EVOLUTION OF THE SUBCONTINENTAL LITHOSPHERE DURING MESOZOIC TETHYAN RIFTING: CONSTRAINTS FROM THE EXTERNAL LIGURIAN MANTLE SECTION (NORTHERN APENNINE, ITALY)

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Torino 19-21 September 2022

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a cura della Società Geologica Italiana

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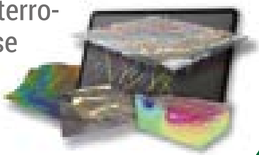

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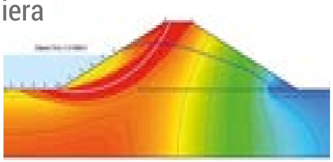

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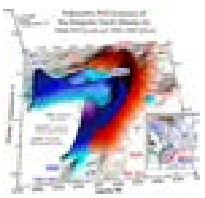

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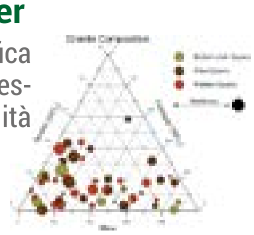

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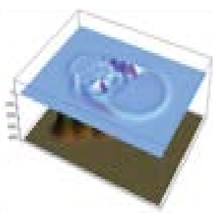

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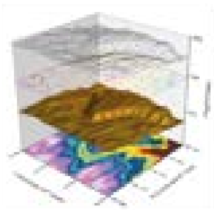

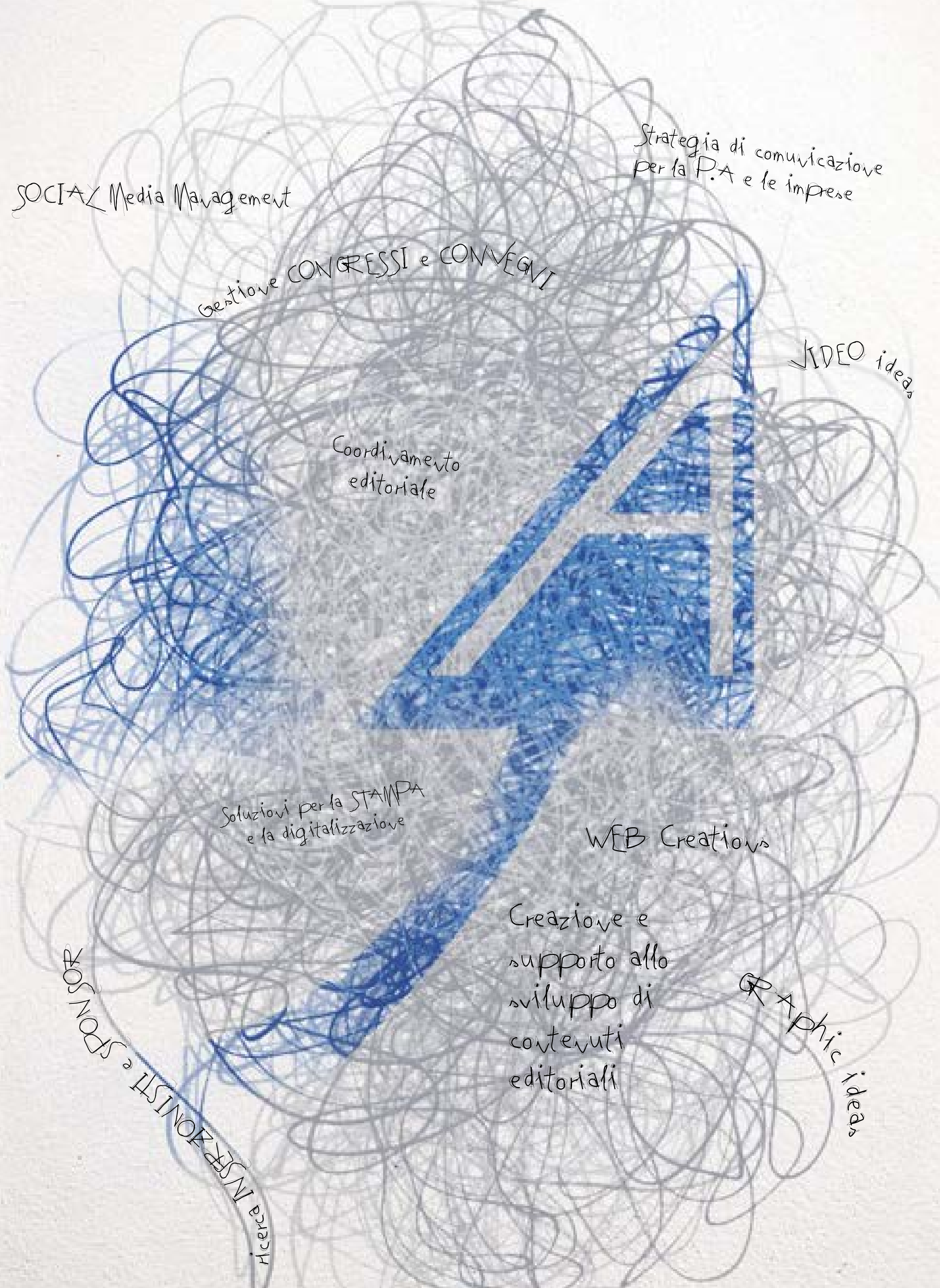
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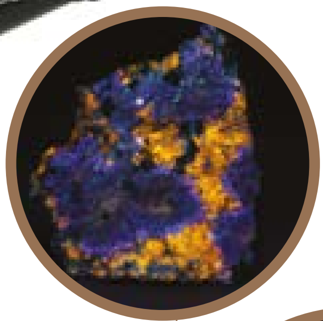

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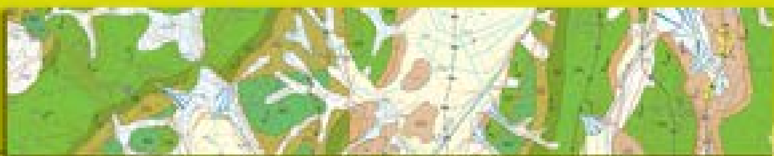

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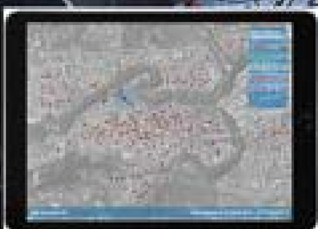

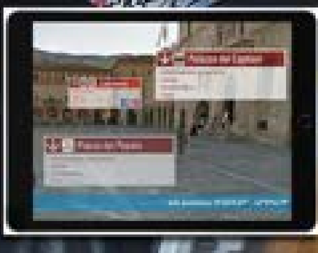

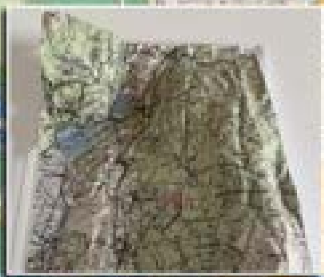

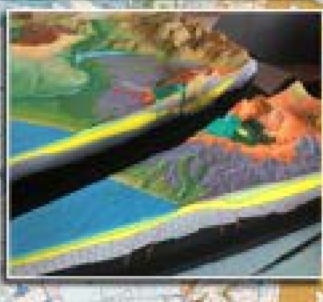

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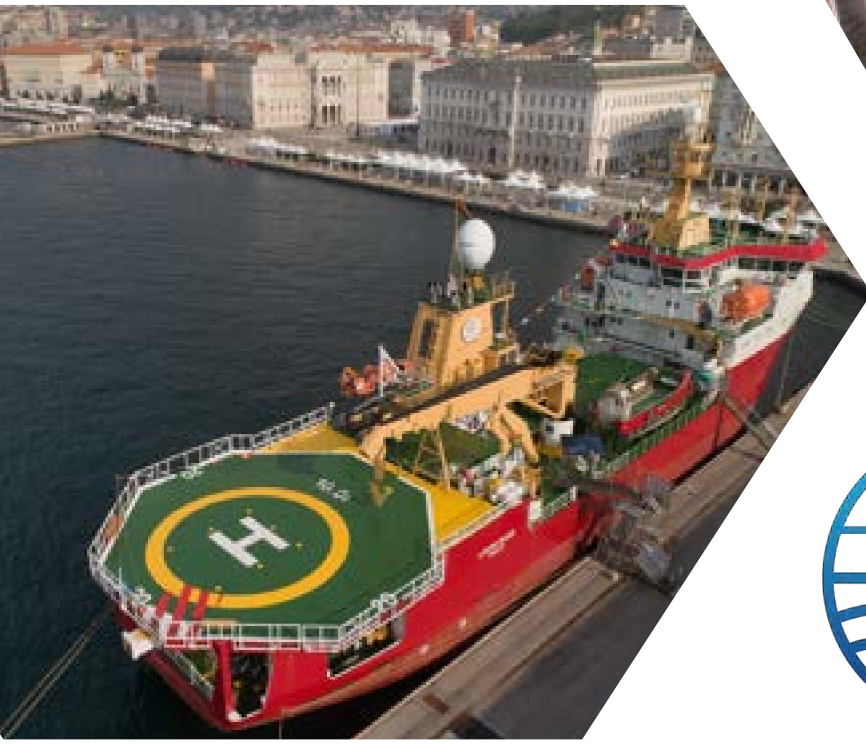

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# PLENARY SESSIONS

# Critical raw materials for a green future

Herrington R.J.*[1-2]

[1] Earth Sciences Department, Natural History Museum London (UK). [2] Economic Mineral Deposits, Imperial College London (UK).

*Corresponding author e-mail:* rington@nhm.ac.uk

*Keywords:* sustainable mining, green technologies, low carbon future, metals.

Clean technologies and infrastructure for our low carbon future carry intense mineral demands. The ambition remains to recycle and reuse as much as we can; however, new-mined resources will be required at least until 2050 to enable green technologies and infrastructure despite the massive improvements in reuse and recycling of existing end-of-use products and wastes. Growth trends suggest that mining will still play a role after 2050 since demand for metals will increase as the developing world moves toward per capita usage of materials comparable to the developed world.

There are sufficient geological resources to deliver the required metals, but we must carefully balance the need to mine with the requirement to tackle environmental and social governance issues and to deliver sustainable development goals, ensuring outcomes are beneficial for both people and planet. In the past, the true values of social impacts and biodiversity loss, as recently highlighted at the COP26 summit, have not been included in mining project evaluations. Particularly with regard to biodiversity, a new approach to designing and evaluating mining projects is needed embracing principles outlined in the recent Dasgupta report[1].

We must carefully, creatively, and systematically secure a diverse range of acceptable sources for the metals we need for a green economy. New frontiers for supply should include novel mineral resources including neglected mined wastes and unconventional new deposits. New processing technologies that involve less invasive, lower energy and cleaner methodologies need to be explored and developing such methodologies will benefit from using nature-based solutions like bioprocessing for both mineral recoveries and for developing sustainable landscapes post-mining. Part of the new ambition would be to seek opportunities for more regulated mining areas in our own backyard, thinking particularly of old mineral districts of Europe, rather than relying on sources with potentially and actually less controllable, fragile, and problematic supply chains.

There is a current debate about the potential of mining our deep ocean, as alternative to terrestrial sources, and this debate needs to be resolved. Based on such a broad analysis, we can then make balanced societal choices about metal and mineral supply from the different sources that will be able to deliver the proposed economic 'Great Reset' that will deliver a good deal for both people and planet. This presentation will discuss the issues raised in a recent paper by Herrington (2021) in more detail.

[1] Final Report - The Economics of Biodiversity: The Dasgupta Review - GOV.UK (www.gov.uk).

Herrington R. (2021) - Mining our green future. Nat. Rev. Mater., 6, 456-458. https://doi.org/10.1038/s41578-021-00325-9.

# The role of Geosciences in the Energy Transition

Salvi F.*

ENI S.p.A., San Donato Milanese (MI).

*Corresponding author e-mail:* Francesca.Salvi@eni.com

*Keywords:* Energy Transition, Geoscience, CCUS, Geo-modelling.

The reduction of the global amount of $CO_2$ emission is mandatory to tackle the climate change. Energy transition processes are ongoing in several countries to achieve the main aims reported in the Paris Agreement signed in 2015, during the COP21.

The main challenge consists in decarbonising and drastically reducing the greenhouse emissions and simultaneously meeting the increasing energy demand of global population: the complexity of the problem demands for a diversified approach and a combination of different actions.

The energy transition progress foresees a gradual change of the energy sources combination: the progressively decrease of the total fossil fuels contribution, carbon and oil mainly, is combined with a relative increase of the gas sharing; increasing the use of renewable sources and geothermal energy; implementing the hydrogen use as energy source and storage and improving the electric vehicle use.

At the same time the decarbonisation path also needs to improve the energy efficiency and increase the carbon capture, utilization and storage (CCUS) projects, to get closer to the Paris Agreement's goals.

Since the geosciences have traditionally played a major role in the O&G exploration and production, one of the questions often occurring among the geoscientists community is which might be their role in the energy transition.

The exploration and production of alternative energy sources require similar or even more expertise in the acquisition, processing and modeling appropriately the surface and subsurface geo-data. Building a geological and geophysical model, representing the geometry of the subsurface and the distribution of the properties of the rocks and their evolution over the time is a fundamental requisite for the evaluation of the geo-resources potential, whether they are hydrocarbons, critical elements for the energy transition (e.g., Lithium, REE), geothermal energy or hydrogen. Similarly, the integration of geological and geophysical studies is mandatory to identify, characterize and monitor, at different scale, sites for the $CO_2$ storage.

Observing, studying and modelling the Earth System are the core of the geosciences, that in this view play a fundamental role in the energy transition, when coupled with the technological innovation and data-sciences and integrated with all the different disciplines in a collaborative system.

# Past hydrological changes in the central Mediterranean: from the regional megadrought to the San Frediano Miracle

Zanchetta G.*

Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* giovanni.zanchetta@unipi.it

*Keywords:* paleohydrology, paleoclimate, Central Mediterranean.

In the last decades, paleoclimatic studies have increased dramatically with the urgency to improve our understanding of the climatic system under the paradigm "The past is the key to the future". A particular focus has been on past "warm" periods as potential analogues (if they can exist) of future warming. However, regional studies have shown that reconstructing past climate is a complex issue posing many challenging questions, the first being chronology and synchronization of events in different paleoclimatic archives. The Mediterranean region represents a good example how different disciplines can be merged to support detailed paleoclimatic reconstructions during the Quaternary. However, a coherent and detailed reconstructions are still lacking, even for the Holocene. In this presentation, some iconic examples of paleoclimatic complexity in the Italian Peninsula will be presented. These examples demonstrate how our ability to reconstruct past climate is far from perfect, requiring significant efforts in the future if geosciences are to continue playing a fundamental role.

# S1.

# Biominerals and environmental mineralogy

*Conveners and Chairpersons*

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# Microbially induced calcite precipitation for environmental applications

Alisi C.*[1], Paganin P.[1], Isca C.[1], Tasso F.[1], Medas D.[2] & Birarda G.[3]

[1] Dipartimento Sostenibilità dei Sistemi Produttivi e Territoriali, ENEA, Roma. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [3] Elettra-Sincrotrone Trieste.

*Corresponding author e-mail:* chiara.alisi@enea.it

*Keywords:* biomineralization, carbonatogenesis, bacteria.

Biologically induced mineralization results from chemical modifications of the microenvironment surrounding the cells, induced by their metabolic activities. The precipitation of several different mineral species can be mediated by bacterial living cells: the Microbial Induced Calcite (MIC) precipitation has been proposed as an alternative strategy for soil stabilization (Dejong et al., 2010), to remove carbon dioxide or to prevent its emission (Silva-Castro et al., 2015), for the restoration of calcareous stones against deterioration, for concrete healing (Zhang et al., 2017) or to remediate environmental matrices by transferring the contaminants present in soils, sediments, and water to less or nontoxic products (Gadd, 2010). The use of calcinogenic bacteria for environmental applications has significant advantages like the possibility of using a product that is physically compatible with carbonate stones and soils; biogenic calcite seems to be more resistant than that produced in an inorganic way, as it is less soluble than the latter. The biological process can improve the precipitation chemistry at the nanoscale, thus allowing deeper penetration of the consolidant. The MIC is coherent, well cemented, and adheres strongly to the substrate; finally, the type of cement and its texture can be adapted by selecting the appropriate bacterium and growth medium.

Apart the known *Bacillus subtilis* that promotes the nucleation of carbonate mineral phases, other strains belonging to genera less studied (*Microbacterium, Stenotrophomonas, Pseudomonas, Rhodococcus*) were preliminary investigated by our research group by IR and powder-XRD, and ESEM showing an enhanced carbonation rate.

Dejong J.T., Mortensen B.M., Martinez B.C. & Nelson D.C. (2010) - Bio-mediated soil improvement. Ecol. Engin., 36(2), 197-201.

Gadd G.M. (2010) - Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiology, 156(3), 609-643.

Silva-Castro G.A., Uad I., Gonzalez-Martinez A., Rivadeneyra A., Gonzalez-Lopez J. & Rivadeneyra M.A. (2015) - Bioprecipitation of Calcium Carbonate Crystals by Bacteria Isolated from Saline Environments Grown in Culture Media Amended with Seawater and Real Brine. BioMed Res. Int., 2015, 816102.

Zhang J., Zhou A., Liu Y., Zhou A., Liu Y., Luan Y., Wang S., Yue X. & Li Z. (2017) - Microbial network of the carbonate precipitation process induced by microbial consortia and the potential application to crack healing in concrete. Sci. Rep., 7, 14600. https://doi.org/10.1038/s41598-017-15177-z.

# Occurrence and distribution of PAHs in different rank Bulgarian coals

Apostolova D.[1], Kostova I.[1], Bechtel A.[2] & Stefanova M.*[3]

[1] Department of Geology, Paleontology and Fossil Fuels, University «St. Kl. Ohridski», Sofia (Bulgaria). [2] Applied Geosciences & Geophysics, Montanuniversit, Leoben (Austria). [3] Bulgarian Academy of Sciences, Sofia (Bulgaria).

*Corresponding author e-mail:* c4909@abv.bg

*Keywords:* coals, PAHs, rank correlation.

Coal is the main energy source in Bulgaria and its combustion in Thermal Power Plants (TPPs) supplies 40% of the electricity of the country. Annually 35.2 Mt of coal is burned, producing 10.4 Mt of solid wastes. The National Energy and Climate Plan 2021-2030 previews a considerable decline in the TPPs share. Despites of the prognosis, the environmental problems triggered by coal exploitation, transportation, combustion, etc. it remains a source for pollution by harmful elements and organic pollutants to all components of the environment. Among them polycyclic aromatic hydrocarbons (PAHs) are of special importance. Totally, coal PAHs content depends on rank, types of fossil sedimentary organic matter and maceral composition. The aim of this study is to track the changes in PAHs composition depending only on the coal rank. Broad range of coals, from Late Carboniferous to Late Miocene, with vitrinite reflectance Ro= 0.17 - 5.20%, from eight Bulgarian basins were studied. For extractable organic matter preparation a protocol described in previous papers was applied. Briefly, ca. 5 g of coal were extracted in a Dionex ASR 200. Further, asphaltenes in the bitumen extracts were precipitated and the soluble portions (maltenes) were fractionated using a Kohnen–Willsch MPLC. PAHs in the aromatic fractions were GC-MS analyzed. The absolute PAHs amounts were determined by inner standard 1,1'-binaphthyl application and later on data were normalized to mg/kg coal. The highest PAHs concentration is registered for the higher rank (bituminous) coals, while the lowest - for the lignites. The PAHs study reveals 3R/4R unsubstituted PAHs dominance in lignite and bituminous coals, and 4R/5R PAHs predominance in the subbituminous coal. The high amounts of alkylated naphthalenes and alkylated phenantrenes in the bituminous coals reflect the diagenetic conversion of the plant-derived terpenoids into alkylated PAHs. For the total PAHs content three series are distinguished: for coals of Miocene/Eocene age -from 1.08 mg/kg to 5.79 mg/kg; for coals of Late Cretaceous/Early Carboniferous age- from 77.9 mg/kg to 137.2 mg/kg; and, for the Late Carboniferous coal - 1.85 mg/kg. The relationship of the total PAHs content vs. Ro shapes as a "bell" and is in a perfect coincidence with the published data for the native PAHs. The maximal PAHs amount of 137.2 mg/kg at Ro- 0.96% for the Late Cretaceous coal lies within the "oil-generation window", Ro=0.5-1.3%.

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# The composition of asbestos bodies in human lungs

Bardelli F.*[1], Pacella A.[2], Borelli V.[3], Di Benedetto F.[4] & Ballirano P.[2]

[1] Istituto di Nanotecnologia, CNR, Roma. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Dipartimento di Scienze della Vita, Università di Trieste. [4] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* fabrizio.bardelli@gmail.com

*Keywords:* asbestos, mesothelioma, crocidolite.

In the lungs, an *in vivo* biomineralization process started by the alveolar macrophages in the attempt to isolate asbestos causes organic and inorganic material to cluster around the foreign fibers. The resulting structures (i.e., asbestos plus a ferruginous coating) are known as asbestos bodies (AB) and become the actual interface between asbestos and the host organism. In fact, although they were generally accepted to be a protective mechanism, *in vivo* and *in vitro* experiments showed that AB are able to induce the production of reactive oxygen species (ROS) and DNA damages, possibly enhancing the cytotoxic properties of asbestos.

The AB are believed to be mainly composed of the Fe-proteins ferritin and/or hemosiderin and mucopolyssaccharides. The presence of (hydroxy)-apatite and Fe-oxides other than ferrihydrite (the mineral core of ferritin) has also been proposed. However, conventional laboratory approaches used to characterize the AB require the removal of the biological tissue by invasive methods (chemical digestion or plasma ashing), which may alter the chemo-physical properties of the AB (Borelli et al., 2007). Non-destructive synchrotron radiation imaging and spectroscopic techniques, which require little or no sample preparation, have recently been applied to the study of AB, revealing their elemental composition, morphology, and mass density (Bardelli et al., 2021). However, two main questions remain open: 1) the exact composition of the Fe-coating in the AB is still unclear; 2) besides recent results (Di Giuseppe et al., 2019; Giacobbe et al., 2021), possible dissolution of amphibole asbestos on long time-scales (decades) is still under debate.

We performed synchrotron X-ray diffraction measurements using a nano-sized X-ray beam (150 nm x 150 nm) to unravel the possible presence of crystalline phases in AB embedded in the original lung tissue, and to check the crystallinity of the asbestos buried inside the AB. Unexpectedly, the results showed that the main phase composing the AB is goethite, and that the inner fiber (crocidolite) maintained a high degree of crystallinity despite the prolonged stay in the lungs (> 10 y). These results may help understanding the role of the AB in the pathogenesis of asbestos related diseases, particularly of malignant pleural mesothelioma.

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# X-ray Fluorescence and Infrared Spectroscopy analyses on fossil and cultured *Helicosphaera carteri* reveal silica presence within coccoliths

Bordiga M.*[1], Gianoncelli A.[2], Birarda G.[2], Pollastri S.[2], Bonanni V.[2], Bedolla D.E.[2-3], Vaccari L.[2], Gariani G.[2], Cerino F.[1], Cabrini M.[1], Beran A.[1], Zuccotti M.[4], Fiorentino G.[4], Cobianchi M.[5] & Lupi C.[5]

[1] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS). [2] Elettra-Sincrotrone Trieste. [3] AREA Science Park, Trieste. [4] Dipartimento di Biologia e Biotecnologie "L. Spallanzani", Università di Pavia. [5] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* mbordiga@ogs.it

*Keywords:* synchrotron light source, silica, fossil and cultured Helicosphaera carteri.

The physiology and proliferation of coccolithophores, one of the main marine calcifiers, are still poorly known even though pivotal to deepen on their role within the global carbon cycle. Recent studies on DNA sequences proved that some living species need silica-like transporters (SILTs) to build their mineralized shell - i.e., the coccoliths (Durak et al., 2016; Langer et al., 2021). To date SILTs have been identified only in few species, but a deeper knowledge on Si-requiring species is important to understand their physiology and distribution, as well as the evolutionary steps driving the SILT strategy. To investigate Si presence within coccoliths, we analyzed living and fossil coccoliths for the first time at three beamlines of Elettra Sincrotrone Trieste: i) Hard X-ray Fluorescence (XRF), ii) Soft X-ray Microscopy and Low Energy X-ray Fluorescence (TwinMic), and iii) Infrared Spectroscopy (SISSI). We selected the species *Helicosphaera carteri* because: a) it is heavily-calcified, b) its big-sized coccoliths make the picking of fossil samples wieldier, c) it belongs to the Zygodiscales family which comprises one species containing SILTs. Fossil coccoliths were picked with a micromanipulator from two deep-sea sediment samples of the NW Pacific (Ocean Drilling Program Site 1209) and deposited during Marine Isotope Stage (MIS) 5 which is considered a good analogue of modern warming, and during the foregoing glacial phase MIS6. To dispel any bias derived from fossilization processes, we also analyzed single coccoliths extracted from monospecific cultures of *H. carteri* grown under 290 ppm of $CO_2$ mimicking MIS5. Preliminary results show for the first time through these newly applied methodologies the Si presence within both living and fossil *H. carteri* coccoliths. More specifically, XRF detected Si in cultured sample at macroscale, whereas TwinMic returned Si distribution maps on single coccoliths. SISSI provided semi-quantitative data on $CaCO_3$ and Si content. Combining the multi-beamline data, we documented higher Si content in the cultured samples than in the fossil ones, possibly due to preservation issues. Our data revealed the potentiality of XRF, TwinMic and SISSI beamlines in analyzing elements, such as Si, contained within both living and fossil coccoliths at species-specific level. This is pivotal in coccolithophore studies since monospecific elemental analyses in the fossil record are extremely complex, if not almost impossible.

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# Impact of Etna's volcanic emission on major ions and trace elements composition of the atmospheric deposition

Brugnone F.*[1], D'Alessandro W.[2], Parello F.[1], Saiano F.[3], Bellomo S.[2], Brusca L.[2], Abita A.M.[4], Li Vigni L.[1] & Calabrese S.[1-2]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] INGV, Palermo. [3] Dipartimento di Scienze Agrarie, Alimentari e Forestali, Università di Palermo. [4] Agenzia Regionale per la Protezione dell'Ambiente, Palermo.

*Corresponding author e-mail:* filippo.brugnone@unipa.it

*Keywords:* volcanic emissions, technology-critical elements, human health.

Mt. Etna, on the eastern coast of Sicily (Italy), is one of the most active volcanoes on the planet and it is widely recognized as a big source of volcanic gases (e.g., $CO_2$ and $SO_2$), halogens, and a lot of trace elements, to the atmosphere in the Mediterranean region. Especially during eruptive periods, Etna's emissions can be dispersed over long distances and cover wide areas. A group of trace elements has been recently brought to attention for their possible environmental and human health impacts, the Technology-critical elements. The current knowledge about their geochemical cycles is still scarce, nevertheless, recent studies (Brugnone et al., 2020) evidenced a contribution from the volcanic activity for some of them (Te, Tl, and REE). In 2021, in the framework of the research project "Pianeta Dinamico", by INGV, a network of 10 bulk collectors was implemented to collect, monthly, atmospheric deposition samples. Four of these collectors are located on the flanks of Mt. Etna, other two are in the urban area of Catania and three are in the industrial area of Priolo, all most of the time downwind of the main craters. The last one, close to Cesarò (Nebrodi Regional Park), represents the regional background. The research aims to produce a database on major ions and trace element compositions of the bulk deposition and here we report the values of the main physical-chemical parameters and the deposition fluxes of major ions and trace elements from the first year of research. The pH ranged from 3.1 to 7.7, with a mean value of 5.6, in samples from the Etna area, while it ranged between 5.2 and 7.6, with a mean value of 6.4, in samples from the other study areas. The EC showed values ranging from 5 to 1032 $\mu S\ cm^{-1}$, with a mean value of 65 $\mu S\ cm^{-1}$. The most abundant ions were $Cl^-$ and $SO_4^{2-}$ for anions, $Na^+$ and $Ca^+$ for cations, whose mean deposition fluxes, considering all sampling sites, were 16.6, 6.8, 8.4, and 6.0 mg $m^{-2}$ d, respectively. The highest deposition fluxes of volcanic refractory elements, such as Al, Fe, and Ti, were measured in the Etna's sites, with mean values of 948, 464, and 34.3 $\mu g\ m^{-2}\ d^{-1}$, respectively, higher than those detected in the other sampling sites, further away from the volcanic source (26.2, 12.4, 0.5 $\mu g\ m^{-2}\ d^{-1}$, respectively). The same trend was also observed for volatile elements of prevailing volcanic origin, such as Tl (0.49 $\mu g\ m^{-2}\ d^{-1}$), Te (0.07 $\mu g\ m^{-2}\ d^{-1}$), As (0.95 $\mu g\ m^{-2}\ d^{-1}$), Se (1.92 $\mu g\ m^{-2}\ d^{-1}$), and Cd (0.39 $\mu g\ m^{-2}\ d^{-1}$). Our preliminary results show that, close to a volcanic area, volcanic emissions must be considered among the major contributors of ions and trace elements to the atmosphere. Their deposition may significantly impact the pedosphere, hydrosphere, and biosphere and directly or indirectly human health.

Brugnone F., D'Alessandro W., Calabrese S., Li Vigni L., Bellomo S., Brusca L., Prano V., Saiano F. & Parello F. (2020) - A Christmas gift: Signature of the $24^{th}$ December 2018 eruption of Mt. Etna on the chemical composition of bulk deposition in eastern Sicily. It. J. Geosci., 139(3), 1-18.

# Effects of Zn contamination on biomineralization processes of benthic foraminiferal tests

Buosi C.*[1], De Giudici G.B.[1], Meneghini C.[2], Medas D.[1], Zuddas P.[3], Iadecola A.[4], Mathon O.[4], Cherchi A.[1] & Kuncser A.C.[5]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze, Università di Roma Tre. [3] UPMC – Sorbonne Universités – Institut des Sciences de la Terre de Paris (France). [4] ESRF, Grenoble (France). [5] Laboratory of Atomic Structures and Defects in Advanced Materials, National Institute of Materials Physics, Bucharest (Romania).

*Corresponding author e-mail:* cbuosi@unica.it

*Keywords:* Zinc biogeochemical cycling, foraminifera, environmental mineralogy.

Benthic foraminifera are an important component of marine communities, playing a key role in ecosystem functioning and biogeochemical cycling. Their sensibility and rapid response to environmental stresses make them an efficient environmental proxy of past and present climate and environmental changes. The Ca-carbonate shells of foraminifera may incorporate trace metals present in the ocean waters through a controlled biomineralization process.

In our study, we applied X-ray absorption and electron spectromicroscopy to reveal the Zn distribution at the nanoscale and its chemical speciation in selected benthic foraminifera species: *Elphidium aculeatum* and *Quinqueloculina seminula*, that were sampled from a heavy-metal polluted area of Sardinia (Italy; De Giudici et al., 2018). These species synthesise their low-Mg and high-Mg shells by extracellular and intracellular mechanism, respectively.

Our analysis reveals that Zn concentration, distribution and chemical speciation differ at the micro- and nano-metric scales of the investigated species. In *Q. seminula*, Zn is more uniformly distributed and occurs in a less ordered environment, which suggests that it is incorporated more easily during the biologically mediated carbonation process. In addition, Zn occurs in an independent and unexpected phase, which is hydrozincite, whose formation is due to foraminiferal cellular processes.

These findings offer a key for a better understanding of the processes ruling the incorporation of Zn in biominerals, their role in biogeochemical cycling and in (paleo)environmental investigations.

De Giudici G., Meneghini C., Medas D., Buosi C., Zuddas P., Iadecola A., Mathon O., Cherchi A. & Kuncser A.C. (2018) - Coordination environment of Zn in foraminifera *Elphidium aculeatum* and *Quinqueloculina seminula* shells from a polluted site. Chem. Geol., 477, 100-111. https://doi.org/10.1016/j.chemgeo.2017.12.009.

# Respirable crystalline silica (RCS) and feldpars: an unconventional harmful exposure scenario

Capella S.*[1-2], Bellis D.[2], Belluso E.[1-2-3], Bullone M.[2-4], Costa G.[1], Ardit M.[5] & Di Benedetto F.[5]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi "G. Scansetti", Università di Torino. [3] Istituto di Geoscienze e Georisorse, CNR, Torino. [4] Dipartimento di Scienze Veterinarie, Università di Torino. [5] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* silvana.capella@unito.it

*Keywords:* respirable crystalline silica, SEM-EDS, horse riding arenas.

Exposure to respirable crystalline silica (RCS) can cause silicosis, a recognized occupational disease. The presence of RCS in equine riding arenas may be a risk factor for the development of silicosis in these animals (Schwartz et al., 1981), but also in human beings working in the equine industry. Currently, a case of lung cancer caused by RCS has been reported in a horse trainer (Yoon et al., 2013).

This study describes for the first time the qualitative and quantitative features of inorganic particles found in equine alveoli and small airways, distinguishing among RCS and non-RCS species. In parallel, the composition of equine working surfaces (soil) is assessed. This approach will help in evaluating possible health consequences due to exposure to equine working surfaces in recreative and professional context.

A total of 10 horses were studied. Based on their clinical presentation and respiratory cytopathology, they were classified as: healthy (control group) or affected by chronic inflammatory (asthma-like) airway diseases (mild and severe asthma groups).

Samples of bronchoalveolar lavage fluid (BALF) and of working surfaces/soils have been collected and investigated respectively by electron microscopy (SEM/EDS, TEM/EDS) and XRPD techniques.

The quality and quantity of Inhaled inorganic particles found in BALF samples from control horses were compared with those found in asthmatic horses. The results highlight an association between the quantity and composition of inhaled inorganic particles (particularly those referable to silicon dioxide) and the presence and severity of bronchoalveolar inflammation in the horses studied.

All the soils investigated contained quartz; feldspars were also often recognized, both sometimes as more abundant species. Together, these data suggest that the silicon dioxide species in BALF can be identified as quartz.

Based on our data, it is plausible to hypothesize that horse riding represents an unconventional exposure to quartz during occupational or recreational-sporting activity. Although limited information is available on the toxic potential of feldspars, they could also represent an additional risk factor for respiratory health and deserves attention in future studies.

The research will subsequently be completed with the evaluation of the presence and quantity of particles dispersed in the air due to trampling by horses. The possible harmfulness of feldspar particles in this context will also be investigated.

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Yoon J.H., Kim B., Choi B.S., Park S.Y., Kwag H.S., Kim I.A. & Jeong J.Y. (2013) - A case report of lung cancer in a horse trainer caused by exposure to respirable crystalline silica: an exposure assessment. Saf Health Work., 4(1), 71-4.

# New mineralogical record of guano-associated phosphates in Colombo Cave (Toirano, Liguria, Italy)

Carbone C.*[1], Balestra V.[2], Belmonte D.[1], Audra P.[3], Columbu A.[4], D'Angeli I.M.[5], Chiesa R.[6] & De Waele J.[7]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [3] Polytech Lab - UPR 7498, Polytech Nice Sophia, Université Côte d'Azur, Nice (France). [4] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [5] Dipartimento di Geoscienze, Università di Padova. [6] Gruppo Speleologico Cycnus, Toirano (SV). [7] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* cristina.carbone@unige.it

*Keywords:* ardealite, newberyite, spheniscidite.

Colombo Cave is part of Toirano karst system and opens at 247 m a.s.l. The wide entrance passage was used during prehistoric times, and a 4.5 m deep archaeological excavation pit is located 10 m from the entrance. The main room is dominated by a large central rock pillar and the floor is completely covered by important ancient bat guano deposits. Samples have beentaken in separate containers and are representative of old guano deposits and a hard-yellow crust covering the guano heap. All samples have been identified by XRD and SEM-EDS analysis.

The results indicate that old guano samples were composed mainly of calcite, quartz, spheniscidite and minor amounts of xenotime (Y), monazite, zircon, and rutile. In particular, spheniscidite $(NH_4,K)(Fe^{3+},Al)_2(PO_4)_2(OH)\cdot 2H_2O$ possibly forms from the reaction of ammonium-rich fresh guano leachates with clay sediments containing Fe and muscovite (source of K and Al) (Sauro et al., 2014). The mineral association in soft yellow and whitish crusts that cover guano is represented by gypsum $CaSO_4\cdot 2H_2O$, brushite $Ca(HPO_4)\cdot 2H_2O$, ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ and newberyite $Mg(HPO_4)\cdot 3H_2O$. Brushite and ardealite occur as cryptocrystalline aggregates varying in color from white-ivory to yellow-ivory, formed by the reaction of sulfuric and phosphoric acid with limestone rock (Hill & Forti, 1997; Puşcaş et al., 2014). Newberyite is less common and likely comes from the interaction of phosphates with Mg-bearing carbonates provided by the disaggregation of the dolomitic host rock. The identification of these minerals is important because they have never been reported from Liguria. Further investigations will be conducted in order to understand the geochemical and minerogenetic processes involved in these guano-associated minerals, and their evolution through time in the damp cave environment (Audra et al., 2019).

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# Emerging pollutants enhances decalcification in marine shelled microbes

Caridi F.*[1], Negri A.[1], Birarda G.[3], Medas D.[2], Buosi C.[2] & Sabbatini A.[1]

[1] Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [3] Elettra-Sincrotrone Trieste.

*Corresponding author e-mail:* a.negri@univpm.it

*Keywords:* emerging pollutants, benthic foraminifera, decalcification.

Marine debris is a global environmental issue. Smoked cigarette butts (CB) are the predominant human coastal litter item together with plastic debris and associated substances that can be bioaccumulated in marine organisms. CB are a vector for the transport and introduction of toxicants, including mainly nicotine, harmful metals, total particulate matter and known carcinogens to aquatic habitats. Also, additives in plastic could cause negative impacts on organisms and accumulate along the food web. In this work, we present the impacts of smoked CB and phthalates on selected species of benthic foraminifera, a group of unicellular eukaryotic organisms, widespread inhabitants of coastal sediments forming part of a key link in marine trophic chains. In particular, foraminiferal cultures of common coastal benthic species have been used to investigate both cellular and metabolic stress after acute and chronic toxicity assays, incorporation of pollutants and potential effects on the biocalcification processes.

Here, for the first time, we evidence nicotine as a biomarker of exposure to the toxicants associated with smoking on benthic foraminifera. Our results demonstrate that nicotine from CB at both sublethal and lethal concentrations (LC50) affects the viability, shell-building mechanism, and cell macromolecular composition of the three studied foraminiferal species each of which exhibited a specific response linked to the type of shell biomineralization. Furthermore, FTIR (Fourier Transform Infrared) microscopy reveals that CB nicotine promotes shell decalcification and alters the composition of cytoplasmic macromolecules (i.e., lipids and proteins) of foraminifera subjected to this emerging pollutant.

Also, our study reveals that plastic-related molecules and plastic debris can be incorporated in the cytoplasm and in the foraminiferal tests analyzed *in situ* and treated *in vitro* with bis-(2-ethylhexyl) phthalate (DEHP) molecule. In particular, the FTIR analysis shows that DEHP can be incorporated in the cytoplasm of the calcareous foraminifer cultured *in vitro*, thus entering the molecular machinery of biomineralization.

In conclusion, we hypothesize that marine debris and its associated additives may produce modifications related to the biomineralization process in foraminifera. This effect would be added to those induced by ocean acidification with negative consequences on the foraminiferal biogenic carbon (C) storage capacity.

# Organic biocement in polychaete bioconstructions from the Mediterranean: perspectives and new challenge in the geobiological research

Deias C.*[1], Sanfilippo R.[1-2], Censi P.[3], Vescogni A.[4], Vespasiano G.[5], Apollaro C.[5], Dominici R.[5], Cipriani M.[5], Miriello D.[5] & Guido A.[5]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [4] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [5] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* claudia.deias@phd.unict.it

*Keywords:* Sabellariidae, biopolymers, environmental proxy.

In marine environments organisms produce minerals through biologically controlled, induced, or influenced processes (Perry et al., 2007). In addition, mineral formation can result from the crystallisation of inorganic compounds after a biologically nucleation phase. These processes lead the building of skeletons or the deposition of organic-derived structures (i.e., microbialites). Exoskeletons can derive also from the secretion of organic polymers cementing detrital grains of different origin and nature.

The chemical relationship between the elemental concentration of biominerals and environmental water is a well-known characteristic of corals which composition mirrors that of seawater. Then the coral composition can represent an affordable environmental and paleo-environmental *proxy*. On the contrary, this evidence is not yet recognised for other marine invertebrates as Polychaetes of the Sabellariidae family that secret a biopolymer in small spots by glands of the body worm and use this material to construct their tube-shaped exoskeleton agglutinating sand grains (Sanfilippo et al., 2019). Accordingly, this study is addressed to fill this gap of knowledge clarifying if the composition of biopolymers secreted by sabellarid polychaetes can mirror that of the environmental water. Whether such a relationship occurs, the composition of the biopolymers could be exploited as environmental *proxy* for the ecosystem where these worms live. For recognising this possibility, bioconstructions formed by aggregate tubes of the two species *Sabellaria alveolata*, and *S. spinulosa*, living on shallow bottoms off the Simeto river mouth (Ionian Sea, Sicily) and the Casarza beach (Adriatic Sea, Abruzzo) were studied, respectively. In this work, C, N, Na, Mg, P, Cl and K concentrations were analysed in both different marine coastal systems in order to collect first data on the occurrence of some biopolymer-water chemical relationships under different environmental conditions.

This is the first stage of the research that will be followed by the detailed biogeochemical study that aims to investigate also concentrations and distributions of several minor and trace elements between biopolymers and environmental waters.

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# Effect of bioprecipitation of secondary minerals mediated by sulphate reducing bacteria (SRB) on metal mobility in mine impacted environment: preliminary data

Dore E.*[1], Fancello D.[1], Marras P.A.[1], Medas D.[1], Rigonat N.[1], Vacca S.[1], Alisi C.[2], Paganin P.[2] & Tasso F.[2]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento Sostenibilità dei Sistemi Produttivi e Territoriali, ENEA, Roma.

*Corresponding author e-mail:* elisabetta.dore@unica.it

*Keywords:* bioprecipitation, SRB, mine area.

Mine and related activities are sources of huge volumes of mine wastes, tailings and residues of metallurgy, often characterized by high contents of metals and semimetals such as Zn, Pb, Fe, As, etc. These materials, when exposed to surface/near surface conditions, can be subjected to oxidation processes leading to the mobilization and dispersion of contaminants in soils and waters.

Centuries of intensive mine exploitation, mainly addressed to zinc (Zn) and lead (Pb) extraction from sulphide and calamine deposits, left a seriously impacted environment in the Iglesiente and Arburese mine districts (SW Sardinia). Studies performed at the watershed scale, showed high sulphate ($SO_4^{2-}$) and metal contents (mainly Zn and Fe) in rivers flowing in the area, however significant differences up to three orders of magnitude have been observed among them: from 6 kg/day of Zn load in Rio San Giorgio to 2000 kg/day in Rio Irvi waters. Microscale investigations (X-Ray Powder Diffraction (XRPD), Scanning Electron Microscopy energy dispersive spectroscopy (SEM-EDS), etc.) carried out on streambed sediments, allowed to recognize the presence of biogeochemical barriers, in well-developed hyporheic zone, that significantly affects metals mobility. Of particular interest is the presence of secondary sulphide minerals (e.g., framboidal $FeS_X$ and ZnS) the precipitation of which is mediated by sulphate reducing bacteria (SRB), under reducing conditions.

With the aim to better understand the bioprecipitation processes, anaerobic batch experiments have been performed at the laboratory scale. Specifically, highly polluted Rio Irvi water (Zn = 550 mg/l) was inoculated with selected native SRB isolated from core sediments sampled along Rio San Giorgio and Rio Naracauli riverbanks. Different SRB microbial communities and novel metal-tolerant sulphidogenic microorganisms have been identified by the next-generation sequencing (NGS) approach.

SEM-EDS analysis carried out on solids recovered at the end of experiments, showed the presence of (bio)precipitates having Zn and S composition and tubular morphology. At the same time, up to 100% of Zn removal has been determined by chemical analysis, performed by inductively coupled plasma optical emission spectroscopy (ICP-OES), of recovered solution (Paganin et al., 2021).

These findings indicate the effectiveness of SRB in limiting metal mobility, suggest their potential in metal recovery, and highlight the importance of selecting native microbial communities already adapted to extreme environments.

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Paganin P., Alisi C., Dore E., Fancello D., Marras P.A., Medas D., Montereali M.R., Naitza S., Rigonat N., Sprocati A.R., Tasso F., Vacca S. & De Giudici G. (2021) - Microbial Diversity of Bacteria Involved in Biomineralization Processes in Mine-Impacted Freshwaters. Front. Microbiol., 12, 778199.

# Potential recovery of metal from plants: a combined XRD-Thermal study on *Juncus acuts*

Fancello D.[1], Scalco J.[1], Medas D.[1], Rodeghero E.[2], Martucci A.[2], Meneghini C.[3] & Dore E.*[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [3] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* elisabetta.dore@unica.it

*Keywords: Juncus acutus*, XRD, thermal analyses.

In the Arburese mine district (SW Sardinia, Italy), centuries of mine exploitation addressed to the extraction of Zn and Pb from sulphides and non-sulphides (calamine) deposits, left a widespread metal pollution. The *Juncus acutus*, a halophyte pioneer plant, was able to adapt in this extreme environment and to affect metal mobility thanks to its capacity to stabilize them in the external roots and rhizosphere.

A method for evaluating the potential of reuse of biomasses for economic purposes is here presented starting from the specific case study of *Juncus acutus*. For this purpose, plants and rhizospheres, collected from the banks of two streams (Rio Naracauli and Rio Irvi) impacted by past mining activity, were used to perform Thermogravimetry and Differential Thermal analyses combined with X-ray Diffraction (XRD) carried out on raw samples and on samples heated ex-situ (by a conventional diffractometer) or in-situ (by synchrotron-based diffraction).

Results showed the presence of mainly quartz, phyllosilicates, and feldspars with minor amounts of sulphides, sulphates, and Fe, Pb, and Zn carbonates concentrated in the rhizosphere of raw samples. The mineral phases, Zn and Fe oxides and willemite, detected in internal roots and stems samples after heating, indicated the presence of metals in the plant tissues. The ex-situ heating was found to be useful in determining the occurrence of metal-bearing phases in plants especially if combined with thermal analyses in order to reveal the temperature stages at which the significant reactions occur. Despite the high resolution proper of a synchrotron light source, the in-situ heating resulted less effective in revealing minor phases in organic samples, maybe due to the scarcity of oxygen within the sample holder that avoid sulphides oxidation and the degradation of organic compounds (Fancello et al., 2019).

This method, if further developed, could be a useful tool in different application fields. The recognition of metals in plant tissues, and the mineralogical form in which they transform after thermal treatment, is an essential information for phytomining by hyperaccumulator plants. Likewise, biochar production from vegetal masses would benefit from the knowledge of the mineral assemblage attainable under different thermal conditions, to find the optimum temperature.

Fancello D., Scalco J., Medas D., Rodeghero E., Martucci A., Meneghini C. & De Giudici G. (2019) - XRD-Thermal Combined Analyses: An Approach to Evaluate the Potential of Phytoremediation, Phytomining, and Biochar Production. Int. J. Env. Res. Pub. He., 16, 1976.

# Mercury in chestnut tree-rings of the Monte Amiata area (Central Italy): impact of past mining activity and present-day geothermal power plants

Fornasaro S.*[1], Ciani F.[2], Morelli G.[3], Rimondi V.[2], Lattanzi P.[3], Cocozza C.[4], Fioravanti M.[4] & Costagliola P.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze. [4] Dipartimento di Scienze e Tecnologie Agrarie, Alimentari, Ambientali e Forestali, Università di Firenze.

*Corresponding author e-mail:* silvia.fornasaro@unipi.it

*Keywords:* dendrochemistry, tree-ring, *Castanea sativa*.

Mercury (Hg) is a global contaminant emitted to the atmosphere from both natural and anthropogenic sources, which have varied over time in response to increased industrialization and pollution control measures. The Monte Amiata Mining District (MAMD; Central Italy) hosts the 3rd largest Hg-district worldwide and an important geothermal field actively exploited for energy. Mining ceased in the 1980s but left an impressive legacy of environmental impact. The exploitation of geothermal energy started in 1959; currently, there are five active plants equipped with emission control systems (AMIS) to reduce Hg and $H_2S$ emissions; however, the efficiency of these systems is not 100% and $Hg^0$ is still emitted from geothermal plants. Due to the Hg availability in the environment, plants are continuously exposed and absorb by resulting low-cost and efficient biological indicators. Specifically, trees store pollutants in tree-rings that have the potential for reconstructing past atmospheric Hg to complement the temporally and spatially limited data provided by the instrumental record, producing high-resolution data with absolutely dated chronologies.

Here, we present a reconstruction of atmospheric $Hg^0$ recorded in chestnut (*Castanea sativa* Mill.) tree-rings (1969−2020) from two different sites of the MAMD: i) site I near the former Abbadia SS mine; ii) site II near the main geothermal power plant. At each site three trees were sampled. A tree from the Appennino Pistoiese (150 km far from MAMD) (reference area) was analyzed for background value. Total Hg concentrations in the tree-rings were quantified with a Milestone tri-cell Direct Mercury Analyzer (DMA-80). The tree-rings in the MAMD provided a temporal reconstruction of Hg exposure at annual resolution. In the mining period Hg concentrations in trees from Abbadia SS varied between 244 and 50 ng/g, whereas in the post-production period after mine closure in the early 1980s, Hg showed a distinct decrease (between 113 and 12 ng/g). The trees close to the geothermal plants almost systematically showed a lower Hg content in their rings with respect to trees located in the mining area. No significant variations were found in tree-rings corresponding to the years of AMIS installation (early 2000s). However, the Hg concentrations varied from 4 to 1.5 ng/g in reference area, indicating that trees are exposed to a modest local anomaly. All samples showed an increase in Hg concentration from hardwood to sapwood (up to an order of magnitude). Chestnut barks, that record the more present-day Hg pollution, systematically showed higher Hg concentrations than sapwood. This study shows that tree-rings may be a good record of Hg deposition in areas affected by mining activity and geothermal plants and can be used for impact minimization and optimal resource and land management. Nevertheless, further investigation of Hg cycling in trees is necessary to satisfactorily interpret this historical Hg record.

# Understanding the environmental impact and recoverability of untapped element from Municipal Solid Waste Incineration (MSWI) ashes

Ghani J.*[1], Dinelli E.[1], Toller S.[1] & Funari V.[1-3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Istituto di Scienze Marine, CNR, Bologna. [3] Dipartimento di Biotecnologie Marine, Stazione Zoologica "Anton Dohrn", Napoli.

*Corresponding author e-mail:* junaid.ghani2@unibo.it

*Keywords:* solid wastes, resource recovery, Aqua regia.

Municipal Solid Waste Incineration (MSWI) plants generate significant amounts of solid wastes such as fly ash (FA) and bottom ash (BA), containing untapped mineable elements such as Cu, Co, Zn, Rare Earth Elements (REE), and Platinum Group Elements (PGE). Accurate determination of these elements in anthropogenic wastes and assessment of their removals are crucial for the circular economy (Funari et al., 2017; Han et al., 2021). Therefore, we collected the FA and BA samples from MSWI plants, located in Ferrara and Forlì cities in Italy, and applied aqua regia digestion method, following the International Organization for Standardization (ISO) protocol (Santoro et al., 2017) to assess recoverability and environmental significance. While the experimental activity was performed at the Geochemistry Lab of ISMAR-CNR (Bologna) of the National Research Council, we determined metal concentration at the laboratory "Bruno Capaccioni" of Department of Biological, Geological and Environmental Science (BiGeA) at University of Bologna, Italy, by ICP-MS. Our objective was to comparatively investigate the recovery of the elements in leaching of different FA and BA samples as well as in fraction samples including bulk (>8 mm), coarse (4-8 mm), medium (1-2 mm) and fine-grained (0.5-1 mm) samples. Our ICP-MS results showed that numerous elements (e.g., Cr, Cu, Ca, Mg, Na, Sr, Er) were enriched compared to extracted analytes from Certified Reference Materials (CRM) subjected to the same leaching procedure. The most significant results were obtained for Al, As, Be, Li, Ba, Cr, Fe, Ca, Na, and Mg. The REE were at low concentration level but Sc, Y, La, Ce and Nd in all the fraction samples. The majority of light REE plus Sc and Y markedly varied in all the fraction samples of Ferrara and Forli MSWI plants. As a result, the contents of elements were found in decreasing order of fine>medium>coarse>bulk in all replicate samples. The elemental composition in BA and FA samples were relatively different in the grain size fractions samples. Furthermore, the concentration of major elements and some trace elements are higher in BA samples rather than FA samples, especially in the fine-grained samples.

This preliminary study emphasized the importance of MSWI ashes used as an alternative source for base metals and REE recovery by aqua regia digestion protocol assisted by Micro-wave digester. The finding of the present study proposed that aqua regia digestion is a low-cost method for better understanding the environmental impact and recoverability of useful elements from anthropogenic materials like MSWI ashes.

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# Unusual biomineralizaztions in an anchialine environment (Zinzulùsa cave, Castro, Italy)

Guido A.*[1], Alifano P.[2], Talà A.[2], Miriello D.[1] & Belmonte G.[2]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce.

*Corresponding author e-mail:* aguido@unical.it

*Keywords:* anchialine cave, bacteria, biomineralization.

The submerged setting of the Zinzulùsa Cave (Castro, Italy) represents a natural geomicrobiological laboratory that make possible the investigation of new biomineralization processes. The peculiar chemical conditions of this anchialine environment derive from complex interactions of sea water with the underground organic-rich sediments. Talà et al. (2021) proposed that sulfate enriched waters of marine origin infiltrate deep along sediments and rocks with greater permeability, and warm-up going upwards, due to the geothermal gradient. During their route, marine waters interact with organic deposits and generate hydrogen sulfide as a result of sulfate reduction. A complex microbial community has been demonstrated to develop on the bottom and on the walls of the cave (Talà et al., 2021), in particular on centimeter thick black crust that form at a depth of 3-4 m. Here we present a new set of micromorphological and biogeochemical data integrated with optical and electron microscopy analyses with UV-Epifluorescence observations, EDS microanalyses and Raman Spectroscopy characterization, in order to investigate possible biomineralization processes involved in the deposition of these black crusts. The crusts show a variable color from the black of the external surface to the white in the most internal part, passing through different tonality of brown to the medium portion. The crusts are formed of very fine anhedral to sub-euhedral crystals organized in irregular laminations. The thinner black external cover, few microns in thickness, is composed of ferromanganiferous oxides, while the remaining part is formed of Ca-phosphate minerals, mostly carbonate-fluoroapatite, independently from the color and texture. Diffuse spheroidal corpuscles, segmented filaments and amorphous organic matter are mixed with the minerals. The organic nature of ferromanganiferous cover and Ca-fluoroapatite is demonstrated by their high fluorescence under UV-excitation and organic bands in Raman spectra. The overall data point to biomineralization processes, induced by microbial metabolic activities or influenced by organic matter taphonomy, for the deposition of both the component of the crusts. In the light of this research, together with the taxonomic characterization of the microbial community (Talà et al., 2021), it is worthy to consider the Zinzulùsa anchialine site a unique ecosystem useful to obtain new insights into prokaryotic mutual interactions in oligotrophic and aphotic conditions, and a natural laboratory for the study of unusual biomineralizations.

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# Pathological biomineralization: compositional and morphological classification of human urinary stones from the Campania region (southern Italy)

Izzo F.*[1], Langella A.[1], Gatta G.D.[2], Germinario C.[3], Grifa C.[3], D'Antonio M.[1], Di Meo M.C.[3], Di Renzo V.[1], Varricchio E.[3], Salzano L.[4], Lotrecchiano G.[4], Saldutto P.[4] & Mercurio M.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [4] UOC Urologia, Azienda Ospedaliera San Pio, Benevento.

*Corresponding author e-mail:* francesco.izzo4@unina.it

*Keywords:* uroliths, environment, mineralogy.

We present the main results of an active collaboration started in 2018 with the San Pio Hospital (Benevento, southern Italy) that aims at a detailed mineralogical investigation of urinary stones of patients from the Campania region.

Forty-nine uroliths (both bladder and kidney stones), surgically collected from patients admitted between the 2018 and 2020 at the Department of Urology of the San Pio Hospital, have been characterized for clinical purposes and environmental biomonitoring from a mineralogical point of view. Clinical interviews were also held, in anonymous form, to gather some useful information about patient's medical history and lifestyle.

Possible causes of urolithiasis and environmental implications were inferred according to the morpho-constitutional classification of the uroliths (Daudon et al., 2014) carried out by means stereomicroscopy, polarized light microscopy, SEM/EDS, and FTIR spectroscopy. Moreover, six bladder stones, representative of the most common mineralogical phases, have been further characterized following a comprehensive analytical approach (Mercurio et al., 2021) that included mainly EMPA/WDS, Synchrotron X-ray Diffraction and Simultaneous Thermal Analyses.

Mineralogical frequency distribution of uroliths from the Campania region can be discussed as a function of both dietary, socio-demographic and environmental risk factors. Whewellite [$CaC_2O_4 \cdot H_2O$] and weddellite [$CaC_2O_4 \cdot 2H_2O$], along with calcium oxalate anhydrous form, represent the main mineralogical phases forming the biominerals here examined. Worth to note is that the fraction of oxalates in the Campania region (ca. 51%) is quite comparable to those of other Mediterranean areas. Frequent uricite [$C_5H_4N_4O_3$] (ca. 33%), mainly observed in bladder stones of older male patients, could be related to incorrect lifestyle and dietary habits. Occurrence of lower fractions of phosphate (i.e., brushite [$CaHPO_4 \cdot 2(H_2O)$] and carbapatite [$Ca_{10}(PO_4CO_3)_6(OH)_8$]) as well as mixed stones (such as, for example, mixtures of ammonium urate [$NH_4C_5H_3N_4O_3$] and calcium oxalates) indicate specific etiopathogenetic mechanisms, suggesting proper therapeutical approaches. Lastly, in selected bladder stones, undesired trace elements such as Cu, Cd, Pb, Cr, Hg and As have been detected, generally as a consequence of the exposure of patients to environmental pollution or contaminated food. Simultaneous occurrence of Se and Hg should denote a methylmercury detoxification process, probably leading to the formation of a very rare compound known as tiemannite.

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# Se in feed coals and fly ashes from coal fired thermoelectric power plants in Bulgaria

Kostova I.*, Apostolova D., Kuncheva J. & Karakolev A.

Department of Geology, Paleontology and Fossil Fuels, University "St. Kl. Ohridski", Sofia (Bulgaria).

*Corresponding author e-mail:* irenko@gea.uni-sofia.bg

*Keywords:* selenium, coals, ashes.

During the industrial coal combustion in thermoelectric power plants (TPPs), some part of Se is released into the environment and another part is associated with solid waste - fly and bottom ashes. The negative effects of Se on the environment and human health are well known and due to it is important to establish the concentration, distribution and mode of occurrence of Se in coals and solid waste production, as well as to study the behavior of Se during combustion process. The study was performed on feed coals and fly ashes from seven Bulgarian TPPs – Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe. Bulk fly ash or fly ash samples from each row of electrostatic precipitators (ESPs) were obtained. Feed coals were also collected at each TPPs.

The goal of the study is to present new data regarding concentration of Se in feed coals and fly ashes from seven Bulgarian coal fired TPPs. The Se was determined by using new methodology, which is more precise and include pre-treatment of the samples and subsequent determination of Se by using ICP-MS.

"Se content in feed coals". The concentration of Se in coals from TPPs vary from 1.03 to 3.60 ppm, where the highest being in the lignite burned in Maritsa East 2 and 3 TPPs (3.60 and 2.50 ppm) and the calculated enrichment/depletion factor (EDF) of Se shows that the content of Se in them is 3.6 and 2.5 times higher than Clark value for Se in world low-grade coals. The content of Se in the bituminous coal burned in TPP Varna (coal from the Donetsk basin) and in TPP Ruse (coal from the Kuznetsk basin) is lower (2.28 and 1.03 ppm), as the EDF value for them shows that the Se content is around and below Clarke value for high grade coal. "Se content in fly ashes". Se in the fly ashes from studied TPPs varies from 1.23 to 65.75 ppm. The low content of Se in fly ashes from almost all TPPs was observed, except for the ashes from Maritsa 3 TPP, where Se varies from 37.96 to 65.75 ppm and gradually increases from the $1^{st}$ to $3^{rd}$ row of ESP. Se in Maritza 3 TPP is from 4.3 to 7.5 times higher than Clarke value.

Increased Se content is found in the lignite burned in Maritza East 2 and 3 TPPs, while in the bituminous coal burned in Varna and Russe TPPs Se is within the average and below average Se content. The low content of Se in fly ashes from almost all TPPs was observed, except Maritsa 3 TPP, where Se is from 4 to 7 times higher than Clarke value.

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# Cd in feed coals and fly ashes from coal fired thermoelectric power plants in Bulgaria

Kostova I.*, Sabeva R., Isaeva E. & Pehlivanova R.

Department of Geology, Paleontology and Fossil Fuels, University "St. Kl. Ohridski", Sofia (Bulgaria).

*Corresponding author e-mail:* irenko@gea.uni-sofia.bg

*Keywords:* cadmium, coals, ashes.

During the industrial coal combustion in thermoelectric power plants (TPPs), some part of Cd is released into the environment and another part is associated with solid waste products. The harmful effects of Cd on the environment and human health are well known and due to this reason, it is important to determine the concentration and distribution of Cd in coals and their solid waste production, as well as to study the behavior of Cd during combustion process. The study was performed on feed coals and fly ashes from seven Bulgarian TPPs – Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe. Bulk fly ash or fly ash samples from each row of electrostatic precipitators (ESPs) were obtained. Feed coals were also collected at each TPPs.

The aim of the present study is to present new data regarding concentration, distribution and mode of occurrence of Cd in feed coals and fly ashes from seven Bulgarian coal fired TPPs. The Cd was determined by using ICP-MS.

"Cd content in feed coals"**.** Cadmium in coals from TPPs vary from 0.14 to 0.29 ppm, where the highest content was observed in the coal burned in Maritsa East 2 and Republika TPPs (0.29 ppm). It should be noted that, in general, the Cd content of coal from all TPPs is around the average coal content in the world (Clark value). "Cd content in fly ashes"**.** Cd in the fly ashes in studied TPPs varies from 0.19 to 3.01 ppm. The low content of Cd in fly ashes from almost all TPPs was observed, except for the ashes from Maritza 3 TPP, where Cd varies from 1.22 to 3.01 ppm. The Cd amount increasing from the 1$^{st}$ to 3$^{rd}$ row of ESP was also observed in fly ashes from the Maritza 3 TPP.

Generally, the concentration of Cd in studied coal and fly ashes from almost all TPPs is around the average or lower than Cd content in comparison with Clark values. The exceptions are the ashes from the 2$^{nd}$ and 3$^{rd}$ row of ESPs from Maritza 3 TPP, where up to 2.5 times higher Cd content is found.

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# Essential elements in the volcanic soils of São Miguel (Azores): linking geology to human and animal health

Linhares D.*, Pimentel A., Garcia P. & Rodrigues A.

Research Institute for Volcanology and Risk Assessment, University of the Azores, Ponta Delgada (Portugal).

*Corresponding author e-mail:* diana.ps.linhares@uac.pt

*Keywords:* volcanism, geochemistry, trace elements.

The relationship between soils and human health has been known since antiquity, but the idea that soils could influence human health has grown throughout time. Nowadays, soils are recognized not only as part of the ecosystem but as having a fundamental role in human survival (Kabata-Pendias & Mukherjee, 2007). Soils are also the main source of major, minor, and trace elements (TE) available in nature and provided by bedrock and associated fluids (Aiuppa et al., 2000; Kelepertsis et al., 2001; Marescotti et al., 2019). For the Azores archipelago, there are some studies that assess the concentration of TE in topsoils (e.g., Amaral et al., 2006; Freitas & Pacheco, 2010; Parelho et al., 2014; Linhares et al., 2015) evidencing an uneven distribution of the essential TE. Recognizing the importance of TE, this study aims to conduct an inventory of environmental indicators for soil and establish correlations among chemical elements in order to predict the possible effects of essential element deficiency or excess on human and animal health.

Sixty-eight samples of agricultural (pastures) topsoil were collected. Soil physicochemical properties and geochemical baselines of selected major and trace elements (Ca, Mg, Fe, Co, Cr, Cu, I, Mn, Mo, Ni, Se, V, and Zn) were determined on composite samples of each grassing area. The results of this study evidence an uneven distribution of the elements (both major and trace elements) in the topsoils of São Miguel. The highest concentrations of major and trace elements were observed in Nordeste and Picos volcanic regions, and the lowest values are mostly found in Furnas/Congro and Povoação volcanic regions. These differences are considered to be of geogenic origin since they result from the weathering of volcanic rocks with different geochemical compositions. Since all the considered elements have a significant role in human health, the uneven distribution of chemical elements in the soils and their possible deficiency and/or toxicity can contribute to several problems in plants and animals, and ultimately in humans since these elements regulate physiological functions in biological systems.

Considering the volcanic origin of São Miguel Island and that the pedogenesis of different volcanic rocks result in different soil compositions, the results from this study pinpoint the importance of a site-by-site approach to risk assessment, which takes into account the individual environmental characteristics of soils and human activities. To further test the environmental risks associated with the presence or absence of essential elements in the soils of São Miguel, we should assess the bioavailability in future works.

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# Natural Radioactivity concentration in natural stones used as building materials

Marrocchino E.*[1], Telloli C.[2], Salvi S.[2], Rizzo A.[2], Taddei F.[3], De Maria A.[3] & Vaccaro C.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara. [2] Dipartimento Fusione e Tecnologie per la Sicurezza Nucleare, ENEA, Bologna. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* mrrlne@unife.it

*Keywords:* natural stone radioactivity, human health, radionuclides.

Building materials of mineral origin, including raw materials used as a constituent in end-products or as a building material in their own right, are known to have a small but not negligible amount of natural radioactivity.

Since the building materials are derived from rocks and soils in the earth's crust, their radioactivity is due to natural radionuclides of Uranium ($^{238}U$), Thorium ($^{232}Th$), and Potassium ($^{40}K$), moreover the concentrations of these nuclides can vary from material to material, and it should therefore be measured as the radiation is hazardous to human health.

The radioactive content in the materials used as building materials is therefore of certain importance because it can significantly affect the annual effective dose equivalent absorbed due to the long residence time of people inside the buildings. In fact, the gamma radiation originating from the walls, floors and ceilings represent the major source of radiation exposure and considering that individuals spend more than 80% of their time indoors, the internal and external radiation exposures from building materials create prolonged exposure situations (Ravisankar et al., 2016).

The knowledge of natural radioactivity levels is useful to set standards and national guidelines for the measurement of natural radioactivity. As regards Italy, the radioactive content of construction materials is regulated by the Legislative Decree 101/2020.

To avoid excessive alarms or, on the contrary, to underestimate the problem, a cognitive investigation was carried out on the radioactivity content in Porphyry rocks sampled in the Atesino Volcanic District (Trentino-Alto Adige region, North of Italy), to possibly identify critical radioactivity concentration.

Trentino Porphyry rocks have gradually gained more and more space in the last 25-30 years also in the market of sawn, flamed, and polished products, which bring it back fully into the family of ornamental stones.

The analyses were done at the ENEA's Traceability Laboratory (FSN-SICNUC-TNMT) specialized in low and very low activity concentrations of radioisotopes in the environment. The gamma spectrometry analyses were performed on the samples reduced to grains, to which, following the EC guidelines, the criteria on the criticality of the materials were applied, calculating three parameters: the activity concentration index (I), the gamma absorbed dose rate (Da) and the annual effective dose (He).

Ravisankar R., Raghu Y., Chandrasekaran A., Suresh Gandhi M., Vijayagopal P. & Venkatraman B. (2016) - Determination of natural radioactivity and the associated radiation hazards in building materials used in Polur, Tiruvannamalai District, Tamilnadu, India using gamma ray spectrometry with statistical approach. J. Geochem. Explor., 163, 41-52.

# Geo-bio-interactions in metal contaminated environments

Medas D.*[1], Buosi C.[1], Carlomagno I.[2], Lattanzi P.[3], Meneghini C.[4] & Podda F.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Elettra-Sincrotrone Trieste. [3] Istituto Di Geoscienze e Georisorse, CNR, Firenze. [4] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* dmedas@unica.it

*Keywords:* geosphere, biosphere, biominerals.

The worldwide pollution of surface and subsurface environments with harmful metals constitutes one of the major threats to both marine and terrestrial living organisms. The interactions between the geosphere and the biosphere can regulate the mobility of metals and their bioavailability by biomineralization processes. The investigation and the exploitation of these biogeochemical interactions can provide scientific and technological advances to control metal dispersion.

Here we illustrate results obtained from the investigations of Zn biomineralizations in cyanobacteria, plant roots and bivalve shells. Specifically, we present a multi-technique (XRD, SEM, XAFS, XRF, STXM, FTIR, and electron microscopies) approach used to assess how (micro)organisms and plants growing in extreme environments (highly metal contaminated areas) adopt specific detoxification strategies in response to the environmental stress. We observe that Zn dispersion is ruled by biological activity through i) the precipitation of hydrozincite ($Zn_5(CO_3)_2(OH)_6$) by the cyanobacterium *Scytonema* sp. (Podda et al., 2000), ii) the formation of a Zn-silicate biomineralization rim at the root epidermis (Medas et al., 2015), iii) the incorporation of Zn into three main different Zn phases in the investigated bivalve shells: Zn phosphate, Zn hydroxycarbonate (hydrozincite), and Zn cysteine.

Our studies reveal that the biomineralization processes represent an effective strategy against Zn contamination, resulting in a strongly resilient system. Achieved results are relevant to clarify biomineralization processes, and their understanding will provide the scientific community with the strong fundamentals for developing efficient bioremediation techniques and environmental monitoring proxies, using recent scientific and technological advances.

*We acknowledge the CeSAR (Centro Servizi d'Ateneo per la Ricerca) of the University of Cagliari, Italy, for SEM analysis.*

Casu M.A., Gianoncelli A., Kuncser A.C., Maraloiu V.A. & De Giudici G. (2018) - Zinc incorporation in marine bivalve shells grown in mine-polluted seabed sediments: a case study in the Malfidano mining area (SW Sardinia, Italy). Environ. Sci. Pollut. Res., 25, 36645-36660.

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# Hemimorphite-like phase bioprecipitation by *Leptolyngbya frigida* in a metal extreme environment

Medas D.*[1], Lattanzi P.[2], Meneghini C.[3] & Podda F.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze. [3] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* dmedas@unica.it

*Keywords:* biomineral, zinc, bacteria.

Several kinds of living organisms play a fundamental role in the precipitation of silica and silicate biominerals, affecting the Si geochemical cycle (Wysokowski et al., 2018; Ikeda, 2021). Diatoms and sponges are the most prominent examples of controlled silica biosynthesis. Also, silica and silicates can be precipitated by plants and bacteria. The fine mechanisms ruling bacterial biomineralizations are not yet fully understood, and the knowledge of their microscopic structures can offer deep insight into the formation processes.

Our work aims to investigate Zn-silicate precipitated by *Leptolyngbya frigida* from waters in a metal extreme environment (Rio Naracauli, SW Sardinia, Italy). At Naracauli, the Zn-silicate biomineralization is a seasonal process that occurs during summer months, when a green biofilm develops along the stream. The biomineralization is rich in Zn, Si and O, and consists of nanoparticles (100-200 nm) that precipitate both on the bacterial filaments and on the extracellular polymeric substances (EPS). X-ray diffraction, $^{29}Si$ nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy and Zn K-edge X-ray absorption spectroscopy revealed a poorly crystalline phase closely resembling hemimorphite $[Zn_4Si_2O_7(OH)_2 \cdot H_2O]$. $^{13}C$ NMR spectra analysis was conducted to investigate the composition of the Zn-silicate biomineral organic matrix, and results showed that C atoms occur in several functional groups such as carbonyl carbons, C rings, O-aliphatic chains, N-aliphatic chains, and aliphatic chains.

We suppose that biochemical conditions around bacteria and EPS favour electrostatic interactions between the deprotonated surface sites on the biopolymers and aqueous $Zn^{2+}$, leading to higher Zn concentrations than in the surrounding bulk phase. Then silicic acid ($H_4SiO_4$) may be adsorbed with the condensation between the silanol group (Si–OH) of dissolved silicic acid and positively charged Zn by forming a metal ion bridge. This bridge may lead to the formation of $Si_2O_7H_6$ dimers, and their stabilization may result in short-range-ordered domains with a hemimorphite-like structure.

Our findings suggest that cell walls and EPS serve as reactive surfaces for the heterogeneous precipitation of the Zn-silicate biomineral, hindering the condensation of silicon dimers. Moreover, we found a $^{29}Si$ NMR band at 85 ppm that could be attributed to a $(C_3H_6O_3)_2Si$ complex. This complex could play a role in the control of silicon polymerization, with implications for Si biomineralization processes.

Ikeda T. (2021) - Bacterial biosilicification: a new insight into the global silicon cycle. Biosci. Biotechnol. Biochem., 85, 1324-1331.

Wysokowski M., Jesionowski T. & Ehrlich H. (2018) - Biosilica as a source for inspiration in biological materials science. Am. Mineral., 103, 665-691.

# Interplay between abiotic and biotic processes for travertine formation in a thermal spring system

Montegrossi G.*[1], Venturi S.[1-2], Crognale S.[3-4], Casentini B.[3], Amalfitano S.[3], Baroni T.[1], Rossetti S.[3], Tassi F.[1-2], Capecchiacci F.[1-2], Vaselli O.[1-2] & Fazi S.[3]

[1] Istituto di Geoscienze e Georisorse, CNR, Firenze. [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Istituto di Ricerca sulle Acque, CNR, Roma.

*Corresponding author e-mail:* montegrossi@igg.cnr.it

*Keywords:* microbial mat, biofilm-mediated mineralization, hot spring.

Active hydrothermal travertine systems are ideal environments to investigate how abiotic and biotic processes affect mineralization mechanisms and the mineral fabric formation. In this study, a biogeochemical characterization of waters, dissolved gases and microbial mats was performed together with a mineralogical investigation on travertine encrustations at Piscine Carletti (*PC*) spring system (Viterbo thermal area, Latium, Italy). The comprehensive model, compiled by means of TOUGHREACT computational tool from measured parameters, revealed that the overall physicochemical environmental conditions were not able to explain the presence of mineralogical phases or fabrics which were largely influenced by microenvironmental conditions induced by microbial mats. The latter consisted of well-structured microbial communities largely shaped by light availability and temperature conditions, which varied along the *PC* system. Nevertheless, mineralogical features were homogeneous throughout the system with euhedral calcite crystals, related to inorganic precipitation induced by $CO_2$ degassing, coexisting with calcite shrubs associated with organomineralization processes, indicating an indirect microbial participation in the deposition process. Similarly, microbial activity played a role in driving calcite redissolution processes, resulting in circular pits on calcite crystal surfaces possibly related to the metabolic activity of S-oxidizing bacteria occurring in the microbial mats. The latter might also explain the apparent contradiction between the undersaturated conditions with respect to gypsum based on measured physicochemical parameters and the recognition of gypsum crystals embedded in microbial mats. Gypsum precipitation was likely induced by supersaturated microenvironmental conditions determined by local increase in sulfate concentration, likely produced by S-oxidizing bacteria. Moreover, the absence of dissolution on gypsum crystals despite the overall undersaturated environmental conditions suggested the capability of microbial mats in modulating environmental mobility of chemical species by providing a protective barrier on gypsum crystals.

# Manganese oxides of caves: a multi-tool geomicrobiological approach to identify their origin and traits

Pellegrini M.*[1], Farda B.[1], Djebaili R.[1], Vaccarelli I.[1], Bernardini S.[2], Ercole C.[1], Bellatreccia F.[2] & Del Gallo M.[1]

[1] Dipartimento di Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università dell'Aquila.
[2] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* marika.pellegrini@univaq.it

*Keywords:* Mn speleothems, environmental mineralogy, environmental microbiology.

Manganese oxides (MnOx) are common and important geomaterials that regulate the availability of various elements and biogeochemical cycling (Bernardini et al., 2021). Among natural environments where MnOx can be found, caves are one of the most interesting ones in which they occur as black crusts or patinas, speleothem stains, or black sedimentary fill deposits (Hill & Forti, 1997). Both biogenic and abiotic models exist for MnOx formation. Different microbial groups can control Mn oxidation when conditions are favourable, competing with the abiotic process (Vaccarelli et al., 2021). Within this context, this study aimed to investigate the mineralogical, geochemical, and microbiological characteristics of caves' Mn patinas. Optical microscopy, SEM-EDS, XRF, XRPD, FT-IR, and Raman spectroscopy were used to determine the structure and characteristics of Mn patinas. SEM-EDS and 16S rRNA sequencing and metagenome function prediction was used to investigate the microbial role in the formation of these deposits and the biotic processes involved. Geochemical analyses revealed that patinas consist of Fe-lenses (fine-mixture of hematite, goethite, and detrital minerals) alternated to Mn-layers (with vernadite, todorokite, and/or ranciéite). An oscillatory Mn and Fe pattern was also observed along with patina growth, suggesting an alternating oxic and suboxic formation environments according to the different phases of the flood occurrences. Microbiological analysis showed the occurrence of *Bacillus, Flavobacterium*, and *Pseudomonas*, $Mn^{2+}$-oxidizing bacteria related to Mn-rich environments (Vaccarelli et al., 2021). Metagenome function analysis predicted the presence of cytochrome-c-oxidase (CcO), superoxide dismutase (SOD), and peroxiredoxin (POD). One of the primary enzymes involved in Mn(II) oxidation is CcO, while SOD and POD reduce the oxidative stress produced by bioreactions. Our results revealed interesting traits of Mn patinas and abiotic and biotic processes involved in their formation. The findings also confirmed the validity of such a multidisciplinary approach to clarify past hydrogeological, mineralogical, and biological processes.

Bernardini S., Bellatreccia F., Columbu A., Vaccarelli I., Pellegrini M., Jurado V., Del Gallo M., Saiz-Jimenez C., Sodo A., Millo C., Jovane L. & De Waele J. (2021) - Morpho-Mineralogical and Bio-Geochemical Description of Cave Manganese Stromatolite-Like Patinas (Grotta del Cervo, Central Italy) and Hints on Their Paleohydrological-Driven Genesis. Front. Earth Sci., 9, 642667.

Hill C. & Forti P. (1997) - Cave Minerals of the World. National Speleological Society, Huntsville

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# Biomineralization processes in microbial communities: role of bacteria, extracellular polymeric substance and viruses

Perri E.*

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* eperri@unical.it

*Keywords:* biomineral, tufa, stromatolite.

The nanostructure and mineral composition of two modern lithifying microbial community were studied and compared, with the aim to understand the processes of biomineralization. One consists of a thick, stromatolite forming, microbial mat from a marine hypersaline sabkha environment, and one consists of a microbial biofilm in a fluvial tufa-forming freshwater setting. Despite the very different environmental conditions and the diverse species of microorganisms present, the mechanisms of mineralization of the organic substrates and the mineral products, show many similarities.

A variety of microorganisms dominated by cyanobacteria, heterotrophic bacteria and viruses (bacteriophages) compose both the communities; microbial-produced vesicles are also present. Extracellular polymer substance (EPS) produced by most of the bacterial forms, is widespread.

The EPS is the unique place where the mineralization takes place, as inside this organic structure bacterial cell walls, viruses, and vesicles can be initial sites of mineral nucleation and successively completely replaced by the mineral. EPS itself can also mineralize, as mineral nanocrystals develop randomly within the polymers replacing their filamentous structure.

In both microbial consortiums, the mineralization of the organic substrates starts with the accumulation in the bacterial EPS, of an amorphous mineral mix of Ca, Si, Al, S and Mg with various proportions, that could have played a fundamental role in the subsequent formation of two types of proto-crystals less than 10 nm in size: nanoparticles (irregular to sub-spherical) and nanofibers (elongated), respectively Ca and Si-Al-Mg rich. The growth of proto-crystals carries to the formation of two mineral species: Ca-carbonate and Mg-silicate crystals with different habitus. The Ca-carbonate continues its growth forming most of the deposit, whereas the silicate, probably for the much less availability of Si and Al ions, the remain.

The presence of several bacterial forms implies several metabolic processes acting within the microbial communities; among these heterotrophic bacteria (mainly sulphate and nitrate reducing) are probably the main responsible for the mediation of mineral formation thanks to their degradation activity of the EPS. In fact, the highly hydrated nature of much EPS represents an environment where ions can accumulate to reach higher concentrations. The microbial degradation of EPS increases the alkalinity and reduces the quantity of cation binding sites, releasing the cations that can be attracted by negatively charged substrates such as virus, vesicles, bacterial walls, and EPS itself, that act as nucleation sites for initiating the mineralization process.

# Potentially toxic elements (PTEs) related to asbestos fibres of chrysotile, tremolite and actinolite in the Calabria and Basilicata regions (Italy)

Punturo R.*[1-2], Ricchiuti C.[1], Pereira D.[3-4] & Bloise A.[5]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] CHARROCK Research Group, University of Salamanca (Spain). [4] Geology Department, University of Salamanca (Spain). [5] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* punturo@unict.it

*Keywords:* asbestos, potentially toxic elements, fibers.

"Asbestos" is a commercial term that includes six fibrous silicate minerals. The Italian law established that chrysotile, amosite, crocidolite, and fibrous actinolite, tremolite, anthophyllite were included under the definition of asbestos (i.e., regulated asbestos).

Epidemiological studies proved that the development of pathologies, such as malignant mesothelioma and lung cancer, is often linked to occupational or environmental exposure to asbestos fibres. Now a day, it is widely accepted by the scientific community that, in addition to many other factors, the potentially toxic elements (PTEs) associated to asbestos may contribute to increasing their toxicity. This contribution compares PTEs in terms of minor and trace element concentrations (Fe, Mn, Cr, Co, Ni, Cu, Zn, Be, V, As, Rb, Sb, Ba, Pb, Sr) in various types of asbestos minerals detected using micro X-ray fluorescence (μ-XRF) and inductively coupled plasma mass spectrometry (ICP-MS) . For this study, we focused on chrysotile, tremolite asbestos and actinolite asbestos contained in serpentinite host rocks cropping out in abandoned quarries in Calabria and Basilicata Regions, Southern Italy (Bloise et al., 2020; Ricchiuti et al., 2021).

In the minerals analyzed, high concentrations of Cr and Be were found in tremolite asbestos and chrysotile respectively, while the pseudo-total concentrations of PTEs in the samples, showed that the largest amounts were detected in tremolite asbestos, followed by actinolite asbestos and chrysotile.

However, since other metals such as Mn and Fe (minor elements) are known to induce toxicity, and considering their input to the overall balance, actinolite contained the largest amount of PTEs and in this case chrysotile proved to be more toxic than tremolite asbestos.

Provided that asbestos can be widespread in air, rocks, soil and water, it is fundamental to quantify their PTEs amount in order to better understand the asbestos-related diseases. Moreover, in the frame of the UNESCO International Geoscience Programme (IGCP)-746 RESOURCES4ALL, a collaborative project among institutions from Europe and Africa, results will permit to understand how serpentinite abandoned quarries of southern Italy, may be monitored and still enhanced.

Bloise A., Ricchiuti C., Punturo R. & Pereira D. (2020) - Potentially toxic elements (PTEs) associated with asbestos chrysotile, tremolite and actinolite in the Calabria region (Italy). Chemical Geology, 558, 119896.

Ricchiuti C., Pereira D., Punturo R., Giorno E., Miriello D. & Bloise A. (2021) - Hazardous Elements in Asbestos Tremolite from the Basilicata Region, Southern Italy: A First Step. Fibers, 9(8), 47.

# Metal removal from metalliferous sediments collected in Thyrrenian seafloor through chemical leaching

Romano J.*[1-2] & Funari V. [2-3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Istituto di Scienze Marine, CNR, Bologna. [3] Dipartimento di Biotecnologie Marine, Stazione Zoologica "Anton Dohrn", Napoli.

*Corresponding author e-mail:* jennifer.romano2@unibo.it

*Keywords:* hydrometallurgy, Fe-Mn crust, leaching.

The global supply for aggregates, critical minerals, and elements such as Rare Elements Earths and metals underpin our economy. Every year millions of tons of minerals are extracted from the mining industry and used in the most diverse industrial fields. The last half century has been characterized by an increase in Population, urbanization, and industrialization, and all these phenomena require more mineral resources. In addition, new technologies require commodities that were not necessary in the past. The Mediterranean seafloor is believed to host metals of commercial interest (Fe, Mn, Cu, Zn) and critical elements (CrE, such as, Co, Cr, Ga, Nb, Sb, REEs). The recent development of technologies for seabed exploration gives us new perspectives to the exploitation of marine resources, Fe-Mn Crust can be considered exploration target. (Hein et al., 2013). Hydrometallurgy is the most suitable extractive technique for the extraction and purification of manganese as compared to all other techniques including biometallurgy and pyrometallurgical processes (Baba et al., 2014). Hydrometallurgy involves treating the ore or mineral concentrate with solutions to dissolve the metals from their host mineral phases. Hydrometallurgy generally uses leaching, in which the ore is piled up into mounds or placed in tanks and mixed with strongly reactive solutions and generally operates at ambient temperatures (Zubkov et al., 2018).

Hydrometallurgical experiment in small scale reactor for three different probably metallic-rich marine samples was performed. Leaching procedure involves the use of an aqueous solution containing a lixiviant and a material containing valuable metal. Samples of iron oxides, manganese oxides and metalliferous sands, collected from the Tyrrhenian seabed (W of Eolo Seamount and NE of Elba Island seafloor for Fe-Mn crust and metalliferous sand, respectively), were analysed. We aimed to evaluate chemical $H_2SO_4$ leaching at two different liquid-solid ratio (10:1 and 5:1, liquid-solid ratio (L/S), respectively) and with different concentration of acid ($H_2S0_4$ 10M and $H_2S0_4$ 15M) used as lixiviant. For leaching procedure some pre-treatment in all the three samples was performed. All the collected samples were dried at low temperature (50°C), grounded, and milled in an agata mortar before the experiment. With the aim of remove water-soluble salts, the powder was washed with distilled water. The leaching yields of several elements, including some of those considered as critical, are provided. The different leaching condition in term of liquid-solid ratio and molarity of liquid, generated solids of different quality. The total element chemistry of solid material was determined on pressed powder pellet by a wavelength dispersive X-Ray Fluorescence instrument. Concerning the original material as we removed and significantly reduced the metals amounts, enriched solutions where metals can be recovered for reuse or further treatment or analysis.

Baba A., Ibrahim L., Adekola F., Bale R., Ghosh M., Sheik A., Pradhan S., Ayanda O. & Folorunsho I. (2014) - Hydrometallurgical Processing of Manganese Ores: A Review. Journal of Minerals and Materials Characterization and Engineering, 2, 230-247.

Hein J.R., Mizell K., Koschinsky A. & Conrad T.A. (2013) - Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources, Ore Geology Reviews, 51.

Zubkov M.V., Plucinski P.K., Dartiguelongue A.C.Y. & Lusty P.A. (2018) - Metal Extraction from Deep-Ocean Mineral Deposits. Elements, 14(5), 319-324.

# Environmental mineralogy in the mining area of Montevecchio Ponente (SW Sardinia)

Sedda L.*, Podda F. & Naitza S.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* lorenzo.sedda96@gmail.com

*Keywords:* biominerals, environmental mineralogy, hydrozincite.

The Montevecchio mining area (Arbus – Guspini, Sardinia SW) has been exploited for centuries, for the extraction of lead and zinc minerals.

The following work focuses on the study and characterization of the sources and contaminants present in the "Cantieri Sanna" from the area of Montevecchio Ponente.

There is a large amount of mining residues in the area downstream of the washing plants, affected by important erosion phenomena, which involve a solid transport of contaminants in solution.

These mineral residues were characterized by diffractometric (XRD) and chemical analysis (ICP-MS), after their solubilization. The whitish biomineral patinas present along the Rio Roia Cani were also analyzed by means of diffractometric analysis and a scanning electron microscope (SEM).

From the analysis carried out, the presence of secondary phases emerged, such as: epsomite, glaucocerinite, goethite, hydroxyapatite, minium, nantokite, plumbojarosite and zincite, indicating a remarkable reactivity of the tailings with atmospheric agents; these results made it possible to identify tailings as a source of contamination. Furthermore, the presence of sub-economic contents of rare earths elements (REE), more particularly of light rare earths elements (LREE), and of Al, Fe, Pb and Zn emerged.

Biomineralization occurs in the area was found in the streambed of rio Roja Cani; it appears like that which forms in the bed of the rio Naracauli, described in detail in Medas et al. (2014).

SEM-EDS analysis confirm that biomineralization is mediated by bacterial activity, due to the filamentous and tubular structures present in biofilms; furthermore, the presence of zinc and oxygen emerges from the compositional maps, confirming that the biomineralization is composed of hydrozincite, as revealed by the XRD analysis.

We argued that this biomineralization rules natural attenuation of zinc as already found in rio Naracauli (Wanty et al., 2013; De Giudici et al., 2014).

De Giudici G., Wanty R.B., Podda F., Kimball B.A., Verplanck P.L., Lattanzi P., Cidu R. & Medas D. (2014) - Quantifying biomineralization of zinc in the rio naracauli (Sardinia, Italy), using a tracer injection and synoptic sampling. Chemical Geology, 384, 110-119. https://doi.org/10.1016/j.chemgeo.2014.07.002.

Medas D., Lattanzi P., Podda F., Meneghini C., Trapananti A., Sprocati A., Casu M.A., Musu E. & De Giudici G. (2014) - The amorphous Zn biomineralization at Naracauli stream, Sardinia: Electron microscopy and X-ray absorption spectroscopy. Environmental Science and Pollution Research, 21(11), 6775-6782. https://doi.org/10.1007/s11356-013-1886-4.

Wanty R.B., Podda F., De Giudici G., Cidu R. & Lattanzi P. (2013) - Zinc isotope and transition-element dynamics accompanying hydrozincite biomineralization in the Rio Naracauli, Sardinia, Italy. Chemical Geology, 337-338, 1-10. https://doi.org/10.1016/j.chemgeo.2012.11.010.

# Aberration-corrected electron microscopy and electron energy-loss spectroscopy applied to the characterization of Fe(II)-oxidizing bacteria-produced organo-mineral stalks

Vigliaturo R.*[1], Dražić G.[2] & Gieré R.[3-4]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Department for Materials Chemistry, National Institute of Chemistry, Ljubljana (Slovenia). [3] Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA (USA). [4] Center of Excellence in Environmental Toxicology, University of Pennsylvania, Philadelphia, PA (USA).

*Corresponding author e-mail:* ruggero.vigliaturo@unito.it

*Keywords:* EELS, Fe redox state, STEM.

Several Fe(II)-oxidizing bacteria (FeOB) from marine and freshwater environments are able to release twisted organo-mineral stalks.

In this study, we have characterized these structures using cutting-edge electron microscopy techniques. The techniques used were: aberration-corrected scanning-transmission electron microscopy (acSTEM), Medium- and High- Angle Annular Dark Field imaging (M/HAADF), and Dual-range Electron Energy-Loss Spectroscopy. Based on the collected data, we are proposing a model that describes the crystal-growth mechanism, the Fe-valence state, the mineralogical state of the stalks, as well as the biogenic contribution to these characteristics and processes.

Even though we used a material science approach in our investigations, we were able to indirectly obtain important information about the involved biological processes.

Our study highlights (Vigliaturo et al., 2020) two main crystal-growth mechanisms: i) based on the aggregation of nanoparticles under a biological control or driven by biologically induced mineralization, ii) an abiogenic growth mechanism based on dissolution and re-precipitation mechanisms having a negligible biological contribution. We can conclude that the organic material acts as a nucleation site and (possibly) template for nanoparticle aggregation, followed by the growth of more ordered crystals.

Vigliaturo R., Marengo A., Bittarello E., Pérez-Rodríguez I., Dražić G. & Gieré R. (2020) - Micro- and nano-scale mineralogical characterization of Fe(II)-oxidizing bacterial stalks. Geobiology, 18, 606-618. https://doi.org/10.1111/gbi.12398.

# S2.

# Learning from the past for a sustainable future: geosciences in/for cultural heritage

*Conveners and Chairpersons*


*Concetta Rispoli (University of Napoli - Federico II)*

*Maria Cristina Caggiani (University of Catania)*

*Alessia Coccato (University of Oxford)*

# The 2-step procedure with Di-ammonium phosphate to consolidate carbonate stones used in cultural heritage

Anfosso M.*[1], Gaggero L.[1], Matteini M.[2], Piquè F.[3] & Vicini S.[4]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Istituto di Scienze del Patrimonio Culturale, CNR, Sesto Fiorentino (FI). [3] Istituto di Materiali e Costruzioni, Scuola Universitaria Professionale della Svizzera Italiana, Mendrisio (Switzerland). [4] Dipartimento di Chimica e Chimica Industriale, Università di Genova.

*Corresponding author e-mail:* milena.anfosso@hotmail.it

*Keywords:* natural stone material, inorganic consolidant, Di-ammonium phosphate.

The knowledge of degradation of stone materials due to ageing processes and to the action of pollution is a key issue in the conservation of cultural heritage. Corrosion and loss of material of sensitive substrates are still the major problems, especially for pieces that are exposed outside; therefore, over the years, different consolidant products have been studied to counter these phenomena. Di-ammonium phosphate (DAP) is an inorganic product thus very compatible with stone materials and specially designed for carbonatic substrate (Matteini et al., 2011). It is no toxic for worker and environment and it is extremely soluble in the water. DAP reacts with the calcium carbonate present in the substrate to create different phases of calcium phosphates, less soluble than carbonate. The aim of this research is to analyze the quality of this product, but also to identify the best protocol for applying DAP. Experiments addressed a 2-step procedure using very low DAP's percentages. Samples of Lecce and Finale stone measuring 5x5x2 cm were used. A first cellulose poultice was applied on samples with solution of 0.5% of DAP in water and left on it for 24 hours. Then, the first poultice was removed and the second one applied in the same way, but with 4% of DAP in water. After the treatment the samples were tested with different analyses to detect calcium phosphates and to test the effectiveness of consolidation. Thanks to the elemental mapping of P by Scanning Electron Microscope coupled with Energy Dispersive Spectrometry a thin veneer of phosphorus on the surface of samples was detected in both lithotypes: in particular 2.11% of P in treated Pietra di Lecce compared with the 1.54% in the untreated one. X-ray fluorescence on the surface of treated samples showed 28.33 wt.% of phosphorus in Pietra di Lecce and 19.29 wt.% in Pietra di Finale. The test of water absorption by capillarity demonstrates that untreated stones absorb more water than treated ones for both types of stones, while the test of evaporation highlights how all absorbed water is released in both lithotypes after four days. Mercury Intrusion Porosimetry (MIP) showed increase of volume of smaller pores in treated stones than untreated. Lastly, the effectiveness of DAP, as consolidating product, was tested with Planar Abrasion Meter, showing that the resistance to abrasion was increased by the treatment of twice up to a depth of 1 mm. As a conclusion, even the phosphate was found in the first layers of the stones the mechanical physical data show how the treatment of DAP in 2-step is effective even at low percentages.

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# Archaeometry and geosciences: the mission of the Center for Research on Archaeometry and Conservation Science (CRACS)

Balassone G.*[1-2-3-4]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] INGV, Osservatorio Vesuviano, Napoli. [4] Istituto per i Polimeri, Compositi e Biomateriali, CNR, Pozzuoli (NA).

*Corresponding author e-mail:* balasson@unina.it

*Keywords:* archaeometry, cultural heritage, case studies.

The Center for Research on Archaeometry and Conservation Science (CRACS) is an academic organization between the Department of Earth Science, Environment and Resources (DiSTAR) of the Federico II University, Naples, and the Department of Science and Technology (DST) of the University of Sannio, Benevento. CRACS intend to promote, organize, and develop the scientific debate and highly interdisciplinary geological studies in Cultural Heritage and Archaeometry. CRACS laboratories have the most advanced instruments for both in-house analyses and portable equipment for on-site non-destructive investigations.

From its foundation (2019), CRACS works in the field of cultural heritage, taking an active part in collaboration on many projects with national and international academic institutions, archaeological museums, monumental sites.

In this contribution, some case studies tackled by CRACS will be presented, spanning from archaeological heritage sites to museums to historical buildings.

Investigations carried out by CRACS on Issos Mosaic (Alexander Mosaic) kept at National Archaeological Museum of Naples (MANN), currently under restoration, were very useful to understand materials that make up tesserae and help to understand the effects of previous restorations that sometimes can be considered detrimental.

Also working with MANN, CRACS investigated natural and artificial geo-materials from facades by means of microcores, endoscopy and termography.

The highest expression of non-destructive instrumentation and techniques can be assessed in archaeological sites, where the preservation of the archaeological asset represents sometimes the greatest limitation to the experimental procedures.

In the case study of *Anfiteatro Flavio* (Pozzuoli), experimental non-desctructive analysis were performed on the sculptural group depicting *San Gennaro* and *San Procolo* and on the majolica altar of the chapel and permitted to achieve information about provenance of raw materials, mix design of binder and their state of alteration/conservation.

# Asbestos in cultural heritage: presence in antique and vintage objects and protocols for restauration and preservation

Belluso E.*[1-2], Capella S.[1-2] & Siviero F.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [3] Area Coordinamento RSPP e attività specifiche sicurezza, Università di Torino.

*Corresponding author e-mail:* elena.belluso@unito.it

*Keywords:* cultural heritage, asbestos, risk prevention.

The numerous physic-chemical properties of asbestos have made it an essential component of many industrial products (asbestos containing material: ACM). Its resistance to fire was known in the ancient East where the fibres were woven to make cloths for the cremation of the dead (Browne, 2003). Its binder property was used as early as 3500 BC in eastern Finland to produce ceramics vessels (Lavento & Hornytzkyj, 1995). Massive use of asbestos was carried out during the Second World War and then in the years between 1960 and 1980, during the period of the rapid economic development. Who does not know, for example, the asbestos-cement roofing and panels installed all over the world?

The harmfulness of asbestos, when its fibres are inhaled, has been known since the twentieth century and now asbestos is classified as a carcinogen. For this reason, asbestos is banned in many countries of the world. To avoid or limit people's exposure to this pollutant, careful checks are carried out to assess whether the ACM's disperse asbestos fibres into the air.

A problem that has not yet been highlighted is that there are many objects that fall within the category of Cultural Heritage in which asbestos is present or even it is a primary constituent.

There are many examples of antique or vintage materials and objects (produced in the 19th and 20th centuries), such as: bikes; musical instruments; radio and movie equipments; supports for oil paintings; mural and wall paintings; artistic installations; safes, raincap style football helmets; decorative ceiling covers; theatre curtains, sculptures, furniture, and vases for garden; lamps and bookcases for interior; advertising flyers, pinball machines; novelty items made by rocks; and many others.

Many of these are actually present in several Museums or in private collections. Sometimes they need to be cleaned or restored. In the case of temporary exhibitions, these objects must be handled for transport and installation and subsequent return. Given that the "asbestos risk" for people is when fibres are air dispersed, the handling of these objects must carry out without causing the fibres air dispersion.

The present research is aimed to show the many different ancient and vintage objects and artworks that contain asbestos.

Regarding their handling, both for the restauration and cleaning works, as well as for their transport, a suitable protocol will be proposed.

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Lavento M. & Hornytzkyj S. (1995) - On asbestos used as temper in Finnish subneolithic, Neolithic and early metal period pottery. Fennoscandia Archaeol., XII, 71-75.

# An innovative analytical approach to the study of pigments and minerals through the use of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for cultural heritage applications

Bertino A.*[1], Caggiani M.C.[1], Fugazzotto M.[1], de Ferri L.[2], Baldan M.[3], Tomaini B.[3], Pojana G.[3], Mangone A.[4-5] & Barone G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Department of Collection Management, Museum of Cultural History, University of Oslo (Norway). [3] Dipartimento di Filosofia e Beni Culturali, Università «Ca' Foscari», Venezia. [4] Dipartimento di Chimica, Università di Bari "Aldo Moro". [5] Centro Interdipartimentale di Ricerca per la Diagnostica dei Beni Culturali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* antonella.bertino98@gmail.com

*Keywords:* pigments, Diffuse Reflectance Infrared Fourier Transform Spectroscopy, database.

A study on a collection of powdered commercial pigments and massive minerals was carried out by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), a spectroscopic technique that is reacently appearing in the panorama of mineralogical and geological studies. DRIFTS is a powerful infrared technique generally applied for the characterization of both organic and inorganic materials, without the need of subjecting samples to a time-consuming preparation or to invasive treatments. Moreover, this non-destructive and non-invasive technique requires the use of a small and lightweight instrumentation which is well suited also for *in situ* analyses.

The collection of studied samples includes commercially available natural and synthetic pigments of different colors and brands, and minerals widely used as pigmenting powders since ancient times, such as malachite, lapis lazuli, azurite, cinnabar, etc. Minerals were selected among the specimens belonging to the Museum of Mineralogy, Petrography and Volcanology of the University of Catania.

The DRIFT spectra of the commercially available pigments, analyzed in powdered form after mixing with KBr, were compared with those obtained from the corresponding mineralogical phases in order to highlight similarities and differences in terms of position and intensity of the signals. It is well known that infrared spectroscopy, when operating in diffuse reflectance can generate spectral discrepancies, due to the different surface appearance (powder/massive; matt/shiny) despite the same chemical and mineralogical composition. The limited number of databases (Manfredi et al., 2017; Miliani et al., 2012) of DRIFT pigments and dyes spectra and the few specific information regarding the attribution of each feature to the corresponding individual vibrational modes for the identification of each species, made the research very compelling and challenging. Thus, the necessity of building up a database of reference spectra to be used in future studies became evident. This is essential in the optics of an increasing use of DRIFTS for the study of archaeological materials, frescoes, museum artifacts, ancient documents and so on, considering its potentialities in terms of versatility and speed and easiness of spectra acquisition.

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Miliani C., Rosi F., Daveri A. & Brunetti B.G. (2012) - Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments. Appl. Phys. A, 106, 295-307.

# Sustainable mineralogical research - A new frontier

Ciriotti M.E.*[1-2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Associazione Micromineralogica Italiana.

*Corresponding author e-mail:* marco.ciriotti45@gmail.com

*Keywords:* sustainability, minerals, deposits.

The research, collection, identification and cataloging of minerals are preparatory stages for the conservation of samples in private and museum collections. As aware citizens attentive to the sustainable management of natural resources, however, we must approach the sampling operations in a perspective that we could define "from a culture of having to a culture of knowledge", conscious of an universe based on knowable physical laws and certain that scientific progress can be measured by the degree of knowledge of these laws.

The concept of sustainability must also be applied to minerals, as for other natural assets, which is nothing more than the characteristic of a process or a state that can be maintained at a certain level indefinitely (or at least as long as possible). A collective social effort is therefore essential to adapt the human consumption of resources to a level of sustainable development: a question of capital importance for the present and the future of humanity (United Nations General Assembly, 1987).

The deposits and sources of minerals in general are not inexhaustible and can be classified according to the combination of the type of evolution over time, their content and their accessibility. The result is an important number of typical situations that allow to say what is correct and what is not correct to do in each of the particular cases.

The analysis of the different situations must be done with the attitude of an educated man, that is, with an attentive look to the future. It is this type of approach that motivates reservations and constraints that do not in any way limit the preparation of important, differently oriented collections: • Leave for others; withdraw in reasonable quantities. • Leave for future generations. • Share with others but also with science. • Leave and protect for testimony and documentation. • Have irreproachable behavior.

United Nations General Assembly (1987) - Report of the World Commission on Environment and Development: Our Common Future. Transmitted to the General Assembly as an Annex to document A/42/427 – Development and International Co-operation: Environment.

# The contribution of archaeometry to the study of inscriptions from the Siracusa catacombs

Coccato A.*[1], Gradante I.[1], Barone G.[2], Mazzoleni P.[2] & Prag J.[1-3]

[1] Faculty of Classics, University of Oxford (UK). [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [3] Merton College, Oxford (UK).

*Corresponding author e-mail:* alessia.coccato@classics.ox.ac.uk

*Keywords:* epigraphy, Sicily, archaeometry.

The catacombs in Siracusa, Sicily (3rd to 6th century AD) constitute a substantial test site within the Crossreads project, which is studying the epigraphic culture of ancient Sicily, and also building a digital open access corpus of all the texts from the island (7th BCE to 7th century AD). The funerary texts and the topography of these underground cemeteries are key to understanding the appearance and consolidation of the Christian community, and, within that framework, increasing attention is being devoted to its material and aesthetic choices.White to grey crystalline marbles are predominant, while polychrome decorative stones, imported or local, are less frequent (*cipollino*, *pavonazzetto*, compact limestones, sandstones, breccias). Red rubrication is predominant, but not exclusive, both on white marbles and on other stones. The reuse of architectural and decorative elements is evident. Moreover, in addition to carved stone, cheaper solutions are also found, such as painting on plaster, engraving the fresh mortar (*graffiti*), or embedding glass tesserae in the mortar.

The non-destructive characterization of stones and pigments is based on autoptic observations, optical digital microscopy, and portable X-ray fluorescence (pXRF). This approach aims at collecting systematic data on the stones, as well as on the inscription production techniques (guidelines, pigment traces, etc.). Chemical data, also using chemometrics, will help to establish preliminary groupings, supporting the definition of a sampling strategy for further laboratory-based analyses (isotopic composition for the crystalline marbles, thin section preparation, etc.). Comparisons across the whole dataset of selected Sicilian inscriptions, as well as with reference materials from known quarries for provenance studies are a long-term aim of this project and are based on on-going fieldwork.

These data convey additional information to that obtained from textual, palaeographic and linguistic studies, promoting a truly interdisciplinary approach where the relationship between choice of materials and visual appearance, with the topographic configuration of the archaeological site, and the content of the inscription, are all considered for the purpose of in-depth historical analysis of the community which created these monuments, and its economic, social and cultural interactions.

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# Study on the compatibility criteria for the formulation of conservation mortars

d'Aniello F.*[1] & De Bonis A.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli.

*Corresponding author e-mail:* francesca.daniello@unina.it

*Keywords:* conservation mortars, compatibility, substrates.

The study aims at deepening the knowledge on the compatibility criteria to formulate conservation mortars suitable for the conservation function to perform in compliance with the UNI 11488:2021 standard. Compatibility with the original materials is one of the fundamental principles for the conservation materials. The latter are defined as "compatible" when they do not create chemical, physical, mechanical, and aesthetic damage to the object to which they are applied. Several aspects should be taken into account for the formulation of conservation mortars: 1) the impossibility of carrying out destructive testing methods on ancient structures and the consequent lack of knowledge of the physical and mechanical behaviour of ancient mortars; 2) the lack of non-destructive testing methods that provide the same information on the physical and mechanical behaviour, not only for mortars but also for masonry walls; 3) a mortar is only a part of a whole structure; 4) the difficulty of reproducing reliable masonry prototypes for laboratory tests; 5) the lack of standards for composite materials.

The starting point for this research project was a bibliographical survey on conservation mortars and on ancient Roman mortars from the Bay of Naples. This allowed the formulation of a mortar (Mortar 0) with an analogous composition to the Roman ones that could be compared to the conservation mortars used nowadays. The Mortar 0 will be applied to four distinct substrates: a brick, a tuff, a limestone, and a lime-based mortar. These were chosen for their different composition and, above all, for their dissimilar rheological properties. The influence between the mortar and the substrates will be evaluated via several analytical techniques amongst which some artificial ageing tests. Subsequently, the same components of the Mortar 0 will be used to formulate twelve mortars by varying the binder/aggregate ratio and the grain size. These mortars will be characterised by means of mineralogical-petrographic and physical-mechanical methods.

This will allow the formulation of "recipes" for the conservation mortars by means of an experimental approach implemented for evaluating the interactions between mortar and substrate. Therefore, by using the same raw materials consciously, it is possible to make conservation mortars with different performances that are more suitable to perform the conservation function. Another advantage will be the use of local raw materials produced with traditional methods that have a low environmental impact thanks to reduced carbon emissions due to transport. Thus, the resulting mixture should be fully compatible from a compositional, physical-mechanical, and aesthetic point of view in continuity with the ancient materials.

# The archaeometric study of pottery production from Southern Atbai Plain (Eastern Sudan)

D'Uva F.*[1], De Bonis A.[1-2], D'Antonio M.[1], Manzo A.[3] & Morra V.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] Dipartimento Asia Africa e Mediterraneo, Università di Napoli "L'Orientale".

*Corresponding author e-mail:* francesco.duva@unina.it

*Keywords:* archaeometry, archaeological pottery, raw materials.

History has recorded, through the remains of the civilizations of the Southern Atbai Plain (Eastern Sudan), the events that attest the presence of different enduring sites, long regional cultural sequence and developed trading network in this territory. The strategic geographical position of the region, the distinct civilizations in the surrounding areas, and the existence of important supply sites of a wide range of raw materials in the territory itself and in Ethio-Eritrean highlands slope justify the different trade routes that cross the Southern Atbai Plain. In this context, an archaeometric study of the ceramics of the area can provide new knowledge in support of archaeology research about ancient trading network of the Northeast Africa. In a preliminary phase of a larger research study, ninety ceramic samples coming from fifteen different sites in Southern Atbai Plain and covering a time span from 6000 BC to 1800 BC, were analysed via a multi-analytical approach (PLM, XRF, XRD, SEM-EDS, TIMS). The raw materials used likely correspond to immature clayey sediments rich in sand attributable to alluvial deposits of the Gash and Atbara rivers. The Gash sediments deriving mainly from the weathering of the Arabian-Nubian Shield (ANS) and the Atbara sediments from the weathering of the Ethiopian Highlands continental flood basalt (CFB). The raw material was usually used without purification so that, in thin section, lithic fragments and loose minerals of the latter are frequently observed. Size and recurrence of lithics are suitable for investigating the paragenesis and texture of the lithotype from which they originated. In doing so, the origin of the raw material can be attributed to the weathering of one or more lithotypes. Seven sediments involved as raw material were recognized, which are respectively characterized by inclusions deriving mainly from the weathering of: epidote-amphibole ortogneiss, muscovite-biotite ortogneiss, epidote-amphibole ortogneiss with the addition of sedimentary calcareous rocks, quartzite, amphibolite, meta-orthopyroxenite and basalt. Even though the wide diffusion of the different lithotypes of ANS, similar in lithology and chemistry, gives a common character to different part of the shield, local differences in the isotopic contents may exist. The first results of isotope analyses states that most of the ceramic samples provide $^{87}Sr/^{86}Sr$ isotope ratios values typical of the mantle source material (0.70418 - 0.70700), however some samples show $^{87}Sr/^{86}Sr$ isotope ratios that diverge towards higher values (0.71078 – 0.71523) akin to those typical of continental crust rocks. In this context, a study of provenance that exploits the Sr-Nd isotopic analysis may confirm local sources of raw material and define the supply sites in the Southern Atbai Plain.

# Petrophysical features of *Pietra di Centola*: a colourful decorative stone from southern Cilento (Italy)

Di Benedetto C.[1], Colella A.[1], d'Aniello F.*[1], De Bonis A.[1-2], Graziano S.F.[2-3], Montesano G.[1], Morra V.[1-2], Rispoli C.[1-2], Verde M.[1] & Cappelletti P.[1-2-4]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] Dipartimento di Farmacia, Università di Napoli «Federico II». [4] Centro Musei delle Scienze Naturali e Fisiche, Università di Napoli «Federico II».

*Corresponding author e-mail:* francesca.daniello@unina.it

*Keywords:* geomaterial, ornamental stone, petrophysical characterisation.

*Pietra di Centola* is an ornamental building stone found near the village of Centola in the Cilento area (southern Italy). The quarry is located on the north-western flank of Monte Chiancone, mainly consisting of Meso-Cenozoic carbonate deposits referable to the succession of Monte Bulgheria. The quarried stone is predominantly composed of marly calcilutites and calcarenites (upper Cretaceous-Oligocene) divided in lithostratigraphical subunits with different chromatic features, changing upwards from variegated grey and beige to red. Geological origin and aesthetic features are similar to the better-known *Scaglia Rossa* formation. *Pietra di Centola* was used, mainly locally, since ancient times. It was employed in some buildings of the medieval village of San Severino di Centola that was definitively abandoned in the last century. For a long period, this building stone was allegedly used only for small building interventions up to the early 70s when it was employed in port and breakwater works. Recently, this ornamental stone had a renewed use in natural stone paving, in sectors of historical and religious restoration and architectural renovations. Nowadays, this stone has gained increasing popularity and is distributed in the national market and exported worldwide.

Despite the recognition of aesthetic qualities characterising this lithotype, the lack of any technical information certainly represents a weak point for a conscious use of this geomaterial. The poor knowledge of its technical properties is the starting point of this study for valorising and fostering this local resource, especially in the light of natural and sustainable architecture.

In this preliminary contribution *Pietra di Centola* has undergone mineralogical and petrophysical characterization, including X-ray powder diffraction (XRPD), Polarized Light Microscopy, He picnometry, ultrasonic wave velocity, water absorption at atmospheric pressure (UNI EN 13755: 2008), compressive strength (UNI EN 1926: 2000), flexural strength (UNI EN 12372: 2006).

Results evidenced how mineralogical and petrographic features influence petrophysical properties of the different lithofacies, especially in terms of porosity, propension to water absorption, and mechanical strength (both flexural and compressive).

The parameters thus obtained will be used to establish quality criteria for the different facies and to make more effective the use of this resource.

# The MagicwHand and Audiobyke projects: following historical routes across the central Apennines for scientific research and development of sustainable tourism

Di Luzio E.*[1], Carfora P. [2] & Barberis W.[3]

[1] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [2] Dipartimento di Lettere e Beni Culturali, Università della Campania «Luigi Vanvitelli», Santa Maria Capua Vetere (CE). [3] Spaceexe s.r.l., Roma.

*Corresponding author e-mail:* emiliano.diluzio@igag.cnr.it

*Keywords:* ancient routes, geoarchaeology, tourism.

The study of the ancient Roman consular roads is an opportunity to observe and study – along the way – the landscape crossed and the interactions with human activities over many centuries. The Via Appia (Quilici & Quilici-Gigli, 2017; Di Luzio & Carfora, 2019) and the *Anterocrium-Amiternum* route, a branch of the ancient Via Salaria (Persichetti, 1909; Quilici, 1993), crossed the impervious Apennine region and still today reveal the signs of the engineering solutions implemented to overcome obstacles, the exploitation of local resources, and a long series of maintenance works.

Over the last few years the Lazio Region financed, through the POR-FESR 2014-2020 calls, two projects aimed at developing collaboration between research institutions, universities and private companies in the field of Geoscience applied to Cultural Heritage and development of sustainable tourism.

The archaeological area of the Via Appia between Fondi and Itri (Latina) and the gorges of Antrodoco (Rieti) preserve tangible signs of the development of the Roman civilization and its passage, two open-air museums which, however, have so far remained off the routes of main tourist itineraries. In the context of the "MagicwHand" and "Audiobyke" Projects, the CNR-IGAG (Institute of Environmental Geology and Geoengineering) and the DILBEC (Department of Letters and Cultural Heritage) of the University of Campania "Luigi Vanvitelli" collaborated with the Spaceexe company providing scientific contents suitable for dissemination through innovative tools dedicated to trekking and cycle-tourism activities. In this contribute, the main results of scientific researches, including geoarchaeological and geomorphological surveys, minero-petrographic and isotopic analyses and geo-hazard evaluations are presented, as well as the state-of-the-art of the high-tech applications.

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# Ceramic technology and painting investigation of archaic architectural remains from the Palatine Hill in Rome

Fugazzotto M.*[1], Stroscio A.[1], Mazzoleni P.[1], Panella C.[2], Russo A.[3], Raneri S.[4] & Barone G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Archeologia, Sapienza Università di Roma. [3] Parco Archeologico del Colosseo, Roma. [4] Istituto di Chimica dei Composti Organo-Metallici, CNR.

*Corresponding author e-mail:* maura.fugazzotto@phd.unict.it

*Keywords:* archaeometry, roman painted terracottas, non-destructive characterization.

Archaic Roman painted antefixes, architectural slabs and *louteria* – retrieved from the north-eastern slope of Palatine Hill, in Rome (Panella & Zeggio, 2017; Panella et al., 2021) – were studied by a multi-analytical approach, providing clues regarding provenance and production technology, both concerning painting layers and ceramic bulks. Considering the importance and uniqueness of the studied materials, non-destructive portable X-Ray Fluorescence have been primarily vastly employed. Moreover, micro-samples of the ceramic bulk were collected for a deeper characterization performed by Optical Microscopy, SEM-EDS, X-Ray Diffraction and micro-Raman Spectroscopy. The comparison with Etruscan reference materials (Barone et al., 2019) and with literature above geological materials from the Roman magmatic province (Peccerillo, 2005) allowed to investigate the characters of the nascent city of Rome and to study its relationship with the coeval Etruscan culture. One of the most interesting results is the similarities recognized with terracottas from the neighbour Etruscan *Veii* rather than with those coming from the most famous *Caere*. Also important is the dentifycation of precious pigments on worthy pieces, beside the most commonly used Fe and Mn based pigments. This research needs to be considered a unique opportunity in investigating this kind of remains, whose high historical and artistic value imposes only non-destructive or micro-destructive analysis, making rare the available scientific data.

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# Archaeometric characterization of painted plasters from the *domus* of *M. Vipsanus Primigenius* at *Abellinum* (Campania region): study of a multilayer technology

Germinario C.[1-2], Covolan M.[3], Mercurio M.[1-2], Musmeci D.[3], Pagano S.*[1], Santoriello A.[3] & Grifa C.[1-2]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] Dipartimento di Scienze del Patrimonio Culturale, Università di Salerno, Fisciano (SA).

*Corresponding author e-mail:* chiara.germinario@unisannio.it

*Keywords:* decorated plasters, multilayer technology, Abellinum.

Situated on the left bank of the Sabato river, the roman city of *Abellinum* represents a living and tangible testimony of the influence of the Roman civilization in Irpinia. The ancient roman colony was built on the remains of a previous Samnite settlement and its evidence outcrops on a plateau not far from the city center of *Atripalda*. Bordered by walls in *opus reticulatum*, the site preserves the remains of the public area of the city, with the baths and the forum. Outstandingly, archaeological excavations unearthed a monumental *domus* with a system building similar typical Pompeian houses, with an atrium and peristyle.

The *domus*, the construction of which began in the Augustan-early imperial age, was likely owned by *M. Vipsanius Primigenius*, a freedman of *Agrippa*, son-in-law of Augustus, as testified by the recovery of a bronze seal in the portico of the peristyle bearing his name. It has all the characteristics of a rich patrician residence, both for the size and for the refinement of the decorations. The rooms of the *domus*, in fact, were finely decorated with Pompeian 3rd and 4th style wall paintings.

From the decorated rooms, eight samples of plasters have been collected with the aim of investigating the technology of wall paintings supports and defining the chromatic palette. The fragments, studied by a multi-analytical approach, have been sampled from two overlapping plasters layers, indicative of different building phases.

All samples are characterized by a multilayer technology; however, interesting differences in the mix designs used for preparing the inner and outer plaster supports have been observed.

The samples from the inner plasters are characterized by the presence of two layers, *arriccio* and *intonachino*, in which fragments of *cocciopesto* have been observed. In particular, the *arriccio* layer has been obtained by adding to the lime-based binder *cocciopesto* and volcanic sand, constituted of pumices, scoriae, clinopyroxene, alkali feldspar, rare olivine and amphibole, whereas ceramic fragments and lower volcanic sands have been mixed to carbonate fragments in the *intonachino*.

Interestingly, in this plasters the pictorial layer lacks. By contrast, the samples from the outer surfaces are characterized by the presence of a pictorial layer applied with "a fresco" or "mezzo fresco" technique on the *intonachino*, prepared with lime binder mixed to carbonate aggregate, which overlays the *arriccio*, constituted of a lime-based layer mainly containing volcanic aggregate.

The walls were decorated with brilliant colors that were analyzed by means of a portable X-Ray fluorescence and Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR), which revealed the use of Fe- and Cu- based pigments to obtain red, yellow, orange, purple, green, and blue decorations.

# A first archaeometric investigation of ancient glass found in Malta: glass groups, materials and degradation

Grima M.*[1], Cagno S.[2] & Vella D.[1]

[1] Department of Metallurgy and Materials Engineering, University of Malta, Msida (Malta). [2] Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, Ås (Norway).

*Corresponding author e-mail:* matthew.grima.18@um.edu.mt

*Keywords:* glass, SEM-EDS, Malta.

In this project, archaeological glass objects found on the Maltese Islands were examined for their elemental composition. This allowed for the objects to be categorised into groups based on their source materials, in the hope of tracing back their place of manufacture and trade origin. No glass manufacturing kiln was ever unearthed in Malta, thus suggesting that Phoenician, Punic and Roman period glass was all imported. Several studies have taken place around the Mediterranean and beyond, leaving the local glass population somewhat lacking from the contributing potential it can have to our own historical legacy, both on a national and international level. All the analytical work carried out on the glass objects was tailored to respect cultural heritage ethics, whereby in general, non-invasive techniques were favoured over invasive ones.

In total, 77 glass items were chosen for analysis. Since surface techniques are a core of the methodology, it was ensured that all glass items were free/partially free of deteriorated patinas and surfaces in order to minimise impacts on the generated results. Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometry (SEM-EDS) of six sacrificial cross-sectional fragments showed a surface layer composed of depleted alkali species followed by a healthy glass core, typical of ancient glass. These surface layers were promoted by the heavy humid burial environment of the majority of this glass collection. Using this knowledge, the remaining glass items were analysed via surface electron probe analysis and successfully organised into five glass groups, namely the natron, the soda-ash, the high potassium, the high lead and the high magnesium groups. Through such groups, it was possible to determine: (i) the level of purity of sand employed to manufacture the glass objects, (ii) obtain opacifier, decolourizer and colourant profiles, (iii) successfully corroborate a site's chronological timeline for the first time through object analysis and (iv) determine that a Horus pendant is made of faience, possibly signalling a Phoenician manufacture. This serves as a great insight into the role that SEM-EDS can play, notwithstanding its lower quantification sensitivity.

# How to sustainably rehabilitate a heritage site after an anthropogenic crisis. The case of Beirut

Hindi N.*[1], Tejado J.J.[2] & Pereira D.[3]

[1] Department of Architecture, Notre Dame University, Zouk Mosbeh (Lebanon). [2] INTROMAC, Cáceres (Spain).
[3] Department of Geology, University of Salamanca (Spain).

*Corresponding author e-mail:* nadine.hindi@gmail.com

*Keywords:* UNESCO, IGCP, sustainability.

On the 4th of August 2020, a double explosion at Beirut Port of the magnitude of 3.5 devastated the port infrastructure and the surrounding neighborhoods, inflicting loss of lives and heritage. But important tangible and intangible heritage of the city was also affected. Some of the most historic neighborhoods suffered severe damages and soon UNESCO showed the concern about the rehabilitation of historic buildings and urban areas, essential to revive the cultural heritage of this historic city. It is very important that original materials and appropriate techniques are used for the reconstruction and restoration of buildings, aiming to preserve Beirut´s urban heritage values (El-Bastawissi et al., 2022). Lebanese vernacular architecture used stone for a significant part of the buildings. Historic buildings in Beirut follow the Mediterranean traditional construction, using a yellow sandstone for the major construction work, and a dolomitic limestone for the ornaments, which were located mainly on the outer façades and obliterated due to the blasts. The immediate action of preserving all stone pieces that were torn apart from the blast, the governmental law that prohibited any kind of full or partial demolition in the affected area, consisting of high number of stone buildings (Law No. 194, dated 16/10/2020) were important factors in the restoration of historic building and the reintegration of Beirut to its original urban landscape. The quarries for those local stone materials are identified (Hamad et al., 1996; El Chami, 2021), the geology of the formations have been published (Walley, 1997), and the technical details of the rehabilitation works are being published gradually (Beirut Heritage Initiative, 2021). This contribution in the seminar aims at exploring the multi-disciplinary socio-economical sustainable approach followed by the civic society, the NGOs and other bodies, in the immediate aftermath of the Port explosion, for the preservation of the built heritage.

*This is a contribution to the IGCP-746 goals.*

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# Archaeometry in consumption contexts: data from the Forum of Cumae

Izzo F.[1-2], Guarino V.[1], Ciotola A.[3], Verde M.*[1], De Bonis A.[1-2], Capaldi C.[3] & Morra V.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] Dipartimento di Studi Umanistici, Università di Napoli «Federico II».

*Corresponding author e-mail:* maria.verde@unina.it

*Keywords:* ancient ceramics, Cumae, provenance.

Since the 18th century the ancient Cumae, the oldest Greek colony in the Western Mediterranean Sea founded in 730 BCE, was subjected to several excavation activities, which have yielded a huge number of ceramic artefacts. Many of these still need to be analysed to define production technologies, provenance of pottery, raw materials used and, consequently, to better understand economy and commercial trades in ancient times. For this purpose, a selection of fifty samples of Roman Coarse Ware collected in the Forum of Cumae underwent to a multi-analytical investigation via mineralogical-petrographic techniques. The obtained results allowed us to gather samples in several petrographic groups including both exotic and local ceramic productions. One of the most representative local ceramic production was the Internal Red-Slip cooking ware (also known as *Rosso Pompeiano*) praised for the peculiar internal red slip manufactured using a low-CaO clays (generally ≤ 6 wt.%) mixed with volcanic sands from the Somma-Vesuvius area. As a function of their chronology, some differences could be preliminary observed. In thin section a birefringent matrix and a bimodal distribution of grains, mainly formed of crystals of clinopyroxenes, alkali feldspars and leucite/plagioclase bearing scoriae fragments, along with minor grog, sporadic crystals of garnet, amphibole and occasional olivine was observed for the samples dated between the end of the 1st century BC and the begin of the 1st century AD. The equivalent firing temperatures range between 800-950°C in oxidizing atmosphere according to the occurrence of hematite and the presence of residual phyllosilicates. On the other hand, the most recent samples (1st century AD – 4th century AD) are rich in quartz and feldspars with minor volcanic components, along with the so-called *calcite ghosts*.

Non-destructive spectroscopic analyses (Raman and FTIR) reveal the occurrence of hematite and phyllosilicates on internal red coatings, as well as carbon black for the *Graue Platte* sample. Sedimentary intakes from the nearby *Volturno* and (potentially) *Clanio* rivers can be also observed in a significant number of utilitarian wares, along with the typical volcanic inclusions of Campania region contexts. In some cases, the presence of granitic fragments or rhyolitic glasses allowed for the identification of exotic samples (probably from the eastern Mediterranean area), whereas common wares imitating African potteries, produced using locally supplied temper, can also be noticed. Noteworthy, the occurrence of samples classified as outliers due to their peculiar textural and compositional features, which provenance determination will shed new light about the production and circulation of ancient ceramics in Cumae between the 2nd century BC to the Late Antiquity.

# ON-Tech – Old New Technology in hydraulic mortars

Medeghini L.*, De Vito C., Calzolari L., Capriotti S. & Mignardi S.

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* laura.medeghini@uniroma1.it

*Keywords:* mortars, sustainability, green materials.

ON-Tech project (Distretto Tecnologico Beni e Attività Culturali – DTC Lazio and Lazio Innova) aims at producing innovative hydraulic mortars for restauration and at characterizing them from the petrographic, chemical, and physical point of view.

The results of archaeometric studies of ancient mortars from the Trajan Aqueduct (Rome, I-II century AD) have brought to light a unique composition of the hydraulic mortars that allowed the monument to survive till now. The restoration mortars are produced according to the ancient recipe of the Roman hydraulic mortar, which proved to be perfect in terms of starting raw materials, grain size and production technology. Therefore, the main objective of the project is to acquire information from our past to make our actions more effective and sustainable to preserve it for future generations.

The technologies and know-how of the partners (Sapienza University of Roma, University of Cassino and Southern Lazio, The National Research Council) with the expertise of the company Tecno Edile Toscana and the stakeholders, represented by restorers from the Central Institute for Restoration, are put in place to produce eco-friendly materials, human safe and compatible with ancient materials (Botticelli et al., 2021).

The present work shows the preliminary results about the characterization of the pozzolan materials from different localities in the surrounding of Bracciano Lake with the aim to identify the differences and to evaluate their quality as raw material for the new products. Optical microscopy (OM), X-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM-EDS) were used to identify the mineralogical petrographic and chemical composition. Vesiculated pyroclastic material, with brown colour matrix, abundant leucite crystals, clinopyroxenes and high porosity are chosen for the experimental step. The pores are characterized by large irregular-elongated shape, and rounded one with smaller size which show yellow glassy edges at PPL with high content of Al and Si.

The experimental mortars will be free of dangerous substances, in a sustainable perspective for the protection of Cultural Heritage. The concept of sustainability will also be extended to its environment and operators, promoting a new conservative approach and minimal intervention in the future. In addition, ON-Tech aims at constant sharing of its outcomes at both informative and commercial level, involving experts but also the general public, to strengthen citizens' sense of responsibility.

Botticelli M., Calzolari L., De Vito C., Mignardi S. & Medeghini L. (2021) - Aqua Traiana, a Roman Infrastructure Embedded in the Present: The Mineralogical Perspective. Minerals, 11, 703.

# Automatic classification of pigments in artworks through FORS and Deep Siamese Network

Melada J.*[1], Bertolaja E.[2], Bonini R.[2], Bonizzoni L.[3], Gargano M.[3], Grifoni E.[3] & Ludwig N.[3]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Master in Scienze per la Conservazione e la Diagnostica dei Beni Culturali, Università di Milano. [3] Dipartimento di Fisica «Aldo Pontremoli», Università di Milano.

*Corresponding author e-mail:* jacopo.melada@unimi.it

*Keywords:* pigments, reflectance spectra, artificial intelligence.

The study of geomaterials composing artworks is of major importance for conservation purposes as well as for obtaining a deeper knowledge of the painting materials and the techniques used by artists. Fiber Optics Reflectance Spectroscopy (FORS) has been used for many decades to acquire information about a painted surface thanks to the principle of selective light absorption. The main advantages of FORS rely on its ease of use, cost-effectiveness, portability, non-invasiveness, and wealth of information acquired. Nevertheless, the identification of the pigment is currently mainly subjective and requires the work of a trained expert. Identification of spectra by means of spectral library search is a widely used method for automating spectral identification through similarity matching (Plutino et al., 2017; Melada et al., 2022). This involves both in situ and in laboratory acquisition of reflectance spectra of known materials to produce a reference database and the selection of the most appropriate searching algorithm which compares spectra of the analyzed paintings with the spectra in the database. The automatization of the process of identification and characterization of painted surfaces and the development of a specific Graphical User Interface (GUI) for this task would be helpful not only to specialists but also to untrained workers. The deployment of a GUI for practical spectrum identification should rely on an algorithm which avoids model retraining, hyperparameter tuning, and problems associated with class unbalance. It must be considered that, based on the architecture of the reference database, there may be many classes and a small number of samples per class. Deep Siamese Neural network which is capable of one-shot-learning is an ideal classifier candidate for dynamic spectrum matching for pigment identification. A Siamese Network is a neural network which is composed of two or more twin networks that shares weights (Liu et al., 2019). It accepts a couple of input spectra and compares the embedded features representation using a distance function. The capabilities of the Siamese Network for pure and mixture pigments classification are compared to similarity-matching algorithms based on distance measures and to classical supervised machine learning estimators.

Liu J., Gibson S.J., Mills J. & Osadchy M. (2019) - Dynamic spectrum matching with one-shot learning. Chemometr. Intell. Lab. Syst., 184, 175-181.

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Plutino A., Richard N., Deborah H., Fernandez-Maloigne C. & Ludwig N.G. (2017) - Spectral divergence for cultural heritage applications. In: Society for Imaging Science and Technology Ed., Color and imaging Conference, 25, 141-146.

# A multi-analytical study of architectural fragments from the Marzamemi II "Church Wreck"

Mirkovic N.[1], Di Fazio M.*[1], De Vito C.[1], Ciccola A.[2], Capuani S.[3-4], Stagno V.[1] & Medeghini L.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Chimica, Sapienza Università di Roma. [3] Istituto dei Sistemi Complessi, CNR, Roma. [4] Dipartimento di Fisica, Sapienza Università di Roma.

*Corresponding author e-mail:* melania.difazio@uniroma1.it

*Keywords:* church wreck, NMR, Green Thessalian stone.

A minero-petrographic and physico-chemical investigation was carried out on several archaeological samples of green architectural stone material from the Marzamemi II site (Sicily). The samples belonged to a Byzantine wreck sunk off the cost of Marzamemi, also known as "Church Wreck". In addition, geological samples from Larisa quarries in Thessaly, Greece, were analysed, with the aim of identifying the area of origin of the geo-materials selected for the realization of the architectural decorations.

Optical Microscopy (OM), Scanning Electron Microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS), X-Ray Powder Diffraction (XRPD), and Raman spectroscopy permitted to define the material as Green Thessalian stone, named also as *verde antico* or *lapis atracius* in the recent times. From a mineralogical point of view, the samples can be defined as ophicarbonate breccia composed of inhomogeneous material that consists of mixtures of serpentine minerals and calcite. Accessory minerals such as magnetite and chromite were also present both in archaeological and quarry samples. The archaeological samples were also studied to define their state of conservation and their degree of degradation caused by their stay underwater for several centuries. Physical characterization of porosity was obtained by Nuclear Magnetic Resonance (NMR) to set the ground for the future conservation procedures.

Indeed, only a wide characterization which consider the material degradation, the material composition and the microclimate is fundamental to address the conservation of such important remains.

# Restoration works in a green perspective: the pavement of the "Palazzo Centrale dell'Università" (Catania, Sicily)

Motta A.*[1], Occhipinti R.[1], Finocchiaro C.[1], Nucatolo G.[2], Starinieri S.[2] & Lazzara G.[3-4]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Centro di Restauro Piacenti S.p.A. – Conservazione del Patrimonio di interesse storico ed artistico, Prato. [3] Dipartimento di Fisica e Chimica "Emilio Segrè", Università di Palermo. [4] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Firenze.

*Corresponding author e-mail:* mottaalfredo5@gmail.com

*Keywords:* restoration, pavement, protective.

The growing interest in the issue of environment safeguard and eco-compatibility has led the scientific research towards the development of new technological and sustainable products in the field of restoration of cultural heritage (Di Turo & Medeghini, 2021). In this respect, the aim of this work is to present a sustainable design strategy for the restoration of the paving of the "Palazzo Centrale dell'Università" (Catania, Sicily)**.** The pavement is made up of black gravels of volcanic rock and white slabs of limestone (*Ragusa Formation*) which create a fine figurative design typical of the Sicilian Baroque style. Despite the recent recovery of the stone surfaces of the paving in 2017, this latter is currently affected by a strong biological attack due to the presence of mosses and lichens that adhere to the stone surface. For this reason, the pavement has been selected as a case study for testing new eco-friendly materials for the cleaning and protective intervention. In particular, this study aims to highlight the difference between traditional biocides (hydrocarbon-based) and eco-friendly ones (water-based or oil-essential based). As regards protective materials, instead, this work seeks to demonstrate the effectiveness of new nanomaterials-based protectives, which are to consider viable alternatives to traditional invasive products.

In collaboration with a Restoration Centre (Piacenti S.p.a.), three different biocide products have been selected and tested on small areas of the pavement with a different light exposure. Then, the stone surfaces have been mechanically cleaned using a brush and a solution of surfactants. For the cleaning intervention, the results have demonstrated the effectiveness of the natural biocidal product which then has been applied to the entire pavement. Through colorimetry, it has been possible to observe the chromatic changes of the pavement during the different phases of the restoration activities.

In parallel, a protective based on nanocomposite was prepared in laboratory and applied using two methods (by brush and spray) on laboratory tests of several types of Sicilian limestone for the artificial aging tests. Subsequently, limestones have been subjected to accelerated degradation tests by a climatic chamber in order to evaluate the protective efficacy of the products on the stone substrate. In addition, samples have been analysed under optical microscope to assess the surface morphology. Then, the contact angle of the samples has been observed to evaluate its wettability and water absorption rate.

Di Turo F. & Medeghini L. (2021) – How Green Possibilities Can Help in a Future Sustainable Conservation of Cultural Heritage in Europe. Sustainability, 13(7), 3609.

# Lead isotopic composition of maiolica made in the Florentine area between the 15th and 19th century

Paghi D.*[1], Manca R.[1-2], Casalini M.[1], Chiarantini L.[3], Bragagni A.[1], Tommasini S.[1] & Benvenuti M.[1-4]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Scienze del Patrimonio Culturale, CNR, Firenze. [3] Centro Interdipartimentale di Microscopia Elettronica e Microanalisi, Università di Firenze. [4] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* rosarosa.manca@unifi.it

*Keywords:* archaeometry, lead isotopes, maiolica.

The production techniques and materials used for the manufacture of Italian maiolica during the Middle Ages and the Renaissance have been broadly studied in the past. However, very little is known about the provenance of the raw materials used to produce the tin- and lead-containing glazes typical of maiolica. This study aims at obtaining a first set of data on the provenance of the lead used as a flux in the production of maiolica glazes in the Florentine area.

Maiolica wares made between the 15th and 19th centuries were analysed using mineralogical and geochemical (lead isotope systematic) methods to trace the origin of Pb and its possible variation over the centuries. Two of the main productions of Tuscany were investigated: the one of Montelupo Fiorentino and the Ginori manufactory in Doccia (Florence, Italy). The analysis of lead isotopes was performed by thermal ionization mass spectrometry (TIMS). Moreover, the samples were analysed by scanning electron microscopy (SEM-EDS) to characterize their layered structure and chemical composition.

Isotope analysis showed that the samples tend to be distributed into distinct groups according to their historical period of production. This indicates the potentiality of discriminating between maiolica produced at different times by lead isotope analysis, although a larger dataset would be needed to confirm this. The comparison with the lead isotope composition of the deposits of the European and circum-Mediterranean area, from which lead was historically extracted, showed that the isotopic composition of the samples differs from that of the Italian deposits, suggesting an import of lead from abroad. The isotopic composition of all the samples is compatible with German ore deposits, in agreement with historical sources: indeed Cipriano Piccolpasso mentions the proverb ‘*piombo todesco, stagnio fiandresco*’ (‘German lead, Flanders tin’) in his famous treatise about maiolica written in c. 1557. At the same time, also the lead deposits of Great Britain (Somerset and Derbyshire), Bulgaria, France (Massif Central), and south-western Switzerland are isotopically compatible with the investigated maiolica glazes and cannot be excluded as possible centres of supply.

In conclusion, lead isotope analysis on the Tuscan manufactories investigated provided promising results for the reconstruction of the evolution of Italian maiolica technology and the commercial and cultural relations in the European and Mediterranean area over time.

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# Preliminary minero-petrographic investigations of different geomaterials from the Temple of Venus in Baia (Phlegraean Fields, Campania region)

Rispoli C.[1], Montesano G.*[1], Russo V.[2] & Cappelletti P.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II».
[2] Dipartimento di Architettura, Università di Napoli «Federico II».

*Corresponding author e-mail:* giovanna.montesano2@unina.it

*Keywords:* minero-petrographic investigations, geomaterials, Phlegraean Fields.

Ancient Romans are widely known for the foundation of one of the greatest empires in history. However, they were also very skilled in using geomaterials for the construction of extremely durable roads, aqueducts, temples and monuments. The study of these geomaterials is therefore of considerable importance in order to understand the secrets of this magnificence.

In this sense, the so-called Temple of Venus, built under Hadrian emperor in the 2nd century A.D. as a thermal fabric, represents an important example of Roman architecture dating to the Imperial Era. The temple is one of the symbol-places of the town of Baia located in the western part of Phlegraean Fields volcanic district (Campania region, southern Italy).

This work stands as a first attempt to investigate geomaterials from different parts of the Temple thanks to a collaboration between the Department of Earth, Environmental and Resources Sciences (DiSTAR), the Department of Architecture (DiArc) of the University of Naples Federico II and the Phlegraean Fields Archaeological Park. It deals with mineralogical and petrographic characterization of a) a mortar containing a brick fragment, b) a scoria and c) a stone material used as *gattone*, i.e., an architectural element with a support function.

Preliminary results deriving from macroscopic, mineralogical analysis (X-Ray Powder Diffraction, XRPD) and Optical Microscopy (OM), (Rispoli et al., 2019) performed at DiSTAR on the different geomaterials are certainly of extreme importance to improve the knowledge of the Roman construction techniques and to support compatible intervention in the conservation phase.

Rispoli C., Fedele L., Di Benedetto C., Esposito R., Graziano S.F., Guarino V., Morra V. & Cappelletti P. (2019) - Characterization of building materials from the Anfiteatro Flavio (Pozzuoli, southern Italy): A mineralogical and petrographic study. Ital. J. Geosci., 138(1), 103-115. https://doi.org/10.3301/IJG.2018.29.

# Provenance study on ceramics from Cales (South Italy) using Sr, Nd and Pb isotopes

Verde M.*[1], De Bonis A.[1-2], D'Antonio M.[1], Renson V.[3], Czujko S.[3], Tomeo A.[4] & Morra V.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II».
[2] Centro di Ricerca per l'Archeometria e le Scienze della Conservazione, Napoli. [3] Research Reactor Center, University of Missouri, Columbia, MO (USA). [4] Soprintendenza Archeologia belle arti e paesaggio per le province di Caserta e Benevento, Caserta.

*Corresponding author e-mail:* maria.verde@unina.it

*Keywords:* ceramics, multi-analytical approach, provenance.

Isotope systematics has widely been explored in archaeological sciences to date objects, define their provenance and describe old human dietary habits. In recent years, this method has also been applied to archaeological ceramics, showing that the isotopic composition of pottery can be related to the isotopic composition of raw materials.

In this research, a total of 125 sherds belonging to different ceramic classes divided in two main groups, fine wares (black glazed pottery, *Terra sigillata*, fine common ware) and coarse wares (common cookware, thin-walled pottery, internal red slip ware, large container) recovered at the archaeological site of *Cales* (currently Calvi Risorta) were studied along with production indicators. A multi-faceted analytical approach via minero-petrographic and geochemical techniques (PLM, XRF, TIMS, MC-ICP-MS) was performed.

The two main groups of fine and coarse wares show distinct petrographic features. Fine wares are characterized by an optically inactive matrix with a bimodal distribution of grains. The inclusions are made of feldspars, quartz, sporadic brown micas, tiny calcite crystals and lithic fragments of both sedimentary (carbonate, occasionally >200 μm) and volcanic nature (trachyte >200 μm), along with microfossils represented by planktonic foraminifers. The coarse wares are mainly characterized by an optical active matrix and a bimodal distribution of grains represented by quartz, feldspars, pyroxenes, brown micas, abundant pumices and trachytic fragments.

The geochemical composition also distinguishes between the two groups of wares. The fine wares show a high-CaO content and the comparison with Campanian clays highlighted a greater affinity with the Mio-Pliocene marine clay sediments of the Apennine sector, which include clays from the area of *Cales*. The coarse wares show a low-CaO content that corresponds with the alluvial clay of Volturno river plain.

The affinity with the raw materials is better established using isotopic analysis. For the first time, the three different isotopic systems of Sr ($^{87}Sr/^{86}Sr$), Nd ($^{143}Nd/^{144}Nd$) and Pb ($^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios, respectively) were combined to better constrain the potential geological sources used as clay raw materials and to more precisely define the pottery provenance. The results highlight the presence of a local production, as already evidenced by minero-petrographic observation, thus attesting the validity and robustness of the method. This innovative approach aims to support traditional ceramic characterization methodologies used in provenance studies by means of a stronger definition of raw material sources.

# Characterization and provenance of historical-contemporaneous marbles from the Waldensian valleys of Piedmont (Cottian Alps, Italy)

Vola G.*[1], Ardit M.[2], Frijia G.[2], Cavallo A.[3], Natali C.[4], Balma Mion C.[5], Lugli F.[6-7] & Primavori P.[8]

[1] Geologist, Bergamo. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [4] Dipartimento di Scienze della Terra, Università di Firenze. [5] Carlo Balma Mion - Studio associato ACT, San Maurizio Canavese (TO). [6] Dipartimento di Beni Culturali, Università di Bologna. [7] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [8] PSC - Primavori Stone Consulting, Milano.

*Corresponding author e-mail:* gabriele.vola@gmail.com

*Keywords:* Piedmont ancient stones, Dora-Maira Massif, Waldensian valleys of Piedmont.

This contribution reports a preliminary archaeometric characterization of silicate-bearing granoblastic marbles from the so-called Waldensian valleys of Piedmont (i.e., Pellice, Germanasca and lower Chisone valleys, Cottian Alps, Italy). These stones, pre-Carboniferous in age, belong to the Dora-Maira Massif of the Penninic domain. "Waldensian" marbles were quarried at least since the XIV century. The XVI century marks the peak in the extraction activity at *Cabitto* quarry of Rocca Bianca relief, and the XIX century that at *Rocca Corba* quarry in the Germanasca Valley (Vola, 2021). On the XX century, the mining activity was mainly concentrated at *La Majera* quarry of Rocca Bianca, and at *Caugis* quarry, in the Subiasco tributary Valley of the Pellice river (Vola, 2020; 2021). These materials were employed for decoration and architectonical purposes in Turin, and later, in Italy and abroad. Fifteen samples representing four lithofacies and commercial types (named "*Statuary white*", "*Bardiglio gray*", "*Zebrato gray*" and "*Cipollino green*" marbles) from the above-mentioned quarries were investigated through a multianalytical approach (Vola et al., 2022). The isotopic signature, combined with the mineral chemistry, allowed tracing marbles origin uniquely (Borghi et al., 2009). The resulting database can be employed either in the cultural heritage, or in the conservation and restoration science, to identify "Waldensian" marbles from different decorative stones with similar microstructural and/or compositional features, but different origin.

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# S3.

# Geosciences for Cultural Heritage

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*Pierluigi Pieruccini (University of Torino)*

*Evdokia Tema (University of Torino)*

# Geoarchaeology of prehistoric Cypriot architecture. Integrated analyses of mudbricks from Middle Bronze Age Erimi

Amadio M.*[1] & Bombardieri L.[2]

[1] Dipartimento di Civiltà e Forme del Sapere, Università di Pisa. [2] Dipartimento di Filologia e Critica delle Letterature Antiche e Moderne, Università di Siena.

*Corresponding author e-mail:* marialucia.amadio@cfs.unipi.it

*Keywords:* earthen architecture, Mediterranean, micromorphology.

Earthen architecture is one of the most impressive expressions of the human ability to create a unique built environment from modest natural resources. For its easy accessibility and the low energy consumption required for its extraction, earth has been chosen by ancient communities to create and shape their built environment. Thanks to its rich archaeological and vernacular earthen architectural heritage, Cyprus represents a key case study for enhancing the current state of the art about earthen architectural practices, analysis and applications in the Mediterranean. The climatic conditions of the island have favoured the development of building techniques based on the manipulation of raw earth since Prehistory. However, this important part of our cultural heritage is in danger due to the rapid degradation of earthen structures in the semi-arid climate of the island. The aim of the paper is to present results obtained from the multi-proxy analysis of mudbrick materials recovered and sampled at the Middle Bronze Age Cypriot site of Erimi-*Laonin tou Porakou* (c. 1950-1650 BC) as pilot geoarchaeological examination of prehistoric earthen architecture in the island. Mudbricks were preliminary examined in the field and further analysed by integrated high-resolution micromorphological, spectroscopic and geochemical analyses with the aim of generating new interdisciplinary data to study degradation agents which impacted on the local earthen architecture and to examine aspects of procurement strategies and interrelation between humans and the local natural environment, as well as forms of social and labour organisation at this prehistoric Cypriot community. The purpose of this study is to contribute to documenting this important part of the island cultural heritage in view of future conservation strategies aimed at preserving and promoting the Mediterranean earthen architecture.

# Geoscience + Archaeology = Geoarchaeology

Angelucci D.E.*

Dipartimento di Lettere e Filosofia, Università di Trento.

*Corresponding author e-mail:* diego.angelucci@unitn.it

*Keywords:* geoarchaeology, archaeological method, soil micromorphology.

Interactions between the Geosciences and Archaeology exist since their appearance. Nowadays, the interface between them is named Geoarchaeology, which is regarded as a specific field of routine archaeological method. This talk focuses on the development of geoarchaeology and examines its role in current archaeology and main tools. The talk also intends to report on the scholars who have worked for bridging the gap between the scientific and the humanistic worlds moving from a geological background.

Geoarchaeology emerged in the '70s within the context of the so-called new archaeology, mostly thanks to English-speaking scholars who began applying sedimentology and geomorphology to the study of archaeological sites and territories – as well as other techniques related to dating, geophysical prospecting or raw material characterization, which are usually considered as belonging to archaeometry rather than geoarchaeology. In the same years, a corpus of norms on archaeological stratigraphy was developed as well (Harris, 1979). During the '80s and '90s, advances in geoarchaeology occurred thanks to the application of other subjects such as soil science or soil micromorphology, with opening of an array of techniques and subfields – e.g., archaeomineralogy or archaeopedology – and an increasing number of research lines and papers.

The present situation of geoarchaeology is rather dynamic. Besides the standardization of procedures and terminology and the development of cross-border techniques combining distinct fields, recent publication of wide-ranging handbooks (e.g., Karkanas & Goldberg, 2019, on site formation processes, or Nicosia & Stoops, 2017, about archaeological micromorphology) gives evidence of the consolidation of the discipline. In addition, a generation of scholars who refer to themselves as "geoarchaeologists" has emerged.

Today, geoarchaeology as "archaeological research using the methods and concepts of the earth sciences" (Butzer, 1982) is almost universally acknowledged by scholars working in archaeological research or dealing with the safeguard of archaeological heritage, and the discipline has developed its own conceptual and methodological framework.

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# The contribution of Geosciences in teaching of Civic Education in secondary schools: experiences of Citizen Science & Engagement in the context of the National Strategies for Sustainable Development (Strategie Aree Interne Valchiavenna)

Bajni G.*[1], Apuani T.[1] & Sterlacchini S.[2]

[1] Dipartimento di Scienze della Terra «A. Desio», Università di Milano. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Milano.

*Corresponding author e-mail:* greta.bajni@unimi.it

*Keywords:* hydrogeological hazard and risk, Citizen Science & Engagement, bottom-up communication.

The dissemination of a culture of respect and value of the territory is an essential component in strategies aimed at guaranteeing the population a future of well-being, social and economic development. The National Sustainable Development Strategy (NSSD) defines the national reference framework for environmental and spatial planning and programming processes in order to implement the sustainable development goals of the United Nations 2030 Agenda. Among the strategic objectives of the NSSD are: "Decrease the exposure of the population to environmental risk factors", "Spread healthy lifestyles and strengthen prevention systems"; "Preventing natural and anthropogenic risks and strengthening resilience".

The authors report on the educational experience carried out with teachers and students from secondary schools as part of the "Strategie Aree Interne Valchiavenna" project, whose aim is to promote a geological culture, on a technical-scientific basis, that leads to respect for the environment through actions aimed at developing a geological-environmental knowledge of the mountains, of their natural resources and, at the same time, of the risks to which people may be potentially exposed, starting a bottom-up cognitive process, based on the concepts of Citizen Science & Engagement, for the protection and management of natural resources, risk prevention, monitoring and mitigation.

The promoted activities were addressed to both teachers and students, providing them with ideas and tools for updating and improving their professional skills on the themes of "hydrogeological hazard and risk" to be included in the Civil Education programmes. The lectures were accompanied by educational workshops in the classroom and guided field activities that included the use of enabling technologies (web apps and geographic information systems) for the collection (directly in the field by using mobile devices), sharing and analysis of geolocalized data.

In addition, following a game-based learning approach, environmental management games were adopted to improve understanding of hazards and awareness of related risks, in order to increase students' soft skills, such as critical thinking, creative problem solving and teamwork.

Laboratory and multimedia educational tools were specifically designed and implemented for the Valchiavenna experimental area, planned in such a way as to make the students the protagonists of their own learning, promoting the observation of geological-environmental elements, landscape forms and processes and the development of risk perception in the mountain environment. Through the realization and use of mobile data collection and environmental monitoring tools a twofold aim was pursued: on the one hand, to develop observational, analytical and communicative skills, which represent an educational element and a tool for cultural development; and on the other hand, to contribute to initiating a process of two-way flow of knowledge of the mountain territory.

# Linking water with rupestrian towns to suggest a geotouristic itinerary around Murge and Premurge areas (MurGEopark, aUGGp, Southern Italy)

Bellini F.*, Cicala M., Festa V., Sabato L. & Tropeano M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* filippo.bellini@uniba.it

*Keywords:* geotourism, rupestrian towns, Premurge.

Geotourism, which is based on the geological knowledge and respect for the crossed territory, could represent one of the means to achieve some goals of the Sustainable Development Agenda 2030. Unluckily, geology alone is not yet a highly appealing tourism topic and could be necessary to highlight links to other cultural attractions. One such links is the connection between geology and the ancestral origin of towns. Taking advantage of this last interest, it could be possible to promote a geotouristic itinerary along rupestrian old towns, such as Laterza, Gravina in Puglia and Matera located around Murge and Premurge (southern Italy). Therefore, these rupestrian towns represent the ideal driving force for introducing geological aspects into touristic itineraries. One of these aspects is understanding where the water was which favoured the development of these urbanized areas. These rupestrian towns developed straddling the border between Murge and Premurge, in areas partly falling within the MurGeopark, an aspiring UNESCO Global Geopark (aUGGp). Locally, Murge and Premurge represent two main structural domains of the Southern Apennines orogenic system, respectively the foreland (the Apulia Foreland, made up of Cretaceous limestones) and the foredeep (the Bradanic Trough, made up of a transgressive-regressive Quaternary succession). Rupestrian towns were digged in transgressive lower Pleistocene coarse-grained carbonate soft-rocks (Calcarenite di Gravina Fm) mantling flanks of morpho-structural highs made up of Cretaceous limestones (Calcare di Altamura Fm). Coarse-grained carbonates are covered by clays (Argille subappennine Fm), in turn covered by regressive lower and middle Pleistocene coarse-grained siliciclastic to mixed deposits (marine terraced deposits) representing the morpho-stratigraphic sub-horizontal top of the whole outcropping succession. Locally, this succession hosts surface aquifers due to the key position of clays, which acts as an aquiclude for the overlying coarse-grained porous deposits. Being the area in uplift since the Middle Pleistocene, the Quaternary succession and its bedrock are deeply and diffusely incised by a drainage network which, reaching the carbonate rocks (both the Quaternary and the underlying Cretaceous ones), produced the spectacular canyons locally called "gravine". Along some walls of these rocky valleys, the presence of an aquifer on diggable rocks locally favoured the rupestrian development of towns, since inhabitants could easily use water collected from springs of this kind of aquifers. The "modern" use of water dates back to the Middle Ages, as proved by the "Fontana Medievale", the "Ponte Acquedotto" and the "Fontana Ferdinandea" located respectively in Laterza, Gravina in Puglia and Matera. Thanks to the link between water and rupestrian town with geology, geoturists can undertake not only a sustainable trip, but also a journey through the history of the anthropization of the area.

# Toward mediterranean inside transport amphoras. Manufactory, provenance and trades reconstruction from VII-VI B.C.

Bisciotti A.*[1], Comodi P.[2], Fastelli M.[2], Zucchini A.[2] & Fiorini L.[3]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Dipartimento di Fisica e Geologia, Università di Perugia. [3] Dipartimento di Ingegneria Civile e Ambientale, Università di Perugia.

*Corresponding author e-mail:* bscndr@unife.it

*Keywords:* archaeometry, transport amphoras, multivariate analysis.

The emporium of Gravisca is a well-documented archaeological site located in the ancient Etruria region nearby the Tarquinia area (VT). Since the VII B.C., and almost to the first part of V B.C., several traders from different Greek settlements of Attic peninsula, Ionia and Magna Graecia were drawn here by the opportunity of good affairs (Fiorini, 2005). The wines and oil exchanged were stored inside transport amphoras that now come widely distribute in fragments as archaeological findings. In this work, eighteen catalogued ceramic fragments (Di Miceli & Fiorini, 2019) from the Gravisca site were studied following an archaeometric approach and coupling (1) petrological observations, conducted through Optical Microscopy, Scanning Electron Microscopy, (2) mineralogical analysis by means of X-Ray Powder Diffraction Data and Rietveld refinements for Quantitative Phase Analysisand (3) chemical analysis of major and trace elements through Inductively Coupled Plasma Spectrometry with further transformation into Log Ratio following the Aitchison approach for compositional data analysis (Aitchison, 1982).

The observed evidence from fabric and texture microstructure has been read in the view of different grades of technological specialization of manufactories. Specific transitions metals and rare earth elements were identified as primary markers for reconstructing different geological native areas of clays deposition. Ward's (Ward, 1963) minimum variance method and agglomerative hierarchical clustering procedure was applied to distinguish between rock setting backgrounds formation from ultramafic, felsic-mafic or metamorphic. Multivariate Statistical Analysis was furthermore extended using principal component analysis to obtain clusters directly related to the specific production centres. The main provenance attribution based on morphological type has been compared to the archaeometry results. Samples from the "Samos-Miletus group" of uncertain attribution have been directly related to Samos manufacture. Moreover, two distinct geographic settlements appear to be operating during VII-VI B.C. that could be identified as 'colonial' factories under the control of Samos. The new data concur with a more straightforward historical reconstruction of archaic poleis manufactory and commercial activity towards Etruria and the Mediterranean area.

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# 3D modeling of geosites in Unesco global geoparks as a tool for geosciences dissemination: examples from the IGCP 741 project "3GEO"

Bollati I.M.[1], Cezar L.[2], Fassoulas C.[3], Forzese M.[4], Tronti G.*[1], Ticozzi N.[1], Zucali M.[1], Pelfini M.[1], Aldighieri B.[5], Goyanes G.[5], Loureiro F.[2], Castro E.[2-6], Nikolakakis E.[3], Fazio E.[4], Maniscalco R.[4] & Maglitto D.[4]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Associação Geopark Estrela, Guarda (Portugal). [3] Natural History Museum of Crete, University of Crete, Heraklion (Greece). [4] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [5] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [6] CERENA-IST, CEG/IGOT, Universidade de Lisboa (Portugal).

*Corresponding author e-mail:* irene.bollati@unimi.it

*Keywords:* 3D modelling, geoheritage, UNESCO IGCP-714.

The UNESCO IGCP 714-3GEO Project (https://en.unesco.org/international-geoscience-programme/projects/714) is focused on implementing outdoor activities for Geosciences promotion (geoclimbing and geotrekking), and empowering them through 3D modelling of rocky outcrops and relevant landforms in UNESCO Global Geoparks (UGGps) and aspiring ones. Indeed, different authors have underlined the efficacy of such tools for managing, promoting and protecting geosites (e.g., Aldighieri et al., 2016; Papadopoulou et al., 2021). Different approaches to produce 2D and 3D models, based mainly on SfM (structure for motion) photogrammetry, using both reflex cameras and Uncrewed Aerial Vehicle technologies bearing optical cameras, have been applied at different study cases in European UGGps. In the Sesia Val Grande UGGp (Italy) and in the surrounding areas, where a complete geological section across the Western Alps is observable, 5 rock cliffs equipped for climbing have been identified for 3D modelling, to analyse in detail rock walls structures and to propose an interactive reading of the types of rock and landforms influencing climbing. In the Eastern Alps, other 3D models have been elaborated in Dolomites, on big wall very famous among alpinists. The Rocca di Cerere UGGp (Italy) offers marvellous landscapes where practicing outdoor sports, visiting archaeological sites and mining parks, and experiencing suggestive geohiking itineraries along cut valleys through amazing inclined calcarenite banks eroded by watercourses. In a context where geotrekking activities combine with the beauty of ancient civilization remains the aim was virtually restoring the geoarchaeological heritage in Mt. Capodarso and Mt. Sabucina, between Enna and Caltanissetta towns. In the Psiloritis UGGp (Greece) under a former INTERREG project titled "GEO-IN" a 3-D model has been produced along the Migias' Geotrail which runs across a gorge and then a plateau in Psiloritis Mountains. The model was used to develop a virtual tour along the trail using 360° panoramas that guide visitor along the important geological, natural and cultural features of the trail. Finally, in the Estrela UGGp (Portugal) several geosites have being surveyed to create 2D and 3D digital models useful for detailed mapping and interpretation of the geosites, monitoring the impact of visitors and producing innovative visitation experience for visual impairment or low mobility public. These are some examples of the outputs that will contribute to the final goal of the IGCP 714 project: the building of a 3D models repository to make these sites available also for people not allowed, for different reasons, to visit the sites, as well as to reinforce the experiences of people having the possibility to practice outdoor activities like geoclimbing and geotrekking at such sites.

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# The stratigraphic architecture of Macco (middle Pliocene) in the Tarquinia Basin as controlling factor in the Monterozzi Necropoli placement

Brandano M.*[1], Ronca S.[1], Cardello L.[2], Rinaldi T.[3], Mura F.[4], Innocenzi F.[1] & Tomassetti L.[5]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [3] Dipartimento di Biologia e Biotecnologie «Charles Darwin», Sapienza Università di Roma. [4] Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Sapienza Università di Roma. [5] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* marco.brandano@uniroma1.it

*Keywords:* stratigraphy, necropolis, Pliocene.

The Middle Pliocene shallow water deposits cropping out in Tuscany and Latium (Central Italy) are represented by a lithostratigraphic unit, known as "Macco" (Fazzini et al., 1972). In the Tarquinia basin, the Macco consists of poorly lithified bioclastic calcarenites intercalated with hybrid sandstones and sandstone often with lateral heteropic transitions. The skeletal assemblage is dominated by free living branches of coralline algae, molluscs and foraminifers deposited in a carbonate ramp environment. The terrigenous fraction is mainly composed of monocrystalline grains of quartz and subordinate detrital micas and feldspars, sedimentary lithoclasts (arenites, siltites, sparse limestones). Glaucony grains and opaques are also present.

Based on new field survey in the area and on the comparison with previous works, a new geological map of Tarquinia area has been produced. Multiscale morphologic and structural analysis shows that morphostructural lineaments are fault-controlled mostly by E-W and NW-SE striking fault and fracture zones, locally interested by calcite-bearing veins. Widespread evidence of transtensive syn-sedimentary tectonics is documented by thickness and facies variations across faults, slumps and fault-related unconformable contacts.

In the Tarquinia area, this lithostratigraphic unit hosts the Etruscan necropolis of Monterozzi, UNESCO site since 2004. The necropolis consists of more than 6000 burials of different typology (room tombs, pit tombs and hole tombs) spanning a chronological period from 7$^{th}$ to 2$^{nd}$ century BC (Cataldi 1993; 2001). The aim of this work is to evaluate how the stratigraphic architecture of Macco may have influenced the distribution of burials.

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# *Aqua Alexandrina* and Fragole tank at Tor Tre Teste (Rome): archaeometric characterization of hydraulic mortars

Calzolari L.*, Baiocchi I., Medeghini L. & Mignardi S.

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* laura.calzolari@uniroma1.it

*Keywords:* hydraulic mortars, ancient Roman aqueducts, archaeometry.

The *Aqua Alexandrina* is a Roman aqueduct built in 226 AD by emperor Severus Alexander to supply water to Baths of Nero. Today only archaeological ruins can testify the magnificence of the last of the 11 aqueducts built in the Roman period for the city of Roma. This study focuses on the characterization of the hydraulic mortars from the archaeological remains at Tor Tre Teste Park, including the *Aqua Alexandrina* and Fragole tank, a cistern probably built before the aqueduct which was part of a *villa*.

The aim of this study is to obtain information about the technology and raw materials used in the mortar production and to verify analogies and differences between the two buildings. A multi-analytical approach has been applied including Optical Microscopy (OM) in thin sections and X-ray Power Diffraction (XRPD) to analyze the mineralogical composition, whereas the Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy (SEM-EDS) was applied to determine the morphological features and the chemical composition of both the aggregate and the binder.

The analyses highlighted how the hydraulic property of the mortar was given, in both monuments, by the presence of an aggregate fraction constituted of artificial and natural materials with pozzolanic behavior. The presence of *Pozzolane Rosse*, a pyroclastic product of Alban Hills, testify a local provenance of the aggregate materials. The presence of under burnt marble fragment suggests the use of this rock as raw material for the binder fraction.

# Still functioning ancient Roman aqueducts: characterization of the mortars of *Aqua Traiana* and *Aqua Virgo*

Calzolari L.*, Medeghini L. & Mignardi S.

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* laura.calzolari@uniroma1.it

*Keywords:* hydraulic mortars, ancient Roman aqueducts, archaeometry.

The aqueducts of ancient Rome were built to resist and the fact that two of them are still functioning is the most powerful assessment of this fact. *Aqua Virgo* (built in 19 BC) and *Aqua Traiana* (built in 109 AD) are still carrying water to Rome, the first from the Aniene Valley and the second from the springs located north of Lake Bracciano (Pace, 2010). The long history of these engineering works is complex and characterized by several intervention, but they are still constituted by the original materials.

The aim of this research is to characterize the original Roman mortars from the inner ducts of the aqueduct, compare them with successive interventions, and understand which materials were used to produce such durable mortars. The cooperation of Sovrintendenza Capitolina ai Beni Culturali, Sovrintendenza Speciale di Roma and ACEA allowed the sampling of mortars, done under the supervision of archaeologists.

A multianalytical approach was chosen, to obtain as much information as possible concerning the binder and the aggregate, their interaction and the hydraulicity of the mortars. Thin sections of the samples were investigated through optical microscopy (OM), scanning electron microscopy (SEM-EDS) and with electron microprobe analysis (EMPA). Powdered samples were investigated with X-ray powder diffraction (XRPD) and the fraction most representative of the binder ($< 63$ µm) was analyzed by thermogravimetric analysis (DSC-TGA) (Bakolas et al., 1998).

Some of the mortar samples analyzed differ from those reported in previous studies in the literature as the binder shows no calcite and instead an amorphous gel-like binder, highly hydraulic, ascribable to hydraulic C-A-S-H phases (Seymour et al., 2022; Torraca, 2009). The aggregate is mainly constituted by natural materials with pozzolanic behavior, as reported by ancient sources. These findings confirm that the ancient Roman technique for the realization of hydraulic mortars allowed to obtain high quality materials.

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# Assessing geodiversity and the potential for a new geopark – The case study of Lumignano and Costozza (Berici Hills, northeastern Italy)

Chimento F.[1], Tusberti F.[1], Brandano M.[3], Breda A.[1], Massironi M.[1], Perissinotto M.L.[2], Tomassetti L.[4] & Preto N.*[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Regione Veneto - Direzione Difesa del Suolo e della Costa, U.O. Servizio Geologico, Venezia. [3] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [4] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* nereo.preto@unipd.it

*Keywords:* geoheritage, geological mapping, Oligocene.

The villages of Lumignano and Costozza are located in the Berici Hills, an isolated group of hills topped by a karst plateau, Northeastern Italy. They are well known among climbers as the cliffs host more than 300 climbing routes. The area has always been attractive for the pervasive presence of caves, quarries and the cliffs that surround and overhang the villages, thus the aim of this work was to unveil the geological heritage of the area for outreaching purposes. Within this work a detailed geological map of the area was done by collecting more than 150 samples of rocks. Rocks samples were cut and polished and then categorized by facies. Five facies associations corresponding to 5 different environments inside a carbonate platform of lower Oligocene age have been mapped. Mapping highlighted the lateral relationship between these facies and the real geometry of the platform, and furthermore new volcanic deposits and faults systems were detected. Three outreach products have been made: a popular science publication in a mountaineering magazine, and then a geological trail and an exhibition, that were presented during the local peas festival. The geological trail is 7 km long, and it makes a ring around the village of Lumignano, it allows to recognize facies, landscapes and caves. In the exhibition, the geological map was presented along with a reconstruction of the carbonate platform in the past, next to 3D models of the most important cliffs and pictures of rock samples. All of this was only possible thanks to detailed mapping that highlighted 32 geoheritage sites in the area. This is an example and a warning on how many geosites are yet to be discovered, and how popularization and valorization of geoheritage will be limited, until geological mapping in Italy will continue to chronically lagging behind.

# A machine learning approach for obsidian provenance studies based on SEM images

Coïsson M.*, Olivetti E., Ansalone P., Martino L. & Ferrara E.

Metrologia dei materiali innovativi e scienze della vita, Istituto Nazionale di Ricerca Metrologica, Torino.

*Corresponding author e-mail:* m.coisson@inrim.it

*Keywords:* obsidians, machine learning, SEM.

Machine learning is emerging as a novel tool for identifying hidden relationships among objects and classes of objects in several scientific domains. Supervised machine learning classifiers, fed with labelled data and suitably trained, may be able to properly recognise unlabelled data, based on multiple similarities that are not obvious to the human eye. In this work, we explore the possibility of exploiting a machine learning approach to a specific case study: the provenance determination of obsidian samples based on the back-scattered electron (BSE) images that may be used to characterise this volcanic rock petrographically (Burton & Krinsley, 1987).

Sourcing of obsidian archaeological artefacts is a well-established way of understanding the socioeconomic context and trade routes of ancient populations since the number of geological sources of this material, e.g., in the Mediterranean region, is limited. Among the several methods of geochemical sourcing, the recognition of the origin of obsidian samples based on the identification of microphenocrysts (granulometry and morphology of crystalline precipitates, embedded within the vitreous matrix) is of utmost importance because it could confirm previous studies aiming at classifying obsidian sources according to the magnetic properties (Zanella et al., 2012; Ferrara et al., 2019). To achieve this goal, we have selected a dataset made of several images of polished obsidian fragments taken with a scanning electron microscope (SEM) operating in backscattered electron contrast. The samples come from flows of different Mediterranean islands, namely: Lipari, Sardinia, Pantelleria, Palmarola, and Melos. Under the SEM, they mainly differ in their general appearance, with a flatter or more granular surface, due to a more or less pronounced porosity in the matrix, and in the amount and morphology of crystalline inclusions. Although some BSE-observable features are pretty distinctive of some sources, the differences among samples with different origins are not always clear enough to allow a direct or correct attribution even to the expert eye.

In this work, we have selected a few supervised machine learning models (e.g., neural network, random forest) to classify the polished obsidian fragments from their SEM images, by extracting from them, through suitable filters, parameters linked to their morphology. The accuracy of this kind of classification, which, as previously commented, could be extremely challenging even for an expert human eye, is verified on testing sets using cross-validation techniques. Suggestions will be given on collecting SEM images with coherent information to build a robust dataset exploitable by machine learning methods.

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# Treatments by titanium dioxide nanoparticle coatings on the surface of the "Arabescato" marble (Carrara variety): a comparison between natural outdoor and accelerated laboratory aging conditions

Curuzzi M.*[1], Renzulli A.[1], Quagliarini E.[2] & Bordini D.[3]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Ingegneria Civile, Edile e Architettura, Università Politecnica delle Marche. [3] S2 S.p.A., Fermignano (PU).

*Corresponding author e-mail:* m.curuzzi@campus.uniurb.it

*Keywords:* titanium dioxide, cultural heritage, self-cleaning.

The use of solutions based on titanium dioxide ($TiO_2$) nanoparticles to obtain protective coatings is extensively reported in literature. The utilization of $TiO_2$-nanocoatings offers many advantages such as a low cost of production and an easy application method on a wide range of materials that make these solutions increasingly used in many sectors. In fact, $TiO_2$-nanocoatings reveal photocatalytic and super-hydrophilicity properties when exposed to ultraviolet light. Covering stone materials with thin coats of $TiO_2$-nanoparticles are revealed self-cleaned and able to avoid the formation of biofouling, water repellent and self-sanifying without altering their physical and aesthetic properties (La Russa et al., 2016; Quagliarini et al., 2018). For examples, the high versatility of $TiO_2$-nanocoatings is also increasingly spreading in the field of Cultural Heritage as a preventive treatment in the preservation of sculptures, paintings and architectural works**.** Previous works were however only focused on data obtained through accelerated aging experiments in laboratory, partially considering the impact of outdoor natural climatic conditions such as rainfall, wind, temperature, pollution and local environmental constraints such as exposure to the geographic cardinal points, buildings design, nature of the ground and presence of local moisture and/or industrial activities (Tran et al., 2014).

In the present work, the white marble commercially known as "Arabescato", belonging to a variety of the "Carrara Marbles" and considered one of the most valuable and sought stone materials in the outdoor and indoor luxury furniture, will be tested as stone material substrate for the application of the $TiO_2$-nanocoatings. The first phase of physical, textural, and mineralogical characterization of the "Arabescato" substrates through the roughness analysis, laser profilometry, porosity, capillary absorption and colorimetry was carried out. The evaluation of the effectiveness of the titanium dioxide nanoparticle treatments will be performed through the comparison between the monitoring of "Arabescato" samples where different types of $TiO_2$-nanocoatings are used and subsequently exposed to both natural outdoor and accelerated laboratory aging conditions.

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# Assessment of mitigation measures and risk scenario of the museum collections: an application to the National Archaeological Museum Villa Frigerj in Chieti (Central Italy)

Falcone F.*[1], Stoppa F.[1], Guglielmelli F.[2], Belfiore V.[3] & Rosatelli G.[1]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti.
[2] SGM Experimentation s.r.l., Laboratori di ingegneria sperimentale, Perugia. [3] Direzione Regionale Musei Abruzzo, Ministero della Cultura, Chieti.

*Corresponding author e-mail:* francesca.falcone@unich.it

*Keywords:* risk management, seismic vulnerability assessment, protection cultural heritage.

Heritage is a precious memory inherited from the past and a resource to protect for the future. The earthquake in L'Aquila in 2009 caused considerable damage, caused by the instability of the museum buildings, the collapse of exhibitors, the breaking of glass shelves, the overturning of objects, the movement of pedestals and the reception of art masterpieces (Indirli et al., 2013). An interdisciplinary study on the danger of damage, vulnerability and exposed value to mitigate the risks of the National Archaeological Museum housed at Villa Frigerj in Chieti, it is necessary to divide the research into four related aspects: a geological assessment including the effects of site amplification, assessment of seismic hazard scenarios, the study of the vulnerability and the dynamic response of the building and finally the assessment of the vulnerability mitigation scenarios both for the building and for the exhibitors (Sangiorgio et al., 2021). Experimental vibrational measurements, integrated with geophysical and geomorphological data, have allowed the verification of the suitability of structural mechanical mitigation systems of exhibitors of museum collections, showcases, bases and pedestals (Yang et al., 2020). Analysis carried out with reference to the provisions of UNI 9916:2014 (assessment of the effects of vibration on buildings), DIN 4150-3, 1999-02 (assessment of the effects of vibration damage on buildings). After assessing whether the building is structurally seismo-resistant (minimum target no level of collapse), exhibitor can also be made Seismo-resistant (Terenzi et al., 2020). We then proceed to the ad hoc adaptation of the collections through the study and development of innovative and experimental shock absorbers/ insulating heatsinks (passive electromagnetic, mechanical). The approach of this study reverses the logic of protecting cultural heritage by transforming it into anctivee preventive action.

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# Geomorphological tools to assess the preservation of the archaeological record of tell-sites in the Kurdistan Region of Iraq

Forti L.*[1-2], Brandolini F.[3], Oselini V.[4], Peyronel L.[5], Pezzotta A.[1], Vacca A.[5] & Zerboni A.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Istituto di Geoscienze e Georisorse, CNR, Pisa. [3] McCord Centre for Landscape, School of History, Classics and Archaeology, Newcastle University (UK). [4] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna. [5] Dipartimento di Studi Letterari, Filologici e Linguistici, Università di Milano.

*Corresponding author e-mail:* luca.forti@unimi.it

*Keywords:* RUSLE model, geoarchaeology, Near East.

Geomorphology offers fresh tools for mapping landforms that are continually modelled by erosional and depositional processes; the same tools can be applied to archaeological contexts. In arid and semi-arid regions, such as the Kurdistan Region of Iraq, the preservation of the archaeological record is mined by ongoing climate changes and human overgrazing. In our work, we present a multiscalar geomorphological surveys of both the landscape around the archaeological sites of Tell Helawa and Tell Aliawa (SW of Erbil) and detail geomorphological mapping of erosional processes acting on the two archaeological settlements. Remote sensing and field survey highlights that at the scale of single tell sites – meaning archaeological mounds – ongoing erosional processes acting along slopes are threatening the preservation of the archaeological record. For the first time, we applied the RUSLE model for soil loss to tells. Data derived from UAV imagery of each tell and their programmatic elaboration highlight that the erosional risk is maximum where the slope gradient is moderately steep, the incision depth of gullies is higher, and grazing (cultivation and herding) intense. Our results suggest that the RUSLE model and other geomorphological tools allow assessing the erosional rate along anthropogenic mound thus estimating the risk of losing the archaeological record. Our approach allows to estimate the amount of soils/sediments loss and propose mitigation strategies to prevent the loss of the archaeological record.

# Widespread Science Museums for the development of a sustainable life strategy in urban areas: an application to the city of Rome

Garuti L.*[1], Corrado S.[1], Cifelli F.[1] & Trippanera D.[2]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Aeromatic s.r.l., Roma.

*Corresponding author e-mail:* lorenzo.garuti@uniroma3.it

*Keywords:* geoeducation, urban sustainable development, virtual fieldtrip.

The use of new medias based on information technologies and multimedia contents has seen a significant increase in recent years, contributing to the dissemination of scientific knowledge. On the other hand, this intense digitization of information caused a progressive decrease in direct experience, essential in scientific disciplines. The direct observation of the territory is even more difficult in a highly anthropized environment, such as big cities. In this context, the development of formative and informative channels, aimed to provide a solid basic knowledge for a sustainable and therefore responsible development of the territory and the communities on it, represents a fundamental tool. This work aims to develop a modern integrated model of scientific information in Geosciences field in order to spread geological knowledge and to contribute to the improvement of life quality in urban areas, taking as an example the city of Rome. A key objective will be to bring citizens closer to the use of the scientific method to reach a broader view of the connection between the territory, geosciences and daily life. It will be essential to promote direct experience, supported by the use of a wide range of multimedia supports, trying to engage people within the learning process, making it active and participatory. Furthermore, the Widespread Museum, proposing cultural itineraries inside not only the single museum or natural site, but also inside the territory that hosts it, allows to connect different sites of interest through thematic itineraries aimed at providing an information service and the enhancement of the territory. Creating an integrated network of outdoor and indoor geological itineraries in central and peripheral sectors of the city will be the core of this project. In this context, developing laboratory paths and multimedia topics with the help of new technologies such as drone detection, virtual reality (VR) contents, 3D objects print and design, will allow greater use and understanding of the scientific results obtained. The city virtual fieldtrip will be developed using the structure-from-motion (SfM) photogrammetry technique from drone-based image collection, the augmented reality (AR) and the virtual reality to visualize geological structures and their features in an urban context. The users in fact, by scanning a QR code or using a VR goggle by remote, will be able to visualize and join a 3D-immersive scientific experience of urban landscapes and monuments, easily accessible and integrated with a detailed and interactive geological description. In addition, for indoor laboratories, 3D object printing will help to create an educational approach that combines digital creation and object manipulation, which contributes to a better knowledge and understanding of Earth's natural processes and their features.

# Chemical and isotopic provenance study of Final Bronze Age glass artefacts from Central Italy

Giannetti F.[1], Avanzinelli R.[1], Braschi E.[2], Cantisani E.[3], Casalini M.*[1], Langone A.[2], Vettori S.[3] & Virili C.[4]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze. [3] Istituto di Scienze del Patrimonio Culturale, CNR, Firenze. [4] Dipartimento di Scienze dell'Antichità, Sapienza Università di Roma.

*Corresponding author e-mail:* martina.casalini@unifi.it

*Keywords:* glass artefacts, Sr-Nd-Pb isotopes, Final Bronze Age, provenance.

The study of ancient glasses provides key information for the reconstruction of the old trading routes, the identification of local production sites and the investigation of the habits and social status of ancient civilizations. During the last decades, the application of trace elements contents and radiogenic isotopes systematics (e.g., Sr, Nd, Pb) in provenance studies has become a powerful tool to discriminate among different (but geologically well defined) sources of raw materials.

We present a detailed study on four glass beads and a vessel's fragment excavated from an archaeological site in central Italy, near the Piediluco Lake (Terni), attributed to the final Bronze-early Iron age. The samples are part of a large series of glass artefacts and were selected for their representative shape (horned, annular, barrel shaped, fragment of vessel), color (from blue to sky blue and aqua green), and decoration (white spiral). The analytical approach aims to investigate the different portions of each sample with the intent to combine major, trace elements and Sr-Nd-Pb isotopes information to identify the raw materials' provenance.

Major elements indicate that the four beads are LMHK (Low Magnesium High Potassium) glasses, due to the low MgO and high $K_2O$ content, which is a typical composition for pre-historical Italian glasses, with Frattesina (Rovigo) being one of the most active centers. The vessel's fragment shows high $Na_2O$ and low MgO instead, and it can be classified as Natron Glass, possibly indicating a different production and/or trade route.

Among trace elements, Zr, Ti, Cr and La are diagnostic of the sand used as silica source. Our results show a good agreement for the two annular beads and the white part of the barrel shaped bead with glasses ascribed to Frattesina, whilst the fragment shows a different signature.

Blue samples can be distinguished by the trace elements used as colourants, namely Co-Cu and Cu-only. The correlation between Co and Cu with other diagnostic trace elements such as Ni, As, Sb and Pb reveals the use of different mineral phases as sources of colouring elements, which may also indicate the exploitation of different ores. White decorations are different, as well: those on the LMHK glass are rich in silica and Ca, whilst white decorations on Natron glass show high Ca and Sb contents, supporting the hypothesis of a different production for this artefact.

Pb isotope results are compared to literature data on Cu and Co ores from the Mediterranean: different bead types correlate with the signature of ore deposits, from the Alpine to the Southalpine and Austrian ore province down to Tuscany. The Pb signature of the vessel is different and may be linked to Eastern Mediterranean ores or to the Spanish Betic Range Ores province; further insights on the possible sources can be done coupling Pb isotopes with specific elements (As, Co, Ni) and thus possible ore minerals (e.g., skutterudite).

# Geoheritage in the Fallère Lake area, Aosta Valley

Gianotti F.*, Forno M.G., Gattiglio M. & Dolce S.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* franco.gianotti@unito.it

*Keywords:* geoheritage, Pleistocene glaciers, deep-seated gravitational slope deformation.

The Fallère Lake area is located in the upper Clusellaz Valley, an about E-W trending valley in the middle Aosta Valley. It is shaped in micaschist and gneiss referred to Fallère and Métailler units (Middle Penninic) near the tectonic contact with calcschist and marble of the Aouilletta Unit (Upper Piedmont Zone).

This area was largely shaped by Pleistocene glaciers, that formed a wide cover of glacial sediments and significant mountonneé rocks (Forno et al., 2012). In addition, it was affected by deep-seated gravitational slope deformation (DSGSD), characterized by extremely fractured rocks and evident morpho-structures involving both bedrock and Quaternary succession (Forno et al., 2013; 2016).

The DSGSD evolution in a glacial environment produced, as observed in other areas (Forno et al., 2020), significant effects both on the facies of Quaternary sediments, that appears particularly rich in rock fragments, and the formation of numerous and wide moraines, that result more extensive than in areas with normal-fractured bedrock. In detail, the glacial phenomena in this geological setting promoted strong erosion and consequent deposition of large amount of glacial sediments, essentially formed by angular small rock fragments, even by small glaciers.

Moreover, this area shows peculiar features connected to DSGSD, comprising a lot of trenches and minor scarps. In detail, the NE-SW elongated Fallère Lake is located along trenches that isolates, from the main Mont Fallère summit, a high morphological sector that forms an evident bulging relief (Forno et al., 2021). Consequently, the investigated area is a significant example of geoheritage both of glacial and DSGSD landforms.

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# The coastal zone conservation and potential: a new perspective from Environmental Function Analysis

Giordano L., Buonocunto F.P.*, Ferraro L. & Milia A.

Istituto di Scienze Marine, CNR, Napoli.

*Corresponding author e-mail:* francescopaolo.buonocunto@cnr.it

*Keywords:* sustainability, EFA, Campania coastal.

In the last decade, the conscious need for sustainable development in coastal zone systems impose a close balance with the anthropogenic environment. Mostly, incorrect management of human activities and geo-environmental resource exploitation are often liable of changing the future of a coastal area leading to land-use conflicts. A comprehensive assessment of the environmental quality of a coastal area can be performed by means of Environmental Function Analysis (EFA) employing physical and biogeochemical versus socioeconomic indicators (Cendrero & Fisher, 1997). The coastal region can be split into geo-environmental and socio-economic components identified by some specific features represented by a set of indicators (Cendrero & Fisher, 1997) supported by a matrix based on the principles of Ecosystem-Based Management (de Groot, 1992). In the era of open data, national geo-databases and environmental agencies reports and databases represent an important resource of information to reduce the subjectivity of EFA indicator construction.

This study reports and compares the application and efficacy of the EFA tool to discover the potential for conservation of two different Campania coastal areas (Italy). The first site is located in the Volturno River Coastal Zone, a human-impacted area in which the study area extends for 50 km$^2$ on-land and seaward. In this case the EFA analysis testified a full conflict of use with a tendency towards high conflict rather than preservation as one might expect (Giordano & Ferraro, 2020). The second EFA site is located in the Sorrento Peninsula and aimed to investigate the conservation potential and the possible anthropic influence on two selected areas extended on-land and seaward for 11 km$^2$ in the Punta Campanella Marine Protected Area (MPA). EFA indicators have been characterized on the base of literature data, geophysical, geological, environmental and socio-economical datasets from national geo-databases including also a bio-indicators analysis.

Moreover, for both case studies the EFA indicators included several environmental components both marine and terrestrial, comprising water column features, inorganic pollutants (heavy metals) and benthic foraminiferal assemblages as well as terrestrial biota, fresh water supply and quality, land use, and natural hazard. Results demonstrated that EFA is adaptable to different case studies ranging from original beach application to territorial management and environmental sustainability assessment in coastal zones.

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# Deformed metaconglomerate of Pinerolo Unit along the Val Germanasca: a twofold geosite

Iaccarino S.* & Petroccia A.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* salvatore.iaccarino@unito.it

*Keywords:* geosites, structural geology, Western Alps.

Understanding the aspects of natural rocks and geological processes is a classical activity in science learning. Often, students struggle with connecting observations to theoretical concepts. Although new modern digital techniques for teaching have been integrated with the traditional Earth Science education mainly due to the last pandemic situation, direct outcrop observation remains fundamental and irreplaceable teaching tool in geology. Deformed metaconglomerate, due to the presence of good strain markers, i.e., pebbles, represents a key lithotype to understand theoretical aspects of structural geology such as finite strain and progressive deformation. In this framework, within the blueschist-facies Pinerolo Unit in the Western Alps (Piedmont, Italy; Vialon, 1966; Borghi et al., 1984), a well-exposed water-polished polygenic metaconglomerate is easily accessible (https://outcropedia.tectask.org/poi/ponte_battarello-cuneo/). This location, proposed as geosite (Petroccia & Iaccarino, 2021), has twofold relevance: (i) it has many implications on both the palaeogeography of the Briançonnais domain and on the later Alpine tectono-metamorphic evolution (Manzotti et al., 2016); and (ii) it recorded several features related to ductile deformation that are clearly observable and recognizable within the outcrop, e.g., the original bedding and its relationship with the subsequent deformation phases (Borghi et al., 1984). The 3D shape of pebbles on different outcrop sections, generally indicates constrictional strain (with L > S tectonite to L tectonite). Starting from the outcrop observations, the integration with different laboratories activity (microtectonics, metamorphic petrology, geochronology), it is possible to open a window for both geologists and for non-specialists on the pre-Alpine and Alpine history. Thanks to the extraordinary features and the clear exposure, this geosite represents a spectacular locality both for the Alpine geology and geoeducational activities, to be valorized.

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# Geosites recognition and geosystem services assessment in Alagna Valsesia (Monte Rosa, W-Alps, Italy): a sustainable development perspective for an Alpine Geopark

Khoso R.B.*[1], Guerini M.[1], Gentilini S.[1-2], Tognetto F.[1], Viani C.[1] & Giardino M.[1-3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Magma Geopark, Egersund (Norway).
[3] Geoparco Sesia-Val Grande, Varallo (VC).

*Corresponding author e-mail:* rasoolbux.khoso@unito.it

*Keywords:* geosites, geosystem services, sustainable development.

In the last century, mountain regions have been deeply influenced by human activities and global drivers of change, resulting in huge alterations and reinterpretation of the balance of these environments (Egan & Price, 2017). Demanding the need to devise new preservation strategies to support mountain regions. Numerous research has been carried out within the Sesia Val Grande UNESCO Global Geopark (UGGp) to recognize and classify geosites and geoheritage sites to enhance and preserve places of significant geological, geomorphological, historical, cultural, or artistic value and to promote geotourism (Tognetto et al., 2021). Until now, 68 geosites have been classified and mapped (Perotti et al., 2020). In this framework, we concentrated in the highest elevation area of the Sesia Val Grande UGGp. Here we examined available data to recognize the geosites within the municipality of Alagna Valsesia and assessed the role of geosites in providing various geosystem services. Landcover maps have been produced by remote sensing analysis to establish the change detection analysis and help understand the changing dynamics of the environment. Regulating, provisioning, knowledge, cultural, and supporting geosystem services have been identified and mapped in the GIS environment, with a broad view on evolutionary scenarios of human-nature interactions. The mapping assessment shows the critical evaluation of the benefits offered by the study area and the vulnerability caused by natural events to the man-made infrastructure development. This approach provides the basis for understanding the natural and human-induced threats to geodiversity and aids in formulating strong planning and management strategies for the Sesia Val Grande UGGp and for sustainable development of human exploited and naturally vulnerable mountain regions. This approach also makes it possible to understand where geoheritage is present and to foster enhancement of sustainable geotourism destinations.

Egan P.A & Price M.F. (2017) - Mountain Ecosystem Services and Climate Change: A Global Overview of Potential Threats and Strategies for Adaptation. United Nations Educational, Scientific and Cultural Organization, France.

Perotti L., Bollati I. M., Viani C., Zanoletti E., Caironi V., Pelfini M. & Giardino, M. (2020) - Fieldtrips and virtual tours as geotourism resources: Examples from the Sesia Val Grande UNESCO Global Geopark (NW Italy). Resources, 9, 63.

Tognetto F., Perotti L., Viani C., Colombo N. & Giardino M. (2021) - Geomorphology and geosystem services of the Indren-Cimalegna area (Monte Rosa Massif - Western Italian Alps). J. Maps, 17, 161-172.

# A Roman kiln excavated at Costigliole Saluzzo connects archaeological, archaeometric and archaeomagnetic investigations

Leite Santos Y.*[1], Tema E.[2-3], Gulmini M.[1], Davit P.[1], Elia D.[4], Meirano V.[4] & Fantino F.[5]

[1] Dipartimento di Chimica, Università di Torino. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Laboratorio di Paleomagnetismo Alpino, Centro Interuniversitario di Magnetismo Naturale «Roberto Lanza», Peveragno (CN). [4] Dipartimento di Studi Storici, Università di Torino. [5] Turin Thermoluminscence Analysis, Torino.

*Corresponding author e-mail:* yuri.leitesantos@unito.it

*Keywords:* archaeometry, archaeomagnetism, baked clay.

The mutual efforts of archaeology and geosciences can provide quality data regarding the characteristics, production technology and dating of archaeological artefacts. This study presents the integrated results of archaeological and archaeometric analyses applied to an ancient kiln discovered at the archaeological site of Costigliole Saluzzo, in Northwest Italy. Since 2003, several archaeological excavations brought into light a large *villa rustica* dated at Roman times, between the first and the third century AD, thanks to stratigraphic and archaeological evidence. In this study, baked clay pieces from a small circular baked clay kiln found in the *villa* were collected and used to better undersand the firing conditions, reconstruct the ancient geomagnetic field and chronologically constrain the kiln last use. 15 samples were taken from different parts of the kiln for archaeomagnetic investigation, oriented in situ with compass and inclinometer, while further 3 samples were used for thermoluminescence (TL) dating. Pieces of the same samples were also used for chemical and Fourier Transform Infra Red (FTIR) analyses. Heating influences specific regions of clays' FTIR absorption spectra, namely those related to the Si–O–Si stretching, to the Si–O–Al bending and to the stretching of bound hydroxyl groups, therefore absorption bands can be used to investigate the temperature distribution in the different parts of the kiln. The obtained archaeomagnetic results show that the baked clays were characterized by a good magnetic stability and systematic alternating field demagnetization procedures successfuly determined the direction of the characteristic remanent magnetization recorded during the last use of the kiln. TL dating, calculated after having estimated both Palaeodose and Annual Dose, suggests that the kiln was most probably last fired in the interval 211 - 531 AD with 95% confidence. Such results integrated with the availabe archaeological evidence suggest that the kiln was still in use during the first part of the 3rd century AD and was abandoned before the last building phase of the roman *villa*, which obliterated it. This study highlights the importance of multidisciplinary investigations and the contribution of different techniques in the investigation of archaeological sites, with archaeology and natural sciences interacting to improve our knowledge of both the archaeological heritage as well as of the past geomagnetic field variations which in turn can be used as dating tool.

# A Multidisciplinary approach for monitoring the conservation state of the sandstones of the Palazzo Ducale in Camerino (MC)

Mammoliti E.*[1], Cupido M.[2], Teloni R.[3], Malavolta M.[1-3], Santini S.[2], Farabollini P.[1], Morici M.[4] & Leoni G.[4]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [3] GeoMORE s.r.l., spin-off Università di Camerino. [4] Scuola di Architettura e Design, Università di Camerino.

*Corresponding author e-mail:* marta.95.cupido@gmail.com

*Keywords:* rock weathering, Equotip hardness tester, geoheritage.

While negative impacts of climate-related and other hazards on urban areas are widely discussed in the scientific literature, their impact on historic buildings is still understudied (Bigio et al., 2014). In this regard, the 2016-2017 seismic sequence in Central Italy, which represents the second major disastrous event in the last decade on the Apennines, caused heavy damage of tens of municipalities, thousands of buildings and mostly important, life losses. These events highlighted the need to involve innovative non-invasive techniques to preserve the existing architectural heritage, carrying out studies on both the structural and decorative elements of historic buildings (e.g., columns, capitals and other stone elements such as architraves or facade adornment).

This is the case of the Palazzo Ducale, one of the main historic buildings in the town of Camerino (Central Italy) protected by the Superintendent for cultural heritage of Marche Region (peripheral body of the current MiBAC Ministero per i Beni e le Attività Culturali), where a multidisciplinary study on the sandstone columns was carried out for its restoration. In this regard, the use of Equotip hardness tester was proposed to implement a new approach for non-destructive evaluation of both the superficial and the internal hardness of the sandstone columns, useful to understand the rule that weathering plays on the mechanical rock properties (Mammoliti et al., 2021).

In addition, a sedimentological study coupled with mineralogical-petrographic analyses (thin sections and XRD) were used to assess the extraction site of the sandstone columns, investigating an outcrop at the Botanical Garden of the city, just beneath the building of Palazzo Ducale. This aspect was essential to find a suitable site to extract rock samples for the Uniaxial Compressive test. In this way, the impossibility of using invasive techniques that could damage historical structures was overcome and a comparison of the mechanical properties was possible.

Eventually, a conservative treatment on the surface was proposed and Equotip has been also tested to verify the effective improvement of rock hardness after the intervention.

Bigio A.G., Ochoa M.C. & Amirtahmasebi R. (2014) - Climate-resilient, Climate-friendly World Heritage Cities. Urban Development Series Knowledge Papers no. 19. World Bank, Washington, DC.

Mammoliti E., Ferretti A., Malavolta M., Teloni R., Ruggeri P. & Roselli G. (2021) - Defining a non-destructive in situ approach for the determination of historical mortar strength using the Equotip hardness tester. Appl. Sci., 11, 4788.

# Using landscape features to understand Bronze Age spatial occupation strategies (Sardinia, Italy)

Mariani G.S.*[1], Brandolini F.[2] & Melis R.T.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] McCord Centre for Landscape, Newcastle University (UK).

*Corresponding author e-mail:* guidos.mariani@unica.it

*Keywords:* geomorphology, Bronze Age, human-landscape interactions.

The exploration of cultural heritage is often not only a matter of material cultures, but a way to reconstruct the lifestyle of past populations. One of the key factors in getting information about sustenance strategies is to look at settlements and their relationship with resources in the surrounding landscape. The spatial organization of human occupation is a function of choices which follow precise rules dictated by both socio-economic and environmental causes. A look at the geology and geomorphology of a landscape gives a helpful perspective in this task. The geological substrate and the landscape features it develops are the main providers of natural resources and leave a mark on land use in past cultures. In choosing the shape of their presence on the territory, populations adapt to local conditions and try to adopt the most fruitful sustenance strategies.

Not much is known about the land occupation strategies of the Nuragic people, the native inhabitants of the island of Sardinia (Italy) during the Bronze Age. The Sardinian physical territory is high in diversity of landscapes and characterized by an uneven distribution of resources. As such, Nuragic populations had to adopt a flexible approach to land use. We investigated this issue in the southwestern corner of Sardinia by combining landscape mapping and spatial statistics tools in an interdisciplinary approach. We looked not only at topographic parameters, but also at the main geological and geomorphological features of the area. With that information, we constructed a map of land units and compared them with the distribution of Bronze Age megalithic towers (Nuraghes).

The location of the vast majority of nuraghes shows a distribution concentrated in low- and mid-elevations, in correspondence with the main waterways, and in proximity with permeable soils. Mountain environments and rough terrain are instead almost completely empty of Nuragic towers. The most densely settled areas are also those with the highest variety of land units, suggesting a preference for complex physical environments in which resources are potentially more diversified. The need for land control, but also for structural stability for megalithic monuments, might also have pushed these populations to choose locations higher than their surroundings on hard geological substrates and low slopes. Tower concentrations are also often not far from the coast, possibly hinting at a close relationship with the sea.

# Strontium isotope analysis for pottery provenance studies along the Nile: does it work?

Maritan L.*[1], Gravagna E.[1], Cavazzini G.[2], Mazzoli C.[1], Usai D.[3] & Salvatori S.[3]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Istituto di Geoscienze e Georisorse, CNR, Padova. [3] Centro Studi Sudanesi e Sub-Sahariani, Treviso.

*Corresponding author e-mail:* lara.maritan@unipd.it

*Keywords:* Sr isotopes, pottery, Nile River.

Provenance of raw materials is extremely important in archaeological studies because it helps to reconstruct possible trades, exchange activities and social organization within ancient societies. Specific petrographic markers and geochemical signatures of reference groups and clay deposits may provide constraints on the possible provenance of raw materials and ceramic products for coarse and fine paste pottery, respectively. Unlike human remains and other materials used in antiquity (such as obsidian, marble and glass), the provenance of pottery has been only recently investigated by isotope analysis and limited to few cases, since the isotopic signature of a potsherd depends on both that of the clay and of the possible added temper. This research explores the possibility of combining petrographic, geochemical and strontium isotope analyses on the study pottery from central-northern Sudan, to understand the social organization, the material culture and their changes occurring from the Mesolithic to the Neolithic period at regional level. Previous archaeometric analyses indicate that the pottery is here characterised by a variety of decorative motives, and produced by river clays tempered with quartz or K-feldspar. For the first ceramic type paste (quartz-tempered), the monotony of the Nubian desert sand did not allow to univocally constrain the provenance of the pottery tempered with quartz sand. On the basis of the Sr isotope ratio and for comparison with sediments collected along Nile and its tributaries, characterised by different isotope signatures in relation to the different rock types outcropping in the respective hydrographic basins, the provenance of pottery was defined. Possible cases of Sr contamination related to the use of the pottery or to post-depositional alteration were also identified and critically analysed in terms also of Sr isotope ratio.

# Soil trail as tool to promote geo- and cultural- heritage

Masseroli A.*, Fracasetti L. & Trombino L.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* anna.masseroli@unimi.it

*Keywords:* geopedology, geoarchaeology.

The soil is a component of geodiversity, and possesses heritage characteristics, being the interface between different spheres, and thus providing knowledge of how the geosphere works and interacts with other Earth subsystems.

To promote soil as element of geoheritage, we aim to realize a geotouristic trail focused on soil and geoarchaeology in the area of Mt. Cusna (2121 m a.s.l.), within the Tuscan-Emilian Apennine National Park (Northern Apennines).

Based on geopedological, geoarchaeological and geomorphological data gathered in over 20 years of research, we plan a multidisciplinary trail, which runs from about 1240 m a.s.l. to 1763 m a.s.l. and it is about 8 km long.

The multidisciplinary and multianalytical approach used to study and characterize this area allowed selecting, along already existing paths, six soil profiles as site of pedological interest, whereas three sites are chosen to show the geomorphological context of the area.

In each of the six sites of pedological interest, the soil evidence allows reconstructing the paleo-environmental and paleo-climatic conditions, and/or retracing the human impact that have affected the area over time.

In detail, the soil mainly recorded, through its physical and chemical properties and pedological features, the influence of climatic variations, the changes in vegetation cover and geomorphological processes, while, in some sites, the presence of traces and/or archaeological findings highlights how human settlements and activities have affected the area over time, too.

In order to communicate the information about the soil trail, illustrative panels were prepared for each site of pedological interest. Every panel contains soil profile characteristics and shows its subdivision into horizons.

To stimulate curiosity and wonder, non-conventional data are also included in each panel, according to the illustrated topic. For instance, soil thin section images (i.e., microphotograph) or archaeological findings pictures were included. The panels are planned either to be installed on site or preferably made available in digital version.

In this way, the interactivity of the trail brings the visitor closer to the soil, often poorly known or even underestimated in its ecological, economic and above all cultural value.

Moreover, promoting the soil variability and the geoarchaeological features, the trail increases the cultural opportunities of the area, since the Mt. Cusna is already a geosite, but focused on stratigraphic, geomorphological and structural geology topics.

# The use of innovative, non-invasive and non-destructive methodologies for the survey of buried archaeological structures: the case study of S. Balbina in Roma (Italy)

Mattia M.*[1], Barone P.M.[2], Facchin G.[3], Narducci R.[4], Portaro M.[1], Rustico L.[4], Soligo M.[1], Tuccimei P.[1], Wueste E.[3] & Bellatreccia F.[1]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] School of Science and Technology, Nottingham Trent University (UK). [3] Archaeology and Classics Program, The American University, Roma. [4] Soprintendenza Speciale Archeologia, Belle Arti e Paesaggio, Roma.

*Corresponding author e-mail:* martina.mattia@uniroma3.it

*Keywords:* total gamma radioactivity, GPR.

The non-invasive and non-destructive methods of exploration and analysis of the subsoil have acquired, over the last years, increasing importance especially in the preservation of archaeological heritage. The possibility of revealing the presence of buried structures and artefacts without moving objects from their original location or before carrying out archaeological excavation, is of great interest to scientists. The aim of this work is therefore to present the joint application of the innovative and non-invasive total gamma radiation measurement technique and the Ground Penetrating Radar (GPR) for the identification of structures buried at a shallow depth. The surveys were carried out in the archaeological area of S. Balbina, so-called for the medieval church dedicated to the Saint. This area is part of a plateau located in the centre of Roma (Italy), on the north-eastern portion of the Roman hill called 'Little Aventine' (the Latin *Aventinus Minor*). From previous works (Wueste et al., 2022) it has emerged as this area is possibly rich in buried structures potentially correlated with ancient visible remains (i.e., the Servian Walls, the *Domus Cilonis* and Santa Balbina church). For the radioactivity measurements a grid of measuring points was established and georeferenced using a total station. A gamma spectrometer with a sodium iodide crystal was used to measure total gamma activity. Data were then processed and mapped with Surfer® (Golden Software), a contouring and analysis software. The results and maps obtained with the total gamma radioactivity technique are subsequently compared with the results obtained by applying on the same site, another non-invasive survey method, the Ground Penetrating Radar. This non-destructive technique is extensively and profitably used for its rapid data collection and its high-resolution images of contrasting subsurface structural or archaeological materials (Barone, 2016). The purpose of the comparison between the two methodologies is to highlight their limitations and prerogatives. The data obtained with these techniques will finally be confirmed or not by subsequent archaeological excavation to be held on the site in summer 2022.

Barone P.M. (2016) - Understanding Buried Anomalies: A Practical Guide to GPR. LAP Lambert Academic Publishing, Germany.

Wueste E., Facchin G. & Barone P.M. (2022) - Aventinus Minor Project: Remote Sensing for Archaeological Research in Rome (Italy). Remote Sens., 14, 959.

# Multi-analytical survey for the conservation and valorization of geoheritage: the case study of the Parco Archeologico-Botanico del Paradiso in Chiavenna (SO)

Melada J.*[1], Arrigoni F.[1], Conforto A.[1], Pigazzi E.[1], Apuani T.[1], Giudici M.[1] & Ludwig N.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Fisica «Aldo Pontremoli», Università di Milano.

*Corresponding author e-mail:* jacopo.melada@unimi.it

*Keywords:* geoheritage, Chiavenna, infrared thermography.

The extraction and trade of soapstone in Valchiavenna is a consolidated tradition since at least a couple of millennia. One of the main trench quarries of the Roman age is located within the archaeological and botanical "Parco del Paradiso"; a place where plant biodiversity, geomorphology of the Alpine environment, archeology and history of the technological tradition combine in a museum and naturalistic educational path. The studied area is included in the larger "Marmitte dei Giganti" natural reserve, at the confluence of two main alpine valleys NS and EW directed. The Valchiavenna basin has already been identified for the study of the Alpine ecosystem due to its high representativeness of geomorphic processes and microclimate peculiarity (Aldighieri & Mazzoleni, 2011). Within this framework, our project aims to support the valorization of the archaeological and botanical park, with a multi-analytical approach. The project consists of two main tasks: i) study of the minero-petrographic and thermophysical properties of the rocks in the ancient soapstone quarry; ii) study of the microclimate of the Colle del Paradiso in relation to the plant species present within the park, to the lithology of the substrate and to geographic location. The outcropping rock belongs to the ultramafic body of the Chiavenna Unit, characterized by a wide local lithological variability, from peridotite to chlorite schist, with calc-silicate boudins and talc schists, the latter exploited for soapstone extraction. *In situ* thermographic acquisitions carried out every two months for at least two consecutive days at three different times of the day (9:00, 13:00, 17:00), made it possible to map the areas of the rock walls of the quarry subject to greater thermal stress. In addition, laboratory thermographic analyses conducted on samples are aimed at characterizing the thermal properties of the material and their variations caused by weathering. The same properties were then estimated *in situ* on large portions of rock through solar loading thermography. The environmental parameters are monitored with a temporal resolution of 10 minutes by means of seven thermos-hygrometers positioned in different points of the area of interest. These data are spatially integrated by a survey with a portable weather station which provides 50 additional measurement points along the path of the botanical park, sampled with the same temporal resolution as the thermographic acquisitions. The output of this work is useful for educational purposes and to investigate the microclimatic characteristics of this peculiar place through the integration of data at different spatial and temporal scales.

Aldighieri B. & Mazzoleni G. (2011) - La Valchiavenna: un bacino pilota per il controllo dell'ambiente alpino. Quaderni di geodinamica Alpina e Quaternaria N° 10, Milano.

# The importance of landslides in the global geological heritage

Morino C.*[1], Coratza P.[2] & Soldati M.[2]

[1] Laboratoire EDYTEM, Université Savoie Mont Blanc, UMR-CNRS 5204, Le Bourget du Lac (France).
[2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* costanza.morino@gmail.com

*Keywords:* landslide, geoheritage.

Our work focusses on highlighting the importance of landslides in the global geoheritage. So far, landslides – despite having been included in the global geoheritage – have received only minimal attention compared to much more popular and spectacular landforms. Our research aims at remedying this shortcoming. We firstly survey the literature to understand to what extent landslides have been considered as part of geoheritage and identified as geosites and/or geomorphosites. There are few cases of landslides defined as geomorphosites, and most of them are located in Europe. We define three new aspects that should be considered when identifying a landslide as a geomorphosite, namely: 1) past and present climate changes, 2) anthropic signature and 3) risk perception. These aspects, added to the values commonly used to define a geosite, are of particular relevance today, as anthropic activities and human-induced climate change are impacting on the environments and human communities all over the world. We emphasise the importance of such aspects by exploring some cases of famous and spectacular landslides worldwide.

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# Gargano Promontory (Apulia, Italy): a natural aspiring candidate for the UNESCO Global Geoparks network

Morsilli M.* & Gianolla P.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* mrh@unife.it

*Keywords:* Gargano, Geopark, Unesco.

The Gargano Promontory, the spur of the Italian peninsula, is one of the best candidate to be inserted in the UNESCO Global Geoparks. Following the general candidature criteria it has a well-defined geographic boundaries and a territory of about 2000 km$^2$, big enough to serve local economic development.

From a geological point of view the geodiversity is very high and include some peculiar features such as: numerous geosites, some of international interest (Punta delle Pietre Nere, Dolina Pozzatina); a natural transect from shallow-water to basinal carbonate rocks of Meso-Cenozoic age; dinosaurs footprints tracksites; spectacular slumpings structures; a complex structural pattern including a very large strike-slip fault and related pull-apart basin (Mattinata Fault); a mature and very well developed karst features (dolinas, polje etc.) and caves; valley and small canyons; marine abrasion surface; vertical sea-cliffs with pocket beaches or km-long sandy beaches; two big lagoons (Lesina and Varano); many natural springs along the coast and also in the internal part (Ischitella, Vico).

The richness of this area includes the very high biodiversity with endemism end ecological singularity that has been preserved through the institution of the Gargano National Park in the ’90, and with a recent transnational UNESCO World Heritage site for the ancient and primeval beech forests (Foresta Umbra).

Other fundamental characteristics include the numerous archaeological remains of international valence such as the Palaeolithic of Cava Pirro Nord and Grotta Paglicci, and some of the oldest chert mines in the Maiolica Formation. In the Holocene cultural remains are related to the Apulian inhabitant testified by many hypogaeum cemetery (e.g. Monte Saraceno, Monte Pucci). During the early Medieval time the legend of apparition of Archangel Michael at Monte Sant’Angelo (AD 493) trigger the history and cultural mixing of the Gargano Promontory. Pilgrims as first travellers and successively crusaders passed for century through the Mattinata Fault, a part of the *Via Sacra Langobardorum*, to reach the sanctuary. The Gargano become during this time the Holy Mountain, a still used name for the hundred thousand pilgrims that all years visit the promontory. In the last 60-70 years the religious tourism was also gradually outpaced by summer tourism with a relatively high impact in some area (Vieste, Peschici), and finally in the last decade the demand shifted to a more sustainable tourism, searching for genuine food and local tradition as well as natural beauties.

In summary, the Gargano Promontory encloses in a relatively small territory a very high geological, ecological, historical, and cultural richness, as well as a strong awareness and attention of the local community to a new form of sustainable developments. All these characteristics, and many others, are the perfect “business card” to candidate the Gargano Promontory as a new aspiring UNESCO Global Geopark.

# Thermal stability of colour and magnetic properties of iron based pigments

Ostorero E.[1], Coïsson M.[1], Iacomussi P.[1], Olivetti E.[1], Giustetto R.[2], Cavaleri T.[3], Piccirillo A.[3] & Ferrara E.*[1]

[1] Istituto Nazionale di Ricerca Metrologica, Torino. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Fondazione Centro per la Conservazione e Restauro «La Venaria Reale», Venaria Reale (TO).

*Corresponding author e-mail:* e.ferrara@inrim.it

*Keywords:* cultural heritage, magnetism, pigments.

Physical-chemical studies on pigments, employed since antiquity for decorating walls, wooden, lithic and ceramic artefacts, are still useful to ascertain their composition and structure, along with the investigation of the related substrates, ligands and lacquers, which reveal information on the sociocultural contexts related to their use. However, difficulties can emerge because of the decay and alterations of the investigated colouring agents. For instance, frequent browning effects may occur due to ligand or substrate degradation, as for copper pigments on papyrus, or to pollution due to mildews, funguses and other parasitic organisms. In this work, we integrate measurements of magnetic, colorimetric and structural properties of iron-based pigments in order to verify their stability and follow the chemical-physical transformations occurring during thermal treatments up to 430°C, with the aim of providing an ordered representation of their degradation processes. These phenomena, in fact, may occur on artworks in the case of particular events – such as natural fires, bombardments or exposure to hot gases (Baraldi & Bensi, 2006). Six pigments have been analyzed, namely 'Yellow Ochre 40301', 'Yellow Ochre 40400', 'Red Ochre 48651', 'Green Earth 41750' (all from "Kremer Pigmente"), Morellone and synthetic $Fe_2O_3$. Their properties have been evaluated using colorimetric (CIE L*c*h*), magnetic (hysteresis loops and FORC) and X-ray diffraction (XRD) measurements, both in the as-received state and after thermal treatments under vacuum at 310 and 430°C, for a duration of 8 hours.

The obtained results pinpoint the stability of $Fe_2O_3$, Red Ochres and Morellone, the colour, phase composition, and magnetic properties of which remain almost unchanged up to 430°C. Green Earth and Yellow Ochres, instead, undergo colour change and modification of magnetic properties when T = 310°C, indicating an evolution both in the structure and granulometry, also caught by FORC experiments.

Crude Yellow Ochres and Green Earth pigments – complex mixtures of natural minerals – exhibit a relevant paramagnetic and superparamagnetic contribution, associated with a faint ferri-magnetic character. The ferromagnetic features (e.g., magnetization and coercive field) of all analyzed samples tend to increase with the temperature of thermal treatment. As well, temperature rising enhances red hues and saturation, though reducing the colour brightness.

In accordance to FORC results, the changes in the magnetic and colour features can be explained in terms of numerical and dimensional growth of iron-oxide granules within the pigments, together with the increase of their oxidative state – from Fe (II) to Fe (III). Fe (II) oxides prevail in yellow and green crude pigments, while in Morellone and red ochres Fe (III) oxides are exclusive or predominant, not showing substantial modification with further thermal treatments.

Baraldi P. & Bensi P. (2006) - Alterazioni delle materie coloranti nelle pitture murali prodotte dalle alte temperature: fonti storiche ed indagini scientifiche. Atti del convegno 'Salvàti dalle fiamme', Lugano, 15-29.

# Iceland, an Open-Air Museum for Geoheritage and Earth Science Communication Purposes

Pasquaré Mariotto F.*[1], Bonali F.L.[2] & Venturini C.[3]

[1] Dipartimento di Scienze Umane e dell'Innovazione per il Territorio, Università dell'Insubria, Varese. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* federico.pasquare@uninsubria.it

*Keywords:* Iceland, geoheritage, geosite.

Geological heritage, better known as geoheritage, has been discussed and reviewed in a number of papers published over the last two decades. Moreover, geoheritage comprises elements of geodiversity, which have scientific, cultural, educational value and can be promoted, popularized and protected through geoscience museums (Venturini & Pasquaré Mariotto, 2019), geoparks (De Grosbois & Eder, 2008) and geotourism (Panizza & Piacente, 2008).

Finally, geoheritage is tightly associated with geological heritage sites, or geosites. These may preliminarily be defined as those parts of the geosphere that are important in terms of the understanding of Earth's history; as far as their social relevance is concerned, they can be regarded as geological or geomorphological objects that may have a scientific, cultural, historical, aesthetic, educational and economic value. In order to describe and assess a number of meaningful geosites, we have chosen Iceland as a key locality, one of the most recognizable and iconic places on Earth, which offers an unparalleled chance to admire the most powerful natural phenomena related to the combination of geodynamic, tectonic and magmatic forces, such as active rifting, volcanic eruptions and subvolcanic intrusions (Gudmundsson, 1995).

This contribution is aimed at illustrating two major Icelandic geoheritage areas and showing their relevance for geosite popularization and promotion, as well as for educational and geoscience communication goals. The two areas are: A) the Snaefellsnes Peninsula, comprising the world-famous Snæfellsjökull volcano; B) the Northern Volcanic Zone (NVZ), where the following volcano-tectonic elements can be observed: (i) a textbook example of a triple-junction interaction between an onshore transform fault and an active rift system; (ii) the Theystareykir Fissure Swarm (ThFS), an active rift zone characterized by a central volcano, several major faults and a great number of eruptive fissures and (iii) the Krafla Fissure Swarm (KFS), another major rift zone also marked by the diffuse presence of eruptive fissures and dominated by the active Krafla Volcano. We have identified and selected a total of 25 geosites from the two areas and, with the purpose of showcasing them, we have made use of the following tools: (i) field photographs, some of which have been reworked by highlighting the most relevant features; (ii) highly detailed images, captured by unmanned aerial vehicles (UAVs) and (iii) 3-D models of field outcrops, based on individual, UAV-captured pictures, further elaborated by using Structure-from-Motion photogrammetry techniques (SfM). Moreover, we have qualitatively evaluated the identified geosites by using three of the above cited criteria (scientific, cultural and educational) wherever they could be applied; such criteria were considered as most suitable for enabling us to carry out a preliminary, and by no means exhaustive, assessment.

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Gudmundsson A. (1995) - Infrastructure and mechanics of volcanic systems in Iceland. J. Volcanol. Geoth. Res., 64, 1-22.

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Venturini C. & Pasquaré Mariotto F. (2019) - Geoheritage promotion through an interactive exhibition: A case study from the Carnic Alps, NE Italy. Geoheritage, 11, 459-469.

# Geoarchaeology and old paradigms: revising Grotta Romanelli's significance for Mediterranean Palaeolithic

Pieruccini P.*[1], Sardella R.[2], Mecozzi B.[2], Forti L.[3], Lanci L.[4], Tema E.[1-5], Lembo G.[6], Muttillo B.[7], Iannucci A.[3], Bona F.[3], Russo Ermolli E.[8], Sadori L.[9], Sigari D.[7] & Mazzini I.[10]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Dipartimento di Scienze della Terra «A. Desio», Università di Milano. [4] Dipartimento di Scienze Pure e Applicate, Università di Urbino «Carlo Bo». [5] Laboratorio di Paleomagnetismo Alpino, Centro Interuniversitario di Magnetismo Naturale «Roberto Lanza», Peveragno (CN). [6] Ministero dell'Istruzione, Ferrara. [7] Dipartimento di Studi Umanistici, Università di Ferrara. [8] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [9] Dipartimento di Biologia Ambientale, Sapienza Università di Roma. [10] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* pierluigi.pieruccini@unito.it

*Keywords:* geoarchaeology, Grotta Romanelli, Quaternary stratigraphy.

During the last century, Grotta Romanelli (Lecce, southern Italy) has been considered as a reference site for the European Late Pleistocene stratigraphy, due to its geomorphological setting and its rich archaeological and palaeontological content. The beginning of the sedimentation inside the cave has been attributed so far to MISs 5e, and the oldest unearthed evidence of human occupation, including evidence of use of fire, was therefore referred to the Middle Palaeolithic. Broad range geoarchaeological investigations were recently carried out in the site: geological/geomorphological surveys and analysis, micromorphology, micropalaeontology, palynology, palaeomagnetism, U/Th, radiocarbon and OSL dating are among the main methods already applied or in progress. The results led to the re-assessment of the litho-, morpho- and chrono-stratigraphical setting, highlighting an earlier human frequentation of the cave (Middle Pleistocene, between MIS 9 and MIS 7), embracing Glacial and Interglacial cycles. These new data provide evidence that the sea reached the cave during the Middle Pleistocene and human occupation occurred long before MISs 5e and persisted beyond the Pleistocene- Holocene boundary providing a new insight within the chronology and characteristics of the human occupation and the terrestrial ecosystem evolution in the Mediterranean area.

# Collaborative geoscience investigations in natural and archaeological heritage sites: the Palazzo Belfort area of Piuro (SO, Italy) case study

Pigazzi E.*[1], Achille C.[2], Apuani T.[1], Bersezio R.[1], Castelletti S.[3] & Marotta F.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Architettura, Ingegneria delle Costruzioni e Ambiente Costruito, Politecnico di Milano. [3] Associazione Italo-Svizzera per gli Scavi di Piuro, Piuro (SO).

*Corresponding author e-mail:* enrico.pigazzi@unimi.it

*Keywords:* historical reconstruction, palimpsest landscape, 3D survey.

Mountain valleys are characterized by an intense geological and geomorphological activity, representing territories into a continuous evolution. In the Alps, this evolution is tightly connected with the human exploitation that has to coexist with the natural processes. Geological mapping of these territories covers a fundamental role for the understanding of the active geological processes and the assessment of hydrogeological risk, but it is also the key tool to interpret their palimpsest landscape evolution. The here presented case study locats in the area of Piuro, a small village of the Italian Bregaglia Valley (Central Alps) famous for the catastrophic landslide that erased the entire ancient town in 1618. Aiming at recostructing the extent of the landslide deposits and of the source area, we realized a 1:10,000 scale geological map and two boreholes (S1: 76 m b.g.s.; S2: 25 m b.g.s.) (Pigazzi et al., 2022) by applying a stratigraphic, structural, and geomorphological approach in the frame of the Interreg project A.M.AL.PI.18 (Interreg V-A IT-CH 2014-2020 Cooperation Program – Axis 2 "Cultural and natural enhancement", Id 594274 - A.M.AL.PI.18 "Alpi in Movimento, Movimento nelle Alpi. Piuro 1618-2018") . Coupling these data with field and remote geomorphological analyses performed on a high resolution, 0.50 m DTM (Marotta et al., 2021), radiocarbon age determinations from borehole samples, and archaeological and historical observations, we constrained the relative depositional chronology of the lithosomes that compose the valley bottom. We proceeded with the sub-surface interpretation of the single sedimentary bodies that were progressively subtracted from the actual topographic surface, to obtain a 3D reconstruction of the interpreted pre- and immediately post-1618 event topographic surfaces. We also proposed a plausible interpretation of the chronological evolution of the valley bottom of Piuro from the post-Last Glacial Maximum to present, that shows how the evolution of this section of the valley has been predominantly dominated by gravitational and torrential related processes for the last ca 10.000 years.

Marotta F., Teruggi S., Achille C., Vassena G.P.M. & Fassi F. (2021) - Integrated Laser Scanner Techniques to Produce High-Resolution DTM of Vegetated Territory. Remote Sens., 13, 2504.

Pigazzi E., Bersezio R., Morcioni A., Tantardini D. & Apuani T. (2022) - Geology of the area of the Piuro 1618 event (Val Bregaglia, Italian Central Alps): the setting of a catastrophic historical landslide. J. Maps, 1-10.

# Geoconservation in Sicily (Italy): the example of the Isola delle Femmine (Palermo)

Randazzo V.*[1], Todaro S.[2], Provenzale S.[3], Di Dio V.[4] & Di Stefano P.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [3] Mistretta (ME). [4] Riserva Naturale di Isola delle Femmine, Palermo.

*Corresponding author e-mail:* vincenzo.randazzo@unimi.it

*Keywords:* geosites, carbonates, Cretaceous.

Isola delle Femmine is a small island of the Tyrrhenian Sea (north of Sicily, Southern Italy) that has been recently established as a geosite. The Italian League for Bird Protection (LIPU)has been entrusted to safeguard the island and specifically the geological aspects, the floristic-vegetational heritage, and the local entomofauna. A tower dating back to the sixteenth century and known as Torre di Fuori characterizes the profile of the island and the suggestive panorama that can be admired from the surroundings of Palermo. A detailed geological survey has been carried out in order to define the most important geological features of the island together with the development of a new geological map based on topographic data and a digital model (1:2.000). Furthermore, a geological pathway through the island has been traced and illustrated. The geological substrate of Isola delle Femmine consists of a Mesozoic carbonate succession belonging to the Panormide Carbonate Platform. Two lithostratigraphic units have been differentiated. The lowest one consists of dolomitic limestones cropping out in the central and northern parts of the island. Despite the absence of biostratigraphic constraints, analogies with comparable deposits from the Palermo Mountains suggested ascribing this unit to the Upper Triassic. The overlying unit consists of well-bedded rudist and stromatolitic limestones organized in peritidal cycles. The macro-and microfacies analysis of these Cretaceous limestones allows attributing this unit to the Lower Cretaceous (i.e., Aptian). Patches of upper Pleistocene skeletal calcarenites rich in benthic foraminifers and calcareous algae, overlap the Mesozoic units. Spectacular speleothems such as stalagmites, decimetre-scale ray calcite ("raggioni") and mammillary calcite suggest a relative long-lasting exposure of the Mesozoic carbonate substrate to groundwater. Isola delle Femmine was thus likely exposed and linked to the mainland (Sicily) and the surrounding area during the Pleistocene as supported by the extent of the coeval glacio-eustatic oscillations (up to 125 m sea-level falls).

# Geoparks as tools for communicating geoscience: A local approach to understand the importance of geology in cultural heritage and human activities

Sánchez Fabián J.A.* & Salman Monte K.

Las Loras UNESCO Global Geopark, San Martín de Perapertú (Spain).

*Corresponding author e-mail:* geoloras@gmail.com

*Keywords:* Geopark, heritage, communication.

Traditionally, the importance of geological and geomorphological characteristics in the configuration of the natural and cultural landscape, as well as in the development of human activities, has been systematically ignored or diminished. This has resulted in a lack of public awareness of the relevance of geology not only in many of our daily activities, but also in our cultural and historical heritage and in the level of socio-economic development achieved in our society today.

UNESCO has launched a new special topic for funding IGCP (International Geoscience Programme) projects on "Enhancing societal acceptance of the sustainable development of Earth´s geological resources" and in the context of this issue we propose the use of Geoparks to communicate the value of geoscience to better understand the relevance that geology has and its influence in aspects of our daily lives, including cultural heritage, traditional land uses and natural resources and how humanity has thrived on the use of these resources.

Global Geoparks are managed by professional teams that combine scientific knowledge, and outreach skills to promote events focussed on an effective transmission of heritage values through actions aimed at schools, the local population, and the general public. They are not traditional spaces such as schools or museums, without imposed restrictions, where the agenda can vary and adapt to the importance of news related to natural resources.

Las Loras Geopark, in Spain, is a territory where the geological and geomorphological characteristics have had special relevance in the historical and socio-economic development of this region. The numerous hanging synclines present in the geopark were used as caves by humans during the Palaeolithic and Neolithic, using them as grazing areas for livestock, and as natural fortresses for the Cantabrian people. Afterwards, the Cretaceous sandstones and dolomites were used to build the magnificent Romanesque churches and monasteries. More recently, lignite was extracted in the area, and even an oil reservoir was discovered, although it never reached a peak in the extraction operation; but still, it continues to be important for the socio-economic development of this area through the oil museum in Sargentes de la Lora and the declaration of this area as an Asset of Cultural Interest by the regional government.

In the framework of the Geopark, several research projects on vernacular architecture, natural hazards, geoheritage, etc. have been carried out. In addition, the Geopark has promoted a research grant programme in which the participating scientists have to devote resources to transferring the new knowledge obtained to the local population in different events, talks or seminars.

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# The role of e-bike in promoting the discover of geodiversity and geoheritage

Senese A.*[1], Bollati I.M.[2], Maragno D.[1], Fugazza D.[1], La Rocca L.[3], Cavanna D.[3], Belotti P.[3], Lauri P.[3], Grimaldi L.[4], Pelfini M.[2] & Diolaiuti G.A.[1]

[1] Dipartimento di Scienze e Politiche Ambientali, Università di Milano. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Regione Lombardia, Milano. [4] Ente Regionale per i Servizi all'Agricoltura e alle Foreste, Regione Lombardia, Milano.

*Corresponding author e-mail:* antonella.senese@unimi.it

*Keywords:* E-bike, ecotourism, geoheritage.

In recent years, electric bicycles (e-bikes) have become one of the fastest growing mobilities. Moreover, the bicycle tourism has started attracting economic and scientific interest especially in the Alps where it represents an upward trend. In fact, the e-bike offers an interesting supplement to conventional bike tourism, opening a new and potentially broader field of vacation activities. In addition, in the last years, Alpine tourism has been generally living a constant growth as well with a consequently increasing of opportunity demand about leisure and sport activities. In this context the e-bike can represent a double opportunity. On the one hand, the e-bike tourist can reach sites that are not accessible with cars or to people not well trained. On the other hand, he can move more slowly than using the car but at the same time he can reach more sites more quickly instead of walking. In this way, the e-bike tourist can better observe, learn about, and appreciate the local geodiversity and the natural and cultural heritage through a fun and healthy sporting activity. However, the accessibility of forests, alpine pastures and open landscapes for mountain bikes differs significantly among the Alpine countries (Probstl-Haider et al., 2018). Therefore, despite the e-bike can be considered a solution for a sustainable tourism and ecotourism (D'Onofrio, 2019), there is a significant question regarding the spatial coverage of destinations for different transport modes, given that most infrastructures are primarily car-centric or pedestrianised. Therefore, a new configuration of roads, walkways and cycle lanes is required, equipping, for instance, routes with recharging stations. Recently some international scientific projects have been developed in order to overcome these limits: one example is the "E-bike" project (Interreg Italy-Swiss) that developed a new long-distance cycleway through the Italian-Swiss Alps.

The cycle path starts in northwestern Italy (Forte di Bard, Aosta Valley) and moves eastward, crossing the Piedmont area to Lake Maggiore. From there, with eco-sustainable crossings, it is possible to discover the Lombardy region, remaining in Italy, or to continue towards the Ticino area and the Lugano region, in Switzerland. Along the cycle path, more than 100 points of interest have been identified, including geoheritage sites, described on the project web portal with in-depth information, images and downloadable audio guides.

Here, we focus on the cycle path of the "E-bike" project from Bormio to the Forni Glacier (Upper Valtellina, Central Italian Alps) in order to investigate the role of the e-bike in promoting the geo-tourism and then in discovering geodiversity and geoheritage. We chose this section of the cycle path since Bormio and its surroundings represent an important destination for Lombardy tourists (both in summer and in winter).

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# The contribution of Geosciences on the determination of the Equivalent Heating Temperatures of ancient baked clays through magnetic measurements: The case of the Sada Nishizuka Kofun, Japan

Tema E.*[1-2], Ferrara E.[3], Hatakeyama T.[4], Matsumoto N.[5] & Mitsumoto J.[6]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Laboratorio di Paleomagnetismo Alpino, Centro Interuniversitario di Magnetismo Naturale «Roberto Lanza», Peveragno (CN). [3] Istituto Nazionale di Ricerca Metrologica, Torino. [4] Institute of Frontier Science and Technology, Okayama University (Japan). [5] Research Institute for the Dynamics of Civilizations, Okayama University (Japan). [6] Graduate School of Humanities and Social Sciences, Okayama University (Japan).

*Corresponding author e-mail:* evdokia.tema@unito.it

*Keywords:* heating temperature, ancient baked clay, magnetic measurements.

Investigating the heating temperatures of ancient baked clay artifacts can offer information about their technology production and enrich our knowledge about the fire control skills in ancient times. Traditionally, chemical and mineralogical analysis, X-ray diffraction, microscopic and microstructural investigation and/or color studies are used to infer the equivalent firing temperatures and gain information on the duration and prevalent atmospheric conditions (reducing/oxidizing) during the ancient heating. More recently, rock magnetism has also been used in such studies based on the principle that magnetic properties of baked clays change upon heating due to mineralogical transformations that take place at different firing temperatures. Here, we present the results obtained from the investigation of the magnetic properties of baked clay fragments belonging to an ancient ceramic coffin excavated at the Sada Nishizuka archaeological site, Okayama prefecture, Japan. The coffin was produced around 630-650 AD and had dimensions of around 160-190 cm in length, 55-65 cm in width, and 70-85 cm in height. Because of their large size and thick vessel walls, the ceramic coffins were most probably fired in large kilns for a long time. Measurements of the magnetic susceptibility changes during stepwise thermal demagnetization, continuous monitoring of the magnetization at increasing heating steps up to 600°C and hysteresis loops before and after heating, reveal changes in magnetic properties at relative low temperatures of around 300-400°C. All studied samples, belonging to different fragments, showed similar behavior, suggesting that the coffin, probably due to its dimensions, has not experienced uniform heating at high temperatures during its production, and thermal equilibrium was reached at relatively low temperatures. Such results indicate that in the open-air, large kilns used for the coffin production, the temperatures reached were not particularly high or at least not enough to cause complete magnetic mineralogy transformations in large and bulk artifacts such as ceramic coffins.

# Multi-scenario approach for flood hazard assessment of Sybaris archaeological site (Calabria region, Italy)

Tufano R.*[1], Guerriero L.[1], Annibali Corona M.[1], Cianflone G.[2], Di Martire D.[1], Ietto F.[2], Novellino A.[3], Rispoli C.[1], Zito C.[1] & Calcaterra D.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [3] Environmental Science Centre, British Geological Survey, Keyworth (UK).

*Corresponding author e-mail:* rita.tufano@unina.it

*Keywords:* Sybaris archaeological site, hydrodynamic model, flood hazard map.

The alluvial plain of Sibari (Calabria region, Italy) hosts the most important Archaic Greek settlement of Magna Graecia in southern Italy: the Sybaris archaeological site. Placed in proximity to the Crati river mouth, this site was repeatedly involved by flood events, as testified by both recent chronicles and ancient documents. Recently, a destructive event occurred in 2013, causing the complete submerging of the archaeological site, while a further event occurred in 2018. During these floods, the four major sectors of the site (Parco del Cavallo, Prolungamento Strada, Casa Bianca and Stombi) were involved and, despite the presence of existing embankments bounding the Crati river, they are still exposed to further events.

On this basis, a specific evaluation of flood hazard at Sybaris archaeological site would be required for supporting the development of a risk management plan and a related improved conservation strategy. In this perspective, a flood hazard analysis was carried out by a combined approach based on probabilistic analysis of the annual maxima rainfalls for runoff estimation and 2D hydrodynamic modelling. First of all, annual maxima rainfalls were analysed by a probabilistic approach using a type I Generalized Extreme Value (GEV) distribution (Gumbel; e.g., Jenkinson, 1955) to estimate Intensity-Duration-Frequency curves for different return periods (i.e., 10-year, 50-year, 100-year and 300-year). Subsequently, considering the dimension of the Crati River basin and the increasing frequency of high magnitude, spatially concentrated, rainfall events, multiple contributing areas scenario were generated. This approach allows to derive multiple runoff hydrographs, estimated by Soil Conservation Service - Curve Number method (SCS, 1972) and for each of them, to set the 2D hydrodynamic modelling. After that, flow depth maps resulted for different return period and for each scenario, were used as a basis for creating flood hazard maps of the Sybaris archaeological site area, consisting in the worst inundation scenario provided by each simulation.

Results from the analysis confirms that the archaeological site is in an area susceptible to flooding and, in case of contributing areas larger than 1000 $km^2$, an event characterized by a return period of 10 years can affect the site. For events generated by contributing areas smaller than 100 $km^2$, an event characterized by a return period of approximately 100 years is required for affecting the site.

The obtained results emphasize the extension of flooded area and describe the hazardous archaeological area linkable to the general subsidence trend of the study area.

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Soil Conservation Service (SCS) (1972) - National Engineering Handbook, Section 4: Hydrology. Department of Agriculture, Washington DC, USA.

# Borcola pass geosite proposal (Italian Pre-Alps)

Zampieri D.*[1], Roghi G.[2] & Dalconi M.C.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* dario.zampieri@unipd.it

*Keywords:* Giovanni Arduino, marble, dolomite.

Within the eastern Italian Southern Alps structural unit, in the southern side of the Borcola pass (Posina, Vicenza) the proposed geosite is of great importance in terms of its multidisciplinary scientific value, aesthetic appeal and educational value. The Posina valley is located in the Venetian Pre-Alps north of Schio (Vicenza). In this area, the injection of Paleogene basaltic dykes along fault/fractures inside the late Triassic Dolomia Principale unit has produced the metamorphism of the dolomitic rock into a marble characterized by the presence of brucite veins.

In the Eighteenth century some marble bodies were studied by the worldwide famous Italian geologist Giovanni Arduino (1779), who understood the origin of the marble. In addition, he performed chemical experiments on the marble by using sulfuric acid and according to Maraschini (1828), later followed by other authors (e.g., von Morlot, 1847; McKenzie, 1991), he was the first to discover the mineral that de Saussure (1792) will dedicate to Déodat de Dolomieu: the dolomite.

The brucite marble has been extracted and used in the Eighteenth century for local church altars, but in the second half of the Twentieth century several quarries operated producing marble fragments for home pavements.

Close to the Borcola pass (1207 m asl), in an easily accessible place, the largest inactive quarry presents a window into the past. From the large quarry square, the artificial 40-meter-high cliff face shows spectacular sub-vertical fault planes adorned by strike-slip lineations belonging to the damage zone of the Schio-Vicenza regional fault (Zampieri et al., 2021).

In the first years of the quarry activity, which started in the Fifties of the Twentieth century, the marble was transported downstream by a cableway, of which a concrete hopper and an iron arrival station structure still exist few kilometers to the south, where the road starts to climb the pass. In the quarry mineral collectors have found beautiful crystals of several Mg-bearing minerals.

In conclusion, the Borcola pass inactive quarry could represent a geosite with several elements of interest covering the history of geosciences, the structural geology, the petrography, the mineralogy and finally the industrial archeology. The beautiful exposition offered by the easily accessible inactive quarry offers an aesthetic appeal of the landscape produced by "interaction of natural and/or human factors". Last but not least, the European path number 5 (from lake Costanza to Verona) passes near the proposed geosite, which can offer an interesting cultural diversion of the path.

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# S4.

# Minerals, rock and museum: from collection to research in a post-pandemic world

*Conveners and Chairpersons*

*Giovanni Pratesi (University of Firenze)*

*Sabrina Nazzareni (University of Perugia)*

*Cristina Carbone (University of Genova)*

*Marco Merlini (University of Milano - La Statale)*

*Germana Barone (University of Catania)*

# DREAMIN, a HUB for the Digital REmote Access of Museum and INfrastructures

Barone G.*[1], Mazzoleni P.[1], Fugazzotto M.[1], Lanzafame G.[1], Sinitò D.[2], Stanco F.[2], Tricomi A.[3], Santagati C.[4], Galizia M.[4], Treffiletti A.[1], Lombardo C.[5], Rizzo C.[4] & Coccato A.[6]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Matematica e Informatica, Università di Catania. [3] Dipartimento di Fisica e Astronomia «E. Majorana», Università di Catania. [4] Dipartimento di Ingegneria Civile e Architettura, Università di Catania. [5] Dipartimento di Scienze Umanistiche, Università di Catania. [6] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK).

*Corresponding author e-mail:* germana.barone@unict.it

*Keywords:* digital museums, accessibility, virtual tours.

DREAMIN (Digital REmote Access Museum and INfrastructures) is a project of the University of Catania for promoting a remote and customized access to museums, collections and monuments belonging to the Catania University Museum Network (SiMuA).

The goal of the project, born during the Covid19 period which strongly prevented the accessibility of cultural structures, is to allow the fulfilment of the cultural, social and entertainment role also in lockdown period.

Thanks to the collaboration between various Departments of the University of Catania (Geology, Computer Science, Physics, Architecture and Engineering) a multiservice system of fruition was thought. Now it is possible to make Virtual Tours of some museums (Museum of Knowledge and Sicilian Mirabilia, Museo of Zoology, Museum of Mineralogy, Petrography and Volcanology, Museum of the Representation), which are integrated with in-depth scientific information, technical and cultural. In particular, it is possible to consult descriptive cards of the exhibited collections and to use wep-apps and interactive games (fresco reconstruction, analytical instrumentation simulations as optical microscope and molecular spectroscopies, the following by remote of real instrumentations, as the pendulum Focault).

An interesting aspect is that all these activities are grouped in a unique free web HUB (https://dreamin.unict.it/), allowing to expand accessibility to museums.

The project was also important for starting a digital cataloguing of the collections exposed in the museums involved in the project, by using the ICCD standards.

The digital platform was published on 22 March 2022 and was a great success for the public, as demonstrated by the numerous visits recorded in the HUB and the related links (about a thousand in a month) as well as newspaper articles, interviews and the subsequent invitation to present the results obtained at the Italian Pavilion at EXPO Dubai 2020.

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# Minerals of Liguria in the historical and modern collections at DISTAV (University of Genova): a masterpiece of geochemical diversity

Belmonte D.*, Carbone C. & Schiaparelli S.

Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* donato.belmonte@unige.it

*Keywords:* Ligurian minerals, DISTAV, museum.

Despite its limited area (less than 5500 $km^2$), Liguria displays an outstanding mineral diversity, with 34 mineral species having their type locality (TL) in its territory. Half of them have been found in the renowned manganese deposits of Val Graveglia and often represent unique findings. Such a valuable heritage has been preserved in the historical and modern mineral collections of the Department of Earth Sciences, Environment and Life (DISTAV) of the University of Genoa, whose first nucleus dates back to the beginning of the XIX century thanks to the effort of the naturalist Domenico Viviani (1772-1840). The historical collections then increased significantly during the XX century mostly due to the monumental work of Arturo Issel (1842-1922), who became the Director of the Museum of Mineralogy and Geology of the University of Genoa and fostered a dense network of scientific and didactical interactions. After that, a number of eminent mineralogists, such as Gabriele Lincio (1874-1938) and Alberto Pelloux (1868-1948), continued the development of the mineral collections by enhancing its quality and diversity. The modern part of the DISTAV mineral collections was built during the 1960s and 1970s by virtue of the fruitful collaboration between the academic community and keen-eyed amateur mineralogists, like Paolo Onofrio Tiragallo (1905-1987), to whom was dedicated a new mineral species found in the Mn ores of Val Graveglia (tiragalloite, IMA1979-061). The recent acquisition of important local mineral collections generously donated by both private citizens and eminent scholars, like Angelo Stagnaro (1940-2018) and prof. Andrea Palenzona (b. 1935), further increased the scientific value of the collections due to the rarity and quality of some specimens. The historical and modern collections of the University of Genova academic museums will get a renovation and full digitalization in the framework of the project "*Università degli Studi di Genova per la Cultura Scientifica (Unige-CS) – ricognizione sistematica, digitalizzazione e diffusione dei Beni Culturali dell'Ateneo genovese*", Bando Diffusione della Cultura Scientifica (Cod. ACPR20_00227), funded by the Ministero dell'Università e della Ricerca (MUR).

# INAIL hidden collection from Villa Giovio (Como, Italy): how quartz, gypsum and hematite rosettes tell the story of silicotics healthcare

Benedetti F., Guercio A., Nappi F. & Rimoldi B.*

Consulenza Tecnica Accertamento Rischi e Prevenzione Centrale, INAIL, Roma.

*Corresponding author e-mail:* b.rimoldi@inail.it

*Keywords:* Villa Giovio, silicosis, healthcare.

The Convalescentiary of Villa Giovio in Como (Italy), which was used until the 1980s, contains a collection of minerals which, although small, represents the historical memory of INAIL (Italian National Institute for Insurance against Accidents at Work) with regard to the mission of caring for technopaths, particularly silicotic patients, who were treated in the Villa.

The patients were mainly workers who had worked in quarries, mines and in the construction of tunnels. In the period between 1960 and 1970, the director of the Convalescentiary, a natural history enthusiast, asked the technopaths arriving at the sanatorium: “bring a mineral from your place of work so that a piece of your history remains here in the sanatorium”, thus initiating the collection of minerals and rocks.

These are samples of rocks, minerals and processing residues that are not necessarily among the most striking or significant from a petrographic and mineralogical point of view: they nevertheless represent stories of life, work, fatigue and the not always healthy conditions of the workplace, as well as evidence of humanity and gratitude.

In 2019, INAIL recovered the collection to realize a permanent exhibition in one of its prestigious building in Rome. The intention is to tell the story of the interweaving of history, geology and medicine, through the description of minerals and rocks, which are symbols of the gratitude of silicosis sufferers; numerous letters of thanks will be displayed, a reminder of what INAIL has done over time.

# Royal Mineralogical Museum of Naples asset digital reproduction and sharing via close-range photogrammetry

Cappelletti P.*[1-2], Amiranda V.[1], Atzori G.[1], Cascella E.[1], Cascini L.[1], D'Acunzo M.[1], Lorusso M.[1], Menna F.[1], Pellino A.[1], Perna G.[1], Petti C.[2], Saracino M.[1], Scarpati S.[1], Sposato M.[1] & Tavani S.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Real Museo Mineralogico, Centro Musei delle Scienze Naturali e Fisiche, Università di Napoli «Federico II».

*Corresponding author e-mail:* piergiulio.cappelletti@unina.it

*Keywords:* digital representation, Royal Mineralogical Museum, virtual models.

In the last 10 years, the improvement in close-range digital photogrammetry has led to a paradigm shift in the acquisition, representation, sharing and analysis of rock exposures and samples (Tavani et al., 2022). 3D models produced by close-range digital photogrammetry are now being routinely employed within both research and educational activities, including geo-heritage sites (Burnham et al., 2022) and museums assets documentation and preservation (Apopei et al., 2021).

Availability of digital replicas, indeed, promotes accessibility, inclusivity, and reproducibility through digital preservation, and has become instrumental towards the delivery of blended teaching during the COVID-19 global pandemic crisis. The employment of these 3D models has been also boosted by the rapid development of standardized exchange formats and free online data repositories.

In this contribution we describe the workflow employed for the acquisition, production, and public sharing of minerals samples from the Royal Mineralogical Museum of Naples (Ghiara & Menditti, 1999). Acquisition was carried out by 11 students of the Virtual Outcrop Models master course at the Department of Earth Sciences of the Federico II University, using both smartphones, and reflex and mirrorless cameras. Image processing was done using the software Zephyr3D, and models were uploaded in Sketchfab, a public repository of 3D models. Problems, errors, and best practice for the acquisition and built of the models are discussed.

In museums, the digital photogrammetry is a great example to sharing cultural heritage, to transferring knowledge in innovative ways. We made about 70 3D mineral models, some of them very rare and precious, to design and production a new Museum's learning resource site and interactive kiosks to help fuel visitor's curiosity, that can move the mineral around and view it from all angles, something that's just not possible with objects in a gallery setting.

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Tavani S., Billi A., Corradetti A., Mercuri M., Bosman A., Cuffaro M., Seers T. & Carminati E. (2022) - Smartphone assisted fieldwork: Towards the digital transition of geoscience fieldwork using LiDAR-equipped iPhones. Earth-Science Rev., 103969. https://doi.org/10.1016/j.earscirev.2022.103969.

# Freshly-fallen meteorite's field research methodology: a citizen science example involving mineralogical museums

Cuppone T.[1], Gardiol D.[2], Morelli M.[3], Serra R.[4], Franza A.[1-5] & Pratesi G.*[1-5]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Osservatorio Astrofisico, Istituto Nazionale di Astrofisica, Torino. [3] Fondazione PARSEC, Prato. [4] Museo del Cielo e della Terra, San Giovanni in Persiceto (BO). [5] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma.

*Corresponding author e-mail:* giovanni.pratesi@unifi.it

*Keywords:* meteorite, PRISMA network, citizen science.

The possibility of unraveling the Solar System's history, especially if done by studying a piece of extra-terrestrial rock (i.e., a meteorite), tantalized scientists in the last two centuries. This is the reason why the recovery of a fresh fall meteorite is crucial to get as much info as possible, also owing to its unweathered nature.

Today the PRISMA network (First Italian Network for Surveillance of Meteor and Atmosphere), consisting of more than 60 all-sky cameras coordinated and managed by the National Institute of Astrophysics (INAF), performs continuous monitoring of the Italian skies at night-time, to detect fireballs and bolides, trace their trajectory to the ground and calculate the strewnfield with the aim to quickly recover possible meteorites (Pratesi et al., 2021). After PRISMA has ascertained the fall of potential meteorite fragments and has alerted the local authorities, a remarkable citizen science experiment begins.

At this point, mineralogical museums – usually asked by people about the discovery of alleged meteorites (Franza et al., 2021) – play an important educational and organizational role in coordinating meteorite research. The procedure starts with setting up a base camp, which must be located near or within the strewnfield. On the basis of the data provided by PRISMA, museum staff coordinate the surveys and organize the activities generally supported by volunteers, citizens, and members of local associations (e.g., amateur astronomers and metal detectors).

Volunteers are then given basic knowledge about the nature of meteorites, their appearance, and their main characteristics by showing real meteorites. Subsequently, they receive information on what to do in case of discovery. Volunteers are also trained on how to move around the strewnfield to carry on a methodical search, avoiding random movements that may leave unexplored areas. Finally, the use of smartphones – nowadays equipped with built-in GPS chips – makes it possible to track the areas already searched and plan further investigations.

This procedure has been set up during the three freshly-fallen meteorites' research that has occurred to date in Italy – e.g., Cavezzo (2020), Temennotte (2021), Quarrata-Agliana (2022) – and have proved to be helpful in guaranteeing a systematic survey of the potential fall area.

In conclusion, mineralogical museums can successfully be extraordinary aggregators of knowledge and interest in the fascinating topic of meteorite research.

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Pratesi G., Moggi Cecchi V., Greenwood R.C., Franchi I.A., Hammond S.J., Di Martino M., Barghini D., Taricco C. & Gardiol D. (2021) - Cavezzo - The double face of a meteorite: Mineralogy, petrography, and geochemistry of a very unusual chondrite. Meteorit. Planet. Sci., 56, 1125-1150.

# In search of lost Italian meteorites. The role of the Museum of Planetary Sciences

Faggi D. & Morelli M.*

Museo di Scienze Planetarie, Fondazione PARSEC, Prato.

*Corresponding author e-mail:* morelli@fondazioneparsec.it

*Keywords:* Italian meteorites, museum, planetological heritage.

The Museum of Planetary Sciences (MSP) in Prato, which is an official repository for the preservation of planetological heritage, preserves a relevant meteorite collection comprising specimens with a high scientific- and/or aesthetic value. Part of these is on display, whilst the majority are kept within humidity-controlled storage cabinets in the warehouse.

MSP meteorite collection has grown in many ways over the years and one of the plan's objectives is to invest in the acquisition – through service, purchases, swaps, and research expeditions – of new representative specimens. MSP pays particular attention to acquiring Italian meteorites, which have become very rare and valuable items. To this end, MSP has launched a review campaign to locate Italian meteorite specimens that may be owned by private parties or have been dispersed over time.

A first attempt concerned the recovery of unknown specimens belonging to the Siena meteorite, which fell in the countryside of Lucignano d'Asso in 1794. Since it was impossible to acquire Siena meteorite specimens on the market, in-depth archival investigations were carried out together with field research on the strew-field area. However, being the Siena meteorite an LL5 chondrite – and thus containing metal and easily degradable – the discovery of samples on the ground was extremely unlikely.

A second investigation was about the Lodi doubtful meteorite (1972). A search of the literature revealed that a possible specimen was recovered, but it had never been analyzed or deposited at a research institution The owners of the specimen made it available and, after a historical analysis of the circumstances of the fall, it was transferred to the MSP for examination At a first glance, the terrestrial origin of the specimen was undoubtful since it was medium rounded, characterized by low sphericity, and constituted by a sphalerite and galena aggregate. Further analysis confirmed the mineralogical composition. On this basis, it was assumed that the specimen came from the nearby Adda River valley where zinc and lead sulfides ores were mined in the past.

The most recent investigation regarded the Vigarano meteorite. Two fragments were recovered in 1910: the smallest was divided into fragments and sold to foreign museums, while the main mass was preserved by the owners of the land on which it had fallen. Today, the main mass is in very poor conservative. However, tiny specimens were given by the owners over the years, and some of them are still well-preserved. In 2022, MSP acquired 8 well-preserved specimens, weighing 12 g. Among them, one sample even shows its original fusion crust. The specimens will be analyzed in the next future to gain new data on their conservation status and their mineralogical, petrographic, spectroscopic, chemical, and isotopic features will be re-examined in the light of the recent developments in meteorite classification procedures.

# Minerals of Modena Province (Northern Apennines, Italy): from museums and private treasures to scientific research and public engagement

Fantini R.*[1], Scacchetti M.[2], Malferrari D.[1], Bartoli O.[3], Bertacchini M.[4] & Ciriotti M.E.[2-5]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] AMI - Associazione Micromineralogica Italiana. [3] Dipartimento di Geoscienze, Università di Padova. [4] Museo Universitario Gemma, Università di Modena and Reggio Emilia. [5] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* riccardo.fantini1@unimore.it

*Keywords:* Modena Province, ophiolites, collections.

The geological and mineralogical knowledge of a region evolves continuously thanks to scientific research. Mineral collections and collectors play two major roles: i) collections provide specimens to enlarge scientific knowledge; ii) collectors should be engaged in scientific research, both inside and outside academia. Mineral collections represent thus a cultural resource of paramount importance in the diffusion of geological sciences toward public stakeholders.

In this work, a comprehensive overview of the mineralogical occurrences of Modena province (Northern Apennines, Italy) is presented exploiting the historical relevance of local museums, and the exceptional quality of local private collections.

The geological setting of Modena province does not display exceptional mineral deposits such as, e.g., those of the Italian Alps. However and more surprisingly, the mineralogical studies are well-grounded in Modena territory since the Estense domination in the 14th century. The initial driving force was the search and exploitation of small copper ore deposits associated with ophiolites, with mines attested up to the Italian autarchy between the First and the Second World War.

The Estense Mineralogical and Geological Museum GEMMA has been a reference point for mineralogical studies of the area since its foundation in 1786. Concerning the interest untied from metal-ores, the mineralogical study of Modena province mainly developed during the 19th and 20th centuries. Mario Malagoli produced the first report on minerals from Modena in 1884, while other studies focused on the morphological crystallography of several species. The high quality of datolite crystals is remarkable, as attested by various scientists during the 19th-20th century and by several beautiful samples of datolite from Modena in the collection of the Vienna Natural History Museum. During the 20th century, mineralogical research in the Modena province spanned from crystallographic to chemical and petrographic studies, mainly focused on ophiolite outcrops. Continued research activity has enlarged the number of identified mineralogical species, while also reporting discoveries of particular aesthetic value in national magazines.

The present work reports an informative overview of the geological setting of Modena province together with an updated review of mineralogical occurrences. Particular attention was devoted to the characterization and identification of minor minerals by X-ray diffraction, electron and optical microscopy, and Raman spectroscopy. A forthcoming publication on the mineralogy of Modena will be accompanied by high-quality images of mineral specimens and a description of several areas of special geological and mineralogical interest.

Besides the scientific aspects, this project contributes to raising social awareness of geological and mineralogical themes, and specifically of the peculiarities of Modena territory, to the local and national community.

# Mineralogy, minerals and collections at the National Museum of Natural History of Paris

Ferraris C.*

Muséum National d'Histoire Naturelle - Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris (France).

*Corresponding author e-mail:* ferraris@mnhn.fr

*Keywords:* minerals, collections, museums.

Sampling the Geology, and therefore the mineral diversity, of our planet: this is the watchword of the National Museum of Natural History in Paris since 1626, when the minerals (to which medical virtues were attributed) entered the Drugstore of the King. The Mineralogical Collection of the National Museum of Natural History is one of the largest in the world, both in terms of volume and its scientific and historical values. For nearly 400 years, almost 140,000 specimens have been acquired, donated or simply collected all over the world. The conservation location of these samples is the Mineralogy and Geology Gallery, the first building built in France (between 1833 and 1839) to be truly a museum – today, the "Treasures of the Earth" exhibition, attracts an average of 70,000 visitors per year that, compared to the 9-10 million visitors of the Louvre Museum, seems negligible, but let's see why it isn't really!

Mineralogy is the oldest and one of the most important scientific disciplines within the wider Geological Sciences. Minerals are the basis of the overwhelming mass of solid matter in the universe and each mineral species is, generally, a natural crystalline substance. According to data from the New Minerals, Nomenclature and Classification Commission (CNMNC) of the International Mineralogical Association (IMA), there are currently about 5800 officially-recognized mineral species. The number of minerals increases steadily from year to year; in the post-war period and until the end of the 1960s, the average number of IMA-approved species per year was 31, increasing to 66/yr between 1970 and 2000, to reach 97/yr in the first twenty years of our century and now with a trend of 130/yr for the last four years.

Is that a great number? This depends on what you compare it with. For example, the number of biological species known today is close to two million, and the number of synthetic chemical compounds, including organic substances, is close to ten million. In comparison to these numbers, the species diversity of the mineral kingdom is clearly relatively small, but a discovery of each new mineral species is a really significant event in the Geological Sciences. The proposed statistics can be compared to others whose importance in an evaluation of a project is surely a crucial aspect. Firstly, one sees an almost logarithmic relationship between the number of mineral species described per year and the number of scientific publications that describe them and take them up for different reasons. However, above all, in a second noteworthy relationship, one sees that the size of the grains of the mineral species described decreased in a constant manner over time. Thus, over the last thirty years, the average size of the grains used for chemical and crystallographic determinations decreased from 1000-500 down to 50-1 microns; furthermore, characterizations at the nanometric scale increased from 4 in the early 2000s to more than 100 in the last ten years. The extreme importance of a new mineral species is therefore understandable, as well as the geological context where it was discovered, the techniques used to determine it, the Institution where the type sample is deposited, and of course the conditions and valorization that the Institution gives to preserve it. The National Museum of Natural History in Paris preserves more than 320 *types* of mineral species.

# Strategies for enhancement and promotion of SiLiBA, the lithotheque of the University of Bari (Italy)

Fioretti G.*[1], Eramo G.[1], Monno A.[1] & Muntoni I.M.[2]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Soprintendenza Archeologia, Belle Arti e Paesaggio per le Province di Barletta-Andria-Trani e Foggia, Ministero della Cultura, Foggia.

*Corresponding author e-mail:* giovanna.fioretti@uniba.it

*Keywords:* cherts, lithotheque, dissemination.

Geological collections assume an undisputed importance since they gather materials for their relevance as specific geological events or for mineral and rock group representativeness, or for historical and educational significance.

SiLiBA, the lithotheque of geological cherts at the Earth and Geoenvironmental Department of the University of Bari Aldo Moro is an example of the scientific and educational value of Universities' geological collections. It is composed of about 900 samples of primary and secondary geological cherts coming mainly from mines and deposits in Apulia and Basilicata (Italy) and from some regions of Croatia. The lithotheque is connected to a laboratory for the characterisation of chert samples. SiLiBA cherts have been studied by means of a non-invasive protocol (Delluniversità et al., 2019) thanks to which, through macroscopic and mesoscopic observations, colourimetric measurements and chemical and micropaleontological analyses, a very large amount of original data, as well as images at different scale, has been produced and collected in a database.

Naturally, for the collection dissemination a fundamental role is played by the most widespread and innovative tools, especially in the historical period we are experiencing, in which the global virtual connection of people, things and ideas is essential for continuing to interact with each other, exchange information and improve themself, both in life and work.

With a view of economic sustainability and resource optimization and in order to create a global connection between archaeologists and geologists, the collection promotion has been improved by means of a dedicated website.

It is articulated into submenus and includes sections containing archaeological information on procurement and manufacturing of cherts in the Prehistory, history of the lithotheque, publications and events and activities, including experimental archaeology laboratories and tutorials.

The website focus is the section concerning the database reports, thanks to which the visitor can consult all the data sheets, setting geographic or geological or by name criteria searching. The SiLiBA site is enriched by a section reporting the interactive 3D reconstruction of the most representative samples.

Even if the input of some data is not yet complete, the site is online and explorable. The future goal is to create a social profile in order to reach as many users as possible, especially in school and university communities, and to publish interesting and original contents that can move people closer to geological collections and to the Earth sciences and to the archaeology field.

Delluniversità E., Muntoni I.M., Allegretta I., Tarantini M., Monno A., Maiorano P., Girone A., Morsilli M., Terzano R. & Eramo G. (2019) - Development of a multiparametric characterisation protocol for chert investigation and application on the Gargano Promontory mines. Archaeol. Anthropol. Sci., 11, 6037-6063.

# *Collectio Mineralium* (1765): recovering a lost mineralogical catalog

Franza A.*[1], Mattes J.[2] & Pratesi G.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Österreichische Akademie der Wissenschaften, Wien (Austria).

*Corresponding author e-mail:* giovanni.pratesi@unifi.it

*Keywords:* Peter Leopold, Collectio Mineralium, mineralogical catalog.

Archival studies in a mineralogical museum not only promote its history but ensure that its records are preserved and available to support the work of its staff as well as to meet the research needs of scholars and the general public.

The goal of this work is therefore to illustrate the (re)discovery of *Collectio Mineralium* (1765), i.e., the catalog of the mineralogical collection belonging to Peter Leopold of Habsburg-Lorraine (1747-1792), Grand Duke of Tuscany (1765-1790) and later Holy Roman Emperor Leopold II (1790-1792). The volume is preserved at the Historical Archive of the University of Firenze Museum System and describes 242 mineralogical specimens mainly coming from today's Hungarian-Slovak mining district. It is interesting to note that Peter Leopold's catalog is not listed in any database for bibliographical research so its critical edition (2022) has made available for the first time this extraordinary primary source for the history of mineralogical collecting.

The *Collectio Mineralium*'s publication process consisted not only in transcribing and translating the text into English but also in the editing of a critical apparatus that – besides investigating the cultural, and scientific background of the volume – allows the historical and modern identification of the mineralogical species, the mining areas, and mining processes reported in the catalog. This analysis enables the determination of emergencies no longer known in different sites, as shown by the international reference database MinDat.org.

In addition to discussing the above-mentioned aspects, this work compares *Collectio Mineralium* to the mineralogical catalogs belonging to Holy Roman Emperor Francis I (1708-1765) and Archduchess Maria Anna of Habsburg-Lorraine (1738-1789). Peter Leopold's father and sister also had private mineralogical collections, both described in catalogs exclusively available in their manuscript form. However, the latter presented minerals collected for scientific and aesthetic purposes, while Peter Leopold's catalog is one of the first examples of commodity collecting since the specimens were got together as evidence of the quantity of monetary minerals that could be extracted from a specific mining site. These data characterize and distinguish *Collectio Mineralium* from the other catalogs of Hapsburg-Lorraine mineralogical collections, as shown by the reconstruction of its genesis that can be found in the official visit that Peter Leopold made to the mining districts of Schemnitz and Kremnitz (today's Banská Štiavnica and Kremnica) in 1764.

In conclusion, this work presents not only a new chapter in Peter Leopold's scientific biography but also brings back to light poorly researched aspects of 18th-century Habsburg mineralogical collecting.

# Trust God but lock your door. Thefts and recoveries of minerals at the Florentine Natural History Museum between the 18th and 19th centuries

Franza A.*[1], Scali F.[2], Fantoni L.[3], Moggi Cecchi V.[3], Garofano L.[4] & Pratesi G.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Scuola di Scienze Matematiche, Fisiche e Naturali, Università di Firenze. [3] Sistema Museale di Ateneo, Università di Firenze. [4] Accademia Italiana di Scienze Forensi, Reggio Emilia.

*Corresponding author e-mail:* annarita.franza@unifi.it

*Keywords:* theft, minerals, museum.

The work focuses on a topic that may escape the attention of scholars and legal practitioners: the crime involving museum mineralogical specimens. Nonetheless, the transnational and wealth dimension of this black market is evidenced by forums such as 'The Lost and Stolen Specimen' on MinDat.org where diverse museums (e.g., Fallbrook Gem and Mineral Museum) spread the news of stolen samples and ask for information leading to their recovery.

In detail, the work examines the historical roots of this phenomenon by investigating the illicit acts committed at the Imperial and Royal Museum of Physics and Natural History in Firenze from its foundation in 1775 to 1868. The analysis of untapped sources preserved at the Historical Archive of the Galileo Museum revealed that 1045 crimes concerning naturalistic specimens were reported to museum management and local authorities during this period.

Because of their scientific, economic, and forensic relevance, the work examines the theft of minerals perpetrated by Ferdinando Raddi in 1818, the thievery of three carved emeralds in 1850, and a robbery of various gold and platinum specimens occurred in 1867. The research carried out at the Historical Archive of the University of Firenze Museum System has allowed the reconstruction of the collecting history of the stolen specimens. Through the examination of the ancient inventories and registers, it was possible to discover that some of them were returned and today are still part of the museum's collections.

The analysis of the aforementioned criminal cases outlined the gradual development of security measures to prevent the misappropriation of mineralogical specimens, such as placing display cases on the shelves, padlocks, and removing the most valuable minerals from the permanent exhibition. Furthermore, this work pointed out how the cataloging of the mineralogical collections was considered not only a tool to report the results of the forensic investigations – e.g., removing the stolen specimens from the general museum catalog highlighting their missing with the term '*involato*' (stolen) – but also as a preventive measure to monitor the status of the mineralogical collections, providing updated data to local authorities in case of suspected criminal misconducts.

In conclusion, this work shows the importance of keeping the spotlight on the vulnerability factors that may affect mineralogical specimens in a museum context, stressing the use of proper methods and practices useful to their mitigation.

# University Earth Sciences Museums: a SWOT analysis

Macrì M.*

Museo Universitario di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* michele.macri@uniroma1.it

*Keywords:* earth sciences, museum, university.

One of the primary tasks in the development of a successful business is the evaluation of its pros and cons: one of the most effective methods is a SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis. Profit, for any business company is the primary goal; yet, an Earth Sciences University Museum is not a business company. The only definition that we can give of "university museum" is that a university museum is a museum - in the International Council of Museums sense - that belongs to an university or, more broadly, to a higher education institution.

Italy has always strongly taken into account the promotion of their university museums; Italy has pioneered the integrated management systems of university heritage, whereby nearly all Italian universities have created formal or informal networks of museums and collections. Yet, Italian university museums shall benefit from an evaluation of their current status and shall devise innovative strategic plans to capitalize upon their uniqueness.

Earth sciences university museums shall integrate research, teaching, conservation and enrichment of their heritage, and promote its dissemination across all types of users. Such strategic plan should not prioritize one of the aforementioned scopes, but rather attempt to integrate all of them.

Albeit not being a business company, an accurate SWOT analysis could be extremely useful to achieve this ambitious goal.

# The importance of the correct labelling in mineralogical collections: a case study

Mauro D.*

Museo di Storia Naturale, Università di Pisa.

*Corresponding author e-mail:* daniela.mauro@unipi.it

*Keywords:* mineralogical collections, Peloritani Mountains, Sicily.

In the framework of a study of sulfide ore minerals from the Peloritani Mountains, two specimens labelled as jamesonite from Alì (Messina Province, Sicily) were identified in the mineralogical collections of the Natural History Museum of the University of Pisa (catalogue numbers 1431 and 1432, respectively). In hand sample, specimen #1431 shows lead-grey metallic prismatic crystals, with a perfect cleavage, associated with a black metallic phase; quartz is the only observed gangue mineral. Specimen #1432 is characterized by lead-grey compact metallic masses associated with silicates. Both specimens were studied through X-ray diffraction and scanning electron microscopy.

The mineralogy of specimen #1431 is simple, being formed by stibnite and minor fülöppite. On the contrary, specimen #1432 was mineralogically very complex: the lead-grey masses are mainly composed by an intermediate member of the geocronite-jordanite series, associated with galena, arsenopyrite, and a lead-antimony sulfosalt (probably boulangerite). Surprisingly, in the studied polished section, domains characterized by the occurrence of reduced phases (native antimony, native arsenic, stibarsen, and dyscrasite), along with an Ag-Pb sulfosalt, were identified. Silicate minerals are diopside, chlorite, and epidote group minerals.

Results of mineralogical investigations on these two samples revealed the occurrence of several rare minerals never reported from the Peloritani Mountains. The identification of fülöppite could be in keeping with the identification of plagionite by Rodolico (1940). The novelty of these findings suggested an accurate check of the real provenance of the studied specimens. Indeed, the comparison with other specimens confidently collected in the Peloritani area suggested some errors in the labels of Pisa's specimens. The solution to this aenigma came from two small labels glued on both samples and resembling some others found on samples bought from the mineral dealer Krantz. After difficult research, a letter dated 9 September 1879 was found: Prof. Meneghini bought the two specimens. Specimen #1431 corresponded to stibnite from Harz (Germany), whereas specimen #1432 was geocronite from the Sala mine (Sweden). After decades, the correct information about these specimens went lost and only an accurate check of available documents allowed to locate their actual origin. This is an important take-at-home message: an acritical study of old mineralogical specimens can lead to totally erroneous results.

Rodolico F. (1940) - Studio a luce riflessa di alcuni minerali italiani. Period. Mineral., 11, 1-14.

# Holotype materials in the mineralogical collections of the Pisa University: a journey into the History and Science and new discovery of 'old' minerals

Mauro D.*[1] & Biagioni C.[2]

[1] Museo di Storia Naturale, Università di Pisa. [2] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* daniela.mauro@unipi.it

*Keywords:* holotype, mineralogical collections, Natural History Museum.

The definition and preservation of holotype materials of new mineral species is a fundamental achievement that has been consolidated in the mineralogical community since the 1970s (Embrey & Hey, 1970). In the meanwhile, a project aimed at locating and listing the type materials for all the known mineral species has been carried out by the Commission on Museums of the International Mineralogical Association.

The mineralogists belonging to the Pisa University have been involved in the study of new mineral species since the beginning of the 20$^{th}$ century, when Giovanni D'Achiardi first described dachiardite-Ca from the pegmatitic dykes of San Piero in Campo, Elba Island, Tuscany (e.g., D'Achiardi, 1906). Currently, the mineralogical collections of the Natural History Museum of the Pisa University preserve the type material of 100 different mineral species, mainly represented by minerals first described in Italy. A critical examination of such materials allowed to reconstruct the evolution of the studies performed by the mineralogists active at the Pisa University. Different research topics allowed the description of several mineral species. Among the most prolific topics, the following can be mentioned: i) crystal-chemistry of feldspathoids from xenoliths embedded in volcanic rocks from central Italy; ii) sulfosalts from hydrothermal veins, with a special reference to the Apuan Alps ore deposits; iii) secondary minerals, with a special focus to sulfate minerals deriving from pyrite weathering; and iv) Bi-Mo minerals from Sardinia.

In the first decades of the 20$^{th}$ century, mineralogists from the Pisa University were particularly interested in the study of minerals from the Larderello area. Among the most important scientific results, Giovanni D'Achiardi (1934) described ginorite, $Ca_2B_{14}O_{20}(OH)_6{\cdot}5H_2O$. According to the Catalogue of Type Minerals Specimen (http://minerctms.canalblog.com/), no data on the type material of ginorite are available. During the examination of the collection of type materials preserved in Pisa, the specimens studied by Giovanni D'Achiardi in 1934 for the definition of this mineral, along with the original hand-written labels, were found. Consequently, type material of ginorite is kept in the mineralogical collections of the Natural History Museum of the Pisa University, with catalogue number 7662.

D'Achiardi G. (1906) - Zeoliti del filone della Speranza presso S. Piero in Campo (Elba). Atti Soc. Toscana Sci. Nat., Processi Verbali, 22, 150-165.
D'Achiardi G. (1934) - Ginorite, nuovo borato di calcio a Sasso Pisano. Period. Mineral., 5, 22-32.
Embrey P.G. & Hey M.H. (1970) - Type specimens in mineralogy. Mineral. Rec., 1, 102-104.

# The estimate of radioactivity in collections of uraniferous minerals: a methodological approach

Moggi Cecchi V.*[1], Fedeli L.[2], Doria S.[3-4], Cupparo I.[5-6], Fabrizi L.[1-7] & Gori C.[8]

[1] Museo di Storia Naturale, Università di Firenze. [2] S.O.C. Fisica Sanitaria Prato e Pistoia, Ospedale San Jacopo, Pistoia. [3] Istituto di Chimica dei Composti Organo-Metallici, CNR, Firenze. [4] European Laboratory For Non Linear Spectroscopy, Università di Firenze. [5] Dipartimento di Fisica, Università di Firenze. [6] Scuola di Scienze della Salute Umana, Università di Firenze. [7] Dipartimento di Scienze della Terra, Università di Firenze. [8] Unità di Fisica Sanitaria, AOU Careggi, Università di Firenze.

*Corresponding author e-mail:* vanni.moggicecchi@unifi.it

*Keywords:* radioactivity, uraniferous minerals, collections.

Uranium is one of the most 'dangerous' elements in social imaginary. This celebrity comes in large part from its use in nuclear weapons, in power plants and from nuclear and radiation accidents (Gaso et al., 2005). Despite its aura, uranium minerals are highly sought-after from mineral's collectors. The best known species are autunite, vandenbrandeite, uraninite, uranophane, uranocircite, torbernite, metatorbenite, sklodowskite, cuprosklodowskite, becquerelite and curite. The specimens may be massive or display crystals with various habits, from equant to needle shaped, sometimes well-developed. However, radioprotection issues arises when dealing with manipulation, storage and exhibitions of such minerals collections (Freedman, 2011; Rowe, 2018). Radiation protection guidelines are not well-established in this field, mostly because the radio-activity estimation of uraniferous minerals is not a trivial issue, due to the manipulation difficulty caused by the emitted ionizing radiation and the dependence of radiometric quantities from several parameters. Samples modelling requires approximations, leading to large uncertainty in the evaluation of the radio-activity (Chernyshev et al., 2014). We therefore propose a new procedure to evaluate uraniferous specimens radio-activity based on simple radiometric measurements, including a detailed description of measured parameters, of the employed instrumentation and of the mathematical formulation of the model developed to obtain the radio-activity of the ores. The proposed methodology takes into consideration sample size, ores composition and measured radiation. The experimental set-up was designed to reduce the measurement uncertainty and extended-source effects were taken under consideration. The procedure was then applied to measure the radio-activity of a group of uraniferous mineral specimens belonging to Natural History Museum of the University of Florence, Italy (Barsotti Collection). This methodology can be easily generalized to other minerals collections, and it represents a guide for uraniferous specimens manipulation, conservation and exhibition.

Chernyshev I.V., Golubev V.N., Chugaev A.V. & Baranova A.N. (2014) - $^{238}U/^{235}U$ isotope ratio variations in minerals from hydrothermal uranium deposits. Geochem. Int., 52, 1013-1029.

Freedman J. (2011) - Storage of the Radioactive Mineral Collections at Plymouth City Museum and Art Gallery, UK. Collections 7(2), 201-212.

Gaso M.I., Segovia N. & Morton O. (2005) - Environmental impact assessment of uranium ore mining and radioactive waste around a storage centre from Mexico. Radioprotection, 40, S739-S745.

Rowe S. (2018) - Managing Small Radioactive Collections in the UK: Experiences from the Polar Museum, Cambridge. J. Conserv. Mus. Stud., 16(1), 4.

# From the underground to the stars. The project for a new planetary and mineralogical museum in Prato

Morelli M.[1], Faggi D.[1], Malesani F.[2], Ciampinelli F.[3], Franza A.[2-4] & Pratesi G.*[2-4]

[1] Fondazione PARSEC, Prato. [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Architetto, Firenze. [4] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma.

*Corresponding author e-mail:* giovanni.pratesi@unifi.it

*Keywords:* museum, planetary sciences, meteorites, minerals.

The Museum of Planetary Sciences in Prato (MSP), founded in 2005 and managed since 2017 by Fondazione PARSEC (FP), houses more than 500 meteorites and about 7000 mineralogical samples – some of which are rare and of great value, because they come from Tuscan mines or mining localities that are now abandoned or no longer accessible.

Today, MSP is animated by an effective synthesis of science and museology, in which the desire for renewal meets the importance of tradition, in a framework where the history of the universe and the planet we inhabit combine.

MSP collections are actively studied, preserved, and enhanced to pass on to the future generations of scientists and amateurs its extraordinary heritage of scientific and historical knowledge, which represents the core value of a museum institution (Pratesi & Franza, 2021). MSP collections offer study materials to scholars whereas the general public has the opportunity to 'see for themselves' and 'touch' the development of these very important branches of science from a classification and laboratory perspective. This is especially true for the meteorite collection since meteorites are the only source of extraterrestrial material available on the Earth.

Recently, the Municipal Administration of Prato promoted a project for joining MSP activities to the other two FP sectors (the Natural Science Centre and the Tuscan Geophysical Institute). A new FP headquarters has therefore been identified at Villa Fiorelli, on the edge of a park containing occurrences of considerable naturalistic interest. This project required extensive reflection on the MSP's future development - in terms of exhibition, education, and research activities.

The project took into consideration various aspects, which were analyzed, discussed, and furthered through a fruitful interaction between different professionals. The analysis of the historical, socio-economic, and cultural context of the MSP, together with the cataloging of its collections (Franza et al., 2022), was considered a priority. Subsequently, the architectural planning began, producing two different designs: the first entirely "superficial", and the second totally "underground". Both designs considered both the current layout of the Museum of Planetary Sciences – whose main exhibition has to be maintained – and the features of the new location site.

Since the structure is in a natural context near an eighteenth-century villa, the underground solution results particularly effective for creating an ambient of over 2000 square meters without causing any environmental or architectural impact.

Franza A., Faggi D., Morelli M., Mancinelli M.L. & Pratesi G. (2022) - Cataloging Italian Meteorite Museum Collections Using the BN-PL National Standard: A Case Study. Cat. Classif. Q., 1-31. https://doi.org/10.1080/01639374.2022.2063466.

Pratesi G. & Franza A. (2021) - Mineralogical, Petrological and Planetological Heritage. The (Italian) story so far. Rend. Lincei Sci. Fis. Nat., 32, 95-116.

# The mineralogical collection of the Department of Physics and Geology of the University of Perugia: a forgotten collection

Nazzareni S.* & Marchetti V.

Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* sabrina.nazzareni@unipg.it

*Keywords:* mineralogical collection, catalogue.

The University of Perugia, in addition to the Galleria di Storia Naturale (CAMS) Museum, has a mineral collection which is partially exposed in the Giovanni Cocco Aula at the Department of Physics and Geology.

As many other Italian Universities, the mineralogical collection was started in the sixties to middle seventies of the XX century by mineralogists of the former Department of Earth Sciences, Giovanni Cocco, Bartolomeo Baldanza, Pier Francesco Zanazzi. Despite the presence of several specimens exposed at the Department space a detailed catalogue of the collection is lacking and only limited information are available.

We started an identification of the specimens of the collection with the aim to produce an updated and accurate internal catalogue which, hopefully, will be the starting point for a new exhibition.

For each specimen we first took a picture and looked for the available information that we reported in the catalogue, then we assigned a new catalogue number. After this first step of the recognition we end up that the collection is composed by ca. 500 specimens.

The collection is composed mainly by minerals (including didactic specimens) covering a wide range of sample size (from micro-mount to some big samples) and mineral families, and a small interesting collection of meteorite, tektites (the Baldanza collection). A recent donation of a former students increased the collection with specimens from Chilean mines.

Unfortunately for a group of specimens we miss some information like mineral classification or origin, and we are going to analyse the specimens and look for the missing data.

A new attention to our mineralogical collection has also the aim to use this important geological heritage for dissemination and communication activity at every level.

# Mineralogical and Petrographic collections preserved in Regional Museum of Natural Sciences of Turin

Senesi M.*[1] & Costa E.[2]

[1] Museo Regionale di Scienze Naturali, Torino. [2] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* massimiliano.senesi@regione.piemonte.it

*Keywords:* mineralogy, MRSN, petrography.

The Regional Museum of Natural Sciences of Turin (MRSN) is located in the former San Giovanni Battista Hospital, built at the end of XVII century under the direction of Amedeo di Castellamonte. In 1978 the Piedmont Region established in this historical site the MRSN Museum .

The museum acquired in loan the Turin University collections, and begins the reorganization, arrangement and cataloging of these collections for conservation, exhibition and educational purposes. It also initiates the establishment of its own heritage through the organization of study and research campaigns, and the collection and purchase of entire collections of particular historical and scientific value.

The collections belonging to the Section of Mineralogy, Petrography and Geology consist, as a whole, of a series of heterogeneous materials, mainly represented by samples of minerals and rocks, but also by samples coming from perforations and tunnels, historical 3D wooden and plastic models, mining tools and laboratory equipment.

The historical core of the Mineralogical, Petrographic and Geological collections comes from the two old museums of the University of Turin, the Museum of Mineralogy and Petrography and the Museum of Geology and Paleontology; the materials are now on loan for the MRSN use, but still property of the University.

The MRSN Museum of Mineralogy and Petrography's own collection consists of rocks, minerals, slabs and meteorites from the Italian territory and from different parts of the world. These samples include some significant topographic subsections and themes of historical and scientific interest, often with high ostensive value.

The 13138 samples of the MRSN Museum of Geology and Paleontology own collection consist of 132 minor collections. Some of them are of essential historical value and others are of particular scientific interest.

The MRSN's mineralogical collection, as a whole, has developed since 1980 until today as a set of samples coming from all over the world. Its aim is to integrate the university collections (not updated since 1950) with the most recent world mineralogical findings.

The samples of the Museum of Geology and Mineral Deposits of the Polytechnic of Turin consist of rocks from the Italian territory and from different parts of the world. The material, now owned by the Piedmont Region, refers to samples and ornamental stones up to the first half of the twentieth century, and partly to historical collections of the nineteenth century.

# Museum collections as a facility for geological research and outreach – Some examples from the Swedish Museum of Natural History

Skogby H.*

Swedish Museum of Natural History Department of Geosciences, Stockholm (Sweden).

*Corresponding author e-mail:* henrik.skogby@nrm.se

*Keywords:* museum, collections, mineralogy.

Museum collections are central for many scientific disciplines, including mineralogy and petrology. Collections are often acquired over long periods, and provide access to specimens that no longer can be found in nature. This is typical for environmental research where, for instance, biocides stored in bones and eggshells can be studied in a time-track mode. However, specimens collected in older times may also be important from a mineralogical perspective where rare samples from closed mines are no longer available, often due to remediation efforts or covering of mine dumps.

The combination of well-curated collections and access to modern equipment and advanced laboratories provides an excellent research environment. It may also provide good opportunities to enhance the interest from Museum visitors and communicate scientific results. At the Swedish Museum of Natural History, efforts are currently made to make the visitors more aware of the Museum's relatively large Research Division. An example of such efforts is "The Lab", a sort of laboratory classroom equipped with microscopes and other instruments where visitors can examine their own material tutored by scientific staff members covering different disciplines at different occasions.

The combination of well-curated collections and well-equipped laboratories has also increased the interest from researchers from abroad to visit the Museum. Although most of the Museum's specimen are accessible via public databases, and in many cases also with digital images, on-site visits are often necessary to select suitable samples and perform analyses. Within mineralogy, we have accommodated a good number of Italian visitors, including Master and PhD students as well as senior researchers. Access have been facilitated by the Erasmus Traineeship program as well as the visiting program "SYNTHESYS" which have provided travel and accommodation support, and has led to numerous collaboration projects.

# Mineralogical crystallography at the Natural History Museum, London: a personal perspective on past, present and future directions of geoscience research at museums

Welch M.D.*

Department of Earth Sciences, Natural History Museum, London (UK).

*Corresponding author e-mail:* m.welch@nhm.ac.uk

*Keywords:* museums, mineralogical crystallography, societal priorities, curiosity-based science.

What is distinctive about geoscience research carried out at museums that sets them apart from most universities? The principal geological asset of a national museum is its comprehensive systematic collection of mineral and rock specimens. How can this asset be used to meet the changing political agendas and societal priorities, while retaining a component of less prescriptive, curiosity-based science that has so often led to significant new research directions? This curiosity-based science has been a significant component of research at the NHM for many years. The freedom to explore such science, together with outstanding mineral collections, makes museums an attractive prospect for a scientific career.

However, with increasing pressure on researchers to deliver financial as well as intellectual benefits for their institutions, there is a danger that museum research becomes too focused on what will attract external funding, so that less fashionable or "serendipitous" science is considered of minor importance and receives less kudos. The result can be a narrowing of scientific endeavour and a significant loss in diversity of the research undertaken.

In this talk I shall use diverse examples from my 30 years of research as a crystallographer at the NHM to illustrate how mineralogy can address these various challenges in a balanced way, while remaining a distinct and vibrant scientific discipline. Examples will include: (a) structure/property correlations of natural frustrated anti-ferromagnets (atacamite/herbertsmithite/claringbullite group); (b) hydroxide perovskites (H-rich materials); (c) the hydrous mineralogy of cold subduction (mantle water); (d) new-to-science minerals.

# S5.

# Sustainability in dimension and ornamental stones industry (from exploitation to application)

*Conveners and Chairpersons*

*Giovanna Antonella Dino (University of Torino)*

*Rossana Bellopede (Politecnico of Torino)*

*Nike Luodes (GTK, Finland)*

*Nereo Preto (University of Padova)*

*Piero Primavori (Freelance consultant, PSC - Primavori Stone Consulting)*

# Mortar based on sludge from carbonate dimension stone processing industry - An experimental and feasibility approach

Azzalini A.*[1], Faria P.[1-2], Lopes L.[1-3], Martins R.[1], Mourão P.[4] & Pires V.[1-5]

[1] Department of Geosciences, University of Évora (Portugal). [2] Department of Geosciences, University of Aveiro (Portugal). [3] Earth Sciences Institute, Pole of the University of Évora (Portugal). [4] Department of Chemistry, Mediterranean Institute for Agriculture, Environment and Development, University of Évora (Portugal). [5] Institute for Advanced Studies and Research, University of Évora (Portugal).

*Corresponding author e-mail:* pagf@uevora.pt

*Keywords:* mortar, dimension stone, marble.

An alternative use is presented for the cutting and finishing residues of dimension stones carbonated rocks, generated in the processing plants, from marble quarries located in the Estremoz Anticline and limestone quarries from the Maciço Calcário Estremenho - Portugal. These by side products, called carbonated sludge or "cream", have a strong capacity to bond with aggregates and allow their use as raw material in mortars, which can later be used to produce stone based composites with a more sustainable base.

Currently, the most used binders to produce these composite materials are polyester and epoxy resins, the latter presenting the high cost of acquisition as its main disadvantage. The study carried out at the Department of Geosciences of the University of Évora, within the scope of the project "Calcinata - Production of lime-based mortar from the calcination of carbonated sludge from the ornamental rock industry (marble and limestone)", aims to demonstrate the feasibility of the technical application of this material, adding economic value to it, so that it is no longer seen as waste and starts to be classified as a by-product of the extractive and transforming industry of carbonated ornamental rocks.

After sampling the carbonated sludge carried out in the main extractive centres of limestone and marble in Portugal, its chemical and physical characterization was carried out, followed by the planning of a series of formulations to understand the behaviour of this material with two types of polyester resin, which after mixing will constitute a material with a high degree of bonding between particles, a primordial condition to be classified as mortar.

After adding the marble and limestone sludges to the resin in defined proportions, three curing times were defined: 7, 14 and 28 days. Subsequently, these samples were subjected to uniaxial compressive strength tests. Viscosity tests were also carried out on a device developed for this purpose. In the next phase and after selecting the ideal binder (sludge + resin) formulations were carried out where the binder was mixed with marble aggregates with different granulometries and different relative proportions. The three marble aggregates used had nominal dimensions between: 2 - 6.3 mm; 6.3 - 12.5 mm, and 10 - 25 mm. After identical curing times to those of the binder formulations, the samples were subjected to uniaxial compressive strength tests and the optimal proportion was defined for the subsequent project stages. Test pieces were then produced for more detailed mechanical and physical tests, such as bending strength, impact, freeze/thaw test, slip test, abrasion resistance, among others, with a view to the complete characterization of these materials.

# The collection of ornamental stones at the Regional Museum of Natural Sciences of Turin

Borghi A.*[1], Gallo L.M.[2] & Senesi M.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Museo Regionale di Scienze Naturali, Torino.

*Corresponding author e-mail:* alessandro.borghi@unito.it

*Keywords:* ornamental stone collection, Museum of Natural Science.

In 1980 the Council of Piedmont Region established the Regional Museum of Natural Sciences (MRSN) with the task, among others, of managing the zoological, mineralogical, geological and paleontological collections of the University of Turin. In particular, the lithological collections of the Museum of Geology and Paleontology and the Museum of Mineralogy and Petrography of the University, entrusted with the mineralogical collections to the management of the Section of Mineralogy, Petrography and Geology, have been over time integrated and updated by new acquisitions and collections. Particularly noteworthy is the occurrence of a collection of natural stone materials, both raw and in slabs with various surface processeing (polished, honed, bushhammered, split, etc.), from all over the world, but with the main objective of representing the best materials, of Italian or foreign origin, sold on the Italian market (Gallo & Fiora, 1998). Alongside this, a series of examples of "extinct" rocks, materials whose quarries have been exhausted or abandoned for some time, occur. In this way, a twofold aim is achieved: to provide a specialized audience (architects, engineers, researchers, teachers, quarrymen, historians and other operators in the sector) with a tool for consultation, study and research for modern lithotypes and, at the same time, to have a term of comparison for rocks no longer on the market, but often still present and described in architecture (Gambino et al., 2007). The lastrotheque consists of tiles, properly inventoried, catalogued and described, measuring 29x41 cm, with a thickness of 2 cm. There are also tiles in standard commercial formats for materials for which it has not yet been possible to obtain "made to measure" specimens from the producers. For each material, several specimens are kept in order to be able to characterize, as far as possible, the salient features of the different product varieties (variations in color, grain, pattern, etc.). For each rock, there are also some plates of variable size (7x10 cm or similar), usually used for studies and laboratory analysis. On the basis of a collaboration developed for over twenty years with the Department of Earth Sciences of the University of Turin, the entire collection is available for consultation for the mineralogical and petrographic characterization of stone materials.

Gallo L.M. & Fiora L. (1998) - Le collezioni di pietre ornamentali al Museo regionale di Scienze Naturali di Torino. Marmi, Pietre, Graniti. Edizione Fiera di Verona, Lugano (CH), 30-33.

Gambino F., Borghi A. & Gallo L.M. (2017) - Dalla collezione di pietre ornamentali del Museo Regionale di Scienze Naturali a *Tourinstones*, un'applicazione per la valorizzazione geoturistica di Torino. Museologia Scientifica Memorie, 17, 206-209.

# Marble quarries sustainability: from scraps to high value-added products

Careddu N.*

Dipartimento di Ingegneria Civile, Ambientale e Architettura, Università di Cagliari.

*Corresponding author e-mail:* ncareddu@unica.it

*Keywords:* dimension stone, secondary raw materials, circular economy.

Huge amounts of stone scraps are produced every day during the quarrying, sawing and processing of carbonate ornamental stones. Most of these materials are landfilled and create serious environmental and health hazards: this practice is no longer compatible with the concept of sustainable development. Thus, it is mandatory to find alternative solutions to recycle them. from the perspective of the circular economy. Scrap from marbles with high calcium carbonate content (> 95%) can become economically attractive because $CaCO_3$ is widely used as functional filler in industrial products having higher added value, such as paper, rubber, paints, pharmaceuticals (Careddu et al., 2014). Focusing in the Orosei Marbles' producing area (North-East Sardinia, Italy), the aim of this report is to compare the performance of various products, through the use of marble scraps (Marras et al., 2022). Furthermore, keeping in mind the marble companies' sustainability, it is strategic to re-thing the concept of landfill with the idea of transforming the landfill itself into a centre for stone materials aimed at secondary processing. Finally, to raise people awareness of the usefulness of quarrying, it will be held and a historical route aimed at industrial tourism will be organized (Careddu et al., 2013).

Careddu N., Marras G. & Siotto G. (2014) - Recovery of sawdust resulting from marble processing plants for future uses in high value added products. J. Clean. Prod., 84, 533-539.

Careddu N., Siotto G., Siotto R. & Tilocca C. (2013) - From landfill to water, land and life: the creation of the Centre for stone materials aimed at secondary processing. Resources Policy, 38, 258-265.

Marras G., Carcangiu G., Meloni P. & Careddu N. (2022) - Circular economy in marble industry: From stone scraps to sustainable water-based paints. Constr. Build. Mater., 325, 126768.

# The Valongo Wharf, Rio de Janeiro, Brazil: a comprehensive history told by its stones

Castro N.*[1-2], Cunha J.B.[1-2], Campos A.P.R. [2], Mozer A.G.S. [1-2] & Mansur K.L.[1]

[1] Departamento de Geologia, Universidade Federal do Rio de Janeiro (Brazil). [2] Centre for Mineral Technology, Ministry of Science, Technology and Innovation, Rio de Janeiro (Brazil).

*Corresponding author e-mail:* ncastro@cetem.gov.br

*Keywords:* Valongo, Rio de Janeiro, natural stones.

Rio de Janeiro's geology and geography, urbanising history and continuous environmental management since 1861, when Emperor Pedro II ordered the reforestation of the Tijuca forest, set the grounds for its World Heritage Cultural Landscape title in 2012. Rio's lithology is composed mainly of gneiss and granite, materials used to build the city from the 16th century. The quarries, all closed, produced building stones up to the 20th century, mostly with enslaved labour.

This work shows the lithological map of the Valongo Wharf, a World Heritage Archaeological Site (Cunha et al., 2020). It is a pier explicitly built to receive enslaved Africans, almost one million of them (UNESCO, 2017). Many Africans who remained in Rio settled in the Valongo region, known as "Little Africa", today acknowledged as the cradle of the Afro-Brazilian culture. The exposed site comprises two levels of pavement, embankment, ramp and drainage structures, all built with local stones. Those stones quarried and set by the enslaved people also tell us about the Earth's history and the other connection Brazil-Africa, as they were formed during the Proterozoic collision of the ancient South American and African continents.

The three prominent proterozoic gneisses of Rio de Janeiro compose the site: Facoidal gneiss, a porphyroblastic biotite orthogneiss, encompassing large k-feldspar crystals with a characteristic augen shape, the most representative heritage stone of Rio (Castro et al., 2021); the Leptinito gneiss, a fine/medium-grained white-coloured garnet leucogneiss, the heritage stone of the oldest buildings (Castro et al., 2022); and, in minor quantities, the Kinzigito gneiss, a dark coarse-grained paragranulite, characterised by biotite/sillimanite bands and large garnet/cordierite crystals. From the same event, aplites, pegmatites and quartzites are also present. Diabase from the Gondwana Supercontinent breakup during the Cretaceous is also found. The ramp and levee of the monument are constituted by blocks of the three types of gneisses. The main alterations observed are scaling, delamination, differential erosion, staining caused by iron and copper old inserts, and wax and paint deposits. Shell incrustations at the front walls of the quay evidence the sea level in the 19th century in a currently land covered portion of the city.

Castro N.F., Mansur K.L., Frascá M.H.B.O. & Silva R.E.C. (2021) - A heritage stone of Rio de Janeiro (Brazil): the Facoidal gneiss. Episodes, 44(1), 59-74.

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# Soapstones from Valmalenco (Sondrio, central Alps): from archeology to modern uses

Cavallo A.*

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* alessandro.cavallo@unimib.it

*Keywords:* soapstone, archaeology, quarry.

The varieties of soapstone from Valmalenco (Sondrio, central Alps) have been known at least since the Middle Ages for their use in Lombardy, and in general throughout northern Italy. The soapstone (*prèda* or *sas de lèvèc*) is a particular rock, with green colour, mainly composed of "soft" minerals (talc and/or chlorite), fine or very fine grained, that can be easily worked at the lathe. They are genetically linked to the serpentinites of the Malenco nappe, rocks formed during the Alpine orogeny from the metamorphism of sub-continental mantle peridotites. From ancient times until the early 60's the product of the quarry was a small block with the shape of a truncated cone, called *ciapùn*. The extraction of the *ciapùn* took place directly from the excavation front with the typical two-pointed pickaxe (*asìsc*) and, once extracted, it was already ready to be transported from the quarry to the lathe for the working of the *lèvèc*. Most of the historic quarries are located in underground tunnels (*trone*), which followed the lode. The use of black powder in Valmalenco for civil purposes has been documented since the 17$^{th}$ century, and it is therefore reasonable to think that this technology could have been used also in the soapstone quarries. In 1964 the technique of continuous drilling (line drilling) of the block surfaces was introduced in the soapstone quarries; in later times, helical wire and diamond wire cutting were also introduced. In Valmalenco there are two main varieties of soapstone: chlorite-schist and talc-schist. For the characterization of the material, both archaeological and samples from the various quarrying sites were characterized by various analytical techniques: optical microscopy on thin sections, XRPD, EDXRF, SEM-EDS and WDS EPMA. The chlorite-schist ("green soapstone") constitutes irregular metric-thickness veins and lenses included in serpentinites, resulting from alpine metamorphic deformation and recrystallization of original gabbroic lenses: it is a fine- to very fine-grained rock, massive to moderately foliated, composed almost exclusively of chlorite (more than 90 wt.%), with small amounts or traces of magnetite, apatite, talc, epidote, diopside, and ilmenite. The talc-schist (or steatite, also called gray soapstone) constitutes sub-vertical veins and lodes, decimetric to metric thickness, included in serpentinites along pre-existing fracture lines, as a result of circulation of hydrothermal fluids in late phases of the Alpine orogeny. The talc schist is generally massive with poor schistosity, and is composed mainly of talc, with smaller amounts of magnesite, dolomite, chlorite, magnetite, and antigorite. The current production of soapstone in Valmalenco, equal to about 20 t/year, is based on the active "Ui" quarry in the municipality of Chiesa in Valmalenco, and the material is used for the realization of handicrafts of high value.

# Towards a 4.0 extractive industry, more sustainable and responsible: best practices connected to dimension and ornamental stones exploitation

Dino G.A.*[1], Mancini S.[1], Cavallo C.[2] & Chiappino C.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Freelance consultant.

*Corresponding author e-mail:* giovanna.dino@unito.it

*Keywords:* 4.0 extractive industry, circular economy, responsability.

In the recent years an increased interest in approaches and best practices aiming at sustainable and responsible mining can be evidenced. The extractive industry, which operates in the field of primary resources, aims to be the key player in the transition from a reality focused on extraction and environmental protection, into an entity that responsibly approaches to the different needs that a modern and sustainable industry requires, such as:

planning, extraction and processing, also thanks to the application of AI and digital tools, aimed at preserving the natural resources, avoiding, or at least limiting, the waste production. When waste production is unavoidable, fundamental is planning how to recover them (technical tests, market analysis, etc.);

preservation of the environment, thanks to guidelines and best practices (from the investigation to the extraction and transformation phases) that aim to prevent impacts and, where unavoidable, intervening to limit their presence within tolerable limits;

transparent comparison to imagine virtuous social models that detect (local) extractive industry as something to promote, guaranteeing not only the proper environment protection, but also producing positive economic and social impacts on the territory (i.e., new jobs, territorial compensation, etc.);

proactive interaction with Public Administration and Governance system towards an effective green deal.

Dimension and ornamental stones industries is one of the main promoters of this "virtuous" approach to raw materials management. Italy shows several examples related to the sustainable use of dimension stone resources. Only as representative virtuous example, here we can cite the exploitation of extractive waste produced by the exploitation of Trentino porphyry, Carrara marble, Granite from Lake Maggiore, Sardinia marble, etc. (Dino et al., 2020; Marras et al., 2022; Vagnon et al., 2020). These virtuous industries are leading other (Italian) industries towards the realisation of 4.0 extractive industry (more responsible, sustainable and digital).

The values of sustainability and responsibility go hand in hand not only with the development of the companies, but of the territory in which they operate, culturally connoting the society and the local habits. Indeed, the areas involved in extractive activities have always been intended as a mirror and witness of changes in local heritage and habits, often thanks to migratory phenomena of quarryman and miners who moved from one country to another to bring experience and expertise: these changes effectively shoot the cultural dynamism of an area.

The 4.0 extractive industry which is sketching out at an Italian level will could be the promoter of a new cultural change in the society.

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# The use of geotechnologies in the sustainable exploitation of geological resources applied to conservation, restoration and structural reinforcement works

Duarte J.*[1-2], Gomes A.[3], Costa F.[4] & Barbosa R.[4-5]

[1] IQGeo, Coimbra (Portugal). [2] Geosciences Center, University of Coimbra (Portugal). [3] Department of Earth Sciences, University of Coimbra (Portugal). [4] Centre for Technology, Restoration and Valorization of Arts, Polytechnic Institute of Tomar (Portugal). [5] Research Center in Information Sciences, Technologies and Architecture, University Institute of Lisbon (Portugal).

*Corresponding author e-mail:* joao.duarte@uc.pt

*Keywords:* conservation, ornamental rocks, geotechnologies.

In architecture, solid stone can have countless uses, as it has been a widely used building material for many centuries, both in its raw state and in dimensioned formats. We can highlight the use of masonry and solid stone walling from monuments of high aesthetic value such as churches, castles and palaces to simple dwellings in historic centres across the country. It is expected that the stones used in architecture will have different characteristics with intensive, varied and long-term use in each region of the country and depending on the type of use. ICOMOS (International Council on Monuments and Sites) recommends a comprehensive characterization of the materials used in conservation, restoration and reinforcement works. We should examine both existing heritage materials and new materials to be introduced. Compatibility with existing materials is critical and can predict the forms of long-term degradation. The degree of degradation to which ornamental rocks are exposed in the built environment, especially in the post-industrial era, increasingly justifies the need for their study and physical and chemical characterization. The main carbonate rocks found in buildings may be sedimentary, such as the limestones in the Codaçal quarries in Porto de Mós, or metamorphic, such as marble in general. In general, carbonate rocks, especially limestones, have different compositions and properties, which are reflected in the behavior of the rock in the formation of different forms of alteration and degradation. In this case study, the sustainable use of the natural resource was planned to apply the best available techniques of geotechnology for the use of the geological resource in conservation, restoration and structural reinforcement works. The aim is to optimize the extraction process, increase the quality of the blocks from the different types of rock present, achieve higher recovery rates, and thus reduce waste production and energy consumption, leading to a reduction in harmful emissions to humans and the environment. The planning of the mining process significantly increases the safety of people and property. To this end, a survey of discontinuities and a geophysical prospection were carried out in the quarry core of Codaçal (Porto de Mós, Leiria), quarry number 5477, in order to characterize the massif geologically and structurally and to better plan the extraction of ornamental rocks. Physical-chemical characterization tests will then be performed on the limestone. The exploration of the site is based on several types of surveys carried out with different methods on a total area of about 11.3 ha. In order to achieve the desired objective, geological-structural surveys were carried out with the aim of mapping the fractures and associated structures, structural mapping using aerial photography, and finally geophysical profiling using the Ground Penetrating Radar (GPR) method.

# Mortars characterisation as a diagnostic element of the variations in the exploitation of Piemonte region georesources during different ages

Mancini S.* & Dino G.A.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* susanna.mancini@unito.it

*Keywords:* archeological mortar characterisation, quarry exploitation, Piemonte region.

Archaeological researches in rural settlement of the Po valley (Piemonte Region, Northern Italy) have identified a large range of buildings and infrastructures, dating from Roman to early Middle Ages (Negro Ponzi Mancini, 1999). Those architectonic elements were characterised by wooden walls made of pebble or brick fragment bases, parts of older and newer walls built with cast-off mortared materials, whose typology does not allow architectural dating. Such a kind of rural architecture is worth of consideration as Cultural Heritage, because witnesses of the development of Piemonte territories over the ages.

As bricks, pebbles and stones found in local territories were frequently reused, once a building had been demolished and/or restructured, the mortar is the only architectural material that was always contemporary to the construction phase. Mortars are made of sand and limestone: sand shows various and usually prevailing local provenance, with small differences, while limestone suitable to produce good mortar are quite rare in Po valley area.

The present research shows the results of the geochemical characterisation, based on the Mg/Ca ratio, of mortars found in rural buildings dating from the early Roman imperial period to the late ancient phases of medieval fortified centres. Limestone provenances were identified by systematic geological and historical investigation; representative samples were collected from ancient quarry sites.

Often the exploited limestone quarries show a fairly constant chemical composition and thus a typical Mg/Ca ratio. The variation in the Mg/Ca ratio was useful to identify the geological formations and likely quarries exploited in the different architectural phases and ages. In some cases, the Mg/Ca ratio was cross-referenced with a third element, Sr, which is normally contained in traces and which strongly characterises the variation in limestones typical of the Po area. The analyses show a wide range of the Mg/Ca ratio characterizing all the samples, but a limited range, due to the origin from single or few quarries, in each group of coeval buildings.

The mortar proved to be an important diagnostic tool to identify the original quarries exploited for limestone production and the period of exploitation (Ortega et al., 2008). The investigation evidenced that quarry sites exploited during the Roman period were often no longer exploited during the medieval period, not only because they were unavailable, but also because of political and road changes: the limestone provenances can thus provide interesting pieces of information on trading road system and its changes in the different periods.

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# Stone recession in cultural heritage investigated by laboratory ageing tests

Mazzoli C.*[1], Salvini S.[1-2], Coletti C.[1], Germinario L.[1], Maritan L.[1], Massironi M.[1] & Pozzobon R.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Ministero della Cultura, Gallerie dell'Accademia di Venezia.

*Corresponding author e-mail:* claudio.mazzoli@unipd.it

*Keywords:* recession rate, ageing test, grain size.

Carbonate rocks (limestones, marbles) are among the most commonly used building materials (both as dimension and ornamental stones), and are highly vulnerable to weathering, especially in polluted areas. One of the main issues in the evaluation of cultural heritage vulnerability is the quantification of the deterioration rate. With this goal in mind, and in the frame of the HYPERION Project, the water-driven recession of stone in cultural heritage was simulated and measured in the laboratory by exposing a set of carbonate rocks, historically exploited and used in northern Italy, to accelerated ageing tests by immersion in rainwaters with different compositions. The tests were run cyclically in an environmental test chamber, alternating wetting and drying phases; at fixed intervals, the recession of each sample was quantified by bulk weight-loss measurements and surface mapping at the confocal microscope. The relationship between the different mineralogy and texture of the stones and the rate and areal development of their recession was investigated, finding that, besides water pH, calcite grain size is the most important controlling decay factor. Correction coefficients were also calculated for obtaining more reliable recession estimations from recession equations known in the literature. The findings of this study can be exploited for predicting stone deterioration in cultural heritage constrained by the relevant environmental context and the expected future climate change.

# Vicenza Stone: nomination as Global Heritage Stone Resource

Milizia E.*[1], Brandano M.[2], Cornale P.[1], Mazzoli C.[3], Perissinotto M.L.[4], Preto N.[3] & Tomassetti L.[5]

[1] LabiGem, Laboratorio Italiano di Gemmologia - Vespa s.r.l., Vicenza. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Dipartimento di Geoscienze, Università di Padova. [4] Regione Veneto, Direzione Difesa del Suolo e della Costa, U.O. Servizio Geologico e Attività Estrattive, Venezia. [5] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* elisa.milizia@labigem.com

*Keywords:* Heritage Stone, limestone, Oligocene.

Vicenza Stone (locally, "Pietra di Vicenza") is a limestone quarried in the Vicenza province of North-eastern Italy. Its use has been documented since the Roman times, and in the 16th century, Andrea Palladio used it of the buildings now part of the "City of Vicenza and the Palladian Villas of the Veneto" UNESCO World Heritage Property. It is a lithofacies of the lower Oligocene Castelgomberto Formation, cropping out in the Venetian Prealps, where it forms massive horizons ranging from 2 to >20 m in thickness, exploited in >100 underground quarries; a ca. 20 quarrying concessions are still open nowadays.

Vicenza Stone is here nominated as a Global Heritage Stone Resource. The designation of "Global Heritage Stone Resource" (GHSR) is maintained by a special commission of the International Union of Geological Sciences, and identifies stones important for the restoration and/or maintenance of historical or public buildings and stone objects. In fact, Vicenza Stone complies with the 6 IUGS criteria for nomination as GHRS: it has been used since Roman times at least, and all over Northern Italy; it is a signature stone in many of the finest buildings by Andrea Palladio and for Palladian architecture in general, making it a cultural icon; it is still being quarried, and its designation as a GHSR may sustain quarrying industry. The production of Vicenza Stone may be continued in a sustainable way, because quarries develop underground, hence, do not have a significant impact on landscape. Besides, there is potential for geoturistic and cultural exploitation of abandoned underground quarries – experiments exist already which have been so far fairly successful.

Data have been collected about the technical properties of Vicenza Stone, its use in architecture, production volumes and geographical diffusion, in order to complete its nomination dossier. The main reason for nominating Vicenza Stone as GHRS remains the role it played in the history of architecture: it has been one of the building materials of choice for the Italian Renaissance architects Andrea Palladio and Vincenzo Scamozzi, among others. Since most works of Palladio made extensive use of it, maintaining the production of Vicenza Stone is now mandatory, in order to ensure the maintenance and restoration of cultural heritage buildings in Palladian style.

# Heritage Stones: the cultural value of natural stones that needs to regain recognition

Pereira D.*

Geology Department, University of Salamanca (Spain).

*Corresponding author e-mail:* mdp@usal.es

*Keywords:* natural stones, Heritage Stones, IUGS.

The International Union of Geological Science (IUGS) is the World's largest association encouraging international cooperation and participation in Earth Sciences. It is made of Commission, Subcommissions and working groups dealing with the most varied geological subjects. Natural Stones are the main subject of the Heritage Stones Subcommission.

Cultural heritage relays many times in the heritage built of stones. For this reason, in 2012 a working group on Heritage Stones was created in the frame of the IUGS. The group was made up by experts on Dimension Stones and it evolved to Task Group and to Subcommission (HSS), achieving a maximum peak of activity by implementing the standard of Global Heritage Stone Resource. More than twenty stones were recognized because their value in cultural and architectonic heritage. Dozens of papers were published in international journals and the group presented the outcomes of the subcommission worldwide. In 2016 this subcommission joined a broader, Heritage Commission, together with a Sites Subcommission: the International Commission of Geoheritage (ICG). In the last two years heritage stones have not been promoted as they used to have, and the impression of the author of this contribution is that if no action is taken, the heritage stones (and therefore natural stones) will be phagocytized by the Sites subcommission, with a possible finalization of the IUGS support. If that is the case, the Heritage Stones working group would have followed a very quick "rise and fall" history, and lots of work done by experts in natural stones will be lost and downgraded. Not because the quality of the work, but because the policy that IUGS has followed in the management of working groups, ignoring the expertise of the members of the subcommission and trying to impose some rules of management that may be good for other traditional commissions, but not to the more technical group that not only deals with nice pictures, like the geosites can be, but on the proper, scientific characterization of rocks, with a complete mineralogical, structural and physical and mechanical properties that will help in restoring or even replacing when needed to maintain the architectonic heritage of the world, some of them recognized by UNESCO as World Heritage sites.

A collaborative work is needed to show IUGS that natural stones are a driver in the economy of societies, both in industry and tourism, but they are also part of the history of civilizations because this is many times engraved on stones.

# Vicenza Stone and the legacy of Andrea Palladio: an appeal for in-depth geological studies

Preto N.*[1], Brandano M.[2], Cornale P.[3], Mazzoli C.[1], Milizia E.[3], Perissinotto M.L.[4] & Tomassetti L.[5]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] LabiGem, Laboratorio Italiano di Gemmologia, Vicenza. [4] Regione Veneto, Direzione Difesa del Suolo e della Costa, U.O. Servizio Geologico, Venezia. [5] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* nereo.preto@unipd.it

*Keywords:* Palladianism, Heritage Stone, sedimentary petrography.

Andrea Palladio (1508 - 1580) was a stonemason, first in Padova and then in Vicenza. He must have been working with Vicenza Stone – an Early Oligocene porous limestone quarried in the Vicenza province since before Roman times – since he was still a child. He then grew to become one of the most influential characters in the history of architecture; the architectural style that stemmed from his work (Palladianism) spread globally and was at the roots of Neoclassicism.

The legacy of Andrea Palladio is preserved in the World Heritage Site of "The city of Vicenza and the Palladian villas" (https://whc.unesco.org/en/list/712/), which is considered unique for its integrity and autenticity, as deliberated by UNESCO since 1994.

A fundamental component of this unique piece of human heritage is Vicenza Stone. Being a stonemason, Palladio (and its disciples and followers likewise, for centuries) knew his dimension stones and chose it carefully. As a result, the city of Vicenza and the villas have a common appearance – given by the color and texture of the stone – which is in continuity with old rural and "poor" architecture and with the landscape of the nearby hills, which backbone is the same early Oligocene formation where the Vicenza Stone is quarried from. Palladio, and more clearly his disciple Vincenzo Scamozzi, were able to distinguish and tell apart types of Vicenza Stone, and were selective about its use. We show that types of Vicenza Stone can still be identified today, and provenance of Vicenza Stone samples can be determined to some degree, with petrographic observations.

The unity of landscape, urban landscape and architectural masterpieces – which blueprint is in large part a dimension stone – deserves recognition and a strategy for conservation. Unfortunately, however, the production of Vicenza Stone is nowadays hitting a historical low. More critically, the few quarries that are still operating do not cover the full variety of stone types which were available to Palladio and its followers. With this contribution, we make an appeal for further studies on the variety of Vicenza Stones, and its use in Palladian architecture, mostly with the aim to guarantee the correctness of future restoration works.

# Stone splitting: the oldest sustainable processing technology

Primavori P.*

PSC - Primavori Stone Consulting, Milano.

*Corresponding author e-mail:* pieprima@gmail.com

*Keywords:* dust, split, rusticity.

Split stone products are part of our daily lives and can be found nearly everywhere, even if they are often unnoticed. Humans have always needed to cut stone into usable sizes and volumes, both to defend, isolate and protect themselves and to create the innumerable works that history, art, architecture and sculpture have handed down to us. Like long ago, today, despite the introduction of ultra-modern technologies for processing, handling and moving, it is still necessary to divide stone and reduce its volume, turning it into products sized to meet our needs. Meaning that stone must still be split. Of all the stone-working technologies, splitting is the one given the least attention, but, at the same time, is probably the one with the highest level of sustainability for each of the three components: environmental, economic and social. There are no stones that cannot be split; in the stone sector, there are stones that cannot be polished, others that cannot be resin-coated, still others that cannot be flamed, and so on. But every stone – truly every one – can be split. Always.

Splitting makes it possible to utilize great amounts of stone materials otherwise destined for dumps, with great advantages from the environmental viewpoint; it is the only technology in the whole stone production chain making it possible to utilize remnants of quarrying, of primary processing (blocks and slabs) and of secondary processing (any-size fragments and various solid residue), creating saleable products from what would have otherwise been discarded. Furthermore, with splitting, lower quality products can be used, creating advantageous economies of scale without compromising stone's aesthetic and economic worth; this is why the intrinsic rusticity and naturalness of split surfaces relegate any stone aesthetic "defect" to the background.

As far as the strictly environmental and safety aspects are concerned, splitting technology is probably unsurpassed in the large panorama of the machines and equipments currently used to process the dimension stones: its performances in terms of dust, gases, emissions, noises, vibrations, operative safety and many other components, together with the total water saving, are indisputable.

The note intends to draw the attention on the splitting activity in the dimension stones sector, its peculiar characteristics, its unlimited versatility and the wide range of obtainable products.

# The asphaltic limestone of the Hyblean Plateau (SE Sicily): from mines to the Late Baroque Towns of the Val di Noto UNESCO site and to European cities

Punturo R.*[1-2], Indelicato V.[1], Fazio E.[1], Lanzafame G.[1], Maniscalco R.[1], Muschella L.[1], Bloise A.[3] & Cirrincione R.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* punturo@unict.it

*Keywords:* Pietra Pece, raw materials, Sicily.

This contribution focuses on "Pietra Pece" (i.e., Pitch Stone), a stone material exploited in south eastern Sicily and used in monumental architecture as well as for paving streets in Europe.

Also known as "asphalt" or "asphaltic rock", pitch stone is a bitumen-impregnated limestone quarried in mines, some of which are still active, and widely used as a valuable stone material in construction, art and hydrocarbon extraction. From a constructive point of view, this material has been used either for facades and as an ornamental material for interiors thanks to its particular chromatic shades (from black to brown with whitish streaks), its water-repellent properties and its malleable behavior when heated that makes it easy to work. After the second world war, the Sicilian bitumen exploited in the Hyblean Plateau was also extensively used for paving streets in European capitals such as Berlin and Paris.

Moreover, after the earthquake that destroyed many cities in south-eastern Sicily in 1693, they were later all rebuilt on or beside towns existing at the time of the earthquake which took place in that year. These cities are considered to represent a considerable collective undertaking, successfully carried out at a high level of architectural and artistic achievement, depicting distinctive innovations in town planning and urban building and for these reasons they internationally recognized and included in the UNESCO World Heritage list ("Late Baroque Towns of the Val di Noto").

Since the use of Pitch Stone in the Hyblean monuments and art is widespread, we collected representative samples of Pitch Stone in from mines and performed optical microscopy, 3D rendering of the fabric by microcomputed X-ray tomography, simulated ultrasonic wave propagation and gas chromatographic study in order to define: (a) the relationship between petrological and petrophysical properties; (b) the percentage of bitumen impregnation and its link to color shades; (c) the amount of hydrocarbons within lithotypes.

Finally, it is worth noting that some of the aforementioned activities are carried out in the frame of the UNESCO International Geoscience Programme (IGCP)-746 *RESOURCES4ALL***,** a collaborative project among institutions from Europe and Africa.

# Assessment of SDG indicators applied to the natural stones cluster in the state of Espírito Santo in Brazil: a step towards sustainable development

Sena do Nascimento J.A., Castro F.F. & Castro N. *

Centre for Mineral Technology, Brazilian Ministry of Science, Technology and Innovation, Rio de Janeiro (Brazil).

*Corresponding author e-mail:* ncastro@cetem.gov.br

*Keywords:* natural stone, SDG.

Brazil is the fifth largest world producer of natural stone, and the state of Espírito Santo holds most of the country's production and exports (ABIROCHAS, 2022). The stone sector accounts for around 10% of the state's GNP (CENTROROCHAS, 2022). Marble quarrying in the South of the state dates back to the 1950s. From the 1970s, the diamond wire cutting technology allowed quarrying of its vast granite deposits in the North. It led to the expansion of all sectors related to natural stone production: processing, transportation, metal-mechanical industry, supplies, marketing and others (Castro et al., 2011). Most of the municipalities host granite or marble quarries (66 of 78), and other natural stone types, i.e., quartzites, are also processed in that state. Their importance to the local economies, together with the existence of the whole supply chain and the degree of cooperation between the stakeholders, merited its recognition and governmental support as the first Mineral-based Local Productive Cluster (APL in Portuguese). The Centre for Mineral Technology (CETEM) has been working for more than twenty years in Espírito Santo, mapping the technological, economic, and environmental issues related to the natural stone industry. With the consolidation of the Sustainable Development Goals (SDG) methodology (UN, 2016) arises the opportunity to construct aligned indicators that can serve as a basis for public policies. This research aims to use the social, economic and technological information bases related to the natural stones production in the state of Espírito Santo to build SDGs monitoring indicators. In this sense, evaluating materials consumption, processing technologies, waste recovery, and the environmental, socio-economic and political challenges will constitute the core for constructing a more rational and socially responsible exploration model of those non-renewable natural resources. A first stage of mapping the stone deposits in the state of Espírito Santo, followed by the evaluation of the productive municipalities' socioeconomic characteristics, has been completed. That allowed the selection of the most relevant SDG indicators. Additionally, technological aspects related to mineral exploration that influence the socioeconomic and environmental dynamics were raised. A database with the most consistent socioeconomic, environmental and technological indicators will be constructed. It is intended to present a model for monitoring this extractive sector in the state of Espírito Santo from the perspective of Sustainable Development.

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# Communicating dimension stone durability, a case-study: a georama in the centre of Bergamo

Signori G.*

Ateneo di Scienze, Lettere ed Arti, Bergamo.

*Corresponding author e-mail:* eurgeol.grazia.signori@gmail.com

*Keywords:* heritage, decorative stones, durability.

The use of ornamental stones has always been bringing within multiple meanings: beauty, decor, prestige, a fashion statement, and, above all, eternity.

Eternity is strongly related to durability and is one of the main expectation of users. It is therefore essential to build tools aimed at communicating this value in order to develop awareness of it in common people and sector professionals, that is, both at an informative level, for example in the context of geo-touristic routes, and at a technical-application level, with the aim of stimulating specific skills to read the stone as a building language and its ability to preserve over time. The Project and research: "ART ON SIGHT: Stones's eternal beauty" aims to it.

In the beginning of the 20th century the lower part of Bergamo city was developed according to a wide furbishing project designed by architect Marcello Piacentini. Here stone is the most distinctive element, coupled with a stylish footprint spread in different and harmonious shapes.

The heart of Bergamo city is therefore an open-air museum, a *georama* that allows to touch, better than any test and tri-al report with labs results, for durability of the litho-types of 100, 80 or 60 years ago.

The aim of the research is the preparation of the technical-scientific material and a specific database which will help to showcase, in terms of scientific and technical details, the heritage buildings starting from their stone soul, highlighting the role of the nature of litho-type and its craftmanship in creating the identity of the city, and in keeping it unchanged over time thanks to the durability of the chosen lithotypes.

The result of the multidisciplinary research developed during the project has brought two different products: the publication of the volume "LOST OCEANS SHIFTING SANDS CHANGING RIVERS RESTING VOLCANOES - A STONE DIORAMA IN THE CENTRE OF BERGAMO", and the interactive and searchable map "ART ON SIGHT: Stones's eternal beauty".

The publication is technical/educational and wishes to highlight and value each litho-type of its kind:

- Durability
- The expressive potential
- The versatility of the processing which has seen an enormous upgrading in the past 100 to 60 years
- The business continuity and the know-how.

All data gathered during the scientific research through a meticulous survey on the use of natural stones in Bergamo, continually rolling out, has been organized in an available database with an interactive map that can be researched in the heritage archive of the Ateneo di Scienze, Lettere ed Arti di Bergamo with this link https://patrimonio.ateneobergamo.it/mappa-pietre-in-vista/.

# Urban stone paving: identity, durability and sustainability. Some cutting-edge cases studies and experiences

Signori G.*[1] & Angheben A.[2]

[1] Ateneo di Scienze, Lettere ed Arti, Bergamo. [2] Italporphyry, Consorzio Italiano Porfido del Trentino, Trento.

*Corresponding author e-mail:* eurgeol.grazia.signori@gmail.com

*Keywords:* sustainability, stone paving, porphyry.

Stone paving either add value to urban landscaping and strongly contribute to making the deep identity of a town.

That's why it is so important to safely maintain urban stone paving. Nowadays road stone paving shall fulfill very serious and heavy requirements due not only to weather, but also to more and more increasing traffic loads, wear and maintenance procedures.

Durability is then the key topic.

We correctly pay a great attention to the stone selection, but what about the technical characteristics of the rest of the stratigraphy beneath the stone paving layer? As an answer, the recently published standard UNI 11714-1:2018 Stone coverings Instructions for the design, installation and maintenance, with the durability requirements as a main issue, introduces a technical approach to the selection of the stratigraphic package according either to the end use (i.e., load class) and the kind of stone paving to be installed.

It applies also to refurbishing projects, where the re-use of stone paving elements is the key-point for the sustainability and virtuous circular economy.

Re-use of stone elements is up to 70-80% in case of traditional durable paving stones, as porphyry cubes (Assisi, Udine, Bressanone, etc.), *sanpietrini* (Rome, Largo Magnanapoli), *basoli* and *masegne* (Napoli, Duomo Street; Bologna, Strada Maggiore; Firenze, d'Azeglio Square), etc., which means that after decades of use, just 20-30% is to be replaced.

While waiting for the Italian eco-sustainable protocol project CAM regarding roads and paving to be published, Consorzio Italporphyry became a precursor of an innovative project for the recovery of the old, worn porphyry paving, thanks also to the availability of an authorized processing center that is a member of the consortium. Sesto a Reghena (PN) refurbishment project was for the recovery of old, badly deteriorated porphyry paving and its re-use for the same site. The old 4/6 cm porphyry paving cubes were recovered by cleaning them in a tumbler and then carefully selecting the ones that could be re-used, for a new, protected pedestrian zone (installed with the pre-mixed mortars from the Mapestone system range) with bars and shops. The road part of the piazza on the other hand, designed to include a drainage function, was paved with "new" 6/8 cm cubes sealed with Mapestone Joint polyurethane binder.

The main inspiration was being able to control limit waste and, at the same time, introduce procedures to demonstrate the sustainability and durability of old materials by enhancing them to extend their service life. Paving is often found to be in poor condition, but most of the porphyry cubes that make up the paving are perfectly sound, so it's a pity to dispose of such a noble product which still has good performance properties and, more importantly, is part of the heritage of local communities.

# Ornamental stones of Piemonte (NW Italy): a geodatabase for the promotion, conservation and dissemination of a scientific, economic and cultural heritage

Storta E.*[1], Barale L.[2], Borghi A.[1], d'Atri A.[1], Dino G.A.[1], Gambino F.[1], Mallen L.[3], Martire L.[1], Morelli M.[3], Nicolò G.[3], Perotti L.[1] & Piana F.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino. [3] Agenzia Regionale per la Protezione Ambientale, Torino.

*Corresponding author e-mail:* elena.storta@unito.it

*Keywords:* ornamental and dimension stones, geological map, Piemonte.

A geodatabase on the ornamental and dimension stones of Piemonte has been implemented referring to a Geo-Lithological Map recently published (Barale et al., 2020). The database is grounded on the Geological Map of Piemonte (Piana et al., 2017) and includes several information such as the scientific and commercial name of stones, the lithological varieties, the quarry location, the petrographic description, as well as the main historical-architectural applications and references. It represents the first complete revision of historical and contemporary stone materials quarried in Piemonte region. The geodatabase represents a source of information for geologists and people working in the fields of Cultural Heritage and geo-environmental sciences. This service is useful for geotouristic and cultural enhancement activities in Piemonte, such as those related with the extraction of stones. It represents also a tool for the creation of geotouristic routes, including sites of scientific and cultural interest (e.g., historical buildings, monuments and historical quarries). The geodatabase is made available through the interactive Geologic Map of Piemonte (GeoPiemonte Map), a web GIS application developed by Arpa Piemonte and CNR-IGG, already hosting the Geological Map of Piemonte (Piana et al., 2017), which was recently updated. Through this application the user will be able to easily access detailed information on the historical-archaeological uses of ornamental stones and their geological properties, by querying the interactive database. A proper scientific language, simplified in order to be suitable for dissemination, has been used: synthetic descriptive cards, both textual and graphic will be also designed.

*This research was carried out through a collaboration between Dipartimento di Scienze della Terra di Torino, CNR-IGG Torino and Arpa Piemonte, with the involvement of Confartigianato Imprese Piemonte. The research is part of the Project: "Carta geo-litologica delle pietre ornamentali del Piemonte: divulgazione on line di un patrimonio scientifico, economico e culturale" co-financed by CRT Foundation and University of Torino.*

Barale L., Borghi A., d'Atri A., Gambino F. & Piana F. (2020) - Ornamental stones of Piemonte (NW Italy): an updated geo-lithological map. J. Maps, 16(2), 867-878. https://doi.org/10.1080/17445647.2020.1837685.

Piana F., Barale L., Compagnoni R., d'Atri A., Fioraso G., Irace A., Mosca P., Tallone S., Monegato G. & Morelli M. (2017) - Geological Map of Piemonte region at 1: 250,000 scale, Explanatory Notes. Mem. Accad. Sci.Torino, Serie V, Cl. Sci. Fis., 41, 2-148.

# The key role of geostructural characterization for a sustainable exploitation of the resource: the case of the dimensional stone of Botticino

Vianello D.*[1], Caselle C.[1], Bonetto S.[1] & Mosca P.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* davide.vianello@unito.it

*Keywords:* Botticino marble, fracture network, quarry planning.

Geological surveys are fundamental part to set up a strategy for sustainable exploitation of the natural resources, defining the geological setting of the area and assessing feasibility and potential production of the quarrying site. Mechanical characterization of the discontinuities network (including stratifications, foliations and fractures) is crucial for estimating the available volume of the resource and its giacimentological framework. Detailed geo-structural analyses of the rock mass are decisive in the exploitation of dimensional stones for which high mechanical and esthetical standards of quarried material are required. Thus, geological-based planning and management of quarry activity is the only feasible way to ensure sustainability of exploitation, reduce mining wastes and mitigate the environmental impact of the quarry.

This contribution aims to define structural setting, spatial relationships of mechanical discontinuities and quality of rock mass in the quarries site of the Botticino village (BS), one of the most famous and appreciated Italian ornamental stone. The "Botticino marble" (commercial term) is a micritic limestone, beige in color, quarried from the upper part of the Corna Formation (Rhaetian-early Sinemurian) of the Southern Alps. The open pit quarries are located on an open anticline with axis NE-SW trending and plunging to SW at low angle due to the evolution of the south-verging Southern Alps. Natural discontinuities in the ore body represent both preferential surfaces for cutting as well as potential failure surfaces. Analysis of mechanical features and relationship of discontinuities is therefore necessary to properly organize the pit and correctly plan the geometry and orientation of the exploitation faces.

Fracture network of rock mass was defined by linear scanline and window sampling and the results were also used for a geological modeling of the quarry site. This approach facilitates the understanding of the giacimentological framework of the resource and represents a useful tool for planning the mining project in order to facilitate extraction and at the same time protect the resource.

# Sustainability in the mining industry: a contribution to achieving social acceptance

Zichella L.[1], Bellopede R.*[1], Marini P.[1], Robledo P.[2] & Vosman L.[2]

[1] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.
[2] Arisa (Advocating Right in South Asia) Foundation, Utrecht (Netehrlands).

*Corresponding author e-mail:* rossana.bellopede@polito.it

*Keywords:* Social License to Operate, cultural heritage, mining due diligence.

Most of the historic Italian buildings, which are part of the cultural heritage, were built using strictly extracted and processed materials in the same region where the building is located. Italy is a large exporter of ornamental stones, but in the last decade also an importer of materials from other countries. These imports are mainly due to low labor costs compared to Italian ones. Examples of sustainability issues related to the extraction and processing of ornamental stones in these countries come from research conducted by Non-Governmental Organizations (NGOs) In such cases, where the extraction process is often poorly regulated and results in excessive and illegal exploitation of resources, with damage to the surrounding natural environment.

The growing awareness of sustainability issues in the natural stone sector over the last ten years has led to the launch of Responsible Business Practices (RBC) initiatives.

At the European level, various legislative documents can represent tools for achieving the social license to operate (SLO) which is fully applicable to the extractive sector, also guaranteeing respect for human rights, often not protected in this sector. After analyzing the regulatory and legal aspects at a European and international level, various cases of European and international natural stone quarrying realities are compared which place SLO as an integral part of their business model. It has been verified that some European companies have developed a series of initiatives to integrate social responsibility into their modus operandi, especially in the light of the Minimum Environmental Criteria (CAM - Italian Ministry for Ecological Transition) requirements necessary for the project and the awarding of public works. In this context is taken into account the importance of the geographic origin of materials (GI), in accordance with the European Commission document COM (2014) 469 final, which extends the protection of geographical indications to non-agricultural materials to make the most of the traditional Europe know-how.

COM 469 (2014) - GREEN PAPER - Making the most out of Europe's traditional know-how: a possible extension of geographical indication protection of the European Union to non-agricultural products. European Commission, Strasbourg.

# S6.

# Palaeomagnetism, Rock Magnetism and Magnetostratigraphy

*CONVENERS AND CHAIRPERSONS*


*Evdokia Tema (University of Torino)*

*Anita di Chiara (INGV, Roma)*

*Francesca Cifelli (Roma Tre University)*

*Massimiliano Porreca (University of Perugia)*

# Anisotropy of out-of-phase magnetic susceptibility of rocks and environmental materials

Chadima M.*[1-2], Hrouda F.[1-3] & Ježek J.[3]

[1] AGICO Ltd., Brno (Czech Republic). [2] Institute of Geology, Czech Academy of Sciences, Prague (Czech Republic).
[3] Faculty of Sciences, Charles University, Prague (Czech Republic).

*Corresponding author e-mail:* chadima@agico.cz

*Keywords:* magnetic fabric, anisotropy of magnetic susceptibility.

The alternating-field magnetic susceptibility can be, in general, resolved into components that are in-phase and out-of-phase with the applied field. While being effectively zero for most geological materials (non-conductive diamagnetic, paramagnetic and many ferromagnetic materials), the out-of-phase susceptibility arises from the presence of (1) ferromagnetic minerals possessing low-field hysteresis (e.g., pyrrhotite, hematite, titanomagnetite), (2) virtually non-magnetic minerals that are conductive electrically (e.g., graphite), or (3) magnetically viscous grains on superparamagnetic / stable single domain boundary (e.g., ultrafine grains of magnetite or maghemite). Using state-of-the-art magnetic susceptibility meters, which are so sensitive to detect even minor out-of-phase contribution to the overall susceptibility signal, anisotropy of out-of-phase susceptibility (opAMS) can be measured. opAMS can be then used as a tool for direct determination of magnetic sub-fabrics carried by the above mentioned rock-forming minerals with non-zero out-of-phase susceptibility. The advantage of the opAMS is its simultaneous measurement with standard AMS in most recent instruments.

Several examples are given: (1) In rocks the susceptibility of which is carried by both magnetite and pyrrhotite, the opAMS indicates the pyrrhotite sub-fabric whose knowledge is important in the investigation of the genesis of ultramafic rocks. (2) In graphite-bearing rocks and graphite ores, the opAMS indicates the preferred orientation of graphite by crystal lattice, which cannot be revealed by standard AMS because of weak diamagnetism of graphite. The knowledge of graphite sub-fabric can help in solving genetic problems of graphite ores. (3) In loess/palaeosol sequences, the opAMS can serve as indicator of preferred orientation of ultrafine particles of magnetite or maghemite that are on transition between superparamagnetic and stable single domain states. The sub-fabric of the ultrafine particles may namely differ from the fabric of multi-domain particles according to geological history of such rocks.

# Rock magnetic study of the Dejvice loess/paleosol sequence (Prague, Czech Republic)

Chadima M.*[1-2], Žatecká M.[3] & Kadlec J.[4(†)]

[1] AGICO Inc., Brno (Czech Republic). [2] Institute of Geology, Czech Academy of Sciences, Prague (Czech Republic). [3] Institute of Geology and Palaeontology, Charles University, Prague (Czech Republic). [4] Institute of Geophysics, Czech Academy of Science, Prague (Czech Republic).

*Corresponding author e-mail:* chadima@agico.cz

*Keywords:* frequency dependent susceptibility, out-of-phase susceptibility, viscous magnetization.

In this contribution, we present a rock magnetic and magnetic fabric study of the Dejvice loess/paleosol sequence with an aim to demonstrate how rock magnetic methods can be very effective tools for detecting paleoenvironmental, pedogenic, and post-depositional processes. This study covers the 15-meter-long loess/paleosol section which was recently temporarily accessible during the underground construction works in the Vienna House Diplomat Hotel in Prague. The exposed part of the sequence contained at least four different paleosol horizons and covered the time interval from ca. 130 ky to recent. For the purpose of this study, 425 orientated samples (8 ccm) were collected evenly covering the studied section.

In general, loess sequences contain variable amount of detrital magnetic particles derided from the source material. In addition, in warmer interglacials periods, pedogenesis results in formation of paleosol horizons which are magnetic enhanced by the in-situ neo-formed nanoscale ferromagnetic particles.

The applied rock-magnetic techniques included measurements of (1) magnetic susceptibility (MS), (2) frequency-dependent susceptibility (kFD), (3) out-of-phase magnetic susceptibility (opMS), and (4) viscous magnetization (Mv). While MS very sensitively reflects the relative amount of all magnetic particles, the other methods (kFD, opMS, and Mv) mirror solely the contribution of the neo-form nanoscale particles. In addition to these rock magnetic parameters, (5) anisotropy of magnetic susceptibility (AMS) was measured in order to obtain magnetic fabric reflecting the preferred orientation of magnetic minerals. Magnetic fabric can be primarily interpreted in terms of paleotransport directions but it may also provide some evidences for post-depositional reworking and/or movements.

All paleosol horizons possess significantly higher values of MS, kFD, opMS and Mv. This indicates that the increased amount of magnetic particles in paleosols is exclusively due to the magnetic enhancement caused by the neo-formation of nanoscale particles during pedogenesis. In addition, the values of kFD, opMS, and Mv mutually intercorrelate very tightly. This indicates that all these independent methods are reliable proxies for the quantification of ultra-file particles in loess/paleosols horizons.

In addition of the paleotransport direction, the magnetic fabric reflects secondary sedimentary processes. This involves the displacement of clastic particles by flowing water and the redeposition of the material along the slope. The direction of movement of these sediments corresponds to the current geomorphology of the surroundings. We can conclude that the section was not deposited solely by the aeolian processes.

# Reconstructing eruptive canters of large pyroclastic density currents using the Anisotropy of magnetic susceptibility

Di Chiara A.*[1-2] & Cangemi B.[1]

[1] INGV, Roma. [2] Scripps Institution of Oceanography, La Jolla, CA (USA).

*Corresponding author e-mail:* anita.dichiara@ingv.it

*Keywords:* Pantelleria, anisotropy of the magnetic susceptibility, ingnimbrites.

The aim of the study is to find the location of the source area and understand the emplacement mode of the explosives eruptions which emplaced large ignimbrites exposed in the volcanic island of Pantelleria (Sicily Channel Italy). The method adopted here is the study of the AMS (Anisotropy of the Magnetic Susceptibility) which uses the magnetic properties of a rock as a proxy for mineral preferred orientations. AMS has been already successfully used to determine pyroclastic dynamics and emplacement modes and identify source vents and flow directions of ignimbrites. The island of Pantelleria (36º 50" N; 11º 57" E) is an ideal location to use the AMS to study large pyroclastic density currents (PDC) to understand the eruptive and emplacement dynamics of the PDC deposits, the ignimbrites. Pantelleria Volcano has been active for at least 330 ka emplacing more than 10 major ignimbrites; comprehensive geochronological defined the stratigraphic succession of these ignimbrite. Nonetheless, despite excellent exposures and well-defined ages, the location of their eruptive centre or centres is not clear. A very recent paper suggested five caldera collapse events, in contrast to the two events reported to date. The youngest caldera (Cinque Denti) correlates with the extensively exposed Green Tuff (GT) ignimbrite (with an Ar/Ar age of 45.7±1 ka). By contrast, deposits connected with the other calderas (e.g., La Vecchia) have not been identified yet. Here, we present the preliminary results of the AMS study of the Green Tuff, and older ignimbrites to unravel their origin and emplacement mode.

# Magnetochronology of late Eocene turbidites (Ventimiglia Flysch Fm) from the western Alps foreland basin

Marini M.[1], Patacci M.[2], Cifelli F.*[3], Mattei M.[3] & Muttoni G.[1]

[1] Dipartimento di Scienze della Terra «A. Desio», Università di Milano. [2] School of Earth and Environment, University of Leeds (UK). [3] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* mattia.marini@unimi.it

*Keywords:* magnetochronology, depositional age model, turbidites.

The late Eocene Ventimiglia Flysch Fm (FYV) of NW Italy is part of the greater Grès d'Annot system, which spans across the French-Italian border and represents the dominantly deep-water sedimentary fill of the foreland basin system of western Alps. Compared to the Grès d'Annot of SE France, the Ventimiglia Flysch Fm. has received relatively little research interest to date, which makes it timely to revaluate its significance, including age and accumulation rates.

Previous studies suggest the up to ca. 1000 m-thick FYV was deposited in a structurally confined elongate basin and is characterized by an overall sheet-like architecture (Dallagiovanna et al., 2012; Marini et al., 2022). The age of FYV is loosely constrained based on biostratigraphic age of the hemipelagic marlstone below (late Bartonian) and an earliest Oligocene foraminiferal assemblage characterizing the upmost part of the unit. This contribution presents the preliminary results of a magnetochronology investigation that aims at providing constraints for a depositional age model.

A total of 170 samples for palaeomagnetic analysis were collected targeting the mudstone component of a ca. 700 m-thick composite stratigraphic section, previously logged bed-by-bed for sedimentary facies. Natural remnant magnetisation (NRM) and anisotropy of magnetic susceptibility (AMS) were measured using a cryogenic magnetometer and an AGICO Kappabridge, respectively.

Results of NRM analysis indicate that the composite stratigraphic section spans two magnetozones, namely a lower and ca. 500 m-thick reverse-polarity zone and an upper normal-polarity zone. Considering the likely age of deposition of FYV from published biostratigraphy, only three reverse polarity chrones (i.e., C15r, C16r and C17r, having durations between 280 and 400 ky) are plausible matches for the zone identified. Although it was not possible to assign conclusively the reverse-polarity zone in the study interval to one of them, this information can be used to constrain the minimum sedimentation rate for FYV, which is 1200 m/Ma, placing it in the upper end of the range of turbidites deposited in large confined basins in active settings. The results of the AMS analysis indicate a disc-shaped fabric subparallel to palaeohorizontal. The direction of K1 varies within the study area and cannot be reconciled with the relatively uniform N-directed palaeoflow, suggesting the observed fabric is tectonic origin.

Dallagiovanna G., Fanucci F., Pellegrini L., Seno S., Bonini L., Decarlis A., Maino M., Morelli D. & Toscani G. (2012) - Note illustrative della Carta Geologica Foglio 257 Dolceacqua e Foglio 270 Ventimiglia alla scala 1:25000. Regione Liguria.

Marini M., Patacci M., Felletti F., Decarlis A. & McCaffrey W. (2022) - The erosionally confined to emergent transition in a slope-derived blocky mass-transport deposit interacting with a turbidite substrate, Ventimiglia Flysch Formation (Grès d'Annot System, north-west Italy). Sedimentology. https://doi.org/10.1111/sed.12968

# Magnetobiochronology of ponded turbidites (Castagnola Fm., Aquitanian) from the Tertiary Piedmont Basin of NW Italy: implications for turbidite deposition

Maron M.*, Marini M., Petrizzo M.R., Felletti F. & Muttoni G.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* mattia.marini@unimi.it

*Keywords:* magnetochronology, depositional age model, turbidites.

This contribution focuses on the ca. 800 m-thick Costa Grande Mb. (CG) of the Castagnola Fm. (Tertiary Piedmont Basin, NW Italy), the turbidite fill of a ponded basin (early Miocene), and aims at: i) retrieving a magnetic polarity stratigraphy for CG; ii) defining an age model by tieing the CG magnetostratigraphy to the reference Geomagnetic Polarity Time Scale (GPTS) with the support of biostratigraphic data from a few hemipelagic beds intercalated in CG; iii) calculating depositional rates and frequency of turbidites by parent flow type; iv) look into whether and how (are they cyclic vs. erratic? Is there a trend?) these quantities changes in time. A base-to-top stratigraphic section of CG, recently logged with cm-scale resolution for sedimentary facies (Marini et al., 2016) was sampled with an average stratigraphic spacing of ca. 7 m yielding 140 samples that were thermally demagnetized to isolate their characteristic component of natural remanent magnetization.

The correlation of the CG magnetostratigraphy with the Late Oligocene-Early Oligocene GPTS was first evaluated with a statistical approach that assumes liner scaling between stratigraphic thickness and time (i.e., constant sediment accumulation rate). Sliding the CG magnetostratigraphy along the GPTS resulted in a total of 28 options, 4 of which above pass the student t-test with a 90% confidence threshold. However, only 1 out of these 4 options agrees with the available biostratigraphic data, suggesting CG was deposited during the early Miocene (from Chron C6AAr.3r to C6Bn.2n) between 21.7 and 22.3 Ma. When only the thin-bedded turbidite component of CG is taken into consideration, the reliability of the selected correlation option improves, suggesting the thin beds of CG might reflect a sort of background deposition by low-density flows with a frequency in the range 0.5-1/ky. Conversely, thicker beds tend to locally cluster in the stratigraphy, suggesting larger parent flows have a lower (0.05-0.3/ky) yet highly variable frequency. These results have important consequences on linking turbidite facies of ancient turbidite systems to likely trigger and parent flow types of submarine sediment gravity flows.

Marini M., Patacci M., Felletti F. & McCaffrey W.D. (2016) - Fill to spill stratigraphic evolution of a confined turbidite mini-basin succession, and its likely well bore expression: The Castagnola Fm, NW Italy. Marine and Petroleum Geology, 69, 94-111.

# Increased weathering and anoxic conditions in the late Norian-early Rhaetian interval from rock magnetism and geochemistry of Pignola-Abriola (Italy) and Kiritihere (New Zealand) sections

Maron M.*[1], Onoue T.[2], Satolli S.[1], Soda K.[3], Sato H.[2-4], Muttoni G.[5] & Rigo M.[4]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Department of Earth and Planetary Sciences, Kyushu University (Japan). [3] Center for Advanced Marine Core Research, Kochi University (Japan).
[4] Dipartimento di Geoscienze, Università di Padova.
[5] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* matteo.maron@unich.it

*Keywords:* Upper Triassic, rock magnetism, paleoclimate.

The late Norian to early Rhaetian (Late Triassic) interval is characterized by an important biotic crisis that involved marine and terrestrial fauna (mainly conodonts, ammonoids, bivalves and theropods). The climate perturbation that began in the Sevatian (upper Norian, ~216 Ma) and persisted up to the Rhaetian (~206 Ma) seems to be linked to the biotic turnover across the Norian/Rhaetian boundary (NRB). To better understand the Norian-Rhaetian climatic perturbation, we applied a rock magnetic investigation to the Upper Triassic marine sections of Pignola-Abriola (Lagonegro Basin, Italy; candidate GSSP for the Rhaetian Stage) and of Kiritehere (North Island, New Zealand), which have been broadly investigated by biostratigraphic and chemostratigraphic studies. The rock magnetic analyses (ARM, IRM, magnetic susceptibility, hysteresis loops) were compared with the latest geochemical data from Pignola-Abriola and Kiritehere, getting a new insight about the paleoclimatic conditions across the Norian/Rhaetian boundary. Both rock magnetic and geochemical data revealed two main phases of increasing weathering in the Sevatian and across the Norian/Rhaetian boundary. The relevant $\delta^{13}C_{org}$ perturbation occurred in concomitance to the Norian-Rhaetian biotic crisis and led to a negative carbon isotope excursion at the NRB, marked by the disappearance of monotids bivalves and close to the first appearance of conodont *Misikella posthernsteini*. Both the $\delta^{13}C_{org}$ negative excursion and the FAD of *M. posthernsteini* have been suggested as markers of the Rhaetian base.

# Reconstructing the past Earth's magnetic field through rocks

Pavón-Carrasco F.J.*[1-2]

[1] Department of Physics of the Earth and Astrophysics, Complutense University of Madrid (Spain). [2] Institute of Geosciences IGEO, CSIC-UCM, Madrid (Spain).

*Corresponding author e-mail:* fjpavon@ucm.es

*Keywords:* paleomagnetism, archeomagnetism, paleomagnetic reconstructions.

The Earth's magnetic field is generated by complex fluid movements located in the outer core and envelops our planet protecting us against the solar wind. The worldwide network of observatories and satellites are providing an accurate picture of the geomagnetic field changes during the last decades. However, it is possible to know the past evolution of the Earth's magnetic field at geological time scales thanks to the ability of some rocks preserving the ambient geomagnetic field (the so-called paleomagnetic information). For the Holocene, the paleomagnetic data derived from certain archeological artifacts, lava flows and core sediments can provide snapshots of the past geomagnetic field and thus, they can be used to reconstruct it at local and global scales. In this talk, a general overview of the state of the art of the Holocene paleomagnetic reconstructions is visited, including some examples of how these paleo-reconstructions can be used as a geological/archeological dating tool.

# Archaeo_dating v8.0: a new release of the archeomagnetic dating tool

Pavón-Carrasco F.J.*[1-2]

[1] Department of Physics of the Earth and Astrophysics, Physics Building, Complutense University of Madrid (Spain).
[2] Geosciences Institute IGEO, CSIC-UCM, Madrid (Spain).

*Corresponding author e-mail:* fjpavon@ucm.es

*Keywords:* archeomagnetic dating, volcanic dating, Matlab.

Here we present a new release version of the Matlab software for paleomagnetic dating called *archaeo_dating*. This version 8.0 includes the most recent paleosecular variation curves of the Earth's magnetic field as well as the regional and global paleoreconstructions covering the last millennia. In this work, we analyze the characteristic of this new version highlighting the use of the new European regional paleoreconstruction SCHA.DIF.4k as a tool for dating archeological and volcanic units for the last 4 millennia.

# Magnetochronology and age-depth depositional models of the Melka Kunture archeological area (Upper Awash, Ethiopia)

Perini S.*[1], Muttoni G.[1], Monesi E.[2], Melis R.T.[2] & Mussi M.[3]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Independent author. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [4] Dipartimento di Scienze dell'Antichità, Sapienza Università di Roma.

*Corresponding author e-mail:* serena.perini@unimi.it

*Keywords:* Pleistocene, human evolution, Melka Kunture.

New magnetostratigraphic results from the Melka Kunture sedimentary sequence, outcropping along the Gombore and Garba gullies in the Upper Awash Valley of Ethiopia, have provided a new temporal framework for human presence in this area of the Ethiopian highlands during the Pleistocene (Gallotti, 2013). Our results have revealed a time-diagnostic magnetochronologic record extending from the Brunhes Chron to the Olduvai Subchron, or possibly the Reunion Subchron, obtained from 9 stratigraphic sections correlated in a regional lithostratigraphic context (Raynal & Kieffer, 2004). By integrating our chronology provided by paleomagnetism (Channell et al., 2020) with other dating methods from the literature (Morgan et al., 2012), we generated linear age models of deposition for the Melka Kunture sedimentary sequence that we used to estimate the mean ages of the main archeological levels therein contained which resulted ranging from ~0.6 Ma to ~2.1 Ma, representing altogether one of the most persistent and prolonged records of human presence of the entire African continent.

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# Late Cenozoic Dynamic Uplift & Subsidence of Central Appalachians & Atlantic Coastal Plain in Eastern North America

Polashenski M.*, Pazzaglia F. & Kodama K.

Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, PA (USA).

*Corresponding author e-mail:* mjp518@lehigh.edu

*Keywords:* geomorphology, magnetostratigraphy, cyclostratigraphy.

We combine a model of base level change for the Delaware River and Brandywine Creek catchments, a new paleomagnetic and cyclostratigraphic-based age model for the inner Coastal Plain, and eustasy to reconstruct a 25-million year record of epeirogenic uplift and subsidence for the U.S. mid-Atlantic passive margin.

Catchment base level change is predicted by a stream-power based linear inversion of fluvial topography that assumes uniform block uplift upstream of the Fall Zone and uniform, steady erosion of 30±5 m/Myr for non-uniform rock erodibility. Several iso-elevation knickpoints in the Delaware and Brandywine catchments are consistent with upstream-propagating transients generated by an unsteady base level fall history at the Fall Zone. Model results show slow rates of Early Miocene basin uplift of ~1 cm/kyr increasing to ~2 cm/kyr in the Middle Miocene. A late Miocene impulsive uplift to ~5.5 cm/kyr at ~8 Ma decreases to ~3 cm/kyr in the Early Pliocene, followed by higher frequency unsteadiness in base level change during the Pleistocene presumably linked to glacio-eustasy.

The corresponding subsidence and depositional record in the sink is recorded by the stratigraphy in the Bethany Beach core (Qj32-27 from ODP Leg 174AX), here re-evaluated in terms of a paleomagnetically-constrained cyclostratigraphic age model with strontium isotope ages and sequence boundaries noted from earlier studies. Optimal sedimentation rates are calculated from the gamma ray data log of continuous lithostratigraphic packages of section using Acycle time series analysis (Li et al., 2019) relating the power spectra to expected astronomical forcings. Inferred polarity intervals based on characteristic remanent inclinations from demagnetization of core samples tie in with the geomagnetic polarity time scale from chron C5 (Late Miocene) through C1 (Middle Pleistocene) to delineate durations of extended hiatuses ranging from ~0.8 to ~2 Myr. Shallow inclinations at ~0.9 Ma are consistent with the Santa Rosa excursion.

These data indicate that base level changes in the source are not coupled to the sink in a simple, obvious way over the record length. Prior to ~12 Ma eustasy and dynamic topography conspire to generate a relatively stable base level for this part of the margin. The two significant unconformities during this time are not linked to any obvious changes in dynamic-driven base level change. After ~12 Ma, acceleration in the rate of subsidence in the sink generally precedes uplift in the sources, suggesting a link to transient and non-uniform dynamic support. We continue to explore the possibility that channel knickpoints - concentrated in basin elevation and response time to the late Miocene pulse of dynamic uplift - record periodic base level fall modulated by short or long eccentricity cycles.

Li M., Hinnov L. & Kump L. (2019) - Acycle: Time-series analysis software for paleoclimate research and education. Computers & Geosciences, 127, 12-22.

# Interpreting the enigmatic inverse magnetic fabric in Miocene dikes from Eastern Iceland

Porreca M.*[1], Trippanera D.[2], Urbani S.[3], Kissel C.[4], Winkler A.[2], Sagnotti L.[2], Nazzareni S.[1] & Acocella V.[3]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] INGV, Roma. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, Gif-sur-Yvette (France).

*Corresponding author e-mail:* massimiliano.porreca@unipg.it

*Keywords:* magnetic fabric, dike, magma flow.

Anisotropy of Magnetic Susceptibility (AMS) is a valid tool to investigate magma flow direction within dikes. However, geometrically inverse magnetic fabric characterized by maximum magnetic susceptibility axis (kmax) perpendicular to the dike wall may complicate the interpretation of flow trajectories. To better understand the nature of this fabric, we present a multiscale study on 19 dikes (383 samples) in the Miocene Alftafjordur volcanic system (Iceland), where 80% of the samples show a geometrically inverse magnetic fabric. We carried out (1) AMS measurements at different magnetic fields and temperatures, along with Anisotropy of Anhysteretic Remanent Magnetization (AARM) analysis; (2) hysteresis loops and FORC diagrams; (3) thin section analysis; (4) structural fieldwork. A variable Ti-content ($0.13_{-x}Ti_xO_4$) titanomagnetite is the main magnetic carrier, and the contribution of the paramagnetic elongated crystals to the magnetic fabric is negligible. Single domain is not the prevailing domain state of the magnetic particles, suggesting that its occurrence cannot be the main cause for the inverse fabric. AMS analysis at different fields and temperatures along with AARM allow us to exclude any mineral phase change of the titanomagnetite across the dike. Nevertheless, kmax is parallel to a diffuse horizontal column-like fracture pattern perpendicularly oriented with respect to the dike strike.

This suggests that the Ti-magnetite mineral orientation during dike cooling was affected by the fracture network progressively developing columnar basalts. This study demonstrates that the interpretation of AMS data on old and deep volcanic bodies is not straightforward and observations at different scales are required.

# Lithology-dependent magnetic fabric in intraplate shear zones in the Northern Apennines, Italy: Constraints from para- and ferromagnetic fabrics

Robustelli Test C.*[1-2], Biedermann A.R.[3], Zanella E.[1-2] & Festa A.[1-4]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Laboratorio di Paleomagnetismo Alpino, Centro Interuniversitario di Magnetismo Naturale «Roberto Lanza», Peveragno (CN). [3] Institute of Geological Sciences, University of Bern (Switzerland). [4] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* claudio.robustellitest@unito.it

*Keywords:* rock magnetism, magnetic fabric, shear zones.

Intraplate shear zones and shallow megathrusts are complex and highly deformed zones displaying a variety of slip behaviours. Lithological heterogeneities are inferred to influence the frictional properties, the slip weakening mechanisms and the degree of shear localization. Magnetic properties of fault rocks (i.e., mineral assemblages, concentration, granulometry and preferred orientation of grains) are known to be sensitive to chemical and physical changes related to the faulting processes. The magnetic mineralogy is lithology dependent, with a variety of subpopulations of grains (different mineralogy and grain size) that may form and alter at distinct diagenetic or deformation stages. Particularly, magnetic fabric is a good proxy for the stress regime variations, providing insight into the relationships between petrofabric and deformation intensity. Since each mineral may respond differently to the deformation mechanisms, separating the preferred orientation of paramagnetic minerals and iron oxides may help to discern multiple deformation events.

We studied the relationships between magnetic and mesoscale structural fabric of three megathrust faults which are developed in carbonate or clay-rich sediments in the Northern Apennines (Italy). The orientation of remanence-bearing grains was isolated performing four separate anisotropy of magnetic remanence experiments. Then, the paramagnetic fabric was derived by high-field torque magnetometry.

Different sensitivity of para- and ferro-magnetic grains to the deformation are observed depending on the lithology. Carbonate-rich rocks reveal a slight variation in the orientation of para- and ferromagnetic fabrics, which suggest similar registration of the strain by different subpopulation of grains. Instead, in clay-rich sediments the ferromagnetic grains show orientations independent from the paramagnetic matrix recording different deformation stages.

Moreover, our results show distinct orientations of the magnetic fabric and changes in ellipsoid shape with strong dependency on the structural position (i.e., distance from the fault plane) and the pervasivity of tectonic features (e.g., cleavage and stylolite).

The magnetic fabric is dominantly oblate with magnetic lineation parallel to the shear sense in the proximity of the shear zone, suggesting shear localization along the main faults. Away from the thrusts, we observed a decrease in the anisotropy degree and magnetic fabrics related to less intense deformation (i.e., intersection lineation fabric), revealing minor to absent evidences of shearing.

Our findings show the potential of rock magnetism to better constrain the role of lithological variation in controlling the internal architecture of shear zones. We recommend detailed sampling at increasing distance to favour the discrimination between localized and distributed deformation. Integration with geochemistry may help strengthen the links between lithology and strain partitioning.

# Syntectonic magmatism and reactivation of collisional structures during late-variscan shearing (SW sardinia, Italy): a contribution from an integrated structural and AMS study

Secchi F.[1], Casini L.[1], Cifelli F.*[2], Naitza S.[3], Carta E.[1] & Oggiano G.[1]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Dipartimento di Scienze, Università di Roma Tre. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* francesca.cifelli@uniroma3.it

*Keywords:* pluton emplacement, AMS data, thermal model.

The Arbus igneous complex (SW Sardinia, Italy) represents a good example of a short time lived post-collisional composite pluton emplaced at shallow crustal level in the external zone of the Variscan chain. The pluton almost consists of granodiorite and leucogranite rock-*suites* emplaced at 304 ± 1 Ma within a main NW trending thrust separating the metamorphic wedge from the fold and thrust belt foreland. The pluton emplaced into a dilatational step over connecting two NW-SE dextral shear zones which belongs to a regional network of post-collisional strike-slip structures marking the transition from collision to post-collisional extension. The microstructure observed for quartz and K-feldspar confirms the lack of significant post-emplacement deformation, indicating only limited high-temperature sub-solidus recrystallization. Anisotropy of Magnetic Susceptivity (AMS) data and field-structural analysis have been carried out to reconstruct the geometry of the pluton and the trajectories of magmatic flow in relation to regional deformation structures. Overall, the magmatic and the magnetic fabrics are broadly discordant with the metamorphic foliation of the country rocks, defining an EW trending elliptical asymmetric sill rooted in the SW quadrant. The reconstructed architecture combined to petrologic observation indicates that accretion of the pluton involved injection of multiple dykes through a sub-vertical feeder zone, combined to lateral flow of the roof controlled by inherited collisional structure. The duration of magmatic activity and the cooling history of the contact metamorphic aureole have been evaluated through a suite of 2D thermal models. All these observations, together with the available geochronological constraints are suggestive of very rapid construction of the pluton. The proposed emplacement model is fully consistent with the regional phase of strike-slip tectonics and widespread magmatism accommodating the large rotation of the Corsica-Sardinia block during the Carboniferous-Permian transition.

# Paleomagnetism of volcanics from the Ecuadorian Andes constrains the significance of Tertiary northern Andean Block extrusion and genesis of the Interandean Valley

Siravo G.*[1], Speranza F.[1], Mulas M.[2] & Costanzo-Alvarez V. [3]

[1] INGV, Roma. [2] Escuela Superior Politécnica del Litoral, Facultad de Ingeniería en Ciencias de la Tierra, Guayaquil (Ecuador). [3] Department of Mechanical and Industrial Engineering, University of Toronto (Canada).

*Corresponding author e-mail:* gaia.siravo@ingv.it

*Keywords:* Northern Andean Block, paleomagnetism, orocline.

GPS and Quaternary slip rate data suggest that the NW South America corner forms a distinct tectonic Northern Andean Block (NAB) drifting at 0.6 cm/yr NE-ward along regional dextral strike-slip faults that bound an oceanic terrane accreted in Late Cretaceous times to W Ecuador and Colombia. Nevertheless, thrust tectonics characterize the external Northern Andes front from Ecuador to Colombia. Thus, the relevance of strike-slip versus thrust tectonics during the Cenozoic and their relation with oceanic terrane accretion are unclear.

Questions on a hypothetical Cenozoic strike-slip deformation also arise from the variable interpretations of the tectonic regime that generated the Ecuadorian Interandean Valley. This tectonic depression, blanketing the eastern side of the Cordillera Occidental, has been alternatively considered as due to extensional, thrust, or strike-slip deformation.

Paleomagnetism may represent an important tool to unravel the Cenozoic tectonic history of the NAB, as peculiar patterns of vertical axis rotations arise from strike-slip and thrust tectonics.

Here we report on the paleomagnetism of 31 mid-upper Eocene to upper Miocene mainly volcanic sites from the Cordilleras Occidental and Real of southern Ecuador. Eleven sites show that the western Cordillera Occidental underwent a 24°±10° clockwise (CW) rotation with respect to South America after late Miocene, while no rotation occurred further east. As the age of rotation and continental sedimentation onset in the Interandean Valley are similar, we relate the regional CW rotation to the emplacement of the Cordillera Occidental nappe onto the Interandean Valley, that in turn is interpreted as a narrow flexural basin formed ahead of the advancing nappe front.

Previous authors documented a post-Cretaceous 28°±9° CW rotation of the Coastal forearc that is statistically indistinguishable from the 24°±10° Neogene CW rotation documented by us in the Cordillera Occidental and Interandean Valley, implying that the whole W Ecuador Andean chain was detached and rotated over a mid-crustal detachment during the last 10 Ma. Eocene-Miocene paleomagnetic inclination values are systematically consistent with those expected for South America, thus excluding latitudinal terrane drift. Our results show that thrust tectonics prevailed over strike-slip displacement in the southern Ecuadorian Andes during the late Cenozoic.

Finally, we note that the reentrant-salient sequence of the Nazca trench-Andean chain from northern Chile to Ecuador mimics closely the edges of the Archean–Paleoproterozoic Amazonian and other minor Cratons of South America. Considering our results on a continental scale, in combination with previous paleomagnetic data we infer that the stiff crust of the Amazonian Craton behaved as a foreland indenter, hampered inland deformation propagation, and caused the formation of what we call the "Ecuadorian Orocline", arisen by opposite-sign nappe rotations around the Craton apex.

# Iron oxide characterization of a deeply weathered high-land lateritic profile from the Deccan Traps: Implications to autochthonous alteration and allochthonous input

Srivastava P.*[1-2], Sangode S.J.[3], Torrent J.[4], Florindo F.[1] & Jovane L.[2]

[1] INGV, Roma. [2] Instituto Oceanográfico, Universidade de São Paulo (Brazil). [3] Department of Geology, Savitribai Phule Pune University (India). [4] Departamento de Agronomía, Universidad de Córdoba (Spain).

*Corresponding author e-mail:* priyeshusrivastava@gmail.com

*Keywords:* laterite, Deccan Traps, environmental magnetism.

The deeply weathered profiles (duricrusts) developed on high-land plateaus of the Deccan Traps are often argued for their origin as a product of an autochthons (in-situ) weathering of Deccan basalts or as an allochthonous enriched ferricrete. The source of iron in latter case has been hypothesized from relief inversion and/or from alteration of aeolian deposits. We investigated geochemical, diffuse reflectance spectroscopy and rock magnetic properties of a ~46 m thick deeply weathered profile from the Patan area in Bamnoli Range of the Western Ghats, India. The sharp distinction between saprolite and laterite (/ferricrete) zones could be identified with dominant ferrimagnetic mineral assemblage in the saprolite zone, and high concentration of antiferromagnetic minerals in ferricrete zone. The index of lateritisation (IOL) ranged between 43 and 98, showing an increasing trends towards the top of profile (from 30 to 46 m) indicating strong lateritisation. Mass balance calculation of major and trace elements showed 80 to 99% of depletion in mobile elements (e.g., $Na_2O$, $K_2O$, CaO), whereas gains in immobile elements (e.g., $TiO_2$) except in top samples. FeO(T) showed very erratic behaviour with several samples showing minimum loss or gain, whereas anomalous gains (>400%) and loss (-86%) were also found in two samples in lateritic (/ferricrete) zone. The allochthonous source of iron oxides in the laterite (/ferricrete) zone was indicated by presence of low coercivity ferrimagnetic mineral. These new data from Patan area provides better understanding on in-situ weathering and allochthonous processes during lateritisation in the Deccan Traps.

# A Late Cretaceous true polar oscillation artifact: further evidence for Earth's long-term rotational stability

Tarduno J.*[1-2], Cottrell R.[1] & Bono R.[3-4]

[1] Earth & Environmental Sciences, University of Rochester, Rochester, NY (USA). [2] Physics & Astronomy, University of Rochester, Rochester, NY (USA). [3] Department of Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, FL (USA). [4] Earth, Ocean and Ecologic Sciences, University of Liverpool (UK).

*Corresponding author e-mail:* john.tarduno@rochester.edu

*Keywords:* paleomagnetism, geodynamics, true polar wander.

Determining Earth's stability with respect to the spin axis sets boundary conditions for understanding the planet's deep mantle, interpreting records of past climate, and understanding the relationship between Earth's rotation and biologic evolution. Global paleomagnetic data sets suggest limited polar wander since the Mid-Cretaceous (Cottrell & Tarduno, 2000; Tarduno & Smirnov, 2001). This conclusion has been challenged by calls for a Late Cretaceous "true polar" oscillation whereby the entire solid Earth rotated by 12 degrees, and then rotated back, 86 to 78 million years ago (Mitchell et al., 2021). This posit is based on new Late Cretaceous paleomagnetic data from the Italian Apennines. We analyze these data and find that the oscillation signal across polarity 33r to 33n greatly exceeds the maximum speed constrained by mantle viscosity and is thus physically implausible. Instead, the data point to an unrecognized overprint magnetization carried by authigenic hematite. This overprint has a differential angular effect on the normal and reversed polarity primary remanences, creating biased magnetic directions and attendant false polar wander. Looking back further in time, rapid "true polar" wander (TPW) has been proposed as a mechanism that promoted evolution in the Cambrian. But, the climate shifts associated with large rapid oscillations of the solid Earth could have drastically disrupted local nascent ecosystems. A re-analysis of sites used to define the TPW hypothesis supports an alternative interpretation: highly variable geomagnetic fields associated with the onset of inner core nucleation (Bono et al., 2019). These analyses suggest the solid Earth was rotationally stable during the Ediacaran and Cambrian, a stability that likely fostered the great radiation of life. These examples demonstrate how Earth is distinct from smaller planetary bodies which may have experienced polar wander. Principal differences are that external forces since the lunar forming impact are too small to drive such motion, and Earth's mantle viscosity structure which dampens large rapid polar motion driven by changes in its mass heterogeneities.

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Tarduno J. & Smirnov A. (2001) - Stability of the Earth with respect to the spin axis for the last 130 million years. Earth Planet. Sci. Lett., 184, 549-553.

# Enriching our knowledge on the Early Neolithic geomagnetic field in Italy: new data from prehistoric backed clays

Tema E.*[1-2], Camps P.[3] & Muntoni I.M.[4]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Laboratorio di Paleomagnetismo Alpino, Centro Interuniversitario di Magnetismo Naturale «Roberto Lanza», Peveragno (CN). [3] Geosciences Montpellier, CNRS-Universite Montpellier (France). [4] Soprintendenza Archeologia, Belle Arti e Paesaggio per le Province di Barletta-Andria-Trani e Foggia, Ministero della Cultura, Foggia.

*Corresponding author e-mail:* evdokia.tema@unito.it

*Keywords:* geomagnetic field, secular variation, Neolithic.

Europe is undoubtedly the geographic area best covered by archaeomagnetic data. However, most of the available data so far are concentrated in the last few millennia while older time periods are still poorly covered. Indeed, retrieving suitable, well dated and still *in situ* baked clays from prehistoric periods is not an easy goal mainly due to the fragility of the structures and the uncertainties on dating. We present here the results of an archaeomagnetic study carried out on three Neolithic hearths with the aim to enrich the Italian reference dataset for the Early Neolithic period and to contribute to the reconstruction of the geomagnetic field secular variation in prehistoric period. A total of 30 oriented samples were collected from three small combustion structures, excavated at the archaeological site of Campi Diomedei (Foggia, Southern Italy). The structures studied were probably used for domestic activities and are dated at 5800-5500 BCE. Magnetic mineralogy experiments show the dominance of a soft coercivity mineral, most probably magnetite, and a very good thermal stability up to around 500 $^{o}$C. Standard thermal demagnetization procedures were used to isolate the direction of the Characteristic Remanent Magnetization acquired by the last use of the structures while the corresponding archaeointensity was determined by the multi-specimen protocol (MSP). The new data are well defined and represent the oldest full geomagnetic field records from archaeological structures in Italy. They have been compared with the very few available data from Neolithic period in the Central Europe and with the available global geomagnetic field models. Such comparison demonstrates that the models show very smooth variations during the Neolithic, underlying the importance of obtaining more reliable data for such prehistoric periods.

# S7.

# Quantitative geology and modeling: an excursion through analogue and numerical modeling and the digital reproduction of outcrops

*Conveners and Chairpersons*

*Daniele Maestrelli (CNR)*

*Amerigo Corradetti (University of Trieste)*

*Silvia Mittempergher (University of Modena and Reggio Emilia)*

*Pietro Sternai (University of Milano – Bicocca)*

*Giovanni Toscani (University of Pavia)*

*Chiara Del Ventisette (University of Firenze)*

# A machine learning based approach to identify natural background concentrations of potentially toxic elements in soils

Ambrosino M.*[1], Albanese S.[2], Ciarcia S.[1], Guagliardi I.[3], Guarino A.[2] & Cicchella D.[1]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Istituto per i Sistemi Agricoli e Forestali del Mediterraneo, CNR, Rende (CS).

*Corresponding author e-mail:* maambrosino@unisannio.it

*Keywords:* machine learning, natural background concentrations, compositional data analysis.

This research suggests a new approach for determining the natural background concentrations of potentially toxic elements (PTEs) in soil, combining compositional data analysis (CoDA) and unsupervised learning. The case study concerns the municipality of Benevento (Southern Italy), in which 156 topsoil samples (10-15 cm) were collected in a 129 km$^2$ area on a 0.5 km grid in the downtown-urbanized area and on 1 km grid in suburban zones. The soils <100 mesh size fraction (150 µm) was analyzed for 26 chemical elements by ICP-ES and ICP-MS after aqua regia digestion.

To separate samples into distinct groups with different geochemical characteristics, we define the optimal number of clusters through the use of the NbClust function available in the R software. Statistical data analysis was performed on centered log-ratio (CLR) transformed data. Afterwards, the samples were separated into 4 groups using the k-means algorithm. Through the Biplot of the Principal Component Analysis (PCA) it was possible to observe the geochemical associations typical of each group. Therefore, by combining the information of the PCA with the map of the clusters distribution, the origin of these associations has been defined.

The results showed the presence of 3 geogenic and 1 anthropogenic clusters. The geochemical associations of the geogenic clusters are clearly attributable to the presence of clays (Ni, Co, Mn, Cr), carbonate rocks (Ca, Mg, Sr) and pyroclastic covers (K, Na, La, U, Th). The anthropogenic cluster (Sb, Pb, Hg, Zn) is associated with vehicular traffic and industrial activity.

In order to evaluating different natural background among significantly different groups, we excluded the anthropogenic cluster and performed the non-parametric statistical test Kolmogorov-Sminrov for the geogenic groups. The result allowed us to determine for which elements the subdivision into three different groups was statistically significant, using 0.05 as the significance interval. All PTEs showed significant differences between the three groups, therefore 3 different background contents were defined using the ProUcl software.

The results of this research showed that, in the study area, the Co natural background concentration exceeds the legal threshold in the area where the clays outcrop, the same happens for the Tl in the areas with pyroclastic covers. For the purposes of the environmental site characterization, the correct determination of natural background concentrations and their dissemination represent a reference value that will avoid making risk assessment errors and, above all, spending unnecessary money each time for further investigations and remediation operations.

The combination of compositional data analysis (CoDA) and unsupervised learning has proved to be a very useful tool for determining natural background concentration.

# Assessing the accuracy and density of photogrammetric point clouds reconstructed by different open-source and commercial software

Casiraghi S.*[1], Bistacchi A.[1], Arienti G.[1], Cannella C.[1], Dal Piaz G.V.[2] & Monopoli B.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Land Technology & Services s.r.l., Treviso.

*Corresponding author e-mail:* s.casiraghi21@campus.unimib.it

*Keywords:* photogrammetry, 3D model reconstruction.

Fracture networks play a key role in many fields, for instance, groundwater resources, geothermal fields, hydrocarbon reservoirs and gas storage. In this context, collecting quantitative and extensive datasets is fundamental to correctly model fractured rock masses. Digital Outcrop Models (DOMs) are a useful tool to collect these datasets. Due to the growing interest in the photogrammetric technique, a multitude of open source and commercial software were developed in past years. In this study, we will investigate the advantage and disadvantages of six different software commonly used for 3D photogrammetric reconstruction, comparing: (1) the accuracy of the reconstruction, (2) the surface and volume density of the resulting dense point clouds, (3) the software optimization in terms of computation time, (4) the possibility to use GPU processing to reduce computation time, (5) the availability of a user-friendly GUI, and (6) the possibility to run batch or command-line processing for repetitive tasks.

The software considered in our comparison are:

- MicMac: A command-line, open-source software developed by IGN (National Institute of Geographic and Forestry Information) and ENSG (National School of Geographic Sciences) in France.
- Meshroom: An open-source 3D Reconstruction Software based on the AliceVision® framework (Griwodz et al., 2021).
- OpenDroneMap® - WebODM®: A command-line toolkit initially born to process UAV images. WebODM provides a web interface to ODM.
- VisualSFM: A GUI application for 3D reconstruction which integrates different tools (Wu, 2011).
- COLMAP®: A Structure From Motion and Multi View Stereo Pipeline, whit a graphical and command-line interface developed by ETH University in Zurich (Schönberger & Frahm, 2016).
- Agisoft Metashape®: A commercial software which is the current standard for dense point cloud processing.

The case study chosen for our comparison is an outcrop of fractured gneiss of the Dent Blanche Nappe, beautifully exposed on the Italian side of the Cervino/Matterhorn in Valtournenche. The dataset is composed of 140 photos, acquired with a Nikon D700 and a 120 mm lens. The dense point clouds obtained with the beforementioned software are processed in CloudCompare to evaluate Surface and Volume density parameters.

This study shows us that starting from the same dataset, different software can give very different results in terms of absolute number of points and surface density, with point clouds that are one or two orders of magnitude less dense than others. Some software produces dense clouds whit errors (e.g., Doubled surfaces) while others produce good dense clouds that can be used in structural geology or geomechanical applications. Apart from Agisoft Metashape®, MicMac and COLMAP® turned out to be a good free and open source solutions for 3D photogrammetric reconstruction, whit reasonable computation time and interesting features.

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# Deformation of Somma-Vesuvius: an analogue/numerical approach

De Matteo A.*[1], Massa B.[2], Castaldo R.[1], D'Auria L.[3-4], James M.[5], Lane S.[5], Pepe S.[1] & Tizzani P.[1]

[1] Istituto per il Rilevamento Elettromagnetico dell'Ambiente, CNR, Napoli. [2] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [3] Instituto Volcanológico de Canarias, Santa Cruz de Tenerife (Spain). [4] Instituto Tecnológico y de Energías Renovables, Environmental Research Division, Santa Cruz de Tenerife (Spain). [5] Lancaster Environment Centre, Lancaster University (UK).

*Corresponding author e-mail:* adadematteo@gmail.com

*Keywords:* Vesuvius, spreading, analogue-numerical modeling.

Many volcanoes experience long-term deformation driven by gravity. The deformation process of the volcanic edifice may influence the evolution of the plumbing system, with consequences for the related volcanic activity and associated hazards. Thus, understanding of the deformation style and related volcano structural evolution represent a critical aspect for risk evaluation. Spreading and sagging are identified as the main gravity-driven deformation styles affecting volcanic edifices built on a ductile substratum. Although Somma-Vesuvius is considered one of the most dangerous and studied volcanoes on the planet, the deformation style affecting its volcanic edifice is still debated. Its asymmetric edifice essentially consists of a truncated cone (Mt. Somma) topped by the small, offset Vesuvius "Gran Cono". The edifice is made up of lavas and pyroclastic deposits emplaced over a relative ductile layer of marine and volcanoclastic sediments. The hypothesis of active spreading deformation at Somma-Vesuvius was first proposed by Borgia et al. (2005), and our research aims to define the state of deformation of Somma-Vesuvius using an integrated numerical/analogue modelling approach (De Matteo et al., 2022).

Numerical modelling of edifice deformation was performed using a finite element method implemented with a three-dimensional time-dependent fluid-dynamic approach. This approach allowed simulations to cover a wide range of scales, from those of analogue models to that of the natural system, by exploring several values of viscosity for the ductile layer. Laboratory analogue models were built at a scale of 1:100.000. We used a mixture of dry quartz-sand and bulking agents to reproduce the volcanic edifice and brittle substratum layers. Polydimethylsiloxane fluids were used to reproduce analogue ductile behaviour. To estimate the vertical and horizontal deformations, analogue models were monitored using four digital cameras and image datasets were processed into sequences of 3-D surface models using structure-from-motion photogrammetry. Horizontal deformation was assessed by tracking feature displacements within a vertical camera image sequence. Results of numerical and analogue modelling were compared with available monitoring data (e.g., DInSAR, GPS, field survey) of the ongoing deformation of Somma-Vesuvius. The results support the hypothesis that a combined spreading-sagging process governs the deformation style of Somma-Vesuvius.

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# Collapsed calderas as a proxy for stress and strain in extensional settings: what analogue models suggest

Facincani P.[1], Maestrelli D.*[2], Sani F.[1], Bonini M.[2], Montanari M.[2], Del Ventisette C.[1-2] & Corti G.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* daniele.maestrelli@gmail.com

*Keywords:* caldera collapse, analogue modelling, caldera elongation.

Collapsed calderas are circular to elongated large depressions originating from the subsidence induced by depletion and/or migration of magma from a shallow or deep reservoir during eruptions. Despite being distributed in all tectonic settings, they are particularly important in extensional settings where are often associated with rifting processes, e.g., the East African Rift System. Therefore, their structural architecture can be strongly perturbed by extensional faults associated with regional extension or related to earlier stages of caldera formation. Calderas often bear an elongated shape in plain view, and have been considered valuable proxies for the regional stress (e.g., Nakamura, 1977) and regional strain (e.g., Casey et al., 2006). Moreover, other authors have related the elongated calderas to the influence of preexisting structures reactivated during extension (Acocella et al., 2003). We therefore aim to investigate the mechanical interactions between collapsed calderas and regional extension leading to elongated edifices. Analogue models of caldera collapse were performed by placing a circular magma chamber (simulated with poly-glycerine) placed below a sand-mixture package. We induced the collapse by draining out the analogue magma from the base, reproducing the classical fault architecture observed at many collapsed calderas (i.e., early inner outward-dipping reverse faults and late outer inward-dipping normal fault). Once completed, the collapsed depression was stretched such that normal faulting produced caldera elongation and segmentation. Finally, we compared the elongation and the structural pattern deriving from the interacting caldera-related and rift-related structures with natural examples from the Main Ethiopian rift. Our results suggest that in extensional settings different interacting factors may contribute to the development of elongated calderas, thereby questioning whether elongated calderas can be considered as a fully reliable proxy for the regional strain.

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# 3D virtual models for geo-educational purposes

Fazio E.*, Forzese M., Maniscalco R. & Punturo R.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* eugenio.fazio@unict.it

*Keywords:* 3D model, geo-education, digital world.

Recent years witnessed a huge boost in digital surveying techniques, mainly due to new technologies and the wider availability of consumer-level products, which are more accessible to a wider range of users. This combination of factors has made it more common to collect images (aerial or ground-based shots) to create highly realistic three-dimensional models of rock outcrops, monuments, and caves using photogrammetry techniques. Today, the use of ultralight drones, portable lidars, tablets, and smartphones equipped with ad hoc sensors, allows the rapid acquisition (a few tens of minutes) of even very large areas (several hundred square meters) with high accuracy and precision data. These tools are particularly useful in the case of vertical walls (cliffs, architectural buildings) because they avoid all the potential risks associated with the operators who have to carry out the surveys and if they are physically indispensable, they have a valuable function of primary analysis of the scenario within which to operate later. Thanks to these new functionalities, in the field of geoscience education, it is possible to set up virtual itineraries of areas of geological interest and to reconstruct three-dimensional models of key outcrops that allow dialogue with students in the classroom or remotely (in the era of Covid's social constraints) 3D reconstructions (virtual or augmented reality) are pivotal for rock samples, minerals (from mesoscopic samples to 3D renderings from microtomography) and fossils studies and dissemination (that can be used on the websites of museum collections). Even if it remains a substitute for direct experience in the field, or an in-person visit to a geological site, or a museum, it is still very valuable teaching support in addition to classical teaching/learning methods.

# A useful method for a quick terrestrial digital acquisition of rock outcrops: an example from the Cap de Creus area (Spain)

Fazio E.*[1], Druguet E.[2] & Carreras J.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Departament de Geologia, Universitat Autònoma de Barcelona (Spain).

*Corresponding author e-mail:* eugenio.fazio@unict.it

*Keywords:* 3D virtual outcrop, structural-geological survey, shear zone.

In some cases, during a geological-structural survey campaign, there may be a need to acquire detailed data in order to subsequently reconstruct a virtual three-dimensional model of an outcrop of scientific interest, but environmental conditions are unfavorable, either due to adverse weather conditions (a particularly windy day) that do not allow drones to take off for aerial filming, or due to limitations imposed by local regulations (military areas, or protected areas, nature reserves to avoid disturbing the fauna present). In such circumstances, the use of a structure-from-motion (Sfm) technique can be very useful to avoid rescheduling the field trip and still obtain appreciable results. The method consists of using a free application and a latest-generation iPad by walking the site to obtain a highly realistic and georeferenced model of the area of interest, which can subsequently be enhanced with orientation data of structures collected manually on the outcrop. Here we propose some examples of outcrops of folds (Carreras & Druguet, 2009) and shear zones (Ponce et al., 2013) collected in the crystalline basement area of Cap de Creus (Eastern Pyrenees), pointing out how this approach may represent time-saving and convenient digital mapping solution.

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Ponce C., Druguet E. & Carreras J. (2013) - Development of shear zone-related lozenges in foliated rocks. Journal of Structural Geology, 50, 176-186.

# Coexistence of brittle and ductile deformation in the Western Ionian Basin as highlighted by seismic data analysis and sequential restoration methods

Gambino S.*[1], Barreca G[1-2], Gross F.[3-4], Monaco C.[1-2-5] & Gutscher M.-A.[6]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di Catania. [3] Institute of Geosciences, Kiel University (Germany). [4] Center for Ocean and Society, Kiel University (Germany). [5] INGV, Osservatorio Etneo, Catania. [6] Geo-Ocean, UMR6538 Univ Brest, CNRS, Ifremer, Plouzané (France).

*Corresponding author e-mail:* salvatore.gambino@unict.it

*Keywords:* ductile deformation, offshore seismic investigation, restoration.

Offshore eastern Sicily, between the Malta Escarpment and the Calabrian Accretionary Wedge, a narrow Plio-Quaternary extensional turbidite basin occurs. The basin is bounded by two active faults systems: 1) the normal, E-dipping Malta Escarpment (MESC) to the West, and 2) the sub-vertical, dextral strike-slip faults of the Alfeo Fault system to the East. The two bounding fault systems have controlled the Pliocene-Quaternary evolution of the basin. However, moving away from the MESC faults, seismic data interpretation reveals that the sedimentary pattern of the Pliocene sequence is affected by localized subsidence with internal reflectors diverging from a structural culmination to the East. Sequential restoration methods allowed for discrimination of two deformation processes in the area: 1) an ongoing regional tectonic stretching controlling the activity of the MESC faults, and 2) a previous diffuse extensional strain affecting the lower Pliocene sequence. The dominant horizontal component of strain suggests that the Pliocene deformation is most likely the result of lateral migration of pre-Pliocene ductile layer. The latter can be associated with the occurrence of underlying salts even though clayey or fluid-rich serpentinite levels cannot be ruled out as shown by diapiric intrusions of various material in the neighbouring areas. Sandbox experiments of progradational sediment loading over ductile layer show how such a material can migrate away due to progradational sediment load, resulting in withdrawal basins and related surrounding highs (see Rojo et al., 2020). 3D Modelling shows that the Messinian top-surface in the area is characterized by sub-circular highs and basins comparable to what is depicted in the available analogue models. Sediment waves pattern detected along a seismic line, which crosses the turbidite basin with a N-S direction, has been used to deduce differential sedimentary load caused by progradational sediment supply (see also Micallef et al., 2018 and Rebesco et al., 2021). Following this evidence and considering the pattern of internal reflectors of the turbidite basin, basins and highs reconstructed through the Messinian top-surface in the Western Ionian Basin can be associated to ductile flow in the pre-Pliocene units. This deformation mechanism was probably triggered by the increasing load of progradational sediments during the Pliocene. In addition, withdrawal basins are found close to the MESC faults and where the higher throws have been measured (see Gambino et al., 2021). This indicates that local thickening of sediments in the hanging-wall block played a significant role in the migration process. As evidenced by Quaternary sub-horizontal seismic reflectors, ductile deformation ended in the Pliocene. This study finally suggests how multiple analytical approaches can be used to identify coeval but distinct deformation mechanisms within the evolution of a sedimentary basin.

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# Reactivation of inherited faults in rift settings: insight from analogue study

Gayrin P.*[1], Maestrelli D.[2], Corti G.[2] & Del Ventisette C.[3-2]

[1] Department of Geosciences, Université Grenoble Alpes (France). [2] Istituto di Geoscienze e Georisorse, CNR, Firenze.
[3] Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* PaulineGayrin@protonmail.com

*Keywords:* normal fault reactivation, rift, analogue modelling.

Continental rifts accommodate extensional stresses via an alternation of brittle deformation (normal faulting) and volcanism (i.e., dykes and lava flow). This latter reshapes the topography of the rift floor, forming fresh new layers of rock that cover ancient faults. Therefore, the influence of the inherited buried faults on the development of the new faults and the processes of linkage at depth between them remains difficult to be investigated. To address the characteristics and growth of normal faults, we perform scaled analogue modelling of brittle-ductile extension to investigate fault growth and reactivation modes, to then compare these with natural data from rift systems.

We reproduce model deformation above an elastic band placed between a fixed and a moving wall, controlled by a stepper motor. We start from a reference model having at the base an elastic band and a 1 cm layer viscous material (PDMS+corundum mixture) used to distribute deformation inside the model. On top of this is a flat, 2-3 cm-thick layer of brittle material (sand mixture). We apply a first phase of orthogonal extension developing a normal faults network, then buried under a variable thickness of brittle material simulating a cover of sedimentary or volcanic deposits, followed by a second phase of extension to study the modalities of reactivation of the inherited faults.

During the experiments, top-view pictures track the progression of the deformation. High resolution perspective photos interpolated creates Digital Elevation Models at regular steps of deformation. The fault network is analyzed using automated tracking (Fatbox, by Wrona et al., 2022) from the top view and semi-automatic mapping and analysis method using the DEMs. The analysis generates D/L profiles used to characterize the style of fault growth and propagation mode, as well the influence of modelling parameters on these latter.

Model results show the development of normal faults creating systems of basins, horst-graben and conjugated faults. We also create a gradient of deformation from one wall to the other representing the different stages of evolution of the fault network, which would happen through time in nature.

The preliminary results show different styles of reactivation depending on the stage of fault development: reactivation according with Constant-Length Fault mode, Propagating Fault mode (e.g., Rotevatn, 2018) and an additional process where the surface above inherited structures first bend, then fracture (without vertical displacement) and finally develop into proper faults propagating and liking laterally. This latter growth mode is in agreement with the process observed by Braham et al. (2021) in Iceland and we can finally compare it with intra-rift faults from other settings.

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# Rift-Rift-Rift triple junctions: insights from analogue and numerical models

Maestrelli D.*[1], Corti G.[1], Brune S.[2-3], Keir D.[4] & Sani F.[4-1]

[1] Istituto di Geoscienze e Georisorse, CNR, Firenze. [2] German Research Centre for Geosciences, Potsdam (Germany). [3] Institute of Geosciences, University of Potsdam, Potsdam-Golm (Germany). [4] Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* daniele.maestrelli@gmail.com

*Keywords:* triple junction, analogue modelling, numerical modelling.

Continental break-up at Rift-Rift-Rift triple junctions commonly represents the "prequel" of oceanic basin formation. Currently, the only directly observable example of a Rift-Rift-Rift setting is the Afar triple junction where the African, Arabian and Somalian plates interact to form three rift branches, two of which are experiencing oceanization (the Gulf of Aden and the Red Sea). The younger of the three (the Main Ethiopian Rift) is still undergoing continental extension. We performed analogue and numerical models simulating continental rifting in a Rift-Rift-Rift triple junction setting to investigate the resulting structural pattern and evolution. By adopting a parametrical approach, we modified the ratio between plate velocities, and we performed single-phase (all the three plates move) and two-phase models (with a first phase where only one plate moves and a second phase where all the three plates move). Additionally, the direction of extension was changed to induce orthogonal extension only in one of the three rift branches. Our single-phase models suggest that differential extension velocities in the rift branches determine the localization of the triple junction, which is located closer to the rift branch experiencing slower extension velocities. Furthermore, imposed velocities affect the distribution of deformation and the resulting pattern of faults. The effect of a faster plate is to favour the formation of structures trending orthogonal to dominant velocity vectors, while faults associated with the movement of the slower plates remain subordinate. In contrast, imposing similar velocities in all rift arms leads to the formation of a symmetric fault pattern at the triple junction, where the distribution of deformation is similar in the three rift branches. Two-phase models reveal high-angle faults interacting at the triple junction, confirming that differential extension velocities in the three rift branches strongly affect the fault pattern development and highlighting geometrical similarities with the Afar triple junction.

# On the relation between the frictional strength of a fault and the presence of structural voids and weak phyllosilicates in the host rock: a numerical approach

Manna L.*[1], Maino M.[1], Casini L.[2], Dabrowski M.[3] & Reali A.[4]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [3] Polish Geological Institute, Warsaw (Poland). [4] Dipartimento di Ingegneria Civile e Architettura, Università di Pavia.

*Corresponding author e-mail:* ludovico.manna01@universitadipavia.it

*Keywords:* rock mechanics, friction, faulting surfaces.

The aim of this study is to perform a parametric analysis of the dependence of the frictional properties of a fault rock on its degree of damage. The study is meant to gain insight into the process of frictional sliding, the mechanism that governs the dynamics of earthquakes (Scholz, 2019), with a particular focus on the nucleation process. The research addresses through a numerical model the experimental evidence at the base of the formulation of the Byerlee's law, namely that the friction coefficient is largely independent on lithology (Byerlee, 1978). The thesis that the model aims to confirm is that fault rocks with different bulk properties can fail in the same way due to the presence of highly concentrated micro- or macroscopic cracks and lamellar phyllosilicates in the host rock, and therefore that the presence of defects in the fault rock is determinant for frictional reactivation. Recent studies have shown that the stress and strain on the interface of a propagating frictional rupture can be successfully reproduced through Linear Elastic Fracture Mechanics (LEFM) solutions (Svelitski & Fineberg, 2014). The purpose is therefore to use a two-dimensional plane strain numerical code based on the Finite Element Method (FEM) in order to simulate the elastic deformation of a medium crossed by elliptical fractures and anisotropic inclusions (such as micas). An analysis based on the study of the principal stresses distribution around the edges of the cracks and inclusions, and the use of Griffith theory of fracture would allow investigating the dependence of the strength of the rock on the porosity of the material, the clustering, the relative orientation and aspect ratio of the cracks. This study provides information on the onset and propagation of frictional ruptures, such as real contact area reduction, slip velocity, number and length of global sliding precursors (the partial slips on the interface that precede global sliding). The calculation of the stress intensity factor and the magnitude and orientation of the principal stresses around the tips of elliptical voids are crucial for the understanding of fracture coalescence and frictional reactivation of shear cracks in an elastic rock, which in turn governs the seismic cycle of natural faults (Brodsky et al., 2016). The numerical simulation will be used as the benchmark of a theoretical model for the study of the dependence of the frictional properties of fault rocks on their degree of damage.

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# Modeling the fate and the transport of heavy metals in a mine-polluted river watershed

Marras P.A.*[1], Zhou L.[2], De Giudici G.B.[1], Medas D.[1] & Dore E.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Academy of Disaster Reduction and Emergency Management, Faculty of Geographical Science, Beijing Normal University (China).

*Corresponding author e-mail:* pierandreamarras@gmail.com

*Keywords:* metals, pollution, river modeling.

Heavy metal pollution is a main issue for integrated watershed management worldwide. Before planning any remediation strategy, it is essential to quantify the input and output fluxes of metal by analyzing the environmental system in all its main components. Physically based models can simulate the behavior of a system, such as a river watershed, starting from the knowledge of the physical processes occurring therein. In this study, the abandoned mining area of the Rio San Giorgio (SW Sardinia) was modeled. Rio San Giorgio catchment is characterized by several mines, wastes and tailing dumps, abandoned after centuries of intense exploitation of Zn and Pb. Among them, the Fanghi Rossi and Campo Pisano dumps are important sources of pollution due to their high contents of contaminants (De Giudici et al., 2017). SWAT (Soil and Water Assessment Tool, Arnold et al., 1998) hydrological model and SWAT-HM (SWAT- Heavy Metal module, Meng et al., 2018) were used to simulate the fate and the transport of the Zn and Pb in the surface waters of Rio San Giorgio. The models were calibrated against measured streamflow and observed concentrations of Zn and Pb. Future simulations were run using Regional Climate Models of the Euro-CORDEX experiment (Giorgi et al., 2009) as climate forcing, to evaluate how pollution could evolve with climate change. Moreover, the impact of the removal of two of the main wastes, namely Fanghi Rossi and Campo Pisano, was simulated. Based on future climate simulations, results showed a small increase (15%) of the mean Zn load is caused by peak loads in occurrence of extreme rainfall events, while mean Pb load showed a significant decrease of around -40%. Waste management scenarios showed that the Fanghi Rossi waste remediation would result in a decrease of -40% of Zn and -34% of Pb loads, while Campo Pisano waste remediation would produce a reduction of -9% of Zn and -35% of Pb loads. The described projections add critical information to support waste management practices. This methodology could be applied in different watersheds affected by mine pollution.

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# Analogue modelling of fault and fracture processes at the outcrop scale: insights from the application of new granular materials in dynamically scaled experiments

Massaro L.*[1], Adam J.[1] & Yamada Y.[1-2]

[1] Department of Earth Sciences, Royal Holloway, University of London (UK). [2] Department of Earth Resources Engineering, Kyushu University, Fukuoka (Japan).

*Corresponding author e-mail:* Luigi.Massaro.2018@live.rhul.ac.uk

*Keywords:* analogue modelling, damage zone, strike-slip tectonics.

Analogue modelling techniques represent an important tool to investigate geological processes in their time and space evolution. Furthermore, dynamically scaled experiments enable the direct comparison between model and rock prototype. The length equivalence (geometrical scaling factor, L*) between the two systems depends on the physical and mechanical properties of prototype and model material. Therefore, the analogue materials applied in the scaled experiment define the model resolution and the range of structures that can be observed.

Granular materials, like quartz sands, show a nonlinear strain-dependent deformation behaviour similar to brittle rocks, resulting, therefore, ideal for the simulation of upper crustal deformation processes (Panien et al., 2006). We applied a new Granular Rock-Analogue Material (GRAM) capable to deform by tensile and shear fractures under variable stress conditions while providing a model resolution corresponding to the outcrop scale (1-100 m). GRAM is an ultra-weak sandstone composed of quartz sand and hemihydrate powder, in different mixing ratios, and water. The mechanical test series, including ring-shear tests and uniaxial compression tests, defined the key properties of the material, deriving a geometrical scaling factor of 1 cm in the model corresponding to 10.65 m in nature (Massaro et al., 2021). Such a model resolution allowed the investigation of the deformation processes characterising the strike-slip fault systems at the damage zones scale.

The strike-slip experiment series were run with different analogue materials, enabling the comparison of the models at different scales. Quartz sand provided a field-scale (100 m - 1 km) model resolution, while GRAM corresponded to the outcrop scale (1 - 100 m). Digital Image Correlation (DIC) techniques allowed the high-resolution monitoring of the deformation during different stages of displacement, comparing the shear zones evolution between the different models. The experiment series demonstrated that the investigation of a geological process at different scales of observation enhances the understanding of its kinematic and dynamic aspects. In this regard, the application of the new GRAM enables the simulation of geological processes in dynamically scaled experiments at a new range of resolutions corresponding to the outcrop scale.

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# Multiscale characterization of a fracture network using NetworkGT and open-source aerial images: the Kuh-e-Asmari anticline case study in Zagros Mts., Iran

Mercuri M.*[1], Tavani S.[2-3], Aldega L.[1], Trippetta F.[1], Bigi S.[1] & Carminati E.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* marco.mercuri@uniroma1.it

*Keywords:* multiscale, fracture, NetworkGT.

Fracture network characterization is a fundamental step for modelling the flow of the different types of geofluids at multiple scales. Classical field methods for collecting and analyzing fracture data sets (i.e., scan-lines or scan-areas; Priest & Hudson, 1981; Mauldon et al., 2001) have limited sample area and the results might be affected by local factors (e.g., facies variations and faults). In poorly- to non-vegetated regions, field-derived data can be integrated with satellite and aerial images providing a "big-picture" of the study area. The availability of open-source, high-resolution aerial and satellite images (e.g., Google Maps, Bing Maps) coupled with the development of specific software and tools (e.g., NetworkGT; Nyberg et al., 2018) allow to digitize and analyse very large and continuous data sets of fractures at multiple scales for a single case study.

In this work, the fracture network affecting the Kuh-e-Asmari anticline, in the Zagros fold-and-thrust belt, has been extracted and analysed at multiple scales leveraging on open-source satellite/aerial images and the NetworkGT tool within QGIS. Three different fracture data sets have been obtained by manually interpreting the images at three fixed scales (1:50.000, 1:5.000 and 1:500). In detail, we analysed the orientation, length distribution, intensity, and topology (Sanderson & Nixon, 2015) of the fracture network comparing the results with structural data from 9 scan-lines performed in the field on the same anticline. Fractures striking roughly parallel (i.e., NW-SE) and perpendicular (i.e., NE-SW) to the anticline axis and a N-S striking set have been individuated in all the datasets, and show a similar log-normal distribution of lengths. Connectivity and frature intensity obviously increase with scale of observation (i.e., from 1:50.000 to 1:500), with the dimensionless intensity and connections per branch (Sanderson & Nixon, 2015) representing the less scale-dependent intensity and connectivity parameters respectively.

In this work we highlight advantages and limitations of each scale of observation and field data. We leverage on our multi-scale dataset to find potential scale relations that, if applied to other case studies, could allow to simulate fracture parameters obtained at a certain scale to other scales of observations.

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# Analogue modelling of magma migration

Montanari D.*[1], Del Ventisette C.[1-2] & Bonini M.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Firenze. [2] Dipartimento di Scienze della Terra, Universittà di Firenze.

*Corresponding author e-mail:* domenico.montanari@igg.cnr.it

*Keywords:* magma migration, sill emplacement, analogue modeling.

We explore the capability of interconnected sills to transport magma in the shallow crust, as well as the effect of multiple magma emplacement on deformation pattern. We analyze this process through analogue models run with synchronous or diachronous magma injection from different, aligned inlets. Experimental results show that the position and activation in time of multiple injection points strongly influence model evolution. In case of synchronous injection at different inlets, intrusions and associated surface deformation are elongated. Forced folds and annular bounding reverse faults are quite elliptical, with the main axis trending sub-parallel to the magma input alignment. Diachronous injection from different sources would instead favor the lateral migration of magma rather than the vertical growth of intrusions. This evolution promotes the development of interconnected intrusions, and suggests that the deformation observed at surface does not necessarily reflect the location and activation timing of their feeders. Overall, our observations have significant implications for the kinematic evolution of sill complexes, timing of intrusion and associated deformation, raising the possibility that interconnected sills may act as channels for long-range lateral magma transport through a succession of sill-fed emplacement events. Model results also suggest that caution should be taken when trying to infer the feeding areas on the basis of the deformation features observed at the surface or in seismic profiles.

# Climatic control on the location of magmatic arcs

Muller V.A.P.*[1], Sternai P.[1], Sue C.[2], Valla P.[2] & Simon-Labric T.[3]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Institute of Earth Sciences ISTerre, Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, Grenoble (France). [3] Centre de Géologie Oisans Alpes, Musée des Minéraux, Bourg-d'Oisans (France).

*Corresponding author e-mail:* v.paivamuller@campus.unimib.it

*Keywords:* volcanic arc, orography, Southern Andes.

Orogens and magmatic arcs at convergent plate margins are primary surface expressions of plate tectonics. Although it is established that climate affects the shape, size, and architecture of orogens via orographic erosion gradients, the upwelling of magmas and surface location of magmatic arcs have been considered insensitive to climate. The Southern Andes and the Cascade Range in the western convergent margin of South and North America, respectively, present a precipitation gradient due to high latitude westerly winds interacting with the topographic barrier. In these sectors, the orographic effect generates an increase in erosion rates on western slopes and an eastward migration of the topographic water divide. Geochronologic data reveal westward migration of late-Cenozoic magmatic activity and Quaternary volcanoes are systematically displaced towards the region of enhanced erosional unloading. This observation lacks a clear tectonic explanation. To adress the possible contribution of orographic erosion on the magma upwelling, we use a fully coupled geodynamic and landscape evolution numerical model and run two sets of numerical simulations. The first set of experiments compares magma upwelling paths when the initial topography is directly above, and shifted laterally, with respect to a pre-imposed mantle melting region. The second set of experiments accounts for asymmetric erosion of a topographic wedge initially centered with respect to the mantle melting region. Results show that the bulk strain and magma upwelling is symmetric when the topography is directly above the mantle melting region without imposed erosion. When the topography is initially lateral, or shifts laterally due to asymmetric erosion, the bulk strain and magma upwelling is asymmetric, feeding volcanism toward the region of enhanced erosion. We thus show that topographic changes due to orography can force a shift in the strain pattern that drive magma upwelling towards the region of topographic unloading. Considering the different structural settings between the Southern Andes and the Cascade Range, the orographic erosion gradient seems the most plausible shared causal mechanism behind the observed late-Cenozoic westward migration of regional magmatic activity.

# Fuelling the transition from Oil to Greener Pastures using Virtual Outcrops and Integrated Reservoir Modelling

Mullins J.R.*[1-2], van der Vegt H.[3] & Howell J.A.[1]

[1] University of Aberdeen (UK). [2] Università di Trieste. [3] Delft University of Technology, Delft (Netherlands).

*Corresponding author e-mail:* mullins.jamesrobert@gmail.com

*Keywords:* virtual outcrop, geomodelling, transition fuels.

Outcrop and more recently, virtual outcrop analogues are commonly used to bridge the gap between 1D well data and 3D seismic datasets. Outcrops provide critical insight in the distribution of spatial heterogeneity in the subsurface and associated connectivity of reservoir quality reservoir facies. Geocellular reservoir models aim to capture numerical representations of heterogeneities that govern the fate of pore fluids in the subsurface; therefore accurate geological facies modelling is a critical step in the reservoir modelling workflow.

The population of geocellular reservoir models are typically reliant on defining the geometry, size and directionality of facies proportions through the manual measurement of object dimensions and variograms from outcrop analogues. These models are typically limited by the quality of the geologilcal exposure and as a result many of the necessary variables cannot be sufficiently specified to guide accurate modelling process in complex reservoirs. Reservoir modelling workflows have long existed for the efficient extraction of hydrocarbons, however these methods are equally applicable for determing long term storage solutions for hydrogen and for carbon capture and storage (CCS).

This study validates a state of-the-art industry workflow that combines process-based forward modelling with the next generation of reservoir modelling algorithms that extract geologically realistic trends, facies relationships and connectivity, while offering conditioning flexibilty to well information. This model was heavily constrained from a high-resolution virtual outcrop model of the Cretaceous Ferron Formation at Ivie Creek Utah. Lessons learnt from the oil industry are explored and applied to the storage of hydrogen and carbon to fuel the energy transition

# Remote Sensing Analysis for Detection of Ground Deformation induced by Large Earthquakes: A First Approach using Copernicus Opensource Dataset

Occhipinti M.*[1], Amorini S.[2] & Porreca M.[1]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] EagleProjects S.p.A., Perugia.

*Corresponding author e-mail:* martina.occhipinti@studenti.unipg.it

*Keywords:* remote sensing, DInSAR, deformation field.

Remote Sensing techniques are methods based on the acquisition of the reflected electromagnetic radiation from the Earth surface in different portions of the electromagnetic spectrum (Campbell, 1996), and are widely applied in several fields, as environmental monitoring or the detection of changes in tropical forests. Another interesting application is the detection of those effects induced by large earthquakes, that can comprise variations in ground deformation (subsidence, seismic ruptures), hydrogeological changes (birth or disappearance of watercourses, changes in the level of soil moisture), gases emissions and temperature anomalies before and after the main shock. The remote sensing dataset is characterized by multispectral images acquired by sensors installed in satellites, built in order to detect the reflectance from the Earth surface. The main goal of this work is to use the dataset from Copernicus satellites for the detection of the effect of large earthquakes on the environment; in particular, in order to study the ground deformation parameter, the dataset from Sentinel-1 satellite will be extracted, that is characterized by radar imagery from SAR. Images processing is executed thanks to SNAP software from ESA (https://earth.esa.int/eogateway/tools/snap) and to Python libraries, that allow to obtain interferometric images to rapidly detect deformation patterns related to large earthquakes. Two case studies are projected to be taken into account: L'Aquila earthquake (2009) and Norcia-Amatrice earthquake (2016). Due to the high number of data from both surveys and remote sensing, the Norcia-Amatrice earthquake will be the first case study in which test this approach, that previews the extraction and interpretation of SAR imagery in order to study effects from large earthquakes. This approach could also lead to the creation of products aimed to the characterization of the landscape from the deformation field point of view, as for example a deformation model appliable in different types of landscape. It's important to underline the relevance of the proposed approach, that can represent a new powerful tool capable to complete and extend field surveys of seismic areas and also to define the behaviour of different environmental processes that are not necessarily related to the seismic risk, as landslides.

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# The quantitative microstructural analysis of mylonitic rocks: the numerical computation of the Earth moving view

Ortolano G.*

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* gaetano.ortolano@unict.it

*Keywords:* interoperability, big-data, microstructural analysis.

Most of the basement rocks can be classified as tectonites (Ramsay & Huber, 1984), namely rocks pervasively characterized by a tectonically induced planar and/or linear fabric formed as the result of the counterbalancing competition between deformation and recovery processes (Wise et al., 1984). The strain shape factor $K= \ln[l_1/l_2]/\ln[l_2/l_3]$ (Ramsay and Huber, 1984) is able to subdivide L- ($K\rightarrow\infty$) from S- ($K\rightarrow 0$) or L-S-tectonites ($K=1$), by measuring the finite maximum ($l_1$), intermediate ($l_2$) and minimum ($l_3$) strain elongation of the Lamé's strain ellipsoid. This purely geometrical approach was recently integrated with the infinitesimal one and by several empirical paleo-piezometer based on the progressive changing in space and time of the: a) Rheological properties; b) Temperature; c) Lithostatic and deviatoric stress field; d) Mineral grain size of pre-and syn-kinematic rock constituent grains; d) Fluid availability, evolving during basement rocks formation.

Very recent enhancements in the field of quantitative image analysis allow for better quantifying fabric parameters (Visalli et al., 2021). These vectorized images, opportunely integrated with sets of classified micro-X-ray maps (Ortolano et al., 2018), have become powerful methods for the quantitative extrapolation of grain-size/-shape distribution parameters subdivided per mineral type (Ortolano et al., 2020a; 2020b).

Results thus obtained are objective and statistically meaningful parameters useful, for instance, for the correct quantification of the effective bulk rock chemistry in the calculation of reliable PT-pseudosections as well as for the extrapolation of fabric parameters for the vorticity analysis and paleo-piezometric purposes.

Examples of the above-mentioned quantitative data extrapolations will be presented for the numerical computation of the Calabrian-Peloritani Orogen (CPO) geodynamic moving view in order to continue to unravel the evolution of this key sector of the Mediterranean geodynamic realm.

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# Thermo-rheological model of a thinned continental crustal section during magma emplacement and exhumation: an updated numerical model for the western Elba Island

Perrini M.*[1], Gola G.[2], Brogi A.[1-2] & Caggianelli A.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* maddalena.perrini@uniba.it

*Keywords:* numerical modelling, magma emplacement and exhumation, Elba Island.

The eastward migrating Neogene-Quaternary extensional tectonics affecting the inner Northern Apennines, the emplacement of magmatic bodies at upper crustal levels and consequent geothermal fluid flow are the main geological processes responsible for the high heat flow anomaly characterizing the whole Tyrrhenian sector of the Italian peninsula. In particular, the Monte Capanne monzogranite, occurring in the western Elba Island, is a late Miocene magmatic body emplaced within a SW-NE trending sub-vertical transfer zone. This strike-slip activity was coeval, at least since upper Miocene, with the development of crustal shear zones enucleated in correspondence with the local brittle-ductile transition, in a E-NE migrating extensional setting, responsible for pluton unroofing and exhumation. In this presentation we provide an updated 3D thermal and rheological numerical model of the crustal sector hosting the magmatic body. The extensional evolution and the associated magma emplacement is reproduced in a numerical domain 20 km deep (down to the base of the continental crust) which includes the main geological features of this crustal sector. The time-dependent temperature distribution is calculated by solving the heat and mass transfer problem accounting for the conductive and advective components as well as the occurrence and exhumation of a ca. 6 km deep, cooling magmatic body. The results of the thermal model are then used to set up rheological profiles useful to interpret the deformation pattern observed in the pluton host rock.

## From the construction of the 3D model to local seismic response analysis

Primofiore I.*[1-2], Baron J.[2], Klin P.[2], Vessia G.[1] & Laurenzano G.[2]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* iprimofiore@ogs.it

*Keywords:* local seismic response, 3D model, numerical simulation of seismic wave propagation.

3D geological models can be used for local seismic response analysis by means of physics-based numerical simulations of 3D seismic wave propagation. In the present work, we set up a 3D model of the asymmetric isolated ridge of Arquata del Tronto (Primofiore et al., 2020), severely damaged during the 2016 seismic sequence in Central Italy. We used the commercial software GeoModeller (Calcagno et al., 2008), which allows building complex and implicit 3D models directly from geological observation and geophysical surveys data. We applied Spectral Element Methods (SPECFEM3D Cartesian, Peter et al., 2011) for the simulations of seismic wave propagation, with the aim of evaluating the topographic site effects in terms of spectral amplification, polarization, and induced torsional motion. In order to separate the site effects caused by the distinct factors involved, we carried out three different versions of the geophysical model, with growing complexity: (1) homogeneous model, (2) with the addition of a thin surface weathering layer, and an alluvial basin (3) with a complex internal structure. The results of the study show that the correlation between the topographic curvature and the seismic amplification decreases with the increasing complexity of the model, for frequencies above 2 Hz. The presence of the alteration layer aggravates the amplification, for frequencies above 4 Hz. The deep geological structure affects the site response only for frequencies below 4 Hz. The results also support a correlation between topographic slope and induced torsional motion (Baron et al., 2022).

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# Thrust Fault Localisation in Multilayers – outcrop tests of idealised models

Sleath P.R.*, Butler R.W.H. & Bond C.E.

Department of Geology and Geophysics, University of Aberdeen (UK).

*Corresponding author e-mail:* p.sleath.20@abdn.ac.uk

*Keywords:* thrusts, faults, deformation.

Interpreting fault systems and understanding fault geometry is highly uncertain and a major risk when developing resources in the subsurface, especially in fold thrust belts where seismic imaging is poor. Researchers rely on conventional textbook models of thrust formation which are based on theory, but is the range of models enough?

As changes in rheology are likely in most multilayers standard models of thrust formation are often not appropriate. The purpose of this work is to test models of thrust formation with actual outcrop structures, to achieve a comprehensive understanding of the variation in localisation behaviour of thrusts, mitigating bias resulting from overuse of the standard models. In the "footwall collapse" model, thrusts form independent of rheology along a base detachment and propagate upwards through a multilayer, branching off old faults at depth with a fault-bend fold forming in the hanging wall (Dahlstrom, 1969; Elliott & Johnson 1980). The "stiff layer" thrusting model relates to the different structural behaviours of a multilayer; the thrust originates and localises in competent horizons as ramps and the thrust tip propagates up and down to create a linked fault system (Eisenstadt & De Paor, 1987). This model has had few tests at outcrop level, so exploring relationships between thrust localisation and stratigraphic variations in various multilayers is important.

Key sites have been studied where multilayers with contrasting competencies have been cut by thrusts in different settings. A first test has been applied to imbricated sandstones and mudstones (SW Wales, UK) and a second to a layer-confined imbricate system within the thinly bedded units of siltstone-fine sandstone encased by thickly bedded competent sandstone beds (S Livorno, Tuscany).

The outcrops show differing competency horizons, and evidence for sedimentology derived rheological controls on thrust fault growth and deformation. Layer parallel thrust faults are common, as detachments are confined along the bedding planes between rheological boundaries. Contradicting the "footwall collapse" model that thrusts propagate up from a detachment. The encasing incompetent rocks show an irregular distribution of strain, the mudstones have a well-developed cleavage that is not present in the siltstones. At both outcrops deformation is localised in areas with a higher proportion of incompetent rocks.

As there is a strong reliance on a few key sites more studies are needed to better understand contractional deformation in multilayers.

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# AFATA (Active FAult Tectonic Analysis): a semi-automatic tool on ArcGIS® for estimating fault offsets on superficial ruptures

Torre D.* & Menichetti M.

Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo".

*Corresponding author e-mail:* d.torre@campus.uniurb.it

*Keywords:* surface ruptures, active fault, GIS toolbox.

The automation of data acquisition and calculation is advancing in many sectors. At the same time, the use of software and the difficulty, in certain cases, in programming languages could lead to various problems.

In relation to the automation of fault offset estimation, many authors have given their contribution (Stewart et al., 2018; Wolfe et al., 2020) combining steps in GIS environment with external programming languages.

AFATA is a new toolbox proposal for ArcGIS® based on Model Builder and on ArcPy language for the evaluation of the three components of rupture offset (vertical, horizontal and along plane offsets) of a normal fault. This tool, that only needs the use of GIS environment, is intuitive and does not require many steps from the user. The semi-automatic process allows the operator to modify and improve the shapefiles on which the analysis is carried out.

The AFATA main inputs are (i) line shapefiles, drawn by the operator, defining the two limits of the fault offset, and (ii) a slope raster obtained through a Digital Elevation Model (DEM) with a resolution comparable with the fault geometry. The result is a line shapefile containing the sampling transects whose frequency is chosen by the user along the fault plane. The measurements (maximum, minimum and average) of the three offset components and the value of the slope angle for each transect are shown in the attribute table.

The application and validation of the proposed toolbox are located in the Central Apennines of Italy on the surface ruptures related to the 2016 earthquakes. The study area was surveyed with a digital geological field survey and with low-altitude aerial photos, using an Unmanned Aerial Vehicle (UAV). A 3D Virtual Outcrops Model (VOM) was generated by the Structure from Motion – MultiView Stereo (SfM-MVS) photogrammetry (Westoby et al., 2012; Tavani et al., 2016); from this, a 0.009 m resolution ortophoto and a 0.02 m resolution DEM were derived for spatial analysis in ArcGIS 10.8.1.

The AFATA application may contribute to obtain a higher number of measurements by regularly scanning the three components of the slip fault, in particular on ruptures difficult to access. The extent of the error for this tool primarly depends on the accuracy with which the user draws the limits; the estimated error obtained on the study area is about 10% of the total slip.

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# 2D numerical simulations of local seismic response at San Salvador (El Salvador) urban center

Vessia G.*[1], Faraone C.[1], Caravaggio S.[1], Rainone M.L.[1], Conoscenti C.[2], Mixco L.[3] & Ramos Castillo A.L.[1-4]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [3] Ministerio de Medio Ambiente y Recursos Naturales, San Salvador (El Salvador). [4] Department of Geophysics, University of El Salvador, San Salvador (El Salvador).

*Corresponding author e-mail:* faraonechiara6@gmail.com

*Keywords:* local seismic response, long period amplifications, San Salvador Urban Center.

In this contribution, we illustrate the results of an ongoing study on the evaluation of the Local Seismic Response LSR of the Metropolitan Area of San Salvador (MASS), the capital of El Salvador. The city of San Salvador is located between the San Salvador volcano and the Ilopango caldera, in a sub-flat area called "Valle de las Hamacas" (Valley of the Hammocks), due to the intense seismic activity. In this area, the affected seismicity is higher than 6 M and is due to the presence of a complex interaction between tectonic structures and volcanic phenomena or a combination of the above, all attributable to the subduction of the Cocos plate below the Caribbean plate. Historically, the main seismic events in the area occurred in 1965 (6.3 M), 1986 (5.5 M), and finally in January and February 2001 (7.7 M and 6.6 M, respectively). Moreover, even frequent seismic swarms occur in the area. The Balsamo, Cuscatlan, and San Salvador formations are present in the MASS, these originated from the effusive and pyroclastic activity of the volcanoes in the study area. These formations have been deposited since the Pliocene and are intercalated with basaltic and andesitic lavas as well as tephritic material. As part of the international cooperation project between Italy – and El Salvador (AICS), the CASTES project centered on natural hazards in the territory of El Salvador was launched. Therefore, a systematic study of the dynamic characterization of the underground soil deposits and rocks soils and the evaluation of the local seismic response LSR has been undertaken. These studies are based on existing data derived from the seismic-mechanical characterization of the subsoil. Analyses of LSR were performed along a 2D section where on-surface accelerometers are also installed at specific seismic stations. The sites studied are Hogar del Niño (HDN), Catholic University (UCA), National Geographic Institute (IGN), Geotechnical Investigation Center (CIG), and Observatorio (OBS). In this paper, we will discuss the results from LSR simulations showing amplification in the range 0.1-0.8 s: it is a large range of periods that is able to affect a large number of different buildings within San Salvador. The calculated amplification factors, related to the past earthquakes that occurred in 2001, are as large as 4 on average. These amplifications can be attributed to both the Tierra Blanca soils (at period range 0.6-0.8 s) and volcanic pyroclastites and epiclastites (at period range 0.1-0.4 s). The long period amplifications might also have triggered the landslides that occurred after the last strong earthquakes of the 2001 seismic sequence.

# UAV-based digital outcrop modelling in adverse conditions: the case study of the Canyon Gramonal (Ica desert, Peru)

Volatili T.*[1], Di Celma C.[1], Pitts A.[1-2], Pierantoni P.P.[1] & Mazzoli S.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] U.S. Geological Survey, Florence Bascom Geoscience Center, Reston, VA (USA).

*Corresponding author e-mail:* tiziano.volatili@unicam.it

*Keywords:* Ica desert, DOM optimization, stratigraphic interpretation.

In the last decade, the use of Digital Outcrop Models (DOM) in geosciences has drastically increased, given the greater affordability and capability of user-friendly photogrammetric-related utilities for solving geological problems. The use of Unmanned Aerial Vehicles (UAV) provided the significant advantage of investigating key outcrops otherwise physically inaccessible. The latter is the case in the present study, where several DOMs of the Canyon Gramonal (Ica province) were produced for stratigraphic analysis within the greater framework of characterizing the evolution of the East Pisco Basin in Southern Peru (Di Celma et al., 2022). The stratigraphic details along the canyon walls were captured over a total length of 1.5 km.

The study area, located in a remote desert environment, presented multiple challenges affecting the UAV survey (e.g., high wind velocity, poor visibility, etc.). Therefore, the photogrammetric survey consisted of flights under different conditions which required an extra effort in the attempt to optimize a non-conventional outcrop scan.

Besides the commonly adopted workflow for Structure from Motion (SfM) photogrammetry, this study involved an extensive post-production phase. The pictures, in RAW format, were edited in graphic software to prevent issues related to improper alignment, possibly linked to the color flatness, typical in desert areas. Secondly, the produced DOM dense point cloud was imported in the CloudCompare software for a cleaning phase before creating the final 3D digital surface model. Finally, the DOM was scaled and georeferenced by natural ground targets identified in aerial imagery.

The stratigraphic interpretation was performed in both the 3D model and high-resolution orthomosaics of the canyon walls. The sedimentary succession exposed at Canyon Gramonal is part of the lower Miocene Chilcatay Formation and comprises a composite sediment wedge interpreted as a coarse-grained, mixed carbonate–siliciclastic subaqueous marine delta (*sensu* Patruno & Helland-Hansen, 2018). The mapping of stratigraphic surfaces and the outcrop study of bed surfaces and facies distribution show that the sediment wedge is composed of three successive sets of delta-scale sigmoidal clinothems that are separated by seaward-dipping erosion surfaces and are preserved in an overall southeastward prograding stacking pattern.

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# S8.

# Perspectives on fluid- and melt-rock interactions by advanced thermodynamics and geochemistry: applications in petrology and geothermy

*Conveners and Chairpersons*

*Martina Casalini (University of Firenze)*

*Enrico Cannaò (University of Milano – La Statale)*

*Fabrizio Tursi (University of Bari)*

*Francesca Piccoli (University of Bern, Switzerland)*

# Deciphering Active Arc vs. post-collisional calc-alkaline magmatism through B and radiogenic isotope data in Aegean-Anatolian Region

Agostini S.*[1], Braschi E.[1], Conticelli S.[3-4], Di Giuseppe P.[1], Francalanci L.[3], Innocenzi F.[5], Lustrino M.[5-4] & Manetti P. [3]

[1] Istituto di Geoscienze e Georisorse, CNR, Pisa. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze, [3] Dipartimento di Scienze della Terra, Università di Firenze. [4] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [5] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* s.agostini@igg.cnr.it

*Keywords:* Arc magmas, petrology, isotope geochemistry.

Aegean-Anatolian region is characterized by a complex geodynamic system related with the African and Arabian convergence under Eurasia and the closure of Tethys Ocean. In this framework, from Miocene onwards, a wide spectrum of calc-alkaline, K-alkaline and ultra-K magmas, with clear orogenic imprint were emplaced throughout the region. Some of these rocks, however, clearly represent magmas emplaced during active subduction, as in South Aegean Arc (Pliocene-Holocene) or Eastern Anatolia (Early-Middle Miocene), some others post-collisional magmas, whose source was previously modified by slab-released fluids, such as in Western Anatolia and Central Anatolia.

Variations of tectonic contexts are mirrored by large differences ratios between Fluid Mobile Elements/ Fluid Immobile Elements (e.g., 1.5$^{87}Sr/^{86}Sr$ from 0.7034 to 0.7091, $^{143}Nd/^{144}Nd$ 0.51235-0.51287), and by even larger variability of B isotopes, with d$^{11}$B ranging from ≈+4‰ to extreme depleted values of -15‰. The combined use of trace elements, radiogenic isotopes and boron isotopes is used to discriminate between fluid released by different subducted domains, such as serpentinized mantle, altered oceanic crust and pelagic/ terrigenous sediments, as well as to trace progressive dehydration of subducted slabs.

# Assessing Alzo's Granite alteration by integration of physical properties

Ballabio N.*[1], Vinciguerra S.[1], Comina C.[1] & Vagnon F.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* nicholas.ballabio@unito.it

*Keywords:* granite, alteration, physical.

Hydrothermal fluids and weathering influence the physical and mechanical properties of rocks. This affects the stability of rock masses and contributes to the rock failure, even at stress level much lower than expected. In this study, we investigated the physical properties of Alzo's granite, a Lower Permian batholite (Boriani & Giobbi, 2004) with granitic and granodioritic composition, outcropping in the lower Sesia Valley and in the Orta's Lake (NW Italy). The sanctuary of Madonna del Sasso rises on an unstable cliff made of this granite (Colombero et al., 2017). In this cliff, the Alzo's granite shows different alteration degrees, from finer grain size and weakly altered units to heavily altered and fractured units. The variation of fracturing and weathering degree strongly affects the geomechanical properties of the material (Colombero et al., 2017) and makes very hard to define strength criterion. Consequently, the assessing of critical thresholds for instability or collapse is challenging.

Laboratory P- and S-waves velocity and apparent electrical resistivity measurements were performed on several blocks sampled at Madonna del Sasso. These samples were collected in different sectors of the cliff to cover different degrees of alteration for a direct comparison with reference properties of the intact granite.

All measurements were performed in dry, wet and in partially saturated conditions in order to understand the effect of different saturation degree and water circulation on the sample properties. Porosity (n) were estimated through Archie's Law (1942). Mechanical properties, such Poisson coefficient ($\nu$), shear modulus (G) and Young's modulus (E) at low deformations were calculated from the ultrasonic measurements.

The results show the need of furthermore detailed investigations to determine the extent of the alteration in the rock mass and to characterised these different sectors from a geomechanical point of view.

Future work will be devoted to: i) compare the laboratory P- and S waves measurements to the theoretically estimated by following the Voigt-Reuss-Hill (VRH) approach in order to assess the contribution of the single mineralogical phases and identify the individual degree of alteration of each mineral; ii) carry out microstructural observations in order to quantify the inner damage and the crack density; iii) apply the Effective Medium Theory (EMT) to define crack density and compared it with those obtained by micro-scale analyses.

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# Melt-rock reaction experiments constrain the nature of crust-mantle interaction during the subduction of the continental crust at mantle depth

Borghini A.*[1], Borghini G.[2] & Ferrero S.[3-4]

[1] Institut für Geowissenschaften, University of Potsdam (Germany). [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [4] Museum für Naturkunde, Leibniz-Institüt für Evolutions- und Biodiversitätsforschung, Berlin (Germany).

*Corresponding author e-mail:* borghini@uni-potsdam.de

*Keywords:* crust-mantle interaction, mantle metasomatism, melt-rock reaction, high-pressure experiments.

Subduction of continental material at mantle depth allows elements transfer from the crust to the mantle via melts and fluids. The interaction between a melt with crustal origin and the mantle in this geological setting was reported in the Granulitgebirge, Bohemian Massif (Borghini et al., 2020). Melt inclusions in eclogites lenses embedded in mantle peridotites were studied and used to constrain the melt nature and the conditions at which metasomatism took place. The melt has granitic composition and trace element signature akin to the continental crust. The interaction of granitic melt with mantle lithologies has been inferred to occur at 1000°C and 2.2 GPa when the slab was subducted at mantle depth. It was suggested that the melt reacted with a mafic / ultramafic layer already present in the peridotites to produce the eclogites in which is now trapped. However, the lack of mineralogical relicts of the protolith leave the nature of the latter still unknown. We performed melt-rock reaction experiments to better define the role of crustal melt-mantle interaction in generating garnet-bearing rocks at the conditions at which metasomatism took place in the Granulitgebirge.

Reaction experiments were carried out using a piston cylinder apparatus on a homogeneous mixture of synthetic glass with the same composition of the granitic melt ($SiO_2$ = 70.95 wt.%, $Al_2O_3$ = 16.84 wt.%, $Na_2O$ = 5.43 wt.%, $K_2O$ = 5.06 wt.%) measured in the inclusions in the Granulitgebirge eclogites and two mantle protoliths, a fertile lherzolite and a spinel clinopyroxenite. The fertile lherzolite was pre-synthesized at the same P-T conditions of the reaction experiments starting from a gel. The pyroxenite is instead a mixture of clinopyroxene and Al-rich spinel separated from a mantle mafic rock (bulk $X_{Mg}$ = 0.74). Initial melt:rock weight proportion is 1:9, in agreement with the rock-dominated metasomatic reaction observed in the Granulitgebirge.

At 2.2 GPa, the reaction between lherzolite and anhydrous granitic melt at 1000 and 1100°C consumed mantle minerals and produced garnet ($Prp_{71}Alm_{13}Grs_9$), orthopyroxene and minor clinopyroxene.

Experimental products after the reaction at 1100°C between melt and spinel clinopyroxenite are garnet ($Prp_{45}Alm_{29}Grs_{24}$) and clinopyroxene coexisting with an andesitic residual melt. These phase assemblage and mineral chemistry are similar to those documented in the Granulitgebirge eclogites thus supporting that the protolith was most likely not peridotitic but a pristine mafic rock. Further experiments are in progress to investigate the influence of pressure and different initial melt/rock ratios on these reactions.

Borghini A., Ferrero S., O'Brien P.J., Laurent O., Günter C. & Ziemann M.A. (2020) - Cryptic metasomatic agent measured in situ in Variscan mantle rocks: Melt inclusions in garnet of eclogite, Granulitgebirge, Germany. J. Metamorph. Geol., 38, 207-234.

# Evidence of Na-metasomatism of phyllite rocks from the Verrucano of Monti Pisani (Tuscany, Italy)

D'Orazio M.*[1], Fulignati P.[1], Gioncada A.[1] & Cavalcante F.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ).

*Corresponding author e-mail:* massimo.dorazio@unipi.it

*Keywords:* albitization, hydrothermal alteration, Monti Pisani.

We report here for the first time the occurrence of albitite rocks in the Middle Triassic "Verruca" Formation (Monti Pisani, Northern Apennine, northern Tuscany, Italy). The albitite is the result of a pervasive Na-metasomatism of phyllites (originally formed by potassic white mica + quartz + chlorite + hematite + albite). The albitisation process took place after the Miocene main phases of Apenninic deformation and was followed by the formation of a system of veins made of Fe-carbonate ± quartz. Hydrothermal alteration continued with the ingression, possibly favored by the increase of permeability due to albitization, of a slightly acidic, oxidizing, aqueous fluid that led to the kaolinization of the albitite and to the complete replacement of the Fe-carbonate of the veins by Fe-hydroxides. This stage was followed by a supergene alteration that led to the formation of a pervasive network of tiny veins of halloysite and colloform (P-Al-Si)-bearing Fe-hydroxides. Finally, the hydrothermally altered rock underwent a localized brittle fracturing without new minerals formed. The most important chemical changes occurred during the whole hydrothermal process were the inversion of the $Na_2O/K_2O$ ratio of the whole rocks (from 0.07 in the pristine phyllite to up to 200 for the kaolinized albitite), the loss of Fe and Mg, and the enrichment of Sb. Light REE and HREE behaved conservatively, whereas MREE were partially lost. The occurrences of hydrothermal alteration are common in central-southern Tuscany, and generally related to the post-collisional extensional regime, lithospheric thinnning, and emplacement of magmatic bodies in the crust. The Monti Pisani kaolinized albitite, altough occurring far from potential magmatic sources, can be considered related to this post-collisional extensional tectonic setting, thus stretching out northward the occurrence of post-Miocene hydrothermal activity in Tuscany.

# Insight into the evolution of the Larderello-Travale granites (Italy) by zircon trace element geochemistry

Farina F.*[1] & Dini A.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* federico.farina@unimi.it

*Keywords:* zircon, trace element, granite.

The peraluminous two-mica and cordierite-bearing granites of the Larderello-Travale (LT) geothermal system (Italy) are shallow-level crustal intrusive rocks generated in a post-collisional extensional setting by melting of Al-rich pelitic protoliths. High precision $^{206}Pb/^{238}U$ zircon ages range from 4.5 to 1.6 Ma indicating at least four main pulses of magmatic activity at ca. 3.6, 3.2, 2.7 and 1.6 Ma, with zircon crystals from the three youngest magmatic events showing significant age spreads of 300-500 ka (Farina et al., 2018).

Zircon crystals in the LT granites range from simple core-to-rim oscillatory zoned grains to more complex crystals with sub-rounded homogeneous or convoluted centres overgrown by oscillatory zoned rims. Most crystals contain inclusions of apatite, K-feldspar, quartz and occasionally monazite. Quite common are also polycrystalline domains made of K-feldspar, biotite, muscovite and quartz representing former melt inclusions. The trace element composition of zircon grains from six samples with age spanning between 3.6 and 1.6 Ma allows defining three groups. Group A comprises grains with euhedral pyramid shape from the oldest magmatic event. These crystals have relatively high U contents (average of 1330 ppm), low Th/U (0.18) and an average Eu/Eu* values of 0.016. Crystals from group B characterize the youngest granites in the LT system. They have very low Eu/Eu* (0.006), high Th/U (0.37) and are extremely enriched in U, Th and HREE, with ca. 20% of grains having U contents higher than 5000 ppm. Finally, group C crystals that formed during the 3.2 and 2.7 Ma magmatic events exhibit transitional chemical features between A and B. The three groups are clearly defined in a ΔFMQ (i.e., $\log fO_{2(sample)} - \log fO_{2(FMQ)}$) vs. Hf plot, in which the formula of Loucks et al. (2020) has been use to determine the difference in oxidation state between the magma from which the zircon crystallized and the fayalite-magnetite-quartz buffer. Group A zircon formed in the most reduced magma (ΔFMQ = -3) while group C in the most oxidized (ΔFMQ from -2 to 1), with the value of ΔFMQ that is inversely correlated with the Hf content. These variations are ascribed to the occurrence of different amounts of reduced organic carbon in the metasedimentary source region. Finally, many grains from the youngest granites exhibit CL-dark centres with convoluted zoning containing densely packed μm-sized rounded inclusions of xenotime, uraninite and coffinite. These centres are partially corroded and overgrown by oscillatory-zoned areas surrounded by U-rich dark rims. The U-Th-REE-rich mineral inclusions hosted with drak-CL domains are likely derived from dissolution-precipitation processes taking place in volatile-saturated evolved low-temperature melts.

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# Healing of gabbro and basalt experimental faults under hydrothermal conditions

Feng W.*[1], Yao L.[2], Gomila R.[1], Ma S.[2] & Di Toro G.[1-3]

[1] Dipartimento di Geoscienze, Università di Padova. [2] State Key Laboratory of Earthquake Dynamics, Institute of Geology, China Earthquake Administration, Beijing (China). [3] INGV, Roma.

*Corresponding author e-mail:* wei.feng@phd.unipd.it

*Keywords:* fault healing, fluid-rock interaction, negative healing rate.

Frictional healing rate $\beta$ or the change of the static friction coefficient ($\Delta\mu$) with log time ($\beta = \Delta\mu/\Delta logt_{hold}$) is a significant parameter in the seismic cycle, controlling the storage of the elastic strain energy in the fault wall rocks and allowing earthquakes to repeatedly occur in pre-existing faults. Fault healing is investigated with slide-hold-slide (SHS) experiments aimed at reproducing the seismic cycle. In the last 40 years, laboratory studies revealed that $\beta > 0$ due to the activation of several fault healing mechanisms including grain growth, dislocation creep, etc. However, most of these experiments were conducted under room conditions, whereas natural earthquakes generally nucleate at ambient temperatures T > 150°C and in presence of pressurized fluids. Under these ambient conditions, fluid-rock interaction (reaction kinetics, pressure-solution transfer, sub-critical crack growth, etc.) may impact severely on $\beta$ and on the magnitude of $\Delta\mu$.

In this study, SHS experiments were performed with a rotary shear machine equipped with a dedicated hydrothermal vessel to investigate the healing behavior of gouge-bearing fault, made of Elta basalt and gabbro. The gouges (grain size < 88 μm) were slid at a slip rate of 10 μm/s, under an effective normal stress of 50 MPa, with temperatures T ranging from 25°C to 400°C and at pore pressure $P_f$ of 0 MPa and 30 MPa. The hold periods between slip events ranged from 3s to 10000s. For each experiment, two sequences of SHS were conducted, with a slip interval of 30 mm, to investigate the dependence of $\beta$ with both cumulative slip and duration of the experiment.

Under room temperature and humidity conditions (T = 25°C and $P_f$ = 0 MPa), the friction healing for both gabbro and basalt gouge increased linearly with hold times ($\beta > 0$), consistently with previous observations. With increasing temperature but $P_f$ = 0 MPa, $\beta > 0$ with the highest value achieved at T = 100°C ($\beta$ = 0.01181±0.00164 for basalt and 0.01767±0.00355 for gabbro). Moreover, $\beta$ was slightly higher in the 2nd sequence than in the 1st sequence, possibly because of the longer slip distance which resulted in smaller grain size distribution favoring fault healing.

Instead, under hydrothermal conditions with $P_f$ = 30 MPa and T = 300°C or T = 400°C for gabbro gouges, in the 2nd sequence, $\beta$ switched from positive to negative with increasing hold time ($\beta$ = 0.0161±0.00169 for holds < 300s and -0.00739±0.00429 for holds > 300s at 300°C, and $\beta$ = 0.00571±0.00199 for holds < 100s and -0.02274±0.00417 for holds > 100s at 400°C, respectively).

The underlying mechanism responsible for the transition from $\beta > 0$ to $\beta < 0$ is unclear, and it will be investigated with microstructural and mineralogical analyses on the experimental fault products. We speculate that the transition, which may result in nature in the switch from seismic to aseismic fault behavior, could be related to the formation of new mineral assemblages associated with fluid-rock interactions. Clearly, this experimental dataset suggests that the healing properties of natural faults are controlled by the feedback of multiple physico-chemical processes associated with the slip history and fluid-rock interaction under hydrothermal conditions.

# Isotopic tracers for provenance analysis of Holocene sediments from the Venetian Polesine area (NE Italy)

Ferrari M.*[1], Natali C.[1], Bragagni A.[1] & Bianchini G.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* mattia.ferrari@unifi.it

*Keywords:* water-rock interaction, sediments traceability, isotope geochemistry.

This study investigates a set of sediments from the easternmost sector of the Po Valley (north of the present-day Po River course), an area filled by alluvia from two interfering fluvial systems (Po and Adige). The investigated samples represent a subset of a wider collection already characterized through X-ray fluorescence (XRF) and classified for their provenance on the basis of the geochemical composition following the criteria reported in Natali & Bianchini (2017).

These samples were selected for the analysis of trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and for lead (Pb)-strontium (Sr) isotope ratios determination by Thermal Ionization Mass Spectrometry (TIMS). The new ICP-MS data showed a lower dispersion and higher consistency with respect to XRF data, as highlighted by the distribution of siderophile-chalcophile elements, leading to a better discrimination of the sediments provenance for the two river systems (i.e., Adige and Po) in the study area, leading to a reclassification of some samples. The Sr and Pb isotopic composition of investigated samples show a variability compatible with the provenance discrimination obtained by the ICP-MS data, and provide further information on the sediment's sources. The obtained isotopic data were compared with those measured in ore deposits from the whole Alpine arc (Giunti, 2010; Artioli et al., 2016) to link different source lithologies with the alluvial sediments. The Pb isotope composition of sediments with Po river geochemical affinity conforms with that of ore deposits from western Alps, whereas sediments with Adige geochemical affinity show a Pb isotopic signature compatible with the Valsugana and Southalpine ore deposits.

The application at a regional scale of these new tracers, allowed to better constrain the geochemical and isotopic features of Po and Adige sources, and to identify further differences in Po affinity sediments settled in various sectors of the easternmost Padanian plain. In particular, sediments with Po affinity from the northern side of the present-day Po River course (Veneto region, this work) show intermediate geochemical features between those of Adige affinity and the Po sediment collected from the southern side (Emilia-Romagna region, Ciarpaglini, 2021), the latter representing the sedimentary deposit with the most genuine signature of the Po river basin source rocks.

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Ciarpaglini A. (2021) - Isotopic characterization of padanian Holocene sediments for the identification of natural and anthropic contributions. MSc Thesis, University of Firenze.

Giunti I. (2010) - Geochemical and isotopic tracers in copper deposits and ancient artifacts: a database for provenance. PhD diss., University of Padova.

Natali C. & Bianchini G. (2017) - Geochemical proxies of sediment provenance in alluvial plains with interfering fluvial systems: A study case from NE Italy. Catena, 157, 67-74.

# Fluid-melt immiscibility during anatexis in Mesoarchean migmatites, Kangerlussuaq basement (Southeast Greenland)

Ferrero S.*[1], Nicoli G.[2] & Gresky K.[2]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Institute of Geosciences, University of Potsdam (Germany).

*Corresponding author e-mail:* silvio.ferrero@unica.it

*Keywords:* nanogranitoids, immiscibility, mesoarchean.

The coexistence of primary crystallized anatectic melt (*nanogranitoids*) and COH fluid inclusions in peritectic garnet is being increasingly recognized as a common occurrence in partially melted rocks. Such occurrence appears to support the current view that a fluid is often present along with a silicate melt under conditions of primary immiscibility when metasediments undergo melting. The large majority of case studies occur in the Phanerozoic eon, while the Precambrian is still poorly represented. Here we characterize the oldest known evidence of fluid melt immiscibility during anatexis from the Mesoarchean basement on the East coast of Greenland by combining petrographic observations, MicroRaman spectroscopy, microprobe investigation and thermodynamic modeling.

The metasedimentary migmatites contain two generations of garnets, a large xenoblastic garnet ($Grt^1$) and a small idioblastic one ($Grt^2$). Both garnet types are almandine- and pyrope-rich with slightly variable grossular component ($Grt^1 > Grt^2$) and both contain primary polycrystalline inclusions with different phase assemblage. MicroRaman investigation shows that these inclusions contain an assemblage consisting of quartz/cristobalite +kokchetavite (a polymorph of K-feldspar) +kumdykolite (a polymorph of albite) ±phlogopite in $Grt^1$. In $Grt^2$ they crystallize instead to quartz +K-feldspar +chlorite, with $H_2O$ locally present. In both cases, the observed phase assemblages are typical of nanogranitoids formed at different conditions and likely to contain two different melts. In both garnet types nanogranitoids occur in the clusters along with primary $CO_2$-$CH_4$ fluid inclusions. Each one of the analyzed inclusions appear to have been affected by post-entrapment modifications, i.e., fluid re-speciation with formation of graphite, and formation of step-daughter minerals such as carbonates, pyrophyllite, quartz and possibly phlogopite. Such occurrence proves for the first time that these rocks experienced partial melting with the formation of garnet, and that this event took place in the presence of COH-rich fluid.

Previous estimates indicated peak metamorphic conditions at 650-700°C and 3-4 kbar, but these calculations were solely based on Fe-Mg exchange thermobarometers and are then likely to reflect re-equilibration in the later stage of the retrograde path. We re-evaluated the metamorphic pressure and temperature conditions with up-to-date phase equilibria modelling. Combined with the identification of nanogranitoids and fluid inclusions, our results suggest metamorphic peak equilibration and partial melting at T > 900°C and P > 7 kbar, and retrograde conditions of ~800°C and 6 kbar. Moreover, the presence of two different silicates melts in two different garnet types suggest the presence of two separated melting events during the PT history of the still poorly investigated Kangerlussuaq basement.

# Petrogenesis and geochemical features of the Lar alkaline igneous complex (SE Iran)

Ghiotto M.*[1], Natali C.[1-2], Bragagni A.[1], Braschi E.[3], Ghafari Bijar S.[4], Avanzinelli R.[1-3], Casalini M.[1], Arvin M.[4] & Conticelli S.[1-2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Geoingegneria e Geologia Ambientale, CNR, Monterotondo (RM). [3] Istituto di Geoscienze e Georisorse, CNR, Firenze. [4] Department of Geology, Shahid Bahonar University, Kerman (Iran).

*Corresponding author e-mail:* matthias.ghiotto@unifi.it

*Keywords:* Lar Igneous complex, shoshonitic/ultrapotassic magmatism, Sistan Suture Zone.

The Lar Igneous Complex is an alkaline complex, Oligocene in age, located in the South Eastern Iran, along the Sistan Suture, a geologic feature separating the Lut from the Helmand (Afghan) block and belonging to the Alpine-Himalayan orogenic belt.

The Lar complex is made of intrusive and hypabyssal igneous rocks with a clear orogenic signature. They show shoshonitic to ultrapotassic affinities with variable degree of silica saturation. Lamprophyres, nepheline-syenites, and phonolites are ultrapotassic silica-undersaturated rocks that crop out intimately associated with silica-saturated to -oversaturated syenitic to trachytic dykes and monzonites. Lamprophyres and nepheline-syenites show peculiar petrographic characteristics with symplectitic crystallisation of nepheline and K-feldspar similar to that found in pseudoleucite textures. The composition of nepheline indicates a possible crystallisation temperature below 700°C. Lamprophyres are characterized by cumulus olivine (Fo content up to 75) and clinopyroxene (mg# up to 0.83), the latter characterised by abundant phlogopite inclusions.

The rocks of the Lar Complex, independently from their degree of silica saturation, show variable enrichments in incompatible trace elements with depletion of HFS with respect to LIL elements typical of subduction-related igneous associations. A decreasing of LREE/HREE ratio is observed passing from silica-undersaturated ($La_N/Yb_N$ from 12 to 22) to silica-saturated and -oversaturated rocks ($La_N/Yb_N$ from 10 to 12), both showing a limited variation in Sr-Nd-Pb isotopic compositions.

Geochemical modelling suggests for the Lar igneous rocks the occurrence of continental crustal contamination processes coupled to crystal fractionation for the most differentiated igneous rocks and highlights a mantle source of their parental magmas modified by a metasomatic agent predominantly constituted by partial melts from carbonate-rich (over subordinate carbonate-poor) recycled sediments at depth within the upper mantle.

# Multiple immiscible liquids formation at shallow Somma-Vesuvius volcanic system

Lima A.*

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* anlima@unina.it

*Keywords:* immiscibility, skarn, Somma Vesuvius.

Melt inclusions represent microscopic droplets of magma trapped in host crystal microcavity during its growing and preserve valuable information on pre-eruptive magma composition and evolution. Previous published data on FI and MI in Somma-Vesuvius (SV) skarn bearing minerals and new ones (unpublished yet), always in SV skarn samples have been collected to try to understand the magma modifications in the shallow magma chamber. Such modifications might explain the stratification as witnessed by the stratigraphic sequence and isotope studies. Another important question is why during open conduit interplinian eruptions often there are explosive phases and VEI increase? Skarns are silicate rocks formed in the transition between magma and carbonate country rock. In this "transition zone" a magma-dominated system interacts with fluid-dominated system. Limestone and dolomitic country rocks melt, because of infiltrative contact metasomatism associated with silicate magmas; $H_2O$ reacts with the chloride, fluoride, borate and carbonate species and the chemical effects of high-temperature hydrolysis may be enhanced by phase separation, permitting multiple immiscible fluid phases formation. Various types of inclusions have been found representative of these environments with close genetic relationships: $CO_2$ fluid inclusions, saline inclusions (SI), saline melt inclusions (SMI), melt inclusions (MI) and, for the first time identified, the composite melt inclusions (CMI). Particularly SMI, MI and CMI record shallow magma chamber immiscibility processes. Until now immiscibility, between silicate melt ± aqueous chloride-rich liquid-carbonate/sulfate melt have been widely documented at SV and in other subvolcanic Italian systems as well. An innovative finding is the immiscibility between silicate liquids recorded by CMI at $T < 1060°C$ and P about 100 MPa. At large scale this kind of immiscibility could explain SV magma chamber stratification. In addition, as experimental studies have demonstrated, immiscibility can occur between liquid when one is Fe- and P-rich and Si-poor and the other Si-rich and Fe and P-poor (Wilson, 1989). White and grey pumices from both Avellino and Pompei Plinian eruptions, show these compositional differences implying that in the shallow magma chamber, during long repose time, stratification could be triggered by silicate liquid immiscibility. Another type of immiscibility between non-silicate (chloride-carbonate-sulfate-$CO_2$) recorded by SMI and CMI at $T < 690°C$, if replicated on a large scale during syneruptive quenching of magma, could be the cause of explosiveness increase of most of interplinian eruptions even at open conduit condition, implementing the eruption VEI.

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# Melt-peridotite interaction at high pressure during subduction: the case study of Borgo (Mt. Duria, Central Alps, Italy)

Malaspina N.*[1], Borghini G.[2], Zanchetta S.[1], Corti M.[1] & Tumiati S.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* nadia.malaspina@unimib.it

*Keywords:* slab-mantle interface, peridotite, melt-peridotite interaction.

The Borgo outcrop in the Mt. Duria Area (Adula-Cima Lunga unit, Central Alps, Italy) is an excellent case study of melt-peridotite interaction occurred in a subducted mantle-crust melange. Retrogressed Grt-peridotites are in direct contact with migmatised eclogites and experienced a common HP (2.8 GPa - 750°C) and post-peak (0.8-1.0 GPa - 850°C) static HT equilibration (Tumiati et al., 2018). Peridotites show a garnet compositional layering crosscut by a subsequent LP chlorite foliation. Eclogite boudins enclosed in migmatites show thin films and interstitial pockets of crystallised melts produced after the partial melting of eclogites at HP conditions (Pellegrino et al., 2020).

The contact between Grt-peridotites and eclogites is marked by a tremolitite layer that also occurs as boudins parallel to the garnet layering in the peridotites, indicating that they formed when peridotites were in the garnet stability field. Thermodynamic modelling of the chemical interaction between the Grt-peridotites and the eclogite-derived melt, suggest that these layers derive from a Grt-websterite precursor formed after the interaction between crustal melts and peridotites at HP.

Bulk rock chemical analyses were conducted on representative samples of Grt-peridotites and tremolitites collected along a profile of about 120 m length, starting from the eclogite-peridotite contact. Tremolitites show a progressive enrichment in LREE from the contact coupled with a complementary depletion of the same elements in the host peridotites. Some fluid immobile elements, such as Zr, progressively decrease in both tremolitites and peridotites. Numerical modelling assuming the eclogite-derived leucosome composition as starting percolating melt well reproduces this REE gradient by two steps of melt-peridotite reaction: a high peridotite assimilation at crust-mantle boundary followed by reactive melt percolation within the adjacent peridotite assuming variable amounts of olivine assimilation and pyroxene + amphibole crystallisation. Percolative reactive flow at decreasing melt mass and high instantaneous melt/peridotite ratio, combined with moderate extents of fractional crystallisation, accounts for the overall REE enrichment and LREE-HREE fractionation observed in tremolitite bulks within the first 30 m of peridotite, with important implication on the understanding of crust-to-mantle mass transfer conditions of the slab/mantle interface.

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# Structural and permeability evolution in the lithocap of a fossil geothermal system (Allumiere quarry, northern Latium, Italy)

Marchesini B.*[1], Tavani S.[2], Mercuri M.[1], Aldega L.[1], Mondillo N.[2], Pizzati M.[3], Balsamo F.[3] & Carminati E.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma.

*Corresponding author e-mail:* barbara.marchesini@uniroma1.it

*Keywords:* faults, alteration, geothermal energy.

Geothermal heat is a crucial source of renewable energy. Its present and future exploitation can be enhanced by the detailed knowledge of structural and chemical-mineralogic processes occurring in situ and their evolution in space and time.

Faults may behave as fluid conduits or fluid barrier. However hydraulic behavior of faults may change in time and space, during their structural evolution. In active geothermal systems, the interaction between hydrothermal fluids and fault rocks may deeply influence the reservoir productivity. In particular, hot and highly reactive fluids may induce severe modification of the physico-chemical properties of fractured rocks. Fossil hydrothermal systems may be used as analogues to study in-situ fluid-rock interaction processes in active geothermal systems.

In this contribution we present the results of a multiscale and multitechnique study carried out in the Allumiere high-sulphidation epithermal system (Tolfa Mountains district, northern Latium, Italy). We document faults and fractures attitude and distribution integrating field data with a virtual outcrop model constructed from drone imagery. We then characterized the mineralogical assemblages of the lithocap using optical petrography, Scanning Electron Microscope (SEM) and X-ray diffraction analysis of representative samples; we also mapped the distribution of the alteration assemblages in relation to major faults orientation.

We observed that the initial circulation of acidic hydrothermal fluids was guided by a major NW-SE-striking fault system, producing a hydrolytic alteration of the Plio-Quaternary pyroclastic rocks, with formation of a generally silicified carapace, variably enriched in alunite and kaolinite, which in turn fades out into a distal illite-smectite-bearing zone, where the country rock appears less altered. This first hydrothermal faulting event caused a permeability reduction of altered rocks, so that following fluid pulse(s) were injected at overpressure conditions. Subsequent exhumation and normal fault reactivation provided the necessary structural pathways for remobilization of alunite and kaolinite, which are enriched in the fault cores.

Latest oxidation of pyrite produced sufficiently acidic solutions that induced leaching of hypogene alunite, which then precipitated in open cavities (i.e., joints), producing a subsequent decrease in permeability.

The reconstruction of the tectonic-hydraulic evolution of a geothermal system is crucial when dealing with the evaluation of reservoir productivity and to make predictions on productional changes during in-situ operation.

# The influence of non-hydrostatic stress on mineral equilibria: insights from molecular dynamics

Mazzucchelli M.L.*[1-2], Moulas E.[1-2], Kaus B.[1-2] & Speck T.[1-3]

[1] Mainz Institute of Multiscale Modelling, Johannes-Gutenberg University of Mainz (Germany). [2] Institute of Geosciences, Johannes-Gutenberg University of Mainz (Germany). [3] Institute of Physics, Johannes-Gutenberg University of Mainz (Germany).

*Corresponding author e-mail:* mmazzucc@uni-mainz.de

*Keywords:* thermodynamics, mineral equilibria, non-hydrostatic stress.

Understanding the underlying mechanisms of geodynamic processes relies on the determination of the pressure-temperature history which is recorded by rocks that have been deformed. In most cases, the interpretation of the conditions attained by rocks is based on the assumption that the stresses in the Earth are hydrostatic, i.e., all the normal components of stress are equal. However, non-hydrostatic stresses are observed in the lithosphere, and the magnitude of the effect of the differential stress on phase equilibria is still actively contested among researchers.

The effect of non-hydrostatic stress on phase equilibria has been explored in several rock-deformation experiments (on mm scale), in which recrystallization of minerals was observed under an applied differential stress (e.g., Richter et al., 2016). However, during experiments, stress and pressure heterogeneities may develop in the sample (e.g., Cionoiu et al., 2019). Therefore, the direct effect of the applied non-hydrostatic stress on the thermodynamics of the reactions cannot be separated from the effect caused by local stress/pressure variations in the sample itself.

Here, we explore the effect of non-hydrostatic stress on the thermodynamics of mineral reactions by investigating a system at the molecular scale. With Molecular Dynamics (MD) we perform coexistence simulations in which two phases are brought in contact and equilibrated at given temperature, pressure, and stress conditions. In such simulations, the stress is kept homogeneous across the entire sample. Our results suggest that the direct effect of non-hydrostatic stress on the solid-liquid equilibria is rather minor for geological applications, consistent with theoretical predictions (Sekerka & Cahn, 2004; Frolov & Mishin, 2010). However, our analysis does not take into account the indirect effect of stress heterogeneities at the sample scale. Spatial variations of stress can reach GPa level and can therefore indirectly affect phase equilibria.

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# Zircon inclusion study as a guide to magmatic processes in a granitic environment: inferences from Gavorrano pluton (Tuscany)

Micheletti F.*, Caggianelli A. & Brogi A.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* francesca.micheletti@uniba.it

*Keywords:* zircon inclusions, SEM microanalyses, granite petrology.

This study presents a Scanning Electronic Microscopy (SEM) characterization by Back-scattered electron (BSE) imaging and semi-quantitative analyses (EDS) of inclusions within igneous zircons from the Gavorrano granitic pluton (Tuscany). The Gavorrano Granite is a small peraluminous granite body of early Pliocene age (4.4 ± 0.6 Ma, Rb/Sr Wr-Bt in Serri et al., 2001) of anatectic origin (S-type granite originated by partial melting of sedimentary protholith). The dominant monzogranite facies is characterized by a generally porphyritic texture with scattered K-feldspar megacrysts up to 8 cm in length. Zoned plagioclase, biotite, and quartz are embedded in a medium-grained matrix mainly composed of quartz and alkali feldspars with pinitized cordierite grains. The most common accessoryphases are apatite, zircon, monazite, magnetite and pyrite. Contact metamorphism of host rocks, belonging to the Tuscan metamorphic Complex, is testified by the occurrence of pelitic and calcsilicate hornfelses and andalusite- and cordierite-bearing spotted schists (Brogi et al., 2021). Separated zircon crystals from the monzogranite are clear and transparent, as there was no radiation damage, given the young age of the rock. They show euhedral shapes and internal zoning patterns typical of a growth under magmatic conditions. Mineral inclusions exposed at the surface of the mount are scattered throughout the oscillatory zoned zircons and show no preferred orientation. Most inclusions, particularly those ones occurring within the smallest zircons (63-125 microns in length), are mono-mineralic (apatite and monazite secondly), as it is typical for the calc-alkaline granitoids, with an euhedral habit indicating they represent earlier-crystallised phases overgrown by later-crystallised zircon. In addition to these, largest zircon crystals (125-250 microns) are present. They are often characterized by sector zoning, suggesting that zircon growth took place when the magmatic environment underwent significant and rapid changes. They also contain numerous composite inclusions of two distinct types: i) globular inclusions of prevalent quartz and K-feldspar and ii) poly-mineralic inclusions bearing quartz + alkali-feldspar + biotite + aluminosilicate phase (andalusite presumably) showing evident signs of resorption, surrounded by a chaotic and convoluted zoning evolving towards unperturbed rhythmic zoning. The former could be interpreted as crystallised melt inclusions while the latter as host rock fragments. This study started with a detailed textural and chemical zircon inclusion analysis and will be coupled with zircon chemistry characterization providing important constraints on the petrogenesis of the Gavorrano pluton.

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# Low temperature thermochronology for geothermal exploration: useful hints from the Larderello-Travale Geothermal Field

Montanari D.*, Ruggieri G., Bonini M. & Balestrieri M.L.

Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* domenico.montanari@igg.cnr.it

*Keywords:* geothermal exploration, magma intrusions.

High enthalpy geothermal fields are mostly associated with magmatic intrusions providing the heat source to make the system work. To identify and locate these features, geothermal exploration generally uses expensive, time-consuming approaches that could also require complex logistics. Here we present the result of a pilot study carried out in the well-known Larderello-Travale geothermal field (Tuscany, Italy), exploring the possibility of an advantageous use of low temperature thermochronology to obtain useful information in implementing the geothermal exploration workflow. The majority of the collected samples, except one retaining the Apatite fission-track age of the undisturbed or almost undisturbed country rocks, cluster in a close time span ranging between 3.1±0.8 and 1.9±1.1 Ma, which clearly matches the known ages of magmatic bodies in the region. We propose that this approach can contribute to the identification of sectors recently affected by thermal perturbations that could have led to the development of hydrothermal systems. This approach has allowed us to imagine the presence of subsurface magmatic intrusions even in areas where currently there are no direct indications. Overall, our results aim to demonstrate how low temperature thermochronology can be a powerful, fast, and cost-effective tool for geothermal exploration, to be used jointly with the classical methods.

# Forward thermodynamic modelling of the uncommon chloritoid + biotite + garnet assemblage: interplay between equilibrium and kinetics

Nerone S.*[1], Groppo C.[1-2] & Rolfo F.[1-2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* sara.nerone@unito.it

*Keywords:* P-T-X relations, $H_2O$ undersaturation, reaction affinity.

In medium-pressure Barrovian terranes, biotite and chloritoid are rarely recognized to be in equilibrium. We report, for the first time, equilibrium relations between chloritoid (Cld), biotite (Bt) and garnet (Grt) in amphibolite-facies phyllites from the Upper portion of the Lesser Himalayan Sequence in eastern Nepal Himalaya. Several studies have investigated the influence of different parameters on the stability of this assemblage, among which pressure (P), temperature (T), bulk rock and fluid compositions (X) (e.g., Sengupta, 2012; Saki et al., 2021). Inspired from these studies, we have applied the forward thermodynamic modelling approach on two representative samples, to test the influence of these parameters on the stability of Cld, Bt and Grt. Two internally consistent datasets and solution model packages have been tested, i.e., hp98 (Holland & Powell, 1998) vs. hp62 (Holland & Powell, 2011), through AFM chemographies; only the hp98 database predicts the coexistence of Cld + Bt for the considered bulk compositions in the simplified KFMASH system. Expanding the modelling to the MnNKCFMASHTO system, however, the calculated P-T isochemical phase diagrams failed in modelling the observed equilibrium relations, predicting Bt appearance at higher temperatures than the Cld stability field. P/T-$a$H$_2$O pseudosections show that low $H_2O$ activities ($a$H$_2$O < 1) due to the presence of $CO_2$ in the fluid do not favour the stability of the observed assemblage. Similarly, X($Fe_2O_3$) has a negligible influence on the stability of the observed assemblage. On the opposite, P/T-M($H_2O$) pseudosections show that $H_2O$-undersaturated conditions expand the Bt stability toward lower temperatures, allowing the formation of the Cld + Bt assemblage at P-T conditions consistent with the results of conventional geothermometry. Kinetic factors could have further contributed to the stability of this assemblage, through thermal overstepping of the Cld-consuming reaction. Preliminary calculations suggest that the reaction affinity of the Cld-consuming reaction is lower than that of the Chl-consuming, Bt-producing reaction, delaying the appearance of staurolite and predicting the coexistence of (metastable) chloritoid and biotite.

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# Petrochronology of chlorite-schists reveals the timing of serpentinites dehydration and metasomatism: new insights from the Zermatt-Saas ophiolite

Piccoli F.* & Rubatto D.

Institute of Geological Sciences, University of Bern (Switzerland).

*Corresponding author e-mail:* francesca.piccoli@geo.unibe.ch

*Keywords:* subduction, serpentinites, geochronology.

Serpentinites dehydration has major implications for geochemical and geodynamic processes in subduction zones because it releases large quantities of fluids that can transport volatiles and other elements to the mantle wedge and, eventually, back to the surface. The interaction of serpentine derived fluids with other slab and/or mantle lithologies can lead to the formation of metasomatic rocks. However, it can be difficult to establish the time span between serpentinite dehydration and metasomatic rock formation. Two main challenges are finding suitable mineral for geochronology and determining the spatial relations between fluid source, i.e., serpentinites, and metasomatic rocks. Moreover, dehydration can be diachronous within a unit. Hence, the knowledge of the timing of dehydration within large oceanic units can shed light on their P-T-t evolution and on potential differences of subduction rates and/or thermal regimes.

In this study, we investigate metasomatic rocks, i.e., chloritized rodingites and mafic dykes, that are embedded within dehydrating serpentinites from the Zermatt-Saas unit (Unter Theodulgletscher unit and Pfwulve pass). Petrological, geochemical and geochronological data on garnet-titanite bearing, zircon-bearing and rutile-titanite-zircon bearing chlorite-schists aim is to constrain the timing of dehydration and the characteristics of serpentinite derived fluids at the source. Compositional maps of garnet acquired by EPMA and LA-ICPMS reveal that a first Ti-rich garnet generation is consumed during chloritization, while a second garnet generation grows in textural equilibrium with chlorite and titanite. Garnet cores are Ti-rich andradite with 2-3 ppm of U. Garnet rims are instead Ti poor. Titanite can thus be petrogenetically linked to the chloritization reaction and consumption of garnet cores. Notably, a Cr-rich garnet rim is observed. This suggests that the last garnet generation records the infiltration of fluids equilibrated with ultramafic rocks.

Titanite from this lithology yields an age of ca. 45 Ma, which indicates that fluid release and chloritization occurred at peak conditions. Zircon in chlorite-schists from Pfwulve displays a preserved magmatic core and a recrystallized metamorphic rim. In situ U-Pb analyses returned a Jurassic age for the zircon cores and an Alpine age for the rims of ca. 47 Ma. Rutile yields a younger age of ca. 37 Ma, whereas titanite from this sample could not be dated. Altogether, our results indicate that within uncertainty the dehydration of serpentinites in the Unter Theodulglatscher unit and at Pfwulve pass happed at the same time, at peak metamorphic conditions.

# Geophysical and geochemical investigations of mud volcanoes in the peri-Adriatic area of the central Marche region

Principi M.*[1], Giuli G.[1], Pierantoni P.P.[1], Spagnoli F.[1-2] & Zambrano M.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Istituto per le Risorse Biologiche e le Biotecnologie Marine, CNR, Ancona.

*Corresponding author e-mail:* michela.principi@studenti.unicam.it

*Keywords:* mud volcanoes, geophysical investigations, geochemical investigations.

Mud volcanoes are geological systems characterized by emission of cold fluids consisting of a mixture of mud water and gas. The settings, driving forces, and expelled material of mud volcanoes is quite variable. These geological features remain an intriguing subject regardless of being known and documented for centuries (Huff & Owen, 2015). Mud vulcanism often occurs in presence of water-saturated fine-grained sediments under pressure from overlying strata, and the eruption of the material could be facilitated or triggered by gas or seismic activity.

This work is framed in a macro project focus on investigating the geological and geochemical characteristics of a series of mud volcanoes distributed along the eastern thrust fronts of the Italian peninsula, more precisely in the Marche region. These structures are distributed on a monocline (NE-dipping) involving Miocene-Pliocene deposits, covering several thrust-related folds and thrust faults in the peri-Adriatic area (Lupi et al., 2016; Maestrelli et al., 2017). The geometry and the mud source of this volcanoes is poorly studied.

Here, we present preliminary results of an integrated methodology (geophysical and geochemical) applied on a key mud volcano located at Monteleone di Fermo to characterize its structure at local scale and the geochemical properties of the expelled material. To reconstruct the 3D subsurface model, comprising the volcano caldera, we integrate the following geophysical methods: (i) 3D Electrical Resistivity Tomography (ERT) using a FullWaver system (Iris); (ii) Passive seismic methods (Refraction Microtremor- ReMi, Horizontal-Vertical Spectral Ratio- HVSR), iii) active seismic methods (Multichannel analysis of surface waves-MASW, seismic refraction). Concerning the geochemical analyses, the mud is subjected to diffractometry and to 4 – Acid "Near Total" Digestion ICP-OES (ppm) test in order to characterize its source rock.

The whole data allow us to determine the near-surface (depth < 100 m) geometry of a mud volcano at local scale and individuate its feed channel. Our study may serve as example methodology for the characterization of similar mud volcanoes in the area. Also, we expect to provide new insight about source and composition of the erupted material.

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# Using the "other" variables in phase equilibrium modelling – enthalpy, activity and chemical potentials as controlling agents in metamorphism

Schorn S.*

Department of Petrology and Geochemistry, University of Graz (Austria).

*Corresponding author e-mail:* simon.schorn@uni-graz.at

*Keywords:* enthalpy, chemical potentials.

Metamorphic processes are typically defined in terms of temperature and pressure that are routinely estimated using thermodynamic modelling. This modelling yields a wealth of thermodynamic data that can be used to investigate this connection and illuminate processes that otherwise appear independent of temperature and pressure. Here the relationship between enthalpy-temperature and composition-activity-chemical potential is applied to classic granulite- and eclogite facies rocks. Calculated enthalpy-temperature paths show that significant heat is consumed by endothermic melting reactions and released during exothermic rehydration that induces a quasi-isothermal state during respective heating and cooling of high-grade metamorphic terranes. This type of reaction-induced thermal buffering can significantly delay heating- and cooling in fertile lithologies such as metapelites, whereas less reactive rocks (e.g., granites) experience more linear temperature-time paths. Constraining the enthalpy involved in metamorphic reactions allows to estimate the effective heat capacity, which is used as input in one-dimensional thermal models to quantify realistic heating-cooling paths of exhuming high-grade metamorphic terranes. Similarly, the conjugate extensive-intensive pair of composition and chemical potential is used to infer the direction of material transport in reactions involved in the transformation of mafic and felsic protoliths at high pressure. Calculated chemical potential relationships applied to reaction textures allow to identify the key components responsible for texture formation and to estimate their relative diffusivities. Phase diagrams contoured for chemical potential and/or activity of $H_2O$ are used to explain hydration gradients between metapelites and embedded dry gabbro that triggered the gabbro-to-eclogite transition and subsequent retrogression during exhumation.

# Development of a Python GUI application to automate EQ3/6 thermodynamic computations

Siron G.*[1], Vitale-Brovarone A.[1] & Matthews S.M.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Institute of Earth Sciences, University of Iceland, Reykjavík (Iceland).

*Corresponding author e-mail:* guillaume.siron@unibo.it

*Keywords:* thermodynamic modeling, fluid speciation, GUI app.

Fluid-rock interactions are one of the most important processes on Earth and play an important role in many metamorphic systems. Nevertheless, even if thermodynamic data for mineral and fluid species are easily accessible though many software packages, in most metamorphic studies, the fluid phase is usually reduced to a simple system, either pure $H_2O$ or a $H_2O$-$CO_2$ mixture. Yet, we know that dissolved elements and ionic aqueous species can play a major role in many metasomatic reactions. Here we present a Python application with a user-friendly graphical user interface (GUI) that allows automation of EQ3/6 thermodynamic fluid speciation computations.

The application computes the fluid speciation using EQ3 computations and then automation of metasomatic reaction through two designs of batch EQ6 computations. The first option computes batches of EQ6 calculations with different fluid-rock ratios set by the user. The user can then plot the resulting compositional variables, i.e., mineral modes, end-member proportions of solid solutions, dissolved elements, and fluid species concentrations. Again, the user interface (UI) allows several plotting possibilities, either 2D plots such as either reaction progress or fluid-rock ratios for a specific reaction progress versus one or more compositional variable(s) or in 3D where up to 2 compositional variables can be represented as surfaces in function of the fluid-rock ratio and the reaction progress. The second design option allows the user to batch process EQ6 computations with different proportions for 3 minerals at a set fluid-rock ratio. Four different resolutions are accessible with one point every 10%, (66 computations) 5% (231), 2.5% (861) and 1% (5151), respectively. As for fluid-rock ratio batch computations, the results can be displayed inside the ternary diagram using a color scale for each run, where the user can choose which variable and which reaction progress is displayed.

We believe that user-friendly applications such as the one presented here will allow more petrologists to introduce fluid speciation into their metamorphic projects. Such effort should allow for a more realistic modeling of the fluid phase and thus of fluid-rock interactions.

# The petrological record of eclogite cycling in an oceanic subduction channel from eastern Australia

Tamblyn R.*[1-2], Hand M.[2], Morrissey L.[3], Anczkiewicz R.[4], Zack T.[5], Phillips G.[6] & Och D.[7-8]

[1] Institut für Geologie, Universität Bern (Switzerland). [2] Department of Earth Sciences, University of Adelaide (Australia). [3] School of Natural and Built Environments, University of South Australia, Adelaide (Australia). [4] Institute of Geological Sciences, Polish Academy of Sciences, Kraków (Poland). [5] Department of Earth Sciences, University of Gothenburg (Sweden). [6] Geological Survey of New South Wales, Maitland (Australia). [7] School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney (Australia).
[8] WSP Parsons Brinckerhoff, Newcastle (Australia).

*Corresponding author e-mail:* renee.tamblyn@geo.unibe.ch

*Keywords:* high-pressure, return flow, eclogite.

Much of what we know about subduction systems comes from the study of palaeosubduction systems, where oceanic crust is exhumed coherently or as chaotic mélange from the subduction channel. High-pressure blueschist and eclogite facies rocks, representing the metamorphosed basaltic oceanic crust, are excellent probes of subduction zone processes. These compositions form useful minerals such as garnet, lawsonite, phengite and accessory phases, which are pressure-temperature sensitive themselves but can also contain inclusion assemblages, can often be dated to find their timing of growth or cooling, and can record information about equilibrated fluid compositions within their isotopic and major and trace element compositions. As such, we can deduce the timing and physical conditions of the path taken by subducted rocks during burial and exhumation, and use this to infer large scale geodynamic processes and tectonic events. Convective return flow of material is becoming recognised as a geodynamic process which occurs within subduction channels, and can result in cycling, reburial and final exhumation of high-pressure blocks within the subduction channel, as predicted from numerical modelling and real-world examples. Lawsonite eclogite and garnet blueschist from mélange at Port Macquarie, eastern Australia, provides an excellent opportunity to investigate such cycling, including the magnitude of depth change and the timeframes it occurred over via detailed petrology, U-Pb, Lu-Hf, Sm-Nd, Rb-Sr and Ar-Ar geochronology, and phase equilibria forward modelling. Lawsonite eclogite contains geochronological and petrological evidence of two cycles of burial and exhumation within the subduction channel over a timeframe of ca. 50 My and a pressure range of at least 1.2 GPa. Garnet blueschist records a different pressure-temperature-time evolution to the lawsonite eclogite, but became accumulated with the eclogite and numerous other low- to high-grade rocks in serpentinite hosted mélange prior to or during exhumation. The suggestion that active and palaeo subduction channels may form mélanges containing materials spanning both a wide range of pressure-temperature conditions, but also timeframes, has repercussions for how we interpret the geology of active and exhumed subduction systems.

# Oxidation of subducted organic matter buffered by marine carbonate rules the carbon isotopic signature of arc emissions

Tumiati S.*[1], Tiraboschi C.[2], Sverjensky D.A.[3], Manning C.E.[4], Vitale-Brovarone A.[5], Boutier A.[6] & Poli S.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Institut für Mineralogie, Universität Münster (Germany). [3] Department of Earth & Planetary Sciences, Johns Hopkins University, Baltimore, MD (USA). [4] Department of Earth, Planetary and Space Sciences, University of California, Los Angeles, CA (USA). [5] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [6] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* simone.tumiati@unimi.it

*Keywords:* carbon isotopes, $CO_2$ cycle, redox.

Open-ocean sediments consist mainly of inorganic calcium carbonate and organic matter (phytoplankton debris), along with minor opal and clays. Once subducted, some carbon is removed from the slab and returns to the atmosphere as $CO_2$ in arc magmas. Its carbon isotopic signature has been thought to reflect that of its subarc source region, implying similar devolatilization extent for both inorganic and organic carbon. We challenged this assumption by experimentally investigating the carbon isotopic exchange in a model metasedimentary system composed of $^{13}C$-$CaCO_3$ + $^{12}C$-graphite, interacting with water at pressure, temperature and redox conditions compatible with an average slab-mantle interface beneath arcs at ≈100 km depth. We show that aqueous fluids rich in $CO_2$ are produced mainly by irreversible oxidative dissolution of graphite, which behaves as a chemically reactive but isotopically inert phase. Conversely, the carbon isotopic composition of $CO_2$ and of the recrystallized carbonate is non-dependent on the organic/inorganic carbon fraction, but it is instead a function of (i) the redox state of the environment and (ii) the fluid-rock ratio. Assuming relatively low fluid-rock ratios realistic for subarc depths where percolation of fluids coming from the underlying oceanic lithosphere dominates, isotopic compositions characterising the global average of volcanic arc $CO_2$ emissions are possible only at relatively oxidizing conditions of deltaFMQ +0.78 to +1.08, which matches the redox state of island-arc-basalt sources.

# Investigating chemical potential gradients to decipher microstructures and mineral assemblages in mylonites

Tursi F.*

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* fabrizio.tursi@uniba.it

*Keywords:* chemical potentials, mineral reactions, ductile deformation.

The use of forward thermodynamic modelling is having increasingly impact on the investigation of tectono-metamorphic processes, particularly when both intensive and extensive thermodynamic variables are considered. In this context, the way new minerals form in rocks affected by ductile shearing, and why relict porphyroblasts are preserved in zones where mineral reactions are generally supposed to be deformation-assisted, can be revealed through the analysis of chemical potential gradients. Here, syn-kinematic mineral assemblages developed in mylonites from the Calabria polymetamorphic terrane were examined through phase equilibrium modelling of the intensive-extensive conjugate pair thermodynamic variables. Results revealed that gradients in chemical potentials have effects on the mineral assemblages of the studied mylonites, and that new syn-kinematic minerals formed in higher-$\mu H_2O$ conditions than the surroundings. In each case study, the fluid that was internally generated by the breakdown of OH-bearing minerals, favoured the development of mylonites' banded fabric. Thermodynamic modelling highlights that during the prograde stage of metamorphism, high-$\mu H_2O$ was necessary to form new minerals while relict, anhydrous porphyroblasts remained stable in condition of low-$\mu H_2O$. This approach provides a more robust interpretation of mylonites microstructures, and evidences that during shearing, the fluid released in the system by devolatilization reactions promotes growth of new minerals and deformation via reaction-induced rheological weakening, favouring ductile deformation.

# S9.

# Ground deformation measurements and Geosciences: applications and outlooks

*Giuseppe Pezzo (INGV Roma)*

*Silvia Bianchini (University of Firenze)*

*Federico Di Traglia (OGS Trieste)*

*Claudia Meisina (University of Pavia)*

# Assessment of the natural and anthropogenic land subsidence along the Upper Adriatic Sea coast

Albano M.*, Trasatti E., Secreti V., Polcari M., Anderlini L., Serpelloni E., Palano M., Pezzo G. & Stramondo S.

INGV, Roma.

*Corresponding author e-mail:* matteo.albano@ingv.it

*Keywords:* SAR, subsidence, Ravenna coast.

In this work, we assessed the last 20 years of onshore and off-shore subsidence along a sector of the Upper Adriatic Sea (Italy) coast by means of ground-based measurements, remote sensing data, and numerical modelling.

The study area encompasses a coastal region of approximately 400 $km^2$ east of Ravenna municipality, where severe ground subsidence has been documented in the past, caused by natural subsidence of soils and by anthropogenic subsidence induced by human activities, such as aquifer exploitation and hydrocarbon extraction (Teatini et al., 2005).

Our approach, based on the synergistic use of remote sensing and in-situ geodetic data, exploited several datasets consisting of Synthetic Aperture Radar (SAR) images provided by Envisat, Cosmo- SkyMed and Sentinel-1 missions, GPS measurements from continuous stations managed by public institutions, local authorities and private companies, and levelling surveys.

Our analysis detected onshore and off-shore subsidence values up to approximately 1-1.5 cm/yr between the Lido Adriano and Lido di Dante coastal villages. Ground subsidence of the same order of magnitude also affected the Angela-Angelina off-shore platform, located approximately 2 km far from the coastline.

The analysis of literature data, together with a specially devised numerical model to estimate the contribution of hydrocarbon extraction to the observed ground subsidence, allowed us to conclude that most of the observed long-wavelength subsidence is related to aquifer overexploitation. Otherwise, the contribution of hydrocarbon extraction is quite limited.

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# Ground deformation in Northeastern Italy by using PS-InSAR and GNSS data

Areggi G.*[1-2], Merryman Boncori J.P.[3], Anderlini L.[2], Rossi G.[4], Serpelloni E.[2], Zuliani D.[4] & Bonini L.[1]

[1] Dipartimento di Matematica e Geoscienze, Università di Trieste. [2] INGV, Bologna. [3] Space Institute, Technical University of Denmark, Lyngby (Denmark). [4] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* giulia.areggi@phd.units.it

*Keywords:* PS-InSAR, GNSS, ground deformation.

We present the results derived from the processing of Interferometric SAR (InSAR) and Global Navigation Satellite System (GNSS) data, showing the mean ground displacement velocities in Northeastern Italy.

Previous studies on this area indicate an active convergence of 1.5-3 mm/yr (e.g., Serpelloni et al., 2016), due to the Adria-Eurasia continent-continent collision. The tectonic activity is also testified by the seismicity distributed along the Southern Alps and Dinaric system. Conversely, the Adriatic coasts and the southern plain are affected by active subsidence with variable rates of 0.5-5 mm/yr (e.g., Tosi et al., 2010).

In the present study, we applied the Stanford Method for Persistent Scatterers (StaMPS), which is based on the detection of coherent and temporally stable pixels in a stack of single-master differential interferograms (Hooper et al., 2012). Starting from Sentinel-1 images, acquired in the 2015-2019 time-span along the ascending and descending orbit tracks, we ran the Persistent Scatterer InSAR (PSI) processing. After the application of spatial-temporal filters and post-processing steps to refine the measurements, we used Adria-fixed GNSS velocities derived by permanent stations in the study area to perform a calibration of the InSAR velocity estimates.

The outcome consists of mean ground velocity maps derived by displacement time series along the radar Line-OF-Sight (LOS) for each satellite track. Moreover, by combining the LOS datasets, we also obtained maps showing the east-west and vertical velocities over the region.

We observe a vertical velocity gradient up to 2 mm/yr across the Carnic Alps and positive vertical trends, with lower values (~1 mm/yr), across the Julian Alps and the Dolomites. Considering the tectonic setting of the area, these signals can be related to strain build up at active tectonic structures. Based on the east-west velocity map, our measurements show a general eastward movement of the study area, increasing toward northeast with rates of 1-2 mm/yr.

The coasts and the southern Venetian-Friulian plain are affected by subsidence, with negative rates of 2-4 mm/yr and slower than 1 mm/yr on the western and eastern sectors respectively, by confirming the correlation with the geological setting.

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# Inflating Source Imaging of the 2009–2013 Unrest Episode at Campi Flegrei Caldera revealed through GPS and DInSAR measurements

Castaldo R., Solaro G.* & Tizzani P.

Istituto per il Rilevamento Elettromagnetico dell'Ambiente, CNR, Napoli.

*Corresponding author e-mail:* solaro.g@irea.cnr.it

*Keywords:* Campi Flegrei caldera, ground deformation, finite element modeling.

Geodetic modelling is a valuable tool to infer volume and geometry of volcanic source system; it represents a key procedure for detecting and characterizing unrest and eruption episodes. In this study, we analyse the 2009–2013 uplift phenomenon at Campi Flegrei (CF) caldera in terms of spatial and temporal variations of the stress/strain field due to the effect of the retrieved inflating source. We start by performing a 3D stationary finite element (FE) modelling of geodetic datasets to retrieve the geometry and location of the deformation source. The geometry of FE domain takes into account both the topography and the bathymetry of the whole caldera. For what concern the definition of domain elastic parameters, we take into account the Vp/Vs distribution from seismic tomography. We optimize our model parameters by exploiting two different geodetic datasets: the GPS data and DInSAR measurements. The modelling results suggest that the best-fit source is a three-axis oblate spheroid ~3 km deep, similar to a sill-like body. Furthermore, in order to verify the reliability of the geometry model results, we calculate the Total Horizontal Derivative (THD) of the vertical velocity component and compare it with those performed with the DInSAR measurements. Subsequently, starting from the same FE modelling domain, we explore a 3D time-dependent FE model, comparing the spatial and temporal distribution of the shear stress and volumetric strain with the seismic swarms beneath the caldera. Finally, We found that low values of shear stress are observed corresponding with the shallow hydrothermal system where low-magnitude earthquakes occur, whereas high values of shear stress are found at depths of about 3 km, where high-magnitude earthquakes nucleate.

# Comparing DInSAR and ground-based monitoring measurements of a rockfill dam during its first impoundment

De Stefano R.*[1], Calcaterra D.[1], Di Martire D.[1], Fiorino A.[2], De Marco S.[2] & Russo G.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II».
[2] Sorical S.p.A., Catanzaro.

*Corresponding author e-mail:* dsrita91@gmail.com

*Keywords:* DInSAR, monitoring, dam.

Monitoring is an essential tool for ensuring safety of large civil engineering works during their construction and service life in terms of maintenance and prevention. Large dams are critical for safety since the catastrophic human and socio-economic consequences in case of failure. Displacements measurements characterize the static response of the dam embankment and its interaction with the soil mass and are traditionally performed by means of assestimeters and inclinometers (dam body displacements) and optical precision levelling and GPS (surface displacements). The integration of ground-based measurements with remote sensing techniques can largely improve the efficiency of monitoring systems. Among the remote sensing techniques, the Synthetic Aperture Radar Differential Interferometry (DInSAR) has been proved its versatility and efficiency for mapping and monitoring deformations of the Earth's surface (Di Martire et al., 2016; Confuorto et al., 2017), subsidence and sinkhole phenomena, as well as infrastructures (Infante et al., 2018). DInSAR technique can implement wide range analysis that exploits the high resolution (3m × 3m) and short revision time (6-8 days) of the Sentinel 1 and COSMO-SkyMed constellations. Due to the availability of a large historical set of data, measured displacements on targets can reliably improve and enlarge the dataset achievable with conventional methods. In this study the suitability of developing an integrated monitoring system, based on the complementary use of remote sensing and traditional techniques, has been verified with reference to the case study of a rockfill dam. Menta embankment Dam is located in Southern Italy and built between 1987 and 2000 as the main reservoir of the new aqueduct system serving the city of Reggio Calabria. DInSAR remote sensing measurements and ground-based traditional monitoring of deformations and displacements have been compared with reference to the first impoundment over a 5 years time interval.

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# Automated assessment of InSAR-based ground displacements at large scale

Festa D.*[1], Confuorto D.[1], Del Soldato M.[1], Raspini F.[1] & Casagli N.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* davide.festa@unifi.it

*Keywords:* InSAR, Machine learning, ground deformation.

Interferometric synthetic aperture radar (InSAR) represents a powerful geodetic technique that allows to measure ground deformations over large temporal and spatial scales with millimeter precision. The launch of the European Space Agency (ESA) C-band Sentinel-1 (S1) satellites has led to set up near real time monitoring services and fostered the intensive mapping of ground displacements across the globe thanks to the enhanced revisiting time (up to 12 days) and the free policy for data dissemination. The recent technological progresses of space-born SAR sensors and the related processing techniques have made available ever-increasing quantities of very accurate monitoring data. Therefore, is of major interest for the scientific community to coordinate the efforts in projecting and implementing automatic solutions aimed at performing integrated analysis of large amounts of data, which can no longer be investigated manually.

In order to efficiently exploit InSAR results at very large scale, here we present a new procedure for the preliminary screening of wide territories affected by active instability phenomena due to both natural hazards and anthropogenic activities. Following an original approach, we implemented the Random forest (i.e., a Machine learning technique) for the automatic recognition of various sources of motion bound to MPs (Measurement Points) with high deformation rates. The methodology relies on the use of an expertly interpreted InSAR training dataset and on generally accessible informative layers concerning geohazard inventories, morphometric and land cover maps. We show the feasibility of our approach by applying it to the ascending and descending orbits deformation maps covering the Northern part of Italy and resulting from the exploitation of the whole S1 archive acquired from March 2015 to December 2018.

Being data-driven and reproducible, the proposed methodology demonstrates the potential applicability of Machine Learning framework for the prompt screening of newly updated InSAR datasets covering very wide areas in continuity with the development of automated ground motion analysis, and thus it may guarantee a valid support in land management and civil protection purposes.

# Seafloor geodesy in shallow water. A practical case: the Campi Flegrei submerged area

Guardato S.*, Donnarumma GP., Riccio R. & Iannaccone G.

INGV, Osservatorio Vesuviano, Napoli.

*Corresponding author e-mail:* sergio.guardato@ingv.it

*Keywords:* seafloor geodesy, pressure sensor, GPS.

Campi Flegrei volcanic complex is one of the most high-risk areas of the world, densely populated, near the city of Naples, and submerged for a significant part. After the 1982–1985 unrest, the Campi Flegrei caldera underwent a phase of subsidence and minor uplift episodes. Changes in seismicity have been observed from 2004, and from 2011 the on-land deformation measurements has indicated a quasi-constant ground uplift of about 90 cm in total, reaching the maximum uplift of the '80s crisis.

From 2016 an innovative multiparameter marine monitoring infrastructure named MEDUSA (Multiparametric Elastic-Beacon-based Devices and Underwater Sensor Acquisition System) has been developed and deployed in the Gulf of Pozzuoli; it represents the first system in the world able to monitor the vertical seafloor movements in a continuous way (De Martino et al., 2014; Iannaccone et al., 2018).

MEDUSA is a permanent infrastructure consisting of four marine multidisciplinary platforms (MMPs) operating as an extension to the marine sector of the on-land geophysical monitoring network of the Campi Flegrei managed by INGV-Osservatorio Vesuviano. Each platform, the deployment depth of which ranges from 40 to 100 m, consists of a buoy connected through a cable to a module placed on the seabed a few meters from the ballast of the buoy. The module is equipped with geophysical and oceanographic sensors, among which a high-resolution pressure sensor. The emerging part of the buoy hosts communication and power systems and control electronics. In addition, on the top of the buoy, a geodetic GPS receiver is installed to monitor the seafloor displacement (De Martino et al., 2020).

We present the results of continuous seafloor displacement measurements over several years performed by MEDUSA infrastructure and we highlight the importance of complementary and alternative methods to investigate a hidden but not negligible part of an active volcanic areas. The results of a feasibility study of an innovative instrument that broaden the seafloor geodesy measurements in the Gulf of Pozzuoli will be outlined.

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# Contraction of Ischia Island revealed by long term geodetic data

Iannarelli M.*[1], Galvani A.[1], Pezzo G.[1], Sepe V.[1] & Ventura G.[2]

[1] INGV, Osservatorio Nazionale Terremoti, Roma. [2] INGV, Roma.

*Corresponding author e-mail:* mirko.iannarelli@ingv.it

*Keywords:* GNSS Network, velocity field, degassing.

The recognition of the processes responsible for the deformation of volcanoes allow us to understand the dynamics of magmatic systems with obvious implication for the evaluation of volcanic hazards. We present data on twenty years (1997–2018) of geodetic measurements on Ischia Island (Italy), which is affected by shallow earthquakes and hydrothermal manifestations. The data from the GPS Network and the leveling route reveal a continuous subsidence with values up to $-15 \pm 2.0$ mm/yr and a centripetal displacement rate. The largest deformations occur on the southern flank of Mt. Epomeo resurgent block. The inversion of GPS and levelling data suggests deflating source located at 4 km depth. Independent geophysical data corroborate the depth of the source inferred from the deformation modeling. Degassing and magma cooling of a reservoir below the southern flank of Mt. Epomeo are responsible for the Ischia deformation pattern. The deformation field appears not associated to the instability of the resurgent block, gravity processes, or tectonics. The temporally discontinuous Ischia shallow seismicity is due to the dynamics of the shallow hydrothermal system and it is not temporally or spatially related to the continuous deflation.

# Assessment of the fire effects on sloping areas via multitemporal satellite images and UAV surveys

Iervolino L.*[1], Peduto D.[1], Fedele A.[2], Somma R.[2-4], Limongiello M.[1] & Barba S.[1]

[1] Dipartimento di Ingegneria Civile, Università di Salerno, Fisciano (SA). [2] INGV, Osservatorio Vesuviano, Napoli. [3] Istituto di Ricerca su Innovazione e Servizi per lo Sviluppo, CNR, Napoli. [4] Istituto di Scienze Marine, CNR, Napoli.

*Corresponding author e-mail:* liervolino@unisa.it

*Keywords:* wildfires, remote sensing.

Wildfires leave a significant mark on the landscape through the combustion of trees and shrubs and changes in soil properties that may cause reduced rainwater infiltration and consequently increased runoff and erosion compared to unburned areas. Intensive erosive processes such as rill erosion, gully erosion, and channel erosion in burned areas have been documented worldwide. The mobilization of sediments downstream and incorporation of additional material within the hydraulic flows along the drainage network may lead to sediment-laden and debris flows. These mass movements may occur because of intense rainfall within a few years after a fire and several times in the same burned basin. The relatively high flow velocities may increase the hazard and risk conditions for people living near the outlets of burned watersheds and thus exposed to the impact of flow processes. In this regard, the assessment of the vegetation condition and the mapping and displacement monitoring are key issues for assessing the hazard of fast-moving landslides on burned sloping areas. Remote sensing techniques are effective tools to obtain spatially distributed information on both vegetation condition and ground displacements. Indeed, satellite-based observations of surface reflectance can be used to calculate vegetation indices, whereas Unmanned Aerial Vehicles (UAVs) can be adopted to perform digital aerial photogrammetry.

In this work, a RTK drone is used to carry out multitemporal photogrammetric data acquisition in two burned areas belonging to the Pizzo d'Alvano massif, Sarno Mountain Range, Campania Region, Italy. Moreover, the vegetation conditions of the two burned areas are assessed by means of multispectral indices starting from Sentinel-2A satellite data. The study sites belong to one of the most landslide-prone areas in Italy that was affected by multiple events in the past, including the disaster of 5-6 May 1998. Recent studies demonstrated that pyroclastic soils in this area are susceptible to post-fire erosion processes, which can supply hyperconcentrated and debris flows threatening the urban centers downstream.

The aim of this work is to better understand the link/relationship between vegetation condition and mass mobilization from burned slopes, via remote sensing techniques. The utility for land managers could reflect in the assessment of post-fire ground displacement response starting from satellite-based vegetation indices in geoenvironmental contexts similar to those examined in the present study.

# Monitoring and Prediction of deformation caused by Landslides Based on Graph Convolutional Network and SAR Imagery

Khalili A.M.*, Guerriero L., Pouralizadeh M., Calcaterra D. & Di Martire D.

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* mohammadamin.khalili@unina.it

*Keywords:* landslides, SAR imagery processing, Graph Neural Networks.

In rural and urban areas, predicting and mapping landslides are complex due to slow movement and human intervention inhibiting the identification of typical morphologies diagnostic (Del Soldato et al., 2017; Noviello et al., 2020). Landslides that affect rural and urban settlements must therefore be detected and tracked in order to identify and predict the landslide boundaries correctly and the vital points of the region and derive information depicting their evolution. Identifying landslides' extent and geometry can be achieved by mapping local signs on buildings and infrastructure if these are correctly mapped and predicted (Guerriero et al., 2021). Recent advances in satellite remote sensing have made it possible to identify, monitor, and map landslides occurring in urban and rural areas and carry out operations on vast areas. By developing Synthetic Aperture Radar (SAR) satellite imagery, the permanent scatter interferometric (PSI) has been implemented to prepare deformation on the Moio della Civitella urban settlement (Salerno province, Italy), whose whole territory is affected by several slow-moving landslides. According to all the sensitive feature of the study area which affected landslide (slope, elevation, curvature, aspect, etc.), graph convolution networks (GCNs) was used to predict the landslide impacts in this study area due to the data points of the study area are highly correlated with one another, and the core assumption of independence among instances in Machine Learning Algorithms (MLA), Artificial Neural Networks (ANN) failed to detect the interrelationship among data points. In the GCNs algorithm, multiple weight coefficients are assigned to each feature. These coefficients are then multiplied together, and a maximum matching strategy is then employed to enlarge the differences between features. The system also performs deep feature mining through GCNs and constructs the relationships between deep features. Therefore, a graph neural network was applied instead in this case study. Each data point is considered a node, and the GCNs task is to predict the landslide of new data points based on what they have learned from the labeled dataset (Liu et al., 2020). In the SAR imagery processing, GCNs achieved the best matching results, proving that this method is superior for predicting deformation.

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# Ongoing sea-level rise and vertical land movements in the Venetian Lagoon: the contribution of Glacial Isostatic Adjustment

Linsalata F.*[1], Melini D.[2] & Spada G.[1]

[1] Dipartimento di Fisica e Astronomia «Augusto Righi», Università di Bologna. [2] INGV, Roma.

*Corresponding author e-mail:* f.linsalata91@gmail.com

*Keywords:* glacial isostatic adjustment, sea-level change, vertical land movements.

The present-day vertical movements in the highly vulnerable Venetian Lagoon result from a number of simultaneously operating mechanisms, also including the Glacial Isostatic Adjustment (GIA) that arises from the interactions between the cryosphere, the solid Earth and the oceans. Although the GIA contribution in northern Adriatic Sea has been discussed several times (Lambeck & Purcell, 2005; Antonioli et al., 2008), significant uncertainties still exist, especially related with the extent and chronology of the Würm Alpine ice-sheet and the rheological profile of the mantle. Here, motivated by the recent publication of updated deglaciation chronologies for both the far and the near field late-Pleistocene ice sheets (Roy & Peltier, 2018; Seguinot et al., 2018), we produce up-to-date estimates of the GIA-induced rates of relative sea-level rise and vertical displacements in the Venetian Lagoon. Using these chronologies in conjunction of high-resolution GIA simulations, we find that GIA is responsible for a complex pattern of geodetic signals across the whole Po plain. However, the GIA rates obtained are generally of the order of a few fractions of millimetres per year, small compared to the signals observed at local tide gauges and at GPS sites close to the Venetian Lagoon. According to our results, GIA should be definitively regarded as a second-order mechanism among those responsible for present-day land movements and relative sea-level variations in the area of Venice.

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# Machine Learning for assessing the spatial probability of trend variations of InSAR-based ground deformations

Medici C.*, Confuorto P., Del Soldato M., Rosi A., Segoni S. & Casagli N.

Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* camilla.medici@unifi.it

*Keywords:* InSAR, machine learning, ground deformations.

The monitoring of geological hazards is a primary activity for land planning and management, due to the induced casualties and economic damage. The MTInSAR (Multi-Temporal Interferometry Synthetic Aperture Radar) techniques are consolidated methods for detecting slow-moving phenomena, e.g., landslides and subsidence.

The wide area coverage, the SAR images availability, and the short revisiting time of the Sentinel-1 constellation combined with the increasingly developed processing techniques, such as the SqueeSAR (Ferretti et al., 2011) foster the possibility of continuous monitoring services even at regional scale. Such ground motion service is currently ongoing over Tuscany region (Italy), and it enables to identify anomalies of movement of radar targets, i.e., trend variations (e.g., accelerations) in the time series of displacement (Raspini et al., 2018).

In this work, we propose an approach for assessing the occurrence probability of anomalies related to landslides and subsidence; this procedure is implemented by using a Machine Learning (ML) algorithm and tested on Tuscany region. The used ML algorithm is the Random Forest, whose input data are about 20,000 anomalies (about 7000 for landslides and 13,000 for subsidence) and ten variables, five of which are related to the morphological and geological setting of the study area and five to the radar system (Confuorto et al., 2022).

The methodology provides two maps of the spatial probability of occurrence of landslides and subsidence anomalies. The reliability of the maps has been verified through a validation procedure, i.e., using subsequent anomalies (2020-2021) to those used as input (2018-2020) and landslide and subsidence inventories. More than 70% of the control anomalies fall within the higher classes of probability of occurrence, both for landslides and for subsidence. Anomalies can be generated even in non-inventoried areas: almost 45% of the non-landslide pixels show high and very high probability of occurrence values, whereas a percentage of about 38% of non-subsidence pixels fall within well-known subsiding areas.

The resulting information, with periodical updates, can be a useful instrument for the authorities for comprehending the main driving forces that lead to terrain deformation anomalies, and for predicting geohazards.

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# Enhancing land subsidence awareness with InSAR data and Deep Transformers

Orlandi D.*[1], Pagli C.[2], Galatolo F.[1], Cimino M.G.C.A.[1] & Perilli N.[3]

[1] Dipartimento di Ingegneria dell'Informazione, Università di Pisa. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Dipartimento di Ingegneria Civile, Università di Pisa.

*Corresponding author e-mail:* diana.orlandi@phd.unipi.it

*Keywords:* InSAR, ground-water over-pumping, transformers.

Land subsidence is a phenomenon that can be caused by human activities such as ground-water over-pumping, with a significant and irreversible impact on ecosystems. Also, an inadequate exploitation of underground water resources can lead to irreversible aquifer compaction and the deceleration of its recharging time (Herrera-García et al., 2021).

Conventional techniques of land subsidence monitoring in areas interested by ground-water extraction use a spatially limited sampling via piezometric measurements, which is often restricted to a few sites. Moreover, in Italy, most of the data collected is owned by singular municipalities and it is not openly available. Thus, detailed information on a broad scale is often lacking. In the last few decades InSAR (Interferometric Synthetic Aperture Radar), has been established as a reliable method for monitoring the subsidence due to ground-water extraction. However, one of the main limitations of InSAR is signal loss of coherence, largely due to changes in the surface conditions between the acquisitions. InSAR-derived surface displacement time-series are often characterized by a low spatial density of point-like targets in non-urban areas with vegetation and cultivated fields. This can limit the capabilities of scientists to monitor the surface deformation. Many processing algorithms have been developed to maximize spatial coverage of InSAR. More recently, researchers started addressing the problem via machine learning based methods, which are well-known in the literature for the dominant performance, the low calibration cost, and the agnostic method.

In this work we present a novel method to overcome incoherence and enhance the spatial density of InSAR-derived surface velocity maps. The method is based on Transformers (Vaswani et al., 2017), a machine learning architecture with dominant performance, low calibration cost and agnostic method. Experimental studies have been carried out over Central and South of Italy, in the regions of Emilia-Romagna, Tuscany and Basilicata. We analyze four-years of surface subsidence (2017-2021) using Sentinel-1 data processed with P-SBAS (Parallel Small Baseline Subset) time-series analysis. Our preliminary results already allow us to observe the full extent of the deformation caused by water resources over-exploitation.

Herrera-García G., Ezquerro P., Tomás R., Béjar-Pizarro M., López-Vinielles J., Rossi M., Mateos R.M., CarreónFreyre D., Lambert J., Teatini P., Cabral-Cano E., Erkens G., Galloway D., Hung W.C., Kakar N., Sneed M., Tosi L., Wang H. & Ye S. (2021) - Mapping the global threat of land subsidence. Science, 371(6524), 34-36.

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# Slow slip events at Mt. Etna volcano

Palano M.*[1], Sparacino F.[1], Gambino P.[2], D'Agostino N.[3] & Calcaterra S.[2]

[1] INGV, Osservatorio Etneo, Catania. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] INGV, Osservatorio Nazionale Terremoti, Roma.

*Corresponding author e-mail:* mimmo.palano@ingv.it

*Keywords:* slow slip event, modelling, Etna volcano.

Mt. Etna is a basaltic Quaternary volcano located on the east coast of Sicily (South Italy) at the front of the Apennine-Maghrebian chain. The volcano developed over the last 500 ka over metamorphic and sedimentary rocks on its western and northern slopes and over Quaternary plastic clays. The different geomechanical properties of these rocks coupled with the inhomogeneous long-term updoming of the volcano have produced a complex basement topography dominated by a 17 km-wide horseshoe-shaped depression beneath the eastern flank. Such a complex basement topography gently dips in SE direction and would lead to the large-scale seaward motion of the eastern flank of Mt. Etna as clearly documented since the early 1980s. At the surface, the unstable sector is defined by a 25 km-wide horseshoe-shaped region, which encompass the sedimentary depression and is bounded by the "NE Rift - Pernicana fault" and by the "South Rift - Mascalucia-Tremestieri - Aci Trezza fault system", respectively on its NE and SE half. By inspecting the time-series of continuous GNSS stations covering the eastern flank of the volcano and spanning the 2006-2016 time interval we detected 11 slow slip events (SSE) with duration grossly ranging from 2 to 67 days. For each recognized SSE, we determine the amount of displacements by averaging site position in the 3 days preceding and following the event. Observed surface deformation for most of the detected slow slip events, concentrates on the south-eastern edge of the unstable flank while the slow slip events involving the north-eastern edge are less frequent. Such a pattern highlights the existence of two distinct families of events, involving two contiguous sectors of the unstable flank, which occasionally slip together in large slow slip events. The displacement fields were used to constrain isotropic half-space elastic inversion models. To determine the spatial distribution of slip for each SSE, we adopted planar source (divided in 15 by 15 squared patches) with a fixed dip of 10°. Achieved results highlight that, for SSEs occurring more frequently, the slip distribution concentrates with values up to 6 cm on the southeastern sector of the planar source, ~10 km off-shore. Regarding the SSEs involving the north-eastern edge of the unstable flank, the slip distribution on the modelled surface concentrates ~12 km off-shore beneath the Riposto Ridge where a ~16-km-long tectonic lineament with a N102° attitude would represent the off-shore prolongation of the most active splay of the Pernicana fault. Finally, equivalent seismic moments of slow slip events occurred in the last ten years (corresponding to magnitudes in the range 5.4-5.9) are larger than those associated to seismic events observed in the last 200 years, suggesting that most of the deformation affecting the eastern flank occurs aseismically.

# A methodology to detect ground deformation events through A-DInSAR Time Series statistical analysis

Pedretti L.*[1], Bordoni M.[1], Vivaldi V.[1], Figini S.[2], Parnigoni M.[3], Grossi A.[3], Lanteri L.[4], Tararbra M.[4], Negro N.[5] & Meisina C.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Scienze Politiche e Sociali, Università di Pavia. [3] RIDS-RES Institute for Data Science, Pavia. [4] Agenzia Regionale per la Protezione Ambientale, Torino. [5] Regione Piemonte, Torino.

*Corresponding author e-mail:* laura.pedretti01@universitadipavia.it

*Keywords:* A-DInSAR, time series, ground deformations.

A-DInSAR Time Series (TS) are powerful tools to identify areas with ground deformations and TS interpretation can help understand the relation between ground movement processes (slow-moving landslides) and triggering factors (snow, heavy rainfall). The availability of Sentinel-1 large datasets with high-temporal resolution of measures and long time period are useful to track the evolution of some ground deformations both in areas where satellite TS can be compared with in-situ monitoring systems, and in areas where in-situ instruments are absent or scarce. However, the analysis of satellite dataset covering large areas could be tricky and time-consuming. This works aims to illustrate a new statistical methodology to identify areas of potential interest for ground deformations by classifying satellite TS trend (uncorrelated, linear, non-linear); by identifying modification of the TS trend, i.e., breaks in non-linear time series related to events (heavy rainfall, the melting of snow); by furnishing the descriptive parameters (beginning and end of the break, length in days, cumulative displacement, the average rate of displacement) to characterize the magnitude and timing of changes in ground motion. The method for events identification of satellite TS is based on three variables: the number of observations, the minimum LOS velocity, and the cumulated displacement threshold. These thresholds should be calibrated according to geomorphological and geological processes and characteristics of a specific or regional site. The methodology has been tested on two Sentinel-1 datasets (2014-2020) available for Piemonte region, in northwestern Italy, an area very prone to slow-moving slope instabilities. The methodology applied to Sentinel-1 will provide a new tool for both back analysis and "near-real-time" monitoring of the territory thanks to the shorter revisiting time with respect to previous satellites. In addition, the methodology can be helpful not only as regards the characterization and mapping of the kinematics of the ground instabilities, but also in the assessment of hazard, risk and susceptibility, becoming a supporting and integrated tool with conventional methods for planning and management of the area. Indeed, any type of satellite datasets with low or high-temporal resolution of measures can be tested to identify any ground instability (slow-moving landslides, subsidence) at local or regional scale.

# Synergistic use of InSAR, GNSS and Leveling data to assess 20 years of onshore nd offshore subsidence along the Upper Adriatic coastal areas

Polcari M.*, Secreti V., Anderlini L., Albano M., Palano M., Serpelloni E., Stramondo S., Trasatti E. & Pezzo G.

INGV, Roma.

*Corresponding author e-mail:* marco.polcari@ingv.it

*Keywords:* InSAR, GNSS, leveling.

We propose a method of investigation based on the complementary use of InSAR data, GNSS measurements and Leveling surveys to assess the onshore and offshore ground subsidence along the coastline in the proximity of the city of Ravenna in the Upper Adriatic Sea (Italy) occurred from 2002 to 2018. This area is indeed hystorically affected by several natural and anthropogenic-induced subsidence phenomena such as soil compaction, groundwater pumping and hydrocarbons extraction. The synergistic use of independent remote sensing and in-situ geodetic data allows to characterise the ground displacement field both in space and time and also to provide a cross-validation of the measurements by comparing the different outcomes. Our dataset consists of i) SAR images provided by Envisat, Cosmo-SkyMed and Sentinel-1 missions, ii) GNSS measurements from continuous stations managed by public institutions, local authorities and private companies and iii) Leveling surveys managed by Eni S.p.A. Experimental results show an onshore and offshore subsidence pattern located in the proximity of Lido di Dante and Fiumi Uniti villages, and at the offshore platform few km far from the coastline, peaking at a linear velocity of about -1.5 cm/yr. It is detected in agreement by all the geodetic data by means the data cross-validation procedure thus shows providing a reliable assessment of the ongoing deformation along a time window of about 20 years. The outcomes highlight how the integration of different remote sensing and in situ geodetic techniques is successful to retrieve deformation history in time and space in complex areas, where different natural and anthropogenic sources concur to the overall deformation pattern.

# GNSS and absolute gravity measurements for a multi-disciplinary study of natural risks in Central Italy

Riguzzi F.[1], Berrino G.[2], Greco F.[3], Amantia A.[3], Iannarelli M.*[1], Massucci A.[1] & Ricciardi G.[2]

[1] INGV, Osservatorio Nazionale Terremoti, Roma. [2] INGV, Osservatorio Vesuviano, Napoli. [3] INGV, Osservatorio Etneo, Catania.

*Corresponding author e-mail:* mirko.iannarelli@ingv.it

*Keywords:* Central Italy, GNSS network, classical topographic survey.

Crustal deformations are widely studied in Italy by analyzing data from GNSS permanent networks. However, deformations can be generated by very different geophysical processes related to tectonics but also to fluid circulation and density variations. Therefore, it is very important to understand if the detected deformations are connected to gravity variations (Greco et al., 2021a).

Since 2018, INGV funded 3 projects aimed to detect ground deformations and gravity variations over different timescale in the area where the recent seismic events of L'Aquila (2009, Mw 6.3) and Amatrice-Norcia (2016, Mw 6.1 and 6.5) took place. The consequent static deformation field reached several centimetres and the modelled impact of such events could have modified the gravity field up to 170 μGal (Riguzzi et al., 2019). Furthermore, the medium-long-term gravity and ground deformation variations related to post-seismic relaxation are expected as consequence of vertical deformation of the Earth surface and/or of the internal boundaries separating layers at depth with different densities. In addition, the L'Aquila area is affected by deformations induced by ground water level changes in the aquifers (Devoti et al., 2018). Therefore, a multidisciplinary approach carrying out joint measurements of deformation and gravity is fundamental to understand the role of each geophysical process. To this aim, a network of 3 (Terni, Popoli, Sant'Angelo Romano) new non-permanent GNSS stations was realized outside the buildings hosting the absolute gravity stations (Greco et al., 2021b). At L'Aquila, a permanent GNSS station managed by the Italian Space Agency (AQUI) is continuously working on the rooftop terrace of the Science Faculty, and positioned vertically with respect to the gravimetric station (AQUIg), which is located 4 floors below (Fortunato et al., 2020). Since 4 absolute gravimetric sites are located indoor, the precise coordinates of the gravity benchmark have been obtained by classical topographic surveys, connecting the indoor site to the outdoor GNSS reference point.

In the poster we describe the procedure and results followed to achieve the coordinates of both the GNSS and the absolute gravimetric sites. Furthermore, we also present the results over the short and the medium-long-term obtained by repetitive combined GNSS and integrated absolute and relative gravity measurements.

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Greco F., Riguzzi F. & Berrino G. (2021a) - Insights into Seismogenetic Areas in Central Italy from Combined Absolute Gravity and GNSS Measurements. Remote Sensing, 13, 4649. https://doi.org/10.3390/rs13224649.

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Riguzzi F., Tan H. & Shen C. (2019) - Surface volume and gravity changes due to significant earthquakes occurred in central Italy from 2009 to 2016. Int. J. Earth Sci., 108, 2047-2056.

# Risk evaluation in critical sites of the metropolitan area of Rome: geophysical-geotechnical characterization of deformation phenomena

Rotella G.*[1], De Ritis R.[2], Argentieri A.[1], Calderoni G.[2], Fabiani M.[1], Marra F.[2], Stefanelli P.[2], Tolomei C.[2], Vitali P.[1], Chiappini M.[2] & Doglioni C.[2]

[1] Città metropolitana di Roma Capitale - Dipartimento IV Servizio 2 "Geologico, difesa del suolo - Rischio idraulico e territoriale", Roma. [2] INGV, Roma.

*Corresponding author e-mail:* g.rotella@cittametropolitanaroma.it

*Keywords:* sinkhole-landslide, InSAR analysis, geophysical prospecting.

The present work concerns the geophysical-geotechnical characterization of deformation phenomena occurring in the metropolitan territory of Rome (Italy). Two sites affected by sinkholes and landslides were investigated within a collaboration agreement between "Città metropolitana Roma Capitale" (CMRC) and "Istituto Nazionale di Geofisica e Vulcanologia" of Rome (INGV). The first, the "Lago Puzzo", is a sinkhole-lake located near Capena (a village placed 30 km North of Rome). In October 2020 a shallow hypocentre and low intensity earthquake occurred in this area. The second site, San Vito Romano (a village placed 50 km East of Rome) shows widespread slow-moving slope movements affecting both the urbanized area and its crossing provincial roads. The two sites are located close to important infrastructures, such as a high-speed railway line, a large overhead power line, and intensely urbanized areas. The investigation, based on an interdisciplinary approach, is aimed to evaluate the two sites geo-structural model and to decipher the evolutionary stages of the respective ongoing phenomena. The remote-detected data (InSAR) have allowed to localize the phenomena and quantify their movements. The seismological spectral analysis techniques have characterized the recent seismic event occurring in the Capena area and the geophysical investigations (e.g., ERT, magnetic and gravimetric surveying) have illuminated the crustal sector of the two sites. The results are relevant for the understanding the deformation mechanisms, for the predicting future evolutions scenarios and, possibly, for the conceptualization of specific time-lapse monitoring systems. Thus, we developed the first fundamental steps towards the definition of the risk mitigation paradigm, that are: detection, mapping and modelling.

# Tectonic and non-tectonic transient deformation in Long Valley Caldera, California, at multiple temporal and spatial scales

Silverii F.*[1], Montgomery-Brown E.K.[2], Pulvirenti F.S.[3], Borsa A.A.[4], Barbour A.J.[5] & Neely W.R.[6]

[1] INGV, Osservatorio Nazionale Terremoti, Roma. [2] U.S. Geological Survey, Cascades Volcano Observatory, Vancouver, WA (USA). [3] Nanjing University of Information Science and Technology, Nanjing (China). [4] Scripps institution of Oceanography, IGPP, San Diego, CA (USA). [5] U.S. Geological Survey, Volcano Science Center, Menlo Park, CA (USA). [6] Department of Geophysics, Stanford University, Stanford, CA (USA).

*Corresponding author e-mail:* francesca.silverii@ingv.it

*Keywords:* GNSS, Long Valley Caldera, transient deformation.

Located at the eastern edge of Sierra Nevada range (SNR), Long Valley Caldera (LVC), California, experiences unrest episodes characterized by increased deformation and earthquake swarms. Furthermore, LVC is affected by hydrological deformation at different spatiotemporal scales controlled by the precipitation falling on SNR. Deformation measurements, such as from Global Navigation Satellite System (GNSS), therefore record superimposed effects of tectonic and non-tectonic processes.

We analyze the deformation at LVC by combining GNSS and hydrological records. Vertical and horizontal components of GNSS displacement show a clear correlation with hydrological trends at both multiyear and seasonal time scales. At the seasonal timescale, deformation is largely controlled by the response to hydrological surface loading. However, several GNSS sites in the south/south-western rim of LVC show anomalous horizontal deformation. This is also where most of the recharging of the LVC hydrothermal system occurs and runoff-induced seismicity was identified. We show that the signal at these sites reflects poroelastic deformation in response to surface water recharge into SNR slopes.

In 2011, the latest inflation episode began at LVC, while Western US was affected by highly variable climatic conditions with alternations of high precipitation and severe drought periods. We show the effect of this multiyear hydrological trend on the GNSS records in LVC. We apply a decomposition method to isolate inflation-related signals from the effect of this hydrological forcing. We finally invert inflation signals using a 3D numerical model to study the evolution of this inflation episode and assess the influence of topography and heterogeneous material properties.

# Copernicus and ground motion: the European Ground Motion Service

Solari L.*[1-2] & Crosetto M.[1]

[1] Centre Tecnològic de Telecomunicacions de Catalunya, Barcelona (Spain). [2] European Environment Agency, Copenhagen (Denmark).

*Corresponding author e-mail:* lorenzo.solari@cttc.cat

*Keywords:* Copernicus, satellite interferometry, ground motion.

Copernicus is the European Union's Earth observation programme and it offers multiple information services ranging from satellite imagery and derived data to in-situ non-spatial data. Copernicus relies on six thematic services to design, manage and distribute a wide spectrum of products. Among the thematic services, the Copernicus Land Monitoring Service (CLMS), operated under the responsibility of the European Environment Agency, provides information about land surface and its bio-geophysical phenomena.

The newest addition to the CLMS portfolio is the European Ground Motion Service (EGMS). The EGMS provides consistent, regular, standardised, harmonised and reliable information regarding natural and anthropogenic ground motion over the Copernicus Participating States and across national borders, with millimetre accuracy. The EGMS is based on the multi-temporal interferometric analysis of Sentinel-1 radar images at full resolution. This technique allows identifying reliable measurement points for which ground motion velocity values and time series of displacement are extracted. The EGMS makes available to users three types of products: (1) Basic, line of sight (LOS) velocity maps in ascending and descending orbits referred to a local reference point; (ii) Calibrated, LOS velocity maps calibrated with a velocity model derived from thousands of global navigation satellite systems time series. In this way, the velocity values are no longer relative to a local reference point and are considered as absolute; (3) Ortho, horizontal (east-west) and vertical (up-down) components of motion extracted from the Calibrated product. The Basic and Ortho products are generated at full resolution whereas the Ortho product is based on a 100 by 100 m resampling grid. All the products are internally quality controlled against service requirements and will go through a validation process performed by a consortium independent from the data production. Users can access all the EGMS products via a data viewer and a data downloader under a free- and open-for-all policy.

The EGMS represents a baseline for ground motion applications at continental, national and local level. It is especially important for the geological and geohazard communities. EGMS data can provide information useful for the identification of anthropogenic or natural subsidence, landslides, volcanic activity and much more. It establishes a baseline for studies dedicated to localised deformation affecting buildings and infrastructure in general. This presentation will give an overview on the technical characteristics of the EGMS and will propose some use cases interpreted under geoscientific aspects.

# A useful tool for the statistical analysis of InSAR datasets

Sparacino F.*[1] & Pezzo G.[2]

[1] INGV, Catania. [2] INGV, Osservatorio Nazionale Terremoti, Roma.

*Corresponding author e-mail:* federica.sparacino@ingv.it

*Keywords:* subsidence, SAR, Matlab-based tool.

Land subsidence represents the main response to deformations induced by multiple natural and anthropic phenomena (i.e., solid and fluid extraction, soil consolidation, aquifer compaction, load-induced compaction, etc.) which take place at different spatial-temporal scales (Bonì et al., 2017). The impacts of land subsidence can be infrastructural, economic, environmental, and social, and it enhances the risk of floods, affecting the human life and activities. Several localities are affected by land subsidence occurring at high rate (Fernandez et al., 2018).

Satellite Synthetic Aperture Radar (SAR) data are used for recent advanced ground deformation investigations to analyse the mechanisms of land subsidence around the world. In particular, these studies use advanced differential interferometric synthetic aperture radar (A-DInSAR) techniques, which are based on the processing of multiple interferograms derived from a large set (at least 20 images) of SAR images. These techniques allow the retrieval of displacement time series of measuring points over wide areas at millimetre resolution and have already been successfully applied to monitoring the evolution of different processes (Bonì et al., 2017).

To rapidly and automatically exploit a generic InSAR dataset distinguishing main components forming the InSAR time series, we developed a Matlab-based tool, which allows to provide information about linear, non-linear, cyclic and/or seasonal components in time series by using frequency analysis. Starting from a generic InSAR dataset, this tool will generate derived datasets as representing the linear, non-linear, and cyclic components. Achieved results are provided by the tool as ascii, together with associated statistical analysis and graphical outputs for time and space visualization. Here we provide examples of SAR dataset exploitation. Such a tool is general and could be applied to several areas of interest. It is a very useful tool because allows the user to have a complete and detailed statistical analysis of the dataset in a short relative time.

Bonì R., Meisina C., Cigna F., Herrera G., Notti D., Bricker S., McCormack H., Tomàs R., Béjar-Pizarro M., Mulas J. & Ezquerro P. (2017) - Exploitation of satellite A-DInSAR time series for detection, characterization and modelling of land subsidence. Geosciences, 7(2), 25.

Fernandez J., Prieto J.F., Escayo J., Camacho A.G., Luzón F., Tiampo K.F., Palano M., Abajo T., Pérez E., Velasco J., Herrero T., Bru G., Molina I., Lòpez J., Rodrìguez-Velasco G., Gòmez I. & Mallorquì J.J. (2018) - Modeling the two- and three-dimensional displacement field in Lorca, Spain, subsidence and the global implications. Scientific reports, 8, 1-14.

# A recent seismic coupling estimation for the Aegean - Anatolian region

Sparacino F.[1], Galuzzi B.G.[2], Palano M.*[1], Segou M.[3] & Chiarabba C.[4]

[1] INGV, Osservatorio Etneo, Catania. [2] Dipartimento di Biotecnologie e Bioscienze, Università di Milano-Bicocca.
[3] British Geological Survey, The Lyell Center, Edinburgh (UK). [4] INGV, Osservatorio Nazionale Terremoti, Roma.

*Corresponding author e-mail:* mimmo.palano@ingv.it

*Keywords:* seismic coupling, seismology, geodesy.

We provide an improved picture of the seismic coupling for the Aegean-Anatolian region by taking advantage of extensive seismic and geodetic datasets. Our approach estimate moment-rates and seismic coupling on 2° x 2° square cells with a 75% overlap and does not require an a priori zonation.

To compute input parameters for the coupling estimation, such as the maximum expected magnitude, the seismogenic thickness and the coefficients of the frequency-magnitude distribution relation we compiled a set of historical and instrumental catalogs from existing seismicity records as well as an extensive combination of recent GNSS velocities integrated with recent literature solutions. Finally, the seismic coupling estimation enables characterizing the crustal deformation modality (seismic versus aseismic), as well as identifying potential seismic cycle gaps over the entire region, thereby providing additional constraints on modern seismic hazard estimates. In particular, seismic coupling is low (<35%) or intermediate (35% - 70%) in most of the study area, while the Karliova triple junction, a N-S-oriented belt along the boundary between western and central Anatolia, and the southeastern Peloponnese are fully coupled, suggesting a full seismic release of the measured deformation budget. Intermediate values of seismic coupling are observed for the eastern and central segments of the Northern and Eastern Anatolian Fault zones, where however the time period since the last large magnitude earthquakes clearly raises the possibility of impending earthquakes. Intermediate values of seismic coupling are also observed for part of the Hellenic volcanic arc, the Kefalonia Transform Fault and the Corinth gulf active faults. Here, considering the available historical records, these intermediate coupling values indicate either significant aseismic deformation or catalog incompleteness. A broad seismic gap is evidenced along the Hellenic subduction zone, because of the reduced coupling and the absence of ~M8 earthquakes in the last 700 years, at least. We conclude that in most of the central Aegean Sea aseismic deformation prevails as suggested by the small value of coupling and the modest seismic release over the last millennium.

# Volcanic and Seismic source Modelling (VSM) - An open tool for geodetic data modelling

Trasatti E.*

INGV, Osservatorio Nazionale Terremoti, Roma.

*Corresponding author e-mail:* elisa.trasatti@ingv.it

*Keywords:* geodetic data inversion, geohazard, open science.

Natural processes and anthropogenic activities often generate changes in the stress state of the crust, and, consequently, measurable surface deformation. Volcanic activity produces surface displacements as a result of phenomena including magma recharge/deployment and migration, and fluid flow. The accurate measurement of surface deformation is one of the most relevant parameters to measure tectonic stress accumulation and for studying the seismic cycle. Improved monitoring capabilities also capture surface deformations related to coastal erosion and its connection to climate change, landslides and deep seated gravitational slopes, and other hydrogeological hazards. In addition, anthropogenic activity such as mining and water pumping cause measurable soil displacement.

Ground deformations are measured by space and terrestrial techniques, reaching sub-millimetric accuracy. Synthetic Aperture Radar (SAR) satellites have been quickly developing in the last decades. GNSS data allows to map nearly 3D deformation patterns, but often the network consists of few benchmarks. The joint use of SAR and GPS data compensate the intrinsic limitations of each technique. Levelling measures the geodetic height of a benchmark. Borehole dilatometers and clinometers provide derivative measurements of the surface displacements.

Theoretical models of deformation sources are commonly employed to investigate the surface displacements observed, for example, in volcanic areas or related to a seismic event. A volcanic source can be represented by a confined part of crust with a certain shape inflating/deflating because of a change in the internal magma/gas pressure. The static seismic source is ideally represented by a tabular discontinuity in the crust undergoing relative movement of both sides. Furthermore, gas reservoir exploitation, water pumping and soil consolidation, can be represented using the same models.

Volcanic and Seismic source Modelling (VSM) is an open source Python tool to model ground deformation detected by satellite and terrestrial geodetic techniques. It allows the user to choose one or more geometrical sources as forward model among sphere, spheroid, ellipsoid, fault, and sill. It supports geodetic from several techniques: interferometric SAR, GNSS, levelling, Electro-optical Distance Measuring, tiltmeters and strainmeters. Two sampling algorithms are available, one is a global optimization algorithm based on the Voronoi cells and the second follows a probabilistic approach to parameters estimation based on the Bayes theorem. VSM can be executed as Python script, in Jupyter Notebook environments or by its Graphical User Interface. Its broad applications range from high level research to teaching, from single studies to near real-time hazard estimates. Potential users range from early career scientists to experts. It is freely available on GitHub (https://github.com/EliTras/VSM). In this contribution I show the functionalities of VSM and test cases.

# S10.

# Evolution of collisional orogens in space and time: the Alpine-Himalayan system in 4 dimensions


*Conveners and Chairpersons*

*Chiara Montomoli (University of Torino)*

*Salvatore Iaccarino (University of Torino)*

*Jean-Luc Epard (University of Lausanne, Switzerland)*

*Paola Manzotti (Stockholm University, Sweden)*

# A new 3D structural model of the North-Western Alps: the Aosta Valley case study (Italy)

Arienti G.*[1], Bistacchi A.[1], Dal Piaz G.V.[2], Dal Piaz G.[3], Monopoli B.[3] & Bertolo D.[4]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Accademia delle Scienze di Torino, Torino. [3] Land Technology & Services s.r.l., Treviso. [4] Regione Autonoma Valle d'Aosta, Dipartimento Programmazione, Risorse Idriche e Territorio, Aosta.

*Corresponding author e-mail:* g.arienti5@campus.unimib.it

*Keywords:* North-western Alps, Aosta Valley, 3D structural model.

The North-Western Alps are one of the best-known orogenic playgrounds worldwide, exposing the stack of the Western Austroalpine, Penninic and Helvetic metamorphic nappes, separated by one or more ophiolitic sutures. Despite having been widely studied in the last two centuries, the reference 3D model is still the Argand's (1911) block diagram, and no updated model that extensively represents the complexity of both ductile and brittle structures exists.

This contribution presents the preliminary results of a new 3D structural model that is being built in the context of the ongoing Italian-Swiss Interreg RESERVAQUA project. The model covers a large area (1300 $km^2$) and runs along the Italian-Swiss boundary ridge, from the Helvetic Mont Blanc massif to the Penninic Monte Rosa nappe.

The new 3D model is based on a high-resolution geological database, as the area is mapped at 1:5000-1:10000 with a dense set of structural stations. The modelling workflow consists of a first step of structural conceptualization in vertical cross-sections, and a second phase of interpolation with advanced implicit algorithms that operate taking advantage of the abundance of structural data, used as constraints.

In this complex metamorphic setting, where thickness variations occur frequently due to ductile and brittle deformative processes (e.g., ductile shear, isoclinal folding, normal faulting), the model geological legend needs to be conceived as a conceptualization of surfaces organized in a hierarchical structure. First order surfaces separate different Alpine domains (e.g., Austroalpine, Penninic); second order surfaces divide different nappes (e.g., Combin and Zermatt-Saas); finally, lower order surfaces are associated to tectono-metamorphic boundaries within single nappes (e.g., Arolla-Valpelline in the Dent Blanche).

An important outcome of the 3D model is the clear distinction between sections of the orogenic wedge that are characterized by different tectonic styles, namely (i) an internal Austroalpine-Upper Penninic domain with sub-horizontal nappe boundaries, blueschist to eclogitic peak metamorphism and diffuse collisional greenschist re-equilibration, and both Oligocene and Miocene brittle normal faults, (ii) the intermediate domain represented by the Grand St-Bernard nappe system, with blueschist peak metamorphism, diffuse greenschist re-equilibration and mainly Miocene brittle faults, and (iii) an external system with low-T greenschist peak metamorphism, foliations consistently SE-dipping, relatively young semi-brittle thrusts and no Miocene or Oligocene normal faults.

In addition to the strictly scientific interest, an updated 3D structural model is essential for many applications, such as those related to circulation and storage of deep water resources hosted in the bedrock, including geothermal fluids. We feel confident that this kind of application would popularize the importance of fundamental studies in tectonics and structural geology in the Alpine belt.

# HP/UHP rocks in the Western Alps: acquiring new (robust) data, constraining old (fashionable) models

Ballèvre M.*

Géosciences Rennes, Université de Rennes (France).

*Corresponding author e-mail:* michel.ballevre@univ-rennes1.fr

*Keywords:* Western Alps, exhumation mechanisms, UHP.

The potential exhumation mechanisms of high-pressure rocks in subduction/collision belts is a long-standing question, that may be answered combining a wealth of sophisticated techniques. Geological mapping, combined with geophysical investigations, reveal the first-order geometrical features of the stacked units. In the Western Alps, the nappe stack has been 'ordered' by E. Argand and co-workers since more than one century. Two major additions to the proposed geometry include (i) the recognition of the gravimetric (positive) anomaly associated to the Ivrea Geophysical Body, thought to reflect the presence of the Adriatic mantle at low depth, and (ii) the investigation of discontinuities in terms of P-T conditions and age between stacked units. The first point is of major importance for understanding the crustal-scale reworking of the nappe stack (backfolding/backthrusting) during Adria indentation, while the second offers clues to the succession of events at depth before collision.

HP/UHP rocks in oceanic and continental rocks have in common four characteristics:

- They reveal a gradient of P-T conditions consistent with low to very low geothermal gradients (5 to 10°C/km) along the former subduction zone.
- The 'subduction gradient' has been destroyed during exhumation. The latter is best interpreted as due to the upward displacement of an extrusion wedge, bounded by (north-westward) propagating ductile thrusts at the base and (south-eastward) 'normal shear sense' ductile faults at the top.
- Exhumation of HP/UHP rocks has taken place shortly after peak burial, i.e., before collision, with the implication that the processes acting during exhumation may have been severely overprinted during collision.
- Erosion only contributes significantly to the exhumation during the final stages of the history, when collision is proceeding.

New discoveries of UHP rocks (Manzotti et al., this meeting) and progress in P-T conditions, age and timing of HP/UHP metamorphism (Nosenzo et al., this meeting) will be used to constrain a geometrical-kinematical model. Strengths and weaknesses of the model will be discussed.

# Tracking a tectono-metamorphic discontinuity within the Greater Himalaya Sequence, NW Himalaya: implications for the orogen metamorphic core assembly and exhumation

Benetti B., Montomoli C.*, Carosi R. & Iaccarino S.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* beatrizyuri.benettisilva@unito.it

*Keywords:* Himalaya Shear zone, High Himalayan Discontinuity, GHS tectonic and metamorphism.

Abrupt modifications of metamorphic, deformation and time path within collisional belts are known as tectono-metamorphic discontinuities. In the Himalaya Orogen, within an exhumed mid-crust mega tectonic unit, the Greater Himalayan Sequence (GHS) a tectonic-metamorphic discontinuity referred as High Himalayan Discontinuity (HHD) has been mapped in the central and eastern portions of the belt. In order to assess the HHD presence in the NW portion of the belt, a multidisciplinary approach comprising fieldwork, microstructural analyses, metamorphic petrology, and *in situ* monazite geochronology was addressed along the GHS in the Alaknanda valley (Garhwal Himalaya, NW India). This applied integrative methodology allowed us to reveal the occurrence of a newly high-temperature ductile shear zone, the Badrinath shear zone (BSZ), within the GHS (Benetti et al., 2021).

The Badrinath mylonite affects sillimanite-bearing migmatitic gneiss from the Upper GHS ($GHS_U$) and displays top-to-the-south thrust-sense of shear. Two main stages of BSZ development were constrained: (1) the pre-mylonitic stage took place during prograde metamorphic path and reached conditions of 700-720°C and 10 kbar during the time interval of 34 and 23 Ma, with incipient partial melting, followed by (2) the mylonitic stage, in which the BSZ underwent nearly-isothermal decompression triggered by the shear activity between 23-19 Ma. Moreover, the rocks from the BSZ footwall, the lower part of GHS (GHSL) experienced metamorphic conditions of ca. 660-700°C and ca. 10-11 kbar followed by decompression nearly ~3 Ma after the BSZ.

The occurrence of an HT shear zone, the contrast in exhumation onset (ca. 3 Ma) and P-T paths between the $GHS_L$ and $GHS_U$, set up a tectono-metamorphic discontinuity inside the GHS in the study area. The BSZ features match with the HHD geological features and represent its prolongation in Garhwal Himalaya, India. The BSZ is the first reported HHD branch in NW Himalaya, corroborating with regional extent of the HHD accomplishing an important role during the GHS exhumation. Such findings support that the deformation was driven by high-temperature shear zones during progressive mid-crust exhumation from top to bottom in the GHS, as highlighted by the model "in-sequence shearing".

Benetti B., Montomoli C., Iaccarino S., Langone A. & Carosi R. (2021) - Mapping tectono-metamorphic discontinuities in orogenic belts: implications for mid-crust exhumation in NW Himalaya. Lithos, 392-393, 106129.

# Topological analysis reveals 1st order kinematics and relative chronology of major tectonic boundaries in the NW Alps

Bistacchi A.*[1], Dal Piaz G.V.[2], Arienti G.[1], Dal Piaz G.[3], Monopoli B.[3] & Bertolo D.[4]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Accademia delle Scienze di Torino. [3] Land Technology & Services s.r.l., Treviso. [4] Regione Autonoma Valle d'Aosta, Dipartimento Programmazione, Risorse Idriche e Territorio, Aosta.

*Corresponding author e-mail:* andrea.bistacchi@unimib.it

*Keywords:* NW Alps, topology.

The analysis of topological relationships allows retrieving fundamental spatial relationships in a set of objects, which are not affected by changes in reference frame, rotation and stretching. In structural geology and tectonics, this kind of analysis has been used to study the distribution of plates on a sphere and the kinematics of their boundaries, and more recently to evaluate the consistency of 3D structural models. With this contribution we discuss the first results of a topological study of the tectonic boundaries of the Austroalpine-Penninic nappe stack in the NW Alps.

This study begun as a way to assess the consistency of a large 3D geological model covering a region of ca. 1300 km$^2$ in Italy and Switzerland, from the Aosta to the Rhone Valleys and from the Mont Blanc to the Monte Rosa (Interreg project ReservAqua). During this project we reconstructed a hierarchical graph (i.e., a discrete topological model) of the boundaries of large tectonic domains (e.g., Austroalpine), nappes (e.g., Dent Blanche), and of major shear zones within the nappes (e.g., Roisan-Cignana Shear Zone), and we populated the graph with properties such as peak metamorphic conditions, age of metamorphism, kinematics, etc.

A common experience when switching from 2D to 3D interpretation and modelling, is obtaining new and unexpected additional outcomes. This was particularly true in this case, and the topological study, in addition to providing constraints for the 3D geomodel, yielded very interesting and sometimes new and surprising results on the relative chronology and kinematics of tectonic boundaries that have been discussed for more than 100 years.

# The Nidar Ophiolite (Ladakh Himalayas, India): construction of fore-arc crust and incipient arc magmatism in the Neo-Tethys

Buchs N., Epard J.-L.* & Müntener O.

Institute of Earth Sciences, University of Lausanne (Switzerland).

*Corresponding author e-mail:* Jean-Luc.Epard@unil.ch

*Keywords:* Himalayas, ophiolite, fore-arc.

The Nidar Ophiolite is a suprasubduction zone ophiolite exposed in the Indus suture zone in the Western Himalayas in Eastern Ladakh (India). Recent detailed mapping and lithostratigraphy of the Nidar Ophiolite (Buchs & Epard, 2019) revealed a complex internal structure and lithologic relationships of the ophiolite. The Nidar Ophiolite consists of an upper mantle unit dominated by harzburgites and dunites, overlain by a crustal sequence composed of layered and isotropic gabbros covered by pillow lavas and lava flows. This crustal sequence represents the compositional build-up of the crust in the Nidar Ophiolite with geochemical signatures of fore-arc basalts. The gabbros are intruded by large intrusive complexes made of wehrlites, olivine-gabbros, gabbronorite, hornblende gabbros, minor plagiogranites and porphyritic subvolcanic basalts to andesites, whereas pillow lavas are intruded by andesitic to dacitic dikes. These intrusions and dikes are related to incipient, hydrous arc magmatism. The fore arc crustal sequence is covered by lower Cretaceous radiolarites followed by volcanosedimentary rocks deposited in a back-arc basin north of the Nidar Ophiolite and south of the Eurasian margin. Bulk rock geochemical data from the build-up and intrusive complexes of the Nidar ophiolite display LILE enrichment relative to REE and HFSE, Nb-Ta negative anomalies, low Ti/V and relatively high Th/Nb ratios, suggesting formation of the magmatic crust in a suprasubduction zone context. Liquids calculated from clinopyroxenes of layered gabbros are similar to the volcanic rocks and indicate two different liquid lines of descent, starting with depleted fore-arc basaltic compositions to construct fore arc crust, followed by more typical arc magmas intruding into the fore-arc crust. New zircon U-Pb dates of four plagiogranites constrain the formation of the ultramafic to felsic intrusive complexes of the Nidar Ophiolite from 132.6 ±1.6 Ma to 129.7 ±1.6 Ma. In-situ Hf isotopic determinations of the dated zircons range from +13 to +15, corresponding to a juvenile mantle reservoir with limited input from subducted sediments.

These findings suggest that the Nidar Ophiolite records the magmatic build-up of nascent intra-oceanic island arc crust related to the Lower Cretaceous subduction of oceanic crust. This scenario is consistent with other Himalayan ophiolites of the Indus-Yarlung-Tsangpo suture zone. The preservation of fore-arc crust with juvenile isotopic signatures over an age range of 132 to 123 Ma and laterally extending over more than 1500 km suggests a major phase of fore-arc extension and arc migration, related to slab retreat, ~10 Ma earlier that the initiation of the Ladakh-Kohistan magmatic arc.

Buchs N. & Epard J.-L. (2019) - Geology of the eastern part of the Tso Morari nappe, the Nidar Ophiolite and the surrounding tectonic units, NW, Himalaya, India. Journal of Maps, 15(2), 38-48. https://doi.org/10.1080/17445647.2018.1541196.

# New geological evidence of the Houiller Briançonnaise Zone from the exploratory tunnel of Saint Martin La Porte (Tunnel Euroalpin Lyon Turin)

Calorio M.*[1], Capurso N.[1], Toso A.[1], Botti E.[1], Ceretto A.[1], Garattoni A.[1], Del Grosso F.[1], Marcelli I.[1], Tira M.[1], Paire U.[1], Serrano B.[2] & Sénémaud J.[2]

[1] Alpina S.p.A., Milano. [2] TELT S.A.S., Torino.

*Corresponding author e-mail:* matteo.calorio@alpina-spa.it

*Keywords:* tunnelling, Houiller Front, faults.

The Saint Martin La Porte exploratory adit, excavated along the axis of the Tunnel Euroalpin Lyon Turin, has the purpose of checking and improving the available geological and geo-mechanical models, understanding the behaviour of Carboniferous rock mass with high overburden in squeezing conditions.

The complexity of the Houiller Briançonnais Zone is confirmed by different geological failures (faults, shear zones, etc.) encountered during the excavation between Pk 10+000 and 12+000 of the south tube. In this work these failures are described from a geological and geomechanical point of view. A final reliable geo-structural model is presented with all the data acquired during the excavation and underground boreholes.

The adit is crossing the contact between the carbonate sediments of the Subbriançonnais Zone (SBZ) to the west and the schisto-metasandstone with coal layers of the Houiller Briançonnais Zone (HBZ) to the east. This contact is represented by the Houiller Front (HF). The most recent deformation phases of the HF (at the scale of the last 5-15 million years) are characterized by an extensional component for normal fault opposed to the oldest movements, as highlighted by the zircon/apatite fission track and focal mechanisms of recent earthquakes (Bertrand et al., 1996).

Bertand J.M., Ailleres L., Gasquet D. & Macaudiére J. (1996) - The Pennine Front in Savoie (Western Alps), a review and new interpretations from the Zone Houillère Briançonnaise. Eclogae Geol. Helv., 89, 297-320.

# Assembly and exhumation of GHS driven by the in-sequence shearing in the Annapurna Range, central-western Nepal

Carano G.*, Montomoli C., Iaccarino S. & Carosi R.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* giorgia.carano@edu.unito.it

*Keywords:* Himalayan Chain, quartz c-axis fabric analysis, meso and microstructural analysis.

In the Annapurna Range (central-western Nepal) the metamorphic core of the Himalaya, the Greater Himalayan Sequence (GHS), crops out between the low-grade rocks of the Tethyan Himalayan Sequence (THS) to the north and the medium- to low-grade rocks of the Lesser Himalayan Sequence (LHS) to the south. Two of the main tectonic discontinuities of the Himalaya separate these Units: the upper South Tibetan Detachment System (STDS) with normal kinematics and the lower Main Central Thrust Zone (MCTZ) with reverse kinematics. In the Modi Khola area other intra-GHS discontinuities are documented (Hodges et al., 1996, Corrie & Kohn, 2011; Shrestha et al., 2020). From the top to the bottom they are: the Modi Khola Shear Zone (MKSZ; 22.5-18.5 Ma; U-Pb on Mnz, Zr and Xtm), the Sinuwa Thrust (ST; 27-23 Ma; U-Th-Pb on Mnz and Lu-Hf on Grt), the Bhanuwa Fault (BT; 23-19 Ma; U-Th-Pb on Mnz, Lu-Hf on Grt). Currently, the BT and the ST were identified only on the base of petrochronological arguments and their kinematics is still debated.

Meso and microscale observations revealed, for the ST, top–to–the–S kinematic indicators. The asymmetry of the quartz c-axis fabric from one sample collected close to the BT, support a top–to–the–S, thrust-sense, kinematics. Quartz fabric analysis was also performed on three samples collected within the MCTZ. The asymmetry of the pole figures indicates a top–to–the–S sense of shear. The quartz fabric opening angle thermometer revealed deformation temperatures of ~525–618°C for the MCTZ and of ~635°C for the BT.

Combining the results with previous literature data, it has been possible to propose a tectono-kinematic model for the exhumation of the GHS. The ST, the BT and the MCTZ are active at different times and at progressively lower structural levels. This is consistent with the in-sequence shearing model documented for other sectors of the Chain (Montomoli et al., 2015; Carosi et al., 2018).

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Hodges K.V., Parrish R.R. & Searle M.P. (1996) - Tectonic evolution of the central Annapurna Range, Nepalese Himalayas. Tectonics, 15(6), 1264-1291.

Montomoli C., Carosi R. & Iaccarino S. (2015) - Tectonometamorphic discontinuities in the Greater Himalayan Sequence: a local or a regional feature? Geol. Soc. Spec. Publ., 412(1), 25-41.

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# Shearing migration in the North Himalayan Gneiss Domes (SE Tibet): a progressive shift of extension from the Cuonadong to the Yalaxiangbo domes

Carosi R.*[1], Chen J.[1] & Cao H.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Institute of Geology, Chinese Academy of Geological Sciences, Beijing (China).

*Corresponding author e-mail:* rodolfo.carosi@unito.it

*Keywords:* Himalaya, gneiss domes, South tibetan Detachment System.

The Cuonadong and the Yalaxiangbo gneiss domes are two North Himalayan Gneiss Domes (NHGD), in eastern Himalaya. They show similar tectonic units separated by an upper ductile/brittle and a lower ductile detachment, with a top-to-the NE sense of shear, linked to the dvelopment of the South Tibetan Detachment System. The sense of shear is the same on the southern and northern limbs of the domes. The upper tectonic unit, above the upper ductile/brittle detachment, includes unmetamorphosed to low-grade metamorphic Triassic-Lower Cretaceous slate and metapsammite of the Tethyan Himalayan Sequence. The middle tectonic unit, sandwiched between the upper and lower detachments, consists of mylonitic granite, staurolite-garnet-two mica schist and biotite-plagioclase gneiss affected by the ductile top-to-the north extensional shear of the lower detachment. The lower tectonic unit consists of mylonitic gneiss, leucogranite plutons, dikes, and sills.

By (LASS-ICP-MS) in situ U-(Th)-Pb monazite petrochronology from sheared samples, we constrained the activity of the lower detachment at ca. 19-18 Ma and the shearing along the upper detachment later than ca. 16-15 Ma (Chen et al., 2018) in the Yalaxiangbo dome. The detachment system is made up by two different shear zones activated in different times and at different structural levels. Our data testify a migration of the deformation from the lower portions to the upper ones (Cottle et al., 2015, Iaccarino et al., 2017, Montemagni et al., 2018, Chen et al., 2018). The ages of shearing of the ductile shear zones in the Cuonadong dome, located nearly 40 km to the South with respect to the Yalaxiangbo dome point out an older activation of the lower ductile shear zone (ca. 25-20 Ma) and a migration of the normal shearing towards the North. This caused an earlier exhumation of the Cuonadong dome with respect to the Yalaxiangbo dome, with similar mechanisms. The two detachments are later folded during the latest stages of exhumation of the domes. New data point out that age of normal shearing not only varies from West to East (Iaccarino et al., 2017) but varies along the same vertical section from ductile to brittle and along a N-S direction showing younger ages to the North in the NHGD.

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Montemagni C., Iaccarino S., Montomoli C., Carosi R., Jain A.K. & Villa I.M. (2018) - Age constraints on the deformation style of the South Tibetan Detachment System in Garhwal Himalaya. Ital. J. Geosci., 137, 175-187.

# Structural and tectono-metamorphic evolution of the Briançonnais units in Aiguille de Chambeyron – Denti di Maniglia Massifs (France, Italy)

Dana D.*[1], Iaccarino S.[1] & Michard A.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino.
[2] Départment Sciences de la Terre, Université Paris-Sud, Orsay (France).

*Corresponding author e-mail:* davide.dana@edu.unito.it

*Keywords:* Briançonnaise, metamorphic wedge, polyphase deformation.

In the Ubaye – Maira Valleys (W Alps), several continental-derived Briançonnais units are stacked between Alpine Tethys-derived units (Gidon et al., 1994). Each Briançonnais units is variably detached and affected by polyphase structural evolution (Michard et al., 2004 and reference therein). In this contribution we carry a contribution towards the reconstruction the structural and metamorphic architecture of the Briançonnais units along this transect. A geological - structural map of the area was realized at the scale 1:15.000, in association with microtectonics and RSCM analysis (Lahfid et al., 2010). Four deformation phases are identified both at the meso and microscale. The first two phases (D1-D2), related to the original top-to-the-W nappe piling, are associated with foliations developed under conditions close to the Alpine metamorphic peak, as suggested by the occurrence of lawsonite / carpholite paragenesis.

Previous tectonic surfaces are transposed by the main deformation phase (D3), developed under retrograde/decompression conditions. D3 dominates the structural-architecture of the transect where backfolding and back-thrusting, with a top-to-the-E transport is the main feature. Various kinematic indicators such as oblique foliations, mineral fish, S-C fabric have made possible to reveal the kinematics of the back-thrust. The folds related to D3 develop a foliation generally dipping to the SW with variable morphology consisting of a crenulation cleavage or disjunctive foliation in greenschist unit and a continuous fine foliation in blueschist units. This S3 foliation is commonly associated to pressure solution and scarce greenschist facies recrystallization. Lastly, a fourth phase (D4) developed in late metamorphic conditions deforms the previous surfaces developing a selective crenulation cleavage. Thermometry, based on RSCM spectroscopy, was performed in order to estimate the Alpine metamorphic peak temperature in each unit. The estimated temperature ranges from 294°C in the more external unit, to 345°C of the innermost Acceglio s.l. units (Michard et al., 2022). Geothermometer based on quartz recrystallization regime were used to determine deformation temperatures, highlighting temperatures near 350°C in the blueschist units manifested by bulging mechanism. Calcite twinning geothermometer and recrystallization regime also have made it possible to identify ranges of strain temperatures similar to those estimated using the RSCM method. Using these constrains, we propose a reconstruction of the structural architecture and tectono-metamorphic evolution of the studied transect in the frame of the subduction/exhumation dynamics of the Briançonnais margin.

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# Records of high-P (eo-)Alpine tectono-metamorphic events in the Variscan lower crust of the Serre Massif (Calabria, southern Italy)

Festa V.[1], Fornelli A.[1], Micheletti F.[1], Spiess R.[2] & Tursi F.*[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* fabrizio.tursi@uniba.it

*Keywords:* rejuvenation of crystalline basements, eo-Alpine tectonics, HP metamorphism.

In the present study we unveil the real significance of mylonitic reworking of polymetamorphic crystalline basement in the Serre Massif of Calabria (southern Italy). We used a multidisciplinary approach to comprehend the structural, microstructural and petrologic changes that occurred along a so far not much considered shear zone affecting the Variscan lower crustal rocks. It was never before studied in detail, although some late Cretaceous ages were reported for these mylonites, suggesting that this shear zone is of prime importance. Our observations reveal now that the formation of the new structural fabric within the shear zone was accompanied by changes in mineral assemblages, in a dominant compressive tectonic regime. During this tectono-metamorphic event, high-P mylonitic mineral assemblages were stabilized, consisting of chloritoid, kyanite, staurolite, garnet and paragonite, whereas plagioclase and biotite became unstable. Peak P–T conditions of 1.26-1.1 GPa and 572–626°C were obtained using THERMOCALC software. These new data question (i) that the Serre Massive represents an undisturbed continuous section of the Variscan crust, as generally suggested in the literature, and (ii) highlights the role of (eo-)Alpine high-P tectonics in the Serre Massif, recorded within mylonite zones, where the Variscan beasement became completely rejuvenated.

# Pre-Orogenic Tectonics in Central Apennines: new insights in the Simbruini Mts. (Central Apennines, Latium)

Fiorini A.*[1], Tavani S.[2], Corradetti A.[3], Mercuri M.[1] & Carminati E.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Dipartimento di Matematica e Geoscienze, Università di Trieste.

*Corresponding author e-mail:* fiorini.1707919@studenti.uniroma1.it

*Keywords:* pre-orogenic tectonics, younger-on-older low-angle faults, Central Apennines.

The Simbruini Mountains are one of the roughly NW-SE oriented ridges forming the Central Apennines, constituted by a Late Triassic to Miocene sedimentary succession deposited in shallow-water carbonate (Triassic-Miocene) to foredeep (Late Miocene) conditions. A pre-thrusting extensional phase has been recognized in this area in previous works (Carminati et al., 2014), testified by occurrence of syn-subduction normal faults associated with deposition of thick breccia deposits (Brecce della Renga Fm., Fabbi & Rossi, 2014). One of the most important tectonic features of the area is the Vallepietra-Filettino-Monte Ortara Line (VFML), a low angle fault with "younger on older" relationships. The kinematics of the VFML is amply debated: some authors consider it as an out of sequence thrust (Carminati et al., 2014), others as a rotated extensional fault (Pace et al., 2014). We contribute on this debate by showing new structural data obtained from geological mapping and virtual outcrop interpretation in the Vallepietra area. The main tectonic contact of the VFML is here scarcely outcropping. Low angle structures in the footwall of VFML, display extensional features. Cross-cutting relationships between inverse, high-angle and low-angle extensional faults and cutoff angles between stratification and low angle extensional faults suggest a pre-orogenic origin and a syn-orogenic rotation of these structures. This also explains their actual low dip angle. The area is characterized by features testifying Cretaceous extensional tectonics, like synsedimentary faults with associated soft sediment deformation structures and anomalous thicknesses of the Lower Cretaceous succession in the hangingwall of VFML. A new tectonic evolution of the area is here proposed. The VFML and the extensional low angle structures originated during a Lower Cretaceous extensional phase. However, a contribution of early Jurassic extensional faulting cannot be excluded due to the proximity with early Jurassic, deep-water, carbonate unit ("Unità Sant'Antonio", Damiani et al., 1998) in nearby areas. The anomalous bending of the lithosphere subducting in late Tertiary under Apennines caused the reactivation of these structures, prior to shortening. During the early Messinian compressive phase, these faults were cut by thrusts and rotated by 40°-50°. In nearby areas, the VFML is characterised by compressive structures, therefore suggesting a compressive reactivation during the orogenic phase for the VFML. In the post-orogenic phase (early Pliocene - Pleistocene) high angle extensional faults cut the previously formed structures.

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# A kinematic reconstruction of the Western Tethys based on the tight fit restoration of the southern N-Atlantic and the "building-block" approach

Frasca G.*[1] & Manatschal G.[2]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Institut Terre et Environnement, Strasbourg (France).

*Corresponding author e-mail:* gianluca.frasca@igg.cnr.it

*Keywords:* rifting, Tethys, kinematic reconstructions.

The Western Tethys is bounded by the European and African plates and interleaving crustal blocks such as Iberia and Adria. Despite being one of the best studied fossil rifted margin systems worldwide, debates remain on size, nature, and kinematic evolution of the Western Tethyan basins as well as on their along strike segmentation. This lack of understanding is due to the difficulty to directly access the distal parts of the rifted margins at present margins and to define the conjugates and the sizes of fossil margins preserved in orogenic settings.

To capture fully in map-view the kinematic evolution, the reconstruction of the Western Tethys rift system is here guided by robust boundary conditions and a tight fit restoration of the Central and N-Atlantic evolution, which implies a peculiar evolution of the Iberian continental block (Frasca et al., 2021). Secondly, we use a newly established "building-block" approach (Manatschal et al., 2022) in which we can restore fossil margins in time and space using "average" width and timing steps. Respecting a unique Alpine data set based on generations of Alpine geologists, we restore the movement of Adria relative Europe and Africa, which allows us to propose new Mesozoic Euler poles for Adria, compatible at a first order and large scale with recently published data and interpretations. We discuss the impact of our results for Triassic to Jurassic depocenters evolution, the age of the Ionian Sea, the segmentation of the Western Tethyan system and the creation of oceanic gateways linking the Atlantic and Tethyan system.

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# Contrasting subsidence-exhumation patterns in the hinterland of the Africa-Eurasia collision zone: the eastern Adjara-Trialeti, western Kura and central Greater Caucasus inverted sedimentary basins (Georgia)

Gusmeo T.*[1], Schito A.[2], Cavazza W.[1], Corrado S.[3], Zattin M.[4], Alania V.[5], Enukidze O.[5] & Pace P.[6-7]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Department of Geology and Petroleum Geology, School of Geosciences, University of Aberdeen (UK). [3] Dipartimento di Scienze, Università di Roma Tre. [4] Dipartimento di Geoscienze, Università di Padova. [5] "M. Nodia" Institute of Geophysics, «I. Javakhishvili» Tbilisi State University (Georgia). [6] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [7] PACE Geoscience, Chieti.

*Corresponding author e-mail:* thomas.gusmeo2@unibo.it

*Keywords:* Caucasus, thermal maturity, thermal modelling.

A multi-proxy thermal maturity dataset constrains the thermal evolution of the sedimentary successions within the eastern Adjara-Trialeti, western Kura and central Greater Caucasus inverted basins in Georgia. Located in the hinterland of the Arabia-Eurasia collision zone, those three basins differ in age, subsidence mechanism and degree of structural inversion. The Adjara-Trialeti back-arc rift basin developed in Paleogene times and its sedimentary fill reached late diagenetic conditions (max ~115°C) during burial before Middle Miocene structural inversion. The western Kura Basin, an Oligocene-Neogene foreland basin which was affected by contrasting and asymmetrical episodes of flexural subsidence in response to loading by the adjacent orogenic belts, acquired a thermal maturity within the late diagenetic realm during tectonic loading by south-directed thin-skinned thrust sheets. The Greater Caucasus formed after the structural inversion of a Jurassic back-arc rift basin where several kms of sedimentary rocks were accumulated, and our results from its southern-central sector indicate increasing paleotemperatures moving towards the axial zone of the orogen, hence from younger to older stratigraphic units, reaching anchizone-epizone conditions (max ~400°C). Additionally, integrating thermal modelling of borehole data, apatite fission-track statistical inverse modelling, and seismic interpretation, we define the complex patterns of subsidence and exhumation registered within the adjacent and structurally interfering Adjara-Trialeti and Kura inverted basins. Applying such multidisciplinary approach, we reconstructed three phases of rapid subsidence in the Adjara-Trialeti basin during late Paleocene-Early Eocene, Middle-Late Eocene and Early Miocene times, which can be associated to discrete tectonic events. Thermal maturity data also indicate that between 1.0 and 1.3 km of the Adjara-Trialeti sedimentary succession were eroded since the onset of structural inversion in the Middle Miocene. In the western Kura Basin we recognised intermittent episodes of flexural subsidence since Oligocene times, in response to competing loading by the Lesser Caucasus, the Adjara-Trialeti fold-and-thrust belt and the Greater Caucasus. Finally, during latest Miocene times, an additional tectonic loading (1.3-1.8 km) was rapidly emplaced due to south-directed thin-skinned thrust sheets, mostly eroded during the Plio-Quaternary.

# Eocene to Miocene metamorphic evolution and tectonic implication of the Ilam Nappe in Nepal Himalaya: Constraints from P–T conditions and monazite petrochronology

Imayama T.*[1], Hoshino R.[1], Yi K.[2] & Kawabata R.[1]

[1] Research Institute of Frontier and Science Technology, Okayama University of Science (Japan). [2] Geochronology Team, Korea Basic Science Institute, Seoul (South Korea).

*Corresponding author e-mail:* imayama@ifst.ous.ac.jp

*Keywords:* Ilam Nappe, P–T conditions, monazite petrochronology.

The Ilam Nappe, consisting of the High Himalayan Crystalline Sequence (HHCS) in far-eastern Nepal, was largely emplaced southward along the Main Central Thrust (MCT). Here we present the P–T–t path of the Ilam Nappe using conventional geothermobarometers, pseudosection modelling, and monazite petrochronology. Amphibole-bearing migmatite just above the MCT experienced prolonged fluid-present melting from a prograde metamorphism at 39–31 Ma to peak upper amphibolite-facies metamorphism (694°C and 10.3 kbar) during 24–19 Ma, followed by cooling. Kyanite-sillimanite migmatites record a prograde metamorphism at 35–28 Ma and peak lower granulite-facies metamorphism (738–765°C and 8.3–9.7 kbar) under kyanite stability via the muscovite dehydration reaction at 25–20 Ma, followed by isothermal decompression under sillimanite stability. The clockwise P–T path and Early-Middle Miocene peak metamorphism of the Ilam Nappe can be correlated to those in the lower-middle HHCS hinterland. The Eocene-Oligocene prograde metamorphism with a low geothermal gradient of 15–25°C/km in the Ilam Nappe and the entire HHCS hinterland could represent the crustal thickening accompanied by large-scale overthrusting before the normal faulting of the South Thrust Detachment System, followed by diachronous extrusions of the upper HHCS along the High Himal Thrust, and of the lower-middle HHCS along the MCT with nappe emplacement. The lower granulite-facies Ilam Nappe was exhumed during the Early-Middle Miocene from the deeper or lower structural level of the HHCS, compared to the earlier Oligocene exhumation of the upper amphibolite-facies Karnali and Kathmandu klippes from the shallower or uppermost structural level of the HHCS.

# Early top-W thrusting in Upper Pennine Bündnerschiefer in the eastern Central Alps

Jakobsson V.* & Ring U.

Department of Geological Sciences, Stockholm University (Sweden).

*Corresponding author e-mail:* Vidark.jakobsson@gmail.com

*Keywords:* Upper Pennine, gabbro, W-directed nappe-stacking.

The Austroalpine domain was formed by Cretaceous top-to-the-W-directed nappe stacking. However, the Paleogene accretion that formed the underlying Pennine domain has traditionally been described by N-S movements, neglecting an E-W component. This study is set up to investigate what role E-W movements played in forming the Upper Pennine domain in the eastern Central (Swiss) Alps. A field study was conducted in the basal Upper Pennine nappe, Avers Bündnerschiefer, with the Juf Gabbro – a rigid mafic unit sitting at the base of the Avers Bündnerschiefer, as the study area. The Juf Gabbro was mapped using a five-fold deformation-intensity scheme. The Juf Gabbro's internal structure is defined by heterogeneously deformed E-W striking metagabbro lenses surrounded by calcschist. Structural data show a D1 phase of penetrative WNW-trending stretching lineation with top-WNW shear-sense indicators – marking the Juf Gabbros and adjacent calcschists main tectonometamorphic imprint. The main foliation is E-W striking and dips moderately to the NNE, and the D1 phase is then folded by subparallel to E-W trending D2 fold axes. These kinematics of the D1 and D2 phases are coherent with the early Cretaceous to Paleogene E-W kinematics of the overlying Upper Pennine and Austroalpine nappes (Platta, Arosa and Err nappes; Handy et al., 1996). The top-SE Avers-Turba mylonite zone crosscuts the E-W striking foliation, constraining the timing of the main tectonometamorphic event to older than the oldest age of top-SE shearing at > 45 Ma (Ring & Glodny, 2021).

Moreover, the top-WNW kinematics have previously been described in the Madris metabasalt (Ring & Glodny, 2021). This metabasalt has experienced blueschist metamorphism of 9 – 12 kbar and 380 – 420°C (Ring, 1992), widely accepted as the metamorphic grade of Avers Bündnerschiefer. The Juf Gabbro show a mineral assemblage of clino-amphibole-talc-chlorite-epidote with no high-P relicts. The point-counting results and pale, colourless pleochroism in chlorite, epidote and clino-amphibole suggest an Al-Mg rich bulk composition, which is consistent with a previous study by Oberhänsli (1978). The Al-Mg-rich bulk composition is suggested for the lack of high-P relicts in the Juf Gabbro – concluding that the main tectonometamorphic imprint of Juf Gabbro occurred under blueschist facies condition. In contrast to the rest of Avers Bündnerschiefer, the Juf Gabbro remain largely unaffected by the later orogenic events and therefore reflects the early kinematics of the entire tectonic nappe. This study suggests that top-WNW imbrication during the early Paleogene formed the Upper Pennine domain (Avers Bündnerschiefer). Avers Bündnerschiefer was already a tectonically cohesive unit once influenced by the top-N kinematics which marks the traditional model of forming the Avers Bündnerschiefer (Schmid et al., 1996).

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# Glacier retreat revealing new details on a complex nappe stack in the Mattmark region (Valais, Switzerland)

Jossevel C.* & Epard J.-L.

Institute of Earth Sciences, University of Lausanne (Switzerland).

*Corresponding author e-mail:* christophecedric.jossevel@unil.ch

*Keywords:* fold nappes, Alpine orogeny, paleogeography.

The Pennine Alps in the Matter and Saas Valleys exhibit tectonic units corresponding to an ocean as well as to a continental margin. They are key areas for the study of the structure of distal domain and paleogeographic reconstruction, despite their complexity due to strong deformation during the Alps' formation. The Monte Rosa and the Zermatt-Saas nappes are the two main tectonic units in the area but although separated from each other by only a few hundred of meters, numerous of tectonic units are sandwiched in between. These units are made of cover and basement and have been neglected during the last decades due to their complexity and the strong shearing they have suffered. However, glacier retreat produces new outcrops offering more complete and continuous information on those units. The Gornergrat nappe, a cover series made of Mesozoic sediments, is one of them and its attribution remains unclear and debated. Recent outcrops close to the Britannia hut, at the base of the Allalinhorn, give new data on the composition and the relation of the tectonic units in this region. Field mapping, lithostratigraphic analyses, structural measurements, and geochronology, allow us to constrain the nature and the origin of the Gornergrat nappe, as well as to propose a paleogeographic reconstruction of the European distal margin.

# Peak metamorphic temperatures in the Alpine tectonic wedge, south Cottian Alps, Italy

Lahfid A.*[1], Michard A.[2], Chopin C.[3], Schmid S.M.[4], Dana D.[5] & Ballèvre M.[6]

[1] Bureau de Recherches Géologiques et Minières, Orléans (France). [2] Départment Sciences de la Terre, Université Paris-Sud, Orsay (France). [3] Ecole Normale Supérieure, CNRS-Université Paris Sciences & Lettres (France). [4] Institut für Geophysik, ETH Zürich (Switzerland). [5] Dipartimento di Scienze della Terra, Università di Torino. [6] CNRS, Géosciences Rennes (France).

*Corresponding author e-mail:* a.lahfid@brgm.fr

*Keywords:* Western Alps, Raman Spectroscopy of Carbonaceous Material (RSCM), blueschist-facies metamorphism.

In the south Cottian Alps, the metamorphic wedge of the Western Alps is widely exposed. It includes, from SW to NE, the Briançonnais internal border (Acceglio units), the ophiolitic Schistes lustrés nappes (Piemonte-Liguria Ocean) and the southern Dora-Maira units derived from the Briançonnais s.l. basement (Michard et al., 2022, and references therein). Located between the Acceglio and Dora-Maira units, the Val Maira-Sampeyre and Val Grana Allochthons (MGA) consist of a Permo-Triassic to Mid Jurassic "Prepiemonte"-type sequence detached from the Briançonnais s.l. basement. The peak metamorphic grade of these tectonic complexes evolves from blueschist- to coesite-eclogite (Brossasco-Isasca unit of Dora-Maira). Here we report new peak temperatures by carrying the RSCM geothermometry approach (see Lahfid et al., 2019) on most of the south Cottian transect with emphasis on the MGA and on the intervening mélange shear zones. TRSCM values range from ~400°C to >500°C, going from the most external Val Grana unit and overlying Queyras schists to the uppermost Dora-Maira unit. We present a new metamorphic map and profiles based on published and new data, including our new thermometric data. We note an overall fit between our TRSCM results and those inferred from the mineral assemblages, where available. The thermal anomaly linked to the rifting evolution that gave birth to the Piemonte-Liguria Ocean was recognized in the poorly metamorphic Adriatic margin SE of the Periadriatic line (Beltrando et al., 2015), but cannot be evidenced in the studied Briançonnais-derived units due to their high metamorphic grade.

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# Double inversion (compressional and extensional) of a rift related extensional fault system in the Apennines wedge

Lavosi G.*[1], Mercuri M.[1], Tavani S.[2-3] & Carminati E.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II". [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* lavosi.1716640@studenti.uniroma1.it

*Keywords:* structural Geology, tectonics, geological mapping.

The Central Apennines are a NW-SE fond-and-thrusts belt developing as the result of the retreating westward subduction of the Apulian plate, that determined firstly a compressional tectonic phase during the Miocene followed by an extensional phase starting from the Pliocene (Carminati et al., 2012). This chain is characterised by a sedimentary succession of Meso-Cenozoic shallow and deep-water carbonates and Cenozoic foredeep clastics, developed from Hettangian time in a platform and basin context, due to a rift episode (Accordi & Carbone, 1988). In the study area, the Lazium-Abruzzi Platform shallow-water succession crops out (SGI-APAT, 2004). In a limited, N-S elongated, part of the study area the Corniola formation, characterised by Early Sinemurian deep-water limestones, not belonging to the Lazium-Abruzzi succession, is anomalousy exposed (Angelucci & Praturlon, 1968). This anomalous outcrop is parallel to a ca. N-S portion of the Celano-Ovindoli-Pezza extensional fault-system, occurring between the Fucino Plan and the Gran Sasso Massif.

To reconstruct the geometry and the kinematics of the Celano-Ovindoli-Pezza faults and the relationships among Jurassic (rift-related) extensional faults and late Cenozoic thrusts and normal faults we performed a detailed geological mapping and a multiscale structural analysis and we built 8 geological cross sections. Combining the field observations with data from the literature we conclude that the presence of the Corniola Fm is related to the opening of a narrow N-S oriented intraplatform basin during Early Jurassic time. Moreover, Miocene thrusts likely reactivated the Jurassic faults in the eastern edge of the basin. In several points, the post-Orogenic extensional faults do not displace thrust faults, but they likely reshear them. The reactivation is not exposed in the northern portion of the study area, where it may occur in the subsurface, while fault reactivation faults is exposed in the central and southern portions.

In conclusion we propose a double inversion of (first compressional in Miocene time and then extensional in Pliocene time) of Jurassic rift-related faults.

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# The Western Alps exhumation history detailed through the eyes of glaucophane-bearing eclogitic rocks: preliminary metamorphic data from the Internal Piedmont Zone

Maffeis A.*[1], Nerone S.[1], Corno A.[1], Caso F.[2] & Petroccia A.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* andrea.maffeis@unito.it

*Keywords:* Western Alps, eclogite, exhumation.

The understanding of the metamorphic evolution of subducted and exhumed oceanic lithosphere is paramount to developing coherent tectonic models of collisional orogens. It is also crucial for understanding deep chemical cycles at convergent margins and the interplay between crustal and mantle wedges. The Western Alps constitute an ideal area for studying subducted and exhumed oceanic units that recorded different P-T conditions and several fundamental studies on the tectono-metamorphic evolution of Alpine units (and subduction zones in general) have been developed. Nevertheless, multiple aspects are still debated, such as the occurrence and the meaning of a late heating event. In this contribution, we present preliminary petrographic and minero-chemical data on a glaucophane-bearing eclogite cropping out in the middle Ala Valley, in the Internal Piedmont Zone, not far from the Gran Paradiso Massif (Caso et al., 2021). These starting data will be fundamental for thermobarometric estimates of this portion of the Internal Piedmont Zone, using the isochemical phase diagram approach. In the studied sample, the main schistosity (Sp) generally occurs as a coarse-grained continuous foliation defined by alternate omphacite- and glaucophane-rich levels, with scattered granoblastic quartz domains and abundant apatite and rutile. The Sp wraps around zoned, almandine-rich, garnet porphyroblasts. They include rutile, apatite, omphacite, and minor paragonite associated with zoisite. Relationships between foliation and garnet suggest that garnet could be interpreted as pre-, syn- to post-tectonic with respect to the metamorphic event related to Sp. Euhedral post-Sp glaucophane crystals have been observed. The retrograde assemblage is represented by local albite, ilmenite, which systematically rims all rutile grains, and by both the sin- and post- tectonic glaucophane characterized by a first thin katophorite mantle, followed by a tremolite/whincite final rim. These preliminary results highlight a polyphasic evolution from HP to LP conditions. The chosen sample is very promising for constraining a detailed exhumation P-T-path of the Internal Piedmont Zone in this less-investigated portion of the Western Alps.

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# Challenges in the interpretation of the metamorphic record in compositionally heterogeneous shear zones - insights from the Central Alps

Maino M.*[1], Schenker F.L.[2], Casini L.[3], Corvò S.[1], Perozzo M.[1], Langone A.[4] & Seno S.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Scienze della Terra, Scuola Universitaria Professionale della Svizzera Italiana, Mendrisio (Switzerland). [3] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [4] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* matteo.maino@unipv.it

*Keywords:* Alps, tectono-metamorphic evolution, non hydrostatic stress.

Following the legacy of Emile Argand, several generations of geologists contributed to the reconstruction of the Alpine-Himalayan orogenic evolution. Throughout this long history of researches, a few key questions stand out, still challenging the geological community. One of the most important is the interpretation of contrasting metamorphic records preserved within closely spaced rocks. The reconstruction of metamorphic histories is based on the estimation of pressure and temperature conditions starting from the assumption that the mineral assemblages always reflect lithostatic pressure and near-equilibrium regional geothermal gradients. These PT paths represent a major tool for tectonic reconstruction as proxies of the burial and exhumation history of the rocks during subduction-exhumation phases.

The occurrence of ultrahigh-pressure and/or high-temperature rocks embedded within significantly lower grade metamorphic rocks rises a major challenge for developing a consistent geodynamic model for exhumation of such deep-seated rocks. Subduction zones are, in fact, efficient player driving material from the surface down into the Earth's mantle. However, the mechanisms to exhume part of this material back to the shallow crust are still highly debated. Scientists generally invoke either mechanical decoupling within a tectonic mélange or spatially variable metamorphic re-equilibration during the retrograde path. Alternative explanations highlight the role of deformation in promoting the coexistence of multiple local equilibria, which cease to correlate with lithostatic conditions and thus burial depths. In this view, the non-hydrostatic stress and the local temperature deviations are accounted as important components potentially modifying the metamorphic system (e.g., Wheeler, 2014; 2020; Moulas et al., 2019; Hess & Ague, 2021).

In this contribution, we integrate structural, petrological and thermochronometric data from classic occurrences of ultra-high pressure and high temperature outcrops of the Adula and Cima Lunga nappes of the Central Alps. The wide dataset comprises new field mapping covering the entire nappes extension (several hundred square kilometres) and structural-petrochronological analyses at the meso- to micro-scale. Our results show the highly variable pressure-temperature-time-deformation paths experienced by the compositionally heterogeneous rocks of the Cima Lunga and Adula nappes. We present evidence of contrasting metamorphic records, potentially contradicting the assumption of a purely lithostatic gradient, as well as of a steady-state regional geothermal gradient. New findings provide arguments to discuss pros and cons of the tectonic models proposed to explain these contrasting metamorphic records.

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Moulas E., Schmalholz S.M., Podladchikov Y., Tajčmanová L., Kostopoulos D. & Baumgartner L. (2019) - Relation between mean stress, thermodynamic, and lithostatic pressure. Journal of metamorphic geology, 37(1), 1-14.

Wheeler J. (2014) - Dramatic effects of stress on metamorphic reactions. Geology, 42(8), 647-650.

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# The deep structure of the Western Alps revealed by the CIFALPS seismic experiments

Malusà M.G.*[1], Guillot S.[2], Zhao L.[3], Paul A.[2], Solarino S.[4] & CIFALPS Working Group

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] ISTerre, CNRS, Université Grenoble Alpes (France). [3] Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing (China). [4] INGV, Osservatorio Nazionale Terremoti, Genova.

*Corresponding author e-mail:* marco.malusa@unimib.it

*Keywords:* subduction, exhumation, Western Alps.

The Alps are the site where classic geologic concepts such as nappe theory, continental subduction and slab breakoff have been first proposed. However, the deep tectonic structure of the Alps has long been poorly constrained by independent geophysical evidence. Here we summarize the main results of the CIFALPS passive seismic experiments carried out since the 2010s by Chinese, French and Italian scientists, with particular emphasis on the transect of the southern Western Alps across the Dora-Maira (U)HP massif (Malusà et al., 2021 and references therein). Major results provided by the application of a wide range of tomographic methods include: (i) the first seismic evidence of European continental crust subducted into the Adriatic upper mantle, beneath the place where coesite was first recognized in continental (U)HP rocks; (ii) evidence of a major involvement of the mantle wedge during (U)HP rock exhumation; (iii) evidence of a serpentinized plate interface favoring continental subduction; (iv) evidence of a continuous slab ruling out the classic model of slab breakoff magmatism; (v) evidence of a polyphase development of anisotropic fabrics in the Alpine mantle. We finally discuss the implications of rifting inheritance and exhumation of deep rocks on the final stages of continental collision, and demonstrate the importance of lateral variations in mantle rock rheology resulting from a complex, but extremely well constrained evolution of the Adria-Europe plate boundary zone starting from the early stages of the Alpine Wilson cycle.

Malusà M.G., Guillot S., Zhao L., Paul A., Solarino S., Dumont T., Schwartz S., Aubert P., Baccheschi P., Eva E., Lu Y., Lyu C., Pondrelli S., Sallimbeni S., Sun W. & Yuan H. (2021) - The Deep Structure of the Alps Based on the CIFALPS Seismic Experiment: A Synthesis. Geochem. Geophys. Geosys., 22(3), e2020GC009466. https://doi.org/10.1029/2020GC009466.

# 3D Vp and Vp/Vs tomographic models of the central Mediterranean area: new insights into the deep structure of the Alpine-Apennine system

Menichelli I.*[1], De Gori P.[2], Improta L.[2], Lucente F.P. [2] & Chiarabba C.[2]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INGV, Roma.

*Corresponding author e-mail:* irene.menichelli@uniroma3.it

*Keywords:* 3D Tomographic images, geodynamic of central-Mediterranean, Alpine-Apennines orogenic system.

The Alp-Array project is a European initiative to advance our understanding of the geodynamics and deep structure of the circum-Mediterranean belts by clarifying the relationship between the Alpine chain and the surrounding orogens, such as the Apennines, Dinarides, and Carpathians. Open questions are mainly based on the deep architecture and connections between these chains. Some broad tomographic investigations of circum-Mediterranean orogens are already been widely discussed, but past models have a low intrinsic resolution. In addition, well-resolved velocity volumes are limited to crustal or deep mantle depths obtained mainly from the analysis of ambient noise, receiver function, and teleseismic data. Here, we present a new Local Earthquakes Tomographic (LET) model computed by analyzing 107 seismic events recorded by AlpArray and RSN (Italian Seismic Network) seismic stations between 2016 and 2018. Only seismic events with magnitude (Mw) ≥ 3.5, recorded by all seismic stations operating in the studied area, were selected for the inversion. The first arrival times of the direct and refracted waves at the Moho depth were hand-picked at larger distances (≤ 1000 km). The strength of the adopted models is based on the high quality of data recorded by a dense seismic array, which allows us to constrain Vp and Vp/Vs anomalies. These models allowed us to address the velocity anomalies to the temperature and compositional variations, defining new constraints on the processes and the kinematics which occurred beneath the study area (Giacomuzzi et al., 2012). For the first time, new high-resolution tomographic images, between 40 and 80 km depth, were computed to define the structure of the crustal-mantle boundary. In particular, cross-sections along different sectors of the Alpine chain show the geometry of the underlying slab and allow to clarify the debates on the polarity change of the Alpine slab (Lippitsch et al., 2003), suggesting the European nature under the whole chain. Furthermore, the structure of the Northern Apennines and Calabrian Arc has been widely investigated to improve our knowledge of the styles of the Adriatic and Ionian subductions. In particular, the delamination processes, the role of fluids, and the induced seismicity beneath the northern Apennines are observable through our seismic and tomographic investigations. Therefore, new insights into the Alpine and Apennines structures, affected by two different subduction styles, have been defined.

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# Prolonged extension in the middle and upper continental crust: insights into the Simplon Shear Zone (Western Alps)

Montemagni C.* & Zanchetta S.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* chiara.montemagni@unimib.it

*Keywords:* Simplon Shear Zone, kinematic vorticity, Ar/Ar geochronology.

The evolution of a shear zone in space and time is strongly influenced by PT conditions, differential stress, pore fluid pressure and time duration of activity (Fossen & Cavalcante, 2017). The understanding of mechanisms controlling the development of a shear zone is thus of paramount importance in constraining the rheology of the continental lithosphere. In particular, crustal scale low-angle normal faults are structures commonly active at mid to upper crustal levels within quartz- and feldspar-rich rocks promoting the exhumation of deep-seated rocks in orogenic post-collisional setting.

We studied the evolution of the Simplon Shear Zone (Switzerland) formed as an extensional detachment accommodating E-W directed lateral extrusion after the collision between Adria and Europe (Mancktelow, 1985). Several tens of kilometres of extension were accommodated by the Simplon Shear Zone, allowing the exhumation of the Lepontine Dome, the deepest part of the Central-Western Alps.

We investigated the evolution of the Simplon Shear Zone constraining the meso-, microstructures and vorticity distribution across the shear zone, its time of activity by $^{40}Ar/^{39}Ar$ dating of syn-shearing micas and its correlation with simple shear component distribution, the estimates of magnitude and variation of differential flow stress and strain rates during shear zone evolution obtained through EBSD-assisted quantitative microstructural analysis. All these data have been combined to reconstruct the structural and temporal evolution of the shear zone as the result of the response of involved rocks to changing PT and stress conditions.

The Simplon Shear Zone evolved from epidote-amphibolite to greenschist facies and then brittle conditions during shearing. A decrease of simple shear component from 88% to 37% towards the top of the shear zone is observed, with mylonites displaying ages within the 12-8 Ma time span. Calculated differential stress (59-78 MPa) and strain rate ($10^{-11}$-$10^{-12}$ $s^{-1}$) are in agreement with values of several other crustal-scale low-angle normal faults developed at medium to shallow crustal levels (Montemagni & Zanchetta, 2022).

Our approach used at different scales revealed that the Simplon Shear Zone experienced a complex evolution, with shear strain that was heterogeneously distributed across the shear zone. Even though this heterogeneity, a general decrease of the simple shear component and increase of the differential flow stress toward the top of the shear zone is clearly defined.

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# An innovative point of view on a classic Himalayan transect: Multistage evolution of the South Tibetan Detachment System along the Kali Gandaki Valley

Nania L.*

Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* laura.nania@unifi.it

*Keywords:* calcite fabric, South Tibetan Detachment System, piezometry.

The Himalayan orogen offers some of the most spectacular natural crustal sections of our Planet, where large-scale overthrusting of the continental lithosphere can be directly investigated. Recent reconstructions have shown that the Himalaya is not a cylindrical belt, and lateral variations along strike need to be further studied to unravel how mid-crustal rocks were exhumed. The South Tibetan Detachment System (STDS) is an example of such regional structures in Himalaya, showing a variable architecture in different areas between Nepal and Bhutan (Kellett et al., 2019 with references). The main structure is a mylonitic zone within amphibolite facies gneiss and greenschist facies metasediments of the Greater Himalayan Sequence and the Tethyan Himalayan Sequence, respectively. Only in few localities, where quartz-bearing rocks occur, a structurally upper brittle fault was later localized. The present contribution aims to provide new data on the main mylonitic zone in central Himalaya, to help explain the different evolution of the STDS and the lack of the younger brittle fault based on the lateral lithological and rheological variations.

The study area is the Kali Gandaki Valley (Western Nepal), where the Annapurna Detachment is the local segment of the STDS. Within a 1-2 km thick mylonitic zone, carbonate rocks are the main lithologies, showing a top-to-the-north sense of shear through asymmetric porphyroclasts and oblique foliations. Calcite accommodated the mylonitic deformation through grain boundary mobility and twinning. Its CPOs indicate that both mechanisms were active during the detachment shearing. The combination of different piezometers and kinematic vorticity gauges point that the two mechanisms dominated on each other at different deformation conditions, highlighting two main progressive deformation stages. Deformation temperatures and strain rates decreased from the stage dominated by grain boundary mobility to the late stage where calcite is deformed by twinning. Differential stress increased, suggesting an exhumation from lower to shallower crustal levels under almost constant general shear conditions. Results support that marbles deformed plastically until the end of the detachment shearing at shallow crustal levels, unlike the quartz-bearing rocks in other areas affected by the STDS. This interpretation can account for the lack of a new localization of a detachment fault at higher structural levels, highlighting the lateral variations of the STDS in the Himalaya also compared to areas where carbonate-bearing rocks occur (e.g., Nania et al., 2022).

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Nania L., Montomoli C., Iaccarino S., Leiss B. & Carosi R. (2022) - Multi-stage evolution of the South Tibetan Detachment System in central Himalaya: Insights from carbonate-bearing rocks. J. Struct. Geol., 158, 104574.

# Rehydration of Variscan upper crust prior to its Alpine reworking as revealed by polycyclic garnet (Dora-Maira Massif, Western Alps)

Nosenzo F.*[1], Manzotti P.[1] & Robyr M.[2]

[1] Department of Geological Sciences, Stockholm University (Sweden). [2] Institute of Earth Sciences, University of Lausanne (Switzerland).

*Corresponding author e-mail:* francesco.nosenzo@geo.su.se

*Keywords:* rehydration, upper crust, polycyclic garnet.

Fluid-present conditions in metamorphic rocks enhance reaction kinetics and favour mineral-chemical re-equilibration. During subduction, oceanic and continental crust dehydrates as a result of break-down of hydrous minerals along an up-pressure (P) up-temperature (T) P–T path. However, polycyclic continental crust may be already partially or totally dry before being subducted. Therefore, its re-equilibration (i.e., reworking) during burial requires interaction with external fluids, a process that may occur prior or during subduction.

In this study, we investigate the behaviour of a slice of Variscan upper continental crust (i.e., the Muret Unit in the northern Dora-Maira Massif) deeply buried (~ 60 km depth) during the Alpine history. Polycyclic micaschists inside and outside a kilometre-scale domain of low strain have been studied in order to estimate the peak P–T conditions reached by the Muret Unit and assess the role of water on the growth of Alpine high P mineral assemblages.

A pre-Alpine amphibolite-facies foliation is still preserved within the low strain domain and is statically overprinted by Alpine high P minerals (phengite, chloritoid, glaucophane, rutile). Outside this domain the same high P minerals define a pervasive Alpine foliation. Polycyclic garnet occurs in the micaschists inside and outside the undeformed domain and displays chemical and textural evidence of growth and dissolution. The first garnet generation is pre-Alpine and grew during the Variscan amphibolite-facies metamorphism (dated at ~ 324 Ma; Nosenzo et al., 2022). Subsequently, pre-Alpine garnet is partially dissolved at the rims and along fractures. A second generation of garnet grew during the Alpine cycle at ~ 21 kbar ~ 550°C. It formed rims and cemented the fractures.

Thermodynamic modelling indicates that the observed Alpine mineral assemblage (g-ctd-ph-gl-ru) developed under $H_2O$-saturated conditions (i.e., in the presence of a free $H_2O$ phase). However, the rock $H_2O$ content ($H_2O$ bounded in the peak mineral assemblage) at the Variscan peak P–T conditions (~ 7 kbar ~ 650°C) is not sufficient to reach $H_2O$-saturation during the Alpine overprint. This requires a minimum rehydration of ~ 0.7 wt% of $H_2O$.

In the micaschist inside the low strain domain, fluid infiltration at greenschist facies occurred during the late Variscan retrogression as indicated by the growth of metamorphic zircon at ~ 304 Ma (Nosenzo et al., 2022). This process may be also responsible for the dissolution of the pre-Alpine garnet.

Nosenzo F., Manzotti P., Poujol M., Ballèvre M. & Langlade J. (2022) - A window into an older orogenic cycle: *P–T* conditions and timing of the pre-Alpine history of the Dora-Maira Massif (Western Alps). J. Metamorph. Geol., 40, 789-821.

# The "Schistes Lustrés" in the Mont Fort and Tsaté nappes (Middle and Upper Penninic, Western Swiss Alps)

Pantet A., Epard J.-L.*, Baumgartner-Mora C., Baumgartner P., Baumgartner L. & Masson H.

Institut des Sciences de la Terre, Université de Lausanne (Switzerland).

*Corresponding author e-mail:* Jean-Luc.Epard@unil.ch

*Keywords:* Western Alps, Penninic, Prepiedmont.

The "Schistes Lustrés" is a volumetrically important formation that outcrops in the highest units of the Penninic nappes stack. Calcschists, partly of Cretaceous age, constitute the dominant lithology. Their association with continental or oceanic crust has been or still is controversial. In the Western Swiss Alps, the "Schistes Lustrés" are classically assigned to the Tsaté nappe (Combin zone s. str.). This nappe is divided into two units, separated by a discontinuous band of strongly deformed Mesozoic rocks, mainly dolomites, called the Frilihorn series.

New stratigraphic and structural observations show that the lower part of the Tsaté nappe is formed by a sedimentary series called "Série Rousse" which is devoid of ophiolitic material and constitute the continuation of the Triassic to Cretaceous Evolène series, itself being part of the cover of the Mont-Fort nappe (Middle Penninics, Prepiedmont domain) (Pantet et al., 2020). This lower part is thus related to the deposition on a continental basement. Above the Frilihorn series, the "Schistes Lustrés" includeophiolitic elements and show preserved stratigraphic contacts with remnants of oceanic crust.The distribution of temperatures obtained by Raman graphite thermometry (RSCM) indicates that the highest temperatures are located at the tectonic limit marked by the Frilihorn Series.

The new data allow us to propose a revised stratigraphy for the "Schistes Lustrés", a more precise attribution to paleogeographic domains and new tectonic subdivisions for the Tsaté and MontFort nappes in the area.

Pantet A., Epard J.-L. & Masson H. (2020) - Mimicking Alpine thrusts by passive deformation of synsedimentary normal faults: a record of the Jurassic extension of the European margin (Mont Fort nappe, Pennine Alps). Swiss J. Geosci., 113(1), 1-25. https://doi.org/10.1186/s00015-020-00366-2.

# Constraining P-T conditions of non-coaxial deformation between subducted continental units: a case study from the Dora-Maira Massif, Western Alps

Petroccia A.[1], Nerone S.*[1], Dana D.[1], Caso F.[2] & Maffeis A.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Terra «A. Desio», Università di Milano.

*Corresponding author e-mail:* sara.nerone@unito.it

*Keywords:* shear zone, P-T path, metamorphic evolution.

The exhumation of subducted continental units within orogenic wedges is driven by ductile shear zones. Thus, elucidating the P-T conditions of non-coaxial deformation is necessary to develop coherent tectonic models. This study examines the boundary between the Sanfront-Pinerolo Unit (Vialon, 1966) and the Ricordone Unit (Bonnet et al., 2022) in the Western Alps. Meso- to microstructural investigations reveal the presence of a km-thick high-strain zone associated with a top-to-the W-SW sense of shear that affected both units. To constrain the metamorphic condition of the mylonitic zone, we selected the most representative sample for mineral chemical analyses and subsequent thermodynamic modelling study. Phengitic (Si = 3.27–3.49 a.p.f.u.) and muscovitic (Si = 3.10–3.22 a.p.f.u.) white mica, biotite and chlorite define a spaced to continuous mylonitic foliation (Sp). Cm-size plagioclase is characterized mostly by albite cores, generally showing an internal foliation (Si) mainly concordant and locally discordant with respect to the external one (Sp). These observations indicate an inter- to syn-tectonic (syn-Sp) albite growth. Oligoclase rims, static on the Sp, represent the last stage of plagioclase growth. Epidote is pre-tectonic relative to the Sp and shows compositions halfway between epidote s.s. and zoisite, as well as allanitic cores. Almandine-rich garnets are homogeneous in composition and syn-tectonic relative to the Sp. They are characterized by strain shadows with biotite and muscovite. Rutile crystals are systematically rimmed by ilmenite. The presence of pre-tectonic epidote and phengite indicates a higher-pressure stage before the main deformational event under higher temperature conditions (Dp), while oligoclase static growth around albite highlights a post-Dp retrograde path. Also, Grt-Bt geothermometer, for the Dp event, returns T > 530°C. Considering the nearby existing estimations (Avigad et al., 2003; Groppo et al., 2019), our new preliminary constraints could further implement the partially known metamorphic evolution of the investigated Alpine mylonite.

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Bonnet G., Chopin C., Locatelli M., Kylander-Clark A.R.C. & Hacker B.R. (2022) - Protracted subduction of the European hyperextended margin revealed by rutile U-Pb geochronology across the Dora-Maira massif (W. Alps). Tectonics, 41(4).

Groppo C., Ferrando S., Gilio M., Botta S., Nosenzo F., Balestro G., Festa A. & Rolfo F. (2019) - What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps). Eur. J. Mineral., 31(4), 665-683.

Vialon P. (1966) - Etude géologique du Massif cristallin Dora-Maira, Alpes cottiennes internes, Italie. Mémoires du Laboratoire de Géologie de la Faculté des Sciences de Grenoble, 4, 193.

# The basement exposed in the southern Calabria: a network of shear zones?

Purrone S.* & Carosi R.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* silviapurrone@hotmail.it

*Keywords:* structural geology, Variscan belt, mylonites.

The Calabria-Peloritani Orogen is a fragment derived from the deformation and metamorphism of the upper to the lower continental crust of the Variscan basement. The current geographic position derives from a migration of the Calabrian arc to the SE, which ended in the Miocene.

The study area is located in the southeast portion of the Serre Massif. It is mainly constituted by paragneiss and phyllite, delimited to the North by the Serre Batholith (emplaced 300-290 Ma). The work focuses on the meso- and micro-structural analysis of the two main tectonic units exposed: the "Mammola Paragneiss Unit" (MPU) and the "Stilo-Pazzano Phyllite Unit" (SPU). Both Units recorded polyphase deformation and regional metamorphism during the Carboniferous and a Late Carboniferous-Early Permian contact metamorphism.

The mesoscale study allowed us to identify two main ductile deformation phases (D2, D3) followed by a brittle event (D4). The microscale study allowed us to highlight both an older relict deformation phase (D1), and to identify three metamorphic events (M1, M2, M3) which show multiple relationships with deformation phases.

D2 is the main deformation event in the area. Thanks to the observed geometry, pervasive foliation S2 and lineation of extension L2, it was possible to associate the phase D2 with a shear event associated with the development of mylonite. At the microscale, it is possible to observe porphyroclasts of quartz, garnet and feldspar that are stretched according to the direction of maximum extension; these elements allowed us to hypothesize that the area was subjected to a ductile deformation event on a regional scale which produces a large network zone.

Quartz dynamic recrystallization, mainly in the Grain Boundary Migration regime, provides deformation temperatures (>500°C) during D2. Active slip system in quartz, identified through the CPO (Crystalographic-preferred orientation) of quartz using the CIP method (Computer Integrated Polarization microscopy), supports this thermal regime.

Combining meso and microscale observation, it was possible to consider the shear zone network as characterized by a top-to-the E-NE sense of shear; compatible with a left transtensive kinematics.

Later, a high-temperature event (M3), linked to the Serre Batholith emplacement, overprint D2 structures as pointed out by static growth of micas, cordierite, andalusite and annealing of quartz.

Considering the chronological constraints related to the Serre Batholith, the paleogeographic position of Calabria and the deforming characteristics of this mylonite belt, compared to other shear zones (Corsica, Argentera, and Sardinia), it is hypothesized that the study area may have been affected by the activity of EVSZ, in a more external position, probably related to the Internal Nappe of Sardinia.

Further deformation, kinematics, flow regime and timing regime analyses are needed to clarify this working hypothesis.

# Tectono-metamorphic evolution of the Briançonnais Units along the southwesternmost sectors of the Alps: Insights from the Marguareis Massif (Western Ligurian Alps)

Sanità E.*[1-2], Di Rosa M.[2], Lardeaux J.M.[3], Marroni M.[2-4] & Pandolfi L.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Géosciences Azur, Université de Nice-Sophia Antipolis (France). [4] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* edoardo.sanita@unifi.it

*Keywords:* Briançonnais Units, HP metamorphism, Marguareis Massif.

In the Marguareis Massif, the SW-verging stack is composed of Helminthoid Flysch located in between Briançonnais Units (European continental margin, Vanossi et al., 1986). The latter are represented by the topmost Marguareis Unit (MU) and the bottommost Cabanaira Unit (CU) both involved in collisional processes into the Alpine wedge starting from middle Eocene age (i.e., Vanossi, 1986). Here, the Briançonnais Units show a Meso-Cenozoic sedimentary succession and recorded, during middle Eocene-late Eocene, a pre-coupling deformation history dealing with the overprinting of fold systems confined to each unit. These are developed at different structural levels. After the coupling of the units (late Eocene-Early Oligocene) the whole tectonic pile shared the same deformation history represented by flat-lying fold system and subsequent faults. Combining micro-scale structural observations, Chlorite-Phengite multi-equilibrium thermo-barometry and Illite Crystallinity index (IC) on middle Eocene metapelites we reconstruct the tectono-metamorphic history of the Briançonnais Units. Microstructural analysis highlights that only the $D1_{MU}$ and $D2_{MU}$ and $D1_{CU}$ events are characterized by metamorphic re-crystallization. The subsequent deformation, indeed, developed at shallower structural levels. $D1_{MU}$ event produced $S1_{MU}$ slaty cleavage marked by preferred orientations of Chl + Phg + Qtz + Alb + K-Fsp + Epd ±Cal whereas the $D2_{MU}$ event is testified by a $S2_{MU}$ crenulation cleavage outlined by Phg + Chl + Qtz + Alb + K-Fesp ± Cal. The $D1_{CU}$ event is represented by a $S1_{CU}$ slaty cleavage marked by very small grains of Chl + Phg + Qtz + Alb ± Cal. Thermobarometric estimations indicate for the $D1_{MU}$-related Chl-Phg couples a Pressure-peak conditions of 1.00-0.90 Gpa and 280-330°C. The retrograde path of the Marguareis Unit is well constrained by the Chl-Phg pairs re-crystallized during the $D2_{MU}$ event at 0.85-0.7 GPa and 230-300°C. For the Cabanaira Unit the IC was measured on the smallest phyllosilicates along the $S1_{CU}$. The latter suggests that the Cabanaira Unit is characterized by an epizonal metamorphic imprint. So, our results show that the prograde path is not recorded in the Marguareis Unit and the Chl-Phg pairs grown along the S1 and S2 foliations depict its retrograde trajectory. The exhumation already started during the D1 and it continues during the D2 up to the shallower structural levels into the Alpine wedge. The Cabanaira Unit seems recorded a different metamorphic history at lower pressure and temperature conditions into the Alpine wedge. So, petrological and structural data indicate that the Marguareis Units recorded HP-LT metamorphic imprint whereas the Cabanaira Unit recorded a epizone-related metamorphic history but both in a continental subduction setting.

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# Structural evolution and Pressure-Temperature-path of the Moglio-Testico Unit (Western Ligurian Alps): a re-appraisal

Sanità E.*[1-2], Di Rosa M.[2], Lardeaux J.M.[3], Marroni M.[2-4] & Pandolfi L.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Géosciences Azur, Université de Nice-Sophia Antipolis (France). [4] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* edoardo.sanita@unifi.it

*Keywords:* HP-LT Metamorphism, Moglio-Testico Unit, Alpine Orogeny.

The Moglio-Testico Unit (Western Ligurian Alps) is classically regarded as a fragment of the Ligure-Piemontese oceanic crust deformed during the building of the Alpine belt (Vanossi et al., 1986) and showing a very low-grade metamorphic imprint (Bonazzi et al., 1987). However, a roboust and updated dataset about its tectono-metamorphic history is lacking. To face these uncertains we performed a geological survey on the Moglio-Testico Unit cropping out between the Tanaro and Arroscia Valleys (Western Ligurian Alps). Here the Moglio-Testico Unit is characterized by a Late Cretaceous-Paleogene(?) sedimentary succession characterized by Palombini Shale that pass upward to a turbiditic sequence. The latter consist of marls and shales intercalated with arenitic beds passing upward to a fine-grained turbidites related to deep-sea to basin-plain environment.

We combined meso- to micro-scale structural analysis with Chlorite-Phengite multi-equilibrium thermo-barometry in order to constrain the tectono-metamorphic evolution of the Moglio-Testico Unit.

Two overprinted fold systems (D1 and D2) confined to the unit were documented. D1 event produced a S1 slaty cleavage associated to F1 isoclinal folds with scattered fold axis and axial planes dipping toward SW and NE. D2 event is marked by S2 crenulation cleavage associated to F2 tight fold showing NW-SE-direct fold axis dipping toward NW and SE and flat-lying to SW and/or NE-dipping axial planes. After the coupling of the units, the subsequent deformation events are represented by a fold system with sub-horizontal axial plane without metamorphic recrystallization and high-angle normal faults, both though to be developed at very shallower structural levels. During the D1 and D2 deformation events metamorphic re-crystallization, i.e., chlorite and phengite (Chl-Phg) grains, along the S1 and S2 foliation planes is present. Thermo-barometric estimations suggest that the Chl-Phg couples along the S1 are in equilibrium at higher pressure and temperature than those growth along the S2, drawing a P-T path coherent with a subduction setting.

Structural analysis and thermo-barometry allowed us to reconstruct the tectono-metamorphic evolution of the Moglio-Testico Unit. Our results indicate that the Moglio-Testico Unit recorded a polyphase deformation history under HP-LT metamorphic conditions probably during its subduction, accretion and subsequent exhumation into the Alpine accretionary wedge.

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# Imaging crust and mantle structure of the Western Alps by geophysical methods: controversies regarding the geological interpretation of the deep structure of the Western Alps

Schmid S.M.*

Institut für Geophysik, ETH Zürich (Switzerland).

*Corresponding author e-mail:* stefan.schmid@erdw.ethz.ch

*Keywords:* Western Alps, mantle lithosphere, crustal structure.

While various authors claimed and still claim slab detachment to have occurred in the Western Alps based on mantle tomography data (e.g., Handy et al., 2021), others (e.g., Malusà et al., 2021) recently proposed that no such slab detachment occurred, seemingly based on p-wave mantle tomography data (Zhao et al., 2016). However, it can be shown that, contrary to the interpretation of their own data by Malusà et al. (2021), the tomography data by Zhao et al. (2016) clearly indicate that such slab detachment occurred if these data are properly analysed in the context of geological data regarding the formation of the arc of the Western Alps. There is in fact no major difference between the mantle tomography data of Zhao et al. (2016) and those of Paffrath et al. (2021). Slab detachment in the Western Alps allows for SE-directed influx of asthenospheric mantle present below the European plate below the Adriatic lithosphere. This accommodates NE-directed roll back of the Apennines. Substantial counterclockwise rotation of western Adria and oroclinal bending is facilitated by a thin orogenic lithosphere (only crust?) present in the southern Western Alps due to slab detachment. A recently constructed large-scale crustal profile across the Western Alps across the Cottian Alps and the southern Dora Maira massif (Michard et al., accepted) based on field evidence reveals massive back thrusting and folding that so far was grossly underestimated. On a lithospheric scale such back-thrusting is supported by mantle tomography indicating that the entire Alpine crust underlying the Dora Maira massif (i.e., half of the internal Western Alps) being part of the European plate is underlain by the Ivrea geophysical anomaly that is part of the Southern Alpine (Adriatic) domain.

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# Low-temperature deformation in the Argentera Massif: distinction between Alpine and Variscan tectonics

Simonetti M.*

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* matteo.simonetti@isprambiente.it

*Keywords:* Argentera Massif, structural analysis, geochronology.

In the Western Alps the Argentera Massif (External Crystalline Massifs) represents a fragment of the dismembered Variscan Belt involved in the alpine tectonics. Most of the Alpine deformation in the basement is concentrated along low-grade ductile, brittle-ductile and brittle shear zones. Low-grade mylonitic and ultramylonitic schists present a deformation age of ~22 ($^{40}Ar/^{39}Ar$ on phengites; Sanchez et al., 2011) suggesting a complete reactivation of the older Variscan Ferriere-Mollières shear zone coupled with the formation of new structures (Fremamorta shear zone, Bersezio Fault). The detailed structural and geochronological study of the Ferriere-Mollières (FMSZ) shear zone revealed that variscan teranspressional deformation is still well preserved and a complex evolution under decreasing temperature from amphibolite facies down to greenschist facies conditions was recognized (Simonetti et al., 2021). The lower grade rocks of the FMSZ are always highly sheared ultramylonites gradually passing to higher grade less sheared rocks (dated between ~340-330 Ma ~320 Ma, U-Th-Pb on monazite) along a continuous deformation gradient without crosscutting relationship. Even if the partial reactivation of some sectors of the FMSZ is recognized in its southern part, the assumption that low-grade deformed rocks were only produced during the alpine event is not always verified. To discriminate between variscan and alpine shearing a detailed structural analysis was made to clarify the relations between sheared high- and low-grade rocks. Thanks to this approach several E-W oriented alpine shear zones with a reverse top-to-the-S sense of shear are recognized (Carosi et al., 2016). One of them is the decametric-scale Colle Panieris thrust which transports variscan amphibole-bearing mylonitic gneiss above Permo-Triassic sediments. The Bersezio Fault and the Fremamorta shear zone represent first-order alpine structures and those newly recognized shear zones are second- and third-order structures that further accommodate the nearly N-S shortening recognized during the Early Miocene. A detailed structural study of such structures at various scale could provide new information to better characterize the alpine deformation of Argentera Massif.

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# Dating the High Himalayan Discontinuity (HHD) in Sikkim (Eastern India)

Stellino L.* & Carosi R.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* letizia.stellino@edu.unito.it

*Keywords:* HHD, Sikkim, monazite.

Multidisciplinary approach, notably improved in the last 20 years in geological mapping, allowed the recognition of the High Himalayan Discontinuity (HHD) in the metamorphic core of the Himalayan belt (GHS). This discontinuity divides the GHS in two tectonic units, and it can be mapped from Western Nepal up to Bhutan for more than 1000 km along the strike (Cottle et al., 2015). According to Montomoli et al. (2015), the HHD and the other discontinuities in the GHS started their activity earlier than the Main Central Thrust; in particular, the HHD was active from ~28 to 18 Ma (monazite U-Th-Pb ages). The prosecution of the HHD in NW India has been recently documented by Benetti et al. (2021) recognizing the Badrinath shear zone (BSZ) in the Garhwal Himalaya, active at ~23 Ma. A strand of the HHD has been documented in Sikkim Himalaya (Chungthang-Thambi thrust; Chakraborty et al., 2019), but its age had not yet been directly constrained.

Our analysis showed that the HHD in Sikkim affected mainly biotite-garnet-bearing mylonitic gneiss. Kinematic indicators (group 1 mica-fish, asymmetric (sigma-type) porphyroclasts, s-c fabric and shear bands), pointed to top-to-the-S/SW sense of shear, in agreement with the BSZ-HHD shearing. Based on microstructural observations, the mylonitic phase that have been recognised in the HHD rocks was characterized by the mineral assemblages Qtz+Kfs+Bt+Ms+Grt+Sill+Pl.

Monazite, a common accessory phase rich in REE, represents a useful tool in petrochronology studies because it has been recognised the important role of the chemical zonings of these minerals, useful to get much information about the metamorphic story of the host-rock, thanks also to the new methods of analysis.

Therefore, 70 monazites (with dimensions from a few tens of μm to ~400 μm), from three samples collected within the HHD in Sikkim, were identified through a Scanning Electron Microscope (SEM-EDS), hosted at Earth Science Department of Turin University, and then, quantitative chemical analysis of these minerals were performed by the electronic microprobe (EMPA) JEOL 8200, hosted at the Earth Sciences Department of Milan University. The maps show a chemical pattern characterized by a depletion of Y and HREE and an enrichment of Th in the core, and a low-Th and high-Y pattern along the rim. Shearing of the HHD occurred during the retrograde path characterized by low Y and high Th rims in monazite.

Furthermore, the monazite U-Th-Pb in situ analysis was carried out using a laser-ablation, inductively coupled, plasma mass spectrometry at the CNR-Istituto di Geoscienze e Georisorse U.O. Pavia (Italy), using an Ar-F 193-nm excimer laser (GeolLas 102 from Micro-Las) coupled with a magnetic sector ICP-MS (Element I from Thermo-Finnigan).

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# Investigating the time of deformation and heat transfer in the Lepontine Dome (Central European Alps)

Tagliaferri A.*[1-2], Schenker F.L.[1], Schmalholz S.M.[2], Ulianov A.[2] & Seno S.[1]

[1] Dipartimento Ambiente Costruzioni e Design, Scuola Universitaria Professionale della Svizzera Italiana, Mendrisio (Switzerland). [2] Institute of Earth Sciences, University of Lausanne (Switzerland).

*Corresponding author e-mail:* alessia.tagliaferri@supsi.ch

*Keywords:* deformation, dating.

Deformation is a main topic when it comes to the study of (poly-)metamorphic crystalline basements: in which stage of the metamorphic history did it occur and how is it correlated to far-field thermo-tectonic processes? We can answer this question adopting a combined approach comprising geological mapping (performed over 30 kmq covering the Valleys of Ticino, Switzerland), meso- and micro-structural analysis, petrology and finally U-Pb geochronology on zircons. We applied this method to the high-grade rocks of the Lepontine nappes constituting the Penninic domain of the Central European Alps.

The Lepontine Dome is a metamorphic and structural dome formed by the nappe-stack of Europe-derived crystalline basement units. It is characterized by a widespread Barrovian metamorphism generally considered to peak end of Oligocene, after nappe formation. The relative mineral-zone and isograde boundaries have an asymmetric-concentric shape, that doesn't coincide with the dome shape defined by regional attitudes of foliation and thrust sheets. This metamorphic pattern suggests a post-thrusting thermal event. However, the pervasive NW-SE-directed amphibolite-facies mineral lineation and the local migmatites, both associated with top-to-the-foreland shearing, indicate that peak temperature conditions reached during nappe emplacement. Hence, a key element to solve this apparent paradox is to unravel the timing of the pervasive high-grade deformation.

Geological survey, focused on a N-S transect along the main tectonic contacts, permitted to sample leucosomes (in shear bands, boudinated and in complex deformed networks) of contact-parallel syn-tectonic migmatites and post-foliation aplitic to pegmatitic dikes to date their genesis through U-Pb zircon dating technique with LA-ICP-MS (Laser Ablation Inductively-Coupled Plasma Mass Spectrometry, 20 µm laser spot) and SIMS (SwissSIMS ion probe, 8x12 µm ions spot).

The ages of metamorphic zircon rims pinpoint at 31-33 Ma the deformation common to all the lithotypes, in different structural levels in the nappe pile, from north to south, coeval with migmatization and leucosomes genesis, hence considered to date the timing of deformation close to peak conditions. While the 22-24 Ma ages of magmatic zircons belonging to post-foliation granitic dikes represent the minimum age of ductile deformation cease, indicating a post-tectonic event affecting only the southernmost units, close to the SSB (Southern Steep Belt).

These events suggest the presence of two main heat pulses: the first related to thrusting, hence pervasive along the nappe boundaries and strictly related to deformation, and the second to magma/fluid advection and/or heat diffusion from the SSB. Which one of these is responsible for the overall Barrovian metamorphism is still unclear and quantitative thermo-kinematic numerical models will help us to discriminate the different scenarios in future studies.

# Petrology and Mineral Chemistry of the Mafic-Ultramafic Rocks from Indus Suture Zone, Western Ladakh: Implications for the Neo-Tethys Subduction

Talat A.*[1], Hiredya C.[2] & Irfan B.[1]

[1] University of Kashmir, Srinagar (India). [2] Inter-University Accelerator Centre, New Delhi (India).

*Corresponding author e-mail:* tahmad001@gmail.com

*Keywords:* Indus Suture Zone, Ladakh, Himalayas, Mafic-Ultramafic rocks.

The Indus Suture Zone (ISZ) of Ladakh Himalaya preserves the ophiolitic remnants of the Neo-Tethys Ocean. Part of these ophiolitic remnants are exposed at Khangral-Chiktan and Dras-Kargil sections along the ISZ, western Ladakh. The observed rock types include mafic-ultramafic cumulates, massive gabbros, diorites and basalts emplaced as faulted blocks over the Mesozoic Dras arc complex. Geochemically, the studied rocks show sub-alkaline tholeiitic characteristics with basalt, basaltic-andesite, andesite to dacite compositional variation. The ultramafic cumulates varies in composition from olivine bearing orthopyroxenite whereas, mafic cumulates from hornblende gabbro norite. The ultramafic cumulates depict nearly flat chondrite normalized REE-patterns [$(La/Yb)_N$ = 0.6–4.1] with prominent positive Eu-anomaly whereas, fractionated patterns are observed in mafic cumulates [$(La/Yb)_N$ = 2.3–3.6], gabbros [$(La/Yb)_N$ = 1.6–7.9], diorites [$(La/Yb)_N$ = 1.9–4.7] and basalts [$(La/Yb)_N$ = 6.4–12.3]. Multi-element patterns depict subduction-related geochemical characteristics such as enriched LILE (e.g., Rb, Ba, Th, U, K, Pb and Sr) and depleted HFSE (e.g., Nb, P, Hf) characteristics compared to primitive mantle. However, pillow basalts depict flat chondrite normalized REE-patterns [$(La/Yb)_N$ = 1–3] similar to NMORB. Presence of Mg-rich olivines, orthopyroxenes and clinopyroxenes while Ti-poor clinopyroxenes in mafic-ultramafic cumulates and gabbros reflect their derivation from previously depleted mantle sources at high pressure and temperature comparable to the base of the modern intra-oceanic island arc tholeiitic sequences. The present mineralogical and geochemical study suggest that the studied rock types exhibit close similarity to intra-oceanic subduction system contemporaneous to Dras-Suru-Shergol-Nidar ophiolitic slices of Ladakh. The latter were responsible for the closure of part of Neo-Tethys Ocean during Late Jurassic to Early Cretaceous.

# Aluminous metapelites as a key to constraining the P-T evolution of the Upper Lesser Himalayan Sequence (Central Nepal)

Tamang S.*[1], Groppo C.[1-2], Rolfo F.[1-2] & Girault F.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino. [3] Institut de Physique du Globe de Paris, CNRS-Université Paris Cité (France).

*Corresponding author e-mail:* shashi.tamang@unito.it

*Keywords:* Himalaya, aluminous metapelites, forward thermodynamic modelling.

The Lesser Himalayan Sequence (LHS) of the Nepal Himalaya is a classic example of an inverted metamorphic sequence, which experienced Barrovian metamorphism during the Himalayan orogenic cycle. Although the LHS represents, in terms of volumes, the bulk of the Himalayan thrust-belt, its metamorphic evolution has been much less constrained than that of the overlying Greater Himalayan Sequence (GHS), the general belief being that it experienced a low-grade metamorphism (i.e., biotite and garnet zones). However, previous studies showed that the upper structural level of the LHS experienced peak temperatures up to 630-650°C, consistent with the sporadic occurrence of staurolite and/or kyanite -bearing lithologies. Moreover, the overall Upper-LHS metamorphic evolution is still poorly defined because the correspondent P-T paths have been rarely reconstructed in detail.

As a contribution to a better understanding of the LHS metamorphic evolution, this study aims at constraining the P-T path of the Upper-LHS in a key area of central Nepal (Ganesh Himal region). The study focuses on aluminous metapelites because these lithologies are more prone to developing low-variant assemblages than other lithologies. The detailed petrographic, microstructural and minerochemical investigation of six aluminous metapelites shows that, in most cases, the peak assemblage includes aluminous porphyroblastic phases (i.e., garnet, staurolite, kyanite, plagioclase) statically overgrowing over the main foliation. The isochemical phase diagram approach, based on the principles of equilibrium thermodynamics, is used to constrain the P-T evolution of the studied samples.

The P-T path constrained for the Upper-LHS is characterized by a prograde moderate increase in both P and T up to peak-P conditions of 8.5-11 kbar, 580-600°C, followed by heating decompression to the thermal peak of 620 ± 20°C, 8.5 ± 0.2 kbar. This "clockwise" path is significantly different from the typical "hairpin" path (i.e., prograde loading followed by cooling decompression) registered in the Lower-LHS and supports those thermo-mechanical models that predict a period of slowdown (or quiescence) of the thrust activity in the lowermost structural levels of the Himalayan thrust-belt.

# From Greater India indentation to Eastward Tibet flow: a comparison between paleomagnetic and GPS data

Todrani A.*[1-2-3], Speranza F.[2], D'Agostino N.[2] & Zhang B.[4]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INGV, Roma. [3] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [4] School of Earth and Space Science, Peking University, Beijing (China).

*Corresponding author e-mail:* alessandro.todrani@uniroma3.it

*Keywords:* Tibet, paleomagnetism, GPS.

The Cenozoic evolution of SE Asia has been commonly related to the India-Eurasia collision and the Tibetan Plateau growth and collapse. The huge amount of geological data acquired in Tibet highlighted that the central Plateau is affected by a NW-SE oriented extension, accommodated by a SE-ward crust flow toward Indochina, channelized between the Sichuan basin and East Himalayan Syntaxis (EHS). Conversely, existing models described the continental crust deformation as accommodated by the extrusion of several hundreds of km wide rigid mega-blocks bounded by continental-scale strike-slip faults, or by tens-to-hundreds km wide quasi-rigid blocks affected by different geodetic velocities. Paleomagnetism is a reliable tool to assess the tectonic style deformation during the geological past, able to evaluate the vertical-axis rotation of crustal blocks and the displacement of the major strike-slip faults. Here we report on the paleomagnetism of middle Cenozoic (< 45 Ma) continental red beds exposed in the intra-continental Mula basin (East Tibet), where we successfully isolated the primary magnetization components from 17 sites supported by a positive fold test. The anisotropy of magnetic susceptibility suggested that post-collision thrust tectonics guided the basin formation and continued after the sediments deposition. Conversely, the paleomagnetic rotation pattern defined scattered rotations from ~30 counterclockwise (CCW) to ~90 clockwise (CW), defining that the Mula basin is dominated by a brittle upper crust fragmented into 2-5 km wide blocks. The lack of strike-slip faults with offset exceeding 1 km occurs among blocks and no regional strike-slip faults were documented nearby, implying that East Tibet is affected by a small crustal block rotation. Moreover, a wealth of paleomagnetic data were collected in Tibet-Indochina during the last fifty years, but their interpretations have been often conflicting. We re-evaluated -with modern and homogeneous criteria- a total of 357 Jurassic-Holocene paleomagnetic data from Tibet-Indochina. We compared the paleomagnetic rotation pattern with the geodetic rotation rate derived from the GPS velocity field, defining that paleomagnetic localities W-NW of EHS show a prevalence of CCW rotation occurred at ~50 Ma, whereas E-NE of EHS few CW rotations after 40 Ma were recorded. Moreover, widespread CW paleomagnetic rotations took place in Northern Indochina at 25-15 Ma after a diffuse remagnetization episode, whereas Pliocene-to-Holocene localities display slight-to-null paleomagnetic rotations. Therefore, we concluded that the scattered paleomagnetic rotation pattern of SE Tibet-N Indochina defines a crust broken in 1-10 km scale block during the EHS indentation between 25-15 Ma. Since 15-10 Ma the thickened Tibet crust started flowing E-SE-ward toward Indochina around EHS, and the present-day geodetic CW rotation is clearly at odds with the highly scattered paleomagnetic rotation pattern.

# S11.

# Composition and evolution of the oceanic lithosphere: a petrological, geochemical and geodynamic perspective


*Conveners and Chairpersons*

*Carlotta Ferrando (University of Pavia)*

*Valentin Basch (University of Pavia)*

*Arianna Secchiari (University of Parma)*

*Manon Bickert (University of Modena and Reggio Emilia)*

*Zeudia Pastore (Norwegian University of Science and Technology)*

 

# Seafloor spreading modes across the Charlie Gibbs transform system (52° - 53° N, Mid Atlantic Ridge)

Basch V.*[1], Skolotnev S.[2], Sanfilippo A.[3], Ligi M.[4], Peyve A.[2]
& the A.N. Strakhov Expedition S50 and A.N. Vavilov Expedition V53 Science Parties

[1] Istituto di Geoscienze e Georisorse, CNR, Pavia. [2] Geological Institute, Russian Academy of Sciences, Moscow (Russia). [3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [4] Istituto di Scienze Marine, CNR, Bologna.

*Corresponding author e-mail:* valentin.basch@gmail.com

*Keywords:* slow-spreading ridges, detachment faults, oceanic core complex.

The prominent Charlie Gibbs right-lateral multi-transform system (52°-53°N) offsets the Mid-Atlantic Ridge (MAR) by ~340 km. The transform system is formed by two distinct transform faults joined by a short ~40 km-long intra-transform spreading centre (ITR). The two adjacent MAR segments are influenced by both the Azores and the Iceland mantle plumes. Recently, high resolution multibeam surveys and a dense sampling program of the entire transform system, including the adjacent magmatically robust southern and northern MAR segments, were carried out during expeditions of R/V Celtic Explorer (Georgiopoulou et al., 2018), R/V A.N. Strakhov (Skolotnev et al., 2021) and A.S. Vavilov (October 2021). The new collected data evidenced a widespread occurrence of large bathymetric highs with corrugated surfaces and exhumed lower crust and mantle rocks on both sides of the intra-transform spreading axis. Morphological analyses of the intra-transform domain and magnetic data indicate that crustal accretion was driven by flip-flop detachment faulting (Cannat et al., 2019), with reduced melt supply and little axial volcanism. Such a tectonic spreading mode persisted for tens of millions of years within the intra-transform domain and led to the consecutive formation of the observed bathymetric highs. The along-axis variability of MORB chemistry and seafloor accretion styles across the Charlie Gibbs transform system are strictly related to changes in melt supply dependent on mantle temperatures and on large-scale mantle heterogeneities. Charlie Gibbs region is therefore a key case study of how seafloor accretion modes at a slow-spreading segment depend critically on the mantle thermal state and on its intrinsic compositional heterogeneity.

**A.N. Strakhov Expedition S50 and A.N. Vavilov Expedition V53 Science Parties***:* Sergey G. Skolotnev, Marco Ligi, Alessio Sanfilippo, Alexander A. Peyve, Yago Nestola, Sergey Yu. Sokolov, Lorenzo Petracchini, Kseniya O. Dobrolyubova, Valentin Basch, Alexey N. Pertsev, Carlotta Ferrando, Alexander N. Ivanenko, Camilla Sani, Anatoly, A. Razumovskiy, Filippo Muccini, Artem S. Bich, Camilla Palmiotto, Yuri V. Brusilovsky, Enrico Bonatti, Konstantin N. Sholukhov, Marco Cuffaro, Ilya A. Veklich, Vitaly N. Dobrolyubov, Ekaterina P. Ponomarenkob, Dmitry A. Kuleshovc, Nikolay A. Shkittin, Tatyana L. Pugachevad, Svetlana A. Dokashenkoe, Elizaveta S. Yakovenkoe, Pavel A. Gladkich.

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# Melt-rock interactions and evolution of the upper mantle at an Oman paleo-spreading centre (OmanDP, Wadi Tayin)

Battifora C.*[1], Basch V.[2], Crispini L.[1] & Rampone E.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* riccared3@gmail.com

*Keywords:* reactive melt percolation; mantle impregnation; depleted melt.

Petrological and geochemical studies of mid-ocean ridge basalts and abyssal peridotites have revealed the complexity of melting processes and melt migration mechanisms associated with the accretion of oceanic lithosphere. Additionally, processes associated with melt transport in the upper mantle below spreading ridges can profoundly impact the chemical evolution of the percolating melts and create lithological, microstructural and chemical heterogeneities within the percolated mantle.

Abyssal peridotites allow the study of mantle processes in present-day oceanic settings, but their sampling is exceptional and limited to the uppermost limit of the oceanic mantle. In contrast, ophiolites expose large mantle sections as well as mantle-crust relationships and make it possible to study large-scale variations in peridotites. During the 2018 onsite campaign, the Oman Drilling Project (OmanDP) has recovered two separate boreholes of the crust-mantle transition (CM sites), respectively 300- and 400-metres deep. In this framework, we study the microstructural and petrochemical complexity associated with multiple episodes of melt-rock interaction, exhumation and intrusion within the Oman upper mantle section. The studied harzburgites recovered at the crust-mantle transition exhibit a composite history of: *i)* high-pressure (spinel-facies) pyroxenite intrusion (e.g., Python & Ceuleneer, 2003); *ii)* spinel-facies sub-solidus (~ 850-900°C) recrystallization, forming granoblastic aggregates of orthopyroxene + clinopyroxene + spinel at the expenses of orthopyroxene porphyroclasts; *iii)* melt reactive porous flow, leading to partial dissolution of spinel-facies pyroxenes in pyroxenite layers and host harzburgite, and crystallization of interstitial olivine; *iv)*plagioclase-facies impregnation of the harzburgites and formation of gabbronoritic veinlets (An = 92 mol%); *v)* MORB-type gabbroic intrusion within the mantle harzburgites (An = 77 mol%, e.g., Python & Ceuleneer, 2003). Impregnation features and subsequent gabbroic intrusions thus track a clear change in the chemistry of migrating melts, possibly related to their hydrated composition (Koepke et al., 2009).

Unravelling the chronology, chemical signature and origin of the different melt percolation and intrusion events recorded in the uppermost mantle is crucial in constraining the very debated evolution of the geodynamic environment in which the Oman lithosphere evolved.

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# Serpentinization of Oceanic Peridotites: implication for geochemical cycles and carbon sequestration

Boschi C.*

Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* chiara.boschi@igg.cnr.it

*Keywords:* serpentinites, carbon sequestration, geochemical cycles.

Ultramafic rocks are a major component of the ocean lithosphere commonly exposed near and along slow- and ultra-slow spreading ridges and in ophiolites environments. The serpentinization of mantle rocks is the reaction of water with the mineral phases olivine and pyroxene to predominantly form serpentine, brucite, and magnetite. The mineralogical assemblages and textures are complex and reflect multiple phases of alteration, deformation, and veining during emplacement, hydrothermal alteration, and weathering. Serpentinization is a widespread process that occurs along mid-ocean ridges where tectonic activity causes exposure of mantle rocks to seawater. It has been studied in modern and fossil oceanic lithosphere as along the Mid-Atlantic Ridge (Früh-Green et al., 2003; Boschi et al., 2013) and at the Ligurian ophiolites (Schwarzenbach et al., 2021), among many others. During serpentinization, various elements (e.g., Mg, Ca, Cl, F, C, S, B, Sr) are exchanged between the rock and the interacting fluid. Additionally, oxidation of $Fe^{2+}$ in the primary mineral phases of olivine and pyroxene is oxidized to $Fe^{3+}$ resulting in the formation of $H_2$, while $CO_2$ can be reduced to $CH_4$; the release of H-rich fluids fueling microbial life is also relevant to the origin of life (Frueh-Green at al., 2003). As the oceanic lithosphere experiences significant geochemical transformation, serpentinization also controls the transport of elements (e.g., $H_2O$, C, S, B, Cl, F) into the mantle, and influences its seismic and rheological properties at convergent plate margins. Finally, serpentinites are also highly reactive with $CO_2$ such that they are prime targets for carbon sequestration (Boschi et al., 2009).

Hence, serpentinization has wide-ranging effects on various tectonic and magmatic processes and numerous geochemical cycles, strongly controlling the chemical exchange between hydrosphere, lithosphere, and biosphere and is considered a key player in the global cycles in the ocean and continental settings.

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# Crustal construction in magmatically robust slow spreading ridge settings

Cannat M.*[1], Chen J.[2] & Olive J.A.[3]

[1] Equipe de Géosciences Marines, Institut de Physique du Globe de Paris, Université de Paris (France). [2] Key Laboratory of Submarine Geosciences, MNR, Second Institute of Oceanography, Hangzhou (China). [3] Laboratoire de Géologie, CNRS - Ecole Normale Supérieure, PSL University, Paris (France).

*Corresponding author e-mail:* cannat@ipgp.fr

*Keywords:* oceanic lithosphere, crustal construction, magma supply.

Spreading modes (i.e., the combination of tectonic, magmatic and hydrothermal processes that control the formation of new oceanic plates at mid-ocean ridges) are now relatively well documented in magma-poor, detachment-dominated, slow-spreading ridge settings. We know less about the structure of slow spread oceanic lithosphere formed in magmatically robust settings. These settings are characteristic of the center of slow spreading ridge segments and represent about 50% of the total length of these ridges. Exposures of mid and lower crustal levels formed in such contexts are lacking in present-day oceans, and there are no clear ophiolitic analogues. While the generally accepted view is that the crust formed in these settings is magmatic, it is clear that its modes of crystallization, and its tectonic structure differ from those of the oceanic crust formed at fast spreading ridges. At fast spreading ridges, the flux of melt is high, the thermal regime is hot, faulting plays a minor role in plate separation, and melt resides at upper crustal depths in a steady state fashion, well within the reach of vigorous axial hydrothermal convection. At magmatically robust slow ridges, the melt flux is lower, and the thermal regime is colder, so that melt can only reside durably at mid crustal to greater depths, out of the reach of the most vigorous (high permeability) hydrothermal systems, while normal faults may develop significant offsets. Seafloor mapping at slow spreading ridge segment centers also commonly points to temporal variations in melt fluxes, and geophysical constraints suggest that melt may also form transient bodies at mid to upper crustal depths, triggering transient high temperature hydrothermal systems. Here, we use recently published thermal models (Chen et al., 2022), and geological constraints from slow spreading ridge segment centers, to explore the potential effects of varying the melt flux and melt emplacement depth with time at a given slow spreading ridge location, on crustal construction processes and on the respective contributions of faults and melt intrusions to accommodating plate divergence.

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# Alpine metamorphism in the far-west: new petrological constraints from the upper Chisone valley (Italian Western Alps)

Corno A.*[1], Mosca P.[2], Groppo C.[1], Borghi A.[1] & Gattiglio M.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* alberto.corno@unito.it

*Keywords:* Western Alps, tectono-metamorphic evolution, phase equilibria modelling.

The Alpine collisional belt comprises tectonic units belonging to different sectors of the continental paleomargins (either Adriatic or European) and of their interposed Piemonte-Liguria ocean (i.e., Alpine Tethys). During the orogeny, the units forming the axial sector of the Western Alps experienced partially different tectono-metamorphic evolutions, recording eclogite- or blueschist-facies metamorphic peaks. The identification of the large-scale tectonic processes driving subduction and exhumation of Alpine units requires first a reconstruction of the pre-collisional paleogeographic setting, and then a characterization of features and distribution of peak metamorphism across the belt.

We investigated these two latter key points in the tectonic pile exposed in the upper Chisone valley (Western Alps), where a progressive westward decrease of the alpine metamorphic peak conditions from eclogite to sub-greenschist facies has been notably described (for a review see Agard, 2021). In the investigated area, the Banchetta-Rognosa unit, consisting of continental and oceanic rock successions, is thought to belong to an ocean-continent transition zone and it is surrounded by different oceanic units made of thick sequences of calcschists and minor meta-ophiolitic bodies, from metric to kilometric in size. In particular, it is sandwiched by the lawsonite-blueschist facies Albergian unit, and juxtaposed to the epidote-blueschist facies Cerogne-Ciantiplagna unit.

The peak P-T conditions of these units were defined through the isochemical phase diagram approach (i.e., P-T pseudosections). The results of phase equilibria modeling point to a metamorphic peak of 20-23 kbar and 450-520°C for the Banchetta-Rognosa unit (Corno et al., 2021), and of 18-21 kbar and 380-430°C for the Albergian unit (Corno et al., 2022).

The constrained metamorphic peak of the Banchetta-Rognosa unit, typical of eclogite-facies conditions, is higher than previously believed as well as higher than that registered in the neighboring Albergian unit. These data allow to extend westward the eclogite-facies metamorphism in this sector of the Alpine axial sector, and to postulate a complex exhumation process to understand the current juxtaposition of units with different metamorphic peaks.

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# Pre-Alpine oceanic tectonostratigraphy of the high-pressure Lanzo Valleys Ophiolites Viù Valley, Western Alps)

De Togni M.*, Gattiglio M. & Balestro G.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* marcello.detogni@unito.it

*Keywords:* tectono-stratigraphy, metaophiolite, Alpine Tethys, Western Alps.

The Western Alpine Ophiolites represent the remnants of the Late Jurassic Alpine Tethys (Ligurian-Piedmont Ocean), and correspond to different tectonic units (i.e., the Piedmont Zone) stacked in the axial sector of the Alpine belt (Balestro et al., 2019). The meta-ophiolite units exposed along the inner Western Alps (i.e., the Internal Piedmont Zone) were metamorphosed under eclogite-facies metamorphic peak conditions and underwent extensive polyphase deformation during the Alpine subduction-exhumation cycle.

The Lanzo Valleys Ophiolites (LVO) tectonically lie both above Dora-Maira Unit (to the South, in Viù Valley) and Gran Paradiso Unit (to the North, in Ala Valley and, to a lesser extent, in Grande Valley), and correspond to an extended but poorly known ophiolitic complex (Leardi & Rossetti, 1985). New lithostratigraphic data have been collected and a new geological map has been realized in Viù Valley in order to improve the knowledge of the oceanic tectonostratigraphy of the LVO (De Togni et al., 2021). Despite the metamorphic-deformation overprint, the main lithological contacts are poorly sheared and not transposed, thus making pre-Alpine tectonostratigraphic reconstruction possible.

The LVO succession consists of serpentinite, metagabbro, metabasalt and metasediments, whose primary lithostratigraphic relationships highlight different stages of the oceanic evolution. Mantle rocks were firstly intruded by gabbroic melts (both Mg-Al and Fe-Ti -rich types) and then serpentinized and exhumed at the seafloor. This was followed by an effusive stage (i.e., metabasalt) and by deposition of carbonatic sediments interlayered by mafic breccia and sandstone, representing the syn-extensional succession. The latter was overlain by post-extensional sediments (i.e., quartzite, impure marble and calcschist), which sealed an articulated ocean floor morphology at Late Jurassic-Early Cretaceous times.

The reconstruction of LVO succession highlights the occurrence of a seafloor characterized by high mobility and tectonically unstable reliefs, evolved during extensional oceanic tectonics. At a regional scale these data can provide new further insights in the Alpine Tethyan evolution and, moreover, in the Alpine geodynamic framework of meta-ophiolites.

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# Evolution of the subcontinental lithosphere during Mesozoic Tethyan rifting: constraints from the External Ligurian mantle section (Northern Apennine, Italy)

Ferrari E.[1], Montanini A.*[1] & Tribuzio R. [2-3]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* alessandra.montanini@unipr.it

*Keywords:* mantle, pyroxenite, rifting.

Our study is focussed on mantle bodies from the External Ligurian ophiolites, within the Monte Gavi and Monte Sant'Agostino areas. Here, two distinct pyroxenite-bearing mantle sections were recognized, mainly based on their plagioclase-facies evolution. The Monte Gavi mantle section is nearly undeformed and records reactive melt infiltration under plagioclase-facies conditions. This process involved both peridotites (clinopyroxene-poor lherzolites) and enclosed spinel pyroxenite layers, and occurred at 0.7–0.8 GPa. In the Monte Gavi peridotites and pyroxenites, the spinel-facies clinopyroxene was replaced by Ca-rich plagioclase and new orthopyroxene, typically associated with secondary clinopyroxene. The reactive melt migration caused increase of $TiO_2$ contents in relict clinopyroxene and spinel, with the latter also recording a $Cr_2O_3$ increase. In the Monte Gavi peridotites and pyroxenites, geothermometers based on slowly diffusing elements (REE and Y) record high temperature conditions (1200-1250°C) related to the melt infiltration event, followed by subsolidus cooling until ca. 900°C. The Monte Sant'Agostino mantle section is characterized by widespread ductile shearing with no evidence of melt infiltration. The deformation recorded by the Monte Sant'Agostino peridotites (clinopyroxene-rich lherzolites) occurred at 750–800°C and 0.3–0.6 GPa, leading to protomylonitic to ultramylonitic textures with extreme grain size reduction (10–50 µm). Compared to the peridotites, the enclosed pyroxenite layers gave higher temperature-pressure estimates for the plagioclase-facies re-equilibration (870–930°C and 0.8–0.9 GPa). We propose that the earlier plagioclase crystallization in the pyroxenites enhanced strain localization and formation of mylonite shear zones in the entire mantle section. We subdivide the subcontinental mantle section from the External Ligurian ophiolites into three distinct domains, developed in response to the rifting evolution that ultimately formed a Middle Jurassic ocean-continent transition: (1) a spinel tectonite domain, characterized by subsolidus static formation of plagioclase, i.e., the Suvero mantle section (Hidas et al., 2020), (2) a plagioclase mylonite domain experiencing melt-absent deformation and (3) a nearly undeformed domain that underwent reactive melt infiltration under plagioclase-facies conditions, exemplified by the the Monte Sant'Agostino and the Monte Gavi mantle sections, respectively. We relate mantle domains (1) and (2) to a rifting-driven uplift in the late Triassic accommodated by large-scale shear zones consisting of anhydrous plagioclase mylonites.

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# Numerical modelling of a curved Mid-oceanic ridge with oblique kinematics along the Knipovich-Mohns segment (Arctic Ocean)

Ficini E.*[1-2], Cuffaro M.[2], Ligi M.[1] & Miglio E.[3]

[1] Istituto di Scienze Marine, CNR, Bologna. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [3] Dipartimento di Matematica, Politecnico di Milano.

*Corresponding author e-mail:* eleonora.ficini@bo.ismar.cnr.it

*Keywords:* mid-ocean ridges, numerical modelling, curved geometry.

Mid-oceanic ridges (MORs) are plate boundaries where two oceanic lithospheric plates move away from each other on either side of a fixed ridge, so that the hot rocks of the underlying mantle (i.e., the asthenosphere) flow upward beneath the MOR. As the plates steadily move away from an oceanic ridge, they are affected by thermal cooling, and these processes favor accretion to the base of the spreading plates. Recent advances in numerical models contribute to describe oceanic rift processes (e.g., Behn et al., 2007; Ligi et al., 2013), although complex geodynamic settings remain relatively unexplored. Here, we use the ASPECT software (Bangerth et al., 2021) to build 3D numerical models of a curved MOR, simulating the Knipovich-Mohns segment geometry in the Arctic Ocean, where plates are driven by strongly oblique spreading rates. The model uses a visco-plastic rheology which includes the approximation of both the asthenospheric and the lithospheric mantle, providing information on the deformation pattern within the mantle, as well as on melting beneath the MOR segments. Preliminary results suggest that the mantle upwelling is mainly focused in the narrow zone where the MOR makes a sharp bend, and provide some asymmetric patterns which affect temperature and viscosity fields, together with strain rate and fraction of melting in that area. This is in agreement with evidence in the field inferred by geophysical data in the region between the Knipovich and Mohns ridges, along the ultraslow-spreading Arctic mid-ocean ridge system. At this latitude, indeed, inversion images of electromagnetic and magnetotelluric data show an asymmetric rise of the mantle focused along the oblique and strongly curved zone, which also coincides with an asymmetric surface uplift at the seafloor (Johansen et al., 2019).

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# The role of melt/olivine ratio in dissolution and reactive crystallization: an experimental and microstructural study (Electron Back-Scattered Diffraction-EBSD) at 0.5 GPa

Grammatica M.*[1-2], Fumagalli P.[1], Borghini G.[1] & Capitani G.C.[3]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* michela.grammatica@unimore.it

*Keywords:* melt-olivine reaction, troctolite, EBSD.

Microstructural and chemical evidence supports the origin of olivine-rich troctolites from dunite infiltration followed by reactive crystallization of interstitial melts. Experiments on the origin of these rocks suggest that the melt/olivine ratio is a fundamental factor in basalt-dunite interactions (Borghini et al., 2018). However, its effects on the chemistry and reactive dissolution and crystallization processes are still not well defined.

The aim of this work is to experimentally evaluate the effect of melt/olivine ratio on mineral chemistry, melt and microstructural evolution of olivine-rich troctolites. We performed piston cylinder experiments at 0.5 GPa, T from 1200 to 1300°C, and 24 hours duration. The starting materials were San Carlos olivine ($Fo_{90}$) and a MORB-type glass (AH6), mixed together in different proportions (i.e., 10, 25 or 50 wt% of melt).

Run products at 1200°C consist of olivine, plagioclase, clinopyroxene and traces of glass, whereas at 1300°C consist only of olivine and glass. Olivine occurs both as large subhedral crystals with straight and lobate rims (~100 µm) or as smaller rounded grains (5-20 µm). At high melt ratio, olivine grain size increases and smaller rounded grains decrease. At 1300°C and high melt ratio, olivine dissolution and crystal growth is promoted, resulting in pronounced olivine grain boundaries tortuosity. At 1200°C, the olivine $X_{Mg}$ is not correlated with the melt amount, whereas at 1300°C, $X_{Mg}$ increases with increasing melt. The NiO content in olivine decreases from 1200 to 1300°C and was found anti-correlated with the melt amount at 1300°C. Clinopyroxene presents a $X_{Mg}$ ~0.87 ± 0.01 and plagioclase a $X_{An}$ ~0.65 ± 0.04. Reacted glasses at 1200°C show higher $SiO_2$ content and lower $X_{Mg}$ than at 1300°C. EBSD analyses suggest that the reaction processes with 50 wt% of melt at 1300°C, strongly affects the pre-existing dunite matrix, favoring annealing. The average intragranular deformation parameter defined by the Grain Orientation Spread (GOS), indicates that no differences occur between the two sets of olivine: the smaller and rounded olivine has a GOS ~0.49 and the larger one with straight and lobate rims has a GOS ~0.41. Hence, in terms of deformation grade, pre-existing olivine and the new crystallized one look similar.

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# Tectonic deformation and variable magma supply along the Mid-Atlantic Ridge axis south of the Romanche transform fault

Maia M.*[1], Briais A.[1], Petracchini L.[2], Cuffaro M.[2], Ligi M.[3], Brunelli D.[3-4], Grenet L.[1] & Hamelin C.[5]

[1] Laboratoire Geo-Ocean, CNRS-IFREMER-UBO-UBS, IUEM, Plouzané (France). [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [3] Istituto di Scienze Marine, CNR, Bologna. [4] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [5] Department of Earth Science, University of Bergen (Norway).

*Corresponding author e-mail:* marcia.maia@univ-brest.fr

*Keywords:* mid-oceanic ridges, Romanche transform fault, geodynamics.

The SMARTIES cruise (Maia et al., 2019) mapped and sampled a portion of the Mid-Atlantic ridge axis south of the Romanche transform fault (TF) and the east ridge-transform intersection (RTI). During the cruise, we acquired new high-resolution bathymetry and gravity data. Twenty-five dives with the French deep-sea submersible Nautile retrieved images, samples and magnetic data at chosen sites across the ridge axis, its flanks, as well as at peculiar off axis features, and at the Romanche TF. Additionally, 19 OBSs were deployed to investigate the regional seismicity over the six weeks of the cruise.

In the present work, we focused on the new high-resolution bathymetry and gravity data to study the crust and lithosphere deformation. The new data set revealed a complex ridge axis, with evidence of a significant decrease in melt supply towards the RTI as well as a marked ridge instability.

The data acquired during the Smarties cruise show large detachment faults marking the spreading style over the entire length of our survey. Furthermore, the survey shows a better-defined ridge axis than what was previously thought, with clear spreading segments offset by large non-transform discontinuities. At least three eastward ridge relocations were identified immediately south of the Romanche TF, rupturing a series of oceanic core complexes (OCCs) located in the African plate, east of the ridge axis. The position of these OCCs is unusual as they are usually observed at the inner part of the RTIs. Seafloor morphology and fault patterns reveal a marked obliquity in both the transform and the spreading directions, especially in the north and center of the study area. Directions orthogonal to the spreading are present in the south and, for older lithosphere, in the center of our study area. In lithosphere older than 10 Ma, the ridge axis seems to form a single magmatic segment between the Romanche and Chain TFs, without obliquity or unusual structures. From around 3 to 10 Ma, OCCs and detachment faults developed in the northern segment of the ridge axis between Romanche and Chain TFs. Overall, the complexity of the ridge axis appears to have increased in the last 3 Ma, with ridge obliquity accompanying the instabilities and ridge jumps. We interpret this pattern as reflecting a progressive decrease in the melt supply, in particular since 3-5 Ma. This may be related to a significant reduction of the ridge spreading rate as seen from kinematic models which allowed the cooling effect of the large offset Romanche TF to dominate the spreading processes in the area.

Maia M., Brunelli D. & Ligi M. (2019) - SMARTIES cruise, RV Pourquoi pas? https://doi.org/10.17600/18001107.

# Chemical and Nd-Hf isotope heterogeneity in depleted mantle domains from the Alpine-Apennine ophiolites.

Montanini A.*[1], Tribuzio R.[2-3], Rumbolo T.[1] & Bosch D.[4]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] Geosciences Montpellier, University of Montpellier (France).

*Corresponding author e-mail:* alessandra.montanini@unipr.it

*Keywords:* residual peridotite, Nd-Hf isotopes, melt-rock interaction.

Here we present geochemical and Nd-Hf isotope data for three depleted mantle bodies from the Northern Apennine (Internal Ligurian, IL), Tuscany (Monti Rognosi, MR) and Western Alps (Monte Civrari, MC) ophiolites. The Internal Liguride and Monti Rognosi peridotites record low to moderate degrees of depletion and display widespread mineralogical and geochemical evidence of melt-rock interaction. Their clinopyroxene compositional variation are mainly related to reactive percolation of residual peridotites by depleted, ortopyroxene-saturated melts in the plagioclase-stability field. Both Sm-Nd and Lu-Hf isotope systems were partially reset by the melt infiltration, but preservation of highly radiogenic $\varepsilon_{Nd}$ (up to +15) at the time of the associated MORB-type magmatism (162 Ma) are consistent with derivation of the IL and MR peridotites from ancient mantle reservoirs that experienced long-term depletion. The Monte Civrari mantle body includes domains of residual spinel harzburgites characterized by $TiO_2$ (0.05-0.15 wt.%) and $Na_2O$ (< 0.1 wt.%)-poor clinopyroxene, with striking LREE depletion ($Ce_N/Sm_N$ = 0.004-0.005), low HREE abundances ($Yb_N \sim$ 5-6) and fractionated HREE ($Gd_N/Yb_N$ = 0.4-0.5). The highly radiogenic Nd-Hf isotope composition of MC peridotites (initial $\varepsilon_{Nd}$ and $\varepsilon_{Nd}$ up to +29 and + 41, respectively) may reflect incorporation of refractory subcontinental lithospheric mantle (SCLM) in the oceanic lithosphere of the Jurassic Alpine Tethys. However, the thermal evolution of the MC mantle body points to rapid cooling and exhumation from asthenospheric conditions, similar to modern abyssal type peridotites (see also McCarthy & Müntener, 2019), which argues against a long residence time in the SCLM after melt extraction. REE and Nd-Hf isotope compositions of the MC peridotites may be reconciled with Jurassic re-melting of an asthenospheric source that underwent a first melting event, starting in the garnet stability field, in Palaeozoic times (> 300 Ma). The Nd-Hf isotopic contrast between Jurassic crustal products (Barry et al., 2017) and associated residual peridotites consolidates the notion that ancient depleted domains may be a significant constituent of the convecting upper mantle.

Barry T.L., Davies J.H., Wolstencroft M., Millar I.L., Zhao Z., Jian P., Safonova I. & Price M. (2017) - Whole-mantle convection with tectonic plates preserves long-term global patterns of upper mantle geochemistry. Sci. Reports, 7, 1-9.

McCarthy A. & Müntener O. (2019) - Evidence for ancient fractional melting, cryptic refertilization and rapid exhumation of Tethyan mantle (Civrari Ophiolite, NW Italy). Contrib. Mineral. Petrol., 174, 69.

# A geophysical study of the Monte Maggiore ultramafic massif

Pastore Z.*[1-2], Church N.[1], Uehara M.[3], Gattacceca J.[3], Zanella E.[4] & Vitale Brovarone A.[2]

[1] Department of Geoscience and Petroleum, Norwegian University of Science and Technology, Trondheim (Norway). [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [3] CEREGE-CNRS - UMR7330, Université Aix-Marseille (France). [4] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* zeudiap@hotmail.com

*Keywords:* serpentinization, magnetic properties, subduction zone.

The Monte Maggiore massif is in the northern end of Corsica and consists of a peridotite body surrounded by gneisses of continental origin. The peridotite body represents sub-continental mantle that underwent tectonic and magmatic evolution during the rifting stage of the Jurassic Ligurian Tethys oceanic basin and successive Alpine subduction to blueschist-facies conditions. The peridotites, mostly plagioclase- and spinel-lherzolites, are intruded by centimeter- to meter-thick gabbroic dykes and are variably serpentinized. Previous studies (e.g., Debret et al., 2014; Magott et al., 2020) have suggested these rocks were affected by at least two main serpentinization episodes, one during oceanization and the second during subduction.

Here, we carried out a ground magnetic survey and analyzed densities and magnetic properties of rocks (> 400 rock specimens) from more than 40 sites across the massif. These data were used to map lithological changes and to identify domains within the massif characterized by different degrees of serpentinization. The serpentinization process can indeed change the mineralogical assemblage and alter the petrophysical properties of the protolith causing significant contrast in magnetic and/or density properties with the unaltered surrounding rocks. Furthermore, we measured the anisotropy of magnetic susceptibility and compared results with the orientation and distribution of fractures and faults as well as with the rocks' layering and mineral foliation to evaluate the control of the Alpine tectonic deformation on the magnetic fabric of the rocks.

The magnetic survey data show a strong magnetic anomaly of up to 3000 nT above background in the southern part of the massif, at the thrusted contact with the gneisses. This anomaly is modelled as a northly dipping heavily serpentinized zone. Magnetic anomalies of lower amplitude and wavelengths between 2 to 300 m are observed both on top of the massif and at lower elevation, closer to the coast. Rock samples show wide ranges of densities and magnetic properties which reflect the petrological changes. Rocks' density ranges from 2.4 g/cm$^3$ to 3.2 g/cm$^3$. Rock magnetic susceptibilities range from $1 \times 10^{-4}$ to 0.2 (SI) with an average magnetic susceptibility of $2.7 \times 10^{-2}$ (SI) and the natural remanent magnetization (NRM) values range from less than 0.001 to 250 A/m with a median NRM of 1.43 A/m.

High-temperature experiments were also performed to investigate the magnetic mineralogy and temperature vs magnetic susceptibility curves suggest the occurrence of end-member magnetite as well as spinels with varying compositions. Demagnetization of the samples using both thermal and alternating field techniques suggest multiple components of the magnetization, compatible with multi-stage serpentinization reactions. Farther microscopy studies will help to get more insights into the magnetic and geological history of the Monte Maggiore peridotites.

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Magott R., Fabbri O. & Fournier M. (2020) - Seismically-induced serpentine dehydration as a possible mechanism of water release in subduction zones. Insights from the Alpine Corsica pseudotachylyte-bearing Monte Maggiore ophiolitic unit. Lithos, 362, 105474.

# An international project to test the 'orphan crust' model through scientific drilling: insights from the Kane Megamullion Oceanic Core Complex (23°N, Mid Atlantic Ridge)

Sanfilippo A.*[1], Dick H.J.B.[2], Klein F.[3], Edgcomb V.[2], Canales J.P.[2], Xu M.[4] & Tivey M.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA (USA). [3] Department of Chemistry and Marine Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA (USA). [4] South China Sea Institute of Oceanology, CAS Key Laboratory of Ocean & Marginal Sea Geology, Guangzhou (China).

*Corresponding author e-mail:* Alessio.Sanfilippo@unipv.it

*Keywords:* oceanic crust, mantle lithosphere, alteration.

Lithosphere at slow and ultraslow-spreading ridges consists of local magmatic centers constituted by gabbroic bodies of variable size and relatively short life spans. These are spaced at intervals of tens of kilometers, separated by serpentinized mantle sections with thin, even missing magmatic crust (Cannat et al., 2006). Here, there seems to be little or no underlying cumulate section to mass balance the lavas back to a primary melt, hence, can be referred as 'orphan crust'. Most deep scientific drilling focused at local magmatic centers (Dick et al., 2000) but the crust between magmatic centers is largely unknown, and often regarded as anomalous. Yet, if large portions of ocean floor are formed by an orphan crust, mantle and plutonic rocks can be subjected to chemical exchange with hot seawater, with important implications for plate tectonics, geochemical cycles, and the biosphere.

With this contribution, we present an IODP proposal to drill two 500-m deep holes on iconic mantle and lower crustal sections exposed at the Kane Megamullion, an oceanic core complex (OCC) located at 23°N on the Mid Atlantic Ridge (MAR) (Dick et al., 2008). Four principal objectives are (i) test the seismic and geologic interpretations of the sub-surface structure; (ii) test the variability of crustal architecture with decreasing melt flux in 3D; (iii) examine hydrothermal alteration processes in lower crustal and mantle lithologies as a function of depth and temperature and (iv) explore heterotrophic and chemolithoautotrophic lifestyles in the lower oceanic crust and upper mantle. This fundamental test is the framework required to fully explore the nature of the ocean crust and mantle at slow spreading ridges, and assess the exchange of heat and mass between the Earth's interior and the oceans taking into account an architecture that is radically different from that envisioned in layered ocean crust models.

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Dick H.J., Tivey M.A. & Tucholke B.E. (2008) - Plutonic foundation of a slow-spread ridge segment: Oceanic core complex at Kane Megamullion, 23°30'N, 45°20'W. Geochem. Geophys. Geosyst., 9.

# Mantle rocks exhumed along an ocean-continent transition: revisiting the Iberian margin peridotites (ODP Leg 149 and 173)

Secchiari A.*[1], Godard M.[2], Montanini A.[1] & Luguet A.[3]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Géosciences Montpellier, Université de Montpellier (France). [3] Institut für Geowissenschaften, Universität Bonn (Germany).

*Corresponding author e-mail:* arianna.secchiari@unipr.it

*Keywords:* mantle, Iberia, IODP.

Investigating peridotite samples exposed along ocean-continent transitions is crucial to shed light on processes occurring in the upper mantle during lithospheric breakup, unravelling, at the same time, source heterogeneity and inheritance.

More than three decades ago, mantle rocks were recovered along the West Iberian margin during several ODP cruises (Leg 103, 149, and 173; see Abe, 2001; Chazot et al., 2005). Despite being one of the few sites worldwide where mantle has been accessed through scientific drilling, Iberian peridotites remain poorly characterized.

Here, we revisit Iberian peridotites through a combined petrological and geochemical study performed on a new set of mantle samples from ODP Holes 899B, 1068A, and 1070A. Hole 899B peridotites are relatively fresh, clinopyroxene-rich (≈ 5-8 vol.%) tectonite harzburgites. They mostly consist of deformed olivine (≈ 80-85 vol.%), showing variable Fo contents (89.1-92.1), and low amount (≈ 10-12 vol.%) of exsolved, Mg-rich orthopyroxene. Dark brown spinel (< 1 vol.%, Cr#=0.198-0.483; $TiO_2$=0.10-0.72) mainly occurs as elongated grains, sometimes rimmed by altered plagioclase.

In contrast to Hole 899B, peridotites from Holes 1068A and 1070A are highly serpentinized. Samples from Hole 1068A have chromian spinel (Cr#=0.253-0.376) mantled by a fine-grain white rim, possibly representing a pseudomorph after plagioclase. Clinopyroxene relics display highly variable $Al_2O_3$ (3.77-7.25 wt.%) and $TiO_2$ contents (0.38-0.75 wt.%), in contrast to the lower and more homogenous values of Hole 1070A samples (3.87-4.70 wt.% and 0.14-0.20 wt.% for $Al_2O_3$ and $TiO_2$, respectively). High Mg# (0.915-0.920) olivine and orthopyroxene with low- to moderate $Al_2O_3$ contents (2.52-3.70 wt.%) are only preserved in Hole 1070A.

In situ trace element investigation revealed convex-upward patterns for Holes 899B and 1068A clinopyroxene, in the range of modern abyssal peridotites. Clinopyroxene shows LREE-depleted segments ($La_N/Sm_N$ = 0.01-0.27) and flat HREE for $Yb_N \approx 10$, coupled to Eu negative anomalies. Orthopyroxene of Hole 899B yields low REE concentrations ($HREE_N \leq 1$) and spoon-shaped patterns, except for the plagioclase-bearing sample, which exhibits a straight pattern ($La_N/Yb_N$ = 0.001-0.02) and negative Eu anomalies. Hump-shaped REE patterns with steep LREE slopes ($La_N/Sm_N$ = 0.003-0.01) and flat HREE segments are observed for Hole 1070A orthopyroxene.

Our preliminary results indicate that the mantle exhumed along the ocean-continent transition of the Iberian margin experienced variable degrees of depletion and melt/rock interaction.

Abe N. (2001) - Petrochemistry of serpentinized peridotite from the Iberia Abyssal Plain (ODP Leg 173): its character intermediate between sub-oceanic and sub-continental upper mantle. Geol. Soc. (London), Spec Publ., 187, 143-159.

Chazot G., Charpentier S., Kornprobst J., Vannucci R. & Luais B. (2005) - Lithospheric mantle evolution during continental Break-up: the West Iberia non-volcanic passive margin. J. Petrol., 46, 2527-2568.

# Onset of hydration in the lower oceanic crust from the Atlantis Bank oceanic core complex (Southwest Indian Ridge)

Tribuzio R.*[1], Ferrando C.[1], Sanfilippo A.[1] & Zanetti A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.
[2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* tribuzio@crystal.unipv.it

*Keywords:* late-stage magmatism, gabbro, amphibole.

We present a petrological and geochemical investigation of amphibole-bearing felsic veins and brown amphibole veins drilled at Atlantis Bank, a gabbroic oceanic core complex from Southwest Indian Ridge. The main purpose is to unravel the interplay among magmatism, hydrothermalism and tectonics during the early exhumation of the lower oceanic crust. Amphibole from the felsic veins has low Mg# [$Mg/(Mg+Fe^{2+}_{tot})$], high contents of $TiO_2$, MnO and $K_2O$, high concentrations of incompatible trace elements (e.g., Nb, Zr, Y and Rare Earth Elements), and negligible Cl. The associated plagioclase has anorthite ranging from 34 to 14 mol%, which negatively correlates with $K_2O$ (0.2 to 0.6 wt%). Geothermometric evaluations for the crystallization of the felsic veins gave a wide temperature interval of 880-680°C, which most likely reflects a magmatic fractional crystallization process controlled by separation of plagioclase and minor amphibole. We envisage that the parental melts of the felsic veins formed by a process of extreme evolution starting from MORB, after crystallization of gabbros rich in Fe-Ti-oxide phases. The brown amphibole veins occur at depth <230 m and typically include minor amounts of plagioclase. In these veins, amphibole has low $K_2O$ and 0.2-0.3 wt% Cl, and the coexisting plagioclase has nearly homogeneous compositions, characterized by about 32 mol% anorthite and low $K_2O$. The crystallization of the brown amphibole veins is estimated to have occurred 790 ± 20°C. Compared to the host gabbros and included clinopyroxenes, amphibole from the brown amphibole veins has lower Mg# and higher $TiO_2$ and MnO, and higher concentrations of incompatible trace elements. These chemical variations argue against a development of the amphibole veins through to interaction of the gabbros with seawater-derived fluids alone. We propose that the onset of the brittle tectonic regime in the exhuming gabbros formed a fracture network that allowed interaction between seawater-derived fluids migrating downward, and late-stage residual melts (i.e., similar to those feeding the felsic veins) rising through the gabbroic sequence.

# Late-stage melt injections in the lower oceanic crust: the amphibole-rich granoblastic dikes within Atlantis Bank (Southwest Indian Ridge)

Tribuzio R.[1], Ferrando C.*[1], Mariani D.[1] & France L.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.
[2] CRPG, CNRS - Université de Lorraine, Nancy (France).

*Corresponding author e-mail:* tribuzio@crystal.unipv.it

*Keywords:* late-stage magmatism, gabbro.

Diabase dikes are described in slow-spreading oceanic crust as representing intrusions of hot primary basaltic melts frozen in a relatively cool host gabbro. These dikes are made up of anhydrous minerals (i.e., mostly plagioclase and clinopyroxene), consistent with the low $H_2O$ contents in most Mid-Ocean Ridge Basalts (MORB). Unexpectedly, most of the sampled diabase dikes drilled into the gabbroic Oceanic Core Complex of Atlantis Bank (57°E, Southwest Indian Ridge; Integrated Ocean Discovery Program Expedition 360, Hole U1473A) include abundant brown amphibole [Amp] (up to 50 vol%) associated with plagioclase [Pl] and accessory amounts of pyroxene, ilmenite and Fe-sulfides, and typically display granoblastic texture. The finding of amphibole-rich felsic material along the dike-gabbro contacts led the Expedition to hypothesize a petrogenetic scenario driven by reaction between late MORB injections and hydrothermally altered gabbros. The present study focuses on the origin of water in the U1473A Amp-rich granoblastic dikes, to elucidate the timing and the chemical evolution of late-stage melt injections in the lower oceanic crust.

The inner domains of the Amp-rich dikes locally preserve intergranular textures with prismatic Pl crystals, and fluidal textures defining a magmatic foliation, and have bulk-rock compositions encompassing those of MORB. The dike rims are characterized by granoblastic texture and display chemically evolved bulk-rock compositions. Brown Amp (edenite to pargasite) has relatively high $TiO_2$ (1.9-3.1 wt%) and low Cl (<0.03 wt%), with no substantial chemical variability within single dikes and associated felsic material. In addition, the oxygen isotopic signature of brown Amp is nearly homogeneous ($\delta^{18}O$ = +5.5‰ ± 0.6), documenting equilibrium conditions with MORB. The anorthite contents in Pl ranges from 63 to 29 mol% and is typically higher in the inner domains of the dikes. Consistently, Amp-Pl equilibrium temperatures are slightly higher (T ~910°C) in dike cores than in dike rims and associated felsic material (T = 830-860°C).

We argue against the involvement of a seawater component in the formation of the Amp-rich dikes. We propose the following scenario for the emplacement of the Amp-rich dikes: (1) primitive basaltic melts intruded into an almost solidified gabbro; (2) the crystallizing dikes interacted with hydrous melts residual after crystallization of olivine, plagioclase and clinopyroxene in the host gabbros; (3) after complete solidification of the dike-gabbro systems, slow cooling conditions triggered recrystallization and development of granoblastic textures into originally fine-grained dike rims.

# S12.

# Growth, recycling and differentiation of the continental crust


*Conveners & Chairpersons*

*Michele Zucali (University of Milano - La Statale)*

*Simona Ferrando (University of Torino)*

*Patrizia Fiannacca (University of Catania)*

*Sergio Rocchi (University of Pisa)*

# Unravelling the tanscrustal magmatic system in the Colli Albani volcanic complex through trace element mapping

Ágreda López M.*[1], Petrelli M.[1], Šala M.[2], Perugini D.[1] & Jorgenson C.[3]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Department of Analytical Chemistry, National Institute of Chemistry, Ljubljana (Slovenia). [3] Department of Earth Sciences, University of Geneva (Switzerland).

*Corresponding author e-mail:* monica.agredalopez@studenti.unipg.it

*Keywords:* mafic magmatic systems, trace element mapping.

Mafic magmas usually erupt effusively due to their low viscosity. However, they sometimes behave explosively, and they can even generate large volume caldera-forming eruptions as observed in the case of the Colli Albani with up to 63 km$^3$ dense rock equivalent per eruption (Giordano & CARG Team, 2010).

The effusive-explosive transition in mafic magmas is a complex problem that is still largely debated (Roggensack et al., 1997; Andújar & Scaillet, 2012). It could represent a significant risk for the surrounding populations, often used to underestimate the hazard of such volcanoes. The Colli Albani is a mafic alkaline volcano located 30 km SE of Rome and has produced both effusive and highly explosive volcanic products.

Trace element mapping in crystals has been previously demonstrated to be useful to decipher textural complexities and chemical variations that helped to understand and reconstruct the pre-eruptive history of an eruption on a crystal-scale (Ubide et al., 2015).

In this study, we present the results of trace-element mapping in clinopyroxenes crystals from the Colli Albani volcano used as a tool to investigate the effusive-explosive transition in this particular complex system. The ultimate aim is to better understand the mantellic and transcrustal processes involved in the generation and evolution of those magmas and to constrain the factors controlling the change in the eruptive style in mafic systems.

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# Use and misuse of geochemical records to decipher fluid regime during crustal melting

Bartoli O.*

Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* omar.bartoli@unipd.it

*Keywords:* anatectic granite, water, migmatite.

The diverse fluid regimes during melting of the metasedimentary crust have been often discriminated on the basis of the composition of anatectic granitoids, with granites indicating fluid-absent melting conditions and trondhjemitic compositions suggesting the addition of external water in the source region. The lack of abundant metasedimentary-derived trondhjemites in the geological record is supposed to prove the minor role of water-fluxed melting in the crustal maturation. In terms of trace elements, instead, Rb, Sr and Ba contents and their ratios have been commonly used to discriminate dehydration vs. water-fluxed melting scenarios. Here I show that reconciling results of melting experiments, thermodynamic modeling and nanogranitoid study brings out a different picture. Equilibrium thermodynamics cannot properly reproduce melt compositions of the selected benchmark experiments, with the latter having trondhjemitic compositions mainly for the metastable behavior of muscovite during laboratory runs. The formation of sufficient volumes of extractable trondhjemitic melts is related to high pressure melting conditions (≥8 kbar at 700°C and ≥11 kbar at 750°C) or K-poor bulk rock compositions, rather than to the only presence of water. At low-to medium-pressure, crustal melts are granites in composition, whatever the fluid regime is. It is inferred that the abundance of anatectic peraluminous granites (compared to metasedimentary-derived trondhjemites) does not imply a dry nature of the orogenic crust. Likewise, the use of LILE (Rb, Sr and Ba) signatures may lead to erroneous conclusions on the fluid regime of the deep continental crust

# Quantifying crustal magma fluxes to unveil their role on volcanic activity, growth of differentiation of the crust and the formation of ore deposits

Caricchi L.*

Department of Earth Sciences, University of Geneva (Switzerland).

*Corresponding author e-mail:* luca.caricchi@unige.ch

*Keywords:* magma flux, plutons, volcanic eruptions.

The rate of magma input into the Earth's crust exerts a first order control on its thermal evolution, the rate of accumulation of eruptible magma, the ratio between plutonic and volcanic material and the capacity of magmatic systems to form ore deposits. As such the flux of magma through the crust is a fundamental parameter defining the temporal evolution of intensive and extensive parameters within magmatic plumbing systems. However, while fundamental, magma injection and transfer occur at inaccessible depth and can only be quantified using indirect methods.

I will first present a series of proxies we have developed to quantify the rate of magma input and transfer through the crust, and then discuss how this parameter can be used to assess the temporal evolution of the thermal and chemical architecture of magmatic plumbing systems, determine the maximum size of impending eruptions, and define the potential of a magmatic systems to be associated with economic mineralisations.

# Probing the hottest melts from Earth's continental crust

Carvalho B.B.*[1], Cesare B.[1], Bartoli O.[1], Satish-Kumar M.[2], Petrelli M.[3], Kawakami T.[4], Hokada T.[5] & Gilio M.[6]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Faculty of Science, Niigata University (Japan). [3] Dipartimento di Fisica e Geologia, Università di Perugia. [4] Department of Geology and Mineralogy, Graduate School of Science, Kyoto University (Japan). [5] Geoscience Group, National Institute of Polar Research, Tokyo (Japan). [6] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* bruna.borgescarvalho@unipd.it

*Keywords:* melt inclusions, granites, ultrahigh temperature metamorphism.

Ultra-high temperature (UHT) metamorphism is considered the most extreme type of regional metamorphism with peak temperature exceeding 900°C and pressure ranging from 5 to 18 kbar. Due to the strongly residual character of UHT granulites the majority of studies have focused on the petrological aspects of solids forming the residuum assemblages and rarely on the geochemical characterization of UHT anatectic melts. Consequently, the impact of UHT anatexis on granite petrogenesis and on the geochemical differentiation of the continental crust still remain unclear. Aiming to fill such gap, in this contribution uses tiny droplets of anatectic melt (i.e., melt inclusions) preserved in peritectic garnet of UHT granulites from Rundvågshetta (Lützow-Holm Complex, East Antarctica) to fully investigate the composition of melts produced by the continental crust at its hottest type of metamorphism.

The rock is a coarse-grained heterogeneous metapelitic granulite with a predominant mafic residual domain and a relatively minor felsic domain. The mineral association in the mafic domain contains orthopyroxene + sillimanite + quartz + garnet + K-feldspar + cordierite + rutile ± sapphirine ± biotite ± plagioclase. In contrast, the more felsic domain is composed of mesoperthite + Qz + garnet + sillimanite + brown biotite + rutile, but is free of orthopyroxene. Cores of garnet porphyroblasts in these melt-rich domains contain clusters of glassy melt inclusions (GI) and crystallized melt inclusions (nanogranitoids; NI) together with multiphase fluid inclusions and accessory phases. Sapphirine + quartz pair may occur as trapped phases within NI and are a good constraint for the entrapment of UHT melt. Zr-in rutile thermometer of crystals closely associated to the melt inclusions indicate temperatures up to 950°C whereas crystals in matrix of the rock reach up to 1000°C.

Glasses are weakly peralkaline to weakly aluminous rhyolites, have high $SiO_2$ (76-78 wt.%), very high $K_2O$ (6.5-10 wt.%) and extremely low CaO and FeO+MgO. $P_2O_5$ contents are low and not consistent with the values predicted by apatite solubility models at T>900°C. Similarly, Zr contents are lower than expected. Micro-Raman investigation suggest that the $H_2O$ contents of these glasses range from 0 to 3.4 wt.%.

Results show that anatexis of metapelites at extremely hot conditions generates highly silicic, weakly peraluminous, strongly potassic magmas with low $H_2O$ contents. Despite the difference in some trace elements, results suggest that UHT melts may represent a component to ferroan (A-type) granites, therefore the UHT anatexis also plays a role on crustal differentiation.

# Permian evolution of the lower continental crust: the example of the Valpelline Unit in the Austroalpine Domain (Western Alps, Italy)

Caso F.*

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* fabiola.caso@unimi.it

*Keywords:* high-temperature deformation, lower continental crust, melt.

High-temperature deformation and metamorphism provide crucial insights into the growth and the evolution of the deep continental crust at different geodynamic contexts (i.e., extensional and compressional). Permian lithospheric extension led to a high-temperature regime that affected the Variscan continental crust, nowadays fragmented and widespread worldwide, and within the Alpine belt. The subsequent Alpine high-pressure and low-temperature imprint, related to the subduction-collision event, has almost totally superimposed this extension-related HT metamorphism, leaving only small portions preserved. The Valpelline Unit (Dent-Blanche Tectonic System, Austroalpine Domain) is an example of those pre-Alpine Permian portions of lower continental crust (i.e., high-grade gneiss, migmatite, amphibolite and marble; Pesenti et al., 2012; Manzotti & Zucali, 2013) that almost completely escaped the Alpine overprint. The production, the segregation and the consumption of melt associated with granulite-facies rocks result in complex meso- and microstructural patterns that make difficult to reconstruct the relationships between metamorphism and deformation (Sawyer, 2008). Despite data about meso-, microstructural evolution and metamorphism in the Valpelline Unit already exist, they are localized in restricted sectors of the entire unit (Manzotti & Zucali, 2013) or outdated (Gardien et al., 1994). Therefore, by combining multiscale structural analysis with geothermobarometric estimates by EMPA chemical analyses, this contribution provides a detailed litho-structural overview, focusing particularly on migmatization processes. Understanding the mechanisms active during melt-present deformation and the resulting fabric relationships represents a solid base needed to address further studies (e.g., P-T-d paths, geochronology, partitioning of REE between melt and restite) on preserved pre-Alpine basements which could provide new interpretations regarding the Permian HT tectonics affecting these deep continental fragments.

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# Melting the mafic crust: multiple anatectic events at Hooper mine, Adirondacks (New York State US)

Ferrero S.*[1], Nicoli G.[2], Darling R.[3], Yakymchuk C.[4], Wunder B.[5] & Tollan P.E.[6]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Institute of Geosciences, University of Potsdam (Germany). [3] Geology Department, State University of New York, Cortland, NY (USA). [4] Department of Earth & Environmental Sciences, University of Waterloo (Canada). [5] German Research Centre for Geosciences, Potsdam (Germany). [6] Department of Earth Sciences, ETH Zürich (Switzerland).

*Corresponding author e-mail:* silvio.ferrero@unica.it

*Keywords:* TTG, nanogranitoids, garnet.

The Adirondacks belong to the Grenville Province and mainly consist of intrusive bodies and limited amounts of sediments, metamorphosed during the Ottawan Orogeny (1090-1050 Ma). The rock exposed in the Gore Mountain area at Hooper Mine are partially melted mafic granulites. This site is located 5 km NW of the Barton Mine, home to the largest garnet megacrysts ever reported. The Hooper mine granulites consist of medium grain size plagioclase, green hornblende and garnet in proportion 60:20:20, and the garnet contains quartz, rutile and melt inclusions (MI), similarly to those reported in Barton Mine (Ferrero et al., 2021).

Two types of garnet were distinguished based on size, chemical zoning, habitus as well as their MI compositions. Type 1 garnets (G1) are large, euhedral porphyroblasts of diameter >5 cm, whereas type 2 garnets (G2) are significantly smaller, <1 cm in diameter, and xenoblastic in shape. In G1 the chemical zoning is weak and inclusions are scattered randomly. G2 are overall similar in composition to G1, with the exception of low Ca and Y in the MI- and quartz-bearing domains. MI in G1 are crystallized to quartz, kumdykolite/albite, amphibole(s) and minor amounts of phlogopite, and can be re-homogenized at 940°C / 1.0 GPa to a trondhjemitic glass. MI in G2 instead crystallize to quartz, kokchetavite/K-feldspar, kumdykolite/albite and phlogopite, and re-homogenize at 900°C / 1.0 GPa to a granitic glass. The latter is close to the T from Ti-in-quartz thermometer in G2, ~850°C at 1.0 GPa. Preliminary data on MI trace elements also show significant differences between the two types of melts, supporting the hypothesis of two separated melting events. Stable O and H isotopes in hornblende ($\delta^2$H: -62 to -73 0/00 and $\delta^{18}$O: 4.7 to 6.7 0/00) records the primary magmatic $\delta^2$H signature of the protolith and indicates that partial melting occurred in a closed isotopic system. Such range of melt compositions, combined with the information previously collected in the Barton Mine, defines a trend characteristic of primitive TTG melts or TTG embryos. When combined with different proportion of peritectic phases (i.e., garnet, plagioclase and quartz), these melts reproduce the full bulk rock TTG chemistry range.

In a nutshell, the Mesoproterozoic mafic lower crust of the Adirondacks appears to be a perfect laboratory to clarify the genetic link between MI, early granitoids, plate tectonics and the formation of the continental crust (Nicoli & Ferrero, 2021).

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# Inferring melting conditions from composition of granitoid rocks: the controversial case of S-type trondhjemites

Fiannacca P.*[1], Basei M.A.S.[2], Cirrincione R.[1] & Russo D.[1]

[1] Dipartimento di Scienze Biologiche Geologiche e Ambientali, Università di Catania. [2] Instituto de Geociências, Universidade de São Paulo (Brazil).

*Corresponding author e-mail:* patrizia.fiannacca@unict.it

*Keywords:* water-fluxed melting, high pressure, collisional belts.

Trondhjemitic plutons and leucosomes of metasedimentary derivation are largely considered the typical product of water-fluxed melting (WFM, e.g., Weinberg & Hasalova, 2015). Nevertheless, some recent studies (Fiannacca et al., 2020; Fiannacca & Cirrincione, 2020; Bartoli et al., 2021) have pointed out that inferring melting conditions only from the geochemical composition of granitoid rocks is not a valid approach. First, it is necessary to assess through microstructural investigations if these compositions truly reflect crystallization from a trondhjemitic magma, since the same compositions can be generated by cumulus or metasomatic processes. Then, the compositional data can be crossed with useful constraints, such as results from experimental work, thermodynamic modelling and nanogranitoid investigations, and linked to the geotectonic context. Late Variscan S-type trondhjemites from the Pizzo Bottino Pluton and host-rock migmatites in the Peloritani Mountains (NE Sicily) have petrographic and geochemical features consistent with their origin as near-pure melts from WFM of metagreywackes, at c. 1.0 GPa and 700°C. Evaluation of the main factors controlling the compositions of granitoid magmas led Fiannacca & Cirrincione (2020) to propose that both high pressure and water are required to produce trondhjemitic melts. In southern Italy, trondhjemites formed close to the collisional baric peak, in accordance with the assumption that WFM generate the earliest melts during prograde orogenic evolution of collisional belts. It is, however, to point out that WFM does not produces only trondhjemites since K-rich granitoids, which typically form by fluid-absent melting, can also be produced by WFM at medium-low pressure. On the other hand, S-type trondhjemites are not usually formed by fluid-absent melting, nor by melting at low pressure. They typically form by water-fluxing melting at high P (and relatively low T), close to the collisional peak. Therefore, despite WFM is not uniquely linked to trondhjemitic composition, S-type trondhjemites can still be considered important markers of crustal evolution, since their occurrence is typically associated with early crustal melting in collision-related settings. On the other hand, the reason why S-type trondhjemites are rather uncommon in the geological record still remains to be explored.

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# Origin of felsic melts by anatexis of arclogites in arc roots: an example from Mercaderes, Colombia

Gianola O.[1], Costa B.[1], Alvaro M.[2], Gilio M.[2], Ferri F.[3] & Cesare B.*[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] EIT RawMaterials CLC South s.r.l., Roma.

*Corresponding author e-mail:* bernardo.cesare@unipd.it

*Keywords:* arc roots, inclusions, thermobarometry.

The Granatifera Tuff formation in the Mercaderes – Rio Mayo region contains abundant xenoliths which sample the entire lithospheric arc section above the subducting Nazca plate. Among the xenoliths, we studied a garnet pyroxenite (arclogite) showing evidence of partial melting.

The rock consists of garnet, clinopyroxene and plagioclase, minor amphibole, accessory rutile, and apatite. Quartz is only present in the cores of garnet, often together with glassy inclusions. The bulk rock composition corresponds to a low-alkali basalt. The rock has an average grain-size of 1.0 ± 0.5 mm and contains a well-developed foliation defined by 2-3 mm-thick monomineralic garnet layers.

Minerals are virtually unzoned: composition of garnet is $Alm_{42\text{-}43}Pyr_{38\text{-}41}Grs_{16\text{-}20}Sps_1$; clinopyroxene contains 15-16% Jd and has a $X_{Mg}$ of 0.73; amphibole is a pargasite with 0.27 apfu Ti, 0.87 apfu Na and $X_{Mg}$ of 0.87; plagioclase composition is $Ab_{72}An_{26}Or_3$.

The garnet frequently contains primary glassy inclusions at the core. Inclusions have a size between 10 and 50 µm, range in shape from irregular to negative crystal, and contain either brown or colorless glass, with one or more shrinkage bubbles. Under SEM inspection the glass shows evidence of local partial crystallization. The composition of the glass in inclusion is rhyolitic and peraluminous (ASI = 1.0–1.2), with an inferred range of $H_2O$ of 0.5-6.0 wt.%. This melt is different from the interstitial glass infiltrated from the host lava of the Granatifera Tuff, which has lower total alkalis.

The presence of primary melt inclusions, along with the occurrence of quartz exclusively as inclusions in garnet, indicate that garnet is a peritectic phase and that the rock contained quartz at the onset of partial melting. Therefore, the studied arclogite is probably the residue after partial melting of a precursor metabasite protolith. To produce a rhyolitic melt and a garnet-bearing residue (but not an omphacitic pyroxene), the degreee of melting must have been low and pressure must have exceeded 1.0 GPa.

We have constrained the P-T conditions of equilibration and possible anatexis of the xenolith by a combination of elastic and intracrystalline geothermobarometry. The intersection of the isomekes defined by the quartz-in-garnet and zircon-in-garnet elastic geothermobarometers with the P-T curve provided by the Fe-Mg intracrystalline geothermometry on clinopyroxene define a P-T field at about 1150-1250°C and 1.7-2.1 GPa. The results locate the origin and melting of the studied arclogite xenolith at a minimum depth of about 55-60 km in the arc root.

This is one of the first and most straightforward examples of the reworking of the sub-arc crust by partial melting, with production of felsic melts and a highly residual and dense restitite.

# The contribution of calcareous pelites in shaping the continental crust: prograde metamorphism, fluid production and melt (un)fertility

Groppo C.*[1-2], Rolfo F.[1-2] & Frezzotti M.L.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.
[3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* chiara.groppo@unito.it

*Keywords:* phase equilibria modelling, hot collisional orogens, decarbonation processes and melt fertility.

Metamorphism and anatexis occurring at middle crustal depths during hot collisional orogenies are important processes involved in the shaping of continental crust; in these geodynamic settings, fluids and melts are produced at progressively higher temperatures, whose amount and composition depend on the P-T history as well as on the protolith's bulk composition. Calcareous pelites are important constituents of sedimentary sequences deposited on passive margins through time and later involved in orogenic processes; their mineralogical composition is transitional between pure pelites (dominated by clay minerals, quartz and feldspars and virtually free of carbonates) and marls (consisting of a mixture of pelitic and carbonatic components). In spite of their relative abundance in the sedimentary record, prograde metamorphism of calcareous pelites is significantly less studied than that of pure pelites with negligible amounts of modal calcite. The fluid and melt productivity of these lithologies is especially poorly investigated, although potentially relevant in influencing the continental crust evolution and growth.

We present the results of mineral equilibria modelling in the system $MnO–Na_2O–K_2O–CaO–FeO–MgO–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2$, with the aim of constraining the prograde evolution of calcareous pelites in hot collisional orogenic settings. A suite of model bulk-rock compositions is used to investigate the influence of different proportions of calcite in the protolith on: (a) the equilibrium assemblages at different pressure, temperature and fluid composition ($P–T–X(CO_2)$) conditions; (b) the melt fertility and, (c) the fluid evolution and the main decarbonation reactions occurring during prograde metamorphism of calcareous pelites. We demonstrate that even a small amount of calcite in the calcareous pelitic protoliths has a strong influence on the final mineral assemblages and compositions, with potential effects on their melt productivity (Groppo et al., 2021). Specifically, it appears that up to ca. 800°C, the melt productivity of calcic metapelites remains low, and melt production occurs gradationally because it is mostly controlled by continuous biotite dehydration melting reactions, rather than by muscovite breakdown. Moreover, the study demonstrates that calcareous pelites could be non-negligible $CO_2$-source rocks in orogenic settings, and that in such contexts, an internal buffered behaviour is likely for most of them.

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# The xenoliths of the Giglio Monzogranite: types and genetical implications

Ibe C.U.*[1], Langone A.[2], Caggianelli A.[1], Tursi F.[1] & Brogi A.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* chinedu.ibe@uniba.it

*Keywords:* xenolith, partial melting, restite.

The Giglio peraluminous monzogranite, emplaced in the upper crust during early Pliocene, is one of the intrusions within the Tuscan magmatic province (TMP). The pluton is exposed for about 20 km$^2$ and has been subdivided in the Arenella, Pietrabona and Le Scole intrusive units (Westermann et al., 1993). With respect to other plutons in the TMP, it is characterized by a notable abundance of metamorphic xenoliths (Barrese et al., 1987), to date not well known for their nature and provenance. For this reason, we carried out a detailed study of mineral assemblages, rock fabric and genesis. Different types of xenoliths were identified. A first one is characterised by the presence of cordierite, sillimanite, feldspars, spinel, aligned biotite flakes and corundum. This xenolith shows an ovoid shape with a light core, primarily made up of plagioclase associated with fibrolitic sillimanite, and a darker margin composed mainly of cordierite (0.56 < Mg<0.58). The compositional and textural features of this xenolith are consistent with a metamorphic restitic origin (Clarke, 1995). They also suggest the breakdown of biotite to produce cordierite in the presence of melt, through the reaction: Bt+Sil = Crd+Spl+Crn+Kfs+melt (in the KFMASH system). A second xenolith type shows a laminated structure characterized by alternation of melanocratic and leucocratic layers. Biotite and spinel constitute the melanocratic layer whereas plagioclase and K-feldspar make up the leucocratic one. Biotite ($X_{Mg}$ 0.46) shows an embayed outline resulting from resorption during partial melting. Elongated spinel-rich aggregates include weakly pleochroic biotite, pinkish relicts of andalusite and some corundum grains. These aggregates are surrounded by plagioclase and cloudy K-feldspar grains towards the host granite. These features suggest that this type of xenolith is migmatitic, with biotite and andalusite being involved in partial melting, probably through the following reaction: Bt+$Al_2SiO_5$+Crn = Spl+Kfs+melt. Excluding the possibility that $Al_2SiO_5$ was originally sillimanite, the presence of andalusite poses some limits to the P-T conditions during partial melting. A provenance of these xenoliths from the source region of the granitic magma is unlikely, since the P-T conditions required for partial melting cannot be easily reached within the stability field of andalusite. An uncommon and very elevated thermal gradient is required. These results could be extended to other xenolith-bearing granitic rocks emplaced at shallow crustal levels as it is the case of the TMP, but further investigations and detailed comparisons are necessary to confirm such extrapolations.

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# Ordovician thermometamorphic events: correlation between the External Zone (Mt Filau-Settiballas area) and the High Grade Metamorphic Complex (Tamarispa area) in Sardinia (Italy)

Mantovani F.*

Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* federico.mantovani@edu.unige.it

*Keywords:* Ordovician thermometamorphism, Giant-Garnet, Sardinia.

In SW Sardinia, the Sulcis-Iglesiente Complex forms part of the External Zone of the Sardinian Variscan chain. In the southernmost Sulcis, the Mt. Filau-Settiballas complex records an exceptional convergence of events quite scarce in other Variscan basement rocks. Costamagna et al. (2016) reported granitic intrusions (Filau Granite, FG) and dikes of the Middle Ordovician age (457 ± 0,17 Ma), associated termometamorphic aureole (Settiballas Spotted Schist, SSS) with marble lens containing Grt, Ves e Wo. The Complex is surrounded and superposed by the Bithia Formation (BF) dated to Middle Cambrian. In the Tamarispa area (NE of Sardinia), in the High Grade Metamorphic Complex (Axial Zone), there are several calc-silicate lenses containing Wo, decimetric Grt, Di e Cc (Franceschelli et al., 2021) in contact with San Lorenzo-Tanaunella Ordovician Orthogneiss (453 ± 8 Ma; Rossi et al., 2009) and within the Brunella Biotitic Gneiss. Structural and petrographic evidences show that the Mt. Filau complex forms an integral part of the SW Sardinia Cambrian-Ordovician succession, which was intruded and metamorphosed by a Middle-Late Ordovician granite. BF could have been the SSS protolith, as well as Brunella Biotitic Gneiss protolith could have been quite analogous to SSS itself. Moreover, FG and San Lorenzo-Tanaunella Orthogneiss have similar emplacement ages. In the Settiballas-Mt. Filau area, the host rocks are affected by Variscan greenschist-facies conditions, whereas the Brunella area attained amphibolite-facies conditions. The pre-Variscan history of southern Sardinia is preserved because the HT/LP metamorphism of the SSS is of higher grade than that in the adjacent BF. However, in northern Sardinia, the same geological framework was overprinted by the Variscan event under amphibolite-facies conditions. The diameters of garnet crystals in calc-silicate lenses in the Tamarispa area (10 to 30 cm), are distinct from other areas in the High Grade Metamorphic Complex suggesting that the growth did not probably result from the Variscan orogenic overprint, but from an older event instead. In the Settiballas-Mt. Filau ML, garnet growth is more clearly related to older contact metamorphism that resulted from the emplacement of the Ordovician FG (Costamagna et al., 2016). Despite differences in term of dimension (mm to cm size in the SW, dm size in the NE), analyses on garnet samples performed by Costamagna et al. (2016), Franceschelli et al. (2021) and University of Firenze shows a high compositional homogeneity (not zoned) and a significant chemical affinity ($Al_{0.3\text{-}1.2}Py_{0.4\text{-}0.5}Grs_{87\text{-}91}Sps_{0.06\text{-}0.2}Adr_{7.4\text{-}8.4}$) between the investigated areas. Age and dynamics of emplacement (Middle-Late Ordovician extensive arc magmatic event), garnets chemical affinities and lithotypes interrelationship highlight a strong correlation between the High Grade Metamorphic Complex sequence in NE and the Cambrian-Ordovician sequence cropping out in SW.

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# Polyphase pyroxenitization of dunites in the lower continental crust: evidence from the Ivrea Mafic Complex (Italian Alps)

Mariani D.*[1], Renna M.R.[2], Zanetti A.[1-3] & Tribuzio R.[1-3]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.
[3] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* davide.mariani01@universitadipavia.it

*Keywords:* reactive melt migration, pyroxenite.

Reaction processes between a percolating melt and an olivine-rich matrix to generate pyroxenites were hypothesized to occur within mafic-ultramafic intrusive sequences from the lower continental crust, both in convergent and extensional tectonic settings (e.g., Jagoutz et al., 2011; Locmelis et al., 2016). These processes may drive the chemical differentiation of mantle-derived magmas emplaced at deep levels of the continental crust. Here, we document the process of dunite pyroxenitization within the Mafic Complex of the Ivrea-Verbano Zone (Southern Alps), which is a gabbronorite-diorite batholith intruding the lower continental crust during the post-Variscan transtensional tectonics. In particular, we present new petrological and geochemical data of an ultramafic lens of inferred cumulus origin localized at deep levels of the Complex.

The studied lens consists of ~60 m thick, spinel-bearing dunites permeated by cm-scale thick pyroxenite veins and mantled by up to 10 m thick pyroxenites along the contact with the enclosing gabbronorites. The contact between the dunites and the external pyroxenites is characterized by orthopyroxene-rich micro-veins in the dunites, and minor embayed olivine in the mantling pyroxenites. Both vein and mantling pyroxenites have an oxide association of Al-spinel and Cr-magnetite, typically associated with relatively high amounts of sulfides (mostly troilite). Away from the contact with the dunites, the mantling pyroxenites lack olivine and spinel, and include accessory amounts of anorthite-rich plagioclase. The mantling pyroxenites display a gradual outward Mg# decrease in pyroxenes, similar to what is observed along mm-scale transects from the dunites to the enclosed pyroxenite veins. The enclosing gabbronorites mostly consist of Fe-rich pyroxenes and anorthite-poor plagioclase. Clinopyroxene from both the pyroxenite veins and the mantling pyroxenites has chondrite-normalized Rare Earth Element (REE) patterns exhibiting a weak negative Eu anomaly. Clinopyroxene from the enclosing gabbronorites differs in the relatively high REE concentrations, pronounced negative Eu anomaly and marked depletion of light REE.

We concude that the pyroxenites formed by reaction of the dunites with externally-derived melts, which had already undergone plagioclase fractionation. The following sequence of events is envisioned: I) the dunite body underwent focused porous melt flow that produced the pyroxenite veins through a replacement-dominated mechanism involving dissolution of olivine and spinel recrystallization. Upon cooling, melt-dunite interaction developed the mantling pyroxenites. The enclosing gabbronorites most likely crystallized after the formation of the dunite-pyroxenite association, from melts genetically unrelated to the pyroxenite-forming ones. In this frame, the process of dunite pyroxenitization occurred before the main event leading to the growth of the Mafic Complex (Quick et al., 1994).

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# The Cima Ghiliè metadacite and its xenoliths (Argentera Massif, Western Alps, Italy): petrography and mineral-chemistry

Moschetti L.*[1], Ferrando S.[1], Compagnoni R.[1] & Radulesco N.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] International University of Monaco, Fontvieille (Monaco).

*Corresponding author e-mail:* linda.moschetti@edu.unito.it

*Keywords:* granulite facies, partial melting.

In the Argentera Massif, the southernmost External Crystalline Massif of the Western Alps, Late-Ordovician (443±3 Ma with $^{206}Pb/^{238}U$ age on zircon; Rubatto et al., 2001) subvolcanic metadacites occur as small bodies (less than 1 $km^2$) intruded into ortho- and paragneisses of the Gesso-Stura-Vesubie Terrane (Compagnoni et al., 2010). A modern petrological investigation of the metadacite still lacks. Moreover, the presence of abundant granulite xenoliths could give relevant information on the pre-Variscan evolution of the Massif. Here, we present the results of petrographic, mineralogical and chemical data on metadacites, and their related xenoliths, cropping out at Cima Ghilié, in the southwestern part of the Argentera Massif. The Cima Ghiliè metadacite, which locally preserves the undeformed porphyritic microstructure, shows transitional contacts to foliated metadacite up to a homogeneous migmatite lacking any evidence of the original igneous protolith. The metadacite is crowded (ca. 15 vol.%) of metamorphic xenoliths, which are easily recognizable in the undeformed portions. Under the microscope, the undeformed metadacite exhibits a mesoporphyritic microstructure with phenocrysts of Pl, Qz, Kfs, Bt and ex-Crd, and microphenocrysts of Pl, Qz and Bt embedded in a microcrystalline groundmass consisting of Qz, Feldspars, very little Bt and euedral Zrn. Nine different kinds of xenoliths, most of them characterized by granulite-facies mineral assemblages, were distinguished. In the deformed metadacite, the xenoliths are strongly stretched along the main foliation, defined by Bt, that wraps around the former phenocrysts. The migmatitic metadacite and some xenoliths are characterized by low volumes of interstitial Bt, Qz and Pl, interpreted as representative of a former melt. Petrographic and minero-chemical data on Bt, Grt, Px, and Pl from xenoliths and metadacite clearly distinguish different mineral generations. Notably, the preservation of the original subvolcanic structure and the lack of a mineral assemblage compatible with the Variscan HP-HT granulite-facies metamorphism seems to be in contrast with the pre-Variscan radiometric age of crystallization of the metadacites. New geochronological analyses on selected samples are necessary to explain this apparent contradiction.

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# Geochemistry and geochronology of the Corno Alto complex (Adamello batholith): evidence for a multi-stage and multi-component process

Mosconi A.*, Tiepolo M., Farina F. & Cannaò E.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* angelica.mosconi@unimi.it

*Keywords:* Adamello, periadriatic magmatism, isotopes.

Granitoid batholiths are important end products of the Earth's long-term compositional differentiation, representing either the addition of juvenile material to the crust or the reworking of older crustal components (Moyen et al., 2021). This study focuses on the Corno Alto complex representing the oldest igneous activity related to the Adamello batholith (Southern Alps). In the field, we recognised three distinct types of granitoid rocks: i) epidote-bearing biotite granodiorites; ii) equigranular and porphyritic tonalites; iii) two-mica granodiorites. Whole-rock chemistry reveals relatively peculiar features with respect to the other units of the Adamello batholith. The Corno Alto rocks exhibit the highest $SiO_2$ contents (up to 71.5 wt%), $K_2O+Na_2O$ up to 7.2%, a strong enrichment in Ba and to a minor extent in Sr (Ba + Sr ≈ 1100-1900 ppm). Other geochemical features include a moderately-to-strong enrichment in LREE over HREE ($La_N/Yb_N > 20$) and Y (Sr/Y > 40).

Cathodoluminescence imaging (CL) of zircons allowed the identification of two main domains: type-A is characterized by oscillatory zoning and mid to low CL response; type-B (mostly at the core) is structureless with mid to high CL. U-Pb geochronology does not reveal a significant age difference between these domains. However, different samples show a roughly east-to-west decrease in age, with main recurring age peaks, at c. 44 Ma, c. 42 Ma, and c. 39 Ma. The different zircon domains have significantly distinct Hf isotopes (up to 18 $\varepsilon_{Hf}$ units of variation) with some values trending towards the isotopic composition of the depleted mantle (DM). Mineral chemistry and in-situ Sr isotopes reveal the sporadic occurrence of corroded calcic plagioclase cores (An90) with a depleted Sr isotopic signature overgrown by albitic rims (An10) with an abrupt enrichment in radiogenic Sr.

These new geochronological data indicate assembly of the Corno Alto complex by multiple magma injections in a relatively large time span of about ~5 Myr. These results refine the current knowledge on the Corno Alto complex age of emplacement given as a single event at 43 Ma (e.g., Ji et al., 2019). Noticeably, the age trend observed in the Corno Alto complex parallel that observed on a larger scale by Ji et al. (2019) being perpendicular to the strike of the European slab. The new data suggest that the effect on the igneous activity of the progressive Eocene-Oligocene slab steepening can be observed even at the scale of the single igneous complex. Hf-Sr isotope systematics and major-trace element mineral chemistry suggest that the Corno Alto is the product of a multi-stage and multi-component process involving: i) a mantle component with a DM signature, likely related to slab-edge effects, and ii) a shallower component with a marked crustal geochemical signature.

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# Crustal growth of the upper crust of the Serre Massif: an overview on the late-Variscan evolution of the southern European Hercynian chain

Ortolano G.*[1], Pagano M.[1], Visalli R.[1], Fazio E.[1], Godard G.[2] & Cirrincione R.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Institut de Physique du Globe de Paris, Université Paris-Diderot (France).

*Corresponding author e-mail:* gaetano.ortolano@unict.it

*Keywords:* microstructural analysis, PT pseudosection, paleopiezometry.

Tectono-metamorphic evolution of metamorphic rocks reflects their burial evolution into the deep crust and subsequent exhumation upon the surface, potentially passing through one or more static metamorphic stages. This induces a continuous change in the intensive variables (e.g., T, P, $fO_2$) through several types of dP/dT gradient, as highlighted by the peculiar continuous adjustment of the mineral assemblages and the solid-solution compositions of different rocks. In order to obtain reliable constraints, a quantitative multiscale analytical approach has to be adopted by means of a sequential stepwise controlled procedure. The first step is the cartographic restitution of the present-day tectonostratigraphic setting of the crystalline basement units, in conjunction with structural, microstructural, and petrographic data. This former analytical phase permits, in turn, the mutual petrogenetic interdependence of the parageneses to be defined, bracketing geochronologically the relative sequence of the evolutionary stages of the basement growth. In other words, it represents the cornerstone of a robust characterization of the deep Earth crust kinematics. The Calabrian Peloritani Orogene (CPO) represents a key sector for the reconstruction of the western Mediterranean microplate movements since the Late-Paleocene. This is because it represents a relic of the southern European Hercynian chain formerly exhumed during the transpressive activity of the Eastern Variscan Shear Zone (Ortolano et al., 2022) before being involved in the Meso- to Late-Alpine evolutionary stages (Cirrincione et al., 2015). In this framework, the Serre Massif crustal section can be interpreted as a relic of the original southern European Variscan Belt devoid of any Alpine metamorphic overprint sandwiched to the south by the Aspromonte-Peloritani tectonic sequence along the Palmi line and, to the north, by the double-verging orogenic system of the Sila Massif and Catena Costiera delimited by the Catanzaro Line. More, in particular, new quantitative multiscale study approaches are focused on the upper crustal level of the Serre Massif consisting in a 2-3 km thick, composed by the basal Mammola Paragneiss Complex (MPC) and the upper Stilo-Pazzano Complex (SPC), separated by a low-angle tectonic detachment. A new geological-structural map (290 $km^2$ at 1:2000 scale) have been produced (Ortolano et al., 2022), followed by a revalidation of the PT constraints obtained by calculation of new effective bulk rock chemistries constrained via quantitative image analysis and by paleopiezometer applied for the first time to the late-Variscan syn-mylonitic quartz grain recrystallization preserved from the post kinematic thermal raising effects of the batholith emplacement. Newly obtained data shed new light on still unsolved questions about the CPO geodynamics, with a special look into the late-Variscan strike-slip kinematics of the southern European Hercynian chain.

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# Alpine Oligocene zircons recycled into Pseudomacigno/Acquadolce units, north-eastern Elba Island

Rocchi S.*[1], Jacobs J.[2] & Masotta M.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Department of Earth Science, University of Bergen (Norway).

*Corresponding author e-mail:* sergio.rocchi@unipi.it

*Keywords:* zircon, provenance, Oligocene.

Acquadolce and Pseudomacigno represent the tectono-stratigraphically youngest units of the western part of the continental margin of Adria plate and are in direct contact with Ligurian oceanic units in eastern Elba Island. The Acquadolce unit shows typical high-pressure mineralogies (Bianco et al., 2015) and a spectacular zircon roller coaster history (Jacobs et al., 2018). Their detrital Oligocene zircons originated in the Alps and were recycled through all stages of the Apennine orogeny, including deep subduction and exhumation. In search for further evidence of Alpine detritus in the Northern Apennines formations of eastern Elba and to better constrain their provenance, we examined the Oligocene Pseudomacigno formation in north-east Elba, whose rocks mainly consist of very low-grade grey metagreywacke, black calcareous phyllites and metasiltstones-sandstones. We performed LA-ICP-MS U-Pb analyses of ca. 140 detrital zircons. The resulting age spectrum shows a major Oligocene age peak, roughly coincident with the Acquadolce age peak from a previous study (Jacobs et al., 2018), thus pointing to a similar maximum deposition age at the very beginning of the Oligocene. Oligocene zircons in Acquadolce represents ~ 15% of the analysed crystals, while in the Pseudomacigno they represent ~ 75%. The pre-Mesozoic part of the age spectrum for Acquadolce is characterized by late Paleozoic (Variscan) and early Ordovician peaks, with the remaining zircon ages mostly of late Neoproterozoic (Panafrican) age. On the other hand, the pre-Mesozoic part of the spectrum of the Pseudomacigno differs significantly from Acquadolce, lacking both Variscan and Ordovician age signals, and showing fewer Grenvillian and other Proterozoic ages. Zircon trace elements concentrations and ratios of both units are comparable and plot in the upper part of the magmatic arc array (well outside the mantle zircon array) in the area representative of post-collisional magmatism. Potential sources on the Adria Plate include the Periadriatic igneous complexes. The plutons themselves are no possible sources, since they were not exhumed before ~ 10 Ma, nevertheless, their ages are important in suggesting ages of potential related volcanic activities. Our study demonstrates that Oligocene zircons of Alpine provenance occur not only in the Acquadolce unit, but also in other Elba tectono-stratigraphically high continental units such as Pseudomacigno. It is thus likely that, during Oligocene, detrital supply from Alpine sources zircons was a common feature of uppermost units of the continental margin of Adria.

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# Cittanova pluton and Serre Batholith: answers to unsettled questions on the southernmost sector of the Serre Massif (Southern Italy) from field and AMS data

Russo D.*[1], Fiannacca P.[1], Mamtani M.A.[2], Fazio E.[1] & Cirrincione R.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Indian Institute of Technology, Kharagpur (India).

*Corresponding author e-mail:* damiano.russo@phd.unict.it

*Keywords:* field relationships, magnetic fabric, central Calabria.

Cittanova pluton mostly consists of fine-grained two-mica granites extending over an area of c. 100 km$^2$ in the southernmost part of the Serre Massif. Its role during Late Variscan magmatism in this exposed cross-section of continental crust is still debated but field relationships of the pluton with more mafic medium-grained biotite ± amphibole granodiorites (BAG) that belong to the Serre Batholith, which forms the intermediate portion of the crustal section, point to a southeast dipping primary contact. Metric and roundish BAG bodies, with both sharp and shaded contacts, are identified in the field within Cittanova granites. Measurement of the anisotropy of magnetic susceptibility (AMS) has been carried out on 132 oriented cubes of both Cittanova and BAG granitoids, in order to understand tectonic relationships between the Cittanova pluton and the Serre Batholith, as well as to obtain possible constraints on the interplay between regional deformation and magma emplacement. In general, both units (Cittanova granite and BAG) show a paramagnetic behaviour, mainly due to the iron contained in biotite. While BAG mean magnetic susceptibility value is 157 x10$^{-6}$ SI unit, Cittanova values are at 54 x10$^{-6}$ SI unit in the north-western side of the pluton and 90 x10$^{-6}$ SI unit in the southeastern part. The distribution of $K_3$ and $K_1$ poles in both Cittanova and BAG magmatic bodies is similar and consistent with a possible NNW-SSE shortening. This reflects an early deformational event, in good agreement with upper crustal Serre rocks stress field and suggests a common deformation history for both Cittanova and BAG rocks. A weak late deformational event (ENE-WSW shortening) is revealed from our new magnetic data. The present work implies two regional compressive tectonic phases, probably active from emplacement to cooling of the two granitoid units and whose evidence have been also recorded in the host rocks from neighbouring areas.

# Structural and geochemical revaluation of appinite dikes along the Cossato-Mergozzo-Brissago Lineament, Ivrea-Verbano Zone, NW Italy

Zucali M.*, Moroni M., Tiepolo M., Masoch J., Romanelli G. & Ferrari E.S.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* michele.zucali@unimi.it

*Keywords:* appinite, geochemistry, microstructures, Permian.

The Appinite Suite in NW Italy consists of swarms of amphibole-rich, ultrabasic to acidic dikes emplaced on both sides of the major Cossato-Mergozzo-Brissago Lineament (CMB) separating the Ivrea-Verbano Zone (IVZ) and the overlying Serie dei Laghi domain (SdL), commonly attibuted to the deep and middle crust, respectively. Our study involved macro- to microtextural and petrographic characterization of dikes and host rocks (kinzigites, amphibolites and sillimanite-bearing micaschists), followed by mineral chemistry, thermo-barometric estimates and C-O isotope analyses. Hornblendite and gabbro dikes display the most complex assemblages and textures, with pargasite-rich chilled margins often enclosing wide pegmatoidal cores with evidence of polyphasic crystallization. Zoned amphibole oikocrysts show wide brown pargasite cores made turbid by ilmenite microinclusions and Fe sulfide droplets and mottled by round pyroxene and anorthite remnants. The green amphibole in the oikocryst coronas and in the plagioclase-rich matrix are intergrown with titanite and calcite. Gabbro-diorite dikes are biotite-rich. Moderate deformation, often localized along chilled margins, caused foliation marked by biotite and green amphibole. Thermobarometric estimates on the complex appinite assemblages suggest a crystallizing path evolving from ~ 10 kbar (30-35 km) down to 6-3 kbar (10-20 km).

Basement rocks recorded prograde paths, from greenschist- to amphibolite-facies with progressive T and P increase to the development of deformation related to CMB shearing. This prograde path is associated with the development of a pervasive foliation, marked by sillimanite and HT-biotite in metapelites wrapping appinite bodies. This event and the final P-T stage recorded in appinite dikes are coincident. Hence, the appinite emplacement might have been coeval with or controlled by the activation of the CMB Lineament, tentatively dated to Permian. However, a pervasive foliation observed in a porphyritic gabbro dike is marked by a peculiar green amphibole-anorthite-quartz-titanite assemblage, interpreted as caused by HT shearing in presence of supercritical brines. Such foliation might be caused by movements along the CMB after the appinite emplacement, hence titanite might provide valuable geochronological data. Our structural and petrological data confirm the current model for IVZ appinites by emplacement of mantle-derived magma, variably contaminated by crustal, anatectic melts, while ascending along deep crustal shear zones like CMB (Mulch et al., 2002). However, our study highlighted both the textural and mineralogical complexity of appinites and their enrichments in magmatic volatiles, including $CO_2$ and S. In particular, C-O isotope compositions of magmatic calcite in hornblendites show mantle-affine signatures concordant with those from the volatile-rich ultramafic pipes and intrusions marking the final magmatic events in the IVZ (Blanks et al., 2020; Chong et al., 2021).

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# S13.

# Earth dynamics to dynamic landscape: feedback between tectonics and landscape evolution


*Conveners & Chaipersons*

*Francesco Pavano (Lehigh University)*

*Ciro Cerrone (University of Napoli - Federico II)*

*Mauro Bonasera (Servizio Geologico d'Italia - ISPRA)*

*Michele Delchiaro (University of Roma - Sapienza)*

*Paola Molin (Roma Tre University)*

*Frank J. Pazzaglia (Lehigh University)*

# Late Quaternary morphotectonic evolution of the Sele River Plain peri-Tyrrhenian graben (southern Italy): new data and constraints from U-series analyses

Ascione A.*[1], Cerrone C.[1], Di Donato V.[1], Valente E.[1], Di Maio G.[2], Soligo M.[3] & Tuccimei P.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Geomed s.r.l. - Geoarcheologia e Geologia Ambientale, Scafati (SA). [3] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* ciro.cerrone@unina.it

*Keywords:* Sele River Plain (southern Italy), Quaternary evolution, U-series dating.

The Sele River Plain corresponds to the inland portion of the Salerno Gulf coastal basin, which is one of the widest coastal grabens along the Tyrrhenian coastal sector of the southern Apennines, Italy. The Sele Plain-Salerno Gulf basin was formed through extensional processes that, since the Late Miocene, led to the opening of the Tyrrhenian back-arc basin. Such processes shaped the modern coastal sector of the Apennines chain, where a horst and graben structure along large fault zones, several km in length, with main NE-SW orientations was formed in Quaternary times. Former studies indicate that Quaternary subsidence allowed the deposition of > 1500 m continental to shallow marine deposits in the Sele Plain basin, which however records a late Quaternary change in the trend of the vertical motions. Such a change is testified by both incision and terracing of the alluvial fill of the inner part of the Sele Plain, and the presence of raised littoral deposits in its coastal part. Existing aminostratigraphy data constrain the age of the beach deposits, raised up to c. 20 m, to MIS 5 and, therefore, point to uplift of ~0.1 mm/y since the Last Interglacial of the formerly subsiding Sele Plain basin.

With the aim of better defining and setting new constraints to the peculiar late Quaternary behaviour of the Sele Plain basin, we are carrying out an integrated morphotectonic and morphostratigraphy analysis of the Sele Plain with a particular focus on its coastal belt, where sea level markers and continental deposits, both outcropping and buried, occur. The study is based on the geomorphological analysis of detailed topographic data (1:5.000 scale maps, 5-m DEM resolution) and field work and is integrated by the analysis of subsurface data from c. 150 pre-existing shallow borehole logs. In addition, the detailed analysis of a shallow (30 m deep) core drilled in the southern part of the study area has been carried out by means of stratigraphic, paleoenvironmental and new U-series analysis from travertine and *Cladocora caespitosa* samples. The geomorphological and stratigraphic data and U/Th dating allow a better definition of the coastline changes in response to the complex interaction between sea level fluctuations and sedimentary inputs, and provide new constraints to the framework of the vertical motions during the late Quaternary.

# Geomorphological remarks in the eastern part of Monte Primo, Central Apennines, Marche, (Italy)

Bufalini M.*[1], Ferrando A.[2], Silvani F.[3] & Bosino A.[4]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [3] Dipartimento di Fisica e Geologia, Università di Perugia. [4] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* margherita.bufalini@unicam.it

*Keywords:* geomorphological mapping, landslides, river terraces deposits, landscape evolution.

This work shows some results of the field investigations carried out during the First Winter School of Geomorphological Survey, held in Camerino (Marche, Italy). A geomorphological map was created applying the new guidelines for geomorphological cartography edited by ISPRA. In addition, the map was digitalized in a GIS environment employing the ISPRA symbology and finally implementing the geomorphological database.

The study area covers approximately 20 km$^2$ and lies west of Camerino, between the village of Spindoli and the eastern slopes of Mt. Primo and Mt. Igno. The geological setting of the area is characterized by the external limb of the Umbria-Marche ridge, composed by asymmetric anticlines of Meso-Cenozoic sedimentary rocks affected by several splaying NE verging thrusts (Mayer et al., 2003). The bedrock is covered by thick sequences of Quaternary scree slope, talus and colluvial deposits.

The main landforms that were detected during the field survey are correlated to the lithological and structural setting of the area, and to fluvial, gravitative and anthropic processes. Selective erosion crests interspersed by litho-structural saddles are evident at the lithological contact between the Scaglia Cinerea and the Bisciaro formations; the crests are aligned in N-S direction.

The bedrock is incised by steep V-shaped valleys. Various orders of river terraces are detectable, highlighting the deepening of the main drainage, which cuts across the semi-consolidated alluvial deposits. The disconformity between the alluvial deposits and the colluvial/gravitational ones is visible due to lateral erosion by the watercourses. Furthermore, the soft sedimentary bedrock, which occasionally crops out, is prone to be eroded by running water. In fact, several forms of rill-interrill, gully erosion and other denudation processes are detectable on the agricultural fields and the uncovered slopes. Denudation scarps, selective structural scarps and landslides scarps are fine example of morphological convergence, underlying an area on which the morphodynamics are still active.

The western part of the study area presents a persistent fault zone on which massive bedrock formations are thrusted on the soft Scaglia Cinerea. The contact is evident, even if it is locally mantled by semi-consolidated scree slope and talus deposits. By the fault zone, the different competence of the bedrock formations favours the presence of translational, rotational and complex landslides, which interest both the geological boundary between the scree and the bedrock and the scree slope itself. Active gravitational trenches were detected in the upper part of a complex landslide near the village of Nibbiano.

In conclusion, the geomorphological evidence highlights an area deeply interested by mass movements as well as soil erosion landforms and features, and this work can be a scientific basis for further studies.

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# Assessment of Quaternary variations of the drainage pattern through morphotectonic investigations in Southern Piedmont (North-western Italy)

Buleo Tebar V.*[1], Bonasera M.[2], Fubelli G.[1] & Racano S.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] Institute of Geosciences, University of Potsdam, Porsdam-Golm (Germany).

*Corresponding author e-mail:* victor.buleotebar@unito.it

*Keywords:* active tectonic, geomorphology, drain age network systems.

Drainage network systems are one of the more responsive elements to recent active tectonic from among all the topographic features. Their anomalies can be significant in areas with high relief energy or less noticeable where intense deposition rates might make capable tectonic signatures not visible. In addition, surface processes are even dominated by changes in climate. Since landscape evolution is the result of the combination of these elements, drainage network systems represent a key element for understanding the role and importance of different factors involved in the processes during Quaternary that have led to the formation of the current relief.

The study area comprises two different zones in Piedmont region (North-Western Italy): the Western Po Plain and the Langhe and Monferrato hills, both located in a complex tectonic framework at which a juxtaposition on a crustal scale between Alpine metamorphic Units and the Ligurian Units of the Apennines takes place. A multi-disciplinary approach is proposed combining geomorphology and geostatistics, with the aim of obtaining a better understanding and knowledge of various aspects of the Quaternary evolution of the area on a regional scale.

A morphometric analysis was carried out based on 5 m resolution DEM supported by geological and geomorphological field surveys. To assess the changes in the river network's direction a quantitative geomorphic analysis of river pattern has been performed through Geographic Information System (GIS) and MATLAB® tools. Different parameters were calculated with the aim of detecting anomalies and the estimation of local uplift and different erosion rates. Following the extraction of longitudinal river profiles, calculating Normalized Channel steepness index ($K_{sn}$) has been possible for assessing river incision, based on local channel slope, contributing drainage area and some other characteristics related to incision processes and basin hydrology. This step has also allowed the identification of knickpoints whose presence represent a deviation of steady-state streams condition and hence a transient phase of potentially landscape changes. These anomalies are present whether they were produced by tectonic deformation or by different factors. In addition, a paleotopographic reconstructions of Pleistocene deposits have allowed the estimation of the thickness of the deposits and the reconstruction of the river patterns during this period.

Preliminary results have provided relevant evidence of potentially recent and important changes in the regional drainage network of Western Po Plain resulting from the combination of tectonic activity during the Early Pleistocene and the climatic variation from the Middle and Late Pleistocene.

# The lithospheric structure of the Corsica-Sardinia Massif: a hint for geomorphic features, neotectonics and current geodynamics of the Western Mediterranean

Cocco F.*[1], Casini L.[2] & Funedda A.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* fabrcocco@unica.it

*Keywords:* isostatic undercompensation, fault reactivation, numerical modelling.

The Corsica-Sardinia Massif (CSM) is set in the middle of western Mediterranean, and it is generally considered a tectonically stable lithospheric block. This background is at odds with the voluminous anorogenic volcanic activity observed in Sardinia, as well as with several geomorphic features such as inverted reliefs, stream captures, deep river incisions and rugged topography with peaks close to 2,000 m above sea level (a.s.l.) in Sardinia and 3,000 m a.s.l. in Corsica, that suggest recent uplift. Moreover, low-magnitude earthquakes along with differential vertical movement recently recorded by high-definition GPS data testify the reactivation of pre-Pleistocene faults.

To investigate the actual geodynamic setting, we model the thermal structure and theoretical gravity anomaly of the CSM resulting from buoyancy, bending moment and horizontal stresses. The lithosphere of CSM is simulated as a thin elastic plate overlying an inviscid asthenosphere. The equations for the balance of forces and heat diffusion/conduction are solved through a Finite Differences scheme on a non-uniform grid composed of 200-by-400 regularly spaced nodes along the horizontal (x,y) directions, and 100 non-uniformly spaced nodes along the vertical (z) axis. The nodes have the minimum vertical spacing of 500 m in the first 40 km of the model, providing an optimal resolution for the crust, topographic surface and the Moho. The geometry and compositional variability of the lithospheric plate is reproduced by using four different layers (sediments, metamorphic upper crust, lower crust, and mantle) characterized by variable volumetric heat production rate, density and thermal conductivity, as well as material-dependent Poisson's ratio and Young's modulus. The thickness of each layer is spatially variable according to geophysical models derived from interpolation of seismic profiles and seismic receiver functions.

Compared to the lithospheric models derived from interpolation of sparse geophysical data, our results evidence a colder and much more homogeneous thermal structure, suggesting that the Campidano and Anglona geothermal highs likely reflect local circulation of fluids along crustal-scale faults. The calculated gravity anomaly fits quite well the results obtained from interpolation of measured geophysical data. Yet, the shape of low gravity anomaly domains matches only partially the distribution of topography, suggesting isostatic undercompensation. This interpretation accounts for the peculiar geomorphic features of Corsica and Sardinia and the observed differential vertical displacements accommodated by reactivation of pre-Pleistocene faults.

# Marine terraces response to subduction earthquake dynamics: a forward modelling approach

Crosetto S.[1], de Montserrat A.[2] & Oncken O.[1-3]

[1] German Research Centre for Geosciences, Potsdam (Germany). [2] ETH Zürich (Switzerland). [3] Institute of Geological Sciences, Freie Universität Berlin (Germany).

*Corresponding author e-mail:* crosetto@gfz-potsdam.de

*Keywords:* marine terraces, earthquake, subduction.

Marine terraces are erosional features that can be preserved if the uplift rate of the topography overcomes the rate of sea level increase. Uplifted marine terraces are observed along the coast of many active margins, and they are frequently used to quantify uplift rates by knowing elevation and age of a terrace, and the sea level position at the time of the terrace formation. While significant advance has been made in the understanding of this process and the role of fluctuating sea level through modelling, major uncertainty pertains to the opportunities and limitations of identifying uplift types - slow vs. fast; continuous vs. discontinuous – that are controlled by a range of tectonic mechanisms.

We explored this question by using a numerical model where terraces can form in conditions of both constant uplift and pulses of rapid uplift. We compared the evolution of terrace sequences formed under constant uplift conditions with sequences subject to variable uplift reproducing cycles of sediment underplating and earthquake clustering, and we explored the influence of the earthquake frequency, i.e., fixed recurrence interval or recurrence interval following a Poisson distribution, on the final geometry of terrace staircase sequences.

Results show that various uplift mechanisms do not produce diagnostic patterns in the staircase morphology; however, earthquakes with recurrence intervals approximated by a Poisson distribution appear to increase the variability of the staircase geometry, and particularly in case of longer recurrence intervals. A preliminary comparison with natural case studies suggests that marine terraces may represent a key feature in contributing to the understanding of the earthquake style at subduction margins.

# A GIS-thermochronology integrated approach to reconstruct the paleo-topography of the Southern Victoria Land (Transantarctic Mountains)

Fioraso M.*[1], Olivetti V.[2], Balestrieri M.L.[3] & Cornamusini G.[1]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Dipartimento di Geoscienze, Università di Padova. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* m.fioraso@student.unisi.it

*Keywords:* thermochronology, erosion, Geographic Information System.

Antarctica is a worldwide unique case for its geological and climatic conditions, where the longest uplifted mountain range on this planet, not related to compressional tectonics, the Transantarctic Mountains (TAM), is located. It constitutes the western shoulder of the West Antarctic Rift System. Three main uplift phases (early Cretaceous, late Cretaceous and Cenozoic) are known to be responsible for the built-up of the mountain chain, the last phase shaped the Present-day topography, beginning in the Eocene.

The study of the main erosional processes on the TAM leads to two main topics: how the changing erosive style shaped the landscape, and how to model the uplift, considering the flexural response due to the erosive unloading of the crustal plate (Stern & ten Brink, 1989). As described in Sugden & Denton (2004), the first Cenozoic glacial phase of warm-based glaciers dominated the Southern Victoria Land (SVL) area between the end of the Eocene and the early Miocene, followed by an alternation of warm- and cold-based glaciers. Since 13 Ma polar conditions have preserved the landscape due to extremely low erosion rates.

In this work, through a test area in the SVL, we integrate digital elevation models with thermochronology and surface exposure dating to reconstruct the paleotopography. We use interpolation and raster calculation tools (Elez et al., 2020) to produce a geophysical relief surface, and published (e.g., Fitzgerald, 1992) and unpublished thermochronological data coupled with topographic profiles useful to estimate the thickness of the eroded crust. A 3-D reconstruction of the eroded cover represents the base for the flexural isostatic response calculation. The spatial analysis of erosion provides new constraints on the amount of tilting and exhumation, as well as to consider the possibility of an increase in local relief due to isostasy.

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# Linear inversion of fluvial topography in the northern Apennines: comparison of base-level fall to crustal shortening

Fisher J.*[1], Pazzaglia F.[1], Anastasio D.[1] & Gallen S.[2]

[1] Department of Earth & Environmental Sciences, Lehigh University, Bethlehem, PA (USA). [2] Department of Geoscience, Colorado State University, Fort Collins, CO (USA).

*Corresponding author e-mail:* jafisher32@gmail.com

*Keywords:* knickpoints, geomorphology, tectonics.

Fluvial terraces, knickpoints, and growth strata carry independent but comparable records of the deformation history in tectonically active mountain belts. In the northern Apennines, these markers are preserved across an actively uplifting, steep mountain front. We take advantage of this setting to model base-level fall histories reconstructed from a linear inversion of fluvial topography on six transverse catchments spanning 110 km along strike from Bologna to Parma. We compare these histories to records of crustal shortening from both shallow and deep thrust structures preserved in growth strata. The fluvial inversion model is based on the detachment-limited stream power model and considers variable erodibility by bedrock lithology. Uplift is assumed to be spatially uniform at the catchment scale and crudely in balance with long-term $^{10}$Be terrestrial cosmogenic nuclide (TCN) erosion rates that range from ~0.3 to 0.7 mm/yr. Rivers record unsteady uplift beginning ~2.25 Ma near Bologna and earlier to the northwest along strike. The rate of base-level fall is comparable with published fault-slip restored from growth strata and incision rates from terrace deposits but do not exhibit a direct correlation. Rather, the modeling demonstrates how orogenic shortening and topographic growth are non-uniform and partitioned along strike of the Apennine mountain front. Rivers record steady uplift in the last ~1 Ma, temporally coincident with overfilling of the Po Plain and reduction of shallow fault-slip, supporting a proposed switch from thin- to thick-skinned crustal shortening. These results are a novel example of base-level fall records assembled from both the erosional source and depositional sink and highlight the versatility of fluvial inversion modeling.

# Surface response to deep subduction dynamics: insight from the Apennines, Italy

Lanari R.*[1], Reitano R.[2], Faccenna C.[2], Piana Agostinetti N.[4] & Ballato P.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze, Università di Roma Tre. [3] German Research Centre for Geosciences, Potsdam (Germany). [4] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* riccardo.lanari@outlook.it

*Keywords:* Apennines, subduction, morphometry.

The topographic elevation of orogenic belts responds to several processes and contributions operating at short and long temporal and spatial (i.e., wavelengths) scales, from the surface to the deep mantle. Although the effect of such contributions on the resulting topography elevation are relatively well understood, the impact of those processes on the morphology, or, on the pattern of crustal deformation/exhumation in orogens has not been yet systematically explored.

We aim to investigate the connection between the morphometric characteristics, exhumation, and deformation from the surface to the depth along and across the Apennines. Specifically, we present four set of observations that are constructed by gathering previous data with new analyses and inferences. Firstly, we provide a new geomorphic and morphometric set of analyses including $k_{sn}$ and $\chi$ to infer the across-divide uplift pattern. Secondly, we present a database of available apatite fission tracks and apatite (U-Th)/He thermochronological cooling ages to deduce exhumational and erosional evolution of the belt. Thirdly, we provide a new compilation based on the age of the youngest lacustrine deposits within each extensional basin along the Apennines to restore the orogenic drainage divide back in time. Fourthly, we detailly show the Moho depth from receiver functions, gathering previous estimates with 27 new ones. From these sets of data, it emerges that: (i) Across the Apennines, the geometries of the surface and the style of deformation and exhumation resemble the geometries of the Moho; (ii) the northern Apennines show asymmetry in topography, deformation style, pattern of exhumation, but also in the geometries of the subducting and the overriding plates; (iii) the Central-Southern Apennines show symmetry in topography, deformation, and exhumation together with a symmetrical Moho geometry

Our work demonstrates that along the Apennines, different ongoing mechanisms (e.g., from subduction to slab break-off) control the overall geometry of surface, crust, and Moho, always resulting in an outstanding coupling between shallower and deeper geometries. Such a coupling might imply that the geometries of the wedge are primarily controlled by internal processes (crustal/mantle) rather than an external contribution (e.g., climate or lithology).

# Exhumation response to climate and tectonic forcing in the southern Patagonian Andes (Torres del Paine and Fitz Roy plutonic complexes)

Muller V.A.P.*[1], Sue C.[2], Valla P.[2], Sternai P.[1], Simon-Labric T.[3], Martinod J.[2], Ghiglione M.[4], Baumgartner L.[5], Herman F.[5], Reiners P.[6], Gautheron C.[2-7], Grujic D.[8], Shuster D.[9], Braun J.[2-10] & Bernett M.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2]Institute des Sciences de la Terre ISTerre, Université de Savoie - Grenoble Alpes, CNRS, IRD, IFSTTAR, Grenoble (France). [3] Centre de Géologie Oisans Alpes, Musée des Minéraux, Bourg-d'Oisans (France). [4] Instituto de Estudios Andinos "Don Pablo Groeber", CONICET, Universidad de Buenos Aires (Argentina). [5] Institut des Sciences de la Terre, Université de Lausanne (Switzerland). [6] Geosciences University of Arizona, Tucson, AZ (USA). [7] Geosciences Paris Saclay, CNRS - Université Paris Saclay, Orsay (France). [8] Department of Earth and Environmental Sciences, Dalhousie University, Halifax (Canada). [9] Earth and Planetary Science, University of California, Berkeley, CA (USA). [10] German Research Centre for Geosciences, Potsdam (Germany).

*Corresponding author e-mail:* v.paivamuller@campus.unimib.it

*Keywords:* Patagonia, thermochronology, glacial erosion.

Alpine landscapes form in mountain belts that likely experienced tectonic uplift during plate's convergence, and efficient erosion dominated by glacial carving and circle retreat. In southern Patagonia late Miocene plutonic complexes are exposed in deep incised valleys with summits topographically above the glacial equilibrium line altitude. Two of the most emblematic ones are the Fitz Roy (Chaltén, 49°S) and the Torres del Paine (51°S) plutonic complexes, ~2 km higher than the mostly flat bottom valley that is partially covered by the Southern Patagonian Icefield. This continental region is located above an asthenospheric window that opens and migrates towards the north since ~16 Ma, and experienced dynamic uplift during episodes of spreading ridge collision with the continental margin. Here we present a new dataset of combined low-temperature thermochronometers from the Chaltén and Torres del Paine plutonic complexes, and their thermal history inversion numerical modeling, to identify the geodynamic processes forcing on the exhumation of the mountain belt. These complexes are separated by 200 km along the strike of the belt, and share a pulse of rapid exhumation at ~ 6 Ma, likely showing that glaciation was regionally starting at this moment. After a period of quiescence, in Torres del Paine the exhumation rate is accelerated from ~2 Ma to the present, interpreted as a signal of the Pleistocene climatic transition creating incise valleys. Before 6 Ma, only pluton cooling is recorded in the Fitz Roy between 16 and 14 Ma, and no significant pulse of cooling is recorded during the time of asthenospheric window emplacement and ridge collision (~12 Ma). We thus propose that the uplift due to asthenospheric upwelling was lower than the resolution of low-temperature thermochronometers (<1 km) or erosion was not suficient to be recorded in our cooling history.

# Tectonics and shore platform development: Rates and patterns of erosion on recently uplifted mudstone and limestone rocks at Kaikōura Peninsula, New Zealand

Omidiji J*[1], Stephenson W.[1], Dickson M.[2] & Norton K.[3]

[1] School of Geography, University of Otago, Dunedin (New Zealand). [2] School of Environment, University of Auckland (New Zealand). [3] School of Geography, Environment and Earth Sciences, Victoria University of Wellington (New Zealand).

*Corresponding author e-mail:* jokotola.omidiji@postgrad.otago.ac.nz

*Keywords:* tectonics, rock coasts, erosion.

On tectonically active rock coasts, there is a dearth of erosion data documenting how rocks adjust (either fast or slow) in response to marine and subaerial processes immediately after coseismic uplift. Here we report erosion rates and evidence of reshaping of shore platform morphology at Kaikōura Peninsula, South Island New Zealand. As a result of the November 2016 Kaikōura 7.8 (Mw) earthquake, platforms around the peninsula were uplifted by ~1.01 m and extended in width. This event ended a 43-year active erosion monitoring campaign but an opportunity to record how rocks respond to sudden environmental change like tectonics was presented. High-resolution topographic data obtained from quarterly surveys over four years using the micro-erosion meters (MEM) and Structure-from-Motion Multi-View Stereo (SfM-MVS) surveys have provided accurate quantitative rates of erosion and visual representation of surface morphologies. MEM erosion data revealed variations in erosion, weathering and deposition rates across lithology, tidal positions, and platform elevation after the uplift. Four-years post-uplift erosion data shows a resetting of erosion rates and faster rock breakdown on mudstone than limestone lithologies compared to pre-uplift rates. Over the 4-year period, surface downwearing rates for all platforms was 2.20 mm/yr, a 100% increase from a pre-uplift rate of 1.10 mm/yr. Average lowering rates on limestone, hard mudstone and soft mudstone platforms are 1.31 mm/yr, 2.13 mm/yr and 3.60 mm/yr, respectively. While previously reported seasonal trends in erosion rates have disappeared as rates are now similar during summer and winter seasons, significant differences in lowering rates now exist across rock lithology and elevation. On one of the harder mudstone rocks, a dramatic increase from a pre-uplift erosion rate of 0.43 mm/yr to 19.23 mm/yr (1-year after uplift) and subsequent decline to 1.54 mm/yr after four years is suggestive of isolated incidents of block detachment and erosion. For the first time, we complement MEM data with available SfM-MVS derived orthomosaics to provide evidence of changing rock morphology and processes such as intense granular disintegration, flaking, algal growth, and boring. On tectonically active rock coasts, the strong fluctuations in erosion rates and platform morphological expressions indicate the actions of not only waves, tides, and weathering processes but also tectonics in shore platform and marine terrace development.

# Long-term exhumation of the western North China Craton: insights from seismic, borehole and geochronological data

Peng H.*[1-2], Wang J.[2], Liu C.[2], Zhang T.[3] & Zattin M.[1-2]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Department of Geology, Northwest University, Xi'an (China).
[3] Exploration and Development Research Institute, Zhongyuan Oilfield Company, SINOPEC Puyang (China).

*Corresponding author e-mail:* pengheng@stumail.nwu.edu.cn

*Keywords:* exhumation, craton, geochronology.

The study of large-scale and long-term sedimentary hiatus and exhumation in vast intraplate basins is very significant for unravelling their tectonic development and morphodynamics. Ordos Basin is an intra-cratonic depressions in the western part of the North China Craton that gradually subsided from the Proterozoic to Mesozoic and contains primarily six post-1.8 Ga unconformities before being affected by a series of Cenozoic tectonic events that gave it its current setting. Given existing thermochronological data that identify Mesozoic–Cenozoic multiphase cooling events, we report the first detailed new apatite fission-track, zircon (U-Th)/He, and zircon U-Pb geochronology on Paleoproterozoic well samples from the oldest sedimentary rocks in the Ordos Basin that reveal cooling events at ca. 2.48~2.43 Ga, 1.97~1.82 Ga, 589~571 Ma, 438 Ma, 285 Ma and 32~18 Ma. Seismic profiles and associated well cross-section interpretations has been used to identify the basin's great unconformities and decipher the stratigraphic pattern. The new data allowed a re-interpretation of the Ordos Basin's amount and timing of erosion and burial. Our results provide new evidence that related unconformities to East Asia orogenic events and give important constraints to petroleum exploration.

# Erosional laws in analogue models

Reitano R.*[1], Faccenna C.[1-2], Funiciello F.[1], Corbi F.[3], Lanari R.[4] & Clementucci R.[1]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] German Research Centre for Geosciences, Potsdam (Germany). [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [4] Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* riccardo.reitano@uniroma3.it

*Keywords:* tectonic geomorphology, analogue modelling, landscape evolution.

The presence of a strong interaction between tectonic deformation and surface processes is widely recognized. Still, the nature of this interaction is difficult to unravel and quantify. In the last decades, analogue landscape evolution models have been widely implemented and employed in different tectonic settings, to complement field campaign studies. Since the aim of these analogue models is to help the interpretation of data coming from natural prototypes, it is important to test how well empirical erosional laws built upon natural landscapes, explain analogue model behavior. We perform a series of experiments for a straight interpretation of the relationship between applied boundary conditions and analogue landscape evolution. The selected analogue material is composed of 40 wt.% of silica powder, 40 wt.% of glass microbeads, and 20 wt.% of PVC powder. The analogue material fills a rectangular box (30×35×5 $cm^3$) placed over a reclined table. Over the box, a series of sprinklers generate a dense mist (i.e., rainfall) that triggers surface processes. The boundary conditions applied to the models are the imposed slope of the reclined table and the rainfall rate. We test three rainfall rates (9, 22, and 70 mm $h^{-1}$) and three imposed slopes (10, 15, and 20°), analyzing how the combination of these boundary conditions results in different landscape metrics (e.g., basins length, basins width, drainage area, channel slope, erosional efficiency) and erosion rates. Results show that in models affected by high rainfall rates (70 mm $h^{-1}$), the implemented analogue material is characterized almost no channelization, and erosion acts uniformly and diffusively over the models' surface. Lower rainfall rates (9, 22 mm $h^{-1}$) allow more discrete channelization instead. On the other hand, as expected, the imposed slope controls the amount of incision, so that the volumes of material removed by erosion increase moving from 10° to 20°. However, even if the maximum incision is generally controlled by the slope, the coupling with rainfall rate tunes the effectiveness of erosion. In this work we compare the imposed boundary conditions with the corresponding erosion rates, using geomorphic markers and landscape metrics to define if and how natural erosional laws apply to analogue landscape evolution models.

# The topographic growth of a mountain chain revealed by hydrography and topography: the case of the Central Apennines

Scaccia D.*, Sembroni A. & Molin P.

Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* david.scaccia@uniroma3.it

*Keywords:* Apennines, uplift, rivers.

Topography is the result of the competition between sub-crustal, crustal and surface processes. In areas characterized by a growing mountain range, the analysis of topography and drainage system proved to be crucial to study such an interaction and, by so doing, to investigate the landscape evolution. The Apennine chain is an active fold-and-thrust belt developed during the Neogene and currently affected by regional uplift and extensional tectonics. In particular, the highest elevations of the central Apennines are not only due to isostasy, but they are also partially supported by mantle upwelling processes, connected with a slab window formed in the early Pleistocene and later enlarged.

In this study, we focused on the geometry of topography (swath profiles, filtered topography) and of fluvial network (river longitudinal profiles, chi-plot, mobility of the regional drainage divide) of the central Apennines to investigate its landscape transient in response to the dynamically supported component of the regional uplift. Finally, we studied the Aniene and Tronto rivers as examples of basins draining respectively the western and eastern sides of the chain. On these basins, we applied a channel stream power linear inverse model to capture the signal of tectonic processes.

The results showed the presence of a topographic bulge centered in the central Apennines and corresponding with an area of shallower Moho and mantle low velocity anomaly. The analysis of hydrography evidenced the sensitivity of river systems to extensional tectonics and to uplift, both inducing perturbations in streams and drainage patterns. In particular, the values of the channel steepness index, recording the along strike variation in regional uplift rate, increase in correspondence with the topographic bulge. The analysis of the mobility of the divide suggests a general condition of stability, although locally the rivers draining the Tyrrhenian side appear to be more aggressive, recording a reorganization of the fluvial network. Finally, the inversion model indicates that: 1) the uplift rate in correspondence with the topographic high reaches a value of 0.88 mm/yr in the Adriatic flank and of 0.68 mm/yr in the Tyrrhenian flank; 2) the uplift forces the drainages to evolve by superimposition to the east and by fluvial piracy to the west.

# The Pleistocene Sardinian composite unconformity surface. Insight on climate and tectonic interplay to reconstruct Western Mediterranean geodynamic evolution

Sechi D.*[1], Andreucci S.[2] & Pascucci V.[1]

[1] Dipartimento di Architettura, Design e Urbanistica, Università di Sassari. [2] Dipartimento di Scienze Chimice e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* dasechi@uniss.it

*Keywords:* marine terraces, Quaternary geodynamic, luminescence dating.

Unconformities correspond to erosional or non depositional surfaces, separating older strata from younger rocks above and encapsulating significant geological gaps. Recent studies on sedimentary sequences filling Quaternary marine terraces have highlighted the possible composite nature of some unconformities and their diachronous character. The presence of such unconformities suggests the possible interplay between regional tectonic and climate driven changes, and when observable along a vast area, it can assume regional importance.

Sardinia Island is located in the centre of the western Mediterranean area, and it has been considered tectonically stable since the Early Pleistocene. It hosts several Pleistocene shallow marine deposits due to their stratigraphic position placed above present sea level, and most of these have been stratigraphically related to the Marine Isotopic Stage (MIS) 5e highstand (116-126 ka), which is considered the last highstand that exceeded the present sea level of +5/9 m.

However, recently, different chrono-stratigraphic reviews of Pleistocene marine successions demonstrated that several of these cannot be related to a single marine event but are the result of the superimposition of two o more events divided by a composite unconformity surface. Thus much of the studied marine terrace sedimentary sequences are composed of more than one transgressive–regressive cycle, related using the Luminescence dating method to the MIS 7 (~200 ka), MIS 5e (~125 ka) and MIS 5c (~100 ka) substages.

In particular, the stratigraphic superimposition of MIS 5c on MIS 5e above present sea level conflicts with the global accepted sea-level curve, which described the MIS 5c placed at around -22 m below the present. This particular chrono-stratigraphic asset for Sardinia Pleistocene marine successions raises different questions: i) Is the highstand of MIS 5c substages well constrained in amplitude and elevation respect to present sea-level positions for the Mediterranean area? ii) Is the Quaternary Relative Sea Level curve of the Mediterranean characterised by unrecognised high-frequency sea level oscillations below the sensitivity of presently available dating methods? iii) Has been the western Mediterranean area characterised by undetected regional versus local tectonic activity during the Pleistocene?

Answering these questions will open new scenarios on the Quaternary geodynamic evolution of the western Mediterranean during the last 300 ka.

# Tectonically driven drainage reorganization in the Eastern Cordillera, Colombia

Siravo G.*[1-2], Becker T.W.[3], Faccenna C.[4-2], Fellin M.G.[5], Gérault M.[6], Herman F.[7], Molin P.[2] & Sembroni A.[2]

[1] INGV, Roma. [2] Dipartimento di Scienze, Università di Roma Tre. [3] Institute for Geophysics and Department of Geological Sciences, Jackson School of Geosciences, University of Texas, Austin, TX (USA). [4] German Research Centre for Geosciences, Potsdam (Germany). [5] Department of Earth Sciences, ETH Zürich (Switzerland). [6] Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA (USA). [7] Institut des Dynamiques de la Surface Terrestre, Faculté des Géosciences et de l'Environnement, Lausanne (Switzerland).

*Corresponding author e-mail:* gaia.siravo@ingv.it

*Keywords:* landscape evolution, flat-slab subduction, inverted orogen.

The topographic growth of a mountain belt is commonly attributed to isostatic balance in response to crustal and lithospheric thickening. However, mantle processes may also dynamically contribute to the topography of the Earth. We investigated the role of these processes in the Eastern Cordillera (EC) of Colombia.

The EC is a double-vergent fold and thrust belt that formed during the Cenozoic by the inversion of a Mesozoic rift. Shortening started in the Paleogene and is still active. The chain is located ~500 km far from the trench where two separate portions of the Nazca plate subducts below the South American plate. North of 5°N, the EC rises above a flat-slab region. Volcanic arc migration implies slab shallowing by ~10 Ma and flattening up to the present-day configuration at ~6 Ma. The occurrence of a high $v_p/v_S$ anomaly and clustered seismicity below the belt at ~160 km depth delineates the slab geometry and has been related to slab dehydration, suggesting the presence of a hydrated mantle wedge. Regional surface uplift started in the Late Miocene/Pliocene. The landscape of the EC that reaches a maximum elevation of ~5000 m (Cocuy Sierra) hosts two plateau-like low-relief surfaces at 2500 m (Chiquinquirà and Tunja highlands) and 1500 m (Mesas). Features like river captures, windgaps, knickpoints, and a disconnected alluvial fan record a transient state of drainage reorganization.

To disentangle the crustal vs. sub-crustal forcing and to investigate the relative timing of drainage network and landscape evolution we: 1) compiled thermochronologic data and inverted for the exhumation history of the chain over the last 20 Ma; 2) tested the hypothesis of a flat-slab and hydrated-mantle wedge induced topographic growth through numerical models; and 3) combined the analysis of topography, hydrography (river longitudinal profiles, morphometric parameters, drainage divide stability), knickpoint migration (celerity model), paleo-longitudinal profile modeling, satellite images, and field observations.

Results indicate that pulses of fast exhumation are found to be associated with the uplift that occurred from ~7 Ma to the present-day. Exhumation rates increased during the Plio–Pleistocene at different wavelengths and amplitudes. The small wavelength and large amplitude signals could be related to shallow crustal deformation, whereas the long wavelength ones likely resulted from the combination of a flat-slab geometry and a weak and buoyant mantle wedge as predicted by the numerical models. All these processes contributed to the landscape evolution: the tectonic deformation strongly influenced the drainage patterns, whereas the sub-crustal related surface uplift caused base-level lowering resulting in an overall drainage re-organization including its integration into the plateaux, fluvial piracy, and knickpoints migration.

# Long-term relief evolution of the Andean chain in the Bongará region (northern Peru): implications for the genesis of supergene ore deposits

Sorrentino A.*[1], Mondillo N.[1-3] & Valente E.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Natural History Museum, London (UK).

*Corresponding author e-mail:* anna.sorrentino2@unina.it

*Keywords:* Zn supergene deposits, Bongará district, morphometric analysis.

In the Bongará district, located in the north-eastern sector of the Peruvian Andes, three mixed sulfide - nonsulfide Zn- Pb ore deposits have been recognized: Mina Grande, Cristal and Florida Canyon, hosted in the carbonate rocks of the Pucarà Group. The Florida Canyon deposit is located in the Eastern Cordillera, within the Utcubamba Basin, and represents one of the most important Zn-Pb MVT deposits of the region. The mineralization is hosted in Triassic rocks and consists mainly of sulfides, with one-third of the resources represented by nonsulfides (Hunt et al., 2017). The Mina Grande and Cristal deposits are comprised in the western margin of the Subandean Fold-and-Thrust Belt, within the Chiriaco Basin, and consist mainly of nonsulfide ores with less sulfides hosted in more recent Jurassic carbonate rocks (Workman & Breede, 2016).

In this study, we performed a morphometric analysis based on the investigation of the topography and the river network features of the two hydrographic basins of the Utcubamba and the Chiriaco rivers, with the aim to determine the relationship between the irregular distribution of vertical motions (e.g., surface uplift) and the genesis of supergene Zn deposits occurring in this district. The research has been conducted through the evaluation of the parameters such as elevation, local relief, swath profile, river longitudinal profiles, slope/area analysis to derive the normalized channel steepness index (ksn) and transformed river profiles ($\chi$-long profiles). The spatial distribution of these indexes allows to derive some considerations about the spatial distribution of vertical motions (e.g., surface uplift). Furthermore, the sharp increase in maximum, mean and minimum elevation moving from the Utcubamba Basin to the Chiriaco Basin, coupled with a jump in the mean Ksn values, suggest that the Chiriaco Basin has experienced either more recent surface uplift or surface uplift at rates higher than the Utcubamba Basin. This trend seems to be confirmed by the uneven erosion that the Florida Canyon and the Mina Grande-Cristal deposits have experienced. In fact, the Utcubamba Basin has been subjected to an uplift protracted in time, resulting in a rugged local relief and lowering the mean and minimum elevations, which would have removed the Jurassic succession and exposed at the weathering the Triassic-hosted Florida Canyon mineralization. In the Chiriaco Basin, the higher surface uplift in terms of time and/or rate has exposed at the weathering the Jurassic-hosted Mina Grande and Cristal deposits allowing the almost complete alteration of primary sulfides and the development of nonsulfide mineralization.

Hunt W., Pennington J., Sepulveda D.H., Poeck J., Osborn J., Gilbertson J. & Tinucci J. (2017) - NI 43-101 Technical Report Preliminary Economic Assessment Florida Canyon Zinc Project Amazonas Department, Peru. SRK Consulting (US).

Workman A. & Breede K. (2016) - Technical Report on the Bongará Zinc Project in the Yambrasbamba Area, Northern Peru. NI 43-101 Technical Report.

# S14.

# Ore deposits for a green future

*Conveners and Chairpersons*

*Nicola Mondillo (University of Napoli - Federico II)*

*Licia Santoro (University of Torino)*

*Marilena Moroni (University of Milano - La Statale)*

*Stefano Naitza (University of Cagliari)*

*Francesco Putzolu (Natural History Museum of London)*

# Chlorine-bromine-iodine systematics as tracer of fluid and metal sources in Sn-W mineralized magmatic-hydrothermal systems

Bongiovanni M.*[1], Fusswinkel T.[1], Marks M.[2] & Kocher S.[3]

[1] Rheinisch-Westfälische Technische Hochschule, Aachen University (Germany). [2] Eberhard Karls Universität Tübingen (Germany). [3] Natural History Museum, London (UK).

*Corresponding author e-mail:* mauro.bongiovanni@emr.rwth-aachen.de

*Keywords:* halogens, fluid inclusions, Sn-W deposits.

Tin is a key element in electronics manufacturing due to its use as solder, and as a nanofilm coating in solar cells and batteries. Tungsten is currently listed as a critical element by the European Commission for the green energy transition. The genesis of Sn-W deposits is typically associated with magmatic-hydrothermal fluids originated in granitic plutons, but the mechanisms of formation are still debated. Classical models (e.g., Heinrich, 1990) propose that fluid-rock interaction and especially mixing of magmatic-hydrothermal fluids with local meteoric, metamorphic or basinal fluids is a key factor in producing high ore grades by lowering Sn and W solubility via dilution (salinity decrease), oxidation, acid neutralization or cooling, but the exact nature and provenance of these external fluids remains debated for many Sn-W mineralized systems worldwide. A better understanding of these fluids would thus significantly contribute to the development of improved predictive models on Sn-W ore deposit formation.

The aim of this study is to conduct a regional-scale halogen study of the Sn-W province of the Cornubian batholith in SW England. The heavier halogens (Cl, Br, I) are well-known for their largely incompatible behaviour in most minerals and during fluid-rock interaction, and thus are ideally suited as fluid provenance tracers (Fusswinkel et al., 2018). However, some of the effects of key processes in magmatic-hydrothermal systems (e.g., fluid exsolution, boiling, fluid phase separation) on halogen signatures are largely unknown, as are the Cl-Br-I systematics of S-type granitic melts. A better understanding of these aspects is required to establish a firm basis for halogen studies in Sn-W magmatic-hydrothermal systems. We present the first results of an integrated study combining in-situ LA-ICP-MS Cl-Br-I analysis of fluid inclusions in hydrothermal quartz with combustion-ion chromatography of granites and mineral separates as a proxy for granitic halogen signatures.

Preliminary petrographic observations consistently witness a progressive decrease of fluid salinity within individual veins, supporting the classical dilution model for such systems. In addition, Br/Cl ratios in whole-rock analyses show a positive correlation with magmatic fractionation. The studied samples range from purely magmatic members (granites of different fractionation degrees), transitional pegmatites and greisen veins, to hydrothermal lodes with Sn-W-Cu mineralization, in order to fully characterize the overall behaviour of halogens in Sn-W systems, and so establish a novel method in the study of such systems worldwide.

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# Vanadium in circular economy and vanadium deposits in the African continent

Boni M.*

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* boni@unina.it

*Keywords:* vanadium, Africa.

Metals and minerals are integral to all renewable energy technologies. Some of them are relatively easy to recycle, making them eminently suitable for a circular economy. A circular economy, in which as much material as possible is re-used rather than discarded to minimize waste, is the model to which all countries should aspire for their long-term future. Vanadium is not an exception to this concept and its use has risen substantially in recent years, as have the number of innovation-driven industries that depend on vanadium for their operations and products. Vanadium batteries continue to support the world's adoption of a circular economy by providing a sustainable, safe and low-cost energy option with a lifecycle of more than 20 years. Over its lifespan, vanadium redox flow battery (VRFB) technology offers the lowest cost per kilowatt-hour stored, and the vanadium chemistry of the battery is also fully reusable and recyclable at the end of project life.

Vanadium can be obtained from primary and secondary sources.The latter mostly consist of metallurgical wastes (from steel industry), tailings and slags from ancient and modern mining areas and plants. Primary vanadium sources are of variable importance, with V-hosting titanomagnetites in the forefront. Africa is a continent enriched in all types of mineral deposits, including vanadium, as a result of its geological legacy. In fact, a large spectrum of vanadium mineralizations with different economic value has been recorded in the African continent, reflecting its geological and climatic evolution. In Africa, not only the resources from Namibia (Otavi Mountainland) and South Africa (Bushveld) are historically well-known and exploited, but also minor occurrences in other countries are rather significant, where vanadium minerals are extracted with old artisanal methods. To ensure sufficient vanadium supply worldwide, even smaller concentrations should be currently regarded as a potential resource, as the graphite-vanadium deposits typical of Eastern Africa and Madagascar, as well as the vanadium credits associated with uranium ores, coal, black shales and oil.

A brief review of the most important vanadium occurrences in several African countries will be reported in this talk, organized as follows:

1. Southern Africa (Botswana, Namibia, South Africa, Zambia, Zimbabwe);
2. Eastern Africa (Burundi, Kenya, Madagascar, Mozambique, Tanzania);
3. Western Africa (Angola, Burkina Faso, Cameroon, DCR Congo);
4. Northern Africa (Algeria, Libya, Mauritania, Morocco, Niger, Tunisia).

# Noble gases as powerful geochemical tools to investigate ore deposits: a case study of Mississippi Valley Type deposits, Jbel Bou Dahar Pb-Zn district, Eastern High Atlas, Morocco

Bouabdellah M.[1], Boukirou W.[1], Caracausi A.*[2], Italiano L.[3] & Zemri O.[1]

[1] Département de Géologie, Faculté des Sciences, Université Mohammed Premier, Rabat (Morocco). [2] INGV, Palermo. [3] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* antonio.caracausi@ingv.it

*Keywords:* noble gases, ore deposits, sulfides.

High economic demand for strategic metals including rare earth elements, due to their extensive use in commercial and scientific applications, is causing a great increase in mineral exploration in recent years. Modern exploration is therefore looking for new deposit types of economic interest at a rate that can meet global demand and challenges for an accelerated energy transition (i.e., green economy).

In this framework, both isotopes and relative amounts of noble gases (e.g., helium, neon, argon, hereafter He, Ne and Ar) trapped within mineral-hosted fluid inclusions could help in constraining the sources (mantle-crust-atmosphere) and evolution of the mineralizing fluids along with ore depositional processes (e.g., fluid mixing, fluid-rock interactions) in a large variety of hydrothermal ore deposit types. In fact, the noble gases and their isotopes are able to provide unique constraints on certain geological processes owing to their inert behavior and because numerous nuclear reactions are recorded in the noble gas isotopic compositions.

Here, we present some preliminary results of He, Ne and Ar isotopes trapped in fluid inclusions in sulfides (pyrite, galena and sphalerite) from the Jbel Bou Dahar carbonate-hosted Pb-Zn-Ba deposit in the eastern High Atlas of Morocco. The Atlas paleorift system in West Africa hosts several world-class Mississippi Valley-type deposits of the Tethyan-Atlantic Pb-Zn ± Cu ± F ± Ba province (Bouabdellah et al., 2016). Among these, the Jbel Bou Dahar district represents an excellent opportunity to establish the evolution of hydrothermal fluids owing to the recent age of emplacement of mineralization and the lack of intensive deformation.

The two-helium isotopes, the primordial $^{3}He$ and $^{4}He$, which is produced by the radiogenic decay of U and Th, clearly indicate the involvement of a dominantly crustal component with traces of a mantle-derived He input. Mixing between these two components is further supported by relationship between argon isotopes ($^{40}Ar/^{36}Ar$) and the Ar-He radiogenic products (e.g., $^{40}Ar^{*}$ by potassium). Furthermore, the combined Ar isotope data ($^{40}Ar/^{36}Ar$) with the atmospheric-derived $^{36}Ar$ and $^{20}Ne$ values reflect input of a meteoric component.

Cross-referencing data from analyses of noble gas isotopic ratios, mineralization from Jbel Bou Dahar deposit would appear to originate from crustal deep hydrothermal systems, given the strong crustal versus magmatic components. These new results are contributing in constraining the nature, source(s), and evolutionary history of the mineralizing system, along with ore depositional processes that led to the formation of the Jbel Bou Dahar Pb-Zn ± Cu ± Ba ores.

Bouabdellah M., Maacha L., Levresse G. & Saddiqi O. (2016) - The Bou Azzer Co-Ni-Fe-As (±Au ± Ag) District of Central Anti-Atlas (Morocco): A Long-Lived Late Hercynian to Triassic Magmatic-Hydrothermal to Low-Sulphidation Epithermal System. In: Bouabdellah M. & Slack, J. Eds., Mineral Deposits of North Africa. Mineral Res. Rev., 229-247. https://doi.org/10.1007/978-3-319-31733-5_810.

# Overview of CRM-bearing minerals in the Co-Ni-As mineralisation of the Punta Corna mining complex, Northern Italy

Bussolesi M.*[1], Grieco G.[2], Cocomazzi G.[2] & Cavallo A.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* micol.bussolesi@gmail.com

*Keywords:* Critical Raw Materials, Co-Ni-As mineralisation.

The Punta Corna mining district, located in the Lanzo Valleys area of Western Alps (Northern Italy), is a system of hydrothermal veins which were exploited in the past for Fe, Ag and later Co. These veins are hosted within metaophiolitic rocks (metabasalts with minor metagabbros, ultramafic rocks and minor metasediments) representing disrupted sections of oceanic lithosphere of Jurassic age. The mineralization is characterized by Co-Ni arsenides in the Eastern sector of Punta Corna, and by siderite in the Western sector, where Co phases are less abundant. Four deposition stages have been recognized (Moroni et al., 2019): i) siderite, ii) baryte, iii) Co-Ni-Fe arsenide, and vi) sulfides and sulfosalts.

This work focuses on the mineralogy and mineral chemistry of CRM-bearing minerals, deposited mainly during the third and fourth stages, in selected mining sites of Punta Corna. The selected mining sites are: San Francesco and Sant'Andrea in the Western part of Punta Corna; Vittorio Amedeo, Nido dell'Aquila, San Giovanni, Carlo Emanuele, Santa Maria, Speranza and Colle Fortuna in the Eastern part; Santa Barbara in the Southern part.

The main CRM phases are: ferroskutterudite $(Fe,Co)As_3$, safflorite $(Co,Fe)As_2$, clinosafflorite $(Co,Fe,Ni)As_2$, tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$, bismuthian tetrahedrite $(Cu,Fe)_{12}(Sb,Bi)_4S_{13}$, bournonite $PbCuSbS_3$, pyrargyrite $Ag_3SbS_3$, a Bi-rich variety of chalcostibite $CuSbS_2$ and an Sb-Bi alloy. Moreover, tiny xenotime $(YPO_4)$ crystals have been detected in some samples.

Co-bearing minerals occur mainly in Eastern Punta Corna, and were not detected in the western part. Ferroskutterudite is abundant in several mining sites, and shows variable Co contents, up to 13.51 wt.%. Safflorite and clinosafflorite (Co up to 16.26 wt.%) are less abundant and were detected only in the San Giovanni mine.

Sb and Bi minerals are widespread in all Punta Corna. Tetrahedrite shows variable Sb contents, up to 30.24 wt.%. Bi partially replaces Sb in the tetrahedrite structure. Bi-tetrahedrite has Sb contents up to 17.33 wt.% and Bi contents up to 15.54 wt.%. Bournonite is not as widespread as tetrahedrite, and was found only in the Santa Barbara mine. Pyrargyrite is rare and limited to the Speranza mining site. Bi-rich varieties of chalcostibite (Sb up to 47.27 wt.%, Bi up to 16.23 wt.%), and a Sb-Bi alloy were detected only in the Carlo Emanuele mining site.

Sb and Bi-bearing phases are lollingite, arsenopyrite and gersdorffite. A mineral approaching lollingite stoichiometry shows variable As substitution by Sb (Sb up to 8.72 wt.%). Arsenopyrite and gersdorffite also display Sb fluctuations, with contents from below detection limit to 13.19 wt.%.

Finally, Co and Sb-rich secondary phases are also present in the complex. They are mostly undetermined oxides and hydroxides with Co contents up to 10.34 wt.% and Sb contents up to 20.06 wt.%.

Tiny xenotime crystals (~10 µm) were detected at Santa Barbara and Santa Maria mining sites.

Moroni M., Rossetti P., Naitza S., Magnani L., Ruggieri G., Aquino A., Tartarotti P., Franklin A., Ferrari E., Castelli D., Oggiano G. & Secchi F. (2019) - Factors controlling hydrothermal nickel and cobalt mineralization - Some suggestions from historical ore deposits in Italy. Minerals, 9(7), 429.

# Critical and other trace metals fractioning within the flotation plant at the Stan Terg Pb-Zn mine, Kosovo: implications on recovery and environmental hazard

Bussolesi M.*[1], Grieco G.[2], Cocomazzi G.[2], Hyseni Q.[3], Cavallo A.[1] & Destefanis E.[4]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Department of Applied Geology and Geophysics, Goce Delcev University, Shtip (North Macedonia). [4] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* micol.bussolesi@gmail.com

*Keywords:* Pb-Zn skarn, Acid Mine Drainage.

The Trepca mines and their processing facilities are located in Northern Kosovo. They exploit a carbonate-replacement deposit consisting of vein-type Pb-Zn mineralization related to Neogene andesite-latite volcanics and intrusive bodies in the area. These are hosted within the Vardar Zone: a suture separating two distinct continental blocks, namely the Pelagonian Zone to the west and the Serbo-Macedonian Massif to the east. The main minerals recovered nowadays from the Stan Terg ore body are galena and sphalerite, but in the past pyrite, arsenopyrite, boulangerite and chalcopyrite were recovered too. The present work, due to the recent interest in increasing mining production in Europe, focuses on the distribution and fractioning of valuable metals along the flotation flowsheet. We studied samples of initial feed, Zn concentrate, Pb concentrate and the final tailing. They were analyzed for major and trace element contents via XRF and ICP-MS and for their mineral chemistry via EMPA. With respect to the initial feed, the Zn concentrate is enriched in the critical metal In (46 ppm) and in Cd (1667 ppm). The Pb concentrate shows interesting enrichments in Bi (1540 ppm) and Sb (1667 ppm), both listed as Critical Raw Material in the EU 2020 report. Microprobe analyses partially confirm the ICP-MS results and highlight an enrichment of Cd within sphalerite and Bi in galena. Sb is below detection limits in all phases except for arsenopyrite, where it is enriched up to 0.85 wt.%. This could suggest that some arsenopyrite reports to the Pb concentrate. The final tailing does not show enrichments in Critical Metals, but in Potentially Toxic Elements (PTE) for the environment. Hg and As, present in high amounts in the feed, report mostly to the tailings, where they respectively show concentrations of 8930 ppm and 1420 ppm. These can result in high release of toxic elements if Acid Mine Drainage (AMD) occurs. The AMD of the tailings was assessed by static Acid Base Accounting tests. Results show that the Net Acid Production Potential (NAPP) is variable, depending on the sulfide to carbonate ratio. Preliminary MP-AES analyses on leached waters from tailing samples highlight absence of acidification and a low amount of dissolved PTE. These could be related to the fast dissolution of carbonates so that a later acidification could be envisaged for tailings showing positive NAPP. Further kinetic tests are required for a better evaluation of environmental hazard.

# The Neoproterozoic high grade metamorphic complex as potencial REE hosted rocks in Oaxaca, southern Mexico

Carrillo-Marrodan L.G.* & Castro-Mora J.

Academic Area of Earth Sciences and Materials, Autonomus University of Hidalgo State, Hidalgo (Mexico).

*Corresponding author e-mail:* ca319073@uaeh.edu.mx

*Keywords:* REE elements, alkaline, petrotectonic.

The Oaxacan complex is located in southern Mexico, Oaxaca state on the surrounding areas of Telixtlahuaca and Nochixtlán villages; it is mainly composed by eight petrotectonic high grade metamorphic units ranging from 1.5 Ga to 960 Ma. (Keppie et al., 2001) Banding foliation is remarkable with a prominent inclination towards NW. This banding foliation obey to a structural arrengement from the top to the bottom of the exposed units.

Nature of the eight main units varies from the structural top represented by a rich amphibole charnokites (1.1 Ga) to the bottom consisted by a well defined migmatite suite; the middle part of the sequence is represented by a rich graphite-phlogopite paragneiss within a *lit par lit* pegmatites bodies, which is the main unit exposed on the area. Going down towards to the bottom there is a rich feldspar sienitic gneiss intruded by local diabase green dykes, this unit is in contact on the lower part with a carbonatite suite intruded by Grenvillian pegmatites (960 Ma). The sequence described outcrops in contact with a series of ortogneiss separated by a precambrian shear known as "Cuajolote Fault" (Solari et al., 2004) that represents a tectonic separation between the paragneiss and the ortogneiss sequences. On the bottom of the sequence described appears the migmatitic exposures (1.3~1.5 Ga) intruded by anorthositic bodies that represents the oldest rocks described all over Mexico.

REE were detected on the alkaline to peralkaline units (sienitic gneiss and carbonatites) and research is ongoing and focused on an extensive sampling to define economic grades and tonnage that could be economically viable for further explotation.

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Solari L.A., Keppie J.D., Ortega-Gutiérrez F., Cameron K.L. & Lopez R. (2004) - ~990 Ma peak granulitic metamorphism and amalgamation of Oaxaquia, Mexico: U-Pb geochronological and common Pb isotopic data. Rev. Mex. Cienc. Geol., 21(2), 212-225.

# Isotopic and trace element signatures of calcite, apatite and zircon from carbonatite liquid associated with Cu-Ni-PGE mineralization

Cherdantseva M.* & Fiorentini M.

Centre of Exploration Targeting, School of Earth Sciences, University of Western Australia, Perth (Australia).

*Corresponding author e-mail:* mariya.cherdantseva@research.uwa.edu.au

*Keywords:* carbonatite liquid, isotopic and trace element composition.

Based on previous detailed mineralogical, petrological and experimental studies, we put forward a model whereby immiscible volatile-rich carbonatite liquid may play a key role in the transportation of Ni-Cu-PGE-rich sulfides from the mantle to the crust. The crystallized product of carbonatite liquid forming haloes surrounding magmatic sulfide globules generally comprises plagioclase, clinopyroxene, amphibole, phlogopite, carbonate, apatite, ilmenite and zircon. This paragenetic association can be found in many examples of magmatic sulfide deposits globally (Sessa et al., 2017; Blanks et al., 2020; Pshenitsyn et al., 2020; Schoneveld et al., 2020). To further refine our model, we have investigated and present here isotopic and trace element composition of accessory minerals (calcite, apatite and zircon) from three mineralized intrusions located at variable depths: lower crustal intrusion - Valmaggia pipe, Italy; middle crustal intrusion - Broken Hill, Australia; upper crustal intrusion - Rudniy, NW Mongolia. Results allowed us to confirm the carbonatitic origin of the haloes surrounding the magmatic sulfide globules and link their signatures in REE distributions among different phases to the depth of emplacement of the individual intrusions. The isotopic signatures of sulfur, carbon and oxygen in apatite, calcite and zircon, respectively, support a mantle source origin for the carbonatite liquid in mineralized intrusions emplaced at different depths and within very different country rocks. The proposed model of carbonatite-enhanced physical transport of magmatic sulfides may lead to a reconsideration of existing paradigms on the formation of orthomagmatic systems, enhancing the predictive and detective capability of exploration techniques to target elusive mineralized systems enriched in nickel, copper and the valuable platinum group metals.

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# Hyperspectral remote and proximal sensing for mineral exploration: the Punta Corna Co-Ni vein system (Piedmont, Italy)

Chirico R.*[1], Mondillo N.[1-2], Laukamp C.[3] & Zanin S.[4]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Natural History Museum, London (UK). [3] CSIRO - Mineral Resources, Kensington (Australia). [4] Altamin Ltd., Oltre il Colle (BG).

*Corresponding author e-mail:* rita.chirico@unina.it

*Keywords:* hyperspectral sensing, mineral exploration, PRISMA, five element vein-type deposits.

The purpose of the study is to highlight the distribution of alteration minerals genetically related to hydrothermally driven metallogenetic processes that occurred in the area of the Punta Corna Cobalt Project, a brownfield exploration prospect owned by Altamin Ltd., located in the Servin Valley in the Western Alps (Piedmont, Italy). More specifically, this work aims to test the capability of hyperspectral remote sensing for producing alteration maps of Visible Near (VNIR)- to Short Wave Infrared (SWIR)-optically active minerals, to be used as support to the mineral exploration in the area. The Punta Corna district is characterized by hydrothermal polymetallic orebodies defined by $Fe^{2+}$-rich carbonates and Co-Ni sulfide mineralization, hosted by E–W-trending subvertical veins with a maximum thickness of 6-7 m. The veins formed during the post-metamorphic structural evolution of the Alpine belt and sharply crosscut the foliation showed by the metaophiolitic host rocks, which generally are affected by intense sericite-quartz-carbonate alteration proximal to ore occurrences (Castelli et al., 2011; Moroni et al., 2019). The methodology is based on mapping of mineral occurrences in terms of relative abundances and composition using feature extraction indices and band ratios applied to hyperspectral satellite and field data. The PRISMA VNIR-SWIR hyperspectral satellite products (Italian Space Agency; ASI, 2020) were tested and combined with images acquired from other multispectral instruments, as well as supported by DEM-based geomorphology. Laboratory hyperspectral IR spectroscopy and mineralogical (XRD) and geochemical (ICP-MS/ES) analyses were carried out to define target alteration minerals and to validate the results obtained from the processing of satellite images. The first results of the study, partly validated through fieldwork, assess that a multi-scale approach based on hyperspectral and multispectral data represents an effective method for mapping alteration minerals associated with the Co-Ni mineralization, i.e., white mica, chlorite, and supergene goethite, since they show diagnostic absorption features at around 2200 nm, 2250 nm and 1550 nm, and 900 nm, respectively (Laukamp et al., 2021). The method can be used as an additional tool for guiding toward prospective areas where Co-Ni-bearing veins occur.

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Moroni M., Rossetti P., Naitza S., Magnani L., Ruggieri G., Aquino A., Tartarotti P., Franklin A., Ferrari E., Castelli D., Oggiano G. & Secchi F. (2019) - Factors Controlling Hydrothermal Nickel and Cobalt Mineralization - Some Suggestions from Historical Ore Deposits in Italy. Minerals, 9, 429.

# The effect of texture and mineralogy on the possible recovery of Sb as a flotation by-product from the Stratoni Pb-Zn-Au skarn deposit (Chalkidiki, Northern Greece)

Cocomazzi G.*[1], Bussolesi M.[2], Grieco G.[1], Cavallo A.[2], Tzamos E.[3] & Lazetera D.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Ecoresources, Thessaloniki (Greece).

*Corresponding author e-mail:* giuseppe.cocomazzi@gmail.com

*Keywords:* antimony, flotation, Chalkidiki.

Antimony is a Critical Raw Material, according to the EU commission 2020 list, strategically important for the global and European economy. Sb occurrences have been reported in the skarn Pb-Zn-Au deposits of the Kassandra Mines, mainly in the Pb concentrates of the flotation plant (Tzamos et al., 2020). The present work focuses distribution of Sb within the Stratoni mineralization of the Chalkidiki peninsula (Northern Greece) and the flotation flowsheet. The Stratoni polymetallic ore consists of a stratabound replacement mineralization hosted within marble horizons. It includes two deposits: Madem Lakkos and Mavres Petres. They have similar mineralization, consisting of lenses of Pb-Zn-Ag ore. The paragenesis is simple, comprising pyrite, sphalerite, galena, arsenopyrite and chalcopyrite. The gangue is rich in quartz, calcite and minor rhodochrosite. The ore samples have been investigated through SEM and EMPA. The only Sb phases detected are boulangerite and rare bournonite. Major and minor Fe-Pb-Zn sulfides, however, show various enrichments in Sb. Boulangerite occurs as tiny crystals (5-10 µm) included in sphalerite, where it is associated to galena. It also forms big prismatic crystals up to 100 µm long replacing galena, pyrite and arsenopyrite. Bournonite occurs in crystals with subhedral shape included in pyrite, or as large subhedral crystals (500-800 µm). Boulangerite and bournonite show homogeneous Sb contents, whose range is respectively 25.60-26.45 wt.%, and 23.37-25.23 wt.%. Antimony is also present in traces within the main base metal sulfides with the following maximum concentrations: pyrite (0.44 wt.%), arsenopyrite (0.13 wt.%), chalcopyrite (0.17 wt.%), sphalerite (0.21 wt.%) and galena (0.28 wt.%). The ore is enriched by flotation in three consecutive stages, that produce lead, zinc and gold concentrates respectively. Each stage includes conditioning, roughing, scavenging and cleaning flotation cells. Feed, some intermediate products, all the concentrates and some tailings of the Olympias and Stratoni mines were sampled and studied using particle size analysis, XRF, XRD, and ICP-MS. Compared with the antimony concentration in the feed (Sb = 1169 ppm), the Pb concentrate is highly enriched (Sb = 20633 ppm) and the Pb discard, that is also the Zn feed, is depleted (Sb = 302 ppm). Zn concentrate is again rich in antimony (Sb = 1170 ppm) compared to its feed, while Zn discard/gold feed is depleted (Sb = 264 ppm). Finally, the production of a gold concentrate, again, results in an antimony enrichment (Sb = 334 ppm) and depletion in the final tailing (Sb = 50 ppm). A sample of old tailing has an antimony content (Sb = 234 ppm) higher than the present tailing. The presence of abundant Sb phases opens up the potentiality to recover the metal as a by-product of lead concentration. Anyway, the presence of tiny Sb phases as inclusions in base metal sulfides and Sb enrichment in base metal phases can negatively affect the recovery rate.

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# Application of the PRISMA satellite hyperspectral sensor to the exploration of Cu-Mo porphyry deposits of the Miocene to Early Pliocene Belt of Central Chile

Corrado F.*[1], Chirico R.[1] & Mondillo N.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Natural History Museum, London (UK)

*Corresponding author e-mail:* frances.corrado@studenti.unina.it

*Keywords:* PRISMA, hyperspectral remote sensing, porphyry Cu-Mo deposits.

This study proposes a methodology based on the use of PRISMA satellite hyperspectral sensor for mapping the alterations associated with magmatic-related ore deposits of the Miocene to Early Pliocene Belt of the Central Andes (Sillitoe & Perello, 2005). The area is characterized by Cu resources mainly hosted by giant porphyry Cu-Mo deposits, emplaced in volcanic and volcaniclastic rocks of the Abanico and Farellones Formations. The bulk of the Co-Mo porphyry endowment is related to the evolution of the granodiorite-dominated San Francisco batholith, which intruded the latter formations and outcrops for an extension of about 200 km$^2$. The ores generally show evidence of zoned hydrothermal alteration patterns. The mineral maps were produced by image processing of products obtained from the PRISMA satellite mission of the Italian Space Agency, which was launched on March 22$^{nd}$, 2019. The PRISMA hyperspectral sensor comprises 234 spectral bands in the Visible Near and Short Wave InfraRed (VNIR-SWIR) regions of the electromagnetic spectrum and it is defined by a spectral resolution of ~13 nm and a spatial resolution of ~30 m (Cogliati et al., 2021). The SWIR 2 wavelength region (from 2000 to 2600 nm) was taken into consideration since it contains diagnostic absorption features of several hydrothermal alteration minerals. Absorption features are caused by combinations of hydroxyl-related fundamental stretching and bending vibrations ($\nu + \delta OH$). Al-bearing sheet silicates (i.e., white micas), kaolin group, chlorite and epidote are characterized by absorption features at around 2200 nm, 2185-2215 nm, 2250 nm and 1550 nm, respectively (Laukamp et al., 2021). Band ratios and feature extraction indexes were applied to several PRISMA scenes covering the areas of interest, in order to determine minerals' relative abundances and compositions, and to map the areas characterized by the occurrence of each target phase. The preliminary results assess that PRISMA allows to reliably define the distribution of the hydrothermal alteration halos and evaluate their relationships, guiding towards the mineralized zones. The proposed method can be considered a cost-effectively and rapid method of mining exploration.

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# Towards the definition of a Sn-W-Mo late Variscan skarn-system in Southwestern Sardinia: evidence from key-areas in the Sulcis-Iglesiente district

Deidda M.L.*[1], De Giudici G.B.[1], Fancello D.[1], Idini A.[1], Tavazzani L.[2] & Kouzmanov K.[3]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Institute of Geochemistry and Petrology, ETH Zürich (Switzerland). [3] Department of Earth Sciences, University of Geneva (Switzerland).

*Corresponding author e-mail:* deiddam.geo@gmail.com

*Keywords:* skarn, Sn-W-Mo, Variscan.

The SW portion of Sardinia (Sulcis-Iglesiente district) hosts many skarn orebodies, spatially and genetically associated to a suite of late-Variscan (289-286 Ma) ilmenite-series granites with a Sn-W-Mo metallogenic signature (Naitza et al., 2017). In order to frame different skarn-forming processes under a regional-scale metallogenic model, three key-areas (the old mines of Perda Niedda, Monte Tamara and Rosas) have been studied. Hosted in the same, variably metasomatized Cambrian carbonate unit (Gonnesa Fm.), these orebodies show a distinctive ore mineral assemblage, including magnetite, Zn-As-Pb-Cu-Fe sulfides - in part referable to pre-existent concentrations in the host rocks (Aponte et al., 1988) - and, as markers of the magmatic source, variable proportions of cassiterite, scheelite, molybdenite and Bi-phases.

The Perda Niedda skarn represents the proximal member of the system. Among prograde and retrograde silicates, garnet and axinite are Sn-rich; hydrothermal alteration of columbo-tantalite-bearing garnet resulted in a magnetite-fluorite-amphibole-chlorite assemblage with abundant cassiterite. Cassiterite and sphalerite are In-rich; magnetite is W-bearing.

Mineralization at Monte Tamara belong to a complex skarn system at variable distance from the causative intrusion. The ores include: 1. a proximal clinopyroxene-garnet-epidote skarn with magnetite, scheelite, cassiterite-stannite, molybdenite, Bi-Pb-Cu-Ag sulfosalts and Zn-Pb-Cu-Fe sulfides (San Pietro); 2. a relatively distal hydrothermal scheelite-arsenopyrite-sphalerite vein with quartz-carbonate gangue (Sinibidraxiu). Here, scheelite prevails over cassiterite (also In-bearing); garnet and epidote are also Sn-enriched.

The Rosas orebodies represent a more distal part of the system. Large-scale fluid circulation exploited a series of structures at the tectonized footwall of the Rosas Shear Zone (Cocco et al., 2022); mineralization mainly occurred in tectonic slices of Cambrian carbonates. Therefore, garnet is subordinate to Mn-rich clinopyroxene and Sn-poor epidote. The main ores consist of Zn-Pb-Cu-Fe sulfides and locally Ag-sulfides. Cassiterite-magnetite-fluorite seams are rare, Bi-phases very rare and scheelite undetected sofar.

In conclusion, skarn orebodies of SW Sardinia can be considered as parts of a regional-scale metallogenic system, related to a specific late-Variscan intrusive suite and developed in the same metasomatized host rocks. This implies that different features between skarn orebodies may reflect local factors (e.g., distality, structural asset, chemical controls related to facies variability in host rocks) within a single skarn system. Based on these evidences, we argue that an updated model for skarn mineralization of SW Sardinia could support further W-Sn-Mo mineral exploration in the future, not only in the deeper parts of these key-areas but also in the many, recurrent and promising skarn occurrences of the whole district.

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# Lithium resources of Italy: an overview

Dini A.[1], Lattanzi P.*[2], Ruggieri G.[2] & Trumpy E.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Pisa. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* pierfrancolattanzi@gmail.com

*Keywords:* lithium, ore deposits, geothermal fluids.

Lithium (Li) was recently added to the European list of critical raw materials because of the booming increase of its use for rechargeable batteries. Italy has no record of Li production, even if it is well known for outstanding Li-mineral specimens from Elba Island pegmatites. On the other hand, the current geopolitical situation suggests the opportunity of a systematic appraisal of the resources.

Most (> 60%) European Li production comes from deposits associated with Late Paleozoic magmatic rocks of segments of the Variscan chain (Gourcerol et al., 2019). In Italy, such rocks occur extensively in Sardinia, but their potential for Li is unknown, and deserves a more systematic exploration. Of potential interest are also Permo-Triassic spodumene pegmatites in the Austroalpine units of central Alps (e.g., Val Racines); most occurrences are probably uneconomic, but at Wolfsberg (Austria) they are the object of current exploration. According to Gourcerol et al. (2019), recent peri-Mediterranean magmatism offers little chances of significant Li resources. Indeed, the previously mentioned Elba Island pegmatites are quite small. Similarly, Tertiary pegmatites of central Alps may offer gem-quality Li-tourmaline samples, but does not appear large enough to warrant bulk mining. However, we notice here that rocks of the Tuscan and Roman Magmatic Provinces (TMP-RMP) have lithium contents (20-60 mg/kg) systematically higher (for the same silica content) than recorded in normal arc igneous rocks worldwide. Specifically, TMP granites contain up to 350 mg/kg Li, mostly hosted by biotite (up to 4 mg/g Li; Dini et al., 2021a).

There are other small Li occurences associated with Mn deposits and metabauxites, and there is a hypothetical potential for sediment-hosted deposits in post-orogenic Lower Permian Alpine basins, where the Li source could have been the penecontemporaneous effusive magmatism. However, the most promising potential seems associated with subsurface fluids (Dini et al., 2021b). High-enthalpy fluids in geothermal fields such as Cesano, Latera, Mofete, Larderello, Amiata may contain up to 480 mg/L Li; a research permit was in fact recently issued for Cesano. Lower temperature thermal waters also may contain significant Li (> 10 mg/L). Moreover, a visionary, but not impossible, perspective may consider deep injection of water to interact with, and extract Li from, magmatic rocks.

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# Co-Ni mineralization in the Punta Corna hydrothermal vein system (Piemonte, Italy): preliminary results

Domenighini G.*[1], Santoro L.[1], Moroni M.[2] & Zanin S.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Altamin Ltd., Oltre il Colle (BG).

*Corresponding author e-mail:* giulia.domenighini@unito.it

*Keywords:* cobalt ore, Co-Ni arsenides, hydrothermal vein system.

The Punta Corna polymetallic hydrothermal vein system is located in the municipalities of Usseglio and Balme, Lanzo Valleys (Piemonte, Italy). The area has been well known since the Middle Ages for the exploitation of Ag, Fe, and minor Co (commonly used for pigments production), until the 20th century.

The global concern about the *green transition* and critical raw materials (CRMs) supply, such as Co, which is critical for the manufacture of electric vehicles and storage power stations, has raised a renewed exploration interest in old mining sites, where the CRMs economic potential was not fully investigated. Since 2018 the Junior Exploration Company AltaMin ltd. owns the exploration license of the Punta Corna area, for assessing the economic viability of the ore.

The deposit consists of a complex vein system interpreted as the product of late Alpine hydrothermal events (Castelli et al., 2011) and it is hosted in the metaophiolitic suite of the Internal Piedmont Zone (IPZ), representing a portion of oceanic lithosphere and its sedimentary cover of the Jurassic Alpine Tethys (Dal Piaz et al., 2003). The IPZ recorded eclogite-facies metamorphism during the early phases of the Alpine orogeny and a re-equilibration under greenschist facies conditions during exhumation. The mineralized veins are almost exclusively hosted in metabasic rocks, locally preserving primary basaltic structures.

Based on literature data, the vein system can be divided into two different areas of geochemical significance: i) the western sector, where Fe mineralization prevails, and ii) the eastern sector, dominated by Co-Ni-Fe arsenides +Fe carbonates, quartz and calcite gangue ± Zn-Cu-Pb-Ag sulfides ± baryte. Mineral assemblage and deposition below 200°C from metal-rich brines (from preliminary fluid inclusion analyses) suggest analogies with five element-vein deposits (Moroni et al., 2019).

The present work is part of a Ph.D. project focused on the geological, geochemical, and mineralogical investigation on the Punta Corna mineralized veins aimed to deepen the knowledge of the structural control of the ore bodies and metal distribution. New field campaigns (Spring-Summer 2022) planned to collect samples and data, are particularly aimed to understand the brittle deformation stages related to the mineralizing events. Petrographic, mineralogical and chemical characterization were performed on 23 new samples collected from different hydrothermal veins by means of optical microscopy, XRD, wet-chemical analyses and SEM-EDS techniques at the University of Torino.

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# Recovering critical and economic metals (In, Sn, Zn, Cu) from mine waste debris and weathered outcrops in the Zn-Fe skarn belt of the Iglesiente-Sulcis region (SW Sardinia): the case of the historical Perda Niedda mining area

Ferrari E.S.*[1], Moroni M.[1], Naitza S.[2], Deidda M.L.[2], Mondragon Mallqi J.[1] & Stucchi M.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* marilena.moroni@unimi.it

*Keywords:* critical metals, metal recovery, mine waste.

Perda Niedda is a historical, poorly known mining area, close to the Arenas-Tiny mine site near Iglesias in SW Sardinia. Mineralization at Perda Niedda consists of several Fe-Zn-rich skarn occurrences developed in the Cambrian Gonnesa limestones over the Oridda monzogranite stock, satellite to the 289 Ma Mt. Linas pluton. Perda Niedda is actually part of a late-Variscan skarn system stretching across the Iglesiente-Sulcis region. Recent studies defined the features of the skarn mineralization: magnetite-sphalerite-fluorite-cassiterite enrichments are associated with retrograde silicate assemblages which deeply replaced prograde skarn facies dominated by andraditic garnet. Critical metals In and Sn are concentrated in cassiterite and Fe-sphalerite (with chalcopyrite disease), and also hosted in widespread garnets and magnetite, as revealed by EPMA and in-situ LA-ICPMS analyses. Twenty samples from several mine dumps and variably mineralized weathered outcrops were collected to verify the fate of In, Sn and associated metals Zn and Cu during weathering. Powdered samples were analyzed by XRD, prior to and after acid attack with aqua regia ($HCl+HNO_3$) aimed at dissolving metals from soluble mineral phases. The resulting solutions were analyzed by Microwave Plasma Atomic Emission Spectrometer (MP-AES). The XRD analyses provided qualitative evaluation of secondary minerals, like Fe- (goethite, lepidochrocite-pharmacosiderite) and Mn-Zn-Fe hydroxides (pyrochroite, chalcophanite), compared to primary minerals (magnetite, cassiterite and andradite) in the starting materials and residues. The solutions from mineralized gossans and weathered mine dump debris recorded high Zn (up to 1 wt.%), Cu (up to 0.7 wt.%) and notable In (0.1 wt.%) contents likely released from Fe-Mn-Zn hydroxide crusts, while the coupled low Sn (280 ppm) might be due to release from magnetite only, because of cassiterite insolubility. Interesting results derived from analyses of poorly mineralized samples still preserving abundant prograde andradite, soluble into HCl (https://www.mindat.org/article.php/553/Solubility+Data+on+646+Common+and+Not+So+Common+Minerals). Their solutions from acid attack provided remarkable Sn contents, up to 0.26 wt.%, with Zn+Cu (up to 2 wt.%) and In (up to 140 ppm). Such pilot study suggests various features involving weathering of mineralized skarns and their economic potential. The first one is the control of the primary minerals in the mobility of valuable metals, in particular In and Sn, when distributed between soluble (sphalerite-magnetite) and insoluble (cassiterite) phases. The second feature regards the role of secondary minerals in efficiently capturing metals liberated during weathering, thereby generating metal-enriched gossans. Last but not least, the role of soluble prograde Ca-garnets acting as initial reservoirs for metals like Sn and In, directly emanated by the granite magma after emplacement, as well as a further potential ore mineral.

# Deformation control on lithium distribution during metamorphism: the eclogitized pegmatites of Koralpe complex

Filippi M.*, Roda M., Zucali M. & Spalla M.I.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* marco.filippi@unimi.it

*Keywords:* lithium, LCT pegmatites, micro-fabric analysis.

Nowadays we are witnessing a renewed interest in Li-Cs-Ta (LCT) pegmatites due to the growing demand for battery metals and new technology. In order to meet the needs of economic development, a substantial review of case studies is currently being undertaken by scientific and industrial communities.

The Koralpe complex (Wolfsberg, Austria) hosts one of the most important lithium deposits in the Alpine region, where spodumene ($LiAlSi_2O_6$) pegmatites were first discovered in the 1980s and reached by underground mining (Göd, 1989). Further exploration is today carried out by European Lithium, which aims to become the first lithium supplier company in Europe.

Pegmatites with albite + quartz + K-feldspar + spodumene + muscovite ± garnet intruded into HT Variscan basement rocks between 245-280 Ma (Göd, 1989; Knoll et al., 2018). During Alpine convergence, the pegmatites were deformed under eclogite and amphibolite facies conditions (Knoll et al., 2018). The syn-metamorphic Alpine foliation is the result of the dynamic recrystallization of igneous minerals during Alpine deformation. This fabric is marked by white mica and quartz and it wraps porphyroclasts of K-feldspar, albite, spodumene, and muscovite. Alpine grossular-rich rims develop around pegmatitic garnets. The Alpine fabrics are heterogeneous and vary from SL tectonitic to mylonitic.

Our contribution investigates the effect of deformation on lithium concentration within pegmatites by comparing highly deformed to less deformed domains where the pegmatitic texture is preserved. In order to assess whether pegmatites acted as an open or close system during Alpine deformation and metamorphism, we also examined the lithium concentrations in the newly formed metamorphic minerals. This goal is achieved by combining underground structural mapping (at 1:100 scale) with mineral chemical analysis and microstructural analysis using the Micro-Fabric Analyser tool (Visalli et al., 2021).

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# Dynamics of metal and volatile flux across the lithosphere

Fiorentini M.*

Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia, Crawley (Australia).

*Corresponding author e-mail:* marco.fiorentini@uwa.edu.au

*Keywords:* critical metals, mineral system, metallogeny.

Ore deposits are loci on Earth where energy and mass flux are greatly enhanced and focussed, acting as magnifying lenses into metal transport, fractionation and concentration mechanisms through the lithosphere. In order to be more predictive about the setting of ore deposits, it is necessary to constrain the dynamics of metal and volatile flux across the lithosphere in space and time. In this framework, the secular change in the geochemical and isotopic composition of mantle magmatism informs on the key changes that our planet has endured during its complex and long-lived geodynamic evolution, providing key insights into the genesis of a wide range of mineral systems that may host commodities that are vital for a transition to a sustainable future.

We provide here a glimpse into the temporal window comprised between ~3.0-2.0 Ga, when it is thought that the bulk of the Earth's continental crust as well as a large proportion of its metallogenic endowment were formed. We focus on the Yilgarn Craton of Western Australia as a natural laboratory, and showcase how the indelible signal of anomalous multiple sulfur isotopes ($\Delta^{33}S \neq 0$) can be used to track the evolving nature of mantle domains that were tapped through time. This novel isotopic tracer can be used in conjunction with other geochemical fingerprinting elements, including tellurium and the platinum group elements, to constrain the complex cycle of volatiles and metals across the lithosphere.

Throughout the Mesoarchean, Al-depleted komatiite magmas and associated nickel-sulfide deposits dominantly display $\Delta^{33}S < 0$. This signature reflects the interaction between mantle magmatism and mafic-dominated crustal environments, and persists into the granitoids in the oldest lithospheric blocks of the craton. In the Neoarchean, Al-undepleted komatiites become dominant, with associated nickel-sulfide deposits displaying consistently positive $\Delta^{33}S$ signatures that, overall, indicate the interaction with more mature crustal environments. In a temporal window comprised between 20-50 million years after komatiite magmatism, volatile-rich calc-alkaline lamprophyres were emplaced. Coevally, the largest gold mineralising event that Earth ever witnessed took place, soon followed by widespread generation of granitoid magmas throughout the craton. The Neoarchean multiple sulfur isotope signature of mantle-derived magmas and associated mineralisation in the Yilgarn Craton is consistently positive.

In the Paleoproterozoic, ultramafic lamprophyres are emplaced in the most juvenile parts of the craton, potentially reflecting the thermal influence of large igneous provinces located several thousand kilometres away. At its margins, significant reworking of Archean material occurs for several hundred million years, controlling the sulfur budget of localised Proterozoic domains, the episodic emplacement of clusters of alkaline magmatism outboard of the craton, as well as the size and nature of precious and base metal deposits.

The geochemical and isotopic composition of mantle- derived magmas preserved in the Yilgarn Craton provides insights into the dynamic interaction between evolving mantle magmatism and changing crustal environments, allowing to decipher planetary magmatic cycles and predict the localisation of large mineral provinces. Most importantly, the geological record associated with a range of mineral systems shows that mantle-derived volatiles may play a crucial role in the physical and chemical transport of chalcophile and highly siderophile elements through the lithosphere.

# Reassessment and sustainable management of national mineral resources, essential raw materials to achieve ecological and digital transition

Fumanti F.*[1], Dacquino C.[1], Siclari M.[1], Verdura M.G.[2], Vigna G.[2], Negri M.[2] & Mining W.G.[2]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Divisione III - Economia circolare e politiche per lo sviluppo ecosostenibile, Ministero dello Sviluppo Economico, Roma.

*Corresponding author e-mail:* fiorenzo.fumanti@isprambiente.it

*Keywords:* mining, extractive waste, national mining strategy.

Italy has a long mining history, dating back to pre-Roman times. Exploitation of metal ores regarded mainly the Alpine Arch, Tuscany, Calabria and Sardinia. Currently there are only 76 operating mines, extracting cement marls, rock salt, feldspar, kaolin, bentonite and other industrial minerals. The extraction of metal ores is limited to the recent restart of a mine in Sardinia. The research and exploitation of metallic minerals has been abandoned at the end of the previous century as the result of a series of inappropriate political-economic choices. This caused the decline of university education and loss of knowledge and training and lifelong learning of mining industry professionals.

Despite its important mining history, nowadays Italy is in a position of rearguard in mineral exploration and in the international race to grab mineral resources. For many minerals, Italy is strongly or, as with metals, totally dependent on foreign markets. The energy crisis, the pandemic and the Ukrainian conflict have shown that it is essential to diversify the raw materials supply chain by also utilising the domestic resources. The Italian scientific community agrees that it is possible that significant mineral resources still exist in Italy, including the so-called Critical Raw Materials. Italy is one of the few countries in the world that does not exploit its metal ores and know little about them, and it is the only European country that does not have its own strategy for supplying solid mineral resources.

Thus, Italy's mining potential needs to be studied and re-evaluated through the joint work of academics, researchers, public administrators and mining professionals, setting, at the same time, the conditions for the creation of a new generation of mining experts. The mining activities, especially those of metal ores, can have a high environmental, sanitary and social impact. In the context of a possible reactivation of metal ores mining and/or the State participation to international mining projects, the "holistic" education of competent persons on sustainable mining of primary and secondary deposits it's essential. Abandoned extractive industries have generated huge quantities of extractive waste deriving from extraction, processing/treatment, drilling etc. The waste may represent potential new deposit of critical and non-critical resources, which could be reused in a circular economy perspective. As part of the National Critical Raw Materials Table, MISE created, in January 2022, the Mining WG. The WG aims to define, by means of a specific project in the frame of an integrated raw materials strategy based first on circularity and environmental protection, the primary and secondary (extractive waste) national mining potential in relation to Critical Raw Materials for the Italian industry, to verify the possibilities of sustainable extraction in Italy, to rebuild high education in mining and develop studies for achieve a social license to operate.

# New insight into ore formation at the Gorno MVT district (Northern Italy)

Giorno M.*[1], Barale L.[2], Bertok C.[1], Burisch M.[3-4], Frenzel M.[4], Looser N.[5], Bernasconi S.M.[5] & Martire L.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino. [3] Technische Universität Bergakademie Freiberg (Germany). [4] Helmholtz-Zentrum Dresden-Rossendorf (Germany). [5] Department of Earth Sciences, ETH Zürich (Switzerland).

*Corresponding author e-mail:* micheleandrea.giorno@unito.it

*Keywords:* ore deposits, hydrothermal, sedimentary basins.

The Gorno mining district (Northern Italy) is an example of the Alpine subclass of Mississippi Valley-type (MVT) deposits. It consists of stratabound Zn-Pb-Ag-F-Ba deposits hosted in carbonate-rich sediments, extending for over ~600 km$^2$ in the Lombardian Alps. Here, a complex series of dolomitization, silicification, brecciation, dissolution, and cementation phenomena affected the lower Carnian stratigraphic succession. High-grade sulfide ore is hosted in the basal portion of the Gorno Formation, consisting of a few meters-thick interval of marly shales, traditionally known as "black shales". Other major orebodies are hosted in the underlying peritidal limestones of the Breno and Calcare Metallifero Bergamasco formations.

Mineralization types are heterogeneous and encompass replacements, dissolution cavity fillings, and breccia cements. Sulfide mineral precipitation was preceded by hydrothermal dolomitization and silicification events. Fluorite and barite prevail in the western part of the district and followed sphalerite deposition.

U-Pb geochronology of ore-related carbonates indicates an early mineral precipitation in a shallow burial setting for the Gorno ore deposits. Fluid inclusion microthermometry documents the involvement of moderately hot, high-salinity brines in ore formation.

Fluid inclusion data, geochemical data, and spatial association of sulfide bodies to organic rich shales support a prominent role for organic carbon in ore deposition. Organic matter and associated hydrocarbons are hence proposed to have acted as reactive barriers that caused reduction of the ore fluid.

# Recycling feldspar wastes as buffer for AMD remediation: preliminary tests on sulfide-rich materials from Sardinia abandoned mines

Grieco G.*[1], Naitza S.[2], Cocomazzi G.[1], Deidda M.L.[2], Bussolesi M.[3], Cazzaniga A.[4] & Zanetta G.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [4] Minerali Industriali s.r.l., Novara.

*Corresponding author e-mail:* giovanni.grieco@unimi.it

*Keywords:* Acid Mine Drainage, circular economy, Sardinia, sulfides.

Acid mine drainage and release of potentially toxic elements are the main source of pollution in sulfide-rich mining sites. In Italy, several regions are affected by environmental pollution caused by the extraction and processing of sulfide minerals. Several studies have assessed the acidification potential of sulfide mine wastes, and suggested some procedures to neutralize the acidity and reduce the high metal content of the waters produced by these materials.

Adding carbonate-based materials, such as lime (Grieco et al., 2021), can neutralize acid mine drainage by raising pH of water and triggering precipitation of metals as hydroxides at the same time, but the treatment processes are often expensive in terms of capital and operating costs.

The aim of this research is to test the neutralizing capacity of a carbonate-bearing buffering material derived from feldspar quarrying in Sardinia.

The Sardinia region has one of the longest mining histories in Italy, and mining dumps are currently causing environmental pollution (Da Pelo et al., 2009).

Selected samples were collected from Campo Pisano and Furtei abandoned mines. Campo Pisano is part of a giant and high-grade MVT and SEDEX Zn-Pb-Fe district with variable proportions of Cd-rich sphalerite, Ag-rich galena and pyrite. The abandoned mine at Furtei exploited an epithermal deposit comprising Cu, Au and Ag sulfides and sulfosalts + base metal minerals (e.g., pyrite, sphalerite).

Grain size, XRD and XRF were used to characterize the samples. The acidification potential was determined through ABA tests. Leaching tests simulated the contaminant release from tailings following the Synthetic Precipitation Leaching Procedure. Leachates were analyzed for major and trace elements through ICP-MS and were then buffered with waste materials from feldspar quarrying, provided by Minerali Industriali. The Potential Toxic Element contents of buffered materials was also determined through ICP-MS.

All samples show positive Net Acid Potential Production, with higher values at Campo Pisano. Leaching tests show very different behavior between the two mines in terms of both acidification and metal contents, with Furtei showing much lower pH and higher metal contents.

Buffering with feldspar waste was very efficient on highly acidic Furtei samples, even though the amount of buffered material required is high. At Campo Pisano were leached solutions are near neutral the addition of buffer has limited impact.

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# Mining a green future

Herrington R.J.*

Centre for Resourcing the Green Economy, Natural History Museum, London (UK).

*Corresponding author e-mail:* r.herrington@nhm.ac.uk

*Keywords:* mining, green, future.

Clean technologies and infrastructure of a low carbon future carry intense mineral demands (https://pubdocs.worldbank.org/en/961711588875536384/Minerals-for-Climate-Action-The-Mineral-Intensity-of-the-Clean-Energy-Transition.pdf). A circular economy would be achievable before 2050, if governments and the private sector get innovation right across the supply chain and ensure that products, such as batteries, can be easily disassembled and recycled. However, growth trends suggest that mining will still play a role, because demand for metals will increase as the developing world reaches the same per capita usage of materials as the developed world.

Our ambition should be to recycle and reuse as much as we can; however, new-mined resources will be required forthe forseeable future to enable green technologies and infrastructure. There are sufficient geological resources to deliver the required metals, but we must carefully balance the need to mine with the requirement to tackle environmental and social governance issues and to deliver sustainable development goals, ensuring outcomes are beneficial for both people and planet. In the past, the true values of biodiversity loss have not been included in mining project evaluations and a new approach is needed embracing principles outlined in the recent Dasgupta report (https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/962785/The_Economics_of_Biodiversity_The_Dasgupta_Review_Full_Report.pdf). Thus, we must carefully, creatively and systematically secure a diverse range of acceptable sources for the metals we demand.

New frontiers for supply should include neglected mined waste and seeking more regulated mining areas in our own backyard rather than relying on sources with less controllable, fragile and problematic supply chains. The debate about mining our deep ocean, as alternative to terrestrial sources, needs to be resolved. Based on such a broad analysis, we can then make balanced societal choices about metal and mineral supply to deliver the 'Great Reset' that is talked about by the World Economic Forum (https://www.weforum.org/great-reset) whilst ensuring a good deal for people and planet.

# Coltan-bearing LCT pegmatites from Nuflo de Chavez Province, Eastern Bolivia

Idini A.*[1], Colonna T.[2], Carmignani L.[3] & Conti P.[3-4]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] GeoExplorer Impresa Sociale, s.r.l. [3] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [4] Centro di Geotecnologie, Università di Siena.

*Corresponding author e-mail:* alfredo.idini@gmail.com

*Keywords:* coltan, tantalum, niobium.

Tantalum (Ta) and Niobium (Nb) are transition metals belonging to the High Field Strength Elements (HFSE). Due to their geochemical affinity their ratio has been used to describe the source, fractionating, and evolution of many geological settings (Tan et al., 2018). Aside from the importance in petrological studies, Ta and Nb are of great importance in the high-tech industry, e.g., manufacture of steel alloys, electronic and optical products. The European Union has identified both Ta and Nb as critical raw materials considering their economic importance and supply risk, as defined by the 2020 final report (EU commission, CRM 2020). One of the most important sources of these elements are the columbite-tantalite minerals (also called *ColTan)*, which is one of the "conflict minerals" in Central Africa that is a cause of the well know environmental and social issues (Bleischwitz et al., 2012). In this work, we present the occurrence of columbite-tantalite from the pegmatites field in the Nuflo de Chavez Province, eastern Bolivia. All the observation and sampling activities were conducted during three months of field surveys in that area, where, to the best of our knowledge, no literature data are present about the coltan, while few companies are operating at artisanal scale. More than 25 outcrops of pegmatite bodies have been mapped, hosted in highly deformed fine-grained sericit schist. All the bodies display an elongated shape, with an average size of 23x8x8 m. They are aligned along a shear zone marked by mylonite structures of mica and garnet, although no evidence of deformation fabric was observed in the pegmatites. The origin of the pegmatites could be explained by the features of the regional setting (Nedel et al., 2020), which indicate the final assemblage of the metamorphic unit and of the sin-to-late granite intrusion belongs to the Sunsass orogeny (1.17-1.08 Ga). The mineralogical assemblage of the major phases is quite simple and points out to LCT pegmatite type: massive microcrystalline quartz, huge microcline crystal (up to 45 cm) partially altered into kaolin, and pluri-centimetric aggregate "mica-book" of fresh muscovite with an average Li content of 5 wt.%. The coltan, estimated at around 3% of the volume of the pegmatites, is represented by centimetric sub-euhedral to euhedral shape crystals and can be easily recognizable included in the microcline. Other accessory minerals are mainly schorlite and beryl. The XRD analysis confirms that the crystal belongs to the columbite (Mn)-tantalite (Mn) series, the elemental analysis performed by ICP-OES of the bulk sample showed an average Ta content of 380 g/kg and 190 g/kg of Nb, confirming that the main phase is tantalite-Mn. The measured low content of U and Th (< 0.1 wt.%) are also significant, as usually these elements can range up to 2 wt.% and in this case transportation and beneficiation process of the coltan concentrate can be very challenging.

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# First insights into fluid evolution in the Taca Taca Bajo porphyry copper system (NW Argentina)

López de Azarevich V.[1], Fulignati P.[2], Gioncada A.*[2], Ortega Pérez M.[1] & Azarevich M.[1]

[1] Centro de Estudios Geológicos Andinos, Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional de Salta (Argentina). [2] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* anna.gioncada@unipi.it

*Keywords:* porphyry copper, ore-forming processes, Argentina.

The Taca Taca Bajo ore deposit is a typical Andean porphyry copper-gold-molybdenum deposit (2203 Mt with an average grade of 0.43% Cu, 0.012% Mo and 0.09 g/t Au measured and indicated resource, First Quantum Minerals Technical Report 2021), sited in NW Argentina. The copper mineralization was first discovered on the Taca Taca property in the mid-1960s. The porphyry deposit consists of 10 km$^2$ of hydrothermally altered rocks showing a central potassic core to peripheral phyllic, argillic and propylitic alteration zones. The hypogene sulphide mineralization was dated to Oligocene and is associated with N-S oriented, rhyodacitic porphyry dykes and a probable small stock that intrudes the Silurian Taca Taca Granite (441 Ma). Two different Oligocene intrusive events were recognized: (i) early-stage rhyodacite that is characterized by phenocrysts of feldspar and quartz hosted in a biotite-rich groundmass; this unit shows a strongly developed stockwork of white to grey early quartz veins; (ii) late-stage intermineral rhyodacite that exhibits scarce phenocrysts of feldspar and quartz hosted in an aplitic groundmass; this unit is cut by a weakly developed quartz vein stockwork. The mineralization of economic interest is distributed into a hypogene (porphyry) paragenesis (potassic and phengitic alteration events), superimposed by a supergene alteration in the central part of the porphyry, hematite-quartz copper-gold veins to the NW and an exotic copper mineralization to the SE.

The aim of the current research is to obtain information on the evolution of the fluids that circulated in the porphyry system from an integrated mineralogical and fluid inclusion study of the different types of veins recognized in core samples from two drill holes, located in collection samples at the University of Salta. Fluid inclusions suitable for microthermometric investigation were found in quartz crystals. The petrography of fluid inclusions allows identifying three types of fluid inclusions at room temperature: Type 1 are multiphase (liquid + vapor + 1 or more daughter minerals) liquid-rich fluid inclusions; Type 2 are two-phase liquid-rich fluid inclusions; Type 3 are two-phase vapor-rich fluid inclusions. Detailed microthermometric investigation under development allow characterizing the P-T-X conditions of the fluids that circulated in the Taca Taca Bajo porphyry copper deposits, shedding light on the ore-forming mechanisms.

# Cooperation projects between EU and Africa towards a more effective sustainable mining. Some case studies: SUGERE and IGCP-746

Mancini S.[1], Dino G.A.*[1], Pereira D.[2], Holden Baptista E.[3], de Ferro Miranda Miguel I.L.[4], Nuvunga F.[5], Silva Victória S.[6], Lasagna M.[1], Bonetto S.[1], De Luca D.A.[1] & Rodrigues N.[7]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Department of Geology, University of Salamanca (Spain). [3] Department of Civil Engineering, Tundavala Politecnical Higher Institute, Lubango (Angola). [4] Department of Geology, University Agostinho Neto, Luanda (Angola). [5] Geological and Mining Department, Higher Institute of Science and Technology of Mozambique, Maputo (Mozambique). [6] Faculty of Sciences and Technology, University of Cabo Verde, Praia (Cape Verde). [7] Earth Sciences Department, University of Coimbra (Portugal).

*Corresponding author e-mail:* giovanna.dino@unito.it

*Keywords:* EU-Africa cooperation projects, sustainability of georesources, geology and mining engineering high education.

According to the UN SDG, the economic development of countries must go hand in hand with the improvement of their environmental, health and social sustainability. In this perspective, the exploitation of georesources must be managed with an interdisciplinary approach that addresses not only technical, economic and environmental issues but also social, legislative and human health ones. At the local level, sustainable development is about meeting defined social, environmental and economic objectives in the long run, ensuring the basic rights of affected individuals and communities.

At present, several cooperation projects related to sustainability in the extractive industry and to the definition of shared operative standards together with other regions, in particular with Africa, are taking place. Examples are the EU-Africa Erasmus+ SUGERE project and the UNESCO IGCP-746. These projects aim to improve capacity building thanks to shared research activities, the revision of curricula, the organization of specific courses and training periods. The culture of sustainability and education are the basis for the development of "critical thought", which is fundamental to face and solve local problems, to acquire ethical values and technical skills that underpin sustainable development.

The path towards environmental and social sustainability of the "wise" use of geological resources leads to a "rethinking" of our way of producing and consuming in an intergenerational perspective through an ever deeper understanding of the ethical value of the interrelationships between socio-economic and natural systems and of their mutual interests and responsibilities, which include:

- maximizing the benefits of regional economic integration and trade (SGD1, SDG17);
- ensuring food security and rural development (SDG2, SDG3);
- boosting education, research and innovation (SDG4),
- engaging together on the global scene to strengthen the multilateral rules-based order, promoting universal values, human rights, democracy, rule of law and gender equality (SDG5, SDG10).
- the creation of decent jobs and value addition through sustainable investments (SDG8);
- improving the business environment and investment climate (SDG9);
- ensuring access to sustainable energy and protecting biodiversity and natural resources (SDG10, SDG 15);
- developing a green growth model, facing climate change (SDG13);
- promoting peace and security (SDG16);
- ensuring well-governed migration and mobility (SDG17).

Positive developments in one of these areas depend on progress in other areas. Such progress can only be achieved by working together based on shared global commitments (i.e., 2030 Agenda for Sustainable Development, Paris Agreement on Climate Change and Agenda 2063).

# Geochemical and petrographic characterization of the Bella Rica hydrothermal gold mineralization (Ponce Enriquez, Ecuador)

Mendoza P.[1], Menoscal M.[1], Villalta M.[1], Fornasaro S.[2], Fulignati P.[2], Gioncada A.*[2], Mulas M.[1], Jimenez Oyola S.[1-3] & Romero Crespo P.[1]

[1] Escuela Superior Politécnica de Litoral, Facultad de Ingeniería en Ciencias de la Tierra, Guayaquil (Ecuador). [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Department of Energy and Fuels, Universidad Politécnica de Madrid (Spain).

*Corresponding author e-mail:* anna.gioncada@unipi.it

*Keywords:* gold mining, volcanic rocks, hydrothermal mineralization.

Bella Rica is sited in the Ponce Enriquez mining district (south of Ecuador), one of the most important gold mining areas in Ecuador, active since 1980's. Gold mesothermal mineralization is hosted within Cretaceous mafic volcanic rocks of Pallatanga Units (Pratt et al., 2005).

The high level of heavy metal(loid)s concentration (As, Cu, Cd, Zn, and Pb) in stream sediments and other matrixes (surface water, soil, and biological) has been discussed in several studies (e.g., Williams et al., 2000; Jiménez-Oyola et al., 2021). The presence of heavy metal(loid)s in the mining district has been considered as due to the superposition of geogenic sources and mining activity. Gold is recovered by leaching with cyanide and flotation in artisanal activity and by a combination of amalgamation with mercury in the illegal mining activity. Despite aforementioned environmental investigations, the studies on the characterization and origin of the Au mineralization are still limited.

With the aim of contributing to the regional geological background, in this study, we present new data on the geochemical and petrographic features of the hydrothermal gold mineralization in the Ponce Enriquez area. Detailed maps of the distribution of selected heavy metal(loid)s are provided. Furthermore, petrologic investigations are carried out with the aim to characterize temperatures and composition of hydrothermal fluids involved in the genesis of Ponce Enriquez ore deposit. These data can help to increase the regional geological knowledge and the promotion of the sustainable development of Ecuador metalliferous mineral sector.

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# Critical metal enrichments in the Fe-Zn skarns of the historical Perda Niedda-Arenas mining areas, Iglesiente, SW Sardinia

Moroni M.*[1], Naitza S.[2], Deidda M.L.[2], Cantaluppi R.[1], Mondragon Mallqi J.[1], Stucchi M.[1], Risplendente A.[1] & Sessa G.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* marilena.moroni@unimi.it

*Keywords:* skarn, critical metals, SW Sardinia.

The historical Perda Niedda and the nearby Arenas-Tiny mine districts host mineralization related to a late-Variscan skarn system stretching across the Iglesiente-Sulcis region in SW Sardinia. Mineralization at the poorly known Perda Niedda (PN) district consists of several Fe-Zn-rich skarn occurrences developed in the Cambrian limestones along the SE margin of the Oridda monzogranite stock, satellite to the 289 Ma Mt. Linas plutonic complex. The W margin of the stock hosts the original extensive Pb-Zn-rich skarns of the Arenas mine. Recent and ongoing studies in both areas are redefining mineral assemblages and outlining previously unreported features of these skarn ores, which are different in spite of proximity. Metals were enriched mainly during retrograde, F-rich skarn stages, while prograde skarn facies were dominated by Ca garnets and clinopyroxenes. At PN the dominant magnetite-sphalerite-cassiterite ore facies is associated with hydrous and F-B-bearing assemblage (fluorite, amphibole, Mn-axinite, chlorite, quartz, calcite) deeply replacing prograde andraditic garnet and hedenbergite-johannsenite skarn. Peculiar Fe-Zn-Sn wrigglite and rare Sn-rich endo-greisen occur along exposed granite contacts. At Arenas galena-sphalerite-chalcopyrite, with minor magnetite, are intergrown with amphibole-vesuvianite-chlorite-calcite-quartz overgrowing prograde grossular-andradite, hedenbergite and wollastonite-fluorite skarn. The retrograde sulfide-oxide mineralization is polyphasic, as suggested by compositional variations in sphalerite, magnetite and cassiterite in orebodies across the whole district. The new researches reveal enrichments of critical metals like major Sn and In and accessory Co and W. At PN cassiterite and Fe-sphalerite are the main hosts of In, although, as revealed by EPMA and in-situ LA-ICPMS analyses, both Sn and In are also substantially enriched in andraditic garnets (also host to Nb-Ta oxide inclusions). Retrograde silicates (e.g., amphiboles, axinite, vesuvianite) partly inherit the Sn endowment. Especially at PN the abundant, polyphasic magnetite displays complex zoning involving Si, Al, Mn as well as Co, Sn, Zn and W, similar to patterns observed in IOCG silician magnetite (Tunnell et al., 2022). At Arenas sphalerite is In-poor and Sn phases were not yet found but both andraditic garnet and magnetite are enriched in Sn. Ca garnets from various skarn bodies in the PN area display trace element contents and both LREE- and HREE-enriched patterns, thereby suggesting locally variable conditions during early skarn development and proximity to the intrusion (Xu et al., 2020). Skarn retrogression and hydrothermal alteration played a major role in the concentration of metals, partly released from prograde minerals. In this sense, garnets seem to be a major early reservoir for metals directly emanated from granitic magma and they may control subsequent polyphase critical metal enrichment and redistribution in ores.

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# Carbonatites and associated REE mineralisation

Pirajno F.*[1] & Yu H.-C.[2]

[1] Centre for Exploration Targeting, University of Western Australia, Crawley (Australia). [2] China University of Geosciences, Beijing (China).

*Corresponding author e-mail:* franco.pirajno@uwa.edu.au

*Keywords:* carbonatites, rare earths deposits.

In this work an introduction and a history of Carbonatites, is presented, followed by key examples in which the first author has extensively worked. Carbonatites are igneous rock with primary carbonate minerals such as:

- Siderite, calcite, dolomite, or ankerite
- Apatite and pyrochlore are often considered essential.

Alkali metasomatism and carbonatite-related deposits contain apatite, fluorite, pyrochlore, baddelyite, bastnäsite and barite. A study, based on Nd, Pb and Sr isotopic systematics, from Oldoinyo Lengai, a 2200 m high nephelinite-phonolite-carbonatite volcano in the East African Rift (northern Tanzania) support a mantle plume source. Carbonatites and associated nephelinitic magmas are thought to be derived from a two-stage process, linked to a mantle plume. In the first stage, melts are generated directly from an upwelling mantle plume. Volatiles released from the plume itself cause intense metasomatism of the overlying lithosphere. In the second stage, low degrees of partial melting in the metasomatised subcontinental lithosphere produce the carbonatite-nephelinite volcanic activity that characterises the Gregory Rift in East Africa.

There are two types of REE, namely: light REE (LREE) and heavy REE (HREE). Further, it must be pointed out that the element Yttrium is not an REE, but it is generally accepted to have it included, due to its chemical similarities with the REEs. The economic REE viability of carbonatites is one of the most important factors that drives a world-wide interest in the origin of carbonatites and associated alkaline complexes and kimberlites. It must be pointed out that REE deposits do not only occur in carbonatites, but are also hosted in peralkaline complexes, pegmatites, phosphorites, ion-adsorption clays and placers, bauxites in karst depressions and laterites. Studies of volcanic carbonatites (such as carbonatite tuffs and lavas of the Oldoinyo Lengai volcano in east Africa) revealed new types of carbonatites i.e., ultra-alkaline carbonatites, consisting of sodium and potassium (with calcium).

In some rare-metal carbonatites, the rock-forming minerals include monazite, bastnäsite, sinkhisite (Lugingol, Mongolia and Bayan-Obo, China) and a number of other rare-metal minerals.

The key examples herein discussed include: the Copperhead carbonatite located in the east Kimberley region of Western Australia, the Kruidfontein Volcanic Complex, near the Bushveld Igneous Complex in South Africa, the Okorusu alkaline complex and associated carbonatites in Namibia, the Gifford Creek Ferrocarbonatite in Western Australia, and the giant world-famous Bayan Obo in China. Of the above, the Gifford Creek Ferrocarbonatite is considered as the distal expression of the Warakurna Large Igneous Province.

# Spatial and compositional effects of intersection zones in the five-element (Ni-Co-As-Bi-Ag) vein system of the Southern Arburèse district (SW Sardinia)

Scano I.*[1], Deidda M.L.[1], Fancello D.[1], Frau F.[1], Moroni M.[2] & Naitza S.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* iscano91@gmail.com

*Keywords:* five-element veins, intersection zones, SW Sardinia.

The Arburèse district (SW Sardinia) is regarded as potential source of critical raw materials related to the large Montevecchio vein system, mined in the past for Pb and Zn ores. In the > 5 km-long, poorly exploited Southern branch of the system, the ores have been defined as five-element (Ni-Co-As-Bi-Ag) polymetallic veins (Moroni et al., 2019). They are hosted in late-Ordovician metasandstones and Silurian carbonaceous shales between two granitoid intrusions: the Arbus (304 Ma) and Mt. Linas (289 Ma) plutons. Investigations in the Perda S'Oliu, Sa Menga, Acqua Is Prunas and Pira Inferida old mines highlighted a pinch-and-swell attitude, with alternating ore shoots and low-mineralized zones. Prevalence of breccia/cockade textures and complex ore mineralogy indicate multiple hydrothermal mineralizing pulses, resulting in the overall mineral assemblages: i) native Bi; ii) Ni-Co arsenides/antimonides and sulfarsenides/sulfantimonides + quartz; iii) Zn, Pb, Cu, Bi sulfides and Cu-Ag-Sb sulfosalts + siderite; iv) quartz; v) pyrite and calcite. As noted in the recent literature on similar European ore deposits (Markl et al., 2016), mineralization processes were mainly controlled a) by redox environments, and b) by intersections with other mineral systems. Native Bi and arsenide precipitation occurred under rapidly evolving reducing conditions, favored by interaction of hydrothermal fluids with carbon-rich lithologies, well represented in Ordovician and Silurian host rocks. Moreover, field surveys in the studied localities pointed out that relevant ore shoots also correspond to intersection zones (IZs) with earlier hydrothermal systems related to the Monte Linas pluton (Deidda et al., 2021). Brecciated domains of IZs were critical both for fluid circulation and entrapment, but also for ore compositions. Indeed, the high-Bi contents of the five-element ore in the Pira Inferida mine are explained by intersection with a granite-related wolframite-quartz (Bi-Au-Te) vein system, from which abundant Bi (±Au) was remobilized. Similarly, in the Sa Menga mine, skarns and veins rich in Ni-Co-bearing arsenopyrite and Fe sulfides were As and metal sources for the cross-cutting five-element ore. In conclusion, where the low-temperature five-element system is close to the inferred contact with the Mt. Linas granite, or it crosscuts the related high-temperature hydrothermal systems selective leaching and reconcentration of Bi, As and other elements might have occurred. Sb abundance seems more related to host rocks chemistry, with increase of Ni-Co antimonides and sulfantimonides far from main IZs. Numerous, unexplored IZs may be assumed as a key targets for further mineral exploration in the Arburèse district, where undiscovered ore shoots may be present at depth.

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# From mining wastes to mineral sources - investigating the REE-bearing occurrences in the Arburèse District (SW Sardinia)

Scano I.*[1], Sedda L.[1], Fancello D.[1], Deidda M.L.[1], Moroni M.[2], Podda F.[1], De Giudici G.B.[1] & Naitza S.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* iscano91@gmail.com

*Keywords:* mining wastes, REE minerals, SW Sardinia.

In recent years, the search for possible sources of REE minerals in Europe involved numerous old mine areas with high volumes of mining wastes that may offer significant amounts of Critical Raw Materials (CRMs). In some cases, strong evidence of CRMs anomalous concentrations arises from environmental characterization of wastes, so that an interesting problem is that of finding their sources, i.e., the original CRMs - rich mineral phases in the residual ore. An excellent example is provided by the Arburèse district of SW Sardinia, for about 150 years a major Pb-Zn source in Italy, now an area under study for remediation of its severe environmental problems, including >10 Mt of waste deposits. The district exploited a large system (>10 km) of low-temperature polymetallic veins hosted in Lower Paleozoic siliciclastic rocks belonging to the Variscan Nappe zone, arranged in two main geometrical trends relative to the late Variscan Arbus pluton: "peripheral" and "intersecting". Recent investigations in the Montevecchio mine area discovered high Zn (up to 2.65 wt.%) and Pb (1.23 wt.%) grades in stratified tailing materials belonging to the Sanna old processing plant. Remarkably, ICP-MS analyses on the same materials revealed total REE+ Y contents attaining about 600 ppm. XRD studies confirmed a tailing composition essentially made of gangue minerals (quartz, siderite and micas) with goethite, baryte and traces of Zn carbonates and Pb sulfates. Chondrite-normalized REE patterns are coherent with the hydrothermal character of the source: however, both the REE mineralogical host(s) in tailings and in the Montevecchio ore are still undetermined. In the search of REE-bearing phases in the ores, some relevant insights are provided by studies on the southern branch of the Arburèse system, where the veins of "peripheral" system are hosted in late Ordovician-Silurian sedimentary sequences. In this part of the district the polymetallic veins assume the character of five-elements (Ni-Co-As-Bi-Ag) veins, with a rich Ni-Co-Fe arsenide – quartz association (1) overprinted by a Zn-Pb-Cu sulfide – siderite – quartz association (2), very similar to that dominating in Montevecchio. Investigations in the Pira Inferida mine sector highlighted the presence of LREE fluorocarbonates (synchysite-Ce and bastnaesite-Ce) and phosphates (monazite) associated with rutile and apatite. LREE minerals have been detected by SEM-EDS as tiny crystals in the quartz-sericitic gangue of the Montevecchio-type (2) mineral association. The same minerals are found in millimetric aggregates in the oxide zone of the veins, sporadically reported by mineral collectors in other mine sites of the same system. Overall, these occurrences, similar to those found in other low-temperature vein systems of Sardinia (e.g., Silius vein system), appear reliable mineral REE sources for Montevecchio mine wastes; they may be therefore used as proxies for REE exploration and assessment in the district.

# District-scale mapping of hydrothermal and supergene alteration zones from PRISMA satellite hyperspectral data in the Coastal Cordillera of northern Chile

Sorrentino A.*[1], Chirico R.[1], Corrado F.[1], Laukamp C.[2] & Mondillo N.[1-3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II". [2] Mineral Resources, Commonwealth Scientific and Industrial Research Organisation, Kensington (Australia). [3] Natural History Museum, London (UK)

*Corresponding author e-mail:* anna.sorrentino2@unina.it

*Keywords:* hyperspectral remote sensing, PRISMA, IOCG.

The Coastal Cordillera of northern Chile hosts several iron oxide-copper-gold (IOCG) deposits of Early Jurassic through Mid-Cretaceous age, hosting also minor amounts of silver and zinc. These deposits display different style of mineralization, such as, veins, hydrothermal breccias, replacement mantos, calcic skarns and combinations of all or many of these deposit types, located in intrusive rocks or within volcano-sedimentary sequences. The host rocks commonly exhibit hydrothermal alteration patterns with both upward and outward zonation. The primary ore bodies underwent a supergene alteration that produced oxidized, iron-rich blankets (Sillitoe, 2003). In this study, we employed the PRISMA satellite remote sensing for identifying and mapping specific minerals associated with the surface-exposed hydrothermal and supergene alteration assemblages which represent vectors to ore deposits. PRISMA is a hyperspectral spaceborne imaging spectrometer funded by the Italian Space Agency and is able to capture images at a spectral resolution of ~13 nm in a continuum of 234 spectral bands in the VNIR and SWIR wavelength range, between 400 and 2500 nm, with hyperspectral resolution and signal-to-noise ratio (SNR) from $\geq$ 200:1 (VNIR) to >100:1 (SWIR 2) (Cogliati et al., 2021; Loizzo et al., 2018). Rock-forming minerals that are optically active in the in the Visible Near (VNIR) to Short Wave Infrared (SWIR) wavelength regions, such as Fe-oxides and hydroxides (hematite-goethite), di- and tri-octahedral phyllosilicates (e.g., micas-kaolinite-chlorite), hydroxyl-bearing sulphates (e.g., alunite) and epidote, can be accurately recognized and mapped, discriminating between different geological targets according to their diagnostic spectral response (Laukamp et al., 2021). Moreover, PRISMA satellite imagery has been processed to determine the relative abundance and composition of the supergene and hydrothermal alteration minerals, applying a range of band ratios in the region around 900 nm and from 2,100 nm to 2,300 nm. The preliminary results highlight that PRISMA satellite allows identifying and mapping alteration minerals associated with hypogene and supergene alteration patterns, vectoring to prospective mineralized areas. Hyperspectral remote sensing can be considered a strategic and transferable tool for cost-effective and rapid mineral exploration at district scale.

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# Structural and stratigraphical characterization of the Vedra Valley sulphides deposit (Oltre il Colle, BG, Italy)

Summino L.*[1], Bertok C.[1], Martire L.[1] & Piana F.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* luca.summino@unito.it

*Keywords:* Gorno district, Southalpine domains, ore geology.

Vedra Valley hosts several sulphides deposits, mainly Zn-Pb sulphides, that have been attributed in literature to MVT deposits. These deposits are strata-bound and hosted in the Upper Triassic stratigraphic succession of the Lombardian Basin (Southalpine Domain): the high-grade mineralization is hosted in shaly beds (*black shales*), placed at the base of the Gorno Formation, and in peritidal limestones and dolostones of the underlying Breno and Calcare Metallifero Bergamasco formations. In the Vedra Valley these formations occur in some thrust-bounded tectonic units, which during the Alpine orogeny have been intensively displaced and arranged in an antiformal stack. Field and petrographic evidence suggest an early post-depositional precipitation of the ore in a shallow burial environment.

Since 2015, Altamin (Energia Minerals) won the concession for the exploration of the Vedra Valley deposits and in 2021 the drilling campaigns confirmed a resource of 7.8 ktons with a grade of 8.6% Zn+Pb. The acquired data, integrated with Altamin borehole data and processing with a specific program for geological 3D modelling (*Micromine*), allowed to create a detailed 3*D* model of the deposits that permits to better understand the link between the mineralization and the structural-stratigraphical setting and to constrain the spatial distribution of the mineralizations.

At least two main phases related to Alpine tectonics have been recognized. The first phase is related to the compressional Alpine tectonics and is divisible in two deformative events. The first event is associated with the development of a km-scale deformation zone, characterized by a system of south-verging, NW dipping thrust faults. This first deformation event caused the development of several thrust planes occurring mainly along the marly-shaly horizons that can be found in the Calcare Metallifero Bergamasco and Gorno Formations and, to a lesser extent, in the limestones and dolostones of Breno and Calcare Metallifero Bergamasco formations. Associated with these thrust faults, back-thrust planes can also be observed. The second deformation event is materialized by two main tear faults, sub-vertical and striking N-S. These tear faults reduced the lateral continuity of the deformation zone to break into several smaller tectonic units to allocate the propagation of the deformative zone.

The second phase is extensional and materialized by a high-angle E-W striking faults system. These faults provoked the displacement of the deformation zone, reducing its N-S continuity.

The Vedra Valley mineralizations have been clearly deformed and displaced by the Alpine orogeny, that provoked the present complex distribution of the orebodies in the Vedra Valley and permit to confirm the pre-Alpine genesis of the mineralization. The shaly-hosted mineralization experienced the most intense deformation, as the main thrust faults of the study area developed mostly along the marly-shaly horizons.

# Origin and metamorphic reworking of the Buca della Vena Tl-rich orebody (Alpi Apuane)

Vezzoni S.*[1], Pieruccioni D.[2], Molli G.[3], Biagioni C.[3] & Dini A.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Pisa. [2] Servizio Geologico d'Italia, ISPRA, Roma. [3] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* simone.vezzoni@igg.cnr.it

*Keywords:* hydrothermal ores, deformation, Buca della Vena mine.

In the last century, with the extensive closure of the mining activities in Italy, also the interest for ore-forming processes declined. A similar fate has befallen the Alpi Apuane ore district (Tuscany) until the discovery of Tl-sulfosalt assemblages as well as the high Tl content in pyrite ores (D'Orazio et al., 2017), which led to a new scientific attraction for this district. The volumetrically most important orebodies consist of pyrite ± baryte ± Fe-oxides which have been the subject of numerous studies (see D'Orazio et al., 2017, for further details). Based on these works, two main contrasting ore-forming models have been suggested: i. epigenetic, related to emplacement of a Miocene granite (Carmignani et al., 1972); ii. syngenetic, with Silurian-Devonian (Orberger et al., 1986) or Middle-Late Triassic age (Cortecci et al., 1985) of the proto-ore.

Buca della Vena mine is one of the main pyrite ± baryte ± Fe-oxides orebody but the ore geometries and host-rock deformation features, as well as the ore tonnage and grade, remain largely unknown. Thus, we propose a detailed field and underground geological-structural investigation of the Buca della Vena mining area. The results argue for significant departure from the proposed models. According to our investigations, the actual ore settings were acquired during two different geological events. The proto-ore was produced by hydrothermal activity related to the Permian magmatic cycle, causing ore-formation, tourmalinization and hydrothermal alteration halo in the lower Cambrian-Middle Ordovician phyllites host-rocks. Finally, the proto-ore, along with the host-rocks, were involved in the Apenninic orogenesis, and were recrystallized, and partially remobilized acquiring the current mineralogical, textural, and structural settings. In addition, we want to emphasise how a field-based approach for the Alpi Apuane, as well as for other ore districts in Italy, can provide a reassessment of the strategic mining potential for critical raw materials.

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# REE-bearing mineralogy in the karst bauxites of the Pedernales peninsula, ominican Republic

Villanova-de-Benavent C.*[1], Proenza J.A.[1], Torró L.[2], Aiglsperger T.[3], Domènech C.[1], Domínguez-Carretero D.[1], Ramírez A.[4] & Rodríguez J.[4]

[1] Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain). [2] Geological Engineering Program, Faculty of Sciences and Engineering, Pontifical Catholic University of Peru, Lima (Peru). [3] Department of Civil Engineering and Natural Resources, Division of Geosciences and Environmental Engineering, Luleå University of Technology (Sweden). [4] Servicio Geológico Nacional, Santo Domingo (Dominican Republic).

*Corresponding author e-mail:* cvillanovadb@ub.edu

*Keywords:* rare earth elements, karst bauxite, monazite, rhabdophane, churchite, bastnäsite, cerianite.

Recently, karst bauxites and other supergene deposits have been considered interesting targets for Rare Earth Elements (REE), amid the increasing demand of critical raw materials, essential to the transition to lower emission energies. The Pedernales peninsula (SW of the Dominican Republic), hosts an extensive karst bauxite occurrence, with numerous deposits scattered between the Sierra de Bahoruco range and a flat, depressed area nearby (Torró et al., 2017). The basement is the basaltic Dumisseau Fm. (Campanian-lower Eocene), overlain by Eocene-Quaternary carbonate rocks, uplifted during the Pliocene (Torró et al., 2017, and references therein). Over one hundred samples were collected, and some were analysed by FUS-ICP, ICP-MS (Actlabs, Canada), and PXRD (CCiT-UB, Spain). REE and Y, contents display wide variations from one deposit to another, and along the bauxite profiles. The highest LREE (La-Nd) in the study area are found in and around the deposits of Las Mercedes, Km-30, Aceitillar and Sombrero, whereas MREE (Sm-Gd), HREE (Tb-Lu) and Y are concentrated in Km-30. The Fe-rich karst bauxites of Pedernales are mostly composed of gibbsite, hematite, and boehmite. Some samples include significant amounts of Mn-oxyhydroxides, and only a few contain kaolinite, which indicates a mature profile.

The compositional and textural characterisation of the thin sections, polished sections and monolayers (from hydroseparation concentrates; www.hslab-barcelona.com), by means of optical microscope, SEM-EDS, EMP, Raman spectroscopy (CCiT-UB, Spain) and QANTMIN (LTU, Sweden) reveals a wide variation in terms of mineralogy and REE distribution. Four groups of REE-bearing minerals were identified: a) euhedral, primary monazite, rich in LREE (Ce, La, Nd); b) secondary rhabdophane-Y±Nd±Dy, churchite-Gd-Dy, or Nd-Sm, and florencite-Nd-Sm, in the form of anhedral grains, crusts around Mn oxyhydroxides or vein infillings; c) secondary bästnasite (enriched in Gd, Nd and Sm) and tengerite (in Gd, Sm, Nd and Y), as rounded grain aggregates of rod-shaped crystals; and d) cerianite.

Nevertheless, the most common REE-bearing mineral in Pedernales are Y-bearing phosphates. It must be noted that some of the studied mineral grains were non-stoichiometric, and further analyses are required for a proper identification and classification. In conclusion, these karst bauxite deposits are, not only significant REE sources, but also excellent natural laboratories to study the REE mobility and mineral stability in supergene environments. In addition, the presence of new minerals cannot be discarded.

Torró L., Proenza J.A., Aiglsperger T., Bover-Arnal T., Villanova-de-Benavent C., Rodríguez-García D., Ramírez A., Rodríguez J., Mosquea L.A. & Salas R. (2017) - Geological, geochemical and mineralogical characteristics of REE-bearing Las Mercedes bauxite deposit, Dominican Republic. Ore Geol. Rev., 89, 114-131.

# Altamin, Italian base and battery metals exploration and production

Zanin S.*

Altamin Ltd., Oltre il Colle (BG).

*Corresponding author e-mail:* szanin@energiaminerals.com

*Keywords:* battery metals, base metals, mineral exploration.

Altamin Limited is an ASX-listed mineral company focused on base and battery metal exploration and brownfield mine development in Italy, with two 100% owned mineral projects and four under license application.

Altamin's operational and management staff are exclusively Italian citizens who are resident in Italy and since operations began in 2015 the company has used Italian exploration & mining contractors and technical consultants. Additional technical expertise is provided by international specialist mining consultants and a technical supervisory team (Australian and UK).

The Company's Gorno Zinc Project, in the Lombardy region of northern Italy, is an advanced, historic mine with well-defined mineralisation. The Gorno project completed two phases of exploration drilling campaigns for a total of 23 km of drilling and a Definitive Feasibility Study is ongoing.

The quality of the zinc and lead concentrates which can be produced by Gorno is unsurpassed in the global market in terms of its lack of impurity elements and its high metal content. As such this demonstrates a long-term clean and premium feed-stock that can be purchased by the significant European metal smelting and refining industry to offset a proportion of the imports of inferior concentrates from the global market.

The Punta Corna Cobalt Project in Piedmont, Italy, historically mined for cobalt, nickel, copper and silver, is an active exploration project with outcropping mineralisation. A historical bulk sample grading 0.6-0.7% Co, plus Ni, Cu, Ag places this project amongst the highest-grade exploration projects in the world and represents a unique opportunity to diversify and expand supply of these critical battery metals from within the European Union Punta Corna Project has an exploration drilling program outlined. Alta's recent sampling has returned high-grade assays over >2 km strike length from multiple sub-parallel veins, with good potential for further mineralised vein discovery and significant depth extension. This project includes the Punta Corna and the Balme licences.

Altamin has lodged applications over Monte Bianco and Corchia, the two most significant copper, cobalt and manganese-rich historical mining districts in Italy (Monte Bianco EL (8,200 ha) in the Liguria region of the Northern Apennines; and Corchia EL (3,500 ha) in the Emilia Romagna region).

Altamin has lodged applications for Exploration Licences over the Campagnano and Galeria areas prospective for lithium in brine the Cesano district in Lazio Region.

# S15.

# Mineralogy and waste: circular economy for a sustainable future


*Conveners & Chairpersons*

*Giancarlo Capitani (University of Milano - Bicocca)*

*Sonia Conte (Istec-CNR Faenza)*

*Linda Pastero (University of Torino)*

*Cecilia Viti (University of Siena)*

# Secondary raw materials for innovative and sustainable ceramic production: recycling the product of thermal inertization of vitreous fibers

Arletti R.*[1], Conte S. [2], Zanelli C. [2], De Iuliis[1] M., di Giuseppe D.[1], Scognamiglio V.[1], Malferrari D.[1], Dondi M.[2] & Gualtieri A.F.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Istituto di Scienza e Tecnologia dei Materiali Ceramici, CNR, Faenza (RA).

*Corresponding author e-mail:* rossella.arletti@unimore.it

*Keywords:* waste recycling, ceramic production, thermal inertization.

Waste recycling could turn into a common practice to improve environmental sustainability of the ceramic manufacturing. Although this industry proved to be able to efficiently recycle its own processing residues, the recourse to pre- and post-consumption wastes from other sectors is still quite limited. Indeed, the main obstacle to a widespread recourse to waste recycling is the lack of knowledge about the effects of different kinds of waste on technological behavior of semi-finish products and technical performance of finished tiles.

In this work, the product of the thermal inertization of exhausted mineral wool is tested as secondary raw material for the realization of high-quality porcelain stoneware. The inertization procedure requires the melting of mineral wool waste packages inside an especially developed experimental pilot plant (Zanatto & Gualtieri, 2002). The basic technology of the experimental plant is based on a melting furnace in oxy-combustion regime according to technological principles already widely used in the production of glass frits. The melting process destroys the fibrous shape of the wool and produces an inert non-hazardous massive glass that is suitable to be recycled for the production of porcelain stoneware

Three different samples were realized adding to a classic porcelain stoneware batch 3,6 and 9 wt.% of inert glass in substitution to standard flux (feldspar), while a fourth samples without any addition was realized and used as benchmark. The material properties were evaluated both on semi-finished products and on fired ones.

During the laboratory-scale simulation of the industrial process, it emerged that the introduction of the secondary raw material does not influence the production process and technological properties of semi-finished product were not perturbed.

As regards firing behavior, the introduction of glass waste has allowed the lowering of the vitrification temperature. Despite a decrease of about 40°C in the maximum temperature of the firing cycle, the specimens containing the waste maintain excellent densification levels.

The only parameter relating to fired products that significantly worsened was the color, as a result of the high iron content present in the waste used.

The mineralogical analysis of the fired products indicated the presence of the same crystalline phases in all the mixtures, even if in different levels. In particular, an high amount of residual plagioclases was observed in the waste-bearing samples with, with a consequent decrease in the glass phase compared to the benchmark. This difference is mirrored in the textures observed: the benchmark shows a more homogeneous glass matrix with respect to waste bearing samples

The results of this study evidenced that the product of the inertization of glass fibers can be recovered and used as a raw material in the production of porcelain stoneware. The results here obtained are therefore transferable to industrial reality.

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# Magnetic zeolites formed from pure sources and wastes: Efficiency in ofloxacin antibiotic water remediation

Belviso C.*[1], Guerra G.[2], Abdolrahimi M.[3-4], Peddis D.[4-5], Maraschi F.[2], Cavalcante F.[1], Ferretti M.[5], Martucci A.[6] & Sturini M.[2]

[1] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ). [2] Dipartimento di Chimica, Università di Pavia. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Istituto di Struttura della Materia, CNR, Montelibretti (RM). [5] Dipartimento di Chimica e Chimica Industriale, Università di Genova. [6] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* claudia.belviso@imaa.cnr.it

*Keywords:* zeolites, wastes, ofloxacin antibiotic.

In this work, red mud (RM) and spinel iron oxide nanoparticles (SPIONs) were added to pure silica/alumina sources (SAs) and fly ash (FA) with the aim of synthesizing and investigating the magnetic behavior of different zeolites. In detail, zeolite A (LTA topology) was synthesized using SAs with the addition of both red mud and spinel iron oxide nanoparticles. Zeolite X (FAU-topology) was formed using fly ash as silica and alumina source with the addition of SPIONs whereas sodalite (SOD-topology) was synthesized mixing FA and RM. All the synthetic products showed magnetic properties. In particular, sodalite displayed ferromagnetic behavior due to the composition of fly ash and red mud used, while the presence of red mud was responsible for antiferromagnetic behavior of zeolite A.

The synthetic zeolites were tested for polluted water remediation by a persistent emerging contaminant (ECs), ofloxacin (OFL) antibiotic. ECs are released from many sources, thus determining diffuse pollution, mainly regarding environmental waters. The emerging contaminants enter the aquatic environment mainly through wastewater due to their low biodegradability in urban wastewater treatment plants (WWTPs). Despite the low concentrations, from ng to a few μg $L^{-1}$, they have a significant probability of being toxic. Among these, antibiotics are of particular concern since their large use in human as well as in veterinary medicine contributes to the generation of antibiotic-resistant bacteria and antibiotic-resistant genes. For the reasons mentioned above, it is mandatory to find new strategies to remove them.

The data indicated that all the synthetic zeolites adsorb a significant percentage of OFL and the materials formed from wastes are more effective in terms of their adsorption capacity, reducing the antibiotic concentration quantitatively in the presence of matrix constituents. Satisfactory recoveries (90–92% in tap water, 83–87% in river water) were obtained for the two zeolites synthesized from industrial waste materials (sodalite and zeolite X). Red mud acts to improve the adsorption performance, especially when added to fly ash, forming a zeolite with SOD topology. OFL adsorption occurs on both the surface grains and porous structures of the FAU topology (Belviso et al., 2021).

Belviso C., Guerra G., Abdolrahimi M., Peddis D., Maraschi F., Cavalcante F., Ferretti M., Martucci A. & Sturini M. (2021) - Efficiency in Ofloxacin Antibiotic Water Remediation by Magnetic Zeolites Formed Combining Pure Sources and Wastes. Processes, 9, 2137.

# 8-bit image analysis as a preliminary method to evaluate residual mortar paste attached on recycle concrete aggregate

Bisciotti A.*, Ardit M. & Cruciani G.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* bscndr@unife.it

*Keywords:* CDW, recycled aggregate, sorting.

Construction and Demolition Waste (CDW) is recognized as a major burden in the construction industry but could also convert into a resource. In fact, the CDW inert materials can potentially be reused in civil engineering as recycled aggregates (RA) (Wang et al., 2021). One limitation is the presence of residual adhered mortar on the surface of CDW which influences the performance of concretes made with RA (de Juan & Gutierrez, 2009). Sorting methods based on hyperspectral imaging are under development (Bonifazi et al., 2018). In this contribution, CDW samples from Pelliccia Scavi s.r.l. (PG, Umbria) were manually separated into three classes of 50 samples each, and classified visually as 1) clean aggregates, 2) partially covered aggregates, and 3) mortar-based aggregates. Pictures from each group were collected using a stereo-microscope with a 15x fixed magnification. The obtained images were then processed through CDWIMAGE, a new software developed to recognize and quantify the portion of residual mortar on the CDW surface. The software, written in Python language, converts RGA input files into a 8-bits (1 byte) pixel matrix. The grayscale of a 8-bit image has 256 possible tones ranging from 0 (black) to 255 (white). From these matrices, a characteristic spectrum of the sample surface is produced in which the intensity is equal to the number of pixels recorded for each of the 256 possible tones. The subtended area in the spectrum region with the highest intensity (the apical point +/- 10 tone values) is calculated by a definite integral using the composite trapezoid rule. The spectrum is then automatically filtered, setting lower and upper threshold values, segmenting the image into regions of interest and background. The procedure allows distinguishing the attached mortar on natural aggregates. The percentage of attached mortar on the CDW surface is then directly estimated. Obtained results have been compared with those from a quantitative phase analysis by X-ray powder diffraction of the same samples, and a close relationship has been observed between estimated percentage of attached mortar on the CDW surface and the content of mineral phases related to chemistry of cementitious materials.

Bonifazi G., Palmieri R. & Serranti S. (2018) - Evaluation of attached mortar on recycled concrete aggregates by hyperspectral imaging. Constr. Build. Mater., 169, 835-842.

de Juan M.S. & Gutièrrez P.A. (2009) - Study on the influence of attached mortar content on the properties of recycled concrete aggregate. Constr. Build. Mater., 23, 872-877.

Wang B., Yan L., Fu Q. & Kasal B. (2021) - A Comprehensive Review on Recycled Aggregate and Recycled Aggregate Concrete. Res. Conserv. Recycl., 171, 105565.

# First experimental results on the use of georesources in waterproofing systems

Calista M.*, Novembre D., Rainone M.L. & Sciarra N.

Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti.

*Corresponding author e-mail:* monia.calista@unich.it

*Keywords:* permeability, landfill.

This work reports the first experimental results on the use of georesources (clays, kaolins and bentonites) as additives in landfill land waterproofing systems. Geotechnical characterization tests were carried out on georesources and on a soil of volcanic origin. The latter was added with georesources in the percentages of 5-10-20-40%. Subsequently, the variation of the permeability coefficient of the vulcanite as a function of the percentage of georesource added was studied. From all the tests it emerged that the georesources used make it possible to lower the permeability of the vulcanite. In particular, a rapid decrease found in mixtures with bentonite is contrasted by one with a milder trend associated with the other georesources. These preliminary results will have to be evaluated in the future in terms of costs and/or benefits.

# On the possible use of F.O.S. / clay mixtures in environmental recovery activities. Preliminary results of chemical-mineralogical and physical-mechanical analyses

Calista M.[1], Novembre D.[1], Pasqualini R.[2], Reale M.[3] & Rainone M.L.*[1]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Deco S.p.A., Pescara. [3] Solved s.r.l. - spin-off Università "G. d'Annunzio", Pescara.

*Corresponding author e-mail:* rainone@unich.it

*Keywords:* FOS, off specification compost, FOS/clay mixture.

The FOS (off specification compost), also known as "stabilized organic fraction", represents the final product of a mechanical-biological treatment (MBT) operated on the organic fraction deriving from the mechanical separation treatment of urban waste downstream of collection. The final phase of this process provides the biological stabilization of the FOS.

In the past decades the intended use of this material, also known as "grey compost", was in the agronomic field. But the environmental requirements in the agronomic field on the one hand and the increasingly accentuated orientation towards quality agricultural productions, have made the prospect of using FOS practically nil in productions destined for both human and animal consumption, thus allocating substantially, the FOS to the landfill.

A possible use in "environmental" recovery activities and not only for landfill "capping", consequently, assumes a great importance ; also considering the quantities of FOS currently produced by the existing MBT plants.

In the technical-scientific literature there are not many references to experiments in this sense, while the legislation is still lacking; especially about the physical-mechanical characteristics of any FOS/clay mixtures.

This note presents the first results of an articulated and multidisciplinary research activity aimed at characterizing the possible types of FOS produced by TMB plants, and at evaluating a potential reuse for environmental purposes conducted through mixing with clays with known geotechnical properties.

The FOS samples used were treated with *Attritor Mill technology* which, using mechanical energy transferred to the materials to be treated, through «mills», produces a very strong comminution (reduction of a material into small fragments) of the materials themselves. The experimentation carried out has shown that the *Attritor-Mill* treatment allows to obtain a progressive and significant dimensional reduction of the materials with a consequent reduction in volume and a significant improvement in some physical-chemical-biological parameters such as the respirometric index.

A chemical-mineralogical and morphological characterization of FOS performed with SEM (Scanning Electron Microscopy), Powder X Ray Diffraction (XRPD) and realease test, was followed by geotechnical laboratory tests conducted on FOS, clays, and FOS/clay mixtures in different proportions.

The results obtained showed a significant improvement in all physical-mechanical parameters and shear-strenght compared to the same parameters of the clay or those of the FOS alone.

# Recycling detoxified cement asbestos in ceramic and cement mortar

Campanale F.*[1], Pellegrino L.[1], Bernasconi A.[2], Galimberti L.[1], Vergani F.[1], Marian N.M.[3], Viti C.[3] & Capitani G.C.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Ideal Standard International, Trichiana (BL). [3] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena.

*Corresponding author e-mail:* fabrizio.campanale@unimib.it

*Keywords:* Asbestos, detoxification, recycling.

Asbestos containing materials (ACMs), although no longer produced, are still abundant in buildings and in the environment and represents a health hazard. Their disposal requires a smarter solution than currently adopted landfilling, and aligned with current policy of circular economy, i.e., detoxification and reuse (Vergani et al., 2022). With this premise, we explored the recycling of ACM thermally treated at 1100°C in the production of Vitreous China (VC) sanitary ware and cement mortar.

The composition of VC may be finally tuned to satisfy the required properties starting from the basic raw materials: i) clay, mostly kaolinite, which provides plasticity to the ceramic mixture; ii) quartz, which acts as filler, forming the skeletal network of the ceramic body; iii) feldspar, a fluxing agent, which promotes greification of the body and the dissolution of component like quartz upon firing (1200-1240°C).

Up to 5 wt.% of thermally treated ACM was added to a ceramic mixture in substitution of quartz (sample S1) and feldspar (sample S2) and fired at 1160°C, 1180°C, 1200°C, 1220°C. Normal production (NP) VC samples fired at the same temperatures were also prepared and studied for a comparison. At T > 1200°C, we found that S1, S2 and NP samples show similar mechanical and aesthetic properties as well as similar degree of greification, suggesting that a partial substitution of thermally treated ACM in the sanitary-ware VC is possible.

The recycling of ACM in the production of cement mortars was explored adding respectively 4 and 7 wt.% of thermally treated ACM in a pre-mixed mortar used in traditional plasters. We determined compressive and flexural strength after hardening time of 7, 14, 28 days, and performed durability tests along a time span of 25 weeks, during which the test samples were subjected to wetting-drying cycles and temperature (20-80°C) cycles.

Our results reveal that addition 4-7 wt.% of thermally treated ACM to widely used pre-mixed mortar for traditional plasters does not affect neither the most important technical properties of the mixture (such as tixiotropy, viscosity, water demand), nor compressive and flexural strength after hardening which are preserved also after repeated temperature and wetting/drying cycles for 25 weeks. These results look therefore very promising towards the recycling of detoxified ACM on cement mortar production.

Vergani F., Galimberti L., Marian N.M., Giorgetti G., Viti C. & Capitani G.C. (2022) - Thermal decomposition of cement–asbestos at 1100°C: how much "safe" is "safe"? J. Mater. Cycles Waste Manag., 24, 297-310.

# Is it waste or urban mine?

Cardinale A.M.[1], Parodi N.*[1], Zotti M.[2] & Carbone C.[2]

[1] Dipartimento di Chimica e Chimica Industriale, Università di Genova. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* nadia.parodi@unige.it

*Keywords:* LDH, urban waste, fungi, REE.

The 2030 Agenda for Sustainable Development, adopted by all United Nations Member States in 2015 provides a shared blueprint for peace and prosperity for people and the planet, now and into the future.

At its heart are the 17 Sustainable Development Goals (SDGs), which are an urgent call for action by all countries - developed and developing - in a global partnership. Among the 17 SDGs, there are few of them strictly environmental: 7-Clean and accessible energy; 13-climate changes; 14-underwater life; 15- life on Earth. To properly address these issues, we need to change our approach and see some problems as resources. Europe is hugely dependent on raw materials, it is the region with the greatest import of resources in the world. Furthermore, in Europe, over 50% of waste is delivered directly to incinerators or landfills, causing, both the risk of environmental damage and the subtraction of valuable resources to the economy and the creation of new jobs. It is estimated (Beasley & Georgeson, 2014) that recovering of raw materials from waste (circular economy) could create 860,000 new jobs by 2030 and lead to a reduction in greenhouse gas emissions of 415 Mt. Just for this purpose nowadays different processes are being studied and set up to recover precious metals and rare earth elements from WEEE (waste from electric and electronic equipment).

Our research group is being working in this field focusing mainly on the recovering of raw materials from the WEEE and the recovering of pollutant from waste water; in both the cases the final objective is to close the recover cycle reusing the elements recovered. Moreover, the applied method has to be as "eco-friendly" as possible. Two main different methods are presented in this work: 1) mycorecovery strategy to pick up lanthanides and precious metals from WEEE, and 2) crystallochemical recovery based on the use of synthetic LDH (layered double hydroxide) to remediate polluted industrial water. In this case, an important application of LDH after the remediation procedure, is the reuse as electrode in lithium and post lithium battery.

Beasley J. & Georgeson R. (2014) - Advancing Resource Efficiency in Europe. European Environmental Bureau, Brussels.

# In situ and ex situ Bottom Ashes (BA) from Municipal Solid Waste Incinerator (MSWI) heating: mineralogical application for solid waste stabilization

De Matteis C.*[1], Toller S.[1] & Tribaudino M.[2]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* chiara.dematteis@unipr.it

*Keywords:* bottom ashes, inertisation, high temperature treatment

Each year in Italy about 30 millions tons of urban waste are produced, of which 5.3 millions are disposed in incinerators. The incineration process produces about one million tons of ashes. Nowadays, a great challenge is the reuse of these materials facing two order of problems: 1) the high reactivity of bottom ashes that may release potentially toxic elements, 2) the unwanted reaction of a non-stabilized material that may hinder possible reuse. Therefore, ashes stabilization is needed before recycling.

A possible stabilization is throughout high temperature treatments. At high temperature more reactive mineralogical phases are stabilized, or as in the case of carbonates, removed (Ardit et al., 2022). Several critical points are however present, as the formation of other unwanted phases, possibly more prone to leaching, the volatilization of Potentially Toxic Elements (PTE), or some changes in hydraulic activity which may compromise reuse as supplementary materials in concrete. Although several investigation were done on the mineralogy and chemistry of the BA after high temperature treatments, systematic investigations on the leaching behaviour at the different temperature products are still missing. Also, there is no information on how this occurs with different grain size; last no study was done on the residuals by in situ observation.

In this work, we investigated a set of sample with different grain size from the Parma Waste to Energy (WtE) plant, preliminary studied with standard 2 h ThermoGravimetric Analysis (TGA) runs, up to 800°C. We have tested three grain size classes samples: 0.062-0.2, 0.3-0.5 and 1-2 mm. They were previously powdered to avoid size surface effect and heated for 24 hours at 200, 400, 600, 800 and 1000°C.

The main results were: 1) the mass loss increases as the grain size decreases, indicating that more reactive phases were concentrated in the lower size grains. This is a quantitative rather than qualitative effect, as XRD results do not show difference in the mineralogical phases composition which are present in samples with different size; 2) the mass loss increases with increasing temperature, with a higher step at 600°C, likely due to the de-carbonation processes; 3) the mass losses obtained from ex situ experiment are greater than those recorded during the TGA analysis.

Parallely, an in situ measurement was performed using an X-ray diffractometer equipped with a hot chamber: the sample was gradually heated and the diffractions were carried out at 200, 400, 600, 800°C. Notably, at the highest temperature we have observed the formation of typical clinker phases as alite, belite and celite. On the same samples leaching test are currently performed, following the procedures codified in EN-12457-2 (Andreola et al., 2019).

Andreola F., Barbieri L., Queiroz Soares B., Karamanov A., Schabbach L.M., Bernardin A.M. & Pich C.T. (2019) - Toxicalogical analysis of ceramic buildings materials - Tiles and glasses - Obtained from post-treated bottom ash. Waste Manag., 90, 50-57.

Ardit M., Zanelli C., Conte S., Molinari C., Cruciani G. & Dondi M. (2022) - Ceramisation of hazardous elements: Benefit and pitfalls of the inertisation trought silicate ceramincs. J. Hazard. Mater., 423, 1-17.

# Application and changing of a Sequential Extraction Procedure (SEP) to analysed chemical-mineralogical composition of Municipal Solid Waste Incineration Bottom Ashes (MSWI BA)

De Matteis C.*[1], Toller S.[1], Mantovani L.[1], Funari V.[2], Dinelli E.[3] & Tribaudino M.[4]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Istituto di Scienze Marine, CNR, Bologna. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [4] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* chiara.dematteis@unipr.it

*Keywords:* bottom ashes, potentially toxic elements, sequential extraction.

Waste management is one of the major challenge in our society. Recycling the ashes from municipal solid waste incinerators (MSWI) as a secondary raw material is a key goal and several processes have been proposed, like inclusion in ceramics or in concrete (Bertolini et al., 2004). However, any form of recycling requires an assessment of the potential pollution for environment and health risk. This can be achieved through a detailed analysis of the chemical and mineralogical composition of MSWI and how it changes when subjected to ageing, leaching and weathering.

MSWI ashes are made by Bottom Ashes (BA), about 20% of the disposed waste, and Fly Ashes (FA), about 4% of the original waste. Whereas FA are classified as dangerous waste, BA, that are the main secondary raw material from incinerators can be recycled. In general, BA are made by crystalline phases, i.e., silicate, carbonate, oxides, sulphates, amorphous glass and metallic inclusion. They are mainly composed by Si, Al, Fe, Ca, Mg, K, Na, S, Cl. However, BA contain also potentially toxic elements (PTE) such as Zn, Pb, Cu, Cr and Ni. Their potential hazard depends on the mineralogical phases they are found, which controls the potential release in the environment. Previous investigations were focussed on the average composition, and only in few recent works the mineralogy was detailed. Indeed, a careful analysis of the mineralogical composition was rarely performed, and owing to the heterogeneous mineralogy of the BA, the PTE (whose concentration is close to the detection limit for SEM-EDS analysis) could be hardly ascribed to specific phases.

In this work we tested a new Sequential Extraction Procedure (SEP; Rauret et al., 1999) to assess the mineralogical composition through sequential leaching of elements (Alam et al., 2019). The procedure was done in five steps: 1) preliminary dissolution of the most soluble phases by dilution in ultrapure water, pH = 7, with solid/water ratio 1:40; 2) mild acetic acid 5M attack to remove carbonates; 3) hydroxilammonium chloride attack to remove reducible phases; 4) hydrogen peroxide and ammonium acetate to remove residual organic matter; 5) acid attack with HF and $HClO_4$ to remove silicates and residual oxides. For each of the steps the eluate was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Ionic Chromatography (IC) and (for major elements) Atomic Absorption (AA). Residual solid portions were analysed by X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF).

Different duration, dilution and procedures were tested for each step. Most critical step was found in the acetic acid dilution for carbonate dissolution.

The mineralogical composition at the different steps and the potential toxicity of the leached residuals within different environmental conditions will be discussed, in order to propose an optimum analytical procedure to detect the criticalities in the disposal and recovery of the BA.

Alam Q., Schollbach K., van Hoek C., van der Laan S., de Wolf T., Brouwers H.J.H. (2019) - In-depth mineralogical quantification of MSWI bottom ash phases and their association with potentially toxic elements. Waste Manag., 87, 1-12.

Bertolini L., Carsana M., Cassago D., Curzio A.Q. & Collepardi M. (2004) - MSWI ashes as mineral additions in concrete. Cement Concr. Res., 34, 1899-1906.

Rauret G., López-Sànchez J.F., Sahuquilllo A., Rubio R., Davidson C., Ure A. & Quevauviller P. (1999) - Improvement of the BCR three steo sequential extraction procedure prior to the certificazion of new sediment and soil reference materials. J. Environ. Monit., 1, 57-61.

# Investigations on industrial wastes for the valorization of their mineral content in the fertilizer industry: preliminary results

Fornari G.*[1], Pinto D.[1], El Chami D.[2] & Clausi M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] TIMAC AGRO Italia S.p.A., Ripalta Arpina (CR).

*Corresponding author e-mail:* gianna.fornari@uniba.it

*Keywords:* minerals, waste, sustainable industry.

In the last decades, the fertilizer industry has been mainly based on the use of non-renewable resources used for plant nutrition. Minerals of commercial interest are removed from natural deposits causing significant social, environmental and economic costs (Bontoux & Bengtsson, 2016). In this perspective, there is an urgent need to implement sustainable methodologies for the preservation of these fundamental non-renewable environmental resources and, at the same time, to provide agricultural soils with the necessary supply of nutrients essential for healthy plant growth (Oliveira et al., 2012). The objective of this study is to offer new solutions for the recovery of industrial wastes thus reducing the environmental problems related to waste management and, at the same time, the excessive exploitation and use of non-renewable natural resources for the production of fertilizers. The research is conducted in collaboration with TIMAC AGRO Italia S.p.A., an Italian company of the French group Roullier, world leader in the production of fertilizers (Amin, 2014).

In this study different types of industrial wastes (i.e., industrial ashes and mineral processing wastes) are characterized from the chemical and mineralogical point of view using the following instrumentations: scanning electron microscopy with EDS microanalysis (SEM-EDS) for morphological, microstructural and microchemical analysis, fluorescence (XRF) for chemical characterization, diffraction (XRD) for mineralogical content, spectroscopy (FTIR) for the identification of functional groups and chemical bonds.

Preliminary investigations show the occurrence in the investigated materials of soil mineral nutrients essential for plant growth (i.e., K, P, Mg, Ca, Si, Fe, Cu, Zn, …) which can be included in new formulations of fertilizers after appropriate verification and eventual removal of potential harmful elements.

Amin N. (2014) - A multi-directional utilization of different ashes. RSC Advances, 4, 62769- 62788.

Bontoux L. & Bengtsson D. (2016) - Using scenarios to assess policy mixes for resource efficiency and eco-innovation in different Fiscal Policy frameworks. Sustainability, 8, 309.

Oliveira M.L., Ward C.R., Izquierdo M., Sampaio C.H., de Brum I.A., Kautzmann R.M., Sabedot S., Querol X. & Silva L.F.O. (2012) - Chemical composition and minerals in pyrite ash of an abandoned sulphuric acid production plant. Sci. Total Environ., 430, 34-47.

# Mortars with recycled aggregates from CDW rubbles of the 2016/2017 earthquakes in central Italy: Petrography and mechanical performance

Galderisi A.[1], Bravo M.[2], Iezzi G.*[1-3], Cruciani G.[4], Paris E.[5] & de Brito J.[6]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Department of Civil Engineering, Barreiro School of Technology, Polytechnic Institute of Setúbal, Lavradio (Portugal). [3] INGV, Roma. [4] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [5] Scuola di Scienze e Tecnologie, Università di Camerino. [6] Instituto Superior Técnico, Universidade de Lisboa (Portugal).

*Corresponding author e-mail:* gianluca.iezzi@unich.it

*Keywords:* CDW rubbles, recycled aggregates, mortars.

This study is focused on the construction and demolition waste (CDW) collected from the rubbles of the Central Italy produced during the 2016/2017 earthquakes. They were first characterised by X-ray powder diffraction (XRPD), then they were used as recycled aggregates (RA) to prepare mortar specimens and finally their physic-mechanical attributes were quantified. These RA were first manually sorted in six groups according to their mesoscopic features: concrete (CO), natural stone (NS), tile (TI). brick (BR), perfored brick (PF) and roof tile (RT) (Galderisi et al., 2022). The colour, density and petrography of the RA was first qualitatively determined by mesoscopic observations, while the abundance of crystalline phases per RA type was determined by the Rietveld method. Their features were compared with virgin aggregates (VA) from Lisbon. The VA are rich in quartz and feldspars, CO of calcite, NS of calcite plus feldspars, Ti of feldspars, mullite plus calcite, BR, PF and RT of feldspars, calcite, pyroxene, melilite and sheet-silicates.

Each group of RA was used alone (100 wt.% of RA) and mixed with VA to prepare 13 types of mortars (12 specimens per type): one reference mortar (RM) made with VA only, six recycled aggregate mortars (RAM) and six recycled plus virgin aggregate mortars (RVAM). The amount of aggregate, cement and water was kept as much as possible constant in the 13 groups. The most relevant physical and mechanical properties of the aggregates and mortars were experimentally quantified, unveiling the significant role of both physical and mineralogical attributes of each type of CDW. Specifically, mortars made with RA only (RAM) rich in CO, NS and TI have good mechanical performance, i.e., higher compressive and flexural strengths than those made with BR, PF and RT. Furthermore, RAM have superior mechanical characteristics to those of corresponding RVAM made with the same type of RA.

These results demonstrate that the physical and mineralogical characteristics of different CDW types are of paramount importance to prepare mortars and concrete. In parallel, the petrography of CDW is also fundamental to sort them as a function of colour, density and especially mineralogical attributes of phases contained in the CDW. For these types of RA from Central Italy, their upcycling reuse for the preparation of mortars or concrete with high and homogeneous physic-mechanical attributes are feasible only by sorting them based on their petrographic properties, i.e., colour, density and paragenesis of phases.

Galderisi A., Iezzi G., Bianchini G., Paris E., de Brito J. (2022) - Petrography of Construction and Demolition Waste (CDW) from Abruzzo Region (Central Italy). Waste Manag., 137, 61-71.

# Use of volcanic minerals for a sustainable future

Lancellotti I.*[1], Altimari F.[1], Andreola F.[1], Barbieri L.[1] & Maggi B.[2]

[1] Dipartimento di Ingegneria "E. Ferrari", Università di Modena e Reggio Emilia. [2] Europomice s.r.l., Milano.

*Corresponding author e-mail:* isabella.lancellotti@unimore.it

*Keywords:* volcanic minerals, sustainability, materials.

Europomice s.r.l. is an Italian mining company that, through the conscious exploitation of its mineral resources, over the years has gained a leading position in the production and marketing of inert volcanic materials, such as pumice, lapillus, zeolite and volcanic mixtures, which meet the needs of nursery gardening, technical green spaces, building industry, and is also active in the market of flux minerals for the ceramic industry.

The company carries out its extraction activity and preparation of finished products and different mixtures in several quarry sites all located in Italy (Tuscany and Lazio).

These materials are naturally expanded due to the acid gases dissolved in the lavas, the resulting solid, not totally crystallized, has alveolar cavities produced by the gases inside the rock. The chemical composition of the pumice's magma ($SiO_2$=56 wt%) causes a high viscosity originating a structure with intercommunicating pores. Instead, the magma of lapillus has a lower $SiO_2$ content, 49 wt%, which lowers the viscosity, therefore it has a lower percentage of pores, but with larger sizes. Finally, the higher amount of $Fe_2O_3$ in lapillus causes red color in contrast with the white color of pumice.

The increased interest in the environment, led Europomice to formulate ecological floor made with *Lapillus* in combination with a *binder*. The main applications will include: cycle paths, forest roads, farm tracks and paths in parks, gardens and farm. The technological advantages of these floors are: better workability, high resistance to atmospheric agents, draining effect and long life with very low maintenance costs.

Other application is green roofs/gardens which are popular in the context of sustainability. They represent a field of application in which structural, constructional, landscaping and agronomic issues must be considered simultaneously. Indeed, the green roof must be able to guarantee the rooting, development and durability of the chosen plant species, and for this it is necessary to reconstruct the natural biological conditions in an artificial environment. For this objective is important to choose suitable materials both from an agronomic point of view and in terms of availability and workability. Vulcanus inerts, thanks to their porous structure, make possible to obtain draining carrying-durable, lightweight and fertile surfaces, all necessary characteristics for the creation of green roofs.

Despite all these applications, a fine fraction, <3 mm, is produced from quarrying operations, which is difficult commercialize. Therefore, a collaboration is active between Europomice s.r.l. and Dept. of Engineering "Enzo Ferrari" of Univ. of Modena and Reggio Emilia for the development of new products for building and agronomic use, such as lightweight aggregates, usually made of expanded clays, expanded clayey schists, vermiculite and perlite and alkali activated materials, aluminosilicate materials consolidated at room temperature.

# Circular economy approach in the management of large volume inorganic wastes: the case of red gypsum from the $TiO_2$ industry

Marian N.M.*[1], Perotti M.[1], Indelicato C.[1], Magrini C.[1], Giorgetti G.[1], Capitani G.C.[2] & Viti C.[1]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* narcisamihaela.ma@student.unisi.it

*Keywords:* recycling, circular economy, red gypsum waste.

The present study deals with the worldwide growing problem of waste production and accumulation. This problem led to the development of circular economy principles, aiming to a valorization and sustainable re-utilization of our wastes.

In this preliminary study, we investigate a special waste from the Tuscan territory (Italy), particularly red gypsum deriving from the $TiO_2$ production. The industrial process is extremely impacting since the production of 1 ton of $TiO_2$ generates ~7 tons of gypsum, which need proper management and disposal. The inorganic waste is produced by the deactivation of sulphuric acid (used to extract $TiO_2$ from ilmenite raw material) with another waste, known as "marmettola", the Carrara marble powders. We analyzed red gypsum wastes produced in more than ten years of the industrial processing, using different chemical-mineralogical techniques such as X-ray fluorescence (XRF), X-ray powder diffraction (XRPD), scanning electron microscopy with energy dispersive X-ray spectrometer (SEM/EDS), and thermal analyses (TA). We therefore explored the possible industrial reuse of red gypsum as secondary raw material in the ceramic industry, following the procedures described in patent n. 0001369219 (GRINN solutions s.r.l.). Ceramic tests have been realized using a surprisingly high amount (up to 70%) of the previously analyzed red gypsum wastes. The main crystalline phases in the ceramic materials are anhydrite, pyroxenes and Fe/Ti oxides, embedded in a glassy matrix.

Preliminary results seem very promising for a definitive solution to red gypsum waste management, thanks to the high % of waste reused in the ceramic products. Further investigations, such as leaching and mechanical test, as well as cost/benefit and Life Cycle Assessment analyses, are needed to upscale the entire process to an industrial perspective.

# On the suitability of phillipsite-chabazite zeolitite rock for ammonia uptake in water: case study from the Pescara river (Italy)

Novembre D.*[1], Gimeno D.[2], Calista M.[1], Mancinelli V.[1] & Miccadei E.[1]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain).

*Corresponding author e-mail:* daniela.novembre@unich.it

*Keywords:* zeolites, ionic exchange, ammonia removal.

Ionic exchange tests have been performed on superficial wastewaters to remove ammonia using a volcanic zeolitized rock from Lazio Region (Central Italy). The zeolitite (natural zeolite) is characterized by chabazite, phillipsite and minor amounts of sanidine, leucite and analcime. After preliminary column experiments in laboratory focused to determine the saturation time of the zeolitite, a pilot plant was built up on a little water course near the area of San Giustino channel (Abruzzo Region, Central Italy). Wastewaters, characterized by starting ammonia value ranging between 5 and 120 mg/l, were filtered with a zeolitic bed. The first experimental results indicate a positive ammonia reduction of about 80-90% and, in all cases, $NH_4^+$ concentration values under the EU law limits. A main purpose of this paper is to evidence that most of studies published on uptake of ammonia by means of zeolitite lead with clinoptilolite-dominant zeolitite despite the large and best performance of phillipsite-chabazite zeolites. Last but not least, a large number of published studies are of difficult comparison because of poor characterization of the zeolitite used.

# Solid-state characterization of high-temperature processed chromium-bearing tannery sludges

Perchiazzi N.*[1], Mugnaioli E.[1], Pollastri S.[2], Franceschini F.[3], Licitra G.[3], Ghezzi L.[1] & Petrini R.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Elettra-Sincrotrone Trieste. [3] Agenzia Regionale per la Protezione Ambientale della Toscana, Pisa.

*Corresponding author e-mail:* natale.perchiazzi@unipi.it

*Keywords:* tannery sludges, pyrolysis products, Cr(VI).

The heavy use of chromium in tannery industry may cause environmental and health concern, due to of the risk of the conversion of the Cr(III) into Cr(VI) compounds, whose carcinogenicity is soundly demonstrated (IARC, 1990). Tannery sludge represents the main solid wastes from the leather industry, characterized by having a plenty of organic substances and a remarkable amount of Cr (Dhal et al., 2013), and the treatment and disposal of this hazardous waste is a major challenge in a sustainable circular economy scheme. Pyrolysis treatment of tannery sludge is considered an effective technology to both reduce solid waste and recycle gas and chemical feedstock, and an increasing number of studies is presently devoted to the study of several aspects involved in the thermal treatment (Kavouras et al., 2015; Tôrres Filho et al., 2016).The present study focuses on incinerated wastes obtained by the pyrolysis of tannery sludges in the industrial district of Santa Croce sull'Arno (Tuscany Region, Italy), one of the largest in Europe.

The high-temperature pyrolitic process volumetrically reduces the original sludge, and would immobilize the chromium (total Cr content in the range 2-4 wt.%), converted in the trivalent form, in a solid.

To date no detailed investigations have been carried out on the type, shape and structure (amorphous, crystalline, disorder, etc.) of this material. Planned studies are focused on the distribution of Cr in the material, with the main goal of understanding the processes which regulate the possible oxidation of Cr(III) to Cr(VI), in order to plan effective remediation and mitigation activities related to reuse.

The obtained results show that this material is a strongly inhomogeneous char, made up by a fine grained carbonaceous matrix, hosting several crystalline or amorphous solids, such as spinel, gypsum, calcite, quartz. Cr(III) oxidation experiments and leaching tests have been performed in order to evaluate the recycling sustainability.

Dhal B., Thatoi H.N., Das N.N. & Pandey B.D. (2013) - Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review. J. Hazard Mater., 250, 272-291.

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Kavouras P., Pantazopoulou E., Varitis S., Vourlias G., Chrissafis K., Dimitrakopulos G.P., Mitrakas M., Zouboulis A.I., Karakostas T. & Xenidis A. (2015) - Incineration of tannery sludge under oxic and anoxic conditions: study of chromium speciation. J. Hazard Mater., 283, 672-679.

Tôrres Filho A., Lange L.C., de Melo G.C.B. & Praes G.E. (2016) - Pyrolysis of chromium rich tanning industrial wastes and utilization of carbonized wastes in metallurgical process. Waste Manag., 48, 448-456.

# Flotation muds as secondary raw materials in ceramic production: a preliminary study

Perotti M.*[1], Marian N.M.[1], Indelicato C.[1], Capitani G.C.[2], Iacoviello F.[3], Salvini R.[1-4] & Viti C.[1]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Department of Chemical Engineering, University College London (UK). [4] Centro di Geotecnologie, Università di Siena.

*Corresponding author e-mail:* matteo.perotti@unisi.it

*Keywords:* secondary raw materials, flotation muds, ceramic production.

Recovery and recycling of valuable materials from industrial waste is one of the main goals in present society. Most natural resources are not renewable (at least at the human time scale), and their availability is running out. The reuse of industrial wastes has the further benefit of limiting landfill disposal. In this respect, recovery of wastes containing precious metals is of primary interest not only in the jewellery industry, but also in the electronics and catalysts industrial sectors. Here we present a preliminary feasibility study focused on flotation muds (FM) derived from precious metals recovery processes. In close collaboration with an Italian innovative start-up, engaged in waste recycling and circular economy sectors, we explored the possibility to reuse FM as secondary raw material (SRM) in the production of thermoformed ceramic products. Two different FM samples have been analysed to determine their chemical and mineralogical characteristics. Subsequently, following a patented process technology, we use exceptionally high amounts of FM (up to 70-85%) to produce ceramic specimens. The latter were finally investigated by means of scanning electron microscopy (SEM-EDS), X-ray diffraction (XRD), X-ray Fluorescence (XRF), high resolution micro-computed tomography (micro-CT) to evaluate their chemical, mineralogical and microstructural (internal porosity, microfabric) features. Moreover, additional tests were carried out to determine the physical and mechanical characteristics of samples with the aim of determining their compressive and flexural strength and frost resistance. In addition, also aggregates from ceramic products were prepared to determine their wear resistance. The main crystalline phases in the ceramic products are gehlenite, anorthite, augite in one sample and diopside, nepheline, anorthite in the second sample. The overall microstructure is very similar to traditional ceramics, where the crystalline grains are associated with minor amorphous matrix and pores with variable size. Our preliminary results confirm that this kind of waste can be successfully re-used in the ceramic industry, resulting in products with high technological performances and competitive with respect to traditional ceramics.

# Discriminating the petrography of CDW *via* rapid spectroscopic tool

Radica F.*[1], Iezzi G.[1-2], Trotta O.[3], Bonifazi G.[3-4] & Serranti S.[3-4]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] INGV, Roma. [3] Dipartimento di Ingegneria Chimica, Materiali, Ambiente, Sapienza Università di Roma. [4] Centro di Ricerca in Biofotonica, Sapienza Università di Roma, Latina.

*Corresponding author e-mail:* francesco.radica@unich.it

*Keywords:* CDW, XRF, SWIR.

Construction & Demolition Wastes (CDW) exceeds 30 wt.% of all waste; after natural (earthquakes, etc.) and social (war) adverse events their amount strongly increases. Consequently, EU imposed their recycling for at least 70 wt.% for limiting their landfills, further excavation of virgin aggregates and thus favouring sustainable industrial processes. However, CDW are extremely heterogeneous materials from a commercial, petrographic and physic-mechanical perspectives. This strongly limits their upcycling recover into new construction materials (Gálvez-Martos et al., 2018). Moreover, the petrography of CDW mirrors available lithotypes (rocks), architectural and historical styles, as well as national (past and present) regulations of a geographical area (Galderisi et al., 2022). An accurate and rapid petrographic characterization will strongly enhance their homogenisation by sorting, thus implementing their upcycling reusing. Till now, sorting is practically limited to grain-size separation after comminution and sieving, more rarely also as a function of density.

To overcome these restrictions, here we show an alternative and efficient petrographic sorting based on spectroscopy. A representative data-set of 18 CDW specimens collected in the Abruzzo region (Central Italy) and already characterised by petrographic methods (XRF and XRPD) are here analysed by non-destructive and extremely rapid Short Wave Infrared (SWIR) spectroscopy or hyperspectral imaging (HSI). The 18 samples are grouped like concrete (CO), natural stone (NS), tile (TI). brick (BR), perfored brick (PF) and roof tile (RT) (Galderisi et al., 2022) and were analysed under reflectance. The same samples were also analysed by portable micro-XRF imaging. The agreement between classic and portable XRF are extremely high for all CDW group, except CO due to their intrinsic heterogeneous texture (cement vs aggregate). The SWIR spectra *via* HSI display three main regions of interest characterised by multicomponent broad bands, vibrating around 1450, 1950 and 2200 nm, mainly corresponding to $H_2O$+OH, $H_2O$ alone and metal-OH plus $CO_3^{2-}$ related features, respectively (Clark et al., 1990). Fitting of bands unveils that the component cantered around 2340 nm increases its area% as a function of CaO; the opposite for $SiO_2$ and $Al_2O_3$. This rapid HSI features is thus useful to discriminate between carbonate- and alumosilicate-rich CDW materials.

Clark R.N., King T.V.V., Klejwa M. & Swayze G. (1990) - High spectral resolution reflectance spectroscopy of minerals. J. Geophys. Res., 95, 12653-12680.

Galderisi A., Iezzi G., Bianchini G., Paris E. & de Brito J. (2022) - Petrography of construction and demolition waste (CDW) from Abruzzo region (Central Italy). Waste Manag., 137, 61-71

Gálvez-Martos J.L., Styles D., Schoenberger H. & Zeschmar-Lahl B. (2018) - Construction and demolition waste best management practice in Europe. Resour. Conserv. Recycl., 136, 166-178.

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# Mineralogy and thermal behavior of treated vitrified solid wastes for recycling

Stabile P.*, Abudurehman A., Carroll M.R. & Paris E.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* paola.stabile@unicam.it

*Keywords:* mineralogy, waste, recycling.

Waste recycling is of relevant importance to recover raw materials otherwise lost and to prevent the disposal in landfills, also avoiding the environmental impacts linked to natural resources exploitation. In particular, regarding Construction and demolition waste (CDW), the EU Waste Framework Directive (WFR 2008/98/EC, modified by the latest Directive (EU) 2018/851) imposes European countries to achieve at least 70% of recycling and/or recovery of CDW by 2020.

This work focuses on CDW coming from the rubble produced by the 2016 seismic events in the Marche Region, for potential recycling as secondary raw materials in the building industry. Given the chemical composition of this CDW (Abudurehman et al., 2021) a series of mixes combining CDW with industrial solid waste has been prepared in an attempt to obtain vitrifiable materials.

Vitrification is, in fact, a good way to gain a strong volume reduction of waste and immobilize potential hazardous elements in the vitrified structure. In this work, a set of experiments was performed at 1200°C, atmospheric pressure and 8-hours duration, incorporating increasing quantities of common solid wastes in the CDW starting material (i.e., 30-50-70 wt.%) like municipal glass, ceramic plates, fly-ash, etc.). Different factors, such as homogeneity, crystallinity and microstructure of the vitrified materials need to be considered prior to spending the product in specific applications. For this reason, the waste mixtures were investigated by optical microscopy, electron probe microanalyses (EPMA) and X-Ray Powder diffraction (XRPD) and results suggest that the vitrification products can be either vitreous or glass-ceramics, mainly depending on the batch composition. For instance, the amorphous content varies from 100 wt.% in products made up of CDW with ceramic powder mixtures to 65 wt.% when CDW was treated along with fly ash.

Thermogravimetric analyses of selected waste mixtures were carried out in order to reconstruct the thermal history of the vitrification process (phases reaction, crystallization of high temperature species, and weight loss). Additionally, another challenge is posed by the fact that glasses obtained from wastes often have widely varying composition (and thus rheological behavior). Therefore, retrieving the viscosity of such materials by Differential Scanning Calorimetry (DSC) measurements has important implications for the identification and quantification of structure effect on the feasible applications of the waste-based products.

Although vitrification process is a highly energy-intensive process, on the other side these studies could contribute to evaluate the possible recycling of the finest fraction of CDW, unsuitable for backfilling and destined only to be landfilled.

Abudurehman A., Stabile P., Carroll M.R., Santulli C., Paris E. (2021) - Mineralogical and chemical characterization of CDW as function of particle size and thermal treatments for potential recycling. Detritus J., 15, 40-50.

# Structural and ion-exchange properties of hydropyrochlore: Towards a potential waste form to immobilize thallium in polluted environments

Taddei A.*, Lepore G.O., Bindi L. & Bonazzi P.

Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* alice.taddei@stud.unifi.it

*Keywords:* hydropyrochlore, XRD/chemical data, soaking experiments.

Hydropyrochlore, ideal formula $(H_2O,\square)_2Nb_2(O,OH)_6(H_2O)$, is a cubic mineral (space group *Fd*-3*m*, *a* = 10.56-10.59 Å, Z = 8) belonging to the pyrochlore supergroup (Atencio et al., 2010). It was described for the first time by van Wambeke (1978) as *kalipyrochlore* while studying carbonatitic rocks from the Lueshe deposit, Kivu (D.R. Congo). In the deposit, hydropyrochlore occurs as a secondary product of primary $(Ca,Na)_2Nb_2O_6(OH,F)$ pyrochlores. Chemical data obtained by electron microprobe analysis match well with data from literature (van Wambeke, 1978) and show that the heavy weathering resulted in a major loss of Ca, Na and F with a simultaneous entry of minor quantities of Sr and K and, most importantly, $H_2O$ (up to about 12 wt% $H_2O$). According to Ercit et al. (1994), $H_2O$ molecules (up to 1.75 apfu) may enter both A and Y sites which, in strongly altered samples, can also show large amounts of vacancies. Partial substitution of O with OH at the X site may also occur. Collectively, all these features make hydropyrochlore an ideal candidate to investigate its capability in the removal of toxic elements from aqueous solutions. The results of previous studies (e.g., Zoppi, 2004 and references therein), hinting at incorporation of thallium within the pyrochlore structure, prompted further studies of the ion exchange mechanisms in hydropyrochlore. In particular, imbibition experiments were performed on single crystals extracted from a large octahedral fragment of hydropyrochlore from the Lueshe carbonatite and the $Tl^+$ incorporation was evaluated through both single-crystal X-ray diffraction (SC-XRD) and electron microprobe analysis (EMPA).

Structural and chemical data were collected before and after the soaking in concentrated solutions containing $Tl^+$ in known molar concentrations for variable imbibition times. After the soaking experiment, SC-XRD data show an increase of the cell parameter of 7-9 ‰. Accordingly, the expansion of the unit cell is associated with a significant increase of electron density at the A site (from ~ 6 to 57 $e^-$ before and after the soaking, respectively) and a decrease at the Y site (from 10 to 3 $e^-$), suggesting that $Tl^+$ was hosted at the A site during the soaking experiment at the expense of $H_3O^+$.

Lastly, in order to check the capacity of hydropyrochlore to retain thallium in its structure, one of the soaked crystals was immersed in water for variable times and analysed through single-crystal XRD.

Atencio D., Andrade M.B., Christy A.G., Gieré R. & Kartashov P.M. (2010) - The pyrochlore supergroup of minerals: Nomenclature. Can. Mineral., 48, 673-698.

Ercit T.S., Hawthorne F.C. & Černý P. (1994) - The structural chemistry of kalipyrochlore, a “hydropyrochlore”. Can. Mineral., 32, 415-420.

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Zoppi M. (2004) - Ossidi di Nb, Ta e Ti: processi di ricristallizzazione e relazioni cristallochimiche. Tesi di Dottorato. Università di Firenze.

# From waste to secondary raw materials: new paths to enable a sustainable use of resources

Tarantino S.C.*

Dipartimento di Chimica, Università di Pavia.

*Corresponding author e-mail:* serenachiara.tarantino@unipv.it

*Keywords:* resources, sustainability, building materials.

Awareness of the finite nature of many resources, including the question of the scarcity of many elements, has grown tremendously over the past few decades. It has become painfully obvious that the linear path of production, where scarce resources are consumed and their value-added products are degraded to waste, has enormous effects on the environment and climate. The concept of circular economy is one of the priority concepts of economic development at the basis of the current EU policy in the field of environmental protection, with the new action plan for the circular economy (CEAP) that the European Commission has adopted in 2020.

The path towards a more sustainable future passes through a road with an efficient use of resources (energy, water, land, minerals), optimization of waste management and value creation. The increased use of secondary and renewable resources will likely be key in achieving sustainable materials use.

This talk addresses some examples of transforming both biosolids and inorganic sludge into secondary raw materials, and their beneficial use in building materials to take a step forward towards the implementation of closed loop material flows.

Examples of development of novel construction materials based on alkali activation of mineral sludge will be illustrated (Clausi et al., 2016, 2018; Occhipinti et al., 2021). Alkali activation offers the opportunity not only to divert such aluminosilicates from landfills, but also to reduce reliance on conventional building materials, which may exhibit large environmental footprints.

Finally, a novel approach to tackle the environmental problem linked to sewage sludge will be shown (LIFE19 ENV/IT/000165, https://life-freedom-project.eu/). This approach, based on the hydrothermal process, converts biosolids into secondary raw materials, which in turn can be used to manufacture structural ceramics that meet the challenges of sustainability and environmental responsibility.

Clausi M., Tarantino S.C, Magnani L.L., Tedeschi C., Riccardi M.P. & Zema M. (2016) - Metakaolin as a precursor of materials for applications in Cultural Heritage: geopolymer-based mortars with ornamental stone aggregates, Appl. Clay Sci., 132-133, 589-599.

Clausi M., Fernandez-Jimenez A., Palomo A., Tarantino S.C. & Zema M. (2018) - Reuse of waste sandstone sludge via alkali activation in matrices of fly ash and metakaolin, Constr. Building Mater., 172, 212-223.

Occhipinti R., Fernandez-Jimenez A., Palomo A., Tarantino S.C. & Zema M. (2021) - Sulfate-bearing clay and Pietra Serena sludge: Raw materials for the development of alkali activated binders, Constr. Building Mater., 301, 124030.

# Earth materials and waste: similarities and differences

Tribaudino M.*

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* mario.tribaudino@unito.it

*Keywords:* waste, anthropogenic materials, mineralogy.

Waste represent the connection between the process of the human exploitation of the earth and the natural geological cycle. In fact, the fate of any waste deposit is that of a future geological deposit, which could be possibly identified as anthropogenic by mineralogical and chemical signature. By this respect wastes in a circular economy or linear approach do not show any difference, but for the fact that circular economy aims to reduce or possibly should cut completely the waste deposits. As a matter of fact, anthropogenic deposits are basically residuals from original waste.

Here we discuss the mineralogical and geochemical differences between waste deposits, with a focus on bottom ashes from incinerators, and the natural earth-made geological deposits. A comparison with continental average crust shows that, once the organic contribution is lost, the waste represent a sink of the manmade materials, with notable similarities in major elements distribution, and a specific imprinting in minor elements, which tells us much about the products and elements most used. Also the mineralogical composition and structures tells us much about the history of the wastes: for instance in bottom ashes local phase equilibria are represented, with dentritic or resorbed structures that recall fast cooled volcanics.

On the other side, major differences between waste and continental crust depositis are in the higher presence of metals, in a specific imprinting from organic chemistry, and in the glassy phases. Glassy phases occur, both from residual glass products, like bottles or windows, and from glass newly formed after heating, this latter with a highly heterogeneous, rich in alkali, composition.

As a conclusion, comparison between the chemical and mineralogical composition of a given waste, in comparison with continental crust composition can give important information on the local production and disposal of waste, on the practice in waste treatment plants, and on possible recycling paths.

# Recycling detoxified cement asbestos in organic compounds

Vergani F.*[1], Campanale F.[1], Perotti M.[2], Marian N.M.[2], Viti C.[2] & Capitani G.C.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena.

*Corresponding author e-mail:* fabrizio.vergani@unimib.it

*Keywords:* cement-asbestos, recycling, organic compounds.

Asbestos minerals, chrysotile and fibrous amphiboles, have been commonly used in construction materials, such as cement-asbestos (CA) slates used in roofing, due to the fibres capability to increase mechanical strength. This asbestos containing material is still largely abundant in buildings and in the environment even if, as universally acknowledged, fibre inhalation causes serious health problems. The present day's strategies to overcome the asbestos issue include confinement, encapsulation and removal. However, a more attractive solution is detoxification and reuse in a contest of circular economy.

In the present work, we evaluate the possibility to reuse thermally treated and deactivated CA powder (a mixture of glass and Ca-Mg silicates typical of cement – details in Vergani et al., 2022) as filler in organic compounds. In particular, the CA powder was used as inorganic filler within flour-elastomers (FKM type, characterized by high resistance to oil and temperature) and bi-component epoxy resins (bisphenol-A, epichlorohydrine based resins) used in flooring. For each application, different proportions of conventional raw materials and deactivated CA powder have been prepared and tested according to conventional quality test protocols and SEM micro-textural observations.

In epoxy resin, the inert CA powder was used either as unique inorganic filler (up to 30 wt.%) or admixed to conventional ones (barite), in different proportions (up to 10 wt.%). Mechanical tests and SEM observations have shown encouraging results for all formulations, even in the case of CA powder as unique filler. In particular, shore hardness exhibits a positive linear correlation with the CA powder quantities in the formulations. Similarly, DSC tests show minor variations in the thermic properties in comparison to the reference blank sample. Finally, particle analysis performed on SEM images reveals that the CA powder is well distributed, in a way comparable to the conventional production using barite as filler.

The employment of the inert CA powder in fluor-elastomers in substitution of wollastonite (~22 wt.%) or barite (~7 and ~14 wt.%) has given some controversial results. Although rheological properties such as cure kinetics, viscosity and scorch temperature are comparable to the standard reference samples, some important physical-mechanical properties worsen, probably linked to dispersion problems. SEM observations show that the CA powder tends to agglomerate, contributing to increase sample porosity with detrimental effects on breaking load, elongation at fracture and related M50 and M100 modules.

These results show that at the present state of art the reuse of deactivated CA-slate as filler in epoxy resin is feasible, whereas the application in elastomers needs some refinement.

Vergani F., Galimberti L., Marian N.M., Viti C. & Capitani G.C. (2022) - Thermal decomposition of cement–asbestos at 1100°C: how much "safe" is "safe"? J. Mater. Cycles Waste Manag., 24, 297-310.

# Potential up-cycling application of Construction and Demolition Waste from the 2016 Central Italy earthquakes

Volpintesta F.*[1], Ossoli E.[1], Reggiani A.[2], Stabile P.[1], Santulli C.[1] & Paris E.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] GeoMITS, Sassuolo (MO).

*Corresponding author e-mail:* francesco.volpintesta@unicam.it

*Keywords:* CDW, geopolymer, recycling.

In EU, Construction and demolition waste (CDW) accounts for about 36 wt.% of the total amount of produced waste. The 2016 seismic crisis in Central Italy generated a huge amount of rubble and, following the disastrous event, the quantity of CDW has drastically increased in the affected areas of the 4 regions involved (Marche, Abruzzo, Umbria, Lazio). CDW accumulation and lack of recycling put at risk the reconstruction in the earthquake-affected area, which will become in next years the largest reconstruction site in Europe. New ways of CDW recycling and applications in the building industry need to be tested, in view also of the EU Green Deal and circular economy regulations.

Recycling of CDW poses numerous critical issues regarding possible decrease in the physical-mechanical properties of the cement-based products which discourages this application. Also, the highly heterogeneous composition of CDW, variable both in space and time leads, in most cases, to mere backfilling applications.

In this study, we tested the possibility to use CDW as the aggregate component in geopolymer-based mortars, for upcycling applications in the building sector. The mineralogical and chemical composition of the CDW samples has been preliminary characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. The CDW of this study is composed mainly of calcite and quartz and, chemically, it is highly enriched in CaO (CaO 39.54, SiO 23.4, $Al_2O_3$ 2.79 wt.%), including also the contribution of cement-based components. Two different CDW grain sizes have been chosen for the tests, 0.08-2 mm and 0-8 mm, the latter being the finest produced by CDW recovery plants and most difficult fraction to recycle.

Geopolymer-based mortars have been produced with the objective to use a minimum of 60 wt.% in the mix, in order to assure a good proportion of waste incorporation. The geopolymer binder has been made using metakaolin as precursor and K-silicate alkaline reagent ($K_2SiO_3$).

Preliminary physical/mechanical tests show promising results in terms of characteristics for possible applications. Flexural and compression resistance results, obtained according to UNI EN 196-1, give about 5 and 30 MPa respectively and are comparable with those of cementitious materials commonly used in the construction sector. Higher CDW contents in mortars showed a progressive increase in porosity and water absorption, and a decrease in density. Other tests, like fire resistance, freeze-thaw, resistance to acid and salt attack, have evidenced the applicability of the geopolymer-based materials in extreme environmental conditions.

The results revealed that this CDW, in spite of its general characteristics (inhomogeneity, high variability) could be effectively recycled using geopolymers for upcycling new products, particularly suitable for application in the green building sector.

# S16.

# The challenge of alkali-activated materials: new chance for a sustainable world

*Conveners & Chairpersons*

*Claudio Finocchiaro (University of Catania)*

*Roberta Occhipinti (University of Catania)*

*Giuseppe Sabatino (University of Messina)*

# Economic and environmental impact assessments of Advanced Geopolymeric materials

Belhamdi H.*[1-2], Visco A.[1-3], Salomone R.[4] & Plutino M.R.[2]

[1] Dipartimento di Ingegneria, Università di Messina. [2] Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo. [3] Istituto dei Polimeri, Compositi e Biomateriali, CNR, Catania. [4] Dipartimento di Economia, Università di Messina.

*Corresponding author e-mail:* hossem.belhamdi@unime.it

*Keywords:* geopolymer, environment, alkaline activator.

In the last decades, the demand for sustainable construction materials has increased to improve the long-term performance of buildings and infrastructures. Therefore, the eco-friendly and economic sustainability of construction materials has begun to attract more and more the attention of researchers and construction practitioners as a viable replacement for Ordinary Portland Cement (OPC) concrete. The use of waste by-products (slag, fly ash, silica fume, and ground granulated blast furnace GGBS, etc.) helps to reduce gas emissions $CO_2$ during the production of geopolymers and enhance the mechanical properties and durability compared to conventional concrete (Ma et al., 2018; Kazemi & Fini, 2022). In this present work, geopolymer materials were prepared using different ratios of alkali-activators mixtures (NaOH and $Na_2SiO_3$) and local industrial solid waste from Sicily territory as a raw material which may resolve the HSE (Health, Safety, and Environment) issues and waste problems. The study aimed to select and characterize raw materials and design the synthesis of geopolymeric materials, through innovative and eco-sustainable approaches, also exploiting waste materials for their production, in order to produce qualitatively good results with the aim of improving and / or create an eco-sustainable product that brings innovation in the class of geopolymeric materials. Furthermore, the cornerstone of the project is, in addition to finding georesources in the Sicilian territory, their analysis and characterization, the creation of geopolymer mixtures and the social impact economic and environmental related to the industrial scale production of this material, with an analysis on a use case from the Sicilian territory.

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Ma C.K., Awang A.Z. & Omar W. (2018) - Structural and material performance of geopolymer concrete: A review. Constr. Build. Mater., 186, 90-102.

# Development of functional and eco-sustainable sol-gel based geopolymers for cultural heritage and buildings applications

Belhamdi H.*[1-2], Sabatino G.[3] & Plutino M.R.[1]

[1] Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo. [2] Dipartimento di Ingegneria, Università di Messina. [3] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.

*Corresponding author e-mail:* hossem.belhamdi@unime.it

*Keywords:* geopolymer, sol-gel, functional materials.

Recently, new synthetic inorganic and organic materials were developed with the aim of promoting their application as protective coatings and/or structural consolidants in construction and cultural heritage sector. In this context, the scientific community paid attention to geopolymers and their new hybrid functional derivatives to design and synthetize innovative and sustainable composites with better chemical resistance, durability and mechanical characteristics. Geopolymers are aluminosilicate-based amorphous inorganic materials obtained through a polymerization process, starting from natural or waste materials with a high content of aluminum or silicon, such as slag (from blast furnaces or from steel mills), clays, flying and volcanic ashes or other aluminosilicate sources (such laterite deriving from tropical areas) (Provis & van Deventer, 2009). They are quite similar to ceramic bodies for their structure and mineralogical properties; nevertheless, geopolymers are featured by scarce rheological properties due to their low viscosity, which make them almost inapplicable in restoration works mostly of vertical buildings. To overcome this problem, thus increasing their chemical, physical and mechanical properties, it is possible to use other copolymers or sol-gel based cross-linkers (polysiloxane oligomers, alcoxysilane agents or epoxy resin precursors), as well as opportune and functional molecules, nanofillers or consolidants: this functionalization of the alkali-activated material improves the performance of the final product, as it allows an increase in the viscosity of the mixture, making the hybrid material more versatile in architectural and renovation of new/ ancient buildings, or in the restoration and conservation of cultural heritage (Ielo et al., 2021). The present work concerns the modification of the geopolymer at the chemical and nanostructural level, through the condensation process in alkaline conditions for the implementation of their properties, in particular by mean of the sol – gel technique, which is an eco-friendly approach to functionalize geopolymers, without high temperature treatments, in accordance with the principles of circular economy and green chemistry. The chemical properties of the final functional geopolymers, together with the precursor ones, were studied by using X-ray fluorescence and diffraction investigations. Finally, corrosion resistance and hydrophobicity of these functional geopolymeric monoliths were tested by immersion and wettability tests.

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Provis J.L. & van Deventer J.S.J. (2009) - Geopolymers: Structures, Processing, Properties and Industrial Applications. Woodhead, Cambridge.

# Design and characterization of alkali-activated binders from water potabilization sludges

Clausi M.* & Pinto D.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* marina.clausi@uniba.it

*Keywords:* water potabilization sludges, wastes, alkali activated binders.

In view of a necessary transition towards circular production processes, an increasing number of disposal materials has started to be considered as resource rather than waste. This change of course requires the development of innovative and environmental-friendly technologies. Alkaline activation technology constitutes a very promising vehicle to reuse and valorize several types of by-products and/or waste.

In this context, wastes deriving from the water potabilization process are attracting attention as potential precursors of alkali activated binders (AABs) by reason both of their clayey nature and the high aluminium content related to the treatment processes (i.e., coagulation and flocculation).

This contribute is aimed at evaluating the potential of new AABs formulated with water potabilization sludges (WPS) coming from two treatment plants serving the Apulian territory (Italy). WPS were used as such and after different pretreatments (thermal and/or mechanical) aimed to enhance their reactivity. Sodium hydroxide (6-8 M) and sodium silicate solutions have been used as activators. A combined use with an Apulian carbonate-rich illitic clay and an additional Si-source (in different proportions) was also proposed with the aim to improve the properties of the pastes.

The obtained products were widely characterized from chemical, mechanical and microstructural points of view. XRPD, FTIR and SEM-EDX analyses demonstrated that the alkaline reaction occurred in all samples. The amount of gel developed was strictly dependent on the Si availability, while the gel composition shifted towards C-N-A-S-H or N-C-A-S-H types, according to the Si and Ca content in the system (i.e., in thermally pretreated samples or in clay-WPS blends). More in general, the encouraging mechanical results suggest the possibility of reuse of WPS either alone or in mixtures as raw materials for the synthesis of AABs.

# Preliminary studies on porous geopolymers for municipal wastewater treatment

Cofano V.*[1], Clausi M.[1], Santoro O.[2] & Pinto D.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] AquaSoil s.r.l., Fasano (BR).

*Corresponding author e-mail:* vito.cofano@uniba.it

*Keywords:* geopolymer, water treatment, sorbent.

In recent years, geopolymer materials have captured attention in wastewater treatment (Mackenzie, 2011) as efficient, environmentally-friendly low-cost adsorbents for elimination, decontamination, and purification of inorganic and organic hazardous pollutants from aqueous environments. A significant number of studies focused on the formulation and characterization of geopolymers due their excellent ability and capacities to adsorb and remove several elements such as dyes (Khan et al., 2015), ammonium (Couto et al., 2016) and sulphate (Runtti et al., 2016) from wastewater. Sorbent geopolymers for wastewater treatment are generally obtained from an aluminosilicate-based raw material (i.e., metakaoline, fly ash or slags) and an alkaline activator (NaOH and/or sodium silicate) with additives such as foaming agent and surfactant to increase their porosity and adsorptive properties.

This study deals with preliminary investigation of physical, chemical and mineralogical properties of porous geopolymers synthesized with the aim to be used in the experimental wastewater treatment line managed by Aquasoil s.r.l. located in Fasano (BR). Geopolymers were synthesised by using metakaolinite as allumosilate precursor and both sodium hydroxide and sodium silicate as alkaline activators. Hydrogen peroxide, oil and polysorbate surfactant, were used to promote porosity. The prepared samples were characterized by XRD, XRF, FT-IR and SEM. Integrity test and images analysis, acquired by digital camera, were also performed. The results show that geopolimerization occurred in all samples, but the amount and type of alkaline activation and of different additives influence significatively porosity, pore-size distribution and compressive strength. The incorporation of porous geopolymers into the current wastewater purification system is expected to be an efficient and economical method, allowing at the same time recycling of industrial waste products.

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Runtti H., Luukkonen T., Niskanen M., Tuomikoski S., Kangas T., Tynjälä P., Tolonen E.T., Sarkkinen M., Kemppainen K., Rämö J. & Lassi U. (2016) - Sulphate removal over bariummodified blast-furnace-slag geopolymer. J. Hazard. Mater., 317, 373-384.

# Restoration tests with alkali activated mortars based on Mt. Etna volcanic ash: the mosaics of Monreale Cathedral (Palermo, Italy)

Finocchiaro C.*[1], Caggiani M.C.[1], Coccato A.[1], Fugazzotto M.[1], Lanzafame G.[1], Nucatolo G.[3], Occhipinti R.[1], Portale S.[1-2], Stranieri S.[3] & Stroscio A.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Scienze Umanistiche, Università di Catania. [3] Centro di Restauro Piacenti S.p.A. - Conservazione del Patrimonio di interesse storico ed artistico, Prato.

*Corresponding author e-mail:* claudio.finocchiaro@unict.it

*Keywords:* restorarion, alkali activation, volcanic ash.

Within the Advanced Green Materials for Cultural Heritage (AGM for CuHe) project (PNR 2015-2020, Area di Specializzazione "Cultural Heritage" CUP E66C18000380005), the Monreale's Cathedral, located in the Metropolitan City of Palermo (Sicily), has been chosen as pilot restoration site. Since 2015 this site is part of the Arab-Norman Palermo and the Cathedral Churches of Cefalù and Monreale UNESCO Heritage, whose magnificence is given by the mosaic's extension (around 6.340 $m^2$), even higher than that of the Basilica of San Marco in Venice (Italy) and second in the world only to the church of Santa Sofia in Constantinople (Turkey). The internal facades are decorated by stone and glass mosaics, remaining the spirit of Byzantine culture. After a preliminary diagnostic campaign on the mosaic decorations located on the South aisle, which showed some deteriorations, specific interventions have been designed though the application of alkali activated materials (AAMs) in the optic of the green economy and sustainable restoration. Indeed, AAMs are assumed as a green alternative to traditional concrete and with high versatility, so they might respond to the increasing necessity of sustainability in conservation/restoration processes ensuring at the same time compatibility and durability of the interventions. Thanks to the satisfying results of previously studies on alkali activated materials (AAMs) based on volcanic ash from Mt. Etna volcano (Italy) (Barone et al., 2020, 2021; Finocchiaro et al., 2020; Occhipinti et al., 2022), a small area, was selected for the tests. The restoration tests were performed in collaboration with a well-known restoration company (Piacenti S.p.A.), whose steps have foreseen: i) the application of bedding and finishing mortars for the filling of *lacunae*; ii) the reposition of detached original *tesserae*; iii) the replica of the mosaic decorations by engraving and painting on the finishing mortar. This *in situ* activity has allowed to evaluate the criticisms related to the preparation and application of these kind of materials in restoration sites.

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Occhipinti, R., Caggiani, M.C., Andriulo, F., Barone, G., de Ferri, L., Mazzoleni, P. (2022) - Effect of atmospheric exposure on alkali activated binders and mortars from Mt. Etna volcanic precursors. Materials Letters, 315, 131940.

# Sorel cement: properties and utilization

Gatta G.D.*[1], Battiston T.[1] & Comboni D.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (Francia).

*Corresponding author e-mail:* diego.gatta@unimi.it

*Keywords:* Sorel cement, magnesium oxychloride cement, elastic properties.

Sorel cement (also called "magnesium oxychloride cement") is a non-hydraulic cement, produced by a mixture of magnesium oxide (magnesia) with magnesium chloride (often in the form $MgCl_2 \cdot 6H_2O$), with a weight ratio of 2.5-3.5 parts MgO to 1 part $MgCl_2$. Its recipe and properties are known since 1867. If compared to the more common Portland cement, discovered in the same period, the Sorel cement shows higher compressive strength, better resilience and capacity of bonding fillers (e.g., gravel, sand, expanded clays, glass fibres or even wood particles). However, when the Sorel cement is exposed to water, for a prolonged period, tends to dissolve. In addition, the presence of Cl ions makes Sorel cement incompatible with steel reinforcement, promoting metal corrosion phenomena. These two limitations represent the main criticalities of the Sorel cement, and are responsible for the success of the Portland cement against the Sorel one. However, the new route toward building materials produced with less energetic protocols is leading to a revaluation of the Sorel cement. The clinker manufacturing process is, in fact, highly energetic ($T_{max}$ 1450-1500°C), whereas the highest temperature usually necessary to produce Sorel cement is that required to promote the dissociation of $MgCO_3$ to $MgO+CO_2$, which nominally does not exceed 650°C. However, the production of highly reactive magnesia requires higher temperatures. At present, Sorel cement is used to make industrial flooring, fire retardant materials, or insulation boards. In addition, magnesium oxychloride cement is one of material used to fabricate the engineered barriers for deep geological repositories of high-level nuclear waste in salt-rock formations.

The aim of this presentation is to report our preliminary experimental findings on the crystal-chemistry of lab-made Sorel cement and on the behaviour of its crystalline components at non-ambient conditions, in order to provide their compositional, thermal and compressional parameters. The crystalline phases usually found in Sorel cement consist of complex magnesium oxychlorides (mainly, but no exclusively, the so-called "phase 3" $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ and "phase 5" $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) and brucite, sometimes coupled with unreacted periclase or magnesium chlorocarbonates. The fractions of the crystalline components depend on the initial cement formulation, but even by setting time and other variables (e.g., the reaction with $CO_2$). A multi-methodological approach has been used, including in-situ X-ray diffraction experiments at non-ambient conditions at the ID15b beamline, ESRF, Grenoble (France).

# Volcanic scraps as mineral resources for the design of sustainable alkali activates materials

Lancellotti I.*[1], Altimari F.[1], Barbieri L.[1] & Maggi B.[2]

[1] Dipartimento di Ingegneria "E. Ferrari", Università di Modena e Reggio Emilia. [2] Europomice s.r.l., Milano.

*Corresponding author e-mail:* isabella.lancellotti@unimore.it

*Keywords:* alkali activation, volcanic scraps, sustainability.

In the Vulsini Volcanic District (Italy) there are inert deposits such as pumice, lapillus and feldspathic sands of considerable commercial interest. The aim of the work was to valorize these extracted scraps whose fineness considerably limits their commercialization. If, therefore, this unsold material is used to restore the same quarry, it is subject to an additional cost of transport from the plant to the quarry; if it is piled up in areas within the quarry's jurisdiction (authorized as a landfill within the quarry) and then resold from these areas, a regional tax is paid. Anyway, a certain quantity of these sands are sold for street substrate, ceramics and filler for fertilizers. Following this information and with a view to increasing the quantities recoverable for industrial use, the geopolymerization appears to be a concrete opportunity.

The average chemical analysis of pumice and lapillus showed the presence of silica at 56.6% and 49.10% respectively, and of alumina at 18.6% and 18.3% respectively. Moreover, the pumice rock is constituted by around 80% of glassy phase and lapillus around 20%. Due to their chemical composition, in this work the volcanic materials were exploited to obtain alkaline-activated materials to be used in construction sector by substituting percentages of metakaolin in order to save it. The powders were mixed together and then the alkaline solution, 8M NaOH and sodium silicate or sodium aluminate, were added and the paste was stirred for few minutes to obtain a homogeneous mixture that could be poured into the mould, with distilled water added if necessary.

From the characterization of samples appears that volcanic minerals are suitable to obtain geo-polymeric materials and their presence does not hinder geopolymerization process. In particular, for geopolymers obtained using sodium silicate as alkaline activator appears that pH remains constant with values typical for metakaolin geopolymers. Conductivity shows different behavior depending on the presence of pumice or lapillus. Pumice maintains low values while lapillus leads to higher values of conductivity. This can be related to the chemical composition of lapillus richer in Ca, Mg and Na, but also to the more porous structure of lapillus-based geopolymers. Indeed, the porosity, ranging around 32-33% for pumice samples, increases up to 45% for the formulation based on 80% of lapillus. The best mechanical performance was achieved by lapillus samples (compressive strength in the range 35-38 MPa for lapillus compositions against 6-8 MPa of pumice ones).

For samples obtained by using sodium aluminate as alkaline activator lower mechanical performance were obtained. Geopolymers with high percentages of pumice presented an average compression strength of 7.3 $N/mm^2$, while for lapillus-containing samples low resistance values were obtained, suggesting that sodium silicate acts better in inducing geopolimerization.

# Alkali activated materials: the experience in Modena

Lancellotti I.[1], Dal Poggetto G.[1], Kamseu E.[1-2], Andreola F.[1], Barbieri L.[1], Romagnoli M.[1] & Leonelli C.*[1]

[1] Dipartimento di Ingegneria "E. Ferrari", Università di Modena e Reggio Emilia. [2] Mipromalo Research, Yaoundé (Cameroon).

*Corresponding author e-mail:* cristina.leonelli@unimore.it

*Keywords:* alkali activation, binder, sustainability.

The action of alkali on aluminosilicates, such as clays, has been investigated since 1927. At those times, it was scientifically proved that unless the alkali is very dilute (pH = 9), the clay begins to break down, giving silicates and aluminates when immersed in alkaline solutions. Specifically, with sodium hydroxide the clays are easily soluble, and with calcium they are insoluble, whilst barium and potassium occupy intermediate positions. Sodium hydroxide attacked the kaolin group minerals more strongly than it did montmorillonite, metabentonite, or illite. Metakaolin was more soluble than kaolin in alkaline media; results on various samples suggest the existence of at least one alkali-kaolin compound and one alkali-metakaolin compound already in 1946. From clays and fired clays, the experiments expanded to other aluminosilicates, fly ash, bauxites, nephelines, etc..

With this base knowledge of the highly reactive metastable aluminosilicates, containing variable amounts of Ca and Fe compounds, the alkaline attack became a facile route to form a cementitious material with high mechanical performance, and nowadays we have a novel class of engineered binders: the alkali activated materials-AAMs.

The experience at the Dept. of Engineering, Univ. of Modena and Reggio Emilia started in 2008 within a strong international collaboration with Mipromalo. Metakaolin, unfired clays, laterites from Cameroon, aluminosilicate industrial by-products were successfully activated to produce solid "ceramic-like" manufacts. Foaming agents were tested to produce lightweight panels, and fillers of different nature were added to reinforce and toughen the fragile structure. The aluminosilicate source characterization, the fresh geopolymeric pastes rheological behavior and the densified products performance are the field of expertise covered by the Research Group. A special attention has been posed on the chemical bonding generated during the reticulation process. With the addition of heavy metals and hazardous cations, the chemical frame of the AAMs was completed and patented. Urban solid wastes in the form of recycled glass containers, bottom ash or fly ash from incinerator plants, have been studied as replacements for the aluminosilicate source or the sodium silicate solution.

Over the years, the Research Group has reached out to local, national, international partners, working together on research projects or international committees (RILEM and ICG-TC05).

# The ancient Odéon from Teatro Romano (Catania Sicily): a pilot site for the application of Alkali Activated Materials in Cultural Heritage conservation

Occhipinti R.*[1], Bertino A., Finocchiaro C.[1], Fugazzotto M.[1], Motta A., Portale S.[1],[2] Stroscio A.[1], Baudo S.[3], Nucatolo G.[4] & Starinieri S.[4]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Scienze Umanistiche, Università di Catania. [3] SB Engineering s.r.l, Catania. [4] Centro di Restauro Piacenti S.p.A. - Conservazione del Patrimonio di interesse storico ed artistico, Prato.

*Corresponding author e-mail:* roberta.occhipinti@unict.it

*Keywords:* alkali activated materials, green restoration, circular economy.

Current practices tend to include modern techniques and innovative materials, with high-tech features to apply in conservation-restoration of Cultural Heritage, ensuring both aesthetic compatibility and adequate properties with regards to the original rock substrate.

In the framework of the project funded by the PNR "Advanced Green Materials for Cultural Heritage" (CUP E66C18000380005), Alkali Activated Materials (AAMs) have been developed and proposed as alternative to traditional materials in restoration intervention at "Odéon of Catania", a monument dated back to the II century A.D. located in the historical city center. In collaboration with Piacenti S.p.A, alkali activated mortars were prepared in order to test: i) the reproduction of a Roman capital originally made by the Etnean basalt); ii) in situ reintegration of the deteriorated brick's masonry; iii) in situ reproduction of prototype of a wall at real scale by imitating the aspect of the brick's masonry of the Odéon itself. All the activities were carried out with the supervision of Piacenti S.p.A. and SB Engineering s.r.l.

The volcanic ash of the recent eruptive events of Mount Etna were used as precursors for the reproduction of Roman capital (60x30x25 cm) and for the basement of the prototype wall. Ceramic wastes were used as precursors to prepare mortars for the in-situ restoration and for the reproduction of bricks.

As foreseen by the AGM project and with a view to large-scale industrial production, companies (SB Engineering s.r.l, M.E.G.A.RES. s.r.l., Costruzioni Edil Ponti-Società Cooperativa, LBC Società Cooperativa Artigiana a.r.l.) have been involved in the manufacture and operational phase of the application of the developed AAMs. The results obtained have demonstrated that local low-cost materials are suitable for the reproduction and restoration in terms of technical properties and aesthetical compatibility. The monitoring of the restored objects has led to promising results about their durability. Moreover, it has been demonstrated that these materials can be easily obtained with site tools, under varying environmental conditions.

# Upcycling of stone composite waste into geopolymer-based mortars for applications in the building sector

Ossoli E.*, Volpintesta F., Stabile P., Santulli C. & Paris E.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* elena.ossoli@unicam.it

*Keywords:* stone-composite, waste recycling, geopolymers.

Stone composite (or engineered stones) are versatile materials, widely used in different sector such as automotive, aerospace and civil engineering. The most common stone composites in the market of building materials consist in polymer matrix composites (PMC) incorporating quartz, or sometimes glass fragments, as inorganic filler component, resins and pigment. Despite being highly versatile and durable, at end-of-life these materials represent a serious environmental problem for the presence of polymers strongly mixed to the inorganic aggregates, difficult to recycle. For many years, composite waste has been landfilled, but since the composite materials waste is now considered special industrial wastes (hazardous waste) and the landfilling is illegal in many EU countries. The increased popularity of these materials calls for effective recycling processes.

In this study, we tested the possibility to use quartz-composite waste as the aggregate components in geopolymer-based mortars, to produce materials for different upcycling applications in the building industry, as tiles or slabs. Two different composites (A-type: 90 wt.% quartz and 10 wt.% unsaturated polyester resin, B-type: 60 wt.% quartz and 40 wt.% acrylic resin) were characterized by X-ray diffraction (XRD), optical microscopy and Scanning Electron Microscope (SEM), to elucidate their mineralogical and chemical composition, as well as determine grainsize and textural relations among the components.

Geopolymer-based mortars were produced with the objective to introduce up to 70 wt.% of composite waste in the geopolymer matrix, which is made by mixing variable amounts of metakaolin, acting as precursors, K-silicate and water. Preliminary results indicate that the grain-to-matrix boundaries are in perfect contact, and that open porosity does not exceed 20%, with only spherical unconnected pores. Density is between 1.8 and 2.2 g/cm$^3$. Water absorption is between 7.2 and 12.7%. Flexural and compressive tests, carried out according to EN standards for cement, indicate good mechanical properties varying in the range of 39.5-62.5 MPa at 28 days. Thermal and chemical resistance complete the characterization of the materials produced.

These preliminary results revealed that composite materials could be effectively recycled using geopolymers and that the new materials are very promising for upcycling application in the building sector, postponing therefore the end-of-life of these composites, otherwise destined to be landfilled.

# Alkali-activated cements (AAC) as virtuous solution for waste treatment

Parisi F.*[1], Giacobello F.[1], Marcianò G.[1], Mottese A.[1], Nania G.[1], Italiano F.[2], Tripodo A.[1], Sabatino G.[1], Caccamo M.T.[1], Magazù S.[1] & Di Bella M.[2]

[1] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.
[2] INGV, Palermo.

*Corresponding author e-mail:* gsabatino@unime.it

*Keywords:* waste treatment, alkali-activated cements, waste management.

Alkali-activated cements (AAC) are materials with excellent technical properties that can be used as hydraulic binders. Depending on the precursor materials, the mechanical compressive strength can be comparable to that of ordinary Portland cement. In addition, these innovative binder offer high resistance to fire and flame as well as being excellent insulating materials. They are synthesized by alkaline reaction of aluminosilicate raw materials which can also be represented by industrial and municipal waste. In this way, it is possible to limit the environmental impacts and obtain economic benefits for local companies according to the principles of the circular economy. In Sicily, most of these waste are disposed in landfill with high economic costs. The purpose of this study is to identifycompanies of the Sicilian territory (Italy) willing to provide waste or secondary products from their industrial activities. The stakeholders in the field of marble, granite and stone industry, mineral quarrying and construction sector have been contacted. In addition, many municipal water purification plants have been identified. We produce a report of the many companies, homogeneously distributed throughout the Sicilian territory, which declared their interest in supplying waste and secondary materials to produce Alkali-activated materials. The realization of such a virtuous system could represent a strong boost for the local/Sicilian economy and, at the same time, could reduce the environmental impacts in terms of atmospheric emissions and energy consumption related to waste management.

## Life cycle assessment of alkali-activated cements realized with ceramic and sewer sludge waste

Parisi F.*[1], Giacobello F.[1], Marcianò G.[1], Mottese A.[1], Nania G.[1], Italiano F.[2], Tripodo A.[1], Sabatino G.[1], Caccamo M.T.[1], Magazù S.[1] & Di Bella M.[2]

[1] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.
[2] INGV, Palermo.

*Corresponding author e-mail:* gsabatino@unime.it

*Keywords:* life cycle assessment, alkali-activated cements, green economy.

Alkali-activated cements (AAC) are innovative synthetic materials, which attract interest as alternative to ordinary Portland cement (OPC) since they are environmentally friendly materials, due to low processing temperature and reduced content of $CO_2$ emissions. These ecological features linked to their peculiar technical properties, such as high strength, high acid resistance, and/or high-temperature resistance, make them very innovative and technological materials. In addition, AAC show good performance if realized by recycling secondary natural or industrial raw materials such as sewage sludge or ceramic material from demolition activities, thus improving strong interest from countries with growing industrialization. Here, we provide the evaluation of the Life Cycle Assessment (LCA) for assessing environmental impacts associated with all the stages of the life-cycle related to the production process of alkali-activated materials based on ceramic and sewer sludge waste. Our study aims to highlights the reduction of global impact and also to stimulate the Sicilian green economy, proposing the employment of local raw materials to increase production of this innovative binder over the Sicilian territory (Italy). To achieve this objective AAC have been produced in laboratory, using waste provided from local companies. The obtained results show, for different scenarios, a considerable reduction of both $CO_2$ emissions and energy consumption, but also a general improvement of the environmental indicators.

# Preliminary studies on the cutting wastes from Sicilian stone industries: a resource for Alkali-Activated Materials

Portale S.*[1-2], Finocchiaro C.[2] & Barone G.[2]

[1] Dipartimento di Scienze Umanistiche, Università di Catania. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* silvia.portale@phd.unict.it

*Keywords:* cutting wastes, stone industry, precursors.

Sicily is a Region extremely rich in natural stones suitable for different uses in building construction, flooring, etc. For this reason, the extraction, sawing and processing activities are widely developed. However, the cutting process inevitably causes large quantities of sludge, a mixture of rock powder and machines cooling water. Globally, the stone industries are responsible for producing about 1000 Kg of cutting waste per 2500 Kg of natural stone (Almeida et al., 2007). The disposal of this waste is regulated by European Waste Codes 010413. Sadly, the sludge is often abandoned indiscriminately in open areas causing a real environmental problem. Therefore, the cutting waste recovery is an ecological challenge: the reuse of these waste materials as construction materials appears to be a viable solution to this problem generating cost reduction, while preserving natural resources. The utilization of stone sludge in alkali activation process has been recently reviewed (Occhipinti et al., 2021).

In this work, three residues of rocks cultivations were selected to determine their potential as precursors in the alkali activation process. The precursors were sampled from local cutting industries and includes Etnean basalts, metamorphic rocks and quartzarenite. To investigate their chemical and mineralogical compositions, these raw materials were characterized by means of X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Fourier Transform-InfraRed spectroscopy (FT-IR).

In particular, the behaviour towards alkali activation process of these sawing sludges either alone or in binary mixtures with metakaolin, a Numidic clay and a common industrial waste such gypsum, was evaluated. Sodium hydroxide and sodium silicate were used in different proportions for the activation process and the binders were cured at room temperature for 28 days.

The promising AAMs were characterized through XRD, FT-IR, and Scanning Electron Microscope (SEM) techniques, to access their mineralogical and microstructural features. Flexural and uniaxial compressive tests were carried out to evaluate their mechanical strength. The obtained results are satisfying the perspective of their potential reuse in the building and restoration fields.

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# The potentiality of volcanic ash from 2021 Cumbre Vieja Eruption (La Palma, Canary Islands, Spain) as starting material for the alkali activation process

Portale S.*[1-2], Occhipinti R.[1], Lanzafame G.[1], Gimeno D.[3] & Barone G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Scienze Umanistiche, Università di Catania. [3] Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain).

*Corresponding author e-mail:* silvia.portale@phd.unict.it

*Keywords:* volcanic ash, starting material, alkali activated material.

The latest eruption of the Cumbre Vieja volcano (La Palma, Canary Islands, Spain), started in September 2021 and lasted about three months, ejected huge quantities of volcanic ash that blanketed the surface of the entire island, reaching considerable thicknesses where closest to the eruptive centre and causing serious damage to residential areas and local cultivations. These natural deposits are considered as a difficult waste to dispose of. Recent works proved volcanic ash as an excellent starting material in the production of Alkali Activated Materials (AAMs) (Barone et al., 2021; Occhipinti et al., 2022).

This work aims to study the potential employment of Cumbre Vieja pyroclasts as precursor for the geopolymerization process, making them suitable in the construction field in the view of promoting the circular economy system. For this reason, samples collected from different sites of the island were characterized to determine their mineralogical and chemical composition before to be used as raw materials.

Mixtures of this precursor alone or in binary blends with metakaolin have been tested, with the aim to produce cementitious binders. Sodium hydroxide (8M) and sodium silicate solution have been used as activators. Lightweight geopolymers have been also prepared by the addition of foaming agents.

AAMs were subjected to X-Ray Diffractometry, FT-IR spectroscopy, Scanning Electron Microscopy and uniaxial compressive testing for a complete mineralogical, textural and physical-mechanical characterization. 3D micro-structure was investigated by synchrotron light computed microtomography at micron scale that provided precise information on the abundance, morphology, and connectivity of the porosity and how it affects the overall structure of the AAMs. Preliminary results evidenced that Cumbre Vieja ash can be efficiently employed as raw material in the geopolymer production, which represent a promising alternative to the conventional building ones with great potential in the construction field.

Barone G., Finocchiaro C., Lancellotti I., Leonelli C., Mazzoleni P., Sgarlata C. & Stroscio A. (2021) - Potentiality of the Use of Pyroclastic Volcanic Residues in the Production of Alkali Activated Material. Waste Biom. Valor. 12, 1075-1094.

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# Radon release from geomaterials used in the synthesis of alkali-activated materials for building purposes

Romano D.*[1], Italiano F.[1], Di Bella M.[1], Mottese A.F.[2], Parisi F.[2], Nania G.[2] & Sabatino G.[2]

[1] INGV, Palermo, ufficio di Milazzo (ME). [2] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e della Terra, Università di Messina.

*Corresponding author e-mail:* davide.romano@ingv.it

*Keywords:* geomaterials, radon exhalation, cultural heritage.

Geomaterials from Sicily have recently been tested as potential raw materials potentially employing for the synthesis of eco-friendly alkali-activated materials to be applied in the field of construction of civil and public buildings as well as in the field of Cultural Heritage for restoration and conservation interventions of building and monuments. Since high radon levels in indoor environments can lead to the development of serious health diseases, evaluating the radon release from building materials becomes fundamental to assess the hazard derived from ionizing radiation (IAEA, 2013).

Here we propose the results of radon emission measurements carried out on samples of Pleistocene clays from the Peloritani Mountains and of industrial wastes known as Electric Arc Furnace Slag (EAF-C), which are considered as the geomaterials most suitable to produce alkali-activated materials. These materials were analysed through alpha spectroscopy in order to investigate the release of $^{222}$Rn in terms of surface exhalation rate. Samples were enclosed in an airtight container connected to a dryer unit filled with $CaSO_4$ desiccant and to an electronic radon detector (RAD 7 Durridge) forming a closed loop in which air circulates. The radon activity concentration in the air volume of the container increases exponentially and tends to an equilibrium value.

The measured exhalation rate show values of 0.03±0.02 and 0.44±0.08 Bq $m^{-2}$ $h^{-1}$ for industrial wastes and clays, respectively. These values are lower than those determined for the Italian building materials usually characterized by high attitude to release radon (e.g., "tufo lionato", "peperino", "black pozzolana", "tufo rosso" and "tufo giallo napoletano"; 0.58-37 Bq $m^{-2}$ $h^{-1}$; Tuccimei et al., 2006). Therefore, we can assume that the use of the studied materials to produce eco-friendly alkali-activated materials for building purposes do not constitute a health threat in terms of radiological risk due to radon emissions.

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# Production of geopolymer binders using Sicilian clay sediments

Stroscio A.* & Mazzoleni P.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* antonio.stroscio@phd.unict.it

*Keywords:* clay sediment, alkali-activated materials, Sicily.

This work is focused on the possibility to use clay sediments, with diverse mineralogical and chemical characteristic, cropping out in Sicily as precursors to geopolymers production (Liu et al., 2019). Different formulations have been prepared using: Plio-pleistocenic clay characterized by high Calcite abundance and illite and smectite dominant clay minerals; and Numidian clay without Calcite and kaolinite rich clay minerals fraction. All the studied clayey sediments were thermally treated at 700°C for 3h and activated with sodium hydroxide solutions (4M, 6M and 8M) and sodium silicate ($SiO_2/Na_2O = 3$), according to the procedure proposed by Gasparini et al. (2013). All geopolymers were cured at 85°C for 20h, to improve the alkaline reaction, and at room temperature (22±3°C) for 28 days keeping the humidity level > 90%. After the curing, an integrity test has been performed to check the chemical stability of geopolymers in water. Specimens were analyzed by chemico-physical and mechanical point of view. X ray diffraction demonstrate that, in addition to the mineralogical phases of the original precursor, a new sol-gel phase was formed as result of polymerization process. Furthermore, crystalline phases have been detected as Tobermorite, in geopolymers with Plio-pleistocene sediments precursor, and Sodalite or Faujasite, in those in which Numidian clays were used, suggesting the formation of more ordered structure (Fernández et al., 1999). Spectroscopic characterization highlighted the shift of the aluminosilicate band towards lower wavelength number attributed to the formation of sodium aluminosilicate gels also evidenced by microanalysis. The compressive strength values ranging from 3.91 MPa to 44.50 MPa are higher in the geopolymers in which sodium silicate solution were used as already reported in literature (Criado et al., 2005; Fernández et al., 1999). According to our results, the obtained geopolymer binders provided good chemico-physical and mechanical characteristics compared to traditional materials utilized in building construction.

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# The effect of natural fibres on geopolymers made using Mt. Etna volcanic ash as precursor

Zafarana S.E.*, Occhipinti R. & Mazzoleni P.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* sabrinazafarana@yahoo.it

*Keywords:* geopolymer composites, volcanic ash, natural fibres.

In the last years the awareness of environmental issues has led to the development of eco-friendly materials that could combine high performance products with the possibility of the re-use of waste materials in both construction and restoration field (Barone et al., 2020).

For Catania the disposal of a large amount of volcanic ash produced by Mt. Etna is seen as a problem. The possibility to turn a waste material into a resource could be a substantial benefit (Barone et al., 2021; Occhipinti et al., 2022). Moreover, the city is located on an active seismic zone so high-quality construction materials are required.

Alkali activated materials have favourable properties such as low curing temperature, recyclability, low cost of the precursors, thermal stability and low density, making them a valid alternative to traditional OPC. Despite these excellent qualities their brittle behaviour imposes constraints in structural design.

To enhance the strength of the geopolymer matrix, both organic and synthetic fibres can be added to the binders to improve mechanical properties (Aydın & Baradan, 2013).

Two types of organic fibres in different length and amount, were used to reinforce Mt. Etna volcanic ash-based geopolymers.

Flexural and compressive strength tests were carried out to compare the mechanical properties of geopolymer composites by using different types of fibres. Moreover, samples were analysed by electron microscope to evaluate the gel formation and the adhesion of the geopolymer matrix to the fibres net.

Preliminary results have shown that the addition of fibres enhances the flexural properties and reduces the shrinkage of the system.

*This research, funded by the PNR "Advanced Green Materials for Cultural Heritage" project, aims to develop natural fibre-reinforced geopolymers for retrofitting seismic areas.*

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# S17.

# Microporous and layered minerals: properties and applications for a sustainable future


*Conveners & Chairpersons*

*Paolo Lotti (University of Milano - La Statale)*

*Giorgia Confalonieri (European Synchrotron Radiation Facility, Grenoble, France)*

*Davide Comboni (European Synchrotron Radiation Facility, Grenoble, France)*

# P-induced crystal fluid interaction: the case of ERI and OFF topology

Battiston T.*[1], Comboni D.[2], Pagliaro F.[1], Lotti P.[1] & Gatta G.D.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (France).

*Corresponding author e-mail:* tommaso.battiston@unimi.it

*Keywords:* microporous materials, zeolites, X-ray diffraction.

The P-induced intrusion of molecules or solvated ions within the nanocavities of open-framework minerals, such as zeolites, has been extensively investigated during last decades (e.g., Gatta et al., 2018, and references within). This peculiar property might be exploited to tailor new multifunctional materials or to enhance industrial catalytic processes involving zeolites (Comboni et al., 2020). In addition, from a geological point of view, a constraint of this phenomena might shed light on the role played by zeolites as fluid carriers in the upper Earth crust, e.g., during the early subduction of altered basalts or oceanic sediments. The aim of the present study is to characterize the high-pressure behavior, promoting the crystal-fluid interaction, on two different natural zeolites species belonging to the ABC-6 family: erionite (AABAAC) and offretite (AAB) (ERI and OFF topology, respectively). Similarities of the framework between these two species resulted in quite common intergrowth, at least in natural samples (Passaglia et al., 1998). Samples were compressed in non-penetrating and penetrating *P*-transmitting fluids (PTFs).

Investigations were conducted via in-situ high pressure single-crystal synchrotron X-ray diffraction, using a diamond anvil cell (DAC), at the ID15b beamline of ESRF (Grenoble, France) and P02.2 of PETRA-III (Hamburg, Germany). Different PTFs have been employed during the experiments: non-penetrating *i*) silicone oil and daphne oil (7575) and potentially penetrating, *ii*) alcohols: water mixtures, *iii)* pure $H_2O$, *iv*) Ne.

The obtained unit-cell P-V patterns revealed the adsorption of $H_2O$ molecules within the structural cavities; in addition, the structure refinements allowed to describe the deformation mechanisms as well as the location of the adsorbed molecules. Interestingly, the magnitude of the absorption phenomena in natural erionite appeared to be comparable with what observed in synthetic zeolites (i.e., $AlPO_4$-5, Lotti et al., 2016), highlighting the great potential of erionite as a mineralogical carrier of fluids in the upper Earth crust.

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# The role of temperature in P-induced crystal fluid interaction: the case of LAU and HEU topology

Battiston T.*[1], Comboni D.[2], Pagliaro F.[1], Lotti P.[1], Gatta G.D.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (France).

*Corresponding author e-mail:* tommaso.battiston@unimi.it

*Keywords:* zeolites, non-ambient conditions, X-ray diffraction.

Zeolites are a class of open-framework aluminosilicate minerals commonly present in soil, oceanic basalts and sediments and diagenetic environments. Zeolites may act as fluid carriers in the upper Earth crust during the early subduction stage thanks to their unique features: the reversible hydration (i.e., the ability of adsorb and release $H_2O$ molecules or other small molecules, e.g., $CO_2$, $CH_4$, $SO_2$) and the ability to overhydrate. During the last decades, the high-pressure (HP) and high-temperature (HT) behavior of natural and synthetic zeolites have been intensively investigated but, at the best of our knowledge, no experiments have ever been conducted combining the effects of both thermodynamic variable. Experiments at these conditions (i.e., simulating the PT gradient), using a $H_2O$-based solution as P-transmitting fluids (PTFs), provide a realistic description of crystal-fluid interaction phenomena.

In this study, we have investigated the HPHT behavior of heulandite and laumontite, two of the most common natural zeolites, whose presence have been described in a wide range of natural environments. The characterization of the crystal-fluid interaction induced by P in these two species has already been performed by Comboni et al. (2018) and Seryotkin (2015) for laumontite and heulandite, respectively, and was adopted as reference in order to evaluate the T gradient effect. In-situ HPHT single-crystal synchrotron X-ray diffraction experiments were performed at the ID15b beamline, at the ESRF, Grenoble (France). The set-up, easily reproducible, consist of a membrane-driven diamond anvil cell (DAC) placed in a resistive heater which allowed to increase the T up to 150(2)°C. Pressure was determined by the ruby florescence method, while temperature was measured using a thermocouple located very close to the P-chamber, allowing a precise determination of both (results were consistent with the values calculated by the Au-powder pattern).

Results of the P-V pattern in laumontite clearly indicated that temperature enhances the $H_2O$ adsorption, giving rise to a volume expansion at $P < 5$ kbar. Previous experimental finding highlighted that hydration of laumontite occurs at ambient condition after ~ 24h, while with the presence of a T gradient required no more that 20 min. Concerning heulandite, preliminary data seems to suggest a higher $H_2O$ adsorption. if compared to that governed by the effect of P only.

Comboni D., Gatta G.D., Lotti P., Merlini M. & Hanfland M. (2018) - Crystal-fluid interactions in laumontite. Microp. Mesop. Mater., 263, 86-95.

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# Synthetic zeolite as targets of fs pulsed laser ablation: effects

Belviso C.*[1], Orlando S.[2], Lettino A.[1], Medici L.[1], Mollica D.[2] & Guarnaccio A.[2]

[1] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ). [2] Istituto di Struttura della Materia, CNR, Montelibretti (RM).

*Corresponding author e-mail:* claudia.belviso@imaa.cnr.it

*Keywords:* femtosecond pulsed laser ablation, LTA typology zeolite, red mud.

Zeolites are microporous crystalline materials characterized by a framework of linked $TO_4$ tetrahedra (where T = Si, Al or others), each consisting of four O atoms surrounding a cation. Many literature data have documented the application of different techniques for the formation of synthetic zeolite with nanocrystal size also using unconventional approaches such as centrifugation-assisted grinding and Pulsed Laser Ablation (PLA). However, the tests on the use of laser to control the synthesis and size of zeolite are still limited whereas fragmentation processes by laser is a well-known method for metallic nanomaterials preparation.

In this work, the effects of Femtosecond Pulsed Laser Ablation (fs PLA) on three different targets of zeolite A (LTA typology) were investigated with the aim to perform nanozeolite re-crystallization process. Zeolite A was synthesized modifying standard IZA protocol without added nanoparticles (LTA), with the addition of red mud (RMFe-LTA) or with the incorporation of nanomagnetite (NMFe-LTA) during the hydrothermal process. fs PLA was performed on each target inside a stainless-steel vacuum chamber characterized by proper transparent windows for the entrance of the laser beam ($\lambda$ = 800 nm). The target was positioned at an angle of 45° with respect to the laser beam normal.

The results show that the chemical composition and crystallographic structure of the zeolitic targets have a significant influence on laser-matter interaction during fs PLA process (Belviso et al., 2022). In detail, the effect of fs PLA treatment on LTA samples is represented by the formation of amorphous material in the ablated area, due to the high local temperature of laser process, and the fast crystallization of formed zeolite nano-nuclei in adjacent areas as a result of the heat propagation. The different behavior characterizing the other two targets is, instead, due to the presence of different Fe nanoparticles. The thermochemical reactions activated by laser ablation on zeolite target characterized by the presence of nanomagnetite contributes to reduce the heat dissipation across NMeFe-LTA sample thus creating the favorable conditions by which the reconstruction of magnetite crystals can be reached from nanomagnetite crystals. Furthermore, under fs laser ablation, the iron oxides probably drive the heat in the molten area thus generating a fast-moving re-solidification front also outside the laser incidence area.

All the ablated targets were analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Belviso C., Orlando S., Lettino A., Medici L., Cavalcante F., Mollica D. & Guarnaccio A. (2022) - Effects of fs pulsed laser ablation on synthetic zeolite targets. Appl. Surf. Sci., 580, 152308.

# Rare Earth recovery from different leaching-like solutions using $NH_4$-exchanged 13X and LTL zeolite

Colombo F.*[1], Confalonieri G.[2], Vezzalini G.[1], Di Renzo F.[3] & Arletti R.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] ESRF, Grenoble (France).
[3] ICGM, CNRS-ENSCM-University of Montpellier (France).

*Corresponding author e-mail:* francesco.colombo@unimore.it

*Keywords:* zeolite, REE, recovery.

The demand of Rare Earth Elements (REEs) is constantly increasing due to their extensive use in many technological fields (e.g., fluid catalytic cracking catalysts, permanent magnets, batteries, fluorescent lamps). The current political scenario considers REEs as strategic resources (Mancheri, 2019). It is therefore essential to find alternative supplies, considering the environmental costs of their mining. REE recovery from wastes is a solution and the interest in the related technologies is increasingly growing. Different methods have been already tested for REE recovery such as precipitation, solvent extraction, adsorption and ion exchange. Despite the well-known ion-exchange properties of zeolites, just a few preliminary works investigated their application for REE separation and recycle (Faghihian, 2005; Duplouy, 2016; Barros, 2019; Mosai, 2019). Thus, we intend exploiting zeolite cation exchange property for the recovery of REEs from liquors obtained from the acid leaching of waste materials. In this work we present a double ion exchange experiment to recover cerium from a very diluted solution (Ce = 0.002 M) using a $NH_4$-exchanged zeolite L. This REE concentration was chosen to test the zeolite in a very extreme condition, representative of the real concentration of leached liquors obtained from spent fluid catalytic cracking (FCC) catalysts. In the first experiment the zeolite was put in contact with the very diluted solution for 72h at room temperature, testing different liquid/solid ratio (i.e., 30, 60, 90, 180, 270, 750 mL/g). The aim of this test was to define the best working conditions, meeting the industrial requirements for low energy consumption and fast recovery. ICP analysis were performed monitoring daily the cerium concentration in the solution. The obtained exchanged zeolites were fully chemically characterized. From the results obtained, the liquid/solid ratio of 90 mL/g shows the best compromise for the cerium ion exchange. Indeed, the 100% of cerium was recovered from the solution in the first 24 h, incorporating in zeolite L porosities 0.55 Ce ions p.u.c.. Once cerium is trapped into the zeolite porosities, a second ion exchange experiment, using $NH_4$ solution, was successfully performed with the aim to recover Ce, for further exploiting.

Further experiments aimed at the recovery of REEs from liquors deriving from phosphor of fluorescent lamps dissolution are in progress and preliminary results will be shown in this work. In particular an $NH_4$-exchanged 13X zeolite is exploited to drawn Ce, La, Eu and Y from solutions mimicking a leached fluorescent lamps liquor (Ce = 0.003M, La = 0.04M, Eu = 0.006M, Y = 0.17M). The zeolite was contacted with the solutions with three different liquid/solid ratio (i.e., 10, 50, 100 mL/g) at room temperature for 24h. The analysis on the solutions and the zeolite after exchange tests gave results very promising, showing a high exchange capacity.

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# Microporous Minerals Catching Sun: UV filters encapsulation in Zeolites

Fantini R.*[1], Vezzalini G.[1], Confalonieri G.[2], Di Renzo F.[3], Mino L.[4], Cavalli R.[5], Argenziano M.[5], Fischer M.[6] & Arletti R.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] ESRF, Grenoble (France). [3] ICGM, CNRS-ENSCM-University of Montpellier (France). [4] Dipartimento di Chimica, Università di Torino. [5] Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino. [6] Faculty of Geosciences, University of Bremen (Germany).

*Corresponding author e-mail:* riccardo.fantini1@unimore.it

*Keywords:* sunscreens, zeolites, cosmetics.

UV radiation plays a major role in skin carcinogenesis, and the diagnosed skin cancers are increasing annually. The research of UV filters (UVfs) is a key topic for the future of material, life, and environmental sciences. Organic and inorganic UVfs have become ubiquitous in many goods, especially personal-care products. Even if UV filters should be effective and photostable, their photodegradation and adverse effects on organisms were reported upon protracted UV exposure.

We recently developed ZEOfilters (Fantini et al., 2021), hybrid UVfs obtained by the encapsulation of octinoxate (OMC) and avobenzone (AVO) into zeolites with different topologies (MOR, FAU, MFI, and LTL) and Si/Al ratios.

The project aims: i) the optimization of ZEOfilters synthesis; ii) the evaluation of their UV filtering performances; iii) the assessment of their efficacy and safety; iv) the investigation of host-guest and guest-guest interactions.

ZEOfilters were characterized by Elemental Analysis, Thermogravimetric Analysis, UV-visible Spectroscopy, FT-IR spectroscopy, and Synchrotron-X-ray Powder Diffraction. Advanced computational studies were also performed to investigate the host-guest interactions. The efficacy and safety of ZEOfilters were evaluated by skin permeation tests, solar exposure tests, and leaching tests into simulated seawater.

The properties of ZEOfilters strongly depend on the zeolite-UVf combination. ZEOfilters based on high-silica zeolites, generally display a low UV filtering power and appear colored due to UV filter protonation. Conversely, LTL- and 13Xencapsulated molecules exhibit an enhanced UV absorbance also compared to bare UV filters.

In the most promising LTL ZEOfilters, FT-IR highlighted a perturbation of the ν(C=O) mode of the OMC carbonyl group. The structural refinement revealed a symmetry reduction from hexagonal to monoclinic of the hybrid, and the bonding of the carbonyl oxygen of OMC with the extraframework K cations. This interaction is probably responsible for the ν(C=O) perturbation in FT-IR. The stabilizing effect of carbonyl-K interactions was already reported for encapsulated, smaller, dye molecules (Fois et al., 2010).

The use of ZEOfilters should provide several advantages: i) the UVf-skin and UVf-UVf interactions should be inhibited; ii) the content of UVf, stabilizers, and other co-formulants may be reduced thanks to the enhanced filtering power and stability of the encapsulated UVfs.

The observed properties are promising for the future development and exploitation of ZEOfilters, which can be a more effective, safe, and eco-friendly alternative to traditional UVfs.

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# P-induced crystal-fluid interactions in 6-membered ring zeolites with EAB topology

Gatta G.D.*[1], Battiston T.[1], Comboni D.[2], Pagliaro F.[1], Lotti P.[1], Migliori M.[3], Giordano G.[3] & Ferrarelli G.[4]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (France). [3] Laboratory Chemical Engineering and Catalysis for Sustainable Processes, Università della Calabria, Rende (CS). [4] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina.

*Corresponding author e-mail:* diego.gatta@unimi.it

*Keywords:* zeolites, crystal-fluid interaction, high pressure.

P-induced intrusion of molecules (or solvated ions) into the structural nano-cavities of a microporous material, e.g., a zeolite, opened a new route to promote a mass transfer from fluids to structurally-incorporated molecules. A full understanding of this phenomenon in natural or synthetic zeolites might expand the number of their utilizations, e.g., in tailoring functional materials or improving catalytic abilities in industrial processes, or for a description of zeolite-fluids interaction in early subduction zones (e.g., Gatta et al., 2018; Comboni et al., 2020).

In this study, synthesis of EAB zeolite samples has been performed following the Aiello-Barrer protocol (Aiello & Barrer, 1970), and then treated in order to obtain the Na- and K-form. Then, we have investigated the high-*P* behaviour, promoting crystal-fluid interaction, of the 2 EAB zeolites by in-situ single-crystal synchrotron X-ray diffraction, using a diamond anvil cell (DAC), at the ID15B beamline of ESRF (Grenoble, France). Distilled $H_2O$, ethanol, methanol and the nominally non-penetrating silicon-oil as hydrostatic pressure transmitting fluids. Compression in non-penetrating silicone oil gives rise to a compressional behaviour without any crystal-fluid interaction, providing a reference for the compressional pattern obtained in nominally penetrating fluids. The results of this research will allow 1) to understand the role played by the pre-existing extraframework population (cations+$H_2O$ molecules) on the adsorption of penetrating molecules, and 2) assess the magnitude of the adsorption by comparing the compressibility of these synthetic microporous compounds.

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# Correlative microscopy of calcareous rocks and related derivative quicklimes applying innovative nano-CT scanning

Indelicato C.*[1], Perotti M.[1], Iacoviello F.[2] & Moreschi R.[3]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Department of Chemical Engineering, University College London (UK). [3] Unicalce S.p.A., Lecco.

*Corresponding author e-mail:* carlo.indelicato@unisi.it

*Keywords:* carbonate rocks, quicklime, porosity, nano-CT, fabric.

One of the main purposes in the lime industry is to determine in which way the quality of products is related to raw materials (i.e., carbonate rocks) properties. Indeed, it has been established that petrographic features of rocks affect the quality of the quicklime. Yet only few studies have investigated in this direction by using innovative methodologies. The main purpose of this work is the investigation on how the raw materials fabric (limestone and dolomitic limestone) is preserved and/or influences the quality of the calcined derivatives (high calcium lime, magnesium oxide, calcium hydroxide). Some studies have correctly highlighted that the quality of the calcined products depends on different types of factors: the geochemistry of the original rock (Beruto et al., 2010; Soltan et al., 2012), the size of the calcined material, parameters such as burning time (so-called soaking time) and applied kiln temperature; on the contrary, the relationships between quicklime properties and the petrographic features of raw material (i.e., mineralogy, microstructure, fabrics etc.) has only been addressed by few studies (Vola et al., 2019). To date, notwithstanding the number of studies by many researchers, it remains unclear to what extent the geopetrographic properties (i.e., different carbonate microfacies) could influence the quality of lime (in terms of porosity, surface area, slaking reactivity) throughout its production process, and this is the main goal of this study.

Petrographic analysis was achieved on different carbonate facies and analyses were carried out on their respective calcined limes through scanning electron microscopy (SEM) and nano-CT. The acquired preliminary data has allowed the detection of observable relations between the raw materials and the fabric of lime products, in particular with regard to grain size. Furthermore, the innovative tomographic use of lime has allowed us to evaluate the porosity and three-dimensionality of calcium oxide crystals and related fabrics.

The set of expected results will lead to a further step in understanding the response of the raw material to the calcination process and the optimization of the production cycle starting from the quarry and ending in the industrial kilns (identification of the most suitable carbonate rock, with positive effects in terms of sustainability which is reflected in the lowering energy consumption, reduction of sterile volume and quarry management).

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# Comparing technological performance of natural zeolite-rich composites for the sorption of non-steroidal anti-inflammatory drugs

Izzo F.*[1], Mercurio M.[2], Germinario C.[2], Grifa C.[2] & Langella A.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento.

*Corresponding author e-mail:* francesco.izzo4@unina.it

*Keywords:* SMNZ, NSAID, emerging contaminants.

Thanks to their properties, natural zeolites have been widely investigated in various contexts, such as environment, pedotechnique, animal feed and oenology. Recently, these tectosilicates have featured as excipients in pharmaceutical preparations and biomedical applications due to their adsorptive and ion exchange capacities, especially as carriers in the drug delivery. The so-called Surface Modified Natural Zeolites (SMNZs), obtained by interaction with some selected cationic surfactants that can replace the native cations, are usually used for this purpose.

One of the latest challenge deals with the removal of some specific pharmaceuticals (i.e., non-steroidal anti-inflammatory drugs, NSAIDs) that act as xenobiotic compounds daily released in water bodies, often responsible for negative effects on living beings in terms of toxicity and persistence. These drug molecules are considered as contaminants of emerging concern (CoEC) or simpler emerging contaminants (ECs), and their removal from wastewaters need of a newer, sustainable, and low-cost remediation agent as SMNZ.

Therefore, the technological performance of selected zeolite-rich rocks toward the sorption of specific drug molecules, after functionalization using five different cationic surfactants (hexadecyltrimethylammonium chloride and bromide, cetylpyridinium chloride, benzalkonium chloride and Arquad®) have been here compared and discussed.

# The role of layered silicates in REE recovery: La uptake and release processes in natural and modified montmorillonites

Lepore G.O.*[1-2], Schingaro E.[3], Mesto E.[3], Lacalamita M.[3], Cristiani C.[4], Gallo Stampino P.[4], Dotelli G.[4], Finocchio E.[5], D'Acapito F.[2] & Giuli G.[6]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto Officina dei Materiali, CNR, Grenoble (France). [3] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [4] Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano. [5] Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova. [6] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* giovanniorazio.lepore@unifi.it

*Keywords:* lanthanum, montmorillonite, uptake/release.

Every year, tons of small Electrical and Electronic Equipment (WEEE) are disposed. The approach known as "urban mining", based on the development of "good practices" for the recovery of precious materials from WEEE, would lead to socioeconomic and environmental benefits. The study of efficient methods for metals recovery is therefore of clear interest. The solid/liquid adsorption process is able to remove metal ions from aqueous solutions with high efficiency and low costs, through a sustainable approach. The efficiency of the process is a key factor, and it depends on the adsorbent materials; thus, the study and development of solids with improved capability is crucial for the implementation at the industrial scale. In recent years, the feasibility of the use of pristine and modified clays for metal recovery has been reported (Padilla-Ortega et al., 2011), specifically the recovery of REs from aqueous solutions (Cristiani et al., 2021). The capture/release results were interpreted in light of the interaction of the single ions with the solid sorbent, and on the basis of the physicochemical properties of the metal ions. Nonetheless, the mechanism of ion-sorbent interactions still needs to be fully clarified.

Here we report the results of ongoing investigations on the performances of montmorillonites for the recovery of La ions from aqueous solutions. The study involves both the assessment of La uptake/release extent and structural investigations aimed at a deeper understanding of the process lying behind La incorporation. An X-Ray Absorption Spectroscopy study was performed at La $L_3$ edge on a set of montmorillonites: two source clays from the Clay Mineral Society repository in pristine form and a polymer-modified with a penta-etylen-hexamine of formula $C_{10}H_{28}N_6$. Ca- and Na-rich montmorillonite were previously contacted with La solutions of known initial concentration. XAS results evidence that La incorporation in the clay-based materials is independent on both polyamine presence and composition of the pristine clay. La-O distances for the first coordination shell range between 2.57 and 2.61 Å with coordination number with O atoms varying from 9 to 12. These results agree with the common interpretation that La incorporation occurs at the interlayer sites of the clays as an outer-sphere complex with water (Munoz-Paez et al., 1995), thus without structural bonding of La inside the clay structure. However, our results also point out the presence of a further La-Si or La-Al distance (at ~ 4.1-4.2 Å), indicating that a further incorporation mechanism must be considered. Indeed, La ions are likely at least partially adsorbed as inner-sphere complexes at the edges and/or at the surface of montmorillonite. The identification of this kind of interaction is of fundamental importance, since inner-sphere complexes are usually considered thermodynamically stable, thus playing an important role among the factors limiting the efficiency of the release process.

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# Adsorption of PFAS to different zeolites: characterization using LC/MS-MS, X-ray diffraction and thermal analysis for industrial application and real environmental conditions

Mancinelli M.*[1], Ahrens L.[2], Bonnet B.[2] & Martucci A.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala (Sweden).

*Corresponding author e-mail:* maura.mancinelli@unife.it

*Keywords:* zeolites, PFAS, water remediation.

Per- polyfluoroalkyl substances (PFAS) are a class of manmade chemicals extremely resistant to chemical, thermal and biological degradation due to the strong carbon-fluorine bonds. Their removal from drinking and natural water is a scientific and social challenge (Buck, 2011). In the present work, the removal efficiency of different organophilic zeolites were investigated: natural chabazite (CHA) and synthetic Y (FAU), Beta (BEA), L (LTL), mordenite (MOR) for 18 PFAS with varying chemical properties and molecular dimensions. Zeolites were selected based on their cost-efficient availability, differing in topology, channel systems, $SiO_2$/$Al_2O_3$ (SAR), and free window apertures and due selectivity, catalytic properties, saturation degree and easy regeneration (Ochoa-Herrera & Sierra-Alvarez, 2008). This study has a two main purposes: to measure the sorption capacity of commercial zeolite for PFAS dissolved in water and to quantify their performance for potential use in wastewater and groundwater remediation, and to understand zeolite structural features for the adsorption of PFAS from aqueous solutions. Zeolites' efficiencies were compared to powdered activated carbon (PAC), the material currently most used in PFAS adsorption remediation technologies, studied at the same conditions. The selected materials were tested among low and high concentrations for 18 PFAS, and four different contaminated real water samples from Uppsala, Sweden. To evaluate the adsorption capacity a series of batch experiments were conducted from 0 to 24h at RT. Concentrations of PFAS in water samples were analysed by solid-phase extraction (SPE) and ultra-performance liquid chromatography coupled to tandem mass spectrometer interfaced with an electrospray ionisation source in a nega-tive-ion mode (UPLC-(-)ESI-MS/MS). Bare and PFAS loaded zeolites powders were characterized by X-ray diffraction and thermal analysis. Uptake of PFAS was greatly influenced by concentration of the solution, PFAS structure, hydrophobicity of the zeolites samples and their 3D pore system size and distribution. XRPD data reveal lattice modifications in unit cell parameters after adsorption maintaining the crystallinity of the samples. Thermal analyses show that PFAS are expelled up to ~700°C and some trapped carbonaceous materials can be degraded until 1400°C. The adsorption efficiency is promising at high and low concentrations of PFAS for all the samples except the L zeolite. The zeolites are not subject to the competitors present in the real water samples and maintain their selectivity in adsorption. Calcined Beta zeolite with SAR=25 is found to be the most efficient material towards long and short-chain PFAS. These findings indicated that these materials can be successfully used for the decontamination of water from PFAS.

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# Preliminary investigations on secondary mineralization processes in pyroclastic rocks from Surtsey (Iceland)

Montesano G.*, Petrosino P., Rispoli C. & Cappelletti P.

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* giovanna.montesano2@unina.it

*Keywords:* Surtsey volcano, palagonitization, hydrothermal alteration.

Alteration of the basaltic glass (sideromelane) and authigenic mineral growth are fundamental mineralogical processes that influence the chemical and material properties of Earth's oceanic crust. These are alteration processes affected the evolution of the very young volcanic island of Surtsey (SW Iceland) since its formation and thus the island represents the most suitable site to investigate all the stages of the evolution process.

The island formed over a 3.5-year episode of explosive and effusive basaltic eruptions from 1963 to 1967, with tephra and lava as main deposits. Visible steam rising from the tephra pile observed in 1967 (Friedman & Williams, 1970) indicated the presence of a hydrothermal system. One year after the discovery of the thermal anomalies, the first signs of palagonitization of the basaltic tephra glass were recorded (Jakobsson, 1978). Surtsey was first drilled in 1979 through a vertically cored drill hole; in 2017, in the frame of the ICDP-sponsored SUSTAIN drilling project, two vertical and one inclined new cores were drilled through the 50-years old still hot Surtsey volcano. Surtsey deposits experienced mobilization of elements by circulating fluids, producing alkaline solutions from which authigenic minerals precipitate.

The present work deals with preliminary minero-petrographic and chemical investigations of pyroclastic rocks from the island of Surtsey through Optical microscopy (OM), X-ray diffraction, scanning electron microscopy (SEM) and energy-dispersion X-ray spectroscopy (EDS). These results will lead to a better understanding of secondary minerogenetic processes affecting Surtsey deposits, which contain mostly zeolites, tobermorite and clay minerals, but also calcium sulphates and calcite.

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# Mineralogical and technological characterization of zeolites from Basin and Range as pozzolanic addition of cement

Montesano G.*[1], Cappelletti P.[1], Caputo D.[2], Liguori B.[2], Campanile A.[2] & Rispoli C.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli «Federico II».

*Corresponding author e-mail:* giovanna.montesano2@unina.it

*Keywords:* zeolites, blended cement, pozzolanic addition.

Cement is a key building material for worldwide infrastructures, but its production is strictly linked to the $CO_2$ emissions which could be limited using supplementary cementitious materials (SCM), such as cement, but requiring a smaller amount of energy for their production. The most suitable SCM is certainly natural *pozzolana*, used for the preparation of hydraulic cements thanks to properties (e.g., the lime setting and the water resistance) deriving from its composition.

Shortage of natural pozzolans has led to the search for materials displaying pozzolanic activity. Among siliceous materials which behave as pozzolans, great attention has been paid to zeolitic tuffs (Liguori et al., 2015), mainly due to the unavailability of natural pozzolan in several countries (including USA) and, conversely, the considerable abundance in these countries of zeolites (Özen et al., 2016). Moreover, zeolitic tuffs can display a better pozzolanic behavior than the pozzolan itself (Liguori et al., 2015).

Here, minero-petrographic, chemical, and technological features of zeolitic tuffs from western USA (Basin and Range district) are reported. Analyzed samples contain erionite, mordenite, clinoptilolite/heulandite and phillipsite, and we evaluated 1) their pozzolanic activity according to European normative (UNI EN 196-5, 2015; Fratini, 1949), and 2) proposed their possible use as addition for blended cements. Results show that all samples provided pozzolanic reactions, but the two samples containing phillipsite displayed a higher reactivity towards CaO. All samples (with some concerns as regards those containing fibrous zeolites) could be thus advantageously employed for the preparation of blended cements, potentially reducing $CO_2$ emissions by 70-90%.

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# Pressure-driven methanol intrusion in MFI-zeolites and its effects on the structural deformation in silicalite-1

Pagliaro F.*[1], Comboni D.[2], Battiston T.[1], Gatta G.D.[1] & Lotti P.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (France).

*Corresponding author e-mail:* francesco.pagliaro@unimi.it

*Keywords:* zeolite, high-pressure, silicalite-1.

The crystal structure of MFI-zeolites is characterized by $SiO_4$ interconnected tetrahedra, which define two major structural channel systems, confined by 10-members rings (10mRs) of tetrahedra running along [010] and sinusoidal cavities along the [100] direction. The MFI-type zeolites are currently used in methanol-to-olefins (MTO) production processes as catalysts, representing an alternative to the high energy-demanding Steam Cracking process, which accounts for 95% of the worldwide olefins production. Under ambient conditions, only the surfaces of the crystallites are supposed to be involved in the MTO processes. Applying a hydrostatic pressure could significantly increase the efficiency of the catalytic process, enhancing the injection of the methanol molecules through the zeolitic channels. In this light, we aimed to study the influence of pressure to improve methanol capability to enter the structural voids of MFI zeolites. For this purpose, six MFI-type zeolites, characterized by slight chemical differences pertaining Fe-, Al- and B-abundance in the siliceous frameworks, balanced by $Na^+$ or $H^+$ as extra-framework cations, have been synthesized. The compressional behavior of these zeolites has been studied by means of *in situ* powder X-ray diffraction up to 2 GPa. A diamond anvil cell (DAC) has been used as a device to generate pressure and both penetrating and non-penetrating fluids have been used as pressure-transmitting media: methanol (able to penetrate the structural voids of the MFI zeolite) and silicone-oil (a polymeric fluid with a kinetic diameter of the molecules larger than the diameters of the structural channels). A different compressional behavior was observed, as a consequence of the intrusion of methanol within the MFI structural channels. The difference in compressibility of the same zeolite sample in silicone oil and methanol has been used as a parameter to evaluate the efficiency of the intrusion process. A comparative analysis of the effect of pressure on the methanol adsorption by the MFI zeolites with different chemical composition may provide useful information on their application as catalysts in the methanol-to-olefins conversion processes. It has been observed that zeolites with higher Fe contents and silicalite-1 (i.e., the 'pure' $SiO_2$ polymorph with a MFI topology) are the least compressible zeolites in methanol (with respect to silicone oil) and, consequently, those with the highest capability to host methanol molecules within their structure.

# Process optimization and characterization of dolomitic hydrated limes with high BET specific surface area for "green applications"

Vola G.*[1], Massa M.[2], Ardit M.[2], Bresciani P.[1], Sarandrea L.[1] & Cruciani G.[2]

[1] Cimprogetti s.r.l., Lime Technologies, Dalmine (BG). [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* g.vola@cimprogetti.com

*Keywords:* semi-hydrated dolomitic lime, fully-hydrated dolomitic lime, periclase hydration kinetics.

This contribution reports preliminary results related to mix-design optimization, physical-chemical, and mineralogical characterization of hydrated dolomitic limes for different "green applications", including acid neutralization and flue gas desulfurization (Oates, 1998). Four different Italian dolostones coming from well-known deposit, were burnt in a muffle furnace at different temperatures, i.e., 950-1050-1150-1250°C, to reproduce different calcination conditions occurring in twin shaft regenerative (TSR) kilns (Vola et al., 2018). Subsequently, dolomitic limes were slaked with warm water and additives for simulating the process occurring into conventional hydrating plants (Bustillo Revuelta, 2021). Different protocols were adopted to improve/facilitate the hydration kinetics of the Mg-oxide, i.e., the conversion rate of periclase into brucite, which is known to be very slow under ambient P-T conditions (Lanas & Alvarez, 2004; Vola et al., 2019). Thus, the starting "water to lime" ratio of 0.67 was progressively increased up to 0.92 via two hydration steps process from "dry" to "wet powders". Whether semi-hydrated dolomitic limes presented an excess of residual moisture (ca. 1-2 wt.%), they had to be dried by an additional thermal treatment under warm air conditions. BET specific surface area, pore-volume, and pore-size distribution from nitrogen gas adsorption isotherms at 77 K were determined. Data from the latter analyses were coupled to those from quantitative phase analysis (QPA) by the Rietveld method on X-ray powder diffraction data (XRPD). Results indicate the complete conversion of CaO-oxide into portlandite hydroxide ($Ca[OH]_2$) can be quite easily reached during the first hydration step. Conversely, the conversion of Mg-oxide into the brucite hydroxide ($Mg[OH]_2$), which occurs after the second hydration step, is still incomplete. In conclusion, the target of a fully-hydrated dolomitic lime product is tricky to achieve without resorting to confined vapor-pressure conditions. However, the optimization of different hydration protocols allowed reaching very high BET specific surface area (52 $m^2/g$), improving technical parameters required for the above-mentioned industrial applications.

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# S18.

# Celebrating the International Year of Mineralogy: two centuries of progress and discoveries


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# Characterization of the blue-growth sectors in elbaite crystals from the San Piero in Campo pegmatites, Elba Island (Tyrrhenian Sea, Italy)

Altieri A.*[1], Pezzotta F.[2], Skogby H.[3], Hålenius U.[3] & Bosi F.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Museo di Storia Naturale, Milano. [3] Department of Geosciences, Swedish Museum of Natural History, Stockholm (Sweden).

*Corresponding author e-mail:* alessandra.altieri@uniroma1.it

*Keywords:* tourmaline, petrogenetic indicator, EMP and OAS analyses.

With their variety of pastel colors, tourmalines from Elba Island are easily recognizable and the main feature, which made them famous, is the dark-colored termination frequently occurring at the analogous pole. Such unusual termination includes multiple thin growth sectors of blackish, brownish, greenish, purplish, or even bluish colors. Tourmalines with blue hues are the rarest ones, making them always been sought after by mineral collectors from all over the world. However, this exceptional and unusual color variety has hindered studies concerning their crystal-chemical characteristics as well as the origin and chemical composition of fluids involved in their crystallization. Two tourmaline crystals with a blue-growth sector at the analogous pole, respectively from the San Silvestro and the Fucili pegmatites, located in the area of the San Piero in Campo village, have been described for the first time through electron microprobe (EMP) and optical absorption spectroscopy (OAS) analyses to define their crystal-chemical aspects and the causes of the color. Chemical data suggest that both tourmalines can be classified as elbaite, ideally $Na(Li_{1.5}Al_{1.5})Al_6Si_6O_{18}(BO_3)_3(OH)_3OH$, and that the upper part of each crystal is characterized by an increased amount in Fe (FeO up to ~1 wt.%). Spectra recorded on the blue-growth sector of both samples show two major absorption bands centered at ~13800 $cm^{-1}$ and ~9200 $cm^{-1}$ related to pure *d-d* transitions in [6]-coordinated $Fe^{2+}$, and this suggests that $Fe^{2+}$ is the main color-causing agent. The blue-growth sectors of tourmaline crystals recorded an increase in $Fe^{2+}$ availability in the crystallization environment that can be explained in terms of partial opening of the geochemical system at the scale of the cavity. Microstructural observations of the cavities in which tourmalines were collected reveal that these pockets are associated with a series of micro-fractures, which crosscut also some early formed biotite crystals hosted in the surrounding solid pegmatitic rock and partially altered in white mica along the fractures and at the rim. In our genetic model, late-stage fracturing phenomenon allowed cavity fluids to infiltrate the surrounding solid pegmatite and locally react with biotite, with a subsequent release of Fe to the fluids, and the formation of a new generation of white mica. Thus, tourmaline, being an excellent petrogenetic indicator, registered such event with a bluish slightly $Fe^{2+}$-rich growth sector.

# Dark colored Mn-rich terminations in a tourmaline crystal from Elba Island (Tyrrhenian Sea, Italy): memory of the late-stage opening of the geochemical system

Altieri A.*[1], Pezzotta F.[2], Skogby H.[3], Hålenius U.[3] & Bosi F.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Museo di Storia Naturale, Milano. [3] Department of Geosciences, Swedish Museum of Natural History (Stockholm).

*Corresponding author e-mail:* alessandra.altieri@uniroma1.it

*Keywords:* tourmaline, petrogenetic indicator, miarolitic cavity.

Elba tourmalines are renowned for the beauty and elegance of their pastel colors. Characteristic for these tourmalines are their dark-colored terminations at the analogous pole typically rich in Fe and/or Mn. Tourmaline crystals are excellent petrogenetic indicators due to the ability to register chemical-physical variations of the crystallization environment during their growth. Consequently, dark-colored terminations likely reflect processes that occurred in tourmaline-rich pegmatites during the latest stages of crystallization. However, the mechanisms that led to the availability of Fe and/or Mn in the crystallizing fluids are not yet completely clear. For this purpose, two tourmaline crystal fragments characterized by dark-colored terminations, found within a wide miarolitic cavity of the Rosina pegmatite, located in the area of the San Piero in Campo village, have been studied. Electron microprobe (EMP) and optical absorption spectroscopy (OAS) data suggest that these fragments were originally a whole crystal that underwent a breakage event followed by the simultaneous growth of Mn-rich dark terminations. We assume that a pocket rupture destabilized the crystallization environment within the pocket itself and was responsible for both the crystal to break and the chemical alteration of early-crystallized minerals, such as spessartine. This led to a release of Mn in the pegmatitic melt allowing the formation of the observed dark colored Mn-rich terminations. Thus, these tourmaline crystal fragments and their dark overgrowths represent the memory of the events that led to the mechanical pocket rupture and the subsequent compositional variation of the geochemical system. Additionally, a comparison of the two dark overgrowths formed on both of the broken surfaces, can provide further information on the different growth processes at the antilogous and the analogous poles.

# Tetrahedrite-group minerals: a new life for one of the oldest sulfosalt groups

Biagioni C.*[1] & Sejkora J.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Department of Mineralogy and Petrology, National Museum, Prague (Czech Republic).

*Corresponding author e-mail:* cristian.biagioni@unipi.it

*Keywords:* tetrahedrite group, nomenclature, new mineral species.

Tetrahedrite-group minerals are well-known since the 19th century and were among the first mineral species whose crystal structure was solved during the first decades of the 20th century. Tetrahedrite-group minerals are cubic, space group *I*-43*m*. Their structural formula can be written as $^{M(2)}A_6{}^{M(1)}(B_4C_2)^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$, where non-italicized letters A, B, C, D, Y, and Z represent different chemical constituents hosted at the *M*(2), *M*(1), *X*(3), S(1), and S(2) sites. Biagioni et al. (2020) recognized eleven different valid mineral species belonging to this group. Since then, 15 species have been described, resulting in a total of 26 tetrahedrite-group minerals (updated May 2022). The crystal-chemical variability of the tetrahedrite and tennantite series has been improved through the definition of seven new species, characterized by different C-constituents: Cd, Cu, Hg, Mn, and Ni. The description of tennantite-(Cu) suggested some classification issues regarding the role of minor Fe in Cu-rich tetrahedrite and tennantite series minerals (Biagioni et al., 2022a). An improvement in the understanding of the crystal-chemistry of Ag-rich tetrahedrite group minerals was achieved following the description of species characterized by 12 or 13 S atoms, highlighting the possible occurrence of $(Ag_6)^{4+}$ clusters in these minerals, and through the discovery of the As-isotype of rozhdestvenskayaite-(Zn), suggesting the possible existence of another series within the tetrahedrite group (Sejkora et al., 2021). New data have also been collected on Te-rich tetrahedrite-group minerals, with the definition of stibiogoldfieldite and its Se-analogue stibioústalečite (Biagioni et al., 2022b). Finally, Škácha et al. (2020) described pošepnýite, a tetrahedrite-group mineral having a non-end-member chemical formula and showing the flexibility of the tetrahedrite crystal structure to adapt to wide chemical changes.

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Sejkora J., Biagioni C., Vrtiška L. & Moëlo Y. (2021) - Zvěstovite-(Zn), $Ag_6(Ag_4Zn_2)As_4S_{13}$, a new tetrahedrite-group mineral from Zvěstov, Czech Republic. Mineral. Mag., 85, 716-724.

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# The Mn ore deposit of Scortico-Ravazzone: a Långban-type mineral assemblage from the Apuan Alps (northern Tuscany, Italy)

Biagioni C.*[1], D'Orazio M.[1] & Mauro D.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Museo di Storia Naturale, Università di Pisa.

*Corresponding author e-mail:* cristian.biagioni@unipi.it

*Keywords:* Mn ore deposits, mineral assemblage, Apuan Alps.

The Apuan Alps metamorphic complex (northern Apennines, Italy) is well-known for the occurrence of several small polymetallic ore deposits. Among them, there are some Mn ore deposits having a negligible economic value but showing some peculiar mineralogical features. The Scortico-Ravazzone Mn ore deposit, in the northern sector of the Apuan Alps, is one of these deposits. Ore bodies are conformably hosted in the upper part of the stratigraphic succession of the Apuane Unit, close to the contact with the Tuscan Nappe (e.g., Valduga, 1957). Few mineralogical data are available about this locality (Di Sabatino, 1967; Abrecht, 1989).

A new sampling of this deposit allowed the collection of new mineralogical data, identifying more than 30 different mineral species and two new phases, scorticoite and suenoite (Biagioni et al., 2019a,b). Scorticoite, ideally $Mn_6(Sb\square)(SiO_4)_2O_3(OH)_3$, occurs in association with friedelite, baryte, sarkinite, $Mn_2(AsO_4)(OH)$, and melanostibite, $Mn_2Fe^{3+}Sb^{5+}O_6$. In the same assemblage, radiated aggregates of wiserite, $(Mn^{2+},Mg)_{14}(B_2O_5)_4(OH)_8 \cdot (Si,Mg)(O,OH)_4Cl$, have been identified, as well as euhedral to anhedral brown vitreous crystals of two members of the manganhumite subgroup, i.e., sonolite, $Mn_9(SiO_4)_4(OH)_2$, and alleghanyite, $Mn_5(SiO_4)_2(OH)_2$. Rarely, the association between manganosite, MnO, and hausmannite, $Mn^{2+}Mn^{3+}{}_2O_4$, was observed. Another uncommon assemblage is represented by alabandite, MnS, associated with Mn-bearing yellow sphalerite, Mn-bearing galena, pyrite, and a still unidentified Ni-Fe sulfide. Amphibole supergroup minerals are frequent, as whitish to colorless fibers. In addition to the orthorhombic amphibole suenoite, $\square Mn_2Mg_5Si_8O_{22}(OH)_2$, single-crystal X-ray diffraction studies revealed the presence of monoclinic amphiboles; their crystal-chemical characterization is currently underway.

The mineral assemblages identified in the Scortico-Ravazzone deposit are unusual for the Mn ore deposits of the Apuan Alps and show some similarities with the mineralogy of the Långban-type deposits occurring in Sweden (e.g., Holtstam & Langhof, 2011).

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# Melanostibite, $Mn_2Fe^{3+}Sb^{5+}O_6$: centric or acentric?

Biagioni C.[1], Hålenius U.[2], Musetti S.*[1] & Bonaccorsi E.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Swedish Museum of Natural History, Stockholm (Sweden).

*Corresponding author e-mail:* silvia.musetti@phd.unipi.it

*Keywords:* melanostibite, oxides, crystal structure.

Melanostibite, ideally $Mn_2Fe^{3+}Sb^{5+}O_6$ ($Z$ = 3), was first reported by Igelström (1893) from the Sjö mine, Sweden; Moore (1968) solved its crystal structure. According to him, melanostibite is isotypic with ilmenite, space group $R$-3, having a disordered distribution of $Fe^{3+}$ and $Sb^{5+}$.

During the systematic study of a suite of specimens collected in the Scortico-Ravazzone Mn ore deposit (Apuan Alps, Tuscany, Italy), a few samples with red tabular pseudohexagonal crystals, up to 0.1 mm in size, were identified. Single-crystal X-ray diffraction allowed their identification as melanostibite. Unit-cell parameters are $a$ = 5.2351(3), $c$ = 14.3645(8) Å, $V$ = 340.93(4) Å$^3$. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1|$ = 0.589) suggested the possible acentric nature of the studied sample. The crystal structure was refined in the space group $R$3 down to $R_1$ = 0.0136 for 309 unique reflections with $F_o > 4\sigma(F_o)$ and 33 refined parameters. The crystal structure shows four octahedrally-coordinated cation sites and two anion sites. Among cation sites, two are occupied by $Mn^{2+}$ cations (average bond distances are 2.214 and 2.209 Å), whereas *Fe* and *Sb* sites have bond distances of 2.044 and 1.992 Å, respectively. These sites have Fe and Sb pure occupancies.

In order to check the actual symmetry of melanostibite from the type locality, a new investigation was performed on a sample from the Sjö mine. Unit-cell parameters are $a$ = 5.2357(2), $c$ = 14.3575(7) Å, $V$ = 340.84(3) Å$^3$. The $|E^2 - 1|$ value is 0.739, suggesting the possible acentric nature of the studied sample. The crystal structure refinement in the space group $R$3 converged to $R_1$ = 0.0116 for 640 unique reflections with $F_o > 4\sigma(F_o)$ and 34 refined parameters. Mn-sites have average bond distances of 2.210 and 2.214 Å, whereas *Fe* and *Sb* sites have bond distances of 2.026 and 2.005 Å, respectively. In the Swedish sample, the site occupancy at the *Fe* and *Sb* sites is ($Fe_{0.64}Sb_{0.36}$) and ($Sb_{0.63}Fe_{0.37}$), respectively, suggesting the coupled heterovalent substitution ${}^{Fe}Fe^{3+} + {}^{Sb}Sb^{5+} = {}^{Fe}Sb^{5+} + {}^{Sb}Fe^{3+}$.

Electron microprobe data collected on both samples agree with the formula $Mn_2Fe^{3+}Sb^{5+}O_6$ ($Z$ = 3).

The crystallographic study suggests that melanostibite is actually $R$3, with varying degrees of structural disorder at the *Fe* and *Sb* sites. The crystal chemical formula could be written as $Mn_2(Fe_{1-x}Sb_x)(Sb_{1-x}Fe_x)O_6$ ($Z$ = 3), with the disorder parameter $x$ = 0 and ~ 0.36 in the Italian and Swedish samples, respectively.

Igelström L.J. (1893) - Melanostibian, ein neues Mineral von der Manganerzgrube Sjögrufvan, Kirchspiel Grythyttan, Gouvernement Örebro, Schweden. Z. Krystallogr.Mineral., 21, 246-248.

Moore P.B. (1968) - Substitutions of the type ($Sb^{5+}_{0.5}Fe^{3+}_{0.5}$)–($Ti^{4+}$): the crystal structure of melanostibite. Am. Mineral., 53, 1104-1109.

# Apuanite and versiliaite revisited

Biagioni C.[1], Musetti S.*[1], Holtstam D.[2] & Zaccarini F.[3]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Department of Geosciences, Swedish Museum of Natural History (Sweden). [3] Department of Applied Geological Sciences and Geophysics, University of Leoben (Austria).

*Corresponding author e-mail:* silvia.musetti@phd.unipi.it

*Keywords:* apuanite, versiliaite, oxysulfides.

Apuanite, $(Fe^{2+}_4Fe^{3+}_8)(Fe^{3+}_8Sb^{3+}_{16})O_{48}S_4$, and versiliaite $(Fe^{2+}_4Fe^{3+}_4)(Fe^{3+}_4Sb^{3+}_{12})O_{32}S_2$, are two very rare oxysulfides currently known only from the Buca della Vena mine, Apuan Alps (Tuscany, Italy). Previous studies indicated non-stoichiometry of these compounds, mainly related to a S deficiency (Mellini et al., 1981). The reexamination of a suite of specimens sampled in different occurrences within the abandoned mining works, as well as of holotype material of both species, allowed to explain the origin of the non-stoichiometry.

Single-crystal X-ray diffraction studies were performed on selected samples of apuanite and versiliaite. Apuanite is tetragonal, space group $P4_2/mbc$, with $a$ = 8.3650(4), $c$ = 18.0021(9) Å, $V$ = 1265.70(14) Å$^3$; versiliaite is orthorhombic, space group *Pbam*, with $a$ = 8.4769(7), $b$ = 8.3286(6), $c$ = 11.9267(9) Å, $V$ = 842.03(11) Å$^3$. Electron microprobe data were obtained for all the studied samples. Chemical data for holotype material correspond to the chemical formulae $(Fe^{2+}_{4.06}Zn_{0.18})_{\Sigma 4.24}(Fe^{3+}_{15.58}V^{3+}_{0.58})_{\Sigma 16.16}(Sb^{3+}_{15.79}As^{3+}_{0.01})_{\Sigma 15.80}O_{48.14}(S_{3.61}Cl_{0.27})_{\Sigma 3.88}$ (Z = 1) and $(Fe^{2+}_{3.72}Zn_{0.71})_{\Sigma 4.43}(Fe^{3+}_{7.55}V^{3+}_{0.06})_{\Sigma 7.61}Sb^{3+}_{11.95}O_{32.11}(S_{1.41}Cl_{0.52})_{\Sigma 1.93}$ ($Z$ = 1) for apuanite and versiliaite, respectively. Apuanite and versiliaite show calculated $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ atomic ratios of 0.207 and 0.330, respectively; these values agree with Mössbauer data that point to 0.21(2) and 0.33(2), for these two different oxysulfides.

The observation of systematic deviations from stochiometry (Mellini et al., 1981) is not supported by current data; the anion deficit seems to be mainly related to the presence of undetected Cl. The occurrence of such an element in both apuanite and versiliaite (up to 0.26 and 0.69 Cl wt.%, respectively) is in keeping with the previous identification of chloro-sulfosalts (dadsonite, with ~ 0.40 Cl wt.%; Orlandi et al., 2010) and oxy-chloro-sulfosalts (pillaite and pellouxite, with 0.98 and 0.33 Cl wt%, respectively; Orlandi et al., 2001, 2004), suggesting high chlorinity of hydrothermal fluids.

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Orlandi P., Moëlo Y. & Biagioni C. (2010) - Lead-antimony sulfosalts from Tuscany (Italy). X. Dadsonite from the Buca della Vena mine and Bi-rich izoklakeite from the Seravezza marble quarries. Per. Mineral., 79, 113-121.

Orlandi P., Moëlo Y., Meerschaut A. & Palvadeau P. (2001) - Lead-antimony sulfosalts from Tuscany (Italy). III. Pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$, a new Pb-Sb oxy-chloro-sulfosalt, from Buca della Vena mine. Eur. J. Mineral., 13, 605-610.

Orlandi P., Moëlo Y., Meerschaut A., Palvadeau P. & Leone P. (2004) - Lead-antimony sulfosalts from Tuscany (Italy). VI. Pellouxite, $\sim(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$, a new oxy-chloro-sulfosalt from Buca della Vena mine, Apuan Alps. Eur. J. Mineral., 16, 839-844.

# ID15b, crystallography and Earth sciences

Comboni D.*, Hanfland M. & Garbarino G.

ESRF, Grenoble (France).

*Corresponding author e-mail:* davide.comboni@gmail.com

*Keywords:* crystallography, large-scale facilities, high-pressure.

In the last decades, experiments at non-ambient conditions have greatly benefited from the improvement of home-lab instruments and large-scale facilities allowing to investigate matter at extreme PT conditions (megapascal and temperatures ranging from few to thousands kelvin). Experiments performed at non-ambient conditions devoted to unveil the structure, properties and the deformation mechanisms of minerals and synthetic compounds, improve our knowledge regarding the evolution of planets and allow to tailor future new cutting-edge materials. In this context, Earth sciences have (and still can) greatly benefited from a number of dedicated beamlines, such as ID15b (ESRF), devoted to the determination of structural properties of minerals at non-ambient PT conditions using angle-dispersive-diffraction and diamond anvil cells. ID15b is capable to provide high-quality data, thanks to a bright and focalized X-ray beam ($\lambda \sim 0.410$ Å) that can be made as small as 2x3 $\mu m^2$ and an EIGER2 X 9M CdTe (340x370 mm) flat panel detector. The extremely high brightness of the EBS-ESRF source, the first fourth-generation high-energy synchrotron in the world, allows to perform a completed single crystal data collection in few minutes. In addition to conventional membrane-driven diamond anvil cells, the beamline is equipped with a He-cooled cryostat and external resistive heating devices which allow to perform high-pressure experiments at low temperatures (down to 10K) and high temperatures (up to 600K). An ex-situ Nd-YAG laser system can anneal samples inside the diamond anvil cell at high-temperature, further increasing the range of the investigable T-induced effects allowing to investigate minerals suggested at shallow-crust to mantle-like conditions. At ID15b, Earth-sciences researchers can find a cooperating and competent staff willing to make fruitful suggestion and help during experiments. Allocations of beam time is open to every scientist *via* submission of standard or long-term Research Proposal. This poster is meant to be a showcase of the ID15b beamline, featuring what it can provide for all the Earth-science researchers.

# Phase stability of hydrated borates at high pressure

Comboni D.*[1], Battiston T.[2], Pagliaro F.[2], Lotti P.[2], Hanfland M.[1] & Gatta G.D.[2]

[1] ESRF, Grenoble (France). [2] Dipartimento di Scienze della Terra «A. Desio», Università di Milano.

*Corresponding author e-mail:* davide.comboni@gmail.com

*Keywords:* borates, high-pressure, X-ray crystallography.

Hydrated borates are a class of minerals made by clusters or chains of B$\varphi_x$ groups ($\varphi$ represents an oxygen, an $H_2O$ molecule or an $OH^-$) organized either in tetrahedra or in planar trigonal groups. Hydrated borates are believed to be a cheaper alternative to $B_4C$ for radiation-shielding concretes (Okuno et al., 2005), due to the large cross section (~3840 barns) for thermal neutrons of the isotope $^{10}B$, which represents about 20% of the boron in nature. A comprehensive characterization of the crystal-chemistry, elastic properties, stability and structural behavior of natural borates at varying T and *P* conditions is advisable for modelling and understanding their role when utilized as aggregates in radiation-shielding concretes (Torrenti et al., 2010), in which the components are subject to pressure (by static compression) and temperature (by irradiation). Interestingly, all hydrated borates studied so far at high-pressure display one (or more) phase transition, and the pressure at which the phase transitions occur seems to be correlated to the $H_2O$ content of the minerals (e.g., Comboni et al., 2020, 2021). During the phase transitions, the most dramatic structural change is the increase of the coordination number of part of the $^{III}B$ to $^{IV}B$, by the interaction between the $^{III}B$ and one $H_2O$ molecule or $OH^-$ group, underlying the importance of the hydrogen bond network in the stability of the crystalline structure.

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# A multi-methodological study of syntactic intergrowths and polysomatism in Ca-REE fluorcarbonate minerals from Mount Malosa (Malawi)

Conconi R.*[1], Fumagalli P.[2], Lucotti A.[3] & Capitani G.C.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Dipartimento di Chimica, Materiali e Ingegneria Chimica «G. Natta», Politecnico di Milano.

*Corresponding author e-mail:* r.conconi@campus.unimib.it

*Keywords:* syntactic intergrowths, Ca-REE fluorcarbonate minerals, micro-Raman spectroscopy.

Ca-REE fluorcarbonates play a crucial role for at least two (apparently) distant reasons, one as critical raw materials closely linked to the industrial progress, to the development of modern technologies and environment-friendly green technologies. The other is tied to fundamental research, since they form a polysomatic series and commonly occur as polycrystals characterized by microscale syntactic (crystallographically oriented) intergrowths of different polysomes/polytypes, often with stacking faults at the nanoscale. Their identification and study are therefore not straightforward. We evaluated the potentialities of non-destructive techniques, such as Electron BackScattered Diffraction (EBSD) and Raman spectroscopy, in the characterization of Ca-REE fluorcarbonates at a microscopic scale in order to provide a "road map" for further investigation with destructive techniques, such as Transmission Electron Microscopy (TEM). We investigated well-characterized Ca-REE fluorcarbonates from Mount Malosa (Malawi) (Guastoni et al., 2009; Capitani, 2019), which belong to the bastnäsite-synchysite series.

EBSD was effective to establish the sample orientation, to setup the oriented cuts and to ascertain the effective syntactic relationship among all the detected Ca-REE fluorcarbonate phases, but failed to distinguish among different polysomes. The latter can be easily understood taking into account that electron diffraction (alike X-ray diffraction) is dominated by heavy atoms, and that the Ca-REE fluorcarbonates studied, although monoclinic, have an identical hexagonal stacking of heavy atoms (Ca and REE) as bastnäsite, the only effective hexagonal term.

Micro-Raman spectroscopy, performed on samples with different orientations and characterized by SEM-EDS, allows the distinction of polysomes based on the differences in intensity and position of the symmetric stretching vibration ($v_1$) of the carbonate group ($CO_3^{2-}$), in the region around 1080-1099 $cm^{-1}$. However, as evidenced by TEM-EDS, what appears as a homogeneous polysome in BSE images, actually may be a disordered intergrowth of compositional faults with a bulk composition matching only by accident that of a real polysome. Actually, there are two different types of $CO_3$ layers in the Ca-REE fluorcarbonates structure: those in contact with two CeF-layers (or *e*-layers), and those in contact with one CeF- and one Ca-layer (or *g*-layers; Donnay & Donnay, 1953). We believed that the Raman signal is sensitive to different abundances of *e*- and *g*-layers in the structure, whose proportions vary with composition, and therefore also with the polysome, but not to the order of the layers within the analysed volume, making the distinction by Raman spectroscopy of ordered and disordered intergrowths with similar composition unfeasible.

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# The thermal stability of riebeckite under different oxidation conditions

Della Ventura G.*[1-2-3], Redhammer G.J.[4], Ventruti G.[5], Oberti R.[6], Radica F.[7], Bernardini S.[1-8] & Mihailova B.[8]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INFN, Laboratori Nazionali di Frascati, Frascati (RM). [3] INGV, Roma. [4] Department of Chemistry and Physics of Materials, University of Salzburg (Austria). [5] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [6] Istituto di Geoscienze e Georisorse, CNR, Pavia. [7] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [8] Fachbereich Geowissenschaften, Universität Hamburg (Germany).

*Corresponding author e-mail:* giancarlo.dellaventura@uniroma3.it

*Keywords:* riebeckite, high temperature behavior, X-ray diffraction, FTIR and Mössbauer spectroscopies.

Riebeckite is a relatively common Fe-rich member of the sodic amphiboles subgroup, typically found in acid igneous rocks and in high-grade metamorphic rocks. The fibrous variety is known as the asbestos crocidolite. Here we studied the stability of a near end-member riebeckite from Mt. Malosa (Malawi) at high temperature under different oxidation conditions. The run products obtained after annealing in air vs. in vacuum were studied by Mössbauer spectroscopy, X-ray diffraction and vibrational (FTIR, Raman) spectroscopies. The results show that riebeckite follows two distinct paths depending on the external environment. Under oxidizing conditions, it is stable in the hydrous form up to relatively low temperatures (400-450°C), then it undergoes a rapid (within ~50°C) dehydrogenation forming oxo-riebeckite which is stable up to ~900°C. The final break-down products of the oxo-amphibole include aegirine + cristobalite + hematite. Under vacuum conditions, no Fe oxidation is observed; in the 550-800°C, it decomposes to aegirine + fayalite + cristobalite + $H_2O$.

External oxygen is required for the release of water into the surrounding system, being a pre-requisite for the Fe-amphiboles to be a carrier of $H_2O$ in the lower crust and upper mantle. One important implication of our results is that characterization of the overall oxidation state of iron does not necessarily provide the redox conditions of the environment of formation, because a crystal-chemical rearrangement under reducing conditions allows riebeckite to maintain its $Fe^{3+}/Fe^{2+}$ composition up to higher temperatures. Another important observation is that riebeckite, irrespective of the external oxidation conditions, develops electrical conductivity for increasing temperature, thus being one of the main candidates for the geophysical anomalies observed at convergent plate margins.

# Crystal structure of minerals: from Haüy's hypothesis to Braggs' experimental evidence

Ferraris G.*

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* giovanni.ferraris@unito.it

*Keywords:* crystal structure, integrant molecules, simple molecules.

Molecules and atoms were not yet clear and distinct concepts, when in 1766 P. Macquer defined the *integrant molecule* as a submicroscopic particle consisting of *simple molecules* that, as a matter of fact, correspond to the modern atoms. In his *Essai d'une théorie sur la structure des crystaux* (1784). R.J. Haüy adopted the integrant molecule as polyhedral building block of his general and innovative periodic model of the crystal structure able to explain symmetry and morphology of the mineral crystals. The idea of a polyhedron as basic building block was suggested by the cleavage rhombohedron of calcite that can be reduced to microscopic dimensions by iterated cleavages. Haüy did not conceive empty spaces in the matter; thus, he represented by space-filling polyhedra both integrant and simple molecules. He was conscious of the limits connected with a polyhedral representation of the molecules, but – he wrote – the science did not yet allow a more realistic representation. Finally, Haüy (*Traité de cristallographie*, 1822) defended his model and emphasized the role of the simple molecules in differentiating the chemical compositions of those mineral species that are based on the same type of integrant molecule (parallelepiped, tetrahedron, octahedron, hexagonal prisms, two types of dodecahedra).

Efforts to overtake drawbacks of Haüy's model, such as inability to explain hemihedry, polymorphism and isomorphism, led to discover Bravais lattices, point and space groups. W. H. Wollaston (1813) proposed mixed compact packages of spheres and ellipsoids to explain the relations between structure, morphology and chemical-physical properties of the mineral crystals, including hemihedry. Following pioneer results published by N. Leblanc and F. S. Beudant, around 1820 E. Mitscherlich showed that the crystalline chemical compounds with similar chemical formula which display the same morphology can co-crystallize; he hypothesized that chemical elements can substitute each other to form solid solutions (isomorphism). The atomistic interpretation of isomorphism was soon successfully tested by Mitscherlich and his master J. J. Berzelius by successfully determining (1828) the atomic weights via a procedure involving isomorphous compounds.

L. Pasteur (1848) showed that the racemes of tartrates are not solid solutions, but they are instead fifty-fifty mechanical mixtures of optically active left- and right-handed crystals. Following an earlier hypothesis by A. Fresnel (1824), Pasteur suggested that the optical activity of a crystalline compound is related to the helical arrangement of atoms / molecules in its structure. D.I. Mendeleev (1869) fruitfully exploited the atomistic theory of isomorphism to build his periodic table of elements. In 1883 W. Barlow started to publish theoretical models of crystal structures that one year after the discovery of the X-rays diffraction by M. von Laue in 1912 were experimentally confirmed by W.H. and W.L. Bragg. A new era for mineralogy was open!

# Characterisation of mineralogical specimens from the abandoned Fe-Mn Montaldo Mine, Corsaglia Valley, Cuneo

Giai M.*, Ciriotti M.E. & Costa E.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* matteo.giai@live.it

*Keywords:* mineralogy, Cuneo province, REE minerals, Fe-Mn ore deposit.

The study focused on the mineralogical analyses of samples deriving from the already known mining landfills, located in Frazione Oberti, Montaldo Mine (Cuneo), collected in five different sites located both on the left and on the right sides of the Corsaglia River (Kolitsch et al., 2011). The samples were subjected to several analyses: SEM-EDS, μ-Raman spectroscopy, and optical microscopy of thin sections, which allowed to determine a quite complex mineralogy: in a mineralized mass of braunite, Fe-Mn-oxides and -silicates (cryptomelane/hollandite series, hematite, muscovite), lesser quantities of other mineral species were detected, like: berzeliite, tilasite, montmorillonite, as well as traces of Rare Earth minerals (monazite, gasparite, chernovite, wakefieldite), other manganese species (ranciéite, ramsdellite romanechite) and accessories minerals (zircon, rutile, arsenogoyazite). Also considering the different data obtained by previous studies, it was possible to suppose that the Montaldo reservoir was affected by different metamorphic/hydrothermal events, which followed the deposition of the "Calcari di Val Tanarello" and its quartzarenitic/conglomeratic intecalations. The high concentration of REE and accessories minerals (mainly arsenogoyazite, berzeliite/manganberzeliite, svabite and tilasite) in the montmorillonite, observed also by Kolitsch et al. (2011), could be explained by the cations exchange capacity of this clay, which in presence of certain pH adsorbs more easily incompatible elements on its surface. This study allowed to also classify numerous species in reference of the new rules dictated by IMA, such as As-rich fluorapatite and muscovite-celadonite series phases (Cabella et al., 1992; 1999), and to recognize some species not yet identified in the Montaldo mine: gasparite-(Ce), monazite-(Ce), ramsdellite, ranciéite and wakefieldite-(Ce), where the latter would also be the second discovery in Italy of this species (Tumiati et al., 2020).

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# Chemical and spectroscopic characterization of turquoise samples showing different colour

Landi A.I.*[1], Lepore G.O.[1], Di Benedetto F.[2], Chelazzi L.[3], Della Ventura G.[4], Carretti E.[5] & Bonazzi P.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [3] Centro di Cristallografia Strutturale, Università di Firenze. [4] Dipartimento di Scienze, Università di Roma Tre. [5] Dipartimento di Chimica "Ugo Shiff", Università di Firenze.

*Corresponding author e-mail:* annairene.landi@unifi.it

*Keywords:* turquoise, chemical composition, colour.

Turquoise is the most known species of a mineral group which includes six isostructural end-members with general formula $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_8 \bullet 4H_2O$, $0 \leq x \leq 2$, with A representing a bivalent cation ($Cu^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ca^{2+}$) and B a trivalent cation ($Al^{3+}$, $Fe^{3+}$) (Foord & Taggart, 1998), both in octahedral coordination (Cid-Dresdner, 1965). Thirteen turquoise samples presenting different colours were studied by means of a multi analytical approach: scanning electron microscope (SEM), electron microprobe (EPMA), X-ray powder diffraction (XRPD), thermogravimetric analysis (TGA), diffuse reflectance spectroscopy in the visible light (DRS), electron paramagnetic resonance (EPR), X-ray absorption spectroscopy (XAS) and infrared spectroscopy (IR). The samples belong to the mineralogical section of the Natural History Museum of Università degli Studi di Firenze: one comes from Chile, the provenance of the other twelve sample is unknown. They were categorized into two groups according to their hue, blue or green. Only four of the studied samples, three blue and one green, turned out to be unaltered, showing chemical composition, cell parameters and interatomic distances near to ideal turquoise. Partial vacancy at the A site and a moderate replacement of $Fe^{3+}$ for Al at M3 site, however, indicate solid solution with minor components of planerite and chalcosiderite, respectively. Copper amounts are similar in the three blue samples, the green one having a higher iron content. XAS and EPR analyses indicate that iron is mainly present as $Fe^{3+}$. The basic colour of turquoise is light blue, depending on the octahedrally coordinated $Cu^{2+}$, but, with $Fe^{3+}$ replacing Al, the colour turns to green (Zhang et al., 1984; Foord & Taggart, 1998): the correlation between chemical composition and colour is confirmed in the studied samples. Water contents measured with TGA are in good agreement with those calculated on the basis of the chemical formulae derived from EPMA data. The other specimens are turquoises showing signs of different alteration degree and containing impurity phases which include quartz, amorphous silica (opal?), kaolinite and minor illite. Additional peaks in the turquoise IR spectra, assigned to the presence of kaolinite, are observed in the most altered sample. The correlation between chemical composition and colour is respected also in these samples, although hues are rather tenuous due to the presence of the impurities, as previously noted (Abdu et al., 2011).

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Foord E.E. & Taggart J.E. (1998) - A reexamination of the turquoise group: the mineral aheylite, planerite (redefined), turquoise and coeruleolactite. Mineral. Mag., 62, 93-111.

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# Parahibbingite from Muonionalusta, the first occurrence of β-$Fe_2(OH)_3Cl$ as terrestrial weathering product of an iron meteorite: Structural and spectroscopic characterization

Margheri S.*[1], Holtstam D.[2], Bonazzi P.[1] & Bindi L.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Department of Geosciences, Swedish Museum of Natural History, Stockholm (Sweden).

*Corresponding author e-mail:* simone.margheri@unifi.it

*Keywords:* parahibbingite, Muonionalusta, crystal structure.

Parahibbingite is a recently approved mineral discovered in a drill core from the Karee mine in the Bushveld complex, South Africa (Koděra et al., 2022). It corresponds to the β-form of ferrous-hydroxychloride [β-$Fe_2(OH)_3Cl$] (Oswald & Feitknecht, 1964) and it was often reported as a Cl-rich corrosion product of iron artefacts and it was the subject of numerous studies aimed at the conservation of archaeological finds. Natural and anthropogenic specimens of β-$Fe_2(OH)_3Cl$ typically occur as pulverulent masses included in thin corrosion layers at the metal/oxide interface (Réguer et al., 2015) or as microcrystalline aggregates and reaction rims in pyroxenites (Koděra et al., 2022).

This study reports the first occurrence of well-developed crystals (up to 1 mm in size and covered by a thin coat of akaganéite) of parahibbingite as a terrestrial weathering product of the Muonionalusta iron meteorite. The mineral was found in a small cavity within a granitic fragment that was in direct contact with the alteration crust of a 22 Kg specimen of the Muonionalusta meteorite collected in the Kitkiöjärvi area, Pajala district, Sweden.

Parahibbingite was firstly identified by means of Raman spectroscopy. Then, selected fragments were studied by single-crystal X-ray diffraction. The crystal structure [$a$ = 6.9362(4), $c$ = 14.673(1) Å, V = 611.35(7) Å$^3$, Z = 6; space group $R$-3$m$; R1 = 0.0331] was found to be identical to that observed for some members of the atacamite group (i.e., gillardite, herbertsmithite and tondiite; Malcherek et al., 2014, and reference therein).

In detail, the structure is made up of a network of $Fe^{2+}$ ions alternatively arranged in triangular and Kagomé planes, stacked along the **c** axis. Iron enters two distinct octahedral sites: Fe1, which is coordinated by six oxygen atoms, and Fe2, which is coordinated by four oxygen atoms and two chlorine atoms. Each chlorine atom acts as acceptor of three H-bonds from oxygen atoms and provide a further linking between Kagomé and triangular planes.

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Réguer S., Mirambet F., Rémazeilles C., Vantelona D., Kergourlaya F., Neff D. & Dillmann P. (2015) - Iron corrosion in archaeological context: Structural refinement of the ferrous hydroxychloride β-$Fe_2(OH)_3Cl$. Corros. Sci., 100, 589-598.

# Piemontite from the Pollino Massif (southern Italy): crystal-chemistry and geochemical inferences

Mesto E.*[1], Mongelli G.[2], Sinisi R.[3], Schingaro E.[1] & Lacalamita M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Scienze, Università della Basilicata, Potenza. [3] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ).

*Corresponding author e-mail:* ernesto.mesto@uniba.it

*Keywords:* piemontite, Mn ores, southern Apennine.

The crystal chemistry of piemontite, ideally $Ca_2Al_2Mn^{3+}(Si_2O_7)(SiO_4)O(OH)$, from the Mn mineralization of the Pollino Massif (southern Apennine) has been investigated by combining Electron Microprobe Analysis (EPMA) and Single Crystal X-Ray Diffraction (SCXRD). Samples collected for the presented study were taken near Mormanno village, where the main entrance of an abandoned underground mine is present. The mineralogical association of analysed samples consists of opaque minerals (Mn-bearing silicates and oxides/hydroxides) + quartz + piemontite. Piemontite typically occurs as millimetric prismatic hypidioblasts and aggregates of minute crystals.

EPM analyses revealed a great variability of the CaO/SrO ratio in the studied samples (CaO/SrO ranging from 1.64 to 9.17) but also a chemical zonation of piemontite (1.64 ≤ CaO/SrO ≤ 4.39). Overall, the REE's concentration was found below the detection limits excepting for $Eu_2O_3$ (0.1 wt.%). Unit-cell parameters of the studied piemontite single crystals are $a \sim 8.87$, $b \sim 5.68$, $10.18 \leq c \leq 10.20$ Å, $\beta \sim 115.3°$, $463.97 \leq V \leq 465.61$ Å$^3$. Structure refinements, performed in $P2_1/m$ space group, converged to $R = 3.7\%$ and provided a preferential partitioning of Mn for the *M3* site and a mixed Ca-Sr occupancy at the *A2* site. The studied crystals show similar $(Mn^{3+}+Fe^{3+})_{M1+M3}$ content which is directly correlated to the value of the *b* axis and a different Sr-enrichment (~26 *vs* 12% Sr in *A2*) affecting the values of c·sinβ parameter, unit cell volume and <*A2*-O> distance. The Sr concentration in the *A2* site also strongly affects the elongation of the cavity.

The definition of the crystal chemical features of piemontite may contribute to highlight the role of this mineral as sources of trace elements, such as Sr and Pb, transition metals and REE. Unlike piemontite from similar geological contexts (Frei et al., 2004), the studied crystals have revealed very poor contents of trace metals as much as REEs. However, high amounts of rare earth elements and other trace elements were detected in the studied bulk samples. Previous authors (i.e., Maynard, 2010) have highlighted that, in marine as well as in continental environment, Mn oxides and hydroxides can host significant amounts of trace and REE elements because of their strong and fast sorption and adsorption effect on dissolved elements (Sinisi et al., 2018). This suggests that, also in the studied case, mostly Mn oxides and hydroxides controlled the chemistry of the mineralization whereas the metal uptake process involved piemontite only partially.

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# The new CISUP facilities for Earth Science at the University of Pisa

Mugnaioli E.*[1-2], Folco L.[1-2], Masotta M.[1-2], Biagioni C.[1-2], Paoli G.[1] & Capaccioli S.[1-3]

[1] Centro per l'integrazione della strumentazione scientifica, Università di Pisa. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Dipartimento di Fisica, Università di Pisa.

*Corresponding author e-mail:* enrico.mugnaioli@unipi.it

*Keywords:* crystallography, X-ray diffraction, electron microscopy, electron diffraction, laser ablation.

Innovative research in Earth sciences, particularly in the fields of mineralogy and petrography, requires the combination of more analytical techniques capable of high-accuracy and/or high spatial resolution. Still, it is rare that a single institution has all the necessary equipment and expertise for a thorough characterization of geological samples. This inevitably hinders the possibility to achieve cutting-edge results in a relatively short time, limiting the national/international attractivity of the facilities and the competitiveness with foreigner research groups.

In 2018, the University of Pisa established the Center for Instrument Sharing (CISUP), an interdepartmental body devoted to the creation of a network of existing facilities and to the pondered acquisition of new large analytical instrumentation (https://cisup.unipi.it/). Through CISUP, the Earth science researchers of the University of Pisa can presently benefit of:

- a high-resolution field emission-scanning electron microscope (FE-SEM) operating under high, low and extended low vacuum modes with automated software for large area mapping;
- a 193 nm ArF excimer laser ablation system coupled to an inductively coupled plasma-mass spectrometer (LA-ICP-MS);
- a high-resolution field emission gun transmission electron microscope (HR-FEG-TEM) equipped with a large-area SDD EDS detector and state-of-the-art electron diffraction systems;
- a single-crystal X-ray diffractometer (SC-XRD), with double source (Mo and Cu *K*α radiation) and equipped with a detector having the largest active area so far available for lab-instruments.

Moreover, a focused-ion beam (FIB) SEM-FEG for high resolution imaging, EDS large area mapping system, 3*D* tomography, TEM and APT sample preparation and will be also installed in the next few months.

We believe that the recently installed and to-be-installed CISUP instrumentation will compose an analytical facility of national and international interest, able to valorize the consolidated tradition of the University of Pisa in the view of modern scientific challenges. This new facility will also favor the establishment of national and international scientific collaborations, possibly supporting the whole compartment of the Italian and European Earth sciences.

# Systematics of *M*:O = 1:2 oxide minerals, and adjustments needed in some of their chemical formulae

Pasero M.*[1] & Chukanov N.V.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka (Russia).

*Corresponding author e-mail:* marco.pasero@unipi.it

*Keywords:* oxide minerals, ixiolite, columbite.

More than a hundred minerals, i.e., some 2% of the known mineral species, belong to the subdivision 4.D. (Metal:Oxygen = 1:2 and similar) within the Class 4. (Oxides) of the Strunz-Nickel classification of minerals. In these minerals the metal cation may assume 6- or 8-fold coordination; in the following those generic cations are referred to as *M* or *A*, respectively. Herewith we will concentrate on oxide minerals mainly based on zig-zag chains of edge-sharing octahedra [$MO_6$] or augmented octahedra [$AO_8$].

Assuming ixiolite as the aristotype, with the smallest unit cell volume and basic vectors $\mathbf{a}_0$ 4.8, $\mathbf{b}_0$ 5.7, $\mathbf{c}_0$ 5.1 Å, five topologically-related structure types can be distinguished:

- ixiolite type, $MO_2$, *Pbcn*, with $a = \mathbf{a}_0$, $b = \mathbf{b}_0$, $c = \mathbf{c}_0$ (4 known species);
- wolframite type, $M1M2O_2$, *P*2/*c*, with $a = \mathbf{a}_0$, $b = \mathbf{b}_0$, $c = \mathbf{c}_0$ (8 known species);
- samarskite type, $AM1M2_2O_8$, *P*2/*c*, with $a = 2\mathbf{a}_0$, $b = \mathbf{b}_0$, $c = \mathbf{c}_0$ (6 known species);
- columbite type, $M1M2_2O_6$, *Pbcn*, with $a = 3\mathbf{a}_0$, $b = \mathbf{b}_0$, $c = \mathbf{c}_0$ (11 known species);
- wodginite type, $M1M2M3_2O_8$, *C*2/*c*, with $a = 2\mathbf{a}_0$, $b = 2\mathbf{b}_0$, $c = \mathbf{c}_0$ (5 known species).

Six additional minerals with unknown structure possibily belong to either of the above groups.

As a general rule, each mineral should be defined with an ideal, end-member chemical formula. Among these oxides there are some oddities which need to be fixed up.

Ixiolite is currently assigned the formula $(Ta,Mn,Nb)O_2$, which does not clearly shows which are the species-forming constituents. In ixiolite the dominant cation has charge 5+, therefore given the general stoichiometry $MO_2$ any ideal formula must contain a cation with lower charge or vacancy, based on both the dominant-valency rule and the site total charge approach (Hatert & Burke, 2008; Bosi et al., 2019). Accordingly, since at the type locality (Skogsböle, Finland) it is Ta > Nb, and $Mn^{2+}$ is the dominant charge-compensating cation, the ideal formula of ixiolite should be modified to $(Ta_{2/3}Mn^{2+}{}_{1/3})O_2$. It is worth noting that analyses are known of ixiolite with either $Fe^{2+}$ or $Sc^{3+}$ as DCCC (e.g., Wise et al., 1998), therefore those specimens could apply for distinct mineral species.

The currently IMA-accepted formulae for polycrase-(Y) and euxenite-(Y) are $Y(Ti,Nb)_2(O,OH)_6$. and $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$, respectively. Based on the site total charge approach the formula must match the stoichiometry $M^{3+}(M^{5+}M^{4+})O_6$. Hence the two minerals would have the same ideal formula, namely $Y(NbTi)O_6$. As euxenite is older than polycrase (1840 vs. 1844), polycrase-(Y) should be discredited.

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# Vanadates and associated minerals from the Vesuvian Collection of the Royal Mineralogical Museum of Naples (Italy)

Pellino A.[1], Balassone G.*[1-2], Abad I.[3], Altomare A.[4], Bellatreccia F.[5], Cappelletti C.[1-6], Mondillo N.[1-7], Herrington R.J.[7], Isè C.[1], Petti C.[6] & Rumsey M.S.[7]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] INGV, Osservatorio Vesuviano, Napoli. [3] Departamento de Geologia y Centro de Estudios Avanzados en Ciencias de la Tierra, Energía y Medio Ambiente, Universidad de Jaén (Spagna). [4] Istituto di Cristallografia, CNR, Bari. [5] Dipartimento di Scienze, Università di Roma Tre. [6] Real Museo Mineralogico, Università di Napoli «Federico II». [7] Earth Sciences Department, Natural History Museum, London (UK).

*Corresponding author e-mail:* annamaria.pellino@unina.it

*Keywords:* vanadates, Somma-Vesuvius volcano, sublimates.

In the Royal Mineralogical Museum of the University of Naples Federico II, the Vesuvian Collection contains a group of samples with deep yellow to green-yellow sublimate encrustations on the surface of lavas related to the recent activity of Vesuvius, from 1631 onward. These samples were collected by Arcangelo Scacchi, director of the Museum and renowned mineralogist, who suggested the presence of a new element, *vesbium* (from the old name of Vesuvius) and called *vesbine* the main mineral of these crusts. Further studies suggested that these microcrystalline crusts could be composed of mixed vanadates, corresponding to volborthite, mottramite, descloizite and vesignieite. Recent investigations carried out by Balassone et al. (2019) demonstrated that the *vesbine* samples correspond to a very complex mixture of variable amounts of vanadates (Cu-bearing and Cu-free), like prevailing mottramite, volborthite and vanadinite together with wulfenite and chrysocolla. The present study shows the results of a preliminary study (SEM-EDS, WDS, XRPD, FTIR, Raman and TEM analyses) on a new set of *vesbine* samples from the Vesuvian Collection. Investigations confirm the complexity of these vanadate-rich assemblages and add new data. Cu, Pb, and Cu-Pb vanadates, as volborthite, vanadinite and mottramite, are the prevailing mineral species. These phases are always associated to Cu-hydroxyhalides, mostly atacamite (also Mn- and Pb-bearing) but also botallackite, clinoatacamite and paratacamite. In these assemblages, variable amount of wulfenite-stolzite phases and Cu-carbonates azurite and malachite have been observed together with minor amount of Cu oxides (cuprite and tenorite) and cerussite. In several sample, some silicates have been found, often mixed with vanadates, mainly consisting of chrysocolla, while one sample shows another Cu-silicates tentatively attributed to dioptase. Even though this research is ongoing, preliminary data show that these mineral assemblages could be deposited as volcanic sublimates in a quite wide temperature range.

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# Zoisite-(Pb), a new orthorhombic epidote-related mineral from Jakobsberg, Sweden, and its relationships with hancockite

Perchiazzi N.*[1], Mauro D.[2], Vignola P.[3] & Zaccarini F.[4]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Museo di Storia Naturale, Università di Pisa. [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Milano. [4] Department of Applied Geological Sciences and Geophysics, University of Leoben (Austria).

*Corresponding author e-mail:* natale.perchiazzi@unipi.it

*Keywords:* zoisite-(Pb), epidote group minerals, hancockite.

Zoisite-(Pb), ideally $CaPbAl_3(SiO_4)(Si_2O_7)O(OH)$, was recently discovered in a sample from the Jakobsberg manganese-iron oxide deposit, Värmland, Sweden. Zoisite-(Pb) occurs as pale pink subhedral prisms, associated with calcite, celsian, diopside, grossular, hancockite, "hyalophane", native lead, phlogopite and vesuvianite. Associated feldspars show one of the highest Pb content (~7-8 wt.%) found in nature.

Zoisite-(Pb) and coexisting hancockite, ideally $CaPbAl_2Fe(SiO_4)(Si_2O_7)O(OH)$, are characterized by distinctly different $Al/(Al+Fe_{tot})$ atomic ratios, i.e., ~0.97 and ~0.77, respectively.

Structural features of zoisite and of the epidote group phases were widely investigated (e.g., Franz & Liebscher, 2004; Armbruster et al., 2006). Zoisite-(Pb) is isostructural with zoisite: M12 regular octahedra form octahedral chains, running along b, with the more distorted and larger M3 octahedra, hosting the $Fe^{3+}$ content, linked on both sides of the chains.

M12 octahedral chains are connected through $Si_2O_7$ groups and $SiO_4$ groups, forming the two distinct A1 and A2 cavities. The A1 cavity has a smaller volume, usually hosting Ca only, whereas A2 has a bigger size, more apt to host cations with a ionic radius larger than $Ca^{2+}$, i.e., $Sr^{2+}$ and $Pb^{2+}$.

The presence of dominant $Pb^{2+}$ in the A2 coordination polyhedron reflects in an asymmetrical spatial distribution of its coordinating oxygens, due to the presence of a stereochemically active "lone pair" of $Pb^{2+}$. The effects of the incorporation of Pb on the crystal structure of zoisite-(Pb), hancockite and related synthetic and natural phases are described and discussed. A full chemical and Raman characterization of the Pb bearing epidote hancockite is reported, together with an improved crystal structural model. According to Armbruster et al. (2006) and Mills et al. (2009), zoisite-(Pb), together with zoisite, cannot be included in the epidote supergroup, which includes phases with monoclinic symmetry only. It seems therefore proper to assess the definition of the new zoisite group, to be properly submitted to the IMA-CNMNC. Possible new phases can be guessed for this group, such the Sr analogue of zoisite-(Pb), with ideal chemical formula $CaSrAl_3(SiO_4)(Si_2O_7)O(OH)$.

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# When mineral sciences meet artificial intelligence: an outstanding example about how Mineralogy can continue to surprise us and have a strong impact on other disciplines

Pereti C.[1-2], Bernot K.[3-4], Bindi L.*[5], Fanelli D.[1-2], Guizouarn T.[3], Laufek A.[6], Sessoli R.[7] & Vymazalova A.[6]

[1] Dipartimento di Fisica e Astronomia e Centro Interdipartimentale per lo Studio delle Dinamiche Complesse, Università di Firenze. [2] Istituto Nazionale di Fisica Nucleare, Firenze. [3] Institut des Sciences Chimiques de Rennes, Centre National de la Recherche Scientifique, UMR 6226, Université de Rennes 1 (France). [4] Institut Universitaire de France, Paris (France). [5] Dipartimento di Science della Terra, Università di Firenze. [6] Czech Geological Survey, Prague (Czech Republic). [7] Dipartimento di Chimica «U. Schiff» e Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Università di Firenze.

*Corresponding author e-mail:* luca.bindi@unifi.it

*Keywords:* machine learning, superconduction, monchetundraite.

For several decades, scientists have been trying to identify new superconductors. Mostly, the search consisted of calculations, simulations, and tweaking known superconducting materials in an attempt to achieve more desirable properties. The widespread success of artificial intelligence triggered the development of novel classification strategies, based on machine learning, to accurately identify candidate materials that could putatively display superconducting behaviors. Working along these lines, we here propose a radically novel approach to supervise classification and regression of superconductive materials based on the DeepSets technology. This is a family of deep learning algorithms which operates on sets - the finite enumeration of distinct members (or elements). When applied to the problem of classifying superconducting material and anticipating their associated critical temperature, the proposed procedure yields obvious advantages. The examined compound is in fact associated to a set - of variable dimension - reflecting its chemical composition. We are thus feeding the neural network with the atomistic description of the scrutinized material, a foundational approach, solidly grounded on first principles, that enables one to overcome the limits of generality which are intrinsic to any heuristic approach. In particular, we can quantitatively gauge the weight of each individual atom to the onset of the superconductive transition. The performance of the fully trained Deep Set was challenged against a reference benchmark dataset: a significant portion of the materials certified as superconductors were indeed identified, yielding significantly better scores as compared to currently available technologies. The associated transition temperatures were also predicted with a high degree of confidence. Then, we searched within the complete mineralogical catalogue to look for possible superconducting candidates, as tagged by the trained classification algorithm. A list of minerals was extracted and 38% of the selected candidates were already reported to display a superconducting transition. We then focused our attention on a sublist of 3 minerals, extracted from the above pool of candidates. Next, we carried out a systematic experimental characterisation to resolve the magnetic properties of their synthetic analogues. Remarkably enough, the synthetic equivalent of the mineral monchetundraite ($Pd_2NiTe_2$) was found to exhibit a superconducting transition at 1.06 K, a value remarkably close to 1.18 K, as predicted by the Deep Set algorithm. Guided in the search by apt machine learning protocols, we hence discovered a novel superconducting material, the synthetic analogue of monchetundraite.

# A new thermal and atmospheric conditioning device for in situ single-crystal diffraction is up and running

Zema M.*[1], Ventruti G.[1], Tarantino S.C.[2] & Micelli C.[3]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Chimica, Università di Pavia. [3] KleisTEK, Advanced Electronic Systems, Monopoli (BA).

*Corresponding author e-mail:* michele.zema@uniba.it

*Keywords:* gas blower, high temperature, X-ray diffraction.

Our new thermal and atmospheric conditioning device for in situ and in operando single-crystal X-ray diffraction measurements is operational. The new device makes in-house single-crystal diffraction techniques flexible and fully versatile for studies under different heating and atmospheric conditions. Thanks to its compact design, the device can be easily mounted at a fixed angle above the crystal on any kind of machine, allowing free rotation of all goniometer circles to collect the whole reciprocal space with no restrictions.

It is a gas blower that can make use of air, $N_2$ or other gases to condition and heat the sample, thus allowing studying the behaviour of crystals under different atmospheric and thermal conditions, and performing in operando studies too.

The sample temperature is maintained at the desired set point, with a ±2 K temperature precision, through a PID controller and a thermocouple placed at the exit of the gas stream. The controller can be easily operated through its touch screen to set experimental conditions, i.e., temperature and gas flow. In addition, the device can be fully controlled by an application based on LabView (National Instruments). A furnace calibration procedure makes use of an additional thermocouple mounted on the goniometer head at the same position of the sample, the center of the X-ray beam.

The setup is compatible with standard crystal mounting in quartz capillary (in air; in closed atmosphere of virtually any conditions; under vacuum), which is recommended for variable temperature experiments as the use of quartz wool keeps the crystal in position and avoids mechanical stress on crystal surfaces.

The first test experiments performed using the new device, including the well-known α-β phase transition in quartz in air and the high temperature behaviour of a natural chabasite in $N_2$ (which proved to be very different from its in-air behaviour) will be shown.

The Year of Mineralogy is starting a new era for mineralogy, and this new era is opening new opportunities for investigating samples under in situ conditions so far unexplored.

# S19.

# Slow rock slope deformations in different geodynamic and climatic settings: processes, activity, hazards


*Conveners & Chairpersons*

*Federico Agliardi (University of Milano - Bicocca)*

*Chiara Crippa (University of Milano - Bicocca)*

*Emiliano Di Luzio (CNR - Roma)*

*Carlo Esposito (University of Roma – Sapienza)*

# The lifecycle of large rock slope failures: tracking progressive failure from nucleation to collapse

Agliardi F.*[1], Amitrano D.[2], Riva F.[1], Scuderi M.M.[3] & Collettini C.[3]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Universitè Grenoble-Alpes, ISTerre, Grenoble (France). [3] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* federico.agliardi@unimib.it

*Keywords:* slope creep, progressive slope failure, modeling.

Large rock slope deformations creep slowly for long periods (hundreds to tens of thousands of years) and may eventually evolve into catastrophic rockslides. Modelling the physical processes underlying slope creep is key to anticipate the evolution of rock slope deformations. However, the mechanisms regulating the slow-to-fast transition toward their catastrophic collapse remain elusive, and their understanding requires models able to capture the contributions of different failure processes over time. Here we combine geomorphological field observations, monitoring data, progressive slope failure modeling and unconventional laboratory experiments to track the long-term evolution of the Spriana rockslide (Valmalenco, Italian Central Alps), affected by long-term instability after the Last Glacial Maximum (LGM) and representing an active threat since the early 1900s.

We used an explicit, time-dependent 2D FEM model (DaDyn-RS; Riva et al., 2018) to simulate the long-term progressive failure of the Spriana slope. DaDyn-RS simulates rock damage, strain localization and associated creep, accounting for the damage-dependent evolution of permeability and hydro-mechanical coupling. Then, we used a biaxial apparatus within a pressure vessel to characterize the frictional and hydro-mechanical behavior of the rockslide basal shear zone. We performed creep experiments on natural cataclastic material, in which pore pressure is increased stepwise until runaway failure (Agliardi et al., 2020).

Our results suggest that rockslide nucleation follows a long period of rock mass damage accumulation in subcritical stress conditions. At Spriana, this occurred in paraglacial conditions after post-LGM deglaciation, leading to rockslide nucleation in Early Holocene and full hydro-mechanical differentiation of the basal shear zone in Mid-Holocene, mirrored by slope creep. As the basal shear zone accumulates strain, it becomes thicker and less permeable, favoring the development of perched aquifers. Since then, observed rockslide creep becomes dominated by the hydro-mechanical forcing of external triggers, e.g., rainfall. At Spriana, the full spectrum of observed creep behaviors is modulated by short-term pore pressure changes and related slip-induced undrained conditions. These results lay physically-based foundations to improve forecasting models for large creping rock slope failures.

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# From PS-driven identification to numerical modelling: DSGSDs of Mount Bulgheria in Southern Italy

Annibali Corona M.*, Guerriero L., Di Martire D., Ammirati L. & Calcaterra D.

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* mariagiulia.annibalicorona@unina.it

*Keywords:* DSGSDs, DInSAR, landslide mapping and modelling.

Deep Seated Gravitational Slope Deformations (DSGSDs) are phenomena recognized in a variety of geological and geomorphological conditions. They can't be properly defined as landslide movement s.s. or gravitational tectonics because of their kinematics and typical large-scale character. Such phenomena develop over long time periods and, under specific boundary conditions, a sudden slow to fast transition might be expected. This transition assumes particular importance, because of time-dependent rheology of the involved rock that makes the kinematics of such kind of landslides poorly constrained and can prevent their identification. On this basis this research has the purpose of analyzing the kinematics of the DSGSDs affecting the Mt. Bulgheria in southern Cilento, where a number of events have been recognized in the past. In this perspective and considering their extremely complex characteristics, a multidisciplinary approach has been adopted for the study. A preliminary analysis was carried out examining the geological formations cropping out in the study area and their tectono-stratigraphic relationships. Subsequently, a photogeological analysis of the area was carried out, allowing to draw up a geomorphological model focused on the identification of all diagnostic morphologies of these landslides. These data allowed to recognize all of the DSGSDs affecting the Mt. Bulgheria in southern Cilento. After phenomena identification, the ongoing kinematics was analyzed using Persistent Scatterer data achieved by SENTINEL-1 image processing. Derived LoS (Line of sight) mean velocities are in the range −3.12 and +1.30 cm and −2.87 and +2,65 cm in ascending and descending geometries, respectively. The interpretation of satellite data has led to measure the surface deformations and to interpretate slow ongoing movements. Further the comparison of these data with the results of the previous analysis has allowed to validate and better interpret DSGSDs preliminarly identified. Finally, collected data were used to support slope stability numerical modellings, allowing to extend our understanding of DSGSDs geometry at depth, deriving a potential 3D shape of the analyzed DSGSDs.

# Integrating innovative and conventional survey and analysis techniques in the study of large landslides, some examples from the Abruzzo Apennines.

Calcaterra D.[1], Di Martire D.[1], Francioni M.[2], Guerriero L.[1], Scarascia Mugnozza G.[3], Sciarra N.*[4]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [3] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [4] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti.

*Corresponding author e-mail:* nicola.sciarra@unich.it

*Keywords:* large landslide, monitoring, UAV, numerical modelling.

The study area is included in the epicentral area of the recent 2016/2017 seismic sequence in the Abruzzo Region (Central Italy), characterized by a complex geodynamic setting. We investigated the role of the morphostructural setting, seismic and meteorological factors in the development of large and deep landslides. In February 2017, following a heavy snow precipitation event and a moderate seismic sequence (at the end of the Central Italy 2016-2017 seismic crisis), several landslides affected the NE-Abruzzo chain and piedmont area. This paper is focused on the Ponzano (1) and Borrano (2) landslide (Civitella del Tronto, Teramo) in the NE Abruzzo hilly piedmont and on the Pietracamela (3) landslide (Teramo), NE Abruzzo chain. These typologically quite different landslides can be described as:

(1) a large translational slide-complex landslide, affecting the Miocene-Pliocene sandstone clay bedrock sequence of the piedmont hilly sector;
(2) a translational slide, which occurred along structural plane of rupture within the Laga Formation extremely fractured rock mass;
(3) a deep-seated landslide (up to hundred meters of depth), occurring along the marl and marly limestone sequences of the Marne con Cerrogna Formation and affecting the NE part of the village of Pietracamela.

The Ponzano and Borrano areas are located on the Eastern slope of the Civitella del Tronto WSW-ENE ridge, with a top elevation ranging from 400-550 m a.s.l.. Minor scarps NNW-SSE-oriented are present on top of the landslide area. They feature flat surfaces in the upper-intermediate area and steep scarps in the upper and lower part of the slope. They lie on NNW-SSE oriented hog-back relief developed on marl beds interlayed with arenaceous ones. beds (up to tens of meters) pertaining to the Upper Miocene-Lower Pliocene Laga formation. A thick cover of colluvial deposits blankets the bedrock.

In a different geological context lies the small village of Pietracamela. Pietracamela is located in the Abruzzo region (province of Teramo), few kilometers on the North of the Gran Sasso Mountain (Central Apennines). The village is at an altitude of 1005 meter a.s.l. with a population of ca. 250 people and is one of the most beautiful hamlets in Italy. Three main formations outcrop in the study area. The oldest in age is the "Marne con Cerrogna" Formation (Burdigalian-Toronian) characterized by the alternation of Marl and Marly Limestone. The Marne con Cerrogna Formation is overlaid by the alternating clay and sandstone of the "Laga" Formation (Messinian). The most recent formation characterizing the area is represented by the well cemented conglomerate and breccia of the "Sintema di Pietracamela" (Middle Pleistocene) which in the study area forms the "Capo le Vene" cliff, impending over the village. The three above mentioned landslides largely affect houses and villages located on top of the scarp or on the slope. For each landslide a detailed integrated 3D numerical stability analysis was performed using data gathered from field geological and geomorphological mapping, borehole interpretation, geostructural analysis and photogeological investigation. The 3D models of landslides were extracted from LiDAR and/or UAV surveys data. Satellite interferometry SAR techniques and borehole inclinometers were finally used to improve the understanding about landslide behaviour and constrain the numerical simulations.

# Classification of the state of activity of Deep-seated Gravitational Slope Deformation phenomena of the Aosta Valley Region exploiting Sentinel-1 data processed by SAR tomography

Cignetti M.*[1], Godone D.[1], Notti D.[1], Giordan D.[1], Calò F.[2], Reale D.[2], Verde S.[2] & Fornaro G.[2]

[1] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Torino. [2] Istituto per il Rilevamento Elettromagnetico dell'Ambiente, CNR, Napoli.

*Corresponding author e-mail:* martina.cignetti@irpi.cnr.it

*Keywords:* DsGSD, DInSAR, risk mitigation.

Deep-seated Gravitational Slope Deformations (DsGSDs) are, both in terms of frequency and extension, one of the most widespread phenomena in the alpine territory. Their dynamic, although very slow may last for long period, affecting anthropic elements, representing a relevant natural hazard. Moreover, they may feature distinct deformation sectors, showing a spatial heterogeneity represented by typical morpho-structural lineaments variable rock mass fracturing, or presence of secondary landslides. A characterization of the state of activity of these huge phenomena is mandatory to evaluate their impact on anthropic elements. Leveraging on DInSAR techniques, a dedicated procedure to explore the behavior and define the state of activity of the 279 DsGSDs inventoried in the regional landslide inventory, i.e., IFFI Catalogue, of the Aosta Valley Region (Western Italian Alps) has been implemented. The proposed methodology consists in several steps. Firstly, Sentinel-1 data acquired over ascending and descending orbits have been processed through SAR tomography technique tailored to the processing of multipass SAR data at the full available spatial resolution for the analysis of Persistent Scatterers (PSs), i.e., ground targets which are concentrated in space (with respect to the wavelength and spatial resolution) and whose electromagnetic response is sufficiently coherent over all the observation period. Subsequently, an analysis of PSs dataset within DsGSD polygons, devoted to the assessment of Sentinel-1 data coverage has been carried out. In particular, this analysis involves the application of three indexes considering the PS abundance, the computation of voids in points distributions, and the assessment of PS clustering by the computation of skewness of their nearest neighbor distance. Three thresholds are set for each considered index leading to identifying cases with adequate points number and distribution for a suitable definition of the state of activity. Using post-processing algortims we projected the velocity values, measured along the Line of Sight ($V_{LOS}$), along the steepest slope ($V_{SLOPE}$) to compare DsGSD with different displacement direction, and the E-W and vertical components are also computed. A $V_{SLOPE}$ threshold has been set to distinguish stable and active phenomena, considering the aforementioned heterogeneities and other active phenomena, superimposed on the DsGSD area that could not be directly related to DsGSD evolution. Overall, the implemented methodology provides a valid instrument to rapidly and remotely define the state of activity of these huge phenomena, often wrongly underestimated or neglected in risk management, useful for a better definition of DsGSDs impacts on anthropic elements for a proper land use planning.

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# Regional scale classification of slow rock slope deformations style of activity

Crippa C.*, Frattini P., Crosta G.B., Valbuzzi E. & Agliardi F.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* chiara.crippa1@unimib.it

*Keywords:* DSGSD, regional scale, remote sensing.

Slow rock slope deformations are widely diffused in the European Alps as well as in other mountain ranges. They evolve over thousands of years by progressive failure processes, resulting in slow movements impacting infrastructures and possibly accelerating until catastrophic collapse of entire slope sectors. The complexity of these phenomena, related to progressive failure processes and time-variable hydro-mechanical coupling mirrored by a complex creep behaviour makes difficult to predict their interaction with elements at risk and anticipate their possible evolution towards catastrophic failure. Furthermore, these huge landslides are usually characterized by complex styles of activity associated to slope sectors with different kinematics, strain partitioning into morpho/structural features and different displacement rates.

Their study is thus very challenging since they are widespread and need to be characterized in an extensive way, but the low amount and rates of surface displacements, as well as their spatial complexity, limit the use of traditional ground-based and sub-surface monitoring techniques. Among all the available in-situ and remote-sensing approaches, differential synthetic aperture radar interferometry (DInSAR) proved to be useful for the quantitative measurement of slow slope displacement rate, making possible long-term monitoring of surface deformations maximizing the spatial and temporal coverage at a relatively low cost.

In this perspective, we developed a multi-scale methodology integrating geomorphological mapping, field data and multi-interferogram DInSAR products using an inventory of 208 slow rock slope deformations in Lombardia (Italian Central Alps).

Using PS-InSAR and SqueeSARTM datasets, we developed an original peak analysis of InSAR displacement rates to characterize the degree of segmentation and heterogeneity of mapped phenomena, highlight the occurrence of sectors with differential activity and derive their characteristic displacement rates. Using 2DInSAR velocity decomposition and machine learning classification, we set up an original automatic approach to characterize the kinematics of each landslide. Then, we sequentially combine PCA and K-medoid cluster analysis to identify groups of landslides distinguished by consistent styles of activity, accounting for all the relevant aspects including velocity, kinematics, segmentation, and internal damage.

The final product of our regional scale analysis is a dataset classification into seven synthetic "style of activity groups" which gather all the 208 mapped slow rock slope deformations in Lombardia according to their diagnostic features (e.g., heterogeneity, kinematics, velocity). This classification is useful to identify critical phenomena to prioritize site-specific analyses, and to analyse the damage potential of slow rock slope deformations on specific classes of elements at risk.

# Slow rock slope deformations in rapid tectonic uplift areas: the cases of Yienchi and Yakou (Taiwan)

Crippa C.*[1], Agliardi F.[1], Schibuola R.[1] & Chen R.F.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] National Taipei University of Technology (Taiwan).

*Corresponding author e-mail:* chiara.crippa1@unimib.it

*Keywords:* landslides, remote sensing, geomorphology.

Deep-seated gravitational slope deformations (DSGSD) gained increasing attention in Taiwan due to their catastrophic impacts on lives and infrastructures after Typhoon Morakot in 2009, when over 2700 mm of rainfall in 5 days were recorded. Furthermore, as the main Taiwan island is located on a complex convergent plate boundary, conventional observations and analyses suggest that the island's strong tectonic activity has, along with its subtropical climate, contributed to the formation of deep-seated landslides. These are widespread in high-relief mountain areas where Miocene to Eocene meta-sandstone and slate successions outcrop.

Among them, Tienchih, located in Lalong River of Kaohsiung, and Yakou, few km east in Taitung County, were assessed as highly landslide-prone area after heavy precipitations.

Slopes at Tienchih and Yakou were affected by significant slope collapses during the years also causing severe damages to infrastructures and the closure of the South Cross Island Highway No. 20, a critical roadway connecting the western and eastern sides of S Taiwan, where continuing slope instability has been observed after 2009. At both sites, morpho-structural evidence identified in 1-m resolution LiDAR DEMs suggest that long-term slope deformations occurred well before catastrophic slope destabilization. This is supported by spectacular gravitational deformation structures (i.e., kink folds and shear zones), well exposed at Yakou. On the other hand, dense vegetation and limited rock outcrops make an accurate assessment of the geometry, controls, mechanisms and style of activity of these landslides difficult.

To overcome this difficulties, we carried out a systematic geomorphological mapping of the two areas through field data, remote sensing techniques and optical methods (i.e., 3D LiDAR point cloud comparison) to identify the distribution of gravitational morpho-structures and extract geomorphological descriptors (stream power index, mean slope angle etc.) possibly interplaying in the onset and evolution of the deep seated landslides.

Since the slopes are almost entirely vegetated, we further investigated the relations between NDVI index, rock mass damage and the land surface temperature measured from Landsat8 to identify, both through a multivariate statistical approach and site specific observations, the correlations between the fracturing state, the vegetation and the land surface temperature.

The integration of combined morphometric variables and remote sensing products suggest that long-term progressive failure of slopes was promoted by high tectonically-forced erosion rates and constrained by inherited ductile structures. These preconditioned the location, size and mechanisms of slope sectors more prone to catastrophic failure due to intense rainfall and river bank erosion.

# Slip surfaces associated with seismic faults and gravitational slope deformations in carbonate rocks

Del Rio L.*[1], Moro M.[2], Fondriest M.[3], Saroli M.[4], Masoch S.[1], Doumaz F.[2], Gori S.[2], Falcucci E.[2], Cavallo A.[5], Lutterotti L.[6], Artioli G.[1], Borovin E.[6] & Di Toro G.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] INGV, Roma. [3] Institut des Sciences de la Terre ISTerre, Universitè Grenoble Alpes, Grenoble (France). [4] Dipartimento di Ingegneria Civile e Meccanica, Università di Cassino e del Lazio Meridionale. [5] Laboratorio tecnologico multidisciplinare CERTEMA, Grosseto. [6] Dipartimento di Ingegneria industriale, Università di Trento.

*Corresponding author e-mail:* luca.delrio@studenti.unipd.it

*Keywords:* DGSD, active faults, microstructures.

Active Normal Faulting (NF) affects the carbonate rocks of the Italian Central Apennines since Late Pliocene causing destructive earthquakes and controlling the development of Deep-Seated Gravitational Slope Deformations (DGSDs; Galadini, 2006). Recent paleo-seismological, geological and geomorphological observations pointed out that, in the Central Apennines, some sharp slip surfaces located in the footwall of large seismogenic normal faults accommodate Deep-Seated Gravitational Slope Deformations (Moro et al., 2012).

The principal slip surfaces and associated slip zones of DGSD and NF exhume from different depths (100-500 m for DGSDs, 1-3 km for NFs), and are formed and active over a different range of temperatures (<30°C for DGSDs vs. 0-100°C for NFs), pressures (<15 MPa for DGSDs, 0-80 MPa for NFs) and slip rates (usually $<10^{-3}$ m/s for DGSDs, up to ~1 m/s for NFs). Such large differences in loading conditions should result in the formation of distinctive secondary fault/fracture networks in the damage zones that host the DGSDs, possibly recognizable at the outcrop scale, or in the slip zones microstructures. The individuation of the deformation mechanisms and the discrimination between DGSDs and NFs structures could bring outstanding improvements in geological hazard studies.

To achieve these goals, we investigated four DGSDs located in the footwall of active seismogenic NFs and three normal faults bordering large and small depressions in the central Apennines. we investigated the fracture distribution around DGSDs' and NFs scarps and the microstructures of the associated slip zones. Then, we performed Crystallographic Texture Analyses (CTA) on natural and experimental slip zones in carbonate rocks to identify the Crystallographic Preferred Orientations (CPOs) of microcrystalline aggregates and interpret the deformation mechanisms active during slip.

Based on these studies, we conclude that most DGSDs in the central Apennines re-use pre-existing minor faults or shear fractures located in the footwall of large normal seismogenic faults and that no microstructural indicators can allow to uniquely distinguish between DGSDs and normal faults. Indeed, slip zones associated with both NFs and DGSDs in carbonate rocks have similar cataclastic fabrics and are produced by similar deformation mechanisms (i.e., cataclasis and pressure-solution). This interpretation is further supported by the weak lattice preferred orientation measured with Crystallographic Texture Analyses.

Galadini F. (2006) - Quaternary tectonics and large-scale gravitational deformations with evidence of rock-slide displacements in the Central Apennines (central Italy). Geomorphology, 82, 201-228.

Moro M., Saroli M., Gori S., Falcucci E., Galadini F. & Messina P. (2012) - The interaction between active normal faulting and large-scale gravitational mass movements revealed by paleoseismological techniques: a case study from central Italy. Geomorphology, 151-152, 164-174.

# Time-dependent rock-mass deformations, geological aging and landscape evolution as predisposing factors for large rockslide triggering

Delchiaro M.*, Marmoni G.M., Della Seta M. & Martino S.

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* michele.delchiaro@uniroma1.it

*Keywords:* Mass Rock Creep, landscape evolution, Zagros Mountains.

Gravity-induced slope deformations are usually related to the Mass Rock Creep (MRC) process that acts on a large time-space scale through a continuous and non-linear variation of the stress-strain conditions of entire portions of slopes. Such time-dependent process is viscosity-driven and is also strongly conditioned by tectonics and by the morphological evolution of valley-slope systems. Both uplift and the drainage network evolution can, indeed, kinetically release portions of slopes isolating a rock mass carapace that starts to deform with possible acceleration over time towards an ultimate collapse.

However, the difficulty to demonstrate such a theoretical scheme is represented by the difficulty of estimating accurately the starting time of the process, of discriminating the ongoing stage of the MRC process, as well as of determining the rheology of the jointed rock mass.

The main goal of this research was to distinguish the contribution of geological aging (intended as the evolution over time of fold flanks, moving from the hinterland to the foreland of an active orogen), and of landscape evolution in the development of MRC-driven deformations. The specific objective was to demonstrate and weight the relationships among the aforementioned factors through an experimental methodological approach tested in Lorestan (Zagros Mountains - Iran) along a transept oriented parallel to the direction of propagation of the fold morpho-structures.

Based on time constraints to the pre-failure morpho-evolutionary reconstruction provided for 3 case studies from the analysis of geomorphic markers, a Landscape Evolution Model (LEM) was implemented in MATLAB. The LEM was calibrated through the time constraints provided by dated geomorphic markers and allowed the identification of the moment back in time in which critical morpho-evolutive conditions determined the initiation of the MRC process responsible for ultimate rock failures. The computation of the LEM-based strain rate, and consequently of the displacement rate, was performed through a sensitivity analysis on the viscosity parameter, allowing to reconstruct the deformation history linked to the MRC process of the simulated slopes.

It can be concluded that the landscape evolution modelling, chronologically constrained by the analysis of geomorphic markers, allows reconstructing the creep history of slope-valley systems involved in MRC. The presented method will be joined and compared in a multi-modelling approach with stress-strain numerical modelling with the aim to calibrate the rock mass rheology and to constraint in back analysis the evolution of large-scale viscosity-driven processes.

# Regional inventory of DSGSDs in the Molise region (Central Apennines, Italy): influence of predisposing factors and river incision on the process onset

Delchiaro M.*[1], Discenza M.E.[2], Di Luzio E.[3], Minnillo M.[2], Rouhi J.[1], Di Martire D.[4], Troiani F.[1], Della Seta M.[1] & Esposito C.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Geoservizi s.r.l., Ripalimosani (CB). [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [4] Dipartimento di Scienze della Terra, Università di Napoli «Federico II».

*Corresponding author e-mail:* michele.delchiaro@uniroma1.it

*Keywords:* DSGSD inventory, relative chronology, geomorphic markers.

At the mountain scale, the onset and evolution of Deep-Seated Gravitational Slope Deformations (DSGSDs) are strictly related to different control factors, such as the geological-geomorphological setting of the slope and the relief dynamics (Discenza & Esposito, 2021). Furthermore, as time-dependent phenomena, DSGSDs are significantly related to the timing of landscape evolution and inherited tectonic deformation histories (Di Luzio et al., 2022). In mountain areas that experienced glaciation-deglaciation cycles, during the glacial retreat, slope debuttressing, glacial rebound, stress redistribution, and changes in slope hydrology, as well as rock jointing favor the formations of DSGSDs and rock collapses (Jarman & Harrison, 2019). Within unglaciated mountain areas, the combined effects of tectonics, river incision, and hillslope processes are recognized to generate high-relief and deep-incised river valleys, such as narrow gorges and canyons, that allow the kinetic release for large portions of slopes (Delchiaro et al., 2019). To deepen this topic, i.e., to better constrain the role of predisposing factors (inherited geological and morpho-structural settings) and preparatory conditions (long-term morpho-evolutionary frame), in the frame of an hazard-oriented research project an original DSGSDs inventory was completed for the entire Molise region (Central Apennines, Italy), as it is highly representative of geological-structural conditions widespread in the whole central Apennines. DSGSD phenomena were mapped by means of a combination of aerial and satellite images interpretation, geomorphometric analyses, and field surveys. The study was integrated through InSAR analyses and allowed to determine the main characteristics of DSGSD phenomena. River longitudinal profile analysis, aimed at identifying the position and spatial distribution of the knickpoints, was also performed, integrated by the identification, through an automatic extraction from DEM, of the remnants of fluvial relict surfaces hanging at different heights above the valley bottoms. The latter can be considered as geomorphic markers of the river valley evolution, consequently, are useful to recognize the local and/or regional ancient base levels of erosion. Knickpoints and geomorphic markers were then compared with the DSGSDs elevations and spatial distribution to provide a relative chronology of the deformational process initiation.

By means of these analyses it was possible to establish a general correlation between the analyzed deformations and some conditioning factors, such as geological, geomorphological, structural, and geodynamic setting of the region.

Delchiaro M., Della Seta M., Martino S., Dehbozorgi M. & Nozaem R. (2019) - Reconstruction of river valley evolution before and after the emplacement of the giant Seymareh rock avalanche (Zagros Mts., Iran). Earth Surf. Dyn., 7, 929-947.

Di Luzio E., Discenza M.E., Di Martire D., Putignano M.L., Minnillo M., Esposito C. & Scarascia Mugnozza G. (2022) - Investigation of the Luco Dei Marsi DSGSD revealing the first evidence of a basal shear zone in the central Apennine belt (Italy). Geomorphology, 108249.

Discenza M.E. & Esposito C. (2021) - State-of-art and remarks on some open questions about DSGSDs: Hints from a review of the scientific literature on related topics. Ital. J. Eng. Geol. Environ., 21, 31-59.

Jarman D. & Harrison S. (2019) - Rock slope failure in the British mountains. Geomorphology, 340, 202-233.

# Numerical modelling unravelling the development of a Basal Shear Zone in a tectonic-driven DSGSD (Luco Dei Marsi, Central Apennines)

Discenza M.E.[1], Di Luzio E.*[2], Di Martire D.[3] & Esposito C.[4]

[1] Geoservizi s.r.l., Ripalimosani (CB). [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [4] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* emiliano.diluzio@igag.cnr.it

*Keywords:* numerical modelling, DSGSD, Basal Shear Zone.

Deep-Seated Gravitational Slope Deformations (DSGSDs) are complex, slow-moving phenomena often controlled by inherited structures (Discenza & Esposito, 2021). In some cases, the presence of these structures or the progression of deformation (Agliardi et al., 2001) favours the development of a Basal Shear Zone (BSZ). Over the years, many numerical modelling were performed to study the time-dependent behaviour of DSGSDs and the role of faults, folds, and bedding planes (Discenza et al., 2011; Della Seta et al., 2017).

This research focuses on development of the Luco dei Marsi DSGSD, in which the first evidence of a BSZ in the central Apennines was found (Di Luzio et al., 2022). The DSGSD affects an anticline formed in a carbonate sequence, whose eastern limb is dismembered by Quaternary normal faults featuring the western edge of the Fucino Basin. The slope deformation was revealed by several orders of graben, scarps, and trenches, as well as bulging and landslides. The short-term activity of the process is on the order of a few mm/yr and was revealed by DInSAR time series.

In this work a numerical modelling was performed to investigate the characteristics of DSGSD. Physical and mechanical properties of intact rock were determined through laboratory tests, while geomechanical characteristics of rock mass were determined through field surveys. The model was built up considering the slope debuttressing due to the erosion and the Late Pleistocene faulting along the eastern margin of the slope. In the analyses, both faults and bedding planes were considered to examine the development of deformation and BSZ. The numerical simulation highlights the role played by the structural setting of the relief and the geometry of bedding planes on the onset and evolution of DSGSD.

Agliardi F., Crosta G.B. & Zanchi A. (2001) - Structural constraints on deep-seated slope deformation kinematics. Eng. Geol., 59, 83-102.

Della Seta M., Esposito C., Marmoni G.M., Martino S., Scarascia Mugnozza G. & Troiani F. (2017) - Morpho-structural evolution of the valley-slope systems and related implications on slope-scale gravitational processes: New results from the Mt. Genzana case history (Central Apennines, Italy). Geomorphology, 289, 60-77.

Di Luzio E., Discenza M.E., Di Martire D., Putignano M.L., Minnillo M., Esposito C. & Scarascia Mugnozza G. (2022) - Investigation of the Luco Dei Marsi DSGSD revealing the first evidence of a basal shear zone in the central Apennine belt (Italy). Geomorphology, 108249.

Discenza M.E. & Esposito C. (2021) - State-of-art and remarks on some open questions about DSGSDs: Hints from a review of the scientific literature on related topics. Ital. J. Eng. Geol. Environ., 21, 31-59.

Discenza M.E., Esposito C., Martino S., Petitta M., Prestininzi A. & Scarascia-Mugnozza G. (2011) - The gravitational slope deformation of Mt. Rocchetta ridge (central Apennines, Italy): Geological-evolutionary model and numerical analysis. Bull. Eng. Geol. Environ., 70, 559-575.

# Application of multi-sensor, multi-temporal, multi-scale remote sensing datasets for landslide analysis

Donati D.*[1], Stead D.[2], Rabus B.[3], Engelbrecht J.[4-5], Clague J.J.[2], Francioni M.[6] & Borgatti L.[1]

[1] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna. [2] Department of Earth Sciences, Simon Fraser University, Burnaby (Canada). [3] School of Engineering Science, Simon Fraser University, Burnaby (Canada). [4] BGC Engineering Inc., Vancouver (Canada). [5] Department of Geography and Environmental Studies, Stellenbosch University (South Africa). [6] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo".

*Corresponding author e-mail:* davide.donati17@unibo.it

*Keywords:* remote sensing, landslide, slope characterization.

The size, location, and failure mechanisms of slowly moving landslides are the result of complex interactions of geological, structural, geomorphological, and environmental factors and processes. Additionally, events such as earthquakes, seasonal groundwater changes, glacier retreat, and other mass wasting events can cause a progressive accumulation of damage, weakening the slope and promoting instability. A full understanding of a landslide should rely on a detailed investigation of the slope, based on surface, subsurface, and monitoring data, the collection of which can pose significant logistical and financial challenges, particularly at remote and previously uninvestigated sites. In such cases, remote sensing methods provide datasets that can be instrumental for preliminary landslide interpretation. The research we conducted at Fels landslide (Alaska, USA) shows how a combination of multi-sensor remote sensing datasets allows for a multi-scale, multi-temporal analysis of the slide that provides insights into its failure mechanism and movement, even in absence of subsurface data. We used LiDAR and close-range photogrammetry to perform a structural characterization of the slope. SAR speckle tracking (ST) was used to quantify surface displacement between 2010 and 2020. Historical aerial imagery was used to perform a preliminary analysis of retreat of Fels Glacier. We used the vector inclination method (VIM) and surface change inversion to determine the magnitude, azimuth, plunge, and spatial distribution of surface displacement and thereby infer the thickness of the landslide and the morphology of the basal rupture surface. Displacement maps derived from the SAR ST datasets reveal that structural geology exerts a primary control on the Fels slide. The VIM and surface change inversion show that the landslide has a maximum thickness of around 140 m and is displacing along a multi-planar surface largely controlled by slope-parallel foliation. We show that the magnitude of surface cracking has increased with progressive glacier thinning and retreat over the past century, suggesting that climate change has played a role in the evolution of the slope. The SAR ST datasets also reveal that slope displacements accelerated between 2010 and 2020, highlighting the need for further monitoring of the area. Future analyses will include 3D numerical modelling using LiDAR and photogrammetry data to build the model, and SAR ST datasets to constrain and validate the modelling results. The remote sensing methods we applied at Fels slide are a critical asset in investigations of landslides at other challenging sites. Collection and combined interpretation of datasets can maximize interpretations of landslides.

# Fault-propagation folding, fluvial dynamics, gravitational deformation and rock slope failures: mutual relationships in the Poggio Baldi area (Northern Apennines)

Esposito C.*[1], Di Luzio E.[2], Baleani M.[3], Troiani F.[1], Della Seta M.[1], Bozzano F.[1] & Mazzanti P.[1-3]

[1] Dipartimento di Scienze della Terra e Centro di ricerca previsione, prevenzione e controllo dei rischi geologici, Sapienza Università di Roma. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] NHAZCA s.r.l. - spin-off Sapienza Università di Roma.

*Corresponding author e-mail:* carlo.esposito@uniroma1.it

*Keywords:* Deep-seated Gravitational Slope Deformation, landslide, fault-propagation fold.

Folding of sedimentary rock sequences as inherited from past tectonics events can control various aspects of rock slope stability, including the development of DSGSD (Deep-seated Gravitational Slope Deformation) and large landslides. In these cases, the knowledge of fold geometry and its complexity is much important for deriving conceptual/evolutionary models of gravity-driven deformations and understanding slope failure mechanisms (e.g., Badger, 2002; Humair et al., 2013; Stead & Wolter, 2015).

This work provides further insights into the relationship between slope-scale gravitational processes and fold-related morphostructural features. We present a case study where the kinematic evolution of a complex fault-propagation fold within the Marnoso-Arenacea turbiditic sequence in Northern Apennines has preconditioned the formation of a DSGSD and the onset of the large and still-active Poggio Baldi landslide, with failure episodes documented in 1914 and 2010 (Mazzanti et al., 2021). An inventory of gravity-driven geomorphological features was realized and their distribution within different sectors of the fold structure analysed to conceive a multiple-step geological, conceptual model for the development of the DSGSD.

While fold geometry, characterized by breaking-through thrusts and panel rotations, and the lithological anisotropies within the flysch sequence played the role of predisposing factors, the Quaternary entrenchment of the Bidente River along the fold back-limb was considered as the main cause for the onset of gravitational deformation.

Finally, the reconstruction of the original slope topography in the Poggio Baldi area and the results of remote sensing analyses allowed for the size calculation of the wedge-shaped rock block which detached in 1914, an event that occurred in the wider frame of the DSGSD.

Badger T.C. (2002) - Fracturing within anticlines and its kinematic control on slope stability. Environ. Eng. Geosci., 8, 19-33.

Humair F., Pedrazzini A., Epard J.L., Froese C.R. & Jabedoyff M. (2013) - Structural characterization of Turtle Mountain anticline (Alberta, Canada) and impact on rock slope failure. Tectonophysics, 605, 133-148.

Mazzanti P., Caporossi P., Brunetti A., Mohammadi F.I. & Bozzano F. (2021) - Short-term geomorphological evolution of the Poggio Baldi landslide upper scarp via 3D change detection. Landslides, 18, 2367-2381.

Stead D. & Wolter A. (2015) - Critical review of rock slope failure mechanisms: the importance of structural geology. J. Struct. Geol., 74, 1-23.

# Implications of rock slope deformations in local seismic response and land management: some hints from a case-study in central Apennines, Italy

Esposito C.*[1], Martino S.[1], Troiani F.[1], Della Seta M.[1], Cercato M.[2], Hailemikael S.[3] & Martini G.[3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Ingegneria Civile, Edile e Ambientale, Sapienza Università di Roma. [3] Dipartimento Sostenibilità dei Sistemi Produttivi e Territoriali, ENEA, Frascati (RM).

*Corresponding author e-mail:* carlo.esposito@uniroma1.it

*Keywords:* rock slope deformation, seismic amplification, seismic microzonation.

Slope-scale rock deformations can be seen as both direct and indirect geohazard source. Direct implications are related to the displacements of the deforming mass (up to its possible localized or general collapse). Indirect hazard and risk conditions risks are due to the severe rock-mass damage resulting from such deformations, that make slopes prone to conventional (in terms of volumes) landslides; furthermore, the inherited superimposition of even thick deforming – and, thus, damaged – rock-masses over a less disturbed bedrock (i.e., the mass beneath the deforming zone/surface) can imply a seismic impedance contrast that can cause amplification of seismic motion over areas as wide as the extent of the process which can be on the order of square kilometers. About this latter implication, we here illustrate the results of a detailed seismic microzonation study carried out after the seismic sequence of Central Italy (2016-2017) in support of post-earthquake reconstruction. During these activities mass rock creep deformations of slopes featured by flexural toppling processes were identified in the municipality of Accumoli (Latium Region), involving two urbanized areas. Geophysical investigations (downhole tests, active surface-wave testing and seismic ambient noise measurements) highlighted peaks of the horizontal-to-vertical spectral ratios (HVSR) in a frequency band ranging from 1.5 up to 2.5 Hz in correspondence of the rock mass involved in the flexural toppling. In one of the two areas, H/V calculated on weak-motions recorded during the seismic sequence within the deforming rock mass, showed a clear peak in the H/V frequency range 1.5-2.0 Hz, thus overlapping the range pointed out by HVSR. The local morpho-structural ang geological settings cannot justify a "simple" 1D resonance: the HVSR peaks can be rather related to the 3D volume of intensely jointed rock mass, in agreement with the field evidence of flexural toppling, as these peaks are confined within the deforming mass. In addition, the lack of a clear polarization of the particle motion in the seismic ambient noise dataset suggests that the observed effect should not be linked to the interaction of seismic surface waves with persistent discontinuities in an anisotropic rock mass. According to the National guidelines for seismic microzonation studies, these rock masses have not been identified as unstable, i.e., involved in conventional landslide processes, but have been identified as seismic amplification prone microzones with associated amplification factors of at least 1.5 in the period range 0.1-0.5 s. The identification of such microzones within areas involved in gravity-induced slope deformations is a significant prerequisite for planning strategies of post-earthquake reconstruction.

# Terrestrial data and remote sensing technologies for monitoring a large-scale and low-kinematic landslide in a DSGSD ophiolitic landscape (Ligurian Apennines, Italy)

Faccini F.*[1-2], Allasia P.[2], Ferrando A.[1], Godone D.[2], Notti D.[2] & Poggi F.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Istituto per la Protezione e la Ricerca Idrogeologica, CNR, Torino. [3] Regione Liguria, Direzione Ambiente e Protezione Civile, Settore Interventi Difesa del Suolo, Genova.

*Corresponding author e-mail:* faccini@unige.it

*Keywords:* DSGSDs, large-scale landslides, Ligurian Apennines.

Deep Seated Gravitational Slope Deformations (DSGSDs) are complex phenomena usually triggered by a combination of genetic mechanisms, such as lithological, tectonic, geomorphological and climatic features. In Ligurian mountain the DSGSDs are frequent due to geologic setting and neotectonic activity.

DSGSDs monitoring is a research field with significant implications either for scientific knowledge or for the most geo-engineering issues.

The techniques of remote sensing have allowed in recent years to identify better these deep slope phenomena, which can feature different degrees of hazard.

In this research, we present the monitoring activities of the large-scale landslides on which some villages of Upper Graveglia Valley (Entella river catchment) are settled (Brandolini et al., 2007). The Graveglia Valley is internationally recognized for its ophiolitic sequence with its sedimentary covers and the upper part of the catchment shows geomorphological evidences that could be linked to a DSGSD.

For decades there have been reports of slope instability phenomena in the Upper Valley, outlined by several indirect kinematic indicators.

Based on a project funded by Regione Liguria aimed at geohydrological risk reduction, drilling activities were carried out to identify the stratigraphy and set up a monitoring network (Faccini et al., 2019). An extensive geophysical survey was launched to plan the drilling survey, made by 10 boreholes: two inclinometer cases were installed (one with a robotized system) and eight piezometric cases.

The monitoring instrumentation was completed with a weather station and two GPS benchmarks, to ensure a crosscheck of the displacements.

The monitoring activities also included the use of PSInSAR satellite data over the period 1992-2019 (Allasia et al., 2021). The results of this study show a complex situation: an evolution of the large slope instabilities in several compartments with different kinematics, behaviour and depth of sliding surface and hydrogeological set-up is recognized. The monitoring data analysis also showed a good match between satellite, GPS, and inclinometric probe.

Allasia P., Baldo M., Faccini F., Godone D., Notti D. & Poggi F. (2021) - The Role of Measure of Deep-Seated Displacements in the monitoring Networks on Large-Scale Landslide. In: Casagli N., Tofani V., Sassa K., Bobrowsky P.T. & Takara K. Eds., Understanding and Reducing Landslide Disaster Risk. ICL Contribution to Landslide Disaster Risk Reduction. Springer. https://doi.org/10.1007/978-3-030-60311-3_4.

Brandolini P., Canepa G., Faccini F., Robbiano A. & Terranova R. (2007) - Geomorphological and geo-environmental features of the Graveglia Valley (Ligurian Apennines, Italy). Geogr. Fis. Din. Quat., 30, 99-116.

Faccini F., Elter F.M., Allasia P., Berruti L., Godone D., Notti D. & Poggi F. (2019) - Geological-geomorphological characterisation and monitoring activities of a large slope instabilities in Upper Graveglia Valley (Ligurian Apennine, Italy). Geophys. Res. Abstr., 21, EGU2019-18661-1.

# Deep-seated gravitational slope deformation in the Cavargna Valley (Central Southern Alps): triggering processes and slope evolution

Ferrario M.F.*[1], Livio F.[1], Zerboni A.[2], Mariani G.S.[3], Martinelli E.[1] & Amit R.[4]

[1] Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Como. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [4] Geological Survey of Israel, Jerusalem (Israel).

*Corresponding author e-mail:* francesca.ferrario@uninsubria.it

*Keywords:* DSGSD, prehistoric landslides, prehistoric earthquakes.

Deep-seated gravitational slope deformations (DSGSD) in Alpine and high mountain areas can involve entire slopes and are a source of potential hazard. Possible triggering mechanisms include, among others, post-glacial debuttressing, earthquake-induced ground shaking, or co-seismic surface faulting. The identification of the triggering mechanism has implications for hazard assessment and for a better understanding of slope processes and evolution. We investigate a DSGSD located in the Cavargna Valley (N Italy), applying an integrated approach, including morpho-structural analysis, geologic field survey, trenching, radiocarbon dating and detailed sedimentological analysis (Livio et al., 2022).

The study area was never occupied by extensive ice tongues and thus glacial processes could be ruled out as triggering mechanisms. We reconstructed the local slope evolution, which encompasses phases of soil development and at least two phases of movement since the Middle Holocene. Then, we discuss the climatic vs tectonic triggering mechanism, by comparing the Cavargna Valley site with other DSGSD in the Central Alps and with a dataset of paleoseismic evidence.

We argue that the landslide onset may be due to a seismic triggering, with a possible source located in southern Switzerland. The later evolution of the landslide was instead driven by climatic predisposing conditions (humid and cold), corresponding to a phase of enhanced slope instability.

Livio F.A., Zerboni A., Ferrario M.F., Mariani G.S., Martinelli E. & Amit R. (2022) - Triggering processes of deep-seated gravitational slope deformation (DSGSD) in an un-glaciated area of the Cavargna Valley (Central Southern Alps) during the Middle Holocene. Landslides, 1-17. https://doi.org/10.1007/s10346-022-01892-w.

# Unraveling spatial and temporal heterogeneities of very slow rock-slope deformations with targeted DInSAR analyses

Franzosi F.*[1], Crippa C.[1], Manconi A.[2] & Agliardi F.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Alpine Remote Sensing, CERC, Institute for Snow and Avalanche Research, Davos (Switzerland).

*Corresponding author e-mail:* f.franzosi@campus.unimib.it

*Keywords:* DSGSD, InSAR.

Spaceborne radar interferometry is a powerful tool to characterize landslide activity. However, its application to very slow rock slope deformations (displacement rates < 5 cm/yr) in alpine environments remains challenging due to noise, atmospheric/snow cover effects and heterogeneous deformation patterns related to complex landslide mechanisms.

In this study we combine available SqueeSAR™ data (Sentinel 1A/B, 2015-2017), ad hoc multi-temporal baseline DInSAR processing (2016-2019), GPS data (2015 to 2019) and detailed field mapping to unravel the kinematics, internal segmentation and style of activity of the Mt. Mater deep-seated gravitational slope deformation (DSGSD) in Valle Spluga (Italy). The high relief slope (1500-3000 m.a.s.l.) is made of dominant micaschist and paragneiss of the Stella-Timun complex (Suretta nappe) and ranges in inclination between 33° (< 2500 m a.s.l.) and 25° (> 2500 m a.s.l.). At 2900 m a.s.l. the slope is cut by a sharp triangular headscarp with a vertical downthrow of about 40 m, moving downslope, shallower arcuate scarps mark the transition to two nested large landslides, affecting the slope between 2400 m a.s.l. and 1550 m a.s.l; with highly deformed toes.

Using regional scale processed PSI data, through 2DInSAR decomposition, we highlight the global translational kinematics of the DSGSD. However, to obtain a spatially-distributed characterization of the DSGSD displacement patterns, we process several multi-temporal interferograms and retrieve unwrapped phase and displacement maps according to a targeted approach based on variable temporal baselines (from 24-days to 1-year). In this context: a) 1-year interferograms provide a picture of long-term background DSGSD displacement signals; b) seasonal interferograms highlight displacement trends suggesting a complex response of different slope sectors to hydrological input; c) 24 days interferograms outline a triangular shaped active sector extending between 2500 m a.s.l. and the main DSGSD headscarp, corresponding to the movement of extensive debris cover and periglacial features.

Our analyses clearly outline a composite slope instability and a strong spatial heterogeneity with different nested sectors possibly undergoing different evolutionary trends towards failure. The combined analysis of seasonal interferograms and GPS data further confirm a sensitivity of the different slope sectors to hydrological forcing modulated by snowmelt and rainfalls. The herein results outline the potential of a targeted use of DInSAR, carefully constrained by field geological and morpho-structural data, for the detailed investigation of a complex very slow rock slope deformation successfully unravelling its mechanisms, temporal trends of activity and forcing factors.

Our approach prove to be effective in providing key information for the definition of possible evolutive scenarios for risk analysis and mitigation of a widespread class of slope instabilities.

# From slow to fast surface displacements in complex scenarios: spatial and temporal evolution of the Brienz/Brinzauls deep-seated landslide, Switzerland

Manconi A.*

Alpine Remote Sensing, CERC, Institute for Snow and Avalanche Research, Davos (Switzerland).

*Corresponding author e-mail:* andrea.manconi@slf.ch

*Keywords:* remote sensing, engineering geology, landslide hazard.

Large compound landslides show long-term evolution, which is characterized by non-steady velocities, sudden accelerations and potential failure events. Accurate data is hence important for the analysis and the interpretation of their kinematic behavior, as well as associated hazard potential. Remote sensing techniques have demonstrated to be a valid complement to standard in-situ monitoring. In particular, Differential Synthetic Aperture Radar Interferometry (DInSAR) from satellite-based imagery as well as from ground-based platforms allowed great advances in the identification and monitoring of surface deformation processes. However, the results obtained with currently available DInSAR methods might be hindered by insufficient spatial or temporal resolutions and/or due to intrinsic limitations of the methods used. Another method that gained momentum in recent years is the Digital Image Correlation (DIC), a method allowing to track displacements by comparing pixel groups in multi-temporal imagery acquired from different sensors, mainly optical and radar, and from different platforms (ground-based, airborne, and/or spaceborne). The DIC strategy has been initially adopted to study rapid flow of glaciers, but more and more often this technique is used for the investigation of slope instabilities and landslide events. Despite reduced accuracies compared to DInSAR, the advantage of DIC is the possibility to retrieve information when large surface displacements gradients occur.

We performed an extensive analysis of C-Band SAR datasets (5.6 cm wavelength) acquired from ERS-1/2, Envisat ASAR, Radarsat-2 and Sentinel-1 satellites in the period 1992-2020, in order to reconstruct the spatial and temporal evolution of the surface displacements at the Brienz/Brinzauls landslide complex (hereafter referred to as Brienz), located in canton Graubünden (Switzerland). Moreover, we jointly consider DIC on multi-temporal Digital Terrain Models (DTM) generated form airborne surveys and DInSAR results to compute 3-D surface deformation fields, and validate our results against ground-based GNSS measurements and additional ground-based radar sensors. The aim of this contribution is manifold. First, we demonstrate how spatial and temporal heterogeneities might deeply influence the investigation of displacements in complex landslide scenarios when relying only on DInSAR measurements. Second, we show how a deep and careful analysis of the DInSAR “base products” (i.e., interferograms) can be of great help in complex scenarios. Finally, we perform a strain analysis to highlight areas of strain accumulation and identify possible relationships between kinematic domains, geological boundaries, as well as tectonic structures and rock mass discontinuities.

# S20.

# Landslides from mountain to coastal environments and beyond

*Conveners & Chairpersons*

*Costanza Morino (Université Savoie Mont-Blanc, Le Bourget-du-Lac, France)*

*Mauro Soldati (University of Modena and Reggio Emilia)*

*Philip Deline (Université Savoie Mont-Blanc, Le Bourget-du-Lac, France)*

# Linking stratigraphy, mineralogy and geotechnical properties of claystones involved in the Lacedel landslide, Cortina d'Ampezzo (Dolomites, Italy)

Alverà G.*, Gianolla P., Ghirotti M. & Cruciani G.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* greta.alvera@edu.unife.it

*Keywords:* landslide, stratigraphy, clay minerals.

The Lacedel landslide is a large earth flow resting on the western slope of Cortina d'Ampezzo (BL). It was presumably triggered in the Late Glacial and features a recurring activity to this day (Mantovani et al., 2019). The presence of a carbonate-siliciclastic sequence of the Heiligkreuz Fm. (Upper Triassic) known in the past as Dürrenstein Fm., in particular the Alpe di Specie member ($HKS_4$) (Gianolla et al., 2018), has been identified as the stratigraphic level to which the sliding surfaces of many landslides of the area correspond to. This study is aimed at closely relate the stratigraphical, mineralogical and geotechnical data from 34 samples, collected from outcrops and boreholes, in order to: i) confirm that the $HKS_4$ Fm. represents the basal portion of the Lacedel landslide; ii) determine the nature of the clay minerals present in all the samples; iii) assess the correlations between the nature and amount of clay minerals to their geotechnical properties. To achieve these goals, a detailed stratigraphic sampling of the $HKS_4$ Fm. was carry out in Cortina d'Ampezzo from outcrops of the landslide crown, at the slopes of the Mt. Faloria and along the Assola Stream (Borca di Cadore, BL).

XRD analyses were performed on the collected samples, both as powders of the whole sample and on oriented mounts of the <2 mm fraction in the air dried, ethylene glycol-saturated, and heated forms. The Rietveld method was used for accurate phase quantitative analyses. The oriented mounts were modelled for the complete identification of clay minerals, in particular the illite-smectite (I/S) mixed layers. The results of XRD analyses show that the ratio of non-clay/clay minerals ranges from 0.40 to 2.30 and that the most abundant clay is a I/S mineral with illite content from 45 to 65%, corresponding to mixtures of disordered interstratifications with Reichweite (R) stacking sequence types R1 and R0.

Correlation between the geotechnical properties (Atterberg limits and residual friction angle by ring shear tests) and the proportion and type of clay minerals, together with the correlations between the equivalent basal spacing and liquid limit (Schmitz et al., 2004), and other empirical relationships further developed (Bolla et al., 2020), were tested and improved.

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# Rockfall susceptibility assessment of the "San Michele Arcangelo" historic trail, Aurunci Regional Park, Italy

Annibali Corona M.*, Guerriero L., Di Martire D., Tufano R. & Calcaterra D.

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* mariagiulia.annibalicorona@unina.it

*Keywords:* rockfall, susceptibility analysis, Aurunci Regional Park.

The "San Michele Arcangelo" historic trail is in the Aurunci Regional Park (central Italy). Representing a significant example of historic trail of great religious significance, it forms the cultural asset of the park. The trail, located along the southern slope of Mt. Altino, prone to rockfalls, is hiked every year by thousands of faithfuls on pilgrimage who are exposed to such kind of instabilities. To contribute to a better understanding of the condition of development and evolution of such phenomena, providing a susceptibility scenario able to support the adoption of mitigation measures, a specific analysis was completed on the basis of field and literature data. Photogrammetric reconstruction of accessible slope sectors was completed to derive geomechanical features of outcropping rocks and estimate potential detaching block volume. Possible mechanisms of detachment were analyzed using the reduced complexity Markland test method. Susceptibility to rock block detachment, rockfall propagation and block deposition was analyzed using GIS processing and deterministic/probabilistic propagation analyses. Results indicate: i) the potential for rock blocks detachment by wedge and planar sliding or toppling, ii) the localization at higher elevations over the whole study area of slope sectors susceptible to block detachment, iii) the moderate susceptibility to both propagation and deposition of rock blocks along the trail, iv) the control exerted by the hydrographic network on rockfall propagation, v) the control exerted by screes and slope angle on rockfall deposition.

# Regional Landslide Susceptibility Assessment applying a Machine Learning algorithm to the coastal region of Attica (Greece)

Bausilio G.*[1], Varsama C.[2], Calcaterra D.[1], Guerriero L.[1] & Di Martire D.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Department of Geography, University of the Aegean, Mytilene (Greece).

*Corresponding author e-mail:* giuseppe.bausilio@unina.it

*Keywords:* landslide, machine learning, MaxEnt.

Landslides, defined as "the movement of a mass of rock, earth or debris down a slope" (Cruden, 1991), have a very high impact on human activities. Landslide susceptibility assessment is a powerful instrument that land-use planners and engineers can use as an additional aid for drafting risk mitigation and urban development plans. A Multivariate Statistical Approach (MSA) has been implemented to assess Landslide Susceptibility for the coastal region of Attica (Greece), where the capital city of Athens is located. The chosen algorithm for evaluating landslide susceptibility is the presence-only algorithm Maximum Entropy (MaxEnt) (Phillips & Dudìk, 2008). As a statistical algorithm, MaxEnt is based on the assumption that the analysis of the historical landslides and their relationship with the environmental and triggering factors can be used to predict future phenomena (Corominas et al., 2014). A recently compiled landslide inventory (Tavoularis et al., 2021) has been utilized as presence data, adopting a 5-fold cross-validation method for testing purposes. The performance was assessed through the ROC/AUC approach, obtaining a "good" performance, thus demonstrating the effectiveness of such approach with useful results for land management entities.

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# Geo-structural pattern and permafrost evolution for landslide risk analysis in high mountain area: preliminary results from the 2019-2020 Mt. Viso rockfall (Italian Westrn Alps)

Bormioli D., Morelli M., Nicolò G. & Paro L.*

Agenzia Regionale per la Protezione Ambientale, Torino.

*Corresponding author e-mail:* l.paro@arpa.piemonte.it

*Keywords:* Mt. Viso rockfall, structural analysis, permafrost degradation.

A huge rockfall occurred the 26.12.2019 involving the Sucai Tower at 3100 m a.s.l., located on the NE slope of the Mt. Viso (Western Italian Alps). The main scarp is extended for 160 m vertically with a width of 40-70 m. The accumulation covers about 65,000 $m^2$ and a volume of about 80,000 $m^3$ has been estimated, with some very huge blocks (the largest exceeds 1,000 $m^3$). Smaller rockfalls starting from the same area continued during the following months in the 2020. Boulders and the accumulation zone involve potentially the very popular trail areas enjoyed by mountain climbers and hikers.

Landslide occurred on the Forciolline Metaophyolitic Unit (metabasites listed with epidote and Na-amphibole and green schists) in a rock mass with strong fracturing density that characterizes the slope with different hazard levels.

The geo-structural analysis was conducted through the photo-interpretation of the 3D scene processed starting from ortho-rectified aerial images and extremely detailed altimetric models, derived from Unmanned Aerial Vehicle (UAV) surveys carried out by Arpa Valle d'Aosta. The images were characterized by a 3 cm maximum ground resolution, while the 3D digital altimetric model of the surfaces (DSM) had a resolution of 6 cm. A 3D dense point cloud was also generated starting from the same images.

Two criteria were applied for the discontinuity systems identification:

- automatic, by means of specific software for the processing and analysis of 3D point clouds (CloudCompare along with Facets plugin). Four main discontinuity systems have been recognized.
- visual interpretation based on geometrical and hierarchical discontinuity relationships as usually observed on the field. Three main structural associations (faults, shear zones and fracture systems) have been recognized.

Discontinuities and structural associations have been observed at different scales and represent structural predisposing framework of the Mt. Viso rockfall.

This rockfall fit into a general context of slope instability of the high alpine areas especially in recent years, in which these processes have been related to climate change and permafrost degradation. The lack of measured temperature data inside the rock masses, does not allow to establish a cause-effect relationship between the atmospheric warming, permafrost degradation and slope instability phenomena. Nevertheless, other rockfalls occurred in Piedmont Alps with same altitude and slope aspect, and in the same month of the year, indicating a high probability of triggering due to climate signal. The permafrost data from regional monitoring network highlight a general degradation in all stations, with a trend of permafrost warming of +0.15°C/decade at 35 m of deep at 3000 m a.s.l.

Further analysis of the rock temperature combined with the climate trends, and of the bedrock fracturing condition, are carrying out by Arpa Piemonte aimed to elaborate predictive rockfalls-climate models, useful for risk management.

# Modelling of slopes in the Calabrian coastal area using FEM and LEM method

Campilongo G.*[1], Ponte M.[1], Catanzariti F.[2], Muto F.[1] & Critelli S.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Geostru SC Engsoft s.r.l., Cluj-Napoca (Romania).

*Corresponding author e-mail:* gloria.campilongo@unical.it

*Keywords:* slope stability, Crotone Basin, numerical analysis, Ionian area, Pliocene-Pleistocene.

The study area is part of the geological unit known in scientific literature as "Crotone Basin", which represents the exposed part of a Neogene to present sedimentary basin developed along the Ionian Sea (e.g., Zecchin et al., 2012; 2020) located in the eastern part of the Calabrian Arc, Southern Italy (Mellere et al., 2005). The tectonic evolution of the area is linked to the spreading of the Tyrrhenian backarc Basin during late Serravallian and the subduction of the Ionian lithosphere below the Calabrian Arc (Zecchin et al., 2020) then, the slab rollback phenomena caused a rapid migration of Arc generating an extensional and transtensional regime (Massari et al., 2010). The sequence of events was accompanied by sediment accumulations that recorded important events alternated and occurred through time like subsidence, extension and uplift phenomena (Mellere et al., 2005). The study area is marked by a superimposition of calcarenite terraces (Pleistocene-Holocene) over the Cutro Clay Formation (late Pliocene-earliest Pleistocene). This stratigraphic succession experienced processes of gravitational instability, such as relevant phenomena of coastal erosion which contribute to the rapid retreat of slopes.

Slope stability analyses of two coastal areas of high historical and archaeological value, which show similar types of phenomena due to the same litho-stratigraphic succession, have been carried out through both Limit Equilibrium Method (LEM) and Finite Element Method (FEM) and the results have been compared. Modelling was conducted considering also residual parameters but the analyses showed that the slopes were already unstable in peak conditions. The water table is a relevant and influential factor in the stability analysis of these types of slopes.

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# Coastal cliff retreat and landslide processes: a preliminary quantitative characterization at Portonovo-Trave cliffs (Conero, Ancona, Italy)

Fullin N.*, Duo E., Fabbri S., Ghirotti M. & Ciavola P.

Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* fllncl@unife.it

*Keywords:* cliff erosion, landslide.

Coastal cliff erosion process is the result of the interplay of many drivers: subaerial, marine or endogenic, including rock control in terms of both lithology and structure. Today, the proper quantitative characterization of such a complex process still represents a scientific challenge, despite its importance for hazard and risk assessments, and considering the future projections of increased erosion due to relative sea level rise (Alberti et al., 2022).

Due to this complexity, the identification of the mechanisms and processes underlying cliff erosion-scale slope instability requires a comprehensive analysis. The improvement of remote sensing techniques has enhanced the amount and quality of geological data that can be collected at various scales (Gómez-Pazo et al., 2021), providing optimal approaches for studying coastal cliff erosion.

In this work, the cliff-top retreat rate was assessed on cliffs composed by Neogenic soft rock (flysch, molasse) between Portonovo and Il Trave (Ancona, Italy). Archived orthophotos spanning 1978-2021 were imported in GIS environment and processed with DSAS (Digital Shoreline Analysis System) tool (Himmelstoss et al., 2018). An erosion up to 40 m (RMSE = 5 m) was found in the area of Il Trave, for the analyzed forty-year period.

The DSAS-based results were crosschecked with a morpho-dynamic evaluation based on the analysis of a DEM of Difference (DoD) between a 2012 Lidar (provided by the Regione Marche) and a DEM obtained from a UAV survey (September 2021). Results suggested that those sectors affected by higher erosion rate, also experienced volumetric variation, observable more in the depletion at the cliff-top than in the upgrowing on the cliff-base.

This first characterization of coastal cliff dynamics represents the starting point for future quantitative assessment of spatial/temporal erosion-landslide processes in the area, involving also mechanical characterization of the rock mass, landslide analyses and evaluation of marine forcings.

Alberti S., Olsen M.J., Allan J. & Leshchinsky B. (2022) - Feedback thresholds between coastal retreat and landslide activity. Eng. Geol., 301, 106620.

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# Conditioning factors of high mountain landslides: geological constrains and influences of permafrost degradation in the Italian Alps over the last two decades

Guerini M.*[1], Giardino M.[1], Paranunzio R.[2], Nigrelli G.[3], Turconi L.[3], Luino F.[3] & Chiarle M.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Scienze dell'Atmosfera e del Clima, CNR, Torino. [3] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Torino.

*Corresponding author e-mail:* michele.guerini@unito.it

*Keywords:* landslide, geology, permafrost.

The Alpine environment is extremely vulnerable to natural hazards, particularly in this phase of global warming. In recent years, many researches have focused on the consequences of climate change on different elements of the Alpine environment (e.g., Nigrelli & Chiarle, 2021), but there are relatively few specific studies in which high altitude landslides are analysed as climate indicators.

This work focuses on conditioning factors of high mountain landslides through the analysis of a dataset of 392 slope instability events documented from 2000 to 2020 at above 1500 m a.s.l. in the Italian Alps (Guerini et al., 2021). Dataset analyses aimed at recognising spatio-temporal trends of slope failure occurrence and at investigating diverse landslide susceptibility of slopes with different characteristics, with a focus on geological constraints and permafrost degradation. Spatial and temporal analyses were performed by using GIS software and by applying non-parametric inferential statistic tests.

The outcomes of these analyses show a positive linear trend in the annual frequency of slope instability events throughout the Italian Alps during the last 20 years, and the increase is faster in the 2011-2020 period compared to the 2000-2010 period. In this respect, the mirroring of the trends in the landslide series with the trends in the temperature series is noticeable. The results also show an increased landslides susceptibility within north-facing areas above 2000 m a.s.l. and a clear upward trend in the number of events on permafrost affected slopes, compared to a substantially stable number of documented events on slopes without permafrost.

Contrary to expectations, the analysis of landslide distribution within different lithotypes shows a relative majority of landslides occurred within rocks classified as "medium resistant", also a larger number than in low resistant or soluble rocks. Possible explanations include that, in a periglacial environment, the presence of permafrost may modify the strength characteristics of rocks. Therefore, the belonging of a certain lithotype to a certain resistance class in general could be less discriminating for slope stability than other specific parameters.

The present study provided further evidence of a correlation between climate change, permafrost degradation and increased natural instability at high altitudes. Nevertheless, in a phase of a very fast climate change, further studies are needed to deepen knowledge on predisposing instability factors of high-altitude slopes, allowing better definition of hazard scenarios.

Guerini M., Giardino M., Paranunzio R., Nigrelli G., Turconi L., Luino F. & Chiarle M. (2021) - Slope failures at high elevation in the Italian Alps in the period 2000-2020. PANGAEA. https://doi.org/10.1594/PANGAEA.931824.

Nigrelli G. & Chiarle M. (2021) - Evolution of temperature indices in the periglacial environment of the European Alps in the period 1990-2019. J. Mt. Sci., 18, 2842-2853.

# Identification and characterization of landslide processes in a Mediterranean catchment: The Val d'Arda case study (Northern Apennines, Emilia-Romagna, Italy)

La Licata M.*[1], Bettoni M.[1-2], Bernini A.[1], Bosino A.[3] & Maerker M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Department Engineering for Crop Production, Leibniz Institute for Agricultural Engineering and Bioeconomy, Potsdam (Germany). [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* manuel.lalicata01@universitadipavia.it

*Keywords:* landslides, inventory map, Northern Apennines.

The Emilian Apennines (Northern Apennines) are among the most landslide-prone areas in Italy, due to the prevalence of weak rocks formations, i.e., arenaceous-pelitic flysch and chaotic mélanges. In the Quaternary, landslide processes have been a major geomorphic factor in shaping the landscape of this area. Indeed, most of the landforms are associated with complex large-scale earthflows, mostly developed after the Last Glacial Maximum (Bertolini et al., 2017). Since these ancient wide bodies have to be considered as active in the actual morphoclimatic conditions, their reactivation represents a potential risk for human settlements and urban management (Bertolini & Pizziolo, 2008). Their identification and localization are essential for both the territorial planning and prevention strategies as well as for the general comprehension of the landscape evolution under climatic changes. In this study we investigated the location, extent and characteristics of the landslides in the Val d'Arda, which is an intensively anthropized landslide-prone area in the Emilian Apennines. We applied traditional geomorphological field mapping together with photointerpretation, remote sensing and the analysis of pre-existing databases developed by regional authorities in order to produce a landslide inventory map. Afterward, we analysed the morphological features and the temporal evolution (along a thirty-year period) of some of these landslides by means of high-resolution photogrammetry and the analysis of historical orthophotos. Our results revealed that the study area is highly diversified in terms of type and extent of mass movement processes. Most of the ancient landslides can be classified as complex slide-flow type, which is characterized by a large crown with a relatively steep slide scarp, a narrower middle flow area and a wide basal toe with low slope inclinations. Some of these landslide bodies experimented partial reactivations during the observed time period and, in some cases, show evidence of retrogressive evolution. Moreover, mass movements also include first-time failures, whose morphogenesis, extent and location is mainly controlled by the lithological context and topography, e.g., shallow landslides, mudflows and soil creep on gentle slopes consisting of tectonized clays ("Argille Scagliose" Auctt.) at lower elevations, as well as rock/debris falls and debris flows on very steep slopes made up of flysch. Landslide dams and barrier lakes have also been observed. Our study illustrates the complexity to map and characterize accurately interwoven landslide processes and their dynamics (in landscapes with high landslide hazard). Further analysis will be carried out in order to investigate landslide susceptibilities and the role of different environmental variables as control factors.

Bertolini G. & Pizziolo M. (2008) - Risk assessment strategies for the reactivation of earth flows in the Northern Apennines (Italy). Eng. Geol., 102, 178-192.

Bertolini G., Corsini A. & Tellini C. (2017) - Fingerprints of Large-Scale Landslides in the Landscape of the Emilia Apennines. In: Soldati M. & Marchetti M. Eds., Landscapes and Landforms of Italy. World Geomorphological Landscape., 215-224. Springer.

# The geomorphological record of long runout landslides in the Solar System

Magnarini G.*

Natural History Museum, London (UK).

*Corresponding author e-mail:* giulia.magnarini@nhm.ac.uk

*Keywords:* long runout landslides, planetary geomorphology.

The ubiquity of long runout landslide deposits in the Solar System holds record of catastrophic events, which mechanics is not fully understood, as many fundamental aspects remain unresolved: the effect of gravity and volume; the role of fluids; the origin of their high velocity; the formation and preservation during emplacement of morphological features and internal structures.

On Earth, understanding the hypermobile behaviour of long runout landslides is critical in order to define risk mitigation strategies. However, on our planet, the loss of the geomorphological record of long runout landslides due to fast erosion rates and active geology can lead to the misinterpretation and underestimation of the process. Therefore, the existence of well-preserved extra-terrestrial long runout landslide deposits can be used to obtained geomorphological information not always available on Earth.

This talk will focus on the importance of comparative planetary geology in studying long runout landslides, in the attempt to link their morphology and internal structures to the mechanisms involved during their emplacement. Using several case studies from Mars, Earth, and the Moon, the talk will discuss: a) longitudinal ridges, distinctive morphological structures of long runout landslides, and their scaling relationship with the thickness of the deposit, suggesting the existence of a scale- and environment-independent formation mechanism (Magnarini et al., 2019; 2021a; 2021b); b) the presence of megablocks and the preservation of the original slope stratigraphy within the deposit, suggesting stress fluctuations and lack of turbulence during the landslide emplacement (Magnarini et al., 2021a).

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# Molards, a geomorphological marker of permafrost degradation and landslide dynamics in cold environments

Morino C.*[1], Conway S.[2], Deline P.[1], Magnin F.[1], Noblet A.[2], Svennevig K.[3], Lucas A.[4], Strom A.[5], Dunning S.[6] & Hermanns R.[7]

[1] Laboratoire EDYTEM, Université Savoie Mont Blanc, UMR-CNRS 5204, Le Bourget du Lac (France). [2] CNRS UMR 6112 - Laboratoire de Planétologie et Géosciences Université de Nantes (France). [3] Geological Survey of Denmark and Greenland, Copenhagen (Denmark). [4] CNRS UMR 7154 - Institut de Physique du Globe de Paris, Université de Paris (France). [5] Geodynamics Research Center, JSC Hydroproject Institute, Moscow (Russia). [6] School of Geography, Politics and Sociology, Newcastle University (UK). [7] Geohazards and Earth Observation, Geological Survey of Norway, Trondheim (Norway).

*Corresponding author e-mail:* costanza.morino@gmail.com

*Keywords:* molards, landslide, permafrost.

This study explores the possibility to use the landform called "molard" as a marker of permafrost degradation in arctic, sub-arctic and mountain environments. Molards in permafrost terrains are cones of loose debris that result from thawing of blocks of ice-rich sediments mobilised by a landslide. Such molards cannot form without ground ice, which cements the source material, allowing it to behave like solid during transport. Once the ground ice has thawed, its cementing action is lost, inducing collapse of the material into molards. We reconstruct the permafrost, geological, geographical settings of 52 landslides characterised by molards, compiling data available in the literature. We apply quantitative terrain analysis using high-resolution DEMs to describe, quantify and compare their topographic characteristics, morphometry, dynamics, and molards distribution and density. Our results show that landslides with molards can occur in terrains characterised by various permafrost distribution, from continuous to isolated. These landslides show a variety of morphological and morphometric characteristics, source materials often composed of loose debris or rheologically weak bedrock, and their molard distribution reflects the dynamics of the landslide. In this study, we show that molards are an indicator landform of permafrost degradation under different permafrost, geomorphological and geological conditions, and that they can be used to decipher landslide dynamics in cold environments.

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# Extreme events and criticalities induced on provincial road n° 18 in November 2021 - Management of emergencies for landslides and gravitational phenomena - Assessment of hydrogeological risk and residual hydraulic functions of road crossings - Province of Southern Sardinia - Italy

Mureddu A.*

Provincia del Sud Sardegna, Carbonia (SU).

*Corresponding author e-mail:* mureddu.alessio@tiscali.it

*Keywords:* landslide, hydrogeological risk, hazard zoning.

On the days of 14, 15 and 16 November 2021, a Mediterranean cyclone hit the Sardinia region and in particular the territory of the Province of Southern Sardinia, with storms of extraordinary intensity, especially in localized areas that were hit by major showers. The storms caused the sudden increase in the flows of the streams, with consequent flooding and serious damage to the road infrastructure network. In areas characterized by particular hydrogeological vulnerability, numerous landslides and landslides occurred with the pouring of hundreds of cubic meters of material onto the road platform. Particular intensity in the damage caused was found on the road network of south-eastern Sardinia, in the Sarrabus region, in correspondence with provincial roads n° 17, n° 18, n° 19 and n° 20.

Right on the provincial road n° 18 the following occurred: numerous phenomena linked to gravitational instability and landslides between Km 2+500 and Km 10+700; the collapse of a transversal crossing at Km 22+700 and the partial failure of two others at Km 21+500 and Km 11+750.

In order to protect public safety, the Province of Southern Sardinia has recognized the state of natural disaster by declaring it administratively with Provincial Council Resolution No. 127 of 18.11.2021. In order to protect public safety and implement all the necessary interventions capable of remedying dangerous situations, an ordinance (No. 15 of 17.11.2021) has been issued for the closure and regulation of traffic on the sections in crisis.

Various inspections were carried out by the technicians of the province that and identified various professionals and road contractors companies capable of managing existing emergencies, as well as planning the interventions necessary to restore functionality and study the problems that arose. At the same time, overall studies were launched aimed at identifying possible interventions to reduce the hydrogeological hazard of the area.

The SP18 is characterized by a geological structure headed by granite lithologies of the Hercynian age, with complex variations of facies and series of acid and basic phylonian intrusions, which respectively identify massive lithotypes and more resistant to alteration in the first case, while the basic veins they are easily eroded by surface runoff and identify concave morphologies in correspondence with the road fronts projecting onto the road.

At present, just four months after the succession of the calamitous events, the first resources in the budget have been identified, three interventions have been planned, designed and contracted for the restoration and improvement of the hydraulic risk in correspondence with the three idraulic crossings, of which one already executed and functional, and the other two in the execution phase.

Simultaneously with these first interventions, a first estimate of the costs for the search for funding to be identified in the short-medium term was carried out, involving the authorities responsible for planning the resources regarding M.I.T., “FSC 2021-2027” and P.N.R.R. funds.

The interventions on the landslide area of the SP18 are being defined, with a zoning of the areas by lithotechnical type of hazard, the overall estimate of the costs required for various types of intervention, capable of reducing the causes of danger as much as possible , through reshaping and geomorphological re-profiling of embankments, improvement of drainage properties upstream and removal of runoff water from embankments, installation of retaining walls and adhering networks, as well as localized displacements of the road axis.

# Geomorphological instability and maintenance management of road fronts along SSPP n° 83 and n° 108. Short and medium term planning and management of gravitational phenomena - Interventions on rockfall barriers and adherence containment networks - Province of Southern Sardinia - Italy

Mureddu A.*

Provincia del Sud Sardegna, Carbonia (SU).

*Corresponding author e-mail:* mureddu.alessio@tiscali.it

*Keywords:* landslide, hydrogeological risk, hazard zoning.

The provincial road n° 83, located in the Iglesiente area, is a very important road on the west coast of Sardinia, the only road route capable of connecting the inhabited centers of Fluminimaggiore, Buggerru and Nebida with the neighboring areas of Sulcis and of Guspinese.

Most of the route has a "half-slope" profile, with various areas characterized by long-standing problems linked to gravitational phenomena and areal landslides that occur in an almost cadenced manner. The main risk mitigation and safety measures carried out in recent decades have involved the installation of passive rockfall barriers and retention adherence nets, capable of allowing road management with a good degree of safety.

From a geological point of view, most of the lithologies affected by falling material processes are headed on slope deposits and accumulation glacis, subject to continuous alteration phenomena of the rocks constituting the "Paleozoic Base" that structures the area. The outcrops of metarenaries, metasyltites and metacalcari of the Nebida and Gonnesa Formations are subject to alterations and decay due to the strong action of westerly winds, loaded with marine spray, as well as from erosive phenomena linked to the action of rain and the consequent surface runoff, capable of destabilizing the foot of the slopes and causing localized landslides.

The provincial road n° 108, the main interconnection road axis between the town of the Municipality of Portoscuso - Portovesme industrial port and the municipalities of Gonnesa and Iglesias, is periodically subject to gravitational phenomena linked to collapses and rolling of materials coming from the long decay the section with a "half-ridge" profile.

Along the unstable fronts, over time, adhering containment networks have been put in place several times, capable of locally containing the falls of coarse material, albeit periodically subject to maintenance actions in cases of the formation of important accumulation pockets.

The geological nature of the materials found "in situ" is due to the deposition of powerful pyroclastic and ignimbritic banks genetically linked to the Calcalcaline Oligo-Miocene Volcanic Cycle, which have led to the current discovery of massive competent stone structures, interspersed with localized layers of stratigraphy subject to incipient alteration, from which the phenomena of instability of the rocky fronts jutting out onto the underlying road artery begin. The cause of the alteration manifestations is similar to those persisting on the SP83, that is, strong wind pressure, rich in coastal saline spray, and persistent erosive action carried out by the rainy manifestations and surface runoff waters. The latter persist even more in depth, with spring manifestations that sometimes come to light, thus identifying further areas of triggering of gravitational phenomena.

Through new financial resources that have become available in recent years, the Province of Southern Sardinia is carrying out a more in-depth overall study of the phenomena in progress, in order to further improve the performance of the structures installed. The latter, in recent years, have been manifesting serious problems related to their functionality, probably also due to the near conclusion of their "life cycle". To this end, interventions aimed at replacing barriers and networks are being planned, as well as identifying solutions capable of further mitigating the causes that influence the processes of decay, so as to be able to intervene to a lesser extent on the effects: at the same time evaluating monitoring methods capable of implementing those currently used.

# Evaluation of historical landslide activity (1954-2018) in relation to land-cover changes in the Sillaro River basin, Northern Apennines

Pittau S.*[1], Rossi M.[2] & Brardinoni F.[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Perugia.

*Corresponding author e-mail:* sharon.pittau2@unibo.it

*Keywords:* landslides, historical landslide activity, land-cover changes.

Drainage basins of the Northern Apennines, and in particular those that have developed on the Allochthonous Ligurian Complex, are dominated by intense landslide activity operated by earth slides and flows, and by widespread badland erosion. Today, a long history of deforestation and land cover changes has generated a landscape with sparse, coppice managed, forest cover. In these settings, quantitative knowledge on landslide occurrence in relation to inherited and ongoing land cover changes is limited, hence preventing suitable strategies of land management. To address this gap, we conduct a multi-temporal inventory in clay-dominated terrain of the Sillaro River basin (139 $km^2$) across four lithologies: claystones of the Ligurian (L-claystones), Epiligurian (E-claystones), and Padano-Adriatic (PA-claystones) Units, as well as marls & sandstones of the terrigenous flysch. Historical landslide activity, investigated by visual inspection of 12 sequential aerial photo sets between 1954 and 2018, is quantified in terms of specific landslide density and specific landslide area. Landslides are classified according to movement type (earth slide, flow and complex) and temporal nature (episodic and recurring). Land use change is evaluated across four periods: pre 1955, 1955-1976, 1977-1996, and 1997-2018. To account for the historical variability of meteorological forcing, we examine three precipitation indices: (i) the annual total precipitation (PRCPTOT); (ii) the annual maximum daily precipitation (RX1day); and (iii) the precipitation fraction (R99pTOT) due to extremely wet days.

Results show that recurring landslides prevail over episodic counterparts, and that recurrence at a site can reach a maximum of 9 times across the 12 photo years examined. Landslide activity is highest in claystones and landsliding appears strongly controlled by lithology. Terrain morphometry and lithology affect landslide lengths and areas, whereas land cover appears to play a secondary role in landslide geometry, except in arable crops and meadows where landslides are smaller. Preliminary findings suggest complex interactions between landsliding and land cover types, modulated by slope gradient and lithology. In this sense, further analysis is in progress. Overall, landslide activity is highest between 1997 and 2018, during a period of land-cover stability, where a decrease in total precipitation and increase of extreme events is recorded. In this context, we found high correlation between landslide activity and specific precipitation indices. In particular, badlands, where landslide activity is dominant, resulted being the most sensitive sites to changes in precipitation.

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# Geomorphic impacts of connected debris flows on river corridor during an extreme storm: a case study in the Italian Alps

Scorpio V.*[1], Steger S.[2], Comiti F.[3] & Cavalli M.[4]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Istituto per l'osservazione della Terra, Eurac Research, Bolzano. [3] Facoltà di Scienze e Tecnologie, Libera Università di Bolzano. [4] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Padova.

*Corresponding author e-mail:* vittoria.scorpio@unimore.it

*Keywords:* debris flow, flood, sediment connectivity.

Debris flows and landslides are the most effective sources of sediment supply to the fluvial system in mountain environments. Large amounts of sediment are eroded and transferred from hillslopes to the channels in a short time, during high-intensity precipitation events. In this context, the coupling of hillslopes processes with the channel network is of great importance for river dynamics, as hillslopes that frequently produce debris flows are not necessarily connected to the channel network while structurally connected areas may not produce debris flows, during extreme events.

Results of a study carried out in the Stolla Creek catchment are presented (40 km$^2$ drainage area, Eastern Italian Alps). The catchment was affected by an extreme precipitation in August 2017 (Scorpio et al., 2022). The geomorphic effects of the storm were investigated in the main channel and over the entire basin to assess the: i) predisposing factors for debris flow initiation; ii) quantification of channel morphological changes; iii) impacts of the lateral sediment connectivity to the channel response. Finally, joint debris flow connectivity-susceptibility map that allows identifying zones that are differently relevant in terms of debris flow susceptibility and connectivity was proposed.

A multi-methodical approach was applied. Hillslope and channel processes were mapped and characterized by using multitemporal orthophotos and Digital Terrain Models. Debris-flow connectivity to the main channel was derived by integrating field evidence and GIS-based analyses. Finally, a combined debris flow release connectivity-susceptibility map was obtained by applying a data-driven approach based on statistical learning.

Results show that the flood was caused by rainfall with a short duration (6 h) and a rainfall intensity exceeding 45 mm/h. More than 600 debris flows were triggered in the whole basin. Connected debris flows released large volumes of sediments leading to profound morphological changes in the fluvial corridor. The Stolla channel experienced widening (width ratio between 1.3 and 4.9) accompanied by aggradation up to 1.2 m or incision down to 2.2 m. Nevertheless, only limited volumes of sediments were exported from the catchment outlet, due to the very short duration of the flood. Landforms distribution in the catchment – the structural connectivity at the basin scale – strongly controlled the sediment cascades linking hillslopes processes to the channel. The modelled connectivity-susceptibility map exhibited a very high spatial agreement with the debris flow observations, confirming that the proposed methodology can be applied to support regional-scale hazard assessments or sediment management plans.

Scorpio V., Cavalli M., Steger S., Crema S., Marra F., Zaramella M., Borga M., Marchi L. & Comiti F. (2022) - Storm characteristics dictates sediment dynamic and geomorphic changes in mountain channels: a case study in the Italian Alps. Geomorphology, 403, 108173.

# Triggering conditions and propagation of the 2019 Palma Campania landslide: implication for residual hazard estimation

Sepe C.[1-2], Calcaterra D.[1], Di Martire D.[1], Fusco F.[3], Tufano R.*[1], Vitale E.[1] & Guerriero L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Ingegneria Civile e Meccanica, Università di Cassino e del Lazio Meridionale. [3] Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano.

*Corresponding author e-mail:* rita.tufano@unina.it

*Keywords:* debris flow, pyroclastic deposits, hydrological modeling.

An intense rainfall event occurred on December 19th, 2019, characterized by ~100 mm of rainfall in 20 hours, triggered a flow-like landslide along the Crocelle slope in Palma Campania (Campania region, Italy). Due to its limited magnitude and the presence of mitigation measures at the slope foot, no victims or damage to human settlements were recorded. However, this event represents just one of the repeated fast-moving rainfall-triggered landslides which involve pyroclastic soils in peri-Vesuvian areas. Indeed, a previous higher-magnitude landslide event occurred in February 1986 (Guadagno et al., 1988), along the western sector of the same slope, resulted in eight casualties and settlement destruction.

In this framework, an analysis focused on understanding the characteristics of the 2019 landslide was performed also considering the need to evaluate the residual landslide hazard for this recurrent-landslide site. For such purpose, a coupled analysis of landside initiation and propagation was carried out on the basis of: i) field survey, ii) geotechnical laboratory testing on soil samples collected in the source area, iii) rainfall analysis, iv) hydrological modelling and slope stability analysis, and v) propagation modelling.

Firstly, the engineering-geological slope model of the source area was reconstructed and the main landslide features were deciphered through in situ observations. Rainfall conditions for landslide initiation were analysed through a statistical analysis to derive return periods of rainfall maxima for specific durations. Hydrologic modelling and slope stability analysis allowed to identify timing and location of potential slope instabilities and to decipher characteristics of triggering rainfall in terms of intensity and duration. Obtained results highlight that the simulated rainfall is characterized by a considerably lower return period in comparison to that estimated by probabilistic modelling of maxima, indicating that the landslide initiation is not simply related to the extreme character of rainfall. The propagation model shows that the landslide mass moved from the detachment to the deposit area with an estimated maximum velocity of ~10 m/s, obtaining good correlation between estimated and measured thickness of landslide deposits. Finally, by comparing landslide characteristics with that of the 1986 event, significantly different in terms of magnitude (i.e., volume), it appears that the occurrence of multiple events along a slope might induce a decrease in residual hazard related to a reduction in the expected magnitude of the prospective events and of their frequency due to i) a time-related reduction of available materials along a slope repeatedly affected by landslides and ii) a potential difference behaviour of primary deposit (involved by the 1986 event) compared to remoulded ones (involved by the 2019 event).

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# Assessment of the relation between structural and morphological setting as condition for coastal slope stability

Torre D.*[1], Piacentini D.[2] & Menichetti M.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* d.torre@campus.uniurb.it

*Keywords:* structural geology, coastal slope, Central Adriatic coast.

The influence of the structural and morphological setting along coastal slopes is a well-known topic. In particular, the relationship between slope and bedding attitude as well as fracture spatial distribution play an essential role in the evaluation of the slope morphodynamic evolution within large areas. The proximity of the sea, the high slope inclinations and situationally the occurrence of landslides are some of the difficulties encountered in studying coastal slope, making it necessary to support the traditional field surveys with remote sensing and geomorphometric techniques. The use of spatial analysis and in particular the assessment of morphometric variables, could be a valid approach to investigate coastal slope involved by gravitational processes (Piacentini et al., 2021) and could be integrated with geometric and spatial analysis of joints. This work presents a multi-disciplinary approach to determine the predisposing role of the bedding and rock mass discontinuities in controlling the morphoevolution of rocky coasts.

Previously proposed methods, (Grelle et al., 2011; Santangelo et al., 2015; Francioni et al., 2018), make it possible to carry out a semi-quantitative analysis to identify structural control domains in areas with uniform lithologies. We propose to integrate these approaches with the acquisition, by means of geo-structural, geomorphological and UAV (Unmanned Aerial Vehicle) surveys, of geometric and spatial discontinuity data, integrating values of geomechanical parameters gathered on different lithologies (Uniaxial Compressive Strenght, Schmidt Hammer, Leeb hardness) and performing a kinematic analysis of the slopes.

The proposed approach has been tested on the western coastal sector of the Central Adriatic Sea (Italy) consisting of several lithologies from Cretaceous limestones and marls to the Upper Messinian sandstones and marls and interested by several gravitational processes. Highly detailed surveys using a low altitude flight platform have been carried out to obtain a 3D outcrop model to be analysed in pair with a Digital Terrain Model (DTM) derived by aerial LiDAR (Light Detection and Ranging) data, with a ground resolution of 2x2 m. The 3D model allows to identify several joint families, to implement them to those measured in the field, and successively to compare these located sets with two morphometric variables (Slope and Aspect) computable by spatial analysis in Geographic Information System (GIS) software. The relative relationship between joint families and slope geometry highlights different sectors that can be considered kinematically stable or instable for planar and wedge sliding. The comparison procedure has been implemented in a Python script (ArcPy), which allows a semi-automatic application of the repeated calculation procedures required. The fine-tuned calculation procedure represents a useful tool to provide preliminary information when assessing the likely hazard of coastal instability.

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# A multidisciplinary approach for the characterization of a rockfall-affected river catchment

Traversa G.*[1], Fugazza D.[1], Manara V.[1], Stucchi L.[2], Bocchiola D.[2], Scaioni M.[3], Maugeri M.[1], Diolaiuti G.A.[1] & Senese A.[1]

[1] Dipartimento di Scienze e Politiche Ambientali, Università di Milano. [2] Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano. [3] Dipartimento di Architettura, Ingegneria delle Costruzioni e Ambiente Costruito, Politecnico di Milano.

*Corresponding author e-mail:* giacomo.traversa@unimi.it

*Keywords:* Mera River, Pizzo Cengalo rock avalanche, debris flow.

Italy and Switzerland geographically share important water resources, including the Mera catchment area, a significant asset for economic-productive purposes and a context of considerable environmental importance, as it hosts several Natura 2000 sites. One of the projects developed in order to contribute to a more sustainable management of these resources is the GERIKO-MERA interreg project. Specifically, this project aims to carry out shared activities in support of a common strategy (i.e., a technical-administrative-managerial collaboration), which can be replicated in other similar contexts, thus determining a significant change in the management of common water resources, which currently have different rules and operating methods in the two states and an ineffective communication activity. Particular attention is given to the theme of changes in Mera River geomorphology due to the occurrence of several rock slope collapses (e.g., in 2013 and 2017) of Pizzo Cengalo (Bregaglia Valley, Swiss Alps). In fact, the debris flow affected the solid transport of the river (Walter et al., 2020). To better study fragile and landslide-prone mountain areas such as the Mera catchment area, it is crucial to apply an inter- and multi-disciplinary approach such as the one developed within the GERIKO-MERA interreg project. In order to evaluate the actual conditions of the river, we recently performed several surveys by means of an unmanned aerial vehicle (UAV) both in some selected areas along the river and over the area affected by the rock fall. In addition, we took advantage from the orthophotos available from the Lombardy region geoportal, acquired in the years before and after the rock avalanche. Moreover, in order to develop a common management of water resources but also to better monitor the territory and thus prevent possible rock slope collapses in the future, it is very important to know the spatial and temporal variability of precipitation in the Mera catchment area. In particular, we developed a methodology to obtain high-resolution daily precipitation series from the beginning of the 19$^{th}$ century. Specifically, the developed methodology is based on the well-known anomaly method based on the independent reconstruction of the climatologies (i.e., the climate normals over a standard reference period) and the anomalies (i.e., the deviations from the climatologies with respect to the same baseline period).

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# Hydrologic and erosion response in burned watersheds (Piedmont, western Italian Alps)

Vacha D., Mandrone G.* & Chicco J.M.

Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio, Università di Torino.

*Corresponding author e-mail:* giuseppe.mandrone@unito.it

*Keywords:* wildfire, landslide, soil erosion, GIS.

Post-wildfires geological hazards are an emerging problem for a number of different environments, including areas such as the Alpine Region where the effects of climate change are showing up in the form of unprecedented forest fires, heatwaves, droughts and extreme rainfall events. The risk connected with post-fire processes such as debris-flows and flood-type events is due to the modification of the hydrological properties of the affected watersheds, because of the litter and vegetation removal, the ash deposition and the alteration of the physical properties of soil and rocks (Parise & Cannon, 2012). Erosion and runoff rates increase due to the diminished capacity of rainfall interception by the tree canopies, shrubs and grass. The surface runoff may concentrate in hollows and low order channels carrying the eroded sediments in the waterways, eventually exerting a strong erosive action at the expense of the riverbed sediments with a consequent "in mass" failure. All of these processes can lead to sediment concentration to levels associated with debris flows. (Tang et al., 2019). Given the complex interaction of this multi-hazard chain and the not-straightforward link between the mitigation actions taken and their effectiveness, decision-makers and local authorities might struggle to have adequate decision support allowing for more robust data and comprehensive risk assessment tools. In fact, it is quite common to use the available financial resources to solve localized problems in a post-event scenario, lacking tools able to quantify the cost-benefit ratio as well as to prevent hazards mitigating the related risks. As a result of the modification induced by the wildfires, the increase in susceptibility of the above described events, lacks of available models apart from a few examples, such as in the USA and Australia.

Tests of a modified version of the RUSLE, on GIS, to quantify the post-fire erosive phenomena for a case study in the NW Italian Alps are here presented. By taking advantage of high-resolution rainfall series and data deriving from field surveys, results highlight the marked increase (more than 20 times) in erosion rates, quantified by expressing both the EI (erodibility index), the A (monthly soil loss) and the SL (monthly sediment loss) rise. April, May and June represent the months with a larger share of the total quantities. This is a consequence of the noticeable increase of the Erodibility Index EI, which for the post-fire scenario is more than one order of magnitude higher than the pre-fire one.

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# S21.

# Monitoring and sustainable management of natural and artificial cavities: a contribution toward mitigation of the risk from underground processes

*Conveners & Chairpersons*

*Mario Parise (University of Bari)*

*Bartolomeo Vigna (Politecnico of Torino)*

*Alberto Cina (Politecnico of Torino)*

*Cristina Carbone (University of Genova)*

*Valentina Balestra (Politecnico of Torino)*

# Sediment and water geochemistry shedding light on ecohydrology and anthropogenic impacts in Pertosa-Auletta Cave

Addesso R.*[1], De Waele J.[2] & Baldantoni D.[1]

[1] Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università di Salerno, Fisciano (SA). [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* addros04@gmail.com

*Keywords:* cave ecosystems, anthropogenic impacts, Pertosa-Auletta Cave.

Caves are only seemingly confined ecosystems, as infiltrating waters carry allochthonous materials (such as sediments, organic matter, microorganisms…) through the vertical profile of the soil and the rock fractures from the surface to the hypogean oligotrophic environment, representing an important energy and nutrient source. Studying waters and sediments permits to highlight the cave ecosystem geochemistry and ecohydrology, to understand the biogeochemical processes occurring in the unsaturated zone, but also to assess potential anthropogenic impacts altering their natural equilibrium (Fairchild & Treble, 2009; Muri et al., 2013; Fehér et al., 2016).

In this study, we provide a comprehensive chemical characterization of the dripping and river waters, collected seasonally, during one year, from the four main trails with a different fruition and natural conditions (Tourist, Fossil, Paradise and Active) in the Pertosa-Auletta Cave (Campania, Italy). The geochemical features of clastic sediments from the same areas of the caves were also investigated.

The chemical analysis of the cave waters showed differences among the investigated trails; in the Fossil path, waters appeared to be enriched in P and N compounds probably related to bat guano, without excluding a pollution from the surface related to farm fields above. The seasonal dynamics revealed the highest amount of several elements (Cd, Co, Cu, Mn, Mo, Ni, Pb, Ti, and Zn) in summer, probably due to the dry weather reducing the dilution effect. Organic C, transported by water through leaching from the top soil, constitutes almost the entire C pool. Moreover, drip and river waters did not exhibit relevant differences, showing high concentration of Ca, because of the contact with the calcareous and dolomitic hostrock in which the cave opens. This was also true for the analyzed clastic sediments, which are mainly constituted of carbonate minerals. They showed variable chemical compositions, except for one sample, displaying the highest amount of organic matter and of C, Cu, Mo, N, P, Pb, S and Zn concentrations, visibly contaminated by bat guano, demonstrating the important organic supply delivered to the cave environment by bat colonies (Addesso et al., 2022).

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# Multi-disciplinary studies at an artificial cavity of historical value in the Massafra territory (Taranto province, Apulia)

Andriani G.F., D'Angeli I.M., De Leo D., Diprizio G., Liso I.S.*, Marsico A., Mastrangelo G., Quercia F., Rigamonti S., Romano G., Siniscalchi A. & Parise M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* i.serena.liso@gmail.com

*Keywords:* artificial cavity, geo-electrical survey, laser scanning.

As in the rest of the area around the Gulf of Taranto, the territory of Massafra is characterized by deep valleys (locally called *gravine*) incised in carbonate rocks. This area was deeply interested by development of the rupestrian civilization (Fonseca, 1980), which resulted in many cavities excavated by man, and used for a variety of purposes, including civil settlements and worship sites (Parise et al., 2013). The main *gravine* at Massafra are San Marco (depth 30 m), cutting the town in two, and Madonna della Scala (depth 40 m), outside the inhabited area. This latter host hundreds of cavities of variable size excavated in the calcarenite rock mass (Caprara & Dell'Aquila, 2009). The most famous is definitely Farmacia del Mago Greguro, a complex cave formed by several chambers on the *gravina* left wall. At this site, multidisciplinary researches were carried out in order to evaluate the main characters of the subterranean system and its stability conditions. The geological surveys allowed to identify two calcarenite facies, on the basis of their stratigraphic features and of the physico-mechanical parameters, with the first characterized by finer grain size and lower strength values, and the second (making the pavement of the cavity), coarser and with higher strength. These facies were analyzed in laboratory through geotechnical tests, performed both in natural and saturated conditions. The whole cavity complex, and the nearby Ciclope Cave, were scanned by means of the Terrestrial Laser Scanner. After the field survey, the post-processing on the point clouds was performed in order to built 3D model of cave complex. Three geo-electrical surveys were performed within the cavity and at the top of the hill. In the cave, in order to preserve the natural pavement, cables for marine surveys were used. Further, geomorphological analysis and a detailed characterization of the discontinuities (outside and within the cave) were carried out to collect additional information on the likely failures in the rock mass. All these data represented the backbone for successive engineering geology analysis, aimed at evaluating the stability at the site.

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# Microplastic pollution in show cave sediments

Balestra V.* & Bellopede R.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* valentina.balestra@polito.it

*Keywords:* microplastic pollution, show cave, karst system.

Microplastic (MP) (plastics < 5 mm) are a global issue, which has been widely found in marine and terrestrial environments, contaminating also remote areas, being them extremely mobile. However, MP pollution in underground environment, such as caves and karst aquifers, is still largely unknown. MPs can be ingested by hypogean animals and endanger the fragile ecosystems of the caves. Geologic features are the primary attraction of the show caves, and MPs can irreversibly damage speleothems deposited on them: they can directly damage speleothems, being incorporated into the cave formation growth, sometimes coloring them, or indirectly, by providing nutrients for acid-producing organisms that can dissolve limestone. Moreover, MPs can pollute karst aquifers which are open systems, even susceptible to contamination by surface pollutants. Therefore, the areas above the caves must also be monitored.

To improve the current knowledge of MP pollution, the sediments of three different show caves in Italy (Bossea, Borgio Verezzi and Toirano caves) were sampled and investigated. A new detection technique, based on the optimization of investigation tests used on different kind of sediments was used (Balestra & Bellopede, 2022). MPs were extracted from sediments via density separation and subjected to organic matter removal. Filters were observed with and without UV light under a microscope, exploiting the MPs fluorescence given by the fluorescent whitening agents additives, before and after organic matter removal. MPs were characterized with visual identification and described using the standardized size and colour sorting system (SCS) (Crawford & Quinn, 2016). In Bossea cave, an average of 4390 items/kg dry weight was calculated for the touristic zone and 1600 items/kg dry weight for the speleological/research section of the cave. Fibre (84.9%) was the most abundant shape, suggesting that synthetic clothes of visitors are the main source of MPs pollution in cave. Most MPs were smaller than 1 mm, accounting for 85.4%, of which 58.4% were shorter than 0.5 mm. The highest MP abundance was fluorescent under UV light (87.7%); however, 12.3% of the MPs observed on filters were not fluorescent. Most fluorescent fibres were transparent (84%), whereas blue (46.1%) and black (22.4%) fibres were more common for the non-fluorescent ones. Borgio Verezzi and Toirano caves sediment samples will be used to test an automated counting software designed by a team work of Politecnico di Torino.

Our results highlight the presence of MPs in show caves, and we provide a valid non-invasive and non-expensive analytical technique for the preparation and isolation of MPs from cave sediments, giving useful information for evaluating the environmental risks posed by MPs in caves.

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# Secondary minerals in minothems at Fragnè Mine (Turin, Italy)

Balestra V.*[1-2], Carbone C.[3] & De Waele J.[4]

[1] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [2] Biologia Sotterranea Piemonte, Frabosa Soprana (CN). [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [4] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* valentina.balestra@polito.it

*Keywords:* secondary minerals, mine, minothem.

The Fragnè mine, Chialamberto (TO), is located in the Lanzo valley. The study area is part of the structural complex historically indicated as "area of calcschists and greenstones" or "Piedmont area" formed by mesozoic ophiolitic units of the Piedmontese Ligurian Basin by the tectonic-metamorphic evolution related to the alpine orogenesis (Falletti et al., 2009). The mineralizations are characterized by massive pyrite and Cu-rich pyrite that occurs in greenschist (prasinite) and amphibolite schist. The underground works development is around 5 km, tunnels that branch off into different levels.

In this work, we describe secondary minerals of minothems (Carbone et al., 2016) not yet described in the Fragnè mine and found usually inside natural caves characterized by different mineralogical associations. The results show that all samples are characterized by secondary Fe-rich minerals typical of acid mine drainage areas.

*Blisters* are composed only by schwertmannite, *war-clubs* by schwertmannite and goethite with low crystallinity, and *hair* by epsomite and hexahydrite minerals. Jelly stalactites and jelly stalagmites are characterized by schwertmannite in association with bacterial masses, instead stalactites and stalagmites by jarosite and goethite.

The results shows that a mineralogical transformation occurs from soft to hard minothems: schwertmannite tends to transform into goethite, probably due to ageing processes of schwertmannite or local pH variations, related to bacterial activity, since schwertmannite is a metastable phase which over time tends to turn into goethite (Jönsson et al., 2005).

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# Biocorrosion of speleothems driven by lampenflora: preliminary observations in Bossea show cave (NW-Italy)

Bellopede R.*[1], Balestra V.[1], De Regibus C.[1], Isaia M.[2], Marini P.[1], Nicolosi G.[2], Piano E.[2] & Vigna B.[1]

[1] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [2] Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università di Torino.

*Corresponding author e-mail:* rossana.bellopede@polito.it

*Keywords:* diatoms and cyanobacteria, calcite weathering, scanning electron microscopy.

Speleothems in show caves are often subjected to tourism-driven alterations, including corrosion due to $CO_2$ increase, undersaturated water and photosynthetic biofilms (e.g., Piano et al., 2015; Pulido-Bosch et al., 1997; White et al., 2021). In particular, the growth of the so-called "lampenflora" causes physical, chemical and aesthetic damage to speleothems (Piano et al., 2015). In this work we investigated for the first time the biocorrosion of speleothems at microscopic level due to lampenflora in Bossea Show cave (NW-Italy).

In this cave, the presence of lampenflora was previously documented in Piano et al. (2015) and biocorrosion on speleothems can be observed in different areas along the touristic path. In this work, a first tentative to describe the possible related biocorrosion from a geo-mineralogical point of view was made. Four superficial samples of 1x1 cm of 0.5 maximum thickness were collected on speleothems along the tourist path, in close proximity of halogen lamps. During in situ sampling, the concentration of the main photosynthetic groups composing lampenflora (cyanobacteria, diatoms, and green algae) was measured with Benthotorch®, a portable fluorimeter. The substrate samples were analysed in laboratory by means of scanning electron microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX), in order to assess the alteration degree and the presence of lampenflora possibly responsible of biocorrosion. SEM images of some speleothem samples show high abundance of diatom frustules and the presence of bacteria, algae and fungi. Fluorimeter measures of cyanobacteria, diatoms and green algae amount were then compared to SEM images and EDX results showing in some cases a relation between the speleothems features visible to the naked eyes, the in situ measurements, the degree of alteration of calcite and the presence of bacteria and diatoms frustules at microscope.

Moreover, in light of a long-term study aiming at evaluating changes in calcite crystal habits over time, a homogenous speleothem was collected and divided into several parts, observed and photographed with SEM and placed along the tourist path in areas colonized by lampenflora, near the new LED lamps, where they will remain for about a year. The samples will then be collected and re-examined at SEM to verify and eventually quantify the degree of biocorrosion due to the flashlight after at least one year of exposition.

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# New stability evaluation methods based on discontinuity sets recognition from 3D point clouds aimed at the protection of underground sites

Cardia S.*[1], Palma B.[2] & Parise M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Idrogeo s.r.l., Vico Equense (NA).

*Corresponding author e-mail:* stefano.cardia@uniba.it

*Keywords:* cultural heritage, caves, remote sensing.

Our cultural and natural heritage is an irreplaceable source of life and inspiration. Caves and, in general, the subterranean environment, belong to the natural heritage as they consist of geologic features and landforms which are part of our world and from which we may benefit during our lifetime; at the same time, we also have the responsibility to preserve them for future generations. Such sites generally have great potential for scientific studies, and can be used as outdoor classrooms, enhancing the public understanding and enjoyment. Hypogean environments are fundamental, among other things, to understand surface processes, climatic changes over time, the evolution of landforms, the origin of mineral deposits, and the local hydrogeology; in addition, they should be preserved for their beauty, and for hosting sites of religious and/or social importance.

To solve the problems related to traditional analyses, which can be in various ways expensive and difficult, the implementation of new digitalized methods, such as close- and long-range remote sensing techniques, has become essential to quantitatively describe the structural arrangement of rock masses in such sites over the last two decades. In recent years, the research has been focused mostly on the implementation of new algorithms and methods that take into account the needs related to geology and, in general, the recognition of geometric shapes starting from three-dimensional data. For this reason, new techniques have been developed to standardize the processes of recognition, evaluation and, finally, extraction of the primitive geometries, such as planes and volumetric shapes that represent blocks and discontinuities. This implies the necessity of having robust and reliable methods to determine such features on a rock outcrop. Moreover, these methods have to be easy to use, fast and accurate. This leads today to the tendency of developing automated methods, which often have limitations as concerns processing time, the definition of parameters and, especially, accuracy. We present here an approach that takes into account both the necessity of downsampling a 3D point cloud to speed up computing processing and the necessity of a supervising stage, so that the various step throughout the recognition and, most important, the extraction of sets, is not totally carried out by the machine, but take advantage of case sensitive observations made in situ.

Finally, many characteristics useful for evaluating the stability of rock masses in a wide range of geological environments can therefore be evaluated. These characteristics, together with the analysis of possible kinematics, information on the hydrogeology of the study area and the analysis of the blocks, contribute to the geo-structural and geomechanical characterization of the rock mass in such important sites.

# Environmental monitoring of Su Marmuri cave (Ulassai), a preliminary picture

Cossu Q.A.[1], Cinus D.*[2], Isaia M.[3], Piano E.[3] & Duce P.[2]

[1] Independent Research. [2] Istituto per la Bioeconomia, CNR, Sassari. [3] Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università di Torino.

*Corresponding author e-mail:* daniela.cinus@ibe.cnr.it

*Keywords:* showcave, carrying capacity, environmental impact.

The Su Marmuri cave is located at 874 m a.s.l. on Tisiddu Mountain (Ulassai). A huge sinkhole, evidence of an ancient water drainage, gives access to a large, mostly horizontal, underground tunnel. The difference in height from the entrance to the sinkhole is ~35 m, and the length of the tunnel is about 900 m. Su Marmuri is a remarkable geoheritage site and a hotspot for the conservation of cave fauna, hosting a large winter colony of about 27.000 individuals of *Miniopterus schreibersi*. Rare endemic subterranean arthropods such as the beetle *Ovobathysciola gestroi*, the chilopod *Lithobius doderoi* and the endemic troglophile spider *Lepthyphantes sardous*.

The cave opened to tourists since the mid-1950s and through the years has become an important tourist attraction, with approximately 20.000 tourists/year visiting the cave from May to October. In light of the biological and geological characteristics of the cave and the concurrent pressure of tourism, an environmental monitoring program of Su Marmuri cave started in 2021 (Cinus, et al., 2021), in the framework of the research project of national relevance "Showcave". Preliminary data collected from May to November show an average annual external temperature at the entry point of 15,4°C and an average annual internal temperature of 8,5°C. In the winter season, when the external air masses are cooler than the internal ones, cold air flows into the cavity, acting like a cold air trap. A modest vertical stratification of the internal atmosphere was observed, with a DT between floor and vault (approximately 34 m) equal to about 0,5°C. No horizontal thermal gradient was detected. The relative humidity of the internal air masses is usually close to saturation, showing significant variations only when the incoming winter flow is triggered. Cave anemometric data show a mean air flow of 0,1 m $s^{-1}$, therefore, considering the size of the section where the air flow is measured (approximately 28x24 m), the incoming air flow can be estimated in ~76 $m^3$ $s^{-1}$. Considering an approximate volume of the cave of ~960.000 $m^3$, we estimate that air masses inside the cave could be completely replaced in a few days. Accordingly, the $CO_2$ values recorded inside the cave seems to align this dynamic, attesting a high resilience of the system in recovering the natural conditions. The closure of the cave to tourism in winter prevents the possible environmental consequences of the poor mobility of the cold air masses and the related accumulation of $CO_2$ in the cave.

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# Joint use of historiographic, toponymic, topographical, speleological and geophysical data for the identification of the presumed entrance of the alabaster cave/quarry of Fontegreca (Caserta, Italy)

Cozzolino M., Gentile V. & Mancini M.*

Dipartimento Agricoltura, Ambiente e Alimenti, Università del Molise, Campobasso.

*Corresponding author e-mail:* maxman@unimol.it

*Keywords:* alabaster cave/quarry, Fontegreca, Matese Massif, Multi-methodological analysis, GPR.

The speleological exploration of a cave carried out by Simone Barra in 1696 on the Matese Mountains at Fontegreca (CE) is documented in literature. The author gives a detailed description in which, referring to the concretions, important alabaster deposits that seem to have been excavated (Barra, 1697) are pointed out. The documents that were consulted during the historical research witness the use of alabaster taken from the Fontegreca cave for the construction of the Church of SS. Salvatore in Piedimonte Matese (Marrocco, 1979; Van Gastel, 2012). Topographical surveys carried out in the area of interest have allowed to locate numerous caves and to identify the outcrop area of the alabaster deposits and the presumed entrance to the cave/mine (Mancini, 2017). The study of the toponymy revealed the existence, until the 1960s, of a "cave outside the walls" at the site of the alabaster outcrop, which allowed to narrow the research to a circumscribed area. The geological context was analysed, the evolution of the state of the site was studied and the alabaster outcrops were delimited. The results and the testimonies of a number of people led to the identification of a restricted area where to search for the cave described by Barra. The anthropization of the place, determined by a house, a road and an aqueduct conduit, made the exact localization of the entrance impossible. In order to obtain information from the subsoil, non-invasive geophysical surveys were carried out by using the Ground Penetrating Radar (GPR) technique. In spite of the narrow cross-country road under which the cavity is supposed to be located, the analysis of the acquired parallel profiles confirmed the expected anomalies in the subsurface. The discontinuities affect a band of approximately 5 m at a depth of approximately 1.5 - 2 m from the road surface. Although only direct verification in the field could provide certainty regarding the nature and value of the anomalies found, the results have added some new elements to our knowledge of this site and have laid the foundations for future investigations aimed at identifying not only the cavity, but also an important alabaster mine not yet known in literature.

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# Phosphate crusts from Herbtslabyrinth-Adventhöhle system, Germany: preliminarily results

D'Angeli I.M.[1], Galliano Y.[2], Heil O.[3], Dostern I.[3] & Carbone C.*[2]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [3] Speläologische Arbeitsgemeinschaft Hessen e.V., Breitscheid (Germany).

*Corresponding author e-mail:* cristina.carbone@unige.it

*Keywords:* apatite, bat guano, permafrost cycles.

Subterranean environments are considered extreme sites, but thanks to their stable and conservative conditions are well known to host interesting minerals and particular mineralogical associations. The most abundant cave minerals are those belonging to carbonates, sulfates, and phosphates. Phosphates in association with sulfates are commonly observed in the presence of bat guano (Audra et al., 2019). However, phosphates have also been found to be related to phases of hydraulic activity associated with allogenic recharge (Piccini et al., 2021). Herbstlabyrinth-Advent Cave, in Germany (Melim et al., 2015), is a show cave system. Its non-touristic branches contain copious amounts of bones of *Ursus speleous.*

Mineralogical investigations in these branches allowed to find cryogenic calcite pools, which were studied to understand permafrost and non-permafrost stages (Richter et al., 2010). In these non-touristic branches we collected 5 samples characterized by brownish crusts on collapsed blocks, walls and ceilings. The samples were subjected to XRD and SEM-EDS analyses.

Their composition is mainly dominated by phosphates, characterized by apatite, hydroxyapatite, but also by quartz, calcite, and goethite. Their inner structure is composed of acicular layers of apatite surrounding quartz and calcite crystals. Calcite minerals showed intense pitting on their surface, whereas quartz terminations exhibited evident breaks. We also observed minor amounts of Mn phosphates, zircons and ilmenite. All the crusts are far away from bat guano deposits and we exclude their origin to be linked to the presence of bat colonies. Anyway we are still investigating if as cryocalcite minerals their precipitation may be correlated to permafrost and not permafrost cycles.

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# Potential factors driving the distribution of subterranean invertebrates in karst groundwaters of the Rotolo Cave (southern Italy)

Di Cicco M*.[1], Fiasca B.[1], Galassi D.M.P.[1], Liso I.S.[2], Parise M.[2] & Vaccarelli I.[1]

[1] Dipartimento di Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università dell'Aquila. [2] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro».

*Corresponding author e-mail:* mattia.dicicco@guest.univaq.it

*Keywords:* karst, groundwater, stygofauna.

The Murge area is a typical district of the Apulian karst in southern Italy, where the carbonate rocks host fractured karst aquifers flowing preferentially from the inland zone towards the Adriatic Sea. The area is characterized by thousand-meters-thick carbonate succession, belonging to the Apulia Carbonate Platform. Rotolo Cave, the deepest in Apulia, opens at the bottom of a karst polje (*Canale di Pirro*) located in South-East Murge (Pisano et al., 2020). The polje extends for about 12 km in East-West direction and ends to the Murgia Escarpment. Within this landform polje, numerous sinkholes, endorheic basins, and swallow holes contribute to recharge the aquifer conveying the meteoric waters towards the subsoil via fast and slow infiltration pathways (point or diffuse recharge).

The Rotolo Cave develops within the vadose zone for 264 m and then reaches the groundwater surface. In the unsaturated zone, several intermittent pools are filled with water immediately after intense rainy events. The large pool *Il Laghetto* undergoes water fluctuations over time, reaching the maximum level in springtime, thus suggesting a close connection to the epikarst network. Moreover, about 70 m above the water table, a probable perched aquifer feeds a water flow from fractures, named *La Fontanella*, whose flow rate changes seasonally, never drying up.

In this context a first attempt to combine hydrogeological and ecological analyses was conducted at the Rotolo Cave to understand the relationships between invertebrate distributions and the hydrogeological features of different sampling sites. Several groundwater bodies were sampled and analyzed (May-October 2021) for surveying both environmental and biological parameters, focusing on the aquatic invertebrate fauna living in the unsaturated and saturated karst, respectively. This karst system harbors a diverse and composite array of species across different groundwater habitat types. A total of seven crustacean species belonging to the *Copepoda* and the *Amphipoda*, with various degrees of adaptation to the groundwater life, was found, thus suggesting that the groundwater bodies analyzed could be fed by alternative subsurface flow pathways or recharge areas. In the unsaturated zone, differences in species compositions and abundances among pools were observed, whilst the saturated karst seemed poorer in species. The minimum theoretical number of species living in the system through asymptotic species richness estimators was assessed. Indeed, the faunal sampling underestimated the theoretical actual baseline richness level (range 16.77 - 76.05%), thus suggesting that additional sampling effort is needed, at least for some habitat types. The combined ecological and hydrogeological approach could shed light on groundwater dynamics and species partitioning in deep karst environments where the biological components may work as hydrogeological tracers of the karst system (Di Cicco et al., 2021).

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Pisano L., Zumpano V., Liso I.S. & Parise M. (2020) - Geomorphological and structural characterization of the 'Canale di Pirro' polje, Apulia (Southern Italy). J. Maps, 16, 479-487.

# Survey and inventory of artificial cavities in the historical centre of Genoa (Italy): a contribution to the development of an experimental Underground Master Plan

Faccini F.*[1-2], Bixio R.[2], Ferrando A.[1], Montanari G.[3], Piana P.[4], Saj S.[2], Terrone M.[1] & Traverso M.[2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Centro Studi Sotterranei, Genova. [3] Dipartimento di Italianistica, Romanistica, Antichistica, Arti e Spettacolo, Università di Genova. [4] Dipartimento di Scienze Politiche e Internazionali, Università di Genova.

*Corresponding author e-mail:* faccini@unige.it

*Keywords:* artificial cavities, culverts, Genoa.

Mediterranean cities record the multi-layered nature of phases of urban expansion: historical centres, generally settled in ancient times, underwent significant expansion from the Middle Ages and progressively grew over time (Faccini et al., 2020). Since the second half of the 19th century, and later after the Second World War, cities have undergone uncontrolled development and sometimes irrational urban sprawl.

The morphological modifications of the natural topography have taken place over time, not only in terms of land surface (excavations, filling, sea embankments, hydrographic network modifications), but also with underground works (urban hypogea of a hydraulic, civil, religious, war, mining and transport nature).

The city of Genoa, and in particular its historical centre, shows both significant morphological changes of the original morphology, and on a dense network of underground environments occupying several hectares of subsoil (Bixio et al., 2017, 2019).

These artificial cavities can be analysed either in terms of the potential impact of urban development at land surface on underground spaces, and in terms of geomorphological risk associated with the instability of artificial cavities and consequent propagation of deformations at ground level. In addition, climate change is leading to an intensification of meteo-hydrological phenomena whose ground effects may trigger sink-hole phenomena.

This study presents, on the basis of archive research and original underground surveys, the results of the artificial cavities inventory in the historic centre of Genoa, characterised by great hydro-geomorphological and urban complexity.

The database developed will provide insight into specific urban planning interventions aimed at the conservation and management of Genoa's artificial cavities, which represent a unique cultural heritage and a resource for their historical and socio-economic importance.

The results can represent the starting point of a specific urban planning tool: an underground master plan, as already developed by other European cities, which is fundamental for sustainable and resilient urban planning policies.

Bixio R., Faccini F., Maifredi A., Perasso L., Saj S. & Traverso M. (2017) - The culverted streams in the historical amphitheatre of Genoa city (Italy): flood risk or geoheritage protection?. In: Parise M., Galeazzi C., Bixio R. & Yamac A. Eds., Cappadocia - Hypogea 2017, Proceedings of International Congress of Speleology in Artificial Cavities. Ege Yayinlari, Istanbul, 165-176.

Bixio R., Faccini F., Perasso L., Piana P., Saj S. & Traverso M. (2019) - Second World War Air-Raid Shelters in Genoa (Italy): knowledge, protection and use of an underground historical and cultural heritage in urban environment. In: Zhalov A., Gyorev V. & Delchev P. Eds., Dobrich - Hypogea 2019, Proceedings of International Congress of Speleology in Artificial Cavities. Bulgarian Caving Society, Dobrich, 191-196.

Faccini F., Giardino M., Paliaga G., Perotti L. & Brandolini P. (2020) - Urban geomorphology of Genoa old city (Italy). J. Maps, 17(4), 51-64.

# Karst geomorphology of the Alburni Massif (Campania, Italy)

Fiorillo F.[1], Cafaro S.[2], Pagnozzi M.[1], Leone G.*[1], Liso I.S.[3], Esposito L.[1] & Parise M.[3]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Fondazione MIdA, Pertosa (SA). [3] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro».

*Corresponding author e-mail:* guleone@outlook.com

*Keywords:* karst geomorphology, endorheic basins, caves.

Karst environments are extremely peculiar settings, with unique landscapes showing a variety of landforms, such as dolines, swallets, shafts, karrenfields, poljes, endorheic basins, caves, etc. These features play an important role in hydrological processes, especially in the natural groundwater recharge and groundwater protection. In such a context, mapping the most typical karst landforms, understanding their formation mechanism and the hydraulic role, combined with analyses of geological and geomorphological data, are of crucial importance to fully comprehend the hydrogeological regime. In this contribution, we focus on the Alburni Massif (Campania), one of the most important karst areas in southern Italy. A karst geomorphological map was realized in Geographic Information System (GIS) environment, based on data derived from the available scientific and speleological literature and cartography, analysis of Google Earth Images, high-resolution Digital Elevation Models (DEM), and field activities. The map consists of several layers: the geological, topographic and hydrological layers represent the base maps on which the main karst elements are portrayed. In detail, the geological layer consists of the rock formations and tectonic faults, extracted from the official geological cartography available for the study area. As regards topography, it consists of contour lines and hill-shade map, derived from a 5-meters DEM. The hydrological information regards the main rivers and the basal springs, these latter being generally located at the contact between the limestone and the boundary impermeable flysch formations. To fully characterize the Alburni Massif, the layer dedicated to karst was eventually realized, by selecting the most important features of the karst landscape. These included the cave entrances, together with endorheic basins and dolines, that were mapped in this study for the first time over the entire mountain ridge, also discriminating, whenever possible, the different mechanisms at the origin of the dolines. In addition, other features such as swallets, blind valleys, morphological saddles, etc., were also represented. All these elements are described in this contribution, giving an overview about the geomorphological and karst landforms of the Alburni Massif. Integrated with further information from cave explorations, this amount of data could be of high significance to improve the knowledge of the Alburni karst environment and of its hydrogeological characters.

# Geo-environmental characterization of a gypsum underground quarry site for sustainable remediation strategies

Garello A., Caselle C.*, Bonetto S. & Masciocco L.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* chiara.caselle@unito.it

*Keywords:* underground gypsum quarry, environmental sustainability, mining remediation.

The present study proposes a geological and environmental characterization of an underground gypsum quarry site in Monferrato area (NW Italy). The exploitation is nowadays concluded in a portion of the quarrying area and possible strategies of environmental remediation/reuse are being considered in order to prevent risk from underground processes.

In this framework, the geological, geo-structural and geo-environmental characterization is key for the assessment of environmental sustainability of remediation proposals, with particular attention to the void stability and the potential interaction between the hydro-geological features of the rock mass and remediation solutions.

A detailed on-site geological characterization of tunnels and the analysis of the main discontinuity surfaces (stratigraphic surfaces, joints, fractures and faults) are made in order to verify their lateral and vertical persistence and define potential seepage paths for underground water. The on field geological survey was completed by water samples collection for a hydrochemical characterization of the underground water. Additional analyses on the surface drainage network were performed, in order to evaluate the interactions between surface waters and underground hydrogeological circuits.

# $^{210}$Po in the Gessoso Solfifera Formation of Perticara Mine

Giordani M.*[1], Taussi M.[1], Meli M.A.[2], Roselli C.[2], Betti M.[2] & Mattioli M.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Scienze Biomolecolari, Università di Urbino "Carlo Bo".

*Corresponding author e-mail:* matteo.giordani@uniurb.it

*Keywords:* Perticara mine, epsomite, polonium.

The Perticara sulphur mine is a historically important mine located in the province of Rimini (Italy), known for the large crystals of sulfur that were extracted there, and for the abundance of ore. The mine was developed in the Gessoso-Solfifera Formation, a rock succession mainly formed by gypsum and limestone that is well preserved in the western Romagna Apennines area (Roveri et al., 2003). The Gessoso-Solfifera Formation comprises primary and clastic, resedimented evaporites with interbedded organic-rich shales, which were deposited during the evaporitic and post-evaporitic stages of the Messinian salinity crisis (Roveri et al., 2003).

The Perticara mine was active for a few centuries until the mid-twentieth century. In 2016 the mine was re-explored by the Federazione Speleologica Regionale Emilia Romagna and starting from this data various environmental matrices (rocks, minerals, water, air) were sampled over time. Samples of natural epsomite crystals (general formula $Mg(SO_4)\cdot 7H_2O$), that extensively grow on rock walls and blocks with a fibrous habit, were collected and morphologically and chemically investigated using SEM-EDS, XRPD, ICP-AES and alpha spectrometry measurements.

Most of the fibres are of inhalable size and can be potentially adsorbed from all parts of the respiratory tract. Their solubility and the presence of significant amounts of toxic elements (As, Co, Fe, Mn, Ni, Sr, Ti, Zn) and radioactive isotope $^{210}$Po (and to a less extent $^{228}$Th) make the inhalation of these fibres potentially hazardous to human health. These preliminary results were recently published by Giordani et al. (2022). Moreover, a significant concentration of $^{222}$Rn ($^{238}$U decay series), as well as $CO_2$ and CO in the air of the mine, could play an important role in the accumulation of $^{210}$Po in epsomite, while very few amounts of $^{210}$Po were detected in the water springs and pools inside the mine or in host rocks, but further investigation is needed.

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# Developing mechanically-based charts to address the assessment of underground cave stability

Lollino P.*[1], Fazio N.L.[1], Mevoli F.A.[1], Perrotti M.[2] & Parise M.[3]

[1] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Bari. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro».

*Corresponding author e-mail:* piernicolalollino@gmail.com

*Keywords:* sinkholes, stability charts, FEM method.

Natural or anthropogenic sinkholes threaten diffuse areas of the italian territory. A specific research project aimed at defining an overall methodology for susceptibility analysis and risk mitigation of underground cave sinkholes, from cave identification to modelling failure mechanisms and defining mitigation interventions, has been recently developed. Based on two levels at different scale of analysis, i.e., urban area and single cavity scale, the methodology at the first level is aimed at defining quantitative procedures to assess in a preliminary way the stability of underground caves at the urban area scale. As a matter of fact, when dealing with a large number of cavities, single-cavity scale investigations can be time- and cost-consuming, resulting in huge economical investments. Therefore, a preliminary approach to detect those caves that are characterized by relatively high failure susceptibility level is necessary to make choices for investing more sophisticated analyses.

In particular, the project has furtherly developed a methodology already proposed by Perrotti et al. (2018; 2019) aimed at assessing the stability conditions of underground caves by using charts based on the results of parametric finite element analyses. The use of such stability charts is straightforward since they are based only on simple information regarding the cave geometry and the geo-mechanical parameters. An advanced version of the charts has been proposed in the aforementioned project, which includes also the quantitative assessment of a safety factor range. The enhanced version of the stability charts has been also validated against field data. The methodology is not intended to replace proper site-specific stability analyses and models implementing the actual cave geometry and the rock mass stress-strain state and should be considered only for speditive preliminary stability assessment.

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# The impact of visitors on the microclimate of Italian touristic show caves

Menichetti M.*

Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo".

*Corresponding author e-mail:* marco.menichetti@uniurb.it

*Keywords:* cave microclimate, show caves, cave ecosystem.

In the last years, several important Italian show caves have been installed facilities for touristic exploitation, opening several questions on sustainable use of the karst environment.

The cave microclimate is one of the elements, of the karst ecosystem, that can be taken into account for monitoring the spatial and temporal evolution of the underground atmosphere and hydrosphere. In the last decades, the available technology has permitted to gather many atmospheric physical parameters useful to characterize the spatial and temporal evolutions of the underground microclimate and eventually to prevent and manage possible irreversible modifications.

Several yearly time series of underground atmospheric parameters, collected from the main Italian show caves from Antro del Corchia in the Apuane Alps to Grotta di Monte Cucco and Grotta Grande del Vento-Frasassi in Central Italy are compared. These caves develop for many kilometres and present a complex morphological pattern with several entrances located at different altitudes.

The thermal variations of the underground atmosphere induced by the visitors, in general, reach a maximum few °C and are noticeable until some tens of meters from the touristic trail. They are of short duration and don't succeed to modify the trend over a long period. They follow daily cycles and these variations are compatible with the recovery capacity of the hypogean systems. The airflow across the entrances of the karst systems is mainly controlled by the value of the outside temperature connects to the seasonal variations and day/night cycles. In the studied caves, the airflow is quite complex and however influence only slightly by the presence of the visitors and mainly by the air flux due to the opening of the doors of the artificial tunnels where present. In all cases, the air flows exchanges can reach a discharge of many cubic meters/sec.

The evolution of the concentration of the $CO_2$ in the tourist part of the caves varies by a few hundred ppm, due to the presence of the visitors. The natural variations reach one order of superior magnitude. The opening of the doors of the artificial tunnels and the flow of the outside air tends to dilute the concentration of the $CO_2$ both during the day and for more long trend.

However, these karst system seems enough capable to absorb the thermal perturbations and $CO_2$ increase, restoring and maintaining the pre-existent environmental conditions. The recovery time is controlled by the inertia of the system where the airflow and the hydrogeological condition play an important role. The energetic budget in the underground system seems to be due to an input of about 80% from electric power and the warmth of the visitors which are dissipated by 70% by the air circulation and 20% at the interface air/water/rock. Despite these decades of time-series data on the underground caves, these observations do not enough do not answer for to long term effect on the hypogean ecosystem.

# Karst development intensity - The case of the North Lithuania

Minkevičius V.[1-2], Taminskas J.[1], Mikulėnas V.*[2], Satkūnas J.[1-2] & Danielius S.[1-2]

[1] Nature Research Centre, Vilnius (Lithuania). [2] Lithuanian Geological Survey, Vilnius (Lithuania).

*Corresponding author e-mail:* vidas@lgt.lt

*Keywords:* karstic, denudation, monitoring.

Karstic phenomena in the North Lithuania are related with dissolution of sulphatic (mainly gypsum) interlayers of Upper Devonian formations, that occur under the 1-10 metres thick Quaternary cover. The area of intensive karst comprises territory of 1046 km$^2$. Development of the karstic landscape is characterised by formation of underground cavities, sinkholes, ground fissures, closed depressions and other phenomena. Besides geological conditions, intensity of the karst process is dependent on hydroclimatic factors (Satkūnas et al., 2007).

The monitoring of the karstic landscape is carried out by measuring of intensity of karstic gypsum chemical denudation and inventory (parametrisation) of karstic sinkholes (Mikulėnas at al., 2019). In total, there are counted over 11000 sinkholes of different age and size.

The monitoring of the karstic chemical denudation is carried out in the North Lithuania since 1963. It is based on measurements of chemical composition of surface water and groundwater, thus enabling to determine amount of gypsum (m$^3$/km$^2$) dissolved and removed annually from the karstic region. Mean annual amount of dissolved gypsum is 142 m$^3$/km$^2$ during the period of measurements. It is noted that intensity denudation increased by 30% during the period 1990-2019 and this period is characterised in general by climate change. During two decades of 21$^{st}$ century, the chemical denudation of gypsum here remains quite high – 157 m$^3$/km$^2$. The intensity of gypsum chemical denudation in 2021 was 239 m$^3$/km$^2$ – one of the highest during measurement period. This measurement indicates how many cubic meters of gypsum have been dissolved per square kilometre and it correlates with volume of surface sinkholes. During the year 2018 it was found 38 new sinkholes of different size, in 2019 - 17, in 2020 - 10, in 2021 - 23 and in spring time 2022 - already 40.

In order to prevent loses, engineering geological evaluation (mapping), geohazard areas investigation and relevant management means must be respectively more comprehensive. Definitely it's important to evaluate the loss of land surface due to karst phenomena as well as the velocity of the process (Taminskas at al., 2020).

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# A project addressed toward mitigation of the sinkhole risk

Parise M.*[1], Castellanza R.[2] & Lollino P.[3]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Bari.

*Corresponding author e-mail:* mario.parise@uniba.it

*Keywords:* artificial cavity, sinkholes, instability.

Natural or anthropogenic sinkholes have become a serious hazard in Italy (Parise & Vennari, 2013), often causing damage to society. With the goal to provide a contribution toward mitigation of the related risk, we present the outcomes of a dedicated Project. It consisted in developing a variety of activities to identify and model failure mechanisms, to implement stability analysis and to define possible mitigation interventions. Articulated in two levels (from urban area to single cavity), the approach first aimed at defining the different aspects of the problem and selecting the case studies. Then, innovative survey technologies were applied, integrated by geomechanical studies and geotechnical modeling; further, a detailed economical analysis was performed, taking into account the historical-cultural values, as a necessary step before choosing appropriate stabilization works.

The selected case studies are Canosa di Puglia and Massafra (Apulia), and the San Lazzaro di Savena area (Emilia Romagna). Canosa di Puglia is characterized by many underground calcarenite quarries (type E1 in the Artificial Cavities Classification; Parise et al., 2013), excavated to extract building materials. With expansion of the urban area, a number of sinkholes occurred, also causing casualties. Massafra is characterized by deep valleys incised in the carbonate rocks. In this territory, due to spreading of the rupestrian civilization (Fonseca, 1980), many cavities were dug, especially as worship sites. Eventually, the San Lazzaro di Savena area (Gessi Bolognesi e Calanchi dell'Abbadessa Park) was studied due to co-existence of natural and artificial caves, these latter being extensive gypsum mines, nowadays abandoned.

The proposed multi-disciplinary approach can be applied from metropolitan areas to small cities, and is strongly based upon the main characters of the cave and its interaction with the built-up environment. The final goal is to identify the critical situations, to define the most proper analysis for stability evaluation, and to choose the actions aimed at mantaining the cavity in safety conditions, eventually allowing its public fruition, at least for those of historical and cultural value.

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# Microbial lampenflora composition: the case study of the "Stiffe" show cave

Pellegrini M.*[1], Beatrice F.[1], Djebaili R.[1], Vaccarelli I.[1], Ercole C.[1], Spera D.M.[2], D'Alessandro A.M.[1] & Del Gallo M.[1]

[1] Dipartimento di Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università dell'Aquila.
[2] Quality Engineering s.r.l., Pescara.

*Corresponding author e-mail:* marika.pellegrini@univaq.it

*Keywords:* lampenflora, 16 rRNA metabarcoding, environmental microbiology.

Many caves across the world have been converted into scientific laboratories and tourist attractions. Due to the development of walkways, the presence of tourists, and the installation of artificial lighting, the environment of these caves undergoes numerous changes, impacting the caves' physic-chemical conditions (Piano et al., 2021). Humidity, temperature, $CO_2$ levels, and electrical lighting in cave entrances and speleothems promote the formation of particular photosynthetic communities known as lampenflora (Nikolić et al., 2020). Lampenflora often causes biodeterioration of colonized surfaces, and a range of techniques (physical, mechanical, and chemical) are used to inhibit photosynthesis and spread. However, the study of the lampenflora composition is mandatory to evaluate the suitable devising strategy. In this study, we focused our attention on "Stiffe" cave, one of the show caves of Abruzzo territory characterized by a huge anthropogenic pressure. The «Stiffe» caves, which have been available to the public since the end of 1990, usually receive roughly 45,000 visitors every year. Artificial tunnels and footbridges are part of the accessible touristic trail. Currently, the overall length of the show path is 1 kilometre. The lighting system was created in the early 1990s. To date, there are many types and colours of bulbs inside the cave, and no systematic light bioremediation activities have been carried out. To study microbial lampenflora composition a 16s rRNA metabarcoding was carried out on mats and biofilms sampled on lightened walls. The results underlined huge anthropogenic pressure-driven Bacteria and Archaea communities' alterations. Beyond microbial lineages common to caves habitats (e.g., *Crossiella*), *Cyanobium* (a lampenflora cyanobacterium) (Di Carlo et al., 2016) and SAR324 clade (Marine_group_B) (deep-sea waters lineage) (Flood et al., 2021) were found. This first microbial survey of "Stiffe" cave represents a valid scientific basis to develop useful devising strategies against degrading lampenflora.

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# Towards a sustainable touristic use of show caves: suggestions to control *lampenflora* proliferation

Piano E.*, Nicolosi G. & Isaia M.

Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università di Torino.

*Corresponding author e-mail:* elena.piano@unito.it

*Keywords:* cave tourism, speleothems, cave management.

The conversion of caves into tourist attractions, i.e., show caves, poses serious threats to the conservation of the subterranean environment, among which the extensive growth of photosynthetic biofilms is of particular concern (Cigna, 2019). Caves are naturally dark environments and the lack of light prevents the growth of photosynthetic organisms. When caves are illuminated for touristic purposes, the proliferation of phototrophic alien organisms, the so-called *lampenflora*, dramatically increases. In particular, epilithic prokaryotic and eukaryotic microorganisms can create extended green-brown patinas on cave walls and speleothems, with consequent physical, chemical and aesthetic damage, jeopardizing their touristic value. A comprehensive knowledge of the main drivers of *lampenflora* proliferation is therefore essential to provide general suggestions for management activities to control this phenomenon and guarantee a sustainable touristic use of show caves. To achieve this aim, in the framework of the Project of Relevant National Interest (PRIN) "SHOWCAVE", we collected data relative to the concentration of the three main microorganism groups composing *lampenflora*, namely cyanobacteria, diatoms and green algae, in nine Italian show caves experiencing different touristic fluxes and one wild cave illuminated by natural light. In each cave, we selected one illuminated cave wall or speleothem on average every 50 m from the cave entrance along the touristic path for a total of 211 sampling plots. First, by combining the data obtained from all the examined show caves, we modelled their concentrations against multiple environmental factors possibly favouring their proliferation. With this approach, we could demonstrate that light intensity is the most important driver of *lampenflora* growth, followed by wall moisture and the distance from the cave entrance, confirming the results obtained in a pilot study in the Bossea show cave (Piano et al., 2015). Second, we compared the *lampenflora* concentration in show caves with similar environmental conditions but different tourist use to specifically demonstrate that a higher number of illumination hours leads to significantly increase the proliferation of *lampenflora* (Piano et al., 2021). Third, by comparing the effect of natural versus artificial illumination, we showed that *lampenflora* concentration can increase up to three times under artificial lights. Finally, we highlighted that scheduling recovering periods of complete darkness in show caves may not be an effective method to control *lampenflora*. Overall, our results point out that management activities should be addressed to the reduction of light intensity and the duration of illumination, while scheduling periods of complete darkness seems not an effective strategy to reduce the proliferation of *lampenflora* in show caves.

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# The hidden world of artificial cavities in the northern Campania Plain: architectural variability and cataloging challenge

Ruberti D.*, Fabozzi M.A. & Vigliotti M.

Dipartimento di Ingegneria, Università della Campania "Luigi Vanvitelli", Aversa (CE).

*Corresponding author e-mail:* daniela.ruberti@unicampania.it

*Keywords:* Northern Campania Plain, anthropogenic cavities, geodatabase.

In Campania (southern Italy), sinkholes phenomena induced by the widespread presence of anthropogenic cavities in the Neapolitan and Caserta provinces are frequent and well-known. Nevertheless in many urban centers of this area, cavities have been reported in specific geological investigations although their real extent is almost unknown. In these towns the underground mining activities were performed to extract volcanic tuffs for buildings. The urban development have sealed every signal of the presence of cavities, which thus represent a geological hazard and contribute to subsoil instability of many places.

The need to carry out a survey of underground quarrings in urban centers has two reasons:

a) The anthropic hypogea represent an absolute documentary value, still unduly neglected and little used for the purposes of a correct and sustainable management of the territory, natural resources and historical and artistic heritage. The enhancement and sustainable reuse of hypogea contributes to enhancing the cultural and tourist promotion of a territory.
b) In a correct urban management, the knowledge of the city subsoil is a priority, as the presence of cavities may easily trigger the collapse of the shallow or deeper soils.

The difficulty of drawing up a univocal cataloging system lies in the definition of database framework that includes all the possible architectural, geological and geotechnical elements of the cavities. In fact, the type of extraction is not the same throughout the territory even over short distances as it was strongly conditioned by the lithological characteristics of the volcanoclastic material in the subsoil, as well as by the purpose of extraction.

The construction of a cavity system initially involved an excavation carried out as a "bottle" or a "bell" from the ground level up to the tuff unit, developing at depth according to its thickness. During excavation, access points were realized through the poorly lithified or loose deposits, with a square or pseudo-circular cross-section; sometimes they were supported by containment walls made of tuff bricks resting on the lower tuff bank. A single vertical excavation is sometimes added at certain distance, so as to determine in depth the coalescence of several chambers, also through the construction of narrow tunnels or wide passages, long connecting tunnels, multiple level chambers. Access shafts were often realized with a system of stairs with one or more ramps, with steps directly carved into the tuff.

This contribution will show the main cavity typologies recognized across an area north of Naples, although the study is still far from exhaustive. Data were managed into a GIS environment such as to provide a first proposal of a geological underground database framework.

# Risk of sinkholes in underground mining activities: the importance of monitoring data

Vigna B. & Fiorucci A.*

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* adriano.fiorucci@polito.it

*Keywords:* karst hydrogeology, evaporites, monitoring.

In central-eastern Monferrato area (NW Italy) there are two underground quarries for the extraction of gypsum belonging to the Messinian evaporitic succession. During the excavation works in the Moncalvo quarry in 2005, a karst cavity with pressurized water (0.3 MPa) was intercepted, resulting in inrush and the formation of a sinkhole. After water pumping it was possible to lower the water levels and explore a karst cavity with a development of about 1 km consisting of fully loaded tunnels that stopped at a large collapsed hall that caused the sinkhole. To avoid other situations like this, a study was undertaken to understand the phenomenon by keeping the hydrodynamic and hydrogeochemical parameters under control. The same methodological approach is used in the underground quarry of Calliano where the stratigraphic setting is similar to the previous case while the hydrogeological situation is quite different. The Moncalvo aquifer, based on the data relating to the measurements of water levels carried out on several piezometers in the quarry and outsite and on the interception of the water flows, appears to be set in a rather compact chalky mass with the presence of two different karst systems operating with interconnected conduit drainage (Vigna et al, 2016). On the contrary, the Calliano aquifer has a water circulation in the rock mass set in a network of interconnected fractures that can be considered as a dispersive circulation. The monitoring of water levels shows, in Moncalvo, the presence of two aquifer systems with different hydrodynamic heights and with rather delayed variations with respect to infiltrative processes. This delay is linked to the presence of a powerful cover of low permeable fine deposits from the Upper Messinian. Any interception of other karst cavities with pressurized water and its rapid emptying could cause collapses with consequent sinkholes. In Calliano, underground excavations intercept numerous water flows with low flow rates (few l/s) with a consequent lowering of the piezometric level kept under control by the monitoring system. In this situation, as there are no karst voids of significant size, the risk of sinkholes is extremely low. The chemical control of the intercepted waters shows very well in Moncalvo the presence of water coming from the surface with positive Eh, high nitrates and slightly undersaturated compared to gypsum. In Calliano there are both waters with negative Eh and low concentrations of nitrates linked to a deeper circulation and waters with positive Eh and high nitrates that have a superficial origin. Due to the dispersive circulation, the waters soon reach saturation and are no longer able to dissolve the gypsum.

Vigna B., Fiorucci A. & De Waele J. (2016) - Three conceptual models of groundwater circulation in gypsum rocks: some examples from Northern Italy. Eurokarst 2016, Neuchatel 5-7 September.

# Environmental parameters monitoring in show caves: some examples from NW Italian show caves

Vigna B.*, De Regibus C. & Balestra V.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* bartolomeo.vigna@polito.it

*Keywords:* monitoring, show caves, environmental parameters.

Natural cavities are characterized by particular environmental conditions such as no light and the remarkable stability of the air temperature. These distinctive environmental factors have been able to maintain and preserve speleothems, paleontological and archaeological remains, and particular habitats rich in specialized fauna over the centuries (Balestra et al., 2021). The development of a cave into a show cave requires different modification to create the necessary facilities for tourist use and the passage of several hundred visitors a day can irreversibly damage speleothems and ecosystems (Cigna, 2016; Cigna & Forti, 2013), therefore, it is necessary to pay special attentions and monitor environmental parameters over time. The data should be collected before the construction of the tourist facilities, followed by a constant monitoring of the parameters during the tourist use to examine and verify any possible impacts over time affecting the cavity.

In general, there is a lack of data about the studies on cave environmental conditions before and during the tourist use, especially because there are no reference protocols regarding the main environmental parameters to monitor and how these monitoring must be carried out.

In this work, the main environmental parameters of three different show caves in NW Italy (Bossea Cave, Piedmont, Toirano and Borgio Verezzi caves, Liguria) were monitored. These parameters are the main factors characterizing the delicate cave environment balance and they can be significantly modified by the lighting systems and the tourist passage. A series of instruments with high precision probes were installed in every cave, aiming at environmental monitoring, especially hydrogeology, hypogeal meteorology (temperature and air circulation) and air carbon dioxide concentrations. These instruments must be able to operate in particularly difficult conditions, such as high relative humidity (usually close to 100% in caves) and to detect even very small parameters variations, such as air velocity variations. The probes must be correctly located in different part of the cavities, especially considering the significant air stratifications that often occur in caves, with consequent vertical variations in air temperature and $CO_2$ content. The data recording time is a fundamental parameter too, allowing to examine with precision the possible impacts related to the tourist passages in some areas of the show cave.

Balestra V., Bellopede R., Cina A., De Regibus C., Manzino A., Marini P., Maschio P. & Vigna B. (2021) - Study of the environmental impact in show caves: a multidisciplinary research. Geoing. Ambient. Mineraria, 163-164, 24-35.
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Cigna A.A. & Forti P. (2013) - Caves: the most important geotouristic feature in the world. Tourism and Karst areas, 6, 9-26.

# Environmental characterization of karst caves: evaluation and monitoring for a correct show caves management

Vigna B.*, De Regibus C. & Balestra V.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* bartolomeo.vigna@polito.it

*Keywords:* cave management, environmental characterization, show caves.

The aim of this work is to identify the main environmental parameters characterizing karst cave to be considered for a proper show cave management.

Generally, caves are described considering their "energy level" (Heaton, 1986). The cave vulnerability is high if the energy level is low. However, the distinction between high, medium and low energy levels is extremely subjective and it is not so relevant for the show cave management. The environmental parameters that should be taken into account before and during the show cave opening are: hydrogeology, air temperature and circulation, $CO_2$ and radon concentration, biological components and lint presence and abundance.

Water circulation is an extremely important parameter, being the karst processes directly linked to water inputs from percolation (oversaturated or undersaturated water, absence of inputs related to surface anthropization or climate change, with serious repercussions on the speleothems growth) and/or to the presence of water courses or karst aquifers (water level changes, $CO_2$ and radon inputs). Air temperature and circulation are equally important parameters to monitor. Cavities with high air circulation values are characterized by low air $CO_2$ (of anthropogenic or natural origin) and radon concentrations, however, these strong air circulations can carry powders inside the caves, damaging the speleothems. The air temperature rising related to the lighting system and the tourist presence can affects the formation of different speleothems or calcium carbonate crystallizations (e.g., calcite, aragonite, vaterite). High air $CO_2$ concentration of natural or anthropogenic origin can affects the speleothem corrosion phenomena, as well as different biological components such as lampenflora, guano, decomposing organic matter or lint (hairs, microplastics, fine particles, etc.). However, the presence of these components, associated with particular environmental conditions, can also lead to particular minerals and speleothem formation, as well as promoting the presence of different organisms.

All these parameters must be measured over time through appropriate monitoring systems (Balestra et al., 2021). Suitable instruments, high precision probes, duration and frequency of measurements must be carefully considered. Through this kind of surveys, it is possible to follow any change over time and consequently highlight impacts related to human presence. Across the application of a matrix parametric evaluation system, it will be possible to assess the adequacy of the cave to tourist use and propose valuable solutions for conservation purposes.

Balestra V., Bellopede R., Cina A., De Regibus C., Manzino A., Marini P., Maschio P. & Vigna B. (2021) - Study of the environmental impact in show caves: a multidisciplinary research. Geoing. Ambient. Mineraria, 163-164, 24-35.

Heaton T. (1986) - Caves: a tremendous range in energy environments on earth. Nat. Speleol. Soc. News, 8, 301-304.

# Characterisation of shallow cavities and geological heterogeneities in urban environments: case study from the medieval village of Camporotondo di Fiastrone (MC)

Zaragoza A.*[1], Teloni R.[2] & Zambrano M.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] GeoMORE s.r.l. - spin-off Università di Camerino.

*Corresponding author e-mail:* abel.zaragozaalonzo@unicam.it

*Keywords:* hypogea, Electrical Resistivity Tomography, Ground Penetrating Radar.

The detection and characterisation of underground cavities and critical areas in urban cities has garnered significant interest from both engineering and historical perspectives. The increasing concern for underground structures is related to the proven correlation between the presence of cavities and the seismic amplification phenomena during strong earthquakes (Lancioni et al., 2014). On the other hand, underground structures in urban areas can be of significant historical and cultural heritage interest, representing a touristic attraction. Direct detection is not often possible due to different issues like sealing, filling, collapse, forgotten location, etc. In this regard, indirect identification of cavities through geophysical methods (e.g., GPR and ERT) may represent a valid solution. In some cases, electrical methods, consisting in positioning classic vertical electrodes through drilling the pavement, are not possible because of the historical and architectonic value of the urban pavements (Park et al., 2017).

In this work, an integrated non-invasive study for the characterisation of underground anthropic cavities was conducted in the medieval village of Camporotondo di Fiastrone (MC), in Central Italy. The town is characterised by a series of hypogeous structures excavated in gravelled alluvial terraces, for storage, cooling and likely, defensive purposes. Only some cavities are known and accessible, whereas the location of most of them remains unknown, representing a potential risk for the human activities. In fact, buildings with nearby cavities were highly damaged by the 2016-17 seismic sequence in the central Apennines, Italy (6.5 Mw, 30/10/2016). The methodology combines innovative non-invasive ERT and GPR surveys with geological and stratigraphical analysis of underground sediments using well logs. For the GPR, two different antennas (200MHz, 400MHz) integrated to the SIR 4000 system (GSSI) were used. In the case of the electrical tomography, inexpensive flat electrodes in combination of an electroconductive gel (Vásconez-Maza et al., 2020) were implemented to avoid pavement damages and at the same time, reducing its electrical resistance. This method allowed detecting a complex distribution of unknown cavities under the town centre, useful for the reconstruction of the damaged buildings.

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Park C.S., Jeong J.H., Park H.W. & Kim K. (2017) - Experimental study on electrode method for electrical resistivity survey to detect cavities under road pavements. Sustainability, 9(12), 2320.

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# S22.

# Naturally Occurring Asbestos (NOA): hazard identification, assessment and mitigation


*Conveners & Chairpersons*

*Dario Di Giuseppe (University of Modena and Reggio Emilia)*

*Jasmine Rita Petriglieri (University of Torino)*

*Laura Fornasini (University of Parma)*

*Michele Mattioli (University of Urbino Carlo Bo)*

# Extensive characterization of mineral fibres dispersed in the water system from a naturally occurring asbestos (NOA)-rich area

Avataneo C.*[1-2], Capella S.[1-2], Lasagna M.[1], De Luca D. A.[1] & Belluso E.[1-2-3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [3] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* c.avataneo@unito.it

*Keywords:* NOA, groundwater, TEM.

In Naturally Occurring Asbestos (NOA)-rich areas, fibres dispersion from rocks/soil may occur induced by natural reasons, such as weathering and erosion, or by anthropogenic activities (often also combined). Consequently, migration through different matrices (soil/rocks, water, air) is likely to occur in these areas resulting in a non-negligible fibres presence in the water system.

Asbestos is carcinogenic to humans when respired (IARC, 2012) and, therefore, it is mainly monitored in air. Nowadays, waterborne asbestos is gaining attention since it can constitute a non-conventional exposure cause. As surface and groundwater resources are exploited for agricultural and industrial activities and as source for tap water, water contamination by asbestos could pose two main risks: i) possible water-to-air migration of fibres, thus constituting a secondary source of airborne asbestos (Avataneo et al., 2022), and ii) possible ingestion (noxiousness still debated), particularly if present in tap water.

Therefore, asbestos in water could represent a problem for human health and environment and should be monitored. In North Westerns Alps (Italy), where NOA and other Elongated Mineral Particles (EMP) containing rocks and sediments are widespread (Belluso et al., 2019), possible asbestos diffusion in water has been recently considered as a consequence of interactions between water system and NOA containing rocks and sediments. Two sampling campaigns were settled on the water system (surface and groundwater) of the Lanzo Valleys and Balangero Plain (NW Italy). The results of an extensive electron microscopy study (SEM-EDS and TEM-EDS-SAED) regarding waterborne mineral fibres found in the area will be presented, supported by hydrochemical and geological data, to define how many and which type of fibres are found in water, which are the releasing mother rocks and what could be their path in the environment. Good practices to effectively analyse waterborne fibres will be discussed highlighting differences between surface and groundwater samples. This is to better characterize and monitor asbestos (and EMP) occurrence in surface and groundwater flowing in NOA-rich areas.

The results of this study are expected to have high impact on regulatory aspects, helping in the definition of a shared method to analyse water samples in support of environmental protection agencies.

Avataneo C., Petriglieri J.R., Capella S., Tomatis M., Luiso M., Marangoni G., Lazzari E., Tinazzi S., Lasagna M., De Luca D.A., Bergamini M., Belluso E. & Turci F. (2022) - Chrysotile asbestos migration in air from contaminated water: An experimental simulation. J. Hazard. Mater., 424, 127528.

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# Statistical approach to the construction of a representativeness sample from core drilling based on RQD

Baietto O.*[1], Marini P.[1], Zanetti G.[1], Patti G.[2], Ferraro D.[2], Tagni M.[2] & Tarasi M.[2]

[1] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [2] U.O. Bonifiche e Attività Estrattive, ARPA Lombardia - Dipartimento di Lecco e Sondrio.

*Corresponding author e-mail:* oliviero.baietto@polito.it

*Keywords:* sampling, RQD, asbestos.

One of the main problems in evaluating the presence of asbestos in a rock mass is, in addition to the complexity of the analysis, the representativeness of the sample. In the case of excavation of tunnels for engineering works that have to cross rock formations containing asbestos, it is often fundamental for a good design of the works to know the occurrences of asbestos and, if possible, to estimate its concentration.

Certainly, the best method for studying the lithologies involved is to carry out core drilling along the section that the work will involve. Despite this, even if the study of lithology can be carried out by observing all the extracted cores, it is economically and timely unsustainable to analyze every meter of sample to evaluate the asbestos parameter. In this work, a composite sampling scheme is proposed, based on the statistical examination of the RQD (Rock Quality Designation) parameter which is a geotechnical classification of rocks based on the percentage of fragments longer than 10 cm recovered along the total length of every core run, as measured along the centerline of the core.

The lower is the RQD, the worse is the rock quality. However, it can be assumed that the highest concentrations of asbestos can be found in correspondence with fractures and along fault surfaces, to which cataclastic and mylonite zones are commonly associated, and therefore in the sections with lower RQD. The construction of a representative sample can therefore be hypothesized starting from the analysis of the RQD parameter of each metric core over intervals of 25 (or more) meters or at each change of facies. After analyzing the percentiles of the RQD in the identified interval, a frequency histogram is created in order to identify the number of occurrences corresponding to each percentile. In this way it is possible to identify the metric intervals corresponding to the occurrences and proceed with forming a sample with a proportional contribution according to the previously identified number of occurrences. This methodology strongly limits the subjectivity of the choice of clasts for the subsample and provides a repeatable and statistically reliable method. The sample thus constituted is then taken to a laboratory equipped for a comminution that lead to a more homogeneous sample. After a correct quartering, a suitable aliquot will be reached. The analysis will proceed, according to the regulations in force, after porphyrization and deposition on the membrane of a known aliquot by using a scanning electron microscope.

# Naturally occurring asbestos (NOA) in sedimentary rocks: a case study from the Tertiary Piemonte Basin

Barale L.*[1-2], d'Atri A.[3-1], Petriglieri J.R.[3-1-2], Piana F.[1-2] & Turci F.[4-1-2]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [3] Dipartimento di Scienze della Terra, Università di Torino. [4] Dipartimento di Chimica, Università di Torino.

*Corresponding author e-mail:* luca.barale@igg.cnr.it

*Keywords:* Naturally Occurring Asbestos (NOA), sedimentary rocks, Tertiary Piemonte Basin.

Studies on naturally occurring asbestos (NOA) and on the relevant geo-environmental problems have been traditionally focused on metamorphic rocks (and, more recently, on magmatic rocks). Besides these 'primary' occurrences (i.e., those realted to the in situ growth of NOA minerals), 'secondary', detrital NOA may occurr in sediments, sedimentary rocks and soils derived form the erosion of 'primary' NOA-bearing rocks.

The occurrence of detrital NOA in sediments and soils is increasingly recognized worldwide. However, a few studies exist that investigate the 'sedimentology of NOA', i.e., the mechanisms underlying the genesis, transport, deposition and post-depositional modifications of detrital NOA particles in the different sedimentary environments. A better understanding of these mechanisms would give us the tools to predict the presence and possible concentration of detrital NOA in sediments and sedimentary rocks.

Here we discuss a case study on the occurrence and distribution of detrital NOA within the Oligocene succession of the southern Tertiary Piemonte Basin (NW Italy). Data come from the surveys performed during the excavation of the Terzo Valico high-speed high-capacity railway line as well as from sampling on selected outcrops. Mineralogical and petrographic analyses showed the widespread occurrence of chrysotile and tremolite-actinolite fibres at different stratigraphic levels and in several lithofacies.

# Distinguishing asbestos cement from fiber-reinforced cement through Portable μ-Raman spectroscopy and portable X-ray fluorescence

Bloise A.* & Miriello D.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* andrea.bloise@unical.it

*Keywords:* asbestos, in situ, polyvinyl fibers.

It is now widely acknowledged that asbestos can adversely affect human health; accordingly, in recent decades fiber-reinforced cement (FRC) has been used as a substitute for asbestos cement (AC). In recent years, portable instruments, have been used to successfully identify asbestos fibres in materials and rocks (e.g., Bloise & Miriello, 2018; Petriglieri et al., 2020; Zholobenko et al., 2021; Tabata et al., 2022). Within this context, our study aims to promote the use of portable analytical techniques, in particular μ-Raman spectroscopy coupled with portable microscopy (p-μR) and portable X-ray fluorescence spectrometry (p-XRF) as a means to identify chrysotile fibers in AC (Eternit) and fibers present in the asbestos-free FRC used as a substitute. Our results show that the simultaneous use of portable devices such as p-μR and p-XRF may be useful in quickly identifying fibrous chrysotile asbestos in Eternit, as well as polyvinyl fibers in new materials FRC used as substitutes for Eternit. Chrysotile shows bands in the 800-200 $cm^{-1}$ range, whereas polyvinyl alcohol fibers show bands in the 3000-800 $cm^{-1}$ range. The p-XRF data on the two types of cement could possibly be used as a chemical fingerprint for the two different materials. Given that exposure to asbestos is a serious health hazard, its rapid and reliable detection in situ on residential buildings is important both for citizens and for administrative bodies charged with safeguarding public health. We believe that our study provides valuable insight into the potential use of portable devices for identifying asbestos and asbestos-free materials.

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Petriglieri J.R., Bersani D., Laporte-Magoni C., Tribaudino M., Cavallo A., Salvioli-Mariani E. & Turci F. (2020) - Portable Raman spectrometer for in situ analysis of asbestos and fibrous minerals. App. Sci., 11(1), 287.

Tabata M., Fukuyama M., Yada M. & Toshimitsu F. (2022) - On-site detection of asbestos at the surface of building materials wasted at disaster sites by staining. Waste Manage., 138, 180-188.

Zholobenko V., Rutten F., Zholobenko A. & Holmes A. (2021) - In situ spectroscopic identification of the six types of asbestos. J. Hazard. Mater., 403, 123951.

# Synthesis of Ni-doped tremolite

Bloise A.*

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* andrea.bloise@unical.it

*Keywords:* synthesis, tremolite, asbestos.

Collected data suggests that different factors such as size, chemical characteristics, surface reactivity and biopersistence may be involved in asbestos-related diseases, but the exact mechanisms responsible for cell damage are still unknown. Fe cations ($Fe^{2+}$/$Fe^{3+}$), present in all types of asbestos as an integral component of the crystalline structure or as a substitute cation, seem to play a key role in asbestos toxicity. In addition to Fe, other toxic elements such as Ni and Cr are considered indicators of asbestos pathogenicity, even if their role is not yet fully understood. In this view, asbestos fibers act as complex crystal-chemical reservoirs that release potentially toxic elements (e.g., Fe, Ni, Cr) into the lung cellular environment during dissolution. To understand the pathological mechanisms induced by tremolite asbestos, *in-vitro* studies on biological system-mineral interactions have been performed using natural asbestos. However, since natural asbestos can simultaneously host Fe, Ni, Cr, etc. and often contains additional mineral phases, it is still difficult to accurately determine toxicity factors and the exact role of each toxic element in the pathogenesis of asbestos. In this light, *in-vitro* screening tests using synthetic asbestos fibres having fixed chemical compositions may help correlate asbestos toxicity to its chemical composition. In this study, well-defined Ni-doped tremolite $Ca_2(Mg_4Ni_1)Si_8O_{22}(OH)_2$ fibers were chemically synthesized to be used to subsequently test the role of Ni in asbestos toxicity through *in-vitro* experiments. The Ni-doped tremolite fibres were obtained by hydrothermal synthesis using cristobalite, magnesium, calcium and nickel oxides as starting raw materials. Several runs were carried out, with reaction temperatures in the 780-830°C range and pressures of 1.1 to 2.4 kbar; the reaction time varied from 4 to 16 days (e.g., Bloise et al., 2017). The starting materials and run products were analyzed by X-ray powder diffraction (XRPD) and under scanning and transmission electron microscopes, both equipped with energy-dispersive spectrometry systems (SEM/EDS and TEM/EDS).

Bloise A., Kusiorowski R., Lassinantti Gualtieri M. & Gualtieri A.F. (2017) - Thermal behaviour of mineral fibres. In: Gualtieri A.F. Ed., Mineral fibres: crystal chemistry, chemical-physical properties, biological interaction and toxicity. Eur. Mineral. Union Notes Mineral., 18, 215-252.

# Asbestos fibers in drinking water in Monte Reventino area (Central Calabria)

Bruno M.R.*[1], Sinopoli F.[1], Cannizzaro A.[2], Olori A.[2], Angelosanto F.[2] & Campopiano A.[2]

[1] Dipartimento di medicina, epidemiologia, igiene del lavoro e ambientale, INAIL, Lamezia Terme (CZ). [2] Dipartimento di medicina, epidemiologia, igiene del lavoro e ambientale, INAIL, Monte Porzio Catone (RM).

*Corresponding author e-mail:* ma.bruno@inail.it

*Keywords:* drinking water, tremolite, Naturally Occurring Asbestos (NOA).

The carcinogenicity of asbestos due to inhalation of the fibres is well documented. On the contrary, the situation is more controversial when asbestos fibers are ingested. Exposure to asbestos fibers in drinking water was linked to stomach cancer (Di Ciaula, 2017). However, to date the presence of fibers in drinking water was not associated with a clear excess of cancer. For this reason, the World Health Organisation (WHO) has not "considered it useful to define a guideline value based on health considerations for the presence of asbestos in drinking water" (WHO, 2011). Currently in Italy, as in the rest of the European Union, no limit value was set for asbestos in drinking water. Only the USA regulation set a limit of 7 million fibers/litre.

Asbestos fibers can be found in drinking water essentially for three reasons:

- as a consequence of the asbestos-bearing rocks weathering and erosion;
- release of asbestos fibers from asbestos cement pipes;
- pollution from industrial activities.

Several ophiolitic rocks containing naturally occurring asbestos (NOA) crop in the Central Calabria (Campopiano et al., 2018a; 2018b).

The INAIL Research Centres of Lamezia Terme (Catanzaro) and Monte Porzio Catone (Rome), are carrying out a study to identify the possible presence of asbestos fibers in the drinking water in some Calabrian municipalities and to identify the possible cause of contamination. This work showes the first results.

Sampling was carried out in the province of Catanzaro, Central Calabria. In particular, 18 water samples were collected from public fountains, supplied by local aqueduct, and from springs using 2L volume polyethylene bottles.

A known volume of each sample was filtered through polycarbonate filters with a diameter of 25 mm and a porosity of 0.8 µm; a quarter of each filter was analysed by scanning electron microscope (SEM Zeiss EVO 15 MA), equipped by energy dispersive X-ray microanalysis (EDS Bruker Quantax). Each filter was observed at magnifications of at least 4000X. All asbestos fibers were counted.

Some samples from Monte Reventino, an area rich in ophiolite outcrops, showed the presence of tremolite in fibrous form, asbestos widely widespread in the area, and in prismatic or lamellar form. However, the concentration of asbestos fibres in all drinking water samples analysed was below 5000 f/L. Titanium dioxide fibres were also observed in some samples.

Finally, non-drinking water used for surface washing was sampled; the results were in agreement with the drinking water samples, but the filters were more heavily loaded and difficult to analyse.

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# The problem of environmental asbestos (and EMP) in France

Claire T., Misseri M. & De Salvo S.*

AD-LAB, Brussieu (France)

*Corresponding author e-mail:* sara.desalvo@ad-lab.fr

*Keywords:* France, asbestos, EMP.

Since January 1st 1997 in France, asbestos, composed of 6 different species, amosite, crocidolite, chrysotile, tremolite-asbestos, anthophyllite-asbestos, actinolite-asbestos, was totally banned in a building construction context. Nevertheless, since the mid-2010s, France has started to take an interest in asbestos in an environmental context. This issue was already known in New Caledonia (French territory) during the 2000s, with the addition of minerals not considered as asbestos at that time but leading to similar pathologies (e.g., antigorite). The French National Agency for Food, Environmental and Occupational Health Safety (ANSES) issued two reports: in 2015 on the health effects of amphibole cleavage fragments and in 2017 on elongated mineral particles, structures for which the only discriminating criterion, apart from their elongated shape, is a length/width ratio greater than 3:1. As a reminder, the ISO 22262 standard stipulates that an asbestos fibre must have, in addition to this ratio, parallel or stepped edges. Among these EMPs, ANSES has specified in particular EMPs of interest (EMPi): the 6 asbestos fibres, their 6 chemical counterparts whose structures do not have parallel edges but still have a ratio of 3:1, other amphiboles such as edenite, winchite and richterite but also antigorite and finally erionite. AD-LAB, a COFRAC accredited laboratory since 2013, is composed of geologists and is able to discriminate between asbestos fibres and non-asbestos EMP. All regulatory analyses are carried out in France, using the MET method. There is no threshold. The conclusion must often be established from a few particles, so only a logigram based on recognised criteria can be used. AD-LAB developed a flow chart in 2015 (published in 2021). AD-LAB will therefore present a complementary, foreign view of the analytical approach to this problem at this congress.

# Preliminary data on the recovery of asbestos containing materials for the synthesis of tobermorite

Di Giuseppe D., Gualtieri A.F.*, Malferrari D. & Scognamiglio V.

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* alessandro.gualtieri@unimore.it

*Keywords:* cement asbestos, fibres, tobermorite.

In Italy, asbestos-containing materials (ACM) are banned since 1992 but they are still found to date in many civil and industrial buildings. Their removal is still in progress and the reclamation of asbestos-contaminated sites, namely roofs with cement-asbestos slates (CAS), has now become a priority because their chronic physical-chemical degradation produce a massive dispersion of asbestos fibres with exposure for the population. Disposal in landfills can no longer be considered the ultimate solution and various industrial processes for the safe disposal of CAS have been proposed in the last two decades. Among them, the thermal inertization is currently the most promising solution (Viani et al., 2013) although many different inertization methods are possible.

We are now attempting to explore the possibility of using modest amounts (1 to 5% by weight) of CAS along with other wastes to synthesize a product containing Al-substituted tobermorite (ST), a nanoporous phase with characteristics and properties comparable to those of smectites. ST can be obtained in a simulated hydrothermal environment from materials whose composition falls within the molar ratios $0.80 < Ca/[Si+Al+Fe] < 0.85$ and $0.00 < [Al+Fe]/[Al+Si+Fe] < 0.17$ (Diamond et al., 1966; Malferrari et al., 2022). Since CAS does not normally exhibit this chemical composition, appropriate amounts of other Ca-, Si-, and Al-containing materials must be added to CAS to fall within these ranges; good candidates for this role are wastes like glass and rock wool, household glass containers and the End-of-Waste derived from the thermal inertization of CAS at 1200°C (KRY•AS).

Preliminary tests indicated that in the synthetized material forms ST and carbonates in varying amounts depending on the overall composition of the starting mixture (i.e., the number of elements other than those defined above). The initial characterization will be followed by a careful microscopic analysis to verify the total absence of fibres. The main advantage over thermal inertization is the use of a relatively low temperature process (approx. 120°C rather than about 1200°C). Nevertheless, this contrasts with both the modest recovery of CAS and the need for prior grinding of the slates. On the other hand, the ST, once its safety has been ascertained also through appropriate biological tests, could be used to replace virgin raw materials such as bentonites and zeolitized tuffs.

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Malferrari D., Bernini F., Di Giuseppe D., Scognamiglio V. & Gualtieri A.F. (2022) - Al-Substituted Tobermorites: An Effective Cation Exchanger Synthesized from “end-of-Waste” Materials. ACS Omega, 7(2), 1694-1702.

Viani A., Gualtieri A.F., Pollastri S., Rinaudo C., Croce A. & Urso G. (2013) - Crystal Chemistry of the High Temperature Product of Transformation of Cement-Asbestos. J. Hazard. Mater., 248-249, 69-80.

# *In vitro* assessment of the potential toxicity of fibrous glaucophane

Di Giuseppe D.*[1], Filaferro M.[2], Scarfì S.[3], Mirata S.[3], Vitale G.[4], Bailey M.[5], Harper M.[6] & Gualtieri A.F.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Dipartimento di Scienze Biomediche, Metaboliche e Neuroscienze, Università di Modena e Reggio Emilia. [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [4] Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia. [5] Asbestos TEM Laboratories, Berkeley, CA (USA). [6] Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL (USA).

*Corresponding author e-mail:* dario.dg@libero.it

*Keywords:* fibrous glaucophane, amphibole asbestos, in vitro toxicity.

The health hazard posed by asbestos exposure may also concern other minerals with an asbestos-like crystalline habit. One of these potentially hazardous minerals is fibrous glaucophane which can occur with a fibrous habit similar to regulated amphibole asbestos minerals. Fibrous glaucophane is an important component of the blueschist rocks of the Franciscan Complex (USA) that are commonly mined for construction purposes in northern and central California (e.g., the Calaveras Dam Replacement Project). Dust generated by excavation activities involving blueschist rocks could potentially expose workers and the general public to health risks. For this reason, it was considered to represent a potential health hazard as naturally occurring asbestos (NOA) by the dam owner, the San Francisco Public Utilities Commission, though an evaluation of the potential health hazard of this mineral fibre was not mandatory per local state and federal regulations. In this work, *in vitro* tests on glaucophane from the Franciscan complex were performed to assess the actual potential toxicity/pathogenicity of fibrous glaucophane (Gla). Biological responses of cultured human monocytes and lung mesothelial cells (THP-1 and Met-5A) following 24 and 48h of exposure to different doses of Gla (25, 50 and 100 μg/mL), have been determined by Alamar Blue viability, extracellular lactate dehydrogenase (LDH) and Comet assays. Generation of reactive oxygen species (ROS) has been evaluated performing a luminescent assay. Crocidolite UICC asbestos (100 μg/mL) was also tested for comparison. Results of *in vitro* tests showed that Gla may induce a decrease in cell viability and an increase in LDH release in tested cell cultures in a concentration dependent mode. Overall, the rank of the investigated fibres in increasing order of cytotoxicity is: Gla (25 μg/mL) < Gla (50 μg/mL) < crocidolite (50 μg/mL) < Gla (100 μg/mL). For both the cells lines, Gla was able to induce DNA damage. Moreover, it was found that Gla can induce the formation of ROS. The biological reactivity of Gla observed in this study confirms that this mineral fibre is a cytotoxic agent. Although Gla induced lower toxic effects compared to the carcinogenic crocidolite, the inhalation of its fibres may be hypothetically responsible for the onset of lung diseases. For a conclusive understanding of the toxicity and carcinogenicity mechanisms of fibrous glaucophane, *in vivo* animal tests should be performed to stimulate a critical evaluation and a classification by the International Agency for Research on Cancer (IARC).

# Micro-Raman investigation of an *in vitro* THP-1 cellular model exposed to chrysotile fibres

Fornasini L.*[1-2], Mirata S.[3], Almonti V.[4], Di Giuseppe D.[5], Scognamiglio V.[5], Bersani D.[1], Bassi A.M.[4], Marengo B.[4], Scarfì S.[3], Gualtieri A.F.[5] & Raneri S.[2]

[1] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [2] Istituto di Chimica dei Composti Organo-Metallici, CNR, Pisa. [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [4] Dipartimento di Medicina Sperimentale, Università di Genova. [5] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* laura.fornasini@unipr.it

*Keywords:* Micro-Raman spectroscopy, chrysotile, macrophage.

Asbestos-related diseases are currently a health issue, affecting patients exposed to asbestos fibres. Ongoing toxicological research is of great interest in the investigation of pathogenic mechanisms, including the acute toxicity of carcinogenic mineral fibres (Gualtieri et al., 2019; Mirata et al., 2022). Diameter and length of the fibres are key factors, together with their biodurability (Gualtieri et al., 2019). In addition, surface activity and metals release from the fibres should be considered in the toxicity/pathogenicity of asbestos (Fubini & Mollo, 1995). In chrysotile, the most commercialized asbestos mineral, Fe and other toxic metals (Cr, Ni, Co, Mn, etc.) are intimately associated to the raw material, since both Fe and trace metals are isomorphous substituent for Mg in octahedral sites. The release of metals into the lung environment occurring from the dissolution of fibres by the macrophage phagocytosis is worth considering in chrysotile pathogenicity.

In this work, an *in vitro* THP-1 cellular model of macrophage phenotypes exposed to chrysotile fibres (from Balangero, Italy) were analyzed by micro-Raman spectroscopy to investigate the organic and inorganic products after different exposure times. Clusters of both mineral and cellular materials were observed, including fibrous and non-fibrous species. In addition to chrysotile fibres, antigorite lamellae and balangeroite fibres were identified in the clusters. A few-microns crystals of Fe oxides (mainly magnetite $Fe_3O_4$) and uncommon Fe sulphides (mackinawite Fe(II)S in different oxidized forms) were also distinguished as Fe compounds. Clusters size and concentration rise as treatment time increases, exceeding 100 µm size (observations up to 96 h). Fibres and Fe compounds were identified in prolonged treatment time systems, as well. Furthermore, their Raman signals were weakly recorded even on aggregated formations where fibres or micro-crystals were hardly distinguishable, suggesting a partial dissolution of the inorganic material. Thanks to the micro-Raman investigation, these crucial preliminary findings about the interaction of mineral fibres and Fe-bearing species with macrophages are expected to be helpful in future toxicological studies aimed at understanding pathogenic mechanisms of chrysotile asbestos.

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Mirata S., Almonti V., Di Giuseppe D., Fornasini L., Raneri S., Vernazza S., Bersani D., Gualtieri A.F., Bassi A.M. & Scarfì S. (2022) - The acute toxicity of mineral fibres: a systematic in vitro study using different THP-1 macrophage phenotypes. Int. J. Mol. Sci., 23, 2840.

# Micro-Raman characterization of fibrous glaucophane

Fornasini L.[1], Di Giuseppe D.[2], Salvioli-Mariani E.[3], Andò S.[4], Gualtieri A.F.[2] & Bersani D.*[1]

[1] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [3] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [4] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* danilo.bersani@unipr.it

*Keywords:* Micro-Raman spectroscopy, glaucophane, NOA.

Glaucophane, a typical component of the blueschist facies, is a Na amphibole with ideal formula $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$. Besides pure glaucophane (end-member), solid-solution series are formed with Fe-glaucophane $Na_2Fe^{2+}{}_3Al_2Si_8O_{22}(OH)_2$ and Mg-riebeckite $Na_2Mg_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$, with the substitutions of $Fe^{2+}$ for Mg and $Fe^{3+}$ for Al, respectively. Glaucophane may occur with a fibrous crystal habit, as detected in the blueschist rocks of Franciscan Complex (California, USA) (Di Giuseppe et al., 2019), which are mined as construction material.

Notwithstanding its asbestiform habit, glaucophane has not been classified as asbestos mineral by the International Agency for the Research on Cancer. Nonetheless, the toxicity and pathogenicity of fibrous glaucophane from California was confirmed by an *in vitro* study (Gualtieri et al., 2021). The exposure to fibrous glaucophane should be considered a health hazard as naturally occurring asbestos (NOA) and standard procedures for its identification and risk assessment are recommended.

In this work, micro-Raman spectroscopy was used to investigate the composition of fibrous glaucophane from California in the solid-solution series. A dataset of micro-Raman and SEM-EDS results from the analysis of non-fibrous glaucophane from the Alps was used as calibration model to estimate the $Mg/(Mg+Fe^{2+})$ ratio in Fe-glaucophane and the $Al/(Al^{VI}+Fe^{3+})$ ratio in Mg-riebeckite series.

As well as for amphiboles of the tremolite-actinolite series, the $Mg/(Mg+Fe^{2+})$ molar ratio was obtained from the areas of the OH stretching peaks, which change in number and relative intensity according to the composition (Bersani et al., 2019). At lower wavenumbers, the main Raman feature, at ~670 $cm^{-1}$, attributed to the $Si\text{-}O_b\text{-}Si$ symmetric stretching, shows a splitting - increasing with the relative amount of Mg - that may be used to estimate the $Mg/(Mg+Fe^{2+})$ ratio. The $Al/(Al^{VI}+Fe^{3+})$ ratio was correlated with the relative intensity of the peaks at ~980 $cm^{-1}$ and ~1040 $cm^{-1}$, attributed to the $Si\text{-}O_b\text{-}Si$ asymmetric stretching modes.

Through this model, the chemical composition of fibrous glaucophane from California was obtained from the micro-Raman characterization in a reliable and non-destructive way, as an effective tool for the characterization of fibrous glaucophane.

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# Management and mitigation of asbestos related risk derived from natural occurrences and anthropogenic dispersion

Gaggero L.*[1], Sanguineti E.[1], Yus Gonzales A.[1], Militello G.[1-2], Annis S.[1] & La Maestra S.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Dipartimento di Scienze della Salute, Università di Genova.

*Corresponding author e-mail:* laura.gaggero@unige.it

*Keywords:* asbestiform and fibrous minerals, environmental monitoring, morphology.

Conventional petrography and mineralogy are overcome when addressing the environmental issues related with naturally occurring asbestos, and the related exposure risks. Asbestos-related focal points are: i) the presence of natural outcrops of asbestos-bearing rocks, ii) the cycle of asbestos within natural matrix- es, and iii) the quantitative assessment of asbestos fibers within large volumes of rock.

In this regard, the potential hazard of asbestos occurrence resides i) in outcropping NOA, ii) in driling and excavation of ophiolitic basements, iii) in the management of waste dumps. Whereas the natural outcrops have an intrinsic potential of fiber release, that can only be increased in case of ground instabilities and landslides, whose management can be encompassed in analogy of iii), the two anthropogenic activities need to apply a holistic scientific and engineering approach.

Asbestos as an exogenous component, or during anthropogenic activity, allows the definition of a "fiber-cycle", overall parallel to the hydric cycle.

Tunnelling across formation with Naturally Occurring Asbestos (NOA) can release fibers into the environment, exposing workers, and the population, if fibers spread outside the tunnel, leading to increased risk of developing asbestos-related disease. An intensive monitoring has been carried out during Terzo Valico 100 m tunnel excavation across a serpentinite lens (Cravasco adit), intercalated within calcschists, based on data of 1571 samples of airborne dust, collected between 2014 and 2016 inside the tunnels, and analyzed by SEM-EDS for quantification of workers exposure.

At this chrysotile occurrence, 84% of 128 analyzed samples (from the zone closer to the front rock) were above 2 ff/l. However, thanks to safety measures implemented and tunnel compartmentation in zones, the asbestos fiber concentration did not exceed the Italian standard of occupational exposure (100 ff/l) and 100% of samples collected in the outdoor square were below 1 ff/l. During excavation under normal working conditions, asbestos concentrations were below 2 ff/l in 97.4% of the 668 analyzed samples.

In amphibole bearing host rocks a major concern was raised on the carcinogenic activity of asbestiform vs. cleavage fragments and on critical length of particles. A preliminary literature review did not highlight that cleavage fragments have the same or greater carcinogenic potential than asbestos. Most of the data collected by the different authors suggest that the toxic effect of asbestos fibers increases with length, despite some notable exceptions. However, the extent to which a mineral with an asbestiform habit affects cell behaviour relative to that of a cleavage fragment of the same mineral is object of ongoing investigations.

Recent data and experiments evidence the need to standardize the normative worldwide for the management of asbestos-containing materials, by re-evaluation of sample preparation and quantification of asbestos.

# A fibrous occurrence of antigorite in Val Varenna, Italy: mineralogical characterization in view of hazard evaluation

Gianchiglia F.*[1], Petriglieri J.R.[2-3-4], Ballirano P.[1], Barale L.[4], Pacella A.[1], Piana F.[4], Tomatis M.[2-5], Viti C.[6] & Turci F.[2-4-7]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [3] Dipartimento di Scienze della Terra, Università di Torino. [4] Istituto di Geoscienze e Georisorse, CNR, Torino. [5] Dipartimento di Scienze Veterinarie, Università di Torino. [6] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [7] Dipartimento di Chimica, Università di Torino.

*Corresponding author e-mail:* gianchiglia.1752866@studenti.uniroma1.it

*Keywords:* fibrous antigorite, Naturally Occurring Asbestos, hazard assessment.

The present study reports the detailed minero-chemical characterization of a fibrous antigorite sample coming from a serpentinite body of Varenna Valley (Liguria, Italy) by means of a set of multi-analytical approaches. The crystal structure was investigated by X-ray powder diffraction (XRPD), the morphological investigation was performed by scanning electron microscopy (SEM), and the chemical composition was determined using an electron microprobe (EMP) equipped with five wavelength-dispersive spectrometers (WDS) and Mössbauer spectroscopy (MS). Moreover, an advanced study of the dissolution kinetics was carried out by incubation at 37°C in a modified Gamble's solution (MGS, pH = 6.5) in presence of citrate as chelating agent up to 1 week. Ion leaching was monitored by inductively coupled plasma optical emission spectrometry (ICP-OES).

SEM images revealed the elongated fibrous habit (asbestos-like) of the antigorite sample.

XRPD indicated that the prevailing superstructure periodicity corresponds to m = 17 antigorite polysome. The measured $\Delta 2\theta$ value of 1.42° $2\theta$ is consistent with an M value of 7.99, derived from the regression equation $M = 11.42 - 2.41 \times \Delta 2\theta$ (Uehara, 1998). $Fe^{2+}/Fe^{3+}$ partition was performed using the $Fe^{3+}/Fe^{tot}$ ratio of 0.31 obtained by Mössbauer spectroscopy. In the absence of clear indication, all $Fe^{3+}$ was allocated at the octahedral layer. The formula was normalized based on 8.647 oxygen atoms (Kunze, 1961).

The obtained formula is $(Mg_{2.622}Fe^{2+}_{0.083}Fe^{3+}_{0.037}Al_{0.047}Mn_{0.006})_{\Sigma=2.795}(Si_{1.973}Al_{0.027})_{\Sigma=2.000}O_{5.000}(OH)_{3.647}$.

Results of ICP-OES analyses, following the antigorite sample incubation in MGS, show that the release of Mg, Si, and Al progressively increases with sample incubation time. The dissolution process evidenced two steps: (1) between 0 and 24 h, representing the undersaturation conditions favourable to fibre solubility; (2) after 24 h, representing the near-saturation conditions where element release is slower. In the first stage of dissolution, a preferential release of Mg with respect to Si is observed, in agreement with Madelung site energy (Schott et al., 1981). Moreover, for longer incubation times a nearly congruent dissolution takes place.

The obtained results provided the fundamental background for future works aimed at investigating all physico crystallo-chemical parameters of antigorite fibres that may cause adverse health effects.

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# Synchrotron techniques for the study of asbestos interactions with lungs

Gianoncelli A.*[1], Rizzardi C.[2] & Pascolo L.[3]

[1] Elettra-Sincrotrone Trieste. [2] Dipartimento Universitario Clinico di Scienze mediche, chirurgiche e della salute, Università di Trieste. [3] Istituto di Ricovero e Cura a Carattere Scientifico Materno e Infantile «Burlo Garofolo», Trieste.

*Corresponding author e-mail:* alessandra.gianoncelli@elettra.eu

*Keywords:* SR-XRF mapping, SR-XANES, asbestos.

The analysis of biological matrices at subcellular level dictates the use of multidisciplinary techniques and expertise. For the past decade Synchrotron facilities have been increasingly attracting the interest of the Life Science field thanks to the variety of techniques they can provide the scientific community with. In particular due to the high brilliance of the synchrotron sources and to the continuous development of X-ray optics and detectors, synchrotron-based techniques offer unprecedented opportunities in terms of spatial resolution, combined with high chemical sensitivity.

The present talk will focus on the use of X-ray microscopy, combined with X-ray Fluorescence (XRF) and X-ray absorption near edge structure (XANES) for investigating the interaction of asbestos fibres in lung tissues (Pascolo et al 2011; 2013; 2016; Kourousias et al., 2021) and cells (Cammisuli et al., 2018). With these microscopy and chemical imaging approaches it is in fact possible to obtain a real mapping of the chemical elements contained in a sample, thus chemically and morphologically characterize both fibers and asbestos bodies while monitoring the biological response they cause: such as iron dysmetabolism and mineralization mechanisms.

In particular the talk will report on the utilisation of the TwinMic soft X-ray microscopy station (Gianoncelli et al., 2016) (400-2200 eV) installed at the Elettra synchrotron facility in Trieste, Italy, and that has a unique sensitivity when tracing silicon-based particles and fibres, such as asbestos.

The most recent outcomes will be shown through selected results, highlighting the invaluable contribution of synchrotron-based techniques.

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# Natural $^{210}Po$-rich fibrous epsomite: a human health issue?

Giordani M.*[1], Meli M.A.[2], Roselli C.[2], Betti M.[2], Peruzzi F.[3], Taussi M.[1], Valentini L.[2], Fagiolino I.[4] & Mattioli M.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Scienze Biolomecolari, Università di Urbino "Carlo Bo". [3] Federazione Speleologica Regionale dell'Emilia Romagna, San Lazzaro di Savena (BO). [4] Gruppo C.S.A. S.p.A, Rimini.

*Corresponding author e-mail:* matteo.giordani@uniurb.it

*Keywords:* fibrous minerals, epsomite, soluble fibres.

Biopersistent fibrous minerals are often investigated due to their possible hazard to human health because they can remain in the lungs for a long time. On the contrary, very scarce knowledge exists on the accurate chemical composition and the possible effect of particulates and fibres with higher solubility (in water and biological environments), such as sulphate minerals and other phases.

Natural fibrous epsomite from Perticara Mine (Central Italy) was investigated through SEM-EDS, XRPD, ICP-AES and alpha spectrometry measurements with the aim of reducing this lack of knowledge on a fibrous sulphate mineral.

A significant number of small fibres with inhalable size for humans were observed on the epsomite sample through morphological and morphometrical investigations. The resulting equivalent aerodynamic diameter ($D_{ae}$) of epsomite fibres is 5.09 μm. Accordingly, we can assume that the fraction of measured fibres that can penetrate the respiratory tract is not negligible and that the epsomite fibres can easily penetrate and be deposited in the laryngeal and bronchial respiratory tract.

Chemical analysis revealed the presence of toxic elements (As, Co, Fe, Mn, Ni, Sr, Ti, Zn) and very high amounts of radioactive isotopes on epsomite crystals. In particular, a surprisingly high amount of $^{210}Po$ (5.59 Bq/g) was detected. The first results of this study were recently published by Giordani et al. (2022).

Due to the high solubility of epsomite under lung conditions (37°C and 100% relative humidity; Chipera & Vaniman, 2007), the inhaled fibres rapidly became a solution. Then, the entire load of hazardous elements could be quickly released into the lung environment and adsorbed from all parts of the respiratory tract, with consequent effects on human health.

Epsomite is common in several natural and anthropic environments worldwide, such as caves, mines, geological outcrops, mineral springs, and efflorescence, and also has several medical and pharmaceutical applications (Ruiz-Agudo et al., 2008). For this reason, our findings suggest great caution in handling other natural epsomite samples. The present work can be considered a representative case study of the investigation of the interaction between soluble minerals and human health. These preliminary results can be the basis for further studies on the content of hazardous elements in building materials and on the toxic elements interaction with humans.

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# Characterization of tremolite-asbestos from Mid Atlantic Ridge

Giovanardi T.*[1], Di Giuseppe D.[1], Perchiazzi N.[2], Brunelli D.[1-3], Nodari L.[4], Della Ventura G.[5-6], Malferrari D.[1], Maia M.[7] & Gualtieri A.F.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Istituto di Scienze Marine, CNR, Bologna. [4] Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia, CNR, Padova. [5] Dipartimento di Scienze, Università di Roma Tre. [6] INFN, Laboratori Nazionali di Frascati, Frascati (RM). [7] CNRS-Géosciences Océan UMR 6538, Institut Universitaire Européen de la Mer, Plouzané (France).

*Corresponding author e-mail:* tommaso.giovanardi@gmail.com

*Keywords:* asbestos, tremolite, Mid Atlantic Ridge.

Tremolite, in its fibrous form, is one of the six asbestos minerals. Together with actinolite and anthophyllite, tremolite forms during serpentinization of basic to ultra-basic igneous rocks. In this frame, tremolite is commonly found in ophiolitic complexes which are the principal host formations for these minerals. Due to the fact that human exposition to asbestos occurs in everyday life, the study of fibrous minerals is mainly focalized on their continental deposits. However, the oceanic lithosphere is the more important deposit of mineral fibres and it is also the precursor of most continental ones. Thus, studying the occurrences of asbestos directly in oceanic lithosphere could permit to constrain the formation processes of these minerals and provide information about the compositional evolution and diversity of the oceanic and continental domains.

Here we present the first chemical and structural study of a tremolite asbestos found along the Mid Atlantic Ridge collected from the surface of a normal fault at the eastern intersection of the Romanche Transform Fault. Tremolite is associated with chlorite and lizardite and enveloped in a Mn-oxides crust. This mineralogical association indicate that tremolite asbestos formed through the green shale facies lower than zeolite in a predominantly fluid system. This is in good agreement with chlorite temperature estimations between 202-206°C. Chemical analyses and structure refinements point out a very slight deviation from the ideal crystal chemistry of tremolite. The cationic formula could be expressed as:

$$(Na_{0.25}K_{0.01})_{\Sigma=0.26}\,(Ca_{1.80}Fe^{2+}{}_{0.17}Na_{0.03})_{\Sigma=2}\,(Mg_{4.65}Al_{0.14}Fe^{3+}{}_{0.13}Cr_{0.05}Ti_{0.01}Ni_{0.01}Mn_{0.01})_{\Sigma=5}\,(Si_{7.53}Al_{0.47})_{\Sigma=8}\,O_{22}(OH)_2$$

The high Mg# value of tremolite (0.972) and the absence of talc (whose crystallization is controlled by Si saturation of the system) suggest an ultramafic peridotitic nature of the protolith. In this frame, Ca necessary for tremolite crystallization must derive from carbonate or Ca-rich silicate phases. The occurrence of plagioclase impregnation plagues within serpentinites near the fault suggests that the alteration of plagioclase provides the necessary Ca without Si saturation in the system.

Comparison of continental and oceanic tremolite indicates different chemical and cation-site partitioning for the two domains. In particular, continental tremolites commonly show higher $SiO_2$, MnO, MgO and CaO and lower $TiO_2$, $Al_2O_3$ and $Na_2O$ than oceanic occurrences and are in general closer to the tremolite end-member. This different behaviour is mainly recognizable for Fe- and Mg- relationships with Si, where continental and oceanic tremolites form separate trends. These observations suggest that tremolite within ophiolitic complexes formed under conditions different from the primary oceanic setting, possibly during obduction or the orogenetic cycles. Our study provides useful information differencing fibrous amphibole from continental and oceanic settings.

# The Liberability factor: a new experimental protocol to predict the environmental dispersion of Elongated Mineral Particles

Gomiero C.*[1], Petriglieri J.R.[1-3-4], Barale L.[4-1], Giustetto R.[3], Pacella A.[5], Piana F.[4-1], Campopiano A.[6] & Turci F.[1-2-4]

[1] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [2] Dipartimento di Chimica, Università di Torino. [3] Dipartimento di Scienze della Terra, Università di Torino. [4] Istituto di Geoscienze e Georisorse, CNR, Torino. [5] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [6] Dipartimento di medicina, epidemiologia, igiene del lavoro e ambientale, INAIL, Monte Porzio Catone (RM).

*Corresponding author e-mail:* cecilia.gomiero@unito.it

*Keywords:* naturally occurring asbestos, weathering simulation test, environmental hazard.

The occurrence of asbestos and asbestos-like minerals (NOA) in natural sites may represent a risk for human and environmental health, specifically when natural or anthropic disturbance of NOA-bearing rocks occurs. These actions result in the release of the potentially hazardous Elongated Mineral Particles (EMPs; NIOSH, 2011). The term EMPs covers the six-regulated asbestos and other fibrous minerals that exhibit an aspect ratio (length/width) greater than 3.

We designed a new experimental protocol to quantitatively evaluate the potency of a rock to release EMPs and fibres (according to World Health Organization criteria; WHO, 1997) into the environment. The approach produced a quantitative parameter, namely the “liberability factor” (Lf), and was tested on about 40 meta-ophiolite samples from different NOA-bearing units of Liguria and Calabria.

An adaptation of the method UNI EN 12457-2:2004 for solid waste was used to design a weathering simulation test for the quantification of EMPs released after the application of a standardized mechanical stress. Waterborne EMPs and fibres were measured by Scanning Electron Microscope (SEM-EDS) according to the procedure set up by the Regional Agency for the Protection of the Environment (ARPA Piemonte, 2016). Lf values were expressed as the number of waterborne EMPs suspended per unit volume of water (fibres/L) and converted into the number of waterborne EMPs per mass of the rockfragment tested (fibres/mg). Lf values ranged from 6.5M to 380’000M EMPs/L. Per mass results ranged from 0.1 to 6400M EMPs/mg. The analyzed samples showed the presence of chrysotile, tremolite-actinolite, antigorite, or sepiolite, that exhibited an asbestos-like habit.

By comparing the Lf values to the overall concentration of NOA available in each selected rockmatrix, we speculated on the potency of specific NOA-bearing matrices to liberate and disperse EMPs in the environment. Our results provide a preliminary indication of the potential environmental exposure elicited by specific EMP-containing rocks. The Lf analysis has proven to be a reliable and easy-to-use method in laboratories.

*This study is part of the BRIC 2019 project (grant number ID 57.1) supported by INAIL (Italian National Institute for Insurance against Accidents at Work).*

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# Globalization and asbestos. The issue of the flow of asbestos-contaminated raw materials in the free world market

Gualtieri A.F.*

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* alessandro.gualtieri@unimore.it

*Keywords:* asbestos, raw materials, globalization.

Asbestos is still a problem today and globalization has somehow exacerbated it.

The asbestos minerals chrysotile (serpentine species) and the amphibole species actinolite-tremolite asbestos, amosite, anthophyllite asbestos, and crocidolite are all included by the International Agency for Research on Cancer in the Group 1 “substance carcinogenic to humans” (IARC, 2012). Notwithstanding, a global ban exists today only for the amphibole asbestos species (with the exception of Bolivia and India) while the so called “safe use” (Frank, 2020) of chrysotile is still allowed in 59% of the world’s countries (IBAS, 2022). The countries that exploit and work chrysotile like Russia can export it all over the world without precautions because “no labelling” is imposed for asbestos containing goods by the Rotterdam Convention (IBAS, 2022). Favoured by the free flow of the asbestos containing goods, the values of the Russian asbestos exports in 2020 were estimated at $175 million with the biggest importers being India, Indonesia, China and Sri Lanka (IBAS, 2022).

The outcome of this global asbestos chaos is that countries that have banned all asbestos species including chrysotile (like Italy) may unknowingly import chrysotile-containing materials from the producing countries (like China or Russia). This short circuit also applies to the natural raw materials that eventually contains asbestos minerals as secondary or impurity phases. By way of example, we have recently reported the case of a brucite product from China that can contain chrysotile (Malferrari et al., 2021). The problem may extend to other raw materials with composition and genesis compatible with that of asbestos minerals like Mg-rich silicates and carbonates.

This presentation will discuss the state of the art on the issue of the flow of asbestos-contaminated raw materials in the free world market, present risky case examples and possible solutions.

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# Actions to prevent Naturally Occurring Asbestos (NOA) fibers spreading: the INAIL approach

Guercio A.*

Consulenza Tecnica Accertamento Rischi e Prevenzione Centrale, INAIL, Roma.

*Corresponding author e-mail:* a.guercio@inail.it

*Keywords:* primary spreading, derived spreading, prevention.

The volume “Naturally Occurring Asbestos and workplaces” published by INAIL (Guercio et al., 2021), final achievement of a project focused on the characterization of NOA sites in Italy, examines activities, such as mining and quarrying, stone working, construction of buildings and infrastructures, urban settlements, that may cause potential risk situations and, consequently, asbestos fibers primary spreading and derived spreading.

In Italy, the first prevention action is the knowledge of natural asbestos outcrops; this is based on the mandatory natural asbestos mapping as disciplined by Ministerial Decree 101/03 according to which Local Authorities have to carry on, update yearly and spread detailed mapped information about these sites.

Main information, useful to estimate the probability to intercept asbestos veins, consists in type of rocks or soils, presence and type of asbestos minerals, layering and texture, degree of rock mass fracturing, areal extension and depth of outcrops.

On the basis of the experiences of Local Authorities, enterprises and Universities and of Inail’s studies, the volume provides specific technical and organizational recommendations in order to display all the preventive measures needed before beginning any working operation (prevention through design) to avoid the spreading of airborne asbestos dust during work.

These measures may be different depending on type of asbestos fibres spreading (primary and/or derived). The solutions are divided in “main”, efficient for every activity, and “specific” ones.

Some of the main actions consist in avoiding asbestos mineralized veins during quarrying or excavations, providing dust abatement systems, cleaning and maintenance of equipment and devices.

Specific actions regards maintenance of floor and ramps in quarries and yards, moving and materials handling, vehicles and operating means equipment, device and cleaning, water dust suppression systems, cutting and excavations techniques, job organization aimed to isolate operators from sources of dust and to plan timing of interventions.

This item is focused on the main risk situations for each type of activities (quarrying, excavations, tunnelling, urbanization) and on the related and most adequate measures to prevent asbestos fibers spreading and, eventually, asbestos workers’ risk exposure.

Guercio A., Rimoldi B., Malinconico S., Paglietti F., Conestabile della Staffa B., Bellagamba S., Addia R., Antonelli B., Bellomo D., Bevilacqua R., Bogliolo M.P., Buffa C., Cifelli F., Colafemmina G., Continisio R., Della Penda E., De Simone P., Di Benedetto R., Frusteri L., Galassi R., Mecchia M., Gargano C., Iotti A., Lancellotti D., Marchesi E., Massera S., Nori L., Papapietro N., Santucciu P., Tamigio G., Valori L., Zecchi C. (2021) - Amianto naturale e ambienti di lavoro. Inail, Milano.

# Naturally Occurring Asbestos recognition and response actions in European environmental decision making

Hyskaj A.*[1], Schimek É.[1], Weiszburg T.[1-2] & Harman-Tóth E.[1]

[1] Department of Mineralogy, Eötvös Loránd University, Budapest (Hungary). [2] Department of Environmental Science, Sapientia Hungarian University of Transylvania, Cluj-Napoca (Romania).

*Corresponding author e-mail:* ambra.hyskaj@ttk.elte.hu

*Keywords:* Naturally Occurring Asbestos, policy making, Europe.

All forms of asbestos minerals (chrysotile, tremolite, actinolite, crocidolite, amosite and anthophyllite) are declared carcinogenic to humans (IARC, 2012). Yet, the means to avoid exposure to this mineral group are not fully established. The regulatory framework of asbestos as a hazardous material in Europe focuses on occupational and asbestos containing (industrial) materials exposure only, especially in indoor environments. On the other hand, the natural occurrence of asbestos (NOA) is still unaccounted, leaving opportunity for human exposure to carcinogenic materials.

Since the natural occurrence of asbestos in the environment cannot be avoided or restricted, management of exposure paths is a continuing responsibility towards sustainable environment quality. In accordance with the Aarhus Convention (including here Directive 2003/4/EC and Directive 2003/35/EC of the European Commission) anyone can access information, take part in decision-making and access justice related to the environment. Even though Europe has a number of EMP (elongated mineral particle) experts, there is no legal board to support professionally questions raised by the European citizens. Thus, a multilateral collaboration is needed to create comprehensive guidelines which can be followed by further requests (questions and letters addressed to the European Commission, and a petition for NOA consideration and regulation submitted to the European Parliament). While recommendations and opinions would serve only to advise state members, regulations and directives would serve as legislations to set goals for member states to accomplish. While air quality control expertise is still existing in Europe (due to occupational exposure issues), this expertise needs to be maintained and collaboration strengthened due to NOA, and to advise sustainable land use on the risky areas.

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European Commission (2003b) - Directive 2003/35/EC of the European Parliament and of the Council of 26 May 2003 providing for public participation in respect of the drawing up of certain plans and programmes relating to the environment and amending with regard to public participation and access to justice Council Directives 85/337/EEC and 96/61/EC.

# Potential toxicity of elongated mineral particles: fibrous ferrierite from Northern Italy

Mattioli M.*[1], Ballirano P.[2], Pacella A.[2], Cangiotti M.[1], Di Lorenzo F.[3] & Giordani M.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Laboratory for Waste Management, Paul Scherrer Institute, Villigen (Switzerland).

*Corresponding author e-mail:* michele.mattioli@uniurb.it

*Keywords:* ferrierite, zeolites, toxicity.

Fibrous minerals represent a serious environmental and occupational hazard, and exposure to these fibers is one of the main causes of the development of pulmonary diseases. The asbestos minerals (chrysotile and asbestiform amphiboles) are by far the most infamous. However, other non-regulated fibrous minerals are potentially as dangerous as the regulatory asbestos because they share similar physical and chemical properties. These fibrous minerals are identified with the term elongate mineral particles, EMPs. Here we focused our attention on a natural fibrous zeolite, ferrierite, that has already been reported as a possible risk to human health (Gualtieri et al., 2018). Morphology, mineralogy, crystal structure, chemistry, and surface activity of fibrous ferrierite recently found in Northern Italy were investigated through an integrated approach using SEM-EDS, EMPA, XRPD, and EPR.

The investigated samples contain abundant crystals with prismatic to highly fibrous habits, and very low flexibility. Morphometric data point out the presence of notable amounts of breathable fibers, with a significant fraction of fibers able to penetrate through the respiratory tract and reach the alveolar space (Dae 2.59 - 2.42 μm). Crystals are Mg-rich ferrierites, R is from 0.81 to 0.83, and the prevailing extra-framework cations are in the Mg > (Ca ≈ K) relationship. The Si/Al ratio (4.2-4.8) is higher than that of erionite (Si/Al ~3.5), whose carcinogenicity has been well known. The bond distances refined in the 1.601-1.642 Å range suggest the occurrence of some degree of Si,Al ordering, with Al showing a site-specific occupation preference T1 > T2 > T3 > T4. EPR data show high amounts of adsorbed CAT1 and CAT8 probes for ferrierite samples. The adsorption rates of probes in solid samples and the amount of interacting components confirm the high abilities of these zeolites to adsorb and interact with related chemicals.

This study confirms that fibrous ferrierite has all the credentials to be considered a potential health hazard and should be tested for toxicity. Furthermore, the remarkable similarities that exist between ferrierite and erionite (e.g., asbestiform habit, high content of breathable fibers and fibrils, presence of iron as impurities, high interaction capability, high Si/Al ratio, biodurability), strongly support the hypothesis that both fibrous zeolites may have a high toxicity/pathogenicity potential. Since the occurrence of fibrous ferrierite concerns geological formations which are intensively quarried for application uses, in addition to potential environmental exposure, occupational and environmental exposures also need to be considered.

Gualtieri A.F., Gandolfi N.B., Passaglia E., Pollastri S., Mattioli M., Giordani M., Ottaviani M.F., Cangiotti M., Bloise A., Barca D., Vigliaturo R., Viano A., Pasquali L. & Gualtieri M.L. (2018) - Is fibrous ferrierite a potential health hazard? Characterization and comparison with fibrous erionite. Am. Mineral., 103, 1044-1055.

# The acute toxicity of mineral fibres: a systematic *in vitro* study using different THP-1 macrophage phenotypes

Mirata S.*[1-4], Di Giuseppe D.[2], Almonti V.[3-4], Vernazza S.[3-4], Gualtieri A.F.[2], Bassi A.M.[3-4], Scarfì S.[1-4], Fornasini L.[5], Raneri S.[5] & Bersani D.[6]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [3] Dipartimento di Medicina Sperimentale, Università di Genova. [4] Centro Interuniversitario per la Promozione dei Principi delle 3R nella Didattica e nella Ricerca, Università di Genova. [5] Istituto di Chimica dei Composti Organo-Metallici, CNR, Pisa. [6] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma.

*Corresponding author e-mail:* serenamira94@gmail.com

*Keywords:* mineral fibres, asbestos, carcinogenicity.

Exposure to mineral fibres represents a serious occupational and environmental hazard, since it leads to chronic lung inflammation with the subsequent emergence of fibrotic pulmonary diseases, pneumoconiosis and various types of malignancies. This happens mainly by inhalation, leading to the localization of the mineral fibers in the lung tissue, where macrophages have a fundamental role in both triggering and maintaining the inflammatory response. In fact, three types of differentiated macrophages can be present at the site of injury and contribute to the outcome of the inflammatory process, namely non-activated M0, pro-inflammatory M1 and alternatively activated M2 cells.

To date, no comparative data have been obtained from the concomitant analysis of the acute toxicity and the inflammatory response induced by different mineral fibres in M0, M1 and M2 cells. Thus, we set up an *in vitro* model based on the three macrophage phenotypes, obtained from THP-1 cell differentiation, and then employed to study the acute effects of three types of carcinogenic mineral fibres: UICC standard crocidolite, chrysotile from Balangero and fibrous erionite from Jersey.

The aim of this study was to gain new insights into the different toxicity mechanisms exerted by these mineral fibres after the first 24 h of exposure. Their cytotoxic action in the three macrophage phenotypes was studied by measuring the level of cell death by either cell lysis or apoptosis. Subsequently, we studied the intracellular oxidative state, the intracellular toxic metal release and the presence of DNA damage. Moreover, the inflammatory response was assayed evaluating both the extracellular release and the gene expression profile of several pro-inflammatory cytokines known for having a crucial role in the early inflammatory response and contributing to the onset of chronic diseases and malignancies in the long term. In general, crocidolite and chrysotile were more potent with respect to erionite in triggering ROS production, apoptosis and cytokine release in the three types of differentiated macrophages.

The three mineral fibres apparently act by different toxicity mechanisms. Crocidolite seems to exert its toxic effects mostly as a result of its biodurability, ROS and cytokine production and DNA damage. Chrysotile, due to its low biodurability, displays toxic effects related to the release of toxic metals and the production of ROS and cytokines. Other mechanisms are involved in explaining the toxicity of biodurable fibrous erionite, which induces lower ROS and toxic metal release but exhibits a cation-exchange capacity able to alter the intracellular homeostasis of important cations.

# Opposite polarity static magnetic field system (CMSPC) used to isolate naturally occurring asbestos (NOA): first results

Olori A.[1], Bruno M.R.*[2], Sinopoli F.[2] & Burriesci G.[1]

[1] Dipartimento di medicina, epidemiologia, igiene del lavoro e ambientale, INAIL, Monte Porzio Catone (RM).
[2] Dipartimento di medicina, epidemiologia, igiene del lavoro e ambientale, INAIL, Lamezia Terme (CZ).

*Corresponding author e-mail:* ma.bruno@inail.it

*Keywords:* Naturally Occurring Asbestos, CMSPC, SEM-EDS.

Naturally occurring asbestos (NOA) is a general term applied to the geologic occurrence of any of the six types of asbestos minerals (Bloise et al., 2016; Campopiano et al., 2018a; 2018b). In some of these NOA we found ferromagnetic minerals such as actinolite or antigorite. Fenton reaction explains the toxicity of iron. Iron and hydrogen peroxide are capable of oxidizing a wide range of substrates and causing biological damage. The reaction is complex and capable of generating both hydroxyl radicals and higher oxidation states than iron. So can be important to create a system to isolate and/or to purify ferromagnetic minerals. The present work reports a detailed scheme to construct a batch system for minerals' purification. We created a device to generate a static magnetic field; six magnets with opposite polarity arranged circularly around a cylindrical ceramic container. The batch produces a toroidal static magnetic field. The system has the following technical characteristics: a container in glazed ceramic with a cylindrical shape flared at the top; height of 13 cm with a top diameter of 8 cm and a bottom diameter of 5.5 cm; inverted truncated cone shape; 6 magnets with 4 opposite polarities, 10 cm long and 4 cm apart, fixed around the container. Static magnetic field of the system was measured. The measurements were carried out by positioning the probe at the bottom, at the top and at an intermediate height of the beaker. Each measurement reported is the average of three measurements. At the top of the beaker the measured static field is equal to 0.00235 Tesla (T) ± 0.00004 (23.5 Gauss (G) ± 0.4). At the bottom of the beaker the measured static field is equal to 0.0182 T ± 0,0005 (182 G ± 5). At an intermediate height of the beaker the measured static field is equal to 0.01382 T ± 0.00005 (138.2 G ± 0.5). Measurements were made using the THM1176 Three-axis Hall Magnetometers (Metrolab Instruments SA, Geneva, Switzerland). It is a portable probe with a dynamic range from a few hundred microtesla up to 20 T (HF type) in four spans, bandwidth DC to 1 kHz and ± 1% uncertainty. In the present work, we have carried out preliminary tests on some NOA. Ferromagnetic minerals (PL5 samples) investigated in this work came from an abandoned serpentine quarry located in the Monte Reventino area (Calabria, Italy, longitude 16°18′44″, latitude 39°02′07″), in the northern sector of Calabrian Apennines Peloritan Orogen (Pacella et al., 2021). After mechanical separation, minerals of Tremolite-Actinolite series was treated and dispersed in to the batch. Then they were filtered and analyzed with Microscope. Sample morphology was investigated by analyzing the filters, mounted on a stub and gold coated, using a Scanning Electron Microscopy (SEM) with energy dispersive spectroscopy (EDS) (FEG -SEM Merlin Zeiss). The first results made it possible to isolate and purify Tremolite talc with good percentages.

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# Exploring the potential of portable µRaman for in situ identification of asbestos fibers

Osticioli I.[1], Perotti M.*[2], Indelicato C.[2], Marian N.M.[2], Ciofini D.[1], Mencaglia A.A.[1], Bellagamba S.[3], Malinconico S.[3], Paglietti F.[3], Viti C.[2] & Siano S.[1]

[1] Istituto di Fisica Applicata "N. Carrara", CNR, Sesto Fiorentino (FI). [2] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [3] Dipartimento innovazioni tecnologiche e sicurezza degli impianti, prodotti e insediamenti antropici, Istituto Nazionale Assicurazione Infortuni sul Lavoro, Roma.

*Corresponding author e-mail:* matteo.perotti@unisi.it

*Keywords:* Natural Occurring Asbestos, portable Raman spectroscopy, in situ investigation.

Natural occurring asbestos minerals (NOA) and asbestos containing materials (ACM) are object of serious concerns due to their known danger to human health and related industrial and environmental issues. Rapid detection of asbestos minerals both in natural and anthropic contexts has become a fundamental challenge for assessing health risks. In this respect, vibrational spectroscopy appears to be the most promising approach for recognising in situ the different species of asbestos in rocks (NOA) and ACM. Here, we report a preliminary investigation on the analytical performances of a dedicated compact µRaman device suitably designed to get high portability and analytical reliability. This was equipped with miniaturized laser excitation sources along with a compact, high sensitivity, and high-resolution spectrometer recently marketed. A number of samples of NOA (serpentinite rocks, soils) and of ACM (asbestos cement, tiles) have been analysed by collecting spectra over a broad spectral range (about 150-6000 $cm^{-1}$). The results achieved have been compared with those provided by a benchtop µRaman system, in order to optimize the acquisition parameters and then maximising the performances of the novel portable µRaman instrument. This work shows the latter allowed rather rapid identification of asbestos fibers within different matrices and aggregates. Some problems were encountered in cases where the fibers were dispersed within fluorescent materials or when they were completely embedded or not sufficiently protruding from the surface of the host material. Nevertheless, the results of the mobile instrument were very similar to those achieved using the laboratory system, which allows to foresee a significant application perspective within the present field.

# First results on the erionite risk assessment in Central Italy

Paglietti F.[1], Bellagamba S.[1], Malinconico S.[1], Cecchetti G.[2], Giordani M.[3] & Mattioli M.*[3]

[1] Dipartimento Innovazioni tecnologiche e sicurezza degli impianti, prodotti e insediamenti antropici, INAIL, Monte Porzio Catone (RM). [2] Ecoman s.r.l., Roma. [3] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo".

*Corresponding author e-mail:* michele.mattioli@uniurb.it

*Keywords:* erionite, zeolites, toxicity.

Erionite is a naturally occurring mineral that belongs to a group of silicate minerals called zeolites. It is usually found in volcanic rocks that have been altered by weathering and groundwater. Like naturally occurring asbestos, erionite can occur in a fibrous form; that is why IARC in 1987 included this mineral in Group 1A - carcinogenic substances. Disturbance of this material can generate airborne fibers with physical properties and health effects similar to asbestos.

Although zeolite-bearing volcanic rocks are widespread in the volcanic districts of Central Italy, there are no systematic studies on the distribution of erionite or other similar fibrous zeolites in these areas. This is mainly because previous approaches to the hazard posed by fibrous zeolites were conducted only in areas with uncommon mesotheliomas, such as in Turkey, the United States, and Mexico. In Italy, epidemiological and toxicological knowledge of mesothelioma linked to erionite exposure is extremely scarce, and the phenomenon is still not comprehensively investigated. However, it is known that approximately 20% of national cases of mesothelioma are not linked to occupational exposure to asbestos.

Most of the volcanic rocks from Central Italy possess a considerable thickness and are affected by various secondary mineralization processes similar to those described in other areas where erionite has been widely found. Therefore, it cannot be excluded a priori that erionite or other fibrous zeolites might also be extensively present in these volcanic rocks. Nevertheless, most of these rocks have not been investigated with this aim in mind, and specific studies on the occurrence of fibrous minerals are currently lacking. Given the considerable extension of these volcanic rocks, environmental exposure to this hazardous fibrous zeolite needs to be taken into serious consideration. This is even more important if active mining or quarrying activities are hosted in these rocks, extensively used as construction material.

In the present study, as the first step, the geological units in Lazio Region were surveyed through a geological analysis of the existing literature and extensive fieldwork. Thanks to the extensive quarrying activity in this area, all the extracted volcanic horizons were surveyed and sampled during the fieldwork. About 20 sampling sites were chosen in correspondence with active and disused quarries. Were then collected about one hundred samples of several volcanic formations, cleaned from residual external material, and preliminarily analyzed under a binocular microscope to verify their quality. Representative samples were then investigated by optical microscopy (OM), X-ray powder diffraction (XRPD) analysis, and scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS).

In this work, we report preliminary results of samplings and analysis conducted on some of the several volcanic deposits of Central Italy to identify and quantify the possible occurrence of health-threatening minerals.

# Laboral safety. How Science can increase perception of asbestos-related disease risk

Pereira D.*[1], López A.J.[2], Ramil A.[2] & Bloise A.[3]

[1] Department of Geology, University of Salamanca (Spain). [2] Laboratorio de Aplicaciones Industriais do Láser, Ferrol (Spain). [3] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* mdp@usal.es

*Keywords:* laser cleaning, asbestos, laboral safety.

Health risks are many times overseen when the consequences are not too evident at the short term. In restoration work, some actions can generate particles that may affect the health of workers through inhalation. Such is the case of asbestos fibers coming from the cleaning of buildings or heritage artifacts made of stone, such as serpentinite and other ultramafic rocks, that may contain asbestos (e.g., chrysotile, tremolite, actinolite). Workers at quarries are also exposed to such material, and therefore the results of our work can help to increase the risk perception in workers from the stone sector, but also to construction workers that work in an environment full of dust.

To demonstrate workers the importance of protection to prevent health injuries, we have ablated some samples of serpentinite after making sure that they have chrysotile as major phase mineral through optical microscope and X-ray powder diffraction. Powder obtained in filters coupled to the ablation laser was analyzed, using tools such as optical microscope, X-ray powder diffraction, transmission electron microscope and thermal analysis. The results were very didactic, and the intention is to use them, in the way of graphics and diagrams, to build information security sheets that will alert the workers about the need of using masks when working or to use tools with coupled filters as the one we used for our study. The main goal is to demonstrate that the interdisciplinary combination of scientific approaches can be used for the sake of human health.

*This is a contribution to the IGCP-746 project.*

# Design of a compact device for airborne asbestos measurement: challenges and solutions

Rabiee A.[1], Della Ventura G.*[1-2], Mirzapour F.[3], Paglietti F.[4], Malinconico S.[4] & Bellagamba S.[4]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INFN, Laboratori Nazionali di Frascati, Frascati (RM). [3] HNA-Co, R&D Department, Tehran (Iran). [4] Dipartimento Innovazioni tecnologiche e sicurezza degli impianti, prodotti e insediamenti antropici, INAIL, Monte Porzio Catone (RM).

*Corresponding author e-mail:* giancarlo.dellaventura@uniroma3.it

*Keywords:* airborne asbestos, monitoring, image analysis, deep learning.

Real-time measurement of airborne asbestos is vital to prevent professional hazards, particularly in those working activities subject to potential high exposure to dusts. Conventional methods for airborne asbestos counting are based on phase contrast microscopy (PCM) or fluorescence microscopy (FM); in both techniques the airborne particulate is sampled on filters that are chemically treated for further manual counting. Numerous attempts have been made to speed up the work through image analysis, however the proposed procedures do not allow rapid and automated analyses of the sampled airborne pollution.

To overcome these difficulties, we started a project aimed at designing a portable apparatus with the final goal of providing the workers with a portable system able to monitor the presence of airborne fibres. The device is equipped with a novel sample collector coupled with an LED back-light source and an optical system which can resolve up to 0.7 µm particles. The images are directly acquired from a surface of a Mixed Cellules Ester (MCE) 450 nm, while the air suction is in progress. The advantage of back-light illumination is that even transparent particles smaller (or thinner in case of fibers) than 0.7 µm provide a shadow which is easily detectable, due to edge light diffraction. Using our trained deep learning model for implementing asbestos counting rules, we can identify even hardly visible fibers which are not detectable using conventional image analysis methods; with these latter methods significant misinformation is in fact caused by heterogeneities in the filter surface and illumination. Our automated counting method can provide not only the fibres amount but also its change through time; the designed system can thus alarm the increase in airborne asbestos concentration in risky workplace environments and help reducing the time of workers exposure to asbestos.

# Release of metals and dissolution of mineral fibres in THP1 macrophagic cell-line systems exposed to chrysotile asbestos. A synchrotron-based study

Raneri S.*[1], Fornasini L.[1-2], Gianoncelli A.[3], Villalobos E.[4], Di Giuseppe D.[5], Scognamiglio V.[5], Mirata S.[6], Almonti V.[7], Bonanni V.[3], Parisse P.[8], Bersani D.[2], Bassi A.M.[7], Marengo B.[7], Scarfì S.[6] & Gualtieri A.F.[5]

[1] Istituto di Chimica dei Composti Organo-Metallici, CNR, Pisa. [2] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [3] Elettra-Sincrotrone Trieste. [4] ESRF, Grenoble (France). [5] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [6] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [7] Dipartimento di Medicina Sperimentale, Università di Genova. [8] Istituto Officina dei Materiali, CNR, Trieste.

*Corresponding author e-mail:* simona.raneri@pi.iccom.cnr.it

*Keywords:* SR-XRF, SR-XANES, chrysotile.

In chrysotile, the most commercialized asbestos species, Fe and other metals are worth considering in its potential toxicity (Gualtieri et al., 2019); in fact, large amounts of Fe (>1000 ppm) and trace metals (Cr, Ni, Co, Mn, etc.) are also intimately associated with the raw material. Since both Fe and trace metals are usually isomorphous substituent of Mg in octahedral sites, their release into the lung environment is strictly connected to that of Mg, when fibres are dissolved by the macrophage phagocytosis (Pollastri et al., 2015). Thus, trace elements are potentially involved in the production of reactive oxygen species (ROS), in addition to Fe (Bloise et al., 2016).

In the frame of the PRIN 2017 3X8WA4 project, THP1-cells exposed to chrysotile fibres (from Balangero, Italy) showed the formation of aggregated structures of both fibrous and non-fibrous species, including Fe oxides and sulphides. These clusters have been extensively characterized by micro-Raman analysis but potential dissolution mechanism needs further investigation, looking at the spatial distribution of metals in the biological system and to the molecular structure of the existing species. To this extent, synchrotron-based X-ray imaging and spectroscopy represent an emerging and effective tool for investigating biological systems at the sub-cellular level, able to clarify metals mobilization mechanism, highlighting both their intracellular spatial distribution and the changes in their valence state induced by the fibres-cells interaction (Cammisuli et al., 2018).

A combined approach with AFM and X-ray fluorescence (XRF) elemental mapping with a sub-micrometre resolution, performed respectively at the at the NanoInnovation lab and the TwinMic beamline of the Italian Elettra Synchrotron Facility in Trieste, has been applied on THP-1 cells after different exposure time to fibers (8 h, 24 h, 96 h). On the same samples, at the ID21 beamline (ESRF, Grenoble, France), micro-XANES at the Fe K-edge provided fundamental details about the chemical states of Fe and the potential transformations of Fe sulphides/oxides in the organic environment. Micro-XANES at the Cr Kedge elucidated the possible Cr toxicity, discriminating Cr(III) - from the asbestos fibres - and potential Cr(VI) - as intracellular toxic species.

Results have been compared with those obtained with oxidative stress analysis, genotoxic and DNA damage investigations, cellular toxicity and viability tests. The whole study represents an important step forward in understanding the mechanisms of toxicity/pathogenicity of asbestos with particular emphasis on the role of iron Fe and other toxic metals released during the dissolution processes induced by phagocytosis.

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# Naturally Occurring Asbestos (NOA) fibers spreading: the INAIL approach

Rimoldi B.*

Consulenza Tecnica Accertamento Rischi e Prevenzione Centrale, INAIL, Roma.

*Corresponding author e-mail:* b.rimoldi@inail.it

*Keywords:* primary spreading, derived spreading, prevention.

The Volume "Naturally Occurring Asbestos and workplaces", published by INAIL (Guercio et al., 2021), represents the final achievement of an internal project focused on the characterization of NOA sites in Italy, in order to prevent specific occupational risks.

The NOA Project in INAIL dates back to 2014, following the positive e fertile experience of the regional study in the Valmalenco quarries, realized with the Regione Lombardia and University of Milano Bicocca contributions: to prevent spreading of mineral fibres during quarrying and consequently the transfer to the processing plants, innovative solutions were planned and shared with enterprises, and tested by workers in situ.

The aim of the volume is the dissemination of knowledge through the description and insights of the geological evidences and work activities set in areas of Naturally Occurring Asbestos, to better understand and manage potential risk situations. In the NOA mapping section (chapter 5) a brief overview of known NOA outcrops in Italy is presented.

Main anthropic activities that can disturb NOA-bearing rocks releasing mineral fibres into the air are: mining and quarrying, stone working, construction of buildings, infrastructures and urban settlements. The analysis of the potential risk situations takes place in every working activity subject of the study, and is based on the distinction between asbestos fibres primary spreading and derived spreading: in a quarry, the digging of rocks creates the primary spreading of dust and fibres, while the passing dumpers cause the resuspension of settled dust, so called derived spreading.

The volume provides specific technical prescriptions in order to display all the prevention measures needed before beginning any working operation (prevention through design), if the presence of NOA cannot be ruled out.

The detailed final section of the volume is dedicated to these prevention actions in the following fields: quarrying and working of ornamental stones and gravel, contaminated sites remediation, tunnel excavation/tunneling, excavation for urban settlements, agricultural and forestry works, ballast remediation.

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# Is there a toxic impact of Russian chrysotile on human health? An in vitro study on asbestos human inhalation target lung cells

Vaiasicca S.*[1], Di Valerio S.[1], Cianfruglia L.[2], Armeni T.[2], Marcheggiani F.[3], Tiano L.[3], Di Giuseppe D.[4], Gualtieri A.F.[4], Procopio A.D.[1], Fazioli F.[1] & Pugnaloni A.[1]

[1] Dipartimento di Scienze Cliniche e Molecolari, Università Politecnica delle Marche, Ancona. [2] Dipartimento di Scienze Cliniche Specialistiche e Odontostomatologiche, Università Politecnica delle Marche, Ancona. [3] Dipartimento di Scienze delle Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona. [4] Dipartimento di Science chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* s.vaiasicca@staff.univpm.it

*Keywords:* russian chrysotile, cito/geno toxicity, in vitro assays.

In the last few years studies related to human health hazard involved naturally occurring asbestos (NOA) underlining the environmental problem of airborne mineral fibers (Di Giuseppe et al., 2022). Nowadays the largest consumer of asbestos is China, followed by Russia, India, Kazakhstan, Brazil, Indonesia, Thailand, Vietnam and Ukraine, where the extraction and the use of asbestos to manufacture building materials are possible in a "safe mode" (Cavallo & Rimoldi, 2013). Among asbestos fibers, Chrysotile or "white asbestos", an hydrated magnesium silicate, represents one of the most asbestos fibers involved in industrial area since it owns a high mechanical resistance and flexibility. However, its exposure resulted in a great negative impact on not professionally exposed people health causing disease related to asbestosis, lung cancer and mesothelioma.

Our study focused the attention on Russian chrysotile fibers, divided in two groups based on their length: $< 5$ µm (R1) and $> 5$ µm (R2) and administered in cultures of mesothelial (MeT5A) and alveolar (A549) human cells lines. UICC Crocidolite (Cro-UICC) fiber was considered as positive control fibers and Wollastonite (W) as negative control fibers.

Results obtained in both cells lines showed a decrease of cells viability (by MTT test) and cell vacuolization (by light microscopy investigations) with higher grade after R2 treatment, confirming the higher cytotoxic effects exerted by longer fibers. On the basis of cytotoxic effect, inflammatory status was investigated showing a high release of reactive oxidative species in the cells with the consequent decrease of cellular glutathione, a potent endogenous antioxidant agent to contrast the insult. This status was in line with the high grade of DNA damage, assayed by Comet test, and related to a block in G2/M phase of cell cycle in both cell lines (investigated by flow cytometry).

This status was also established by molecular analysis (rtPCR) confirming the overexpression of genes implicated in cellular inflammation (Il-6) and proliferation (Cdk1 and Dnmt1). Also the analysis of miRNA-126 and -222, two miRNA related to mesothelioma pathway, showed an early upregulation (24 h) in both cell lines, suggesting a role in tumor progression.

This work mimics the possible cyto- and genotoxic impact of Russian chrysotile fibers in lung human tissue. Remarkably, the two cell lines investigated showed different response to treatments: in particular MeT5A cells showed a major sensibility compared to A549 cells, and higher effects after R1 (short fibers) treatments with respect to the long ones. Our data support the risk exerted by short fibers which allow the survival of damaged cells that could undergo tumoral pathways.

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# S23.

# Geology is coming home. A renewed interest in Italian geoscientific tradition


*Conveners & Chairpersons*

*Alessio Argentieri (Città metropolitana di Roma Capitale)*

*Marco Pantaloni (Servizio Geologico d'Italia - ISPRA)*

*Pietro Mosca (CNR - Torino)*

*Luca Barale (CNR - Torino)*

# It's a Hard Life in Maremma: Luciano Bianciardi and history of geology

Argentieri A.*[1-4], De Caterini G.[2-4] & Rossetti F.[3]

[1] Città metropolitana di Roma Capitale - Servizio 2 "Geologico, difesa del suolo, rischio idraulico e territoriale" - Dip. IV "Pianificazione, sviluppo e governo del territorio", Roma. [2] Engeo Praxis s.r.l., Roma. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma.

*Corresponding author e-mail:* a.argentieri@tiscali.it

*Keywords:* history of geology, Luciano Bianciardi, Maremma.

In the literary output of Luciano Bianciardi (Grosseto, 1922 - Milan, 1971), writer, journalist and translator, references to geology and geologists and his native land Maremma represent a key element. Although known primarily for his criticism of social and cultural environment during Italian economic miracle, Bianciardi in his works reveals a strong knowledge of the territory and of its physiography and geological characteristics. History of Tuscany has been strongly influenced by its geological setting, corresponding to the hinterland of the Northern Apennines where, since Miocene-Pliocene times, post-orogenic extensional tectonics caused crustal thinning, exhumation of the metamorphic roots of the orogen, magmatism and diffuse hydrothermal mineralization. Consequently, several ore deposits and ornamental stones crop out on the Tyrrhenian margin of southern Tuscany. Since the Etruscan civilization, mining and exploitation of underground resources were fundamental economic activities in Maremma.

Luciano, born in Grosseto on December 14th 1922, become attracted since childhood by the history of Italian *Risorgimento*. Various characters, directly or indirectly connected with history of geosciences, are cited in Bianciardi's books dedicated to this historical period: Paolo Savi, Giovanni Targioni Tozzetti, Antonio Stoppani, Giuseppe Meneghini and others. A special mention must be made about Leopoldo Pilla, whose death (occurred in 1848 on the battlefield of Curtatone, as commander of the batallon of his students from Pisa) is told in the short story "*Il volontario Sbrana*" (1966).

The social and economic condition of the working class of the by miners was another crucial issue in Bianciardi's view. The first chapter of *"I minatori della Maremma*" (Bianciardi & Cassola, 1956) starts with a geological framework of the region, prelude to a summary of history of mining research and industry. The tragic accident of the explosion in the Ribolla mine in 1954 inspired his best-known book "*La vita agra*" (It's a hard life), published in 1962.

On the centenary of Bianciardi's birth, we thus pay a tribute to the geological attitude of the writer and of the man.

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# Ragazzoni, Cacciamali and Cozzaglio: the 'Brescia geological trinity'

Argentieri A.[1-4], Schirolli P. [2-4-5] & Musumeci D.*[3-4]

[1] Città metropolitana di Roma Capitale - Servizio 2 "Geologico, difesa del suolo, rischio idraulico e territoriale" - Dip. IV "Pianificazione, sviluppo e governo del territorio", Roma. [2] Museo Civico di Scienze Naturali, Brescia. [3] Dipartimento di Scienze Umanistiche, Università di Catania. [4] Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma. [5] Istituto di Geologia Ambientale e Geoingegneria, CNR, Milano.

*Corresponding author e-mail:* daniele.musumeci@phd.unict.it

*Keywords:* Brescia, history of geology, Southern Alps.

Giuseppe Ragazzoni (Brescia 1824-1898) is undoubtedly the forefather of the geological school in Brescia. Pharmacist, teacher, patriot and politician, he was also a pioneer in modern geology, during a crucial stage (Schirolli, 2010). He inherited the interest in Earth sciences by his father Giovanni Battista, who have been in relations with G.B. Brocchi. Giuseppe focused his attention on the Brescia province and on Southern Alps. In more than 30 years of activity, he produced several geological maps and shared generously his knowledge with Italian and foreign scientists, as testified by his intense correspondence (Schirolli, 2010). Ragazzoni was also a mining entrepreneur, and applied his experience to the research and exploitation of ore bodies in the Trompia Valley; he also started with Antonio Stoppani spelaeological studies in the province. As all scientists of the time, Ragazzoni ascribed to vertical uplift the origin of mountain chains.

In 1899, a year after Ragazzoni's death, the *Circolo Speleologico Bresciano "La Maddalena"* was founded by Giovanni Battista Cacciamali, appointed as first President. Cacciamali (Brescia, 1857-1934) was pupil of Ragazzoni, as well as the younger Arturo Cozzaglio (Tremosine sul Garda, 1862-1950). The two scientists, connected by a deep friendship, had conversely two different vision of geology (Cappelletti Alippi, 1972; Corsi, 1984; Zaina, 1962). Carrying on the legacy of their common master, they politely but fiercely debated, through years, over the new orogenic theories that gradually established in the scientific community at the time. As known, between the last decades of the 19th century and the early 20th, the structures of Western Alps progressively unraveled their secrets to the keen eyes of Swiss, French and Italian geologists. A general conversion from autochtonist interpretation to mobilist theories occurred, despite the resistance to change by the austro-hungarian school. Cacciamali firmly believed in the new model, and revised his previous works in terms of translative tectonics. On the other hand, Cozzaglio, having the practical approach of the engineer, blamed generalizing theories and speculation not adequately supported by field observation.

Is a matter of fact that the geological school of Brescia, initially formed by amateur geologists and naturalists, promoted a positive debate over geology of Southern Alps. Around the local institutions ("Ateneo di Scienze, Lettere ed Arti di Brescia"; Speleological Circle; Natural History Museum, established in 1902) a positive cultural environment grew up, thus giving an important contribution to scientific progress between 19th and early 20th century.

The initial thrust was given by a group of "goodfellas" ("*brai gnari*", in the local dialect). Despite the great affection to their hometown, to which all remained deeply rooted for the entire life, they were capable to provide, maybe unawarely, a global perspective from local observations.

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# Clarence Bicknell (1842-1918): botanist, archaeologist, esperantist, and... citizen geologist

Barale L.*[1], Bicknell M.[2] & Massardo E.[2]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Clarence Bicknell Association, Chalfont St. Giles (UK).

*Corresponding author e-mail:* luca.barale@igg.cnr.it

*Keywords:* history of geology, Clarence Bicknell, Federico Sacco.

Clarence Bicknell (1842-1918) was an eclectic naturalist, archaeologist, artist and Esperantist. Born from a wealthy English family, in 1878 he moved to Bordighera (IM), where he spent the rest of his life and where, in 1888, founded the *Museo Bicknell* that still hosts a part of his collections (Lester, 2018). He was particularly versed in botany, and made substantial contributions to the study of the local flora. However, Bicknell's most significant scientific achievement is the systematic inventory and study of the prehistoric rock engravings of the Merveilles and Fontanalba valleys (Maritime Alps), to which he dedicated himself for twenty years, from 1897 until his death. Bicknell has been recently defined as a «*citizen scientist*» (Mariotti, 2019), for his commitment to several scientific disciplines for which he did not receive an academic training. If his contributions to botany and archaeology are universally praised, Bicknell's involvement in other disciplines is still poorly known. Over the years, Bicknell established relationships and maintained correspondence and collaboration with many geologists, including Alberto Pelloux (1868-1948), Federico Sacco (1864-1948), Arturo Issel (1842-1922), Gaetano Rovereto (1870-1952), and the palaeontologist and Esperantist Achille Tellini (1866-1938). With Pelloux, mineralogist and president of the Italian Geological Society in 1934, Bicknell had a sincere friendship, testified by an intense exchange of letters (Bernardini, 1989). Another lasting friendship linked Bicknell to Sacco, geologist and palaeontologist of Torino, author of a monumental treatise on the Tertiary molluscs of Piemonte and Liguria. As reported by Sacco, Bicknell "*donated a rich collection of Pliocene fossils from Liguria to the Geological Museum of Torino, and [...] always shares liberally with me all the material of the valuable collection put together by him and kept in the nice Museum he built in Bordighera*" (Sacco, 1897). These fossils had been collected by Bicknell since his arrival in Bordighera, mainly in the neighbourhood and in the famous Rio Torsero locality (Ceriale, SV). They represented an important set of specimens and are largely figured in Sacco's treatise; many of them are the type specimens of newly described species. Bicknell's contribution to the study of Western Liguria Pliocene faunas was acknowledged with the dedication of two fossil species: the bivalve *Aequipecten bicknelli* (Sacco, 1897), and the gastropod *Scalaria (Parviscala) Bicknelli* (Hornung, 1920) (today *Epitonium bicknelli* (Hornung, 1920).

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# The Alpine field notebooks of Secondo Franchi (1859-1932)

Barale L.[1], Console F.[2], Corno A.[3], Frasca G.[1], Mosca P.*[1] & Pantaloni M.[2]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.
[3] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* pietro.mosca@cnr.it

*Keywords:* Secondo Franchi, field notebooks, Western Alps.

Secondo Franchi (Castell'Alfero-Asti, 1859 – Rome, 1932) was one of the most influential Italian geologists. His maps and research activity were of great importance for the progress of geological knowledge of the Western Alps.

In a recent paper (Barale et al., 2022) we presented a few of Franchi's main contributions to the geology of the Western Alps by integrating published papers with unpublished material archived in the Library of the Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) in Rome. In particular, we have consulted 11 signed field notebooks of Franchi dated between 1890 and 1924, and original maps signed by Franchi and produced for the final publication of the Alpine geological sheets of the Geological Map of Italy at the 1:100,000 scale.

The field notebooks report geological sketches both at outcrop and landscape scale, often with synthetic but accurate explanations, and contain localities and topography for reference such that the geological features portrayed in cross sections and views can be easily located. These notebooks document the skills of the eminent geologist, who approached the study of the Alpine successions by integrating stratigraphy, structural geology, petrography and palaeontology. Franchi undertook an important and systematic revision of the Alpine lithostratigraphy, always supported by a scrupulous search of fossils both in sedimentary and meta-sedimentary successions, and the results of his studies were fundamental to constrain the Mesozoic age of the Zona delle Pietre Verdi.

In addition, beautiful and curious sketches of the world as observed by Franchi during his field activity enrich the field notebooks.

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# Last century approach to the Wegener theory in the school textbooks

Bonaccorsi E.*[1-2], Borghini A.[3], Gioncada A.[1] & Pieraccioni F.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Museo di Storia Naturale, Università di Pisa. [3] Corso di Dottorato Regionale in Scienze della Terra «Pegaso», Università di Pisa.

*Corresponding author e-mail:* elena.bonaccorsi@unipi.it

*Keywords:* Wegener theory, history of science, school textbooks.

Alfred Wegener published his seminal work "The Origin of the Continents and Oceans" in 1915 and updated it in 1920, 1922 and 1929. The reactions of geologists, geophysicists, and paleontologists were primarily one of rejection, though with varying degrees in different national scientific communities. After Wegener's death in 1930, his ideas were largely forgotten until the 1960s. In Italy the continental drift theory arrived quite later and the reaction in the academic environment spanned from the harsh criticism to the scientific curiosity (Carozzi, 1985; Romano et al., 2016). Whereas the scientific community reactions have been analyzed in detail, no data are yet available about the spreading of the theory in the Italian young generation of the first half of the XX century, through the school textbooks. Few studies exist about this topic, as regards school textbooks in Portugal, Spain (Cavadas, 2019) and Brazil (da Costa & de Souza, 2018). The main objective of this preliminary research is to explore if and how the secondary school textbooks dealt with the Wegener's mobilist theory before the scientific formalization of plate tectonics theory.The used methodology is qualitative and based on fifteen available textbooks dated from 1920 to 1954. Nearly all the textbooks dealt with "Geography" and "Geology", in agreement with the Gentile's school reform of 1923 in which the disciplines science, chemistry and geography were joined together in the upper courses. About one half of the textbooks were written by academics, the other were written by specialized school teachers or other. The analysis of text and pictures shows that the didactic transposition of continental drift appears in Italian textbooks after the 1930s, together with the presentation of the previous orogenetic theories (contraction of the Earth; geosynclines; isostasy…). Many textbooks presented critiques of Wegener's work, focused on the lack of explanation for the nature of forces that could move continents at the Earth's surface. Several of the examined textbooks list the geographical, geological, paleontological and biological arguments supporting continental drift, followed by the paleoclimatic arguments, and in few cases by the geophysical arguments.

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# The historical collections preserved at the Regional Museum of Natural Sciences: a multimedia recovery and enhancement action

Borghi A.*[1], Giacobino E.[2], Senesi M.[2] & Gallo M.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Museo Regionale di Scienze Naturali, Torino.

*Corresponding author e-mail:* alessandro.borghi@unito.it

*Keywords:* historic rock collection, Museum of Natural Science, multimedia database.

Since its foundation in 1978, the University historical collections of mineralogy, petrography, geology and paleontology were stored in the Regional Museum of Natural Sciences of Turin (MRSN). The interventions of recovery and reorganization of the historical collections undertaken since 1983, and still active, concern over 15,000 mineralogical and lithological samples cataloged and at least 7000-8000 specimens of minerals and rocks still to be cataloged, belonging to various ancient collections, which for various reasons have merged with the Turin Mineralogical Museum over the course of over 250 years.

In particular, in 1994 a restoration and reorganization operation was undertaken of the so-called “Collection of minerals and rocks of Egypt”, a relatively homogeneous set of over 725 specimens. The intervention on this collection was dictated by a double necessity. First of all, at that time, the first studies on the stone materials of the Egyptian Museum were beginning, with the consequent need to have comparative finds, not being able to use fragments derived directly from the statues for destructive analyzes. At the same time, the MRSN of Turin undertook the preparation of a series of temporary exhibition events in which it was found the need to present mineralogical and petrographic samples within the museum itinerary.

Subsequently, the interest in the enhancement of historical museum collections concerned the collections collected by the “Duca degli Abruzzi” during his numerous travels and explorations.

The Polar Star (*Stella Polare*) collection includes the rock samples collected during the expedition organized to reach the North Pole in the winter of 1899-1900. During the expedition, a large number of scientific data and observations on geology were collected in the Arctic region. These samples represent an important scientific testimony of one of the most courageous and exciting expeditions of the last century. The petrographic collection represents a unicum, both for its historical and scientific value. The collection consists mainly of samples of effusive magmatic rocks, such as tholeiitic basalts, basaltic andesites and sub-intrusive rocks, such as dolerites. In the collection there are also a good number of mineralizations (quartz, opal, chalcedony, calcite and zeolites).

In view of the forthcoming reopening of the MRSN to the public, the design of the new layout of the exhibition hall called “Arca” is underway, which will be dedicated to the main travels and explorations that have enriched the Museum collections over the centuries. The historical and scientific enhancement of these collections allowed to select some samples of rocks and minerals that will be part of the exhibition.

Finally, the finds are being cataloged following the national cataloging standards through the use of the “Memora” application, the web platform used to catalog and enhance the cultural heritage present in the Piemonte Region. In conclusion, the study of these collections made it possible to enhance and deepen the study of materials that represent a historical, scientific and cultural asset to be rediscovered with the help of the multimedia resources now available.

# Felice Giordano a great geoitalian

Dal Piaz G.V.*

Accademia delle Scienze di Torino.

*Corresponding author e-mail:* gv.dalpiaz@gmail.com

*Keywords:* Felice Giordano, Italian Corps of Mines, Geological Survey.

Felice Giordano (1825-1892) was a fellow student and faithful friend of Quintino Sella (1827-1884), both graduated in hydraulic engineering at the University of Turin (1847) and completed their training at the École des Mines in Paris. Recruited by the Royal Corps of Mines, Giordano was appointed director of the Sardinian mining office (1965-1872) and, promoted to chief engineer, he was in charge of the Inspectorate of the Corps of Mines, first in Turin, then in Florence and from 1871 definitively in Rome, where he became the director of the Geological Survey. The new born Kingdom of Italy needed a modern geological map that would help one tackle the intricacies and deal with natural resources and with weaknesses, if any, of the national territory. This was the "great enterprise" conceived and codified by Quintino Sella in his memoir "*Sul modo di fare la carta geologica del Regno d'Italia"* transmitted to the Minister for Agriculture, Filippo Cordova on December 8$^{th}$, 1861; the birth of the Geological Survey ensued. After many years of a troubled development due to inertia and rivalry of university professors and Royal Corps of Mines engineers (Corsi, 2003; 2007; 2013), the project really started only when Giordano got home from his adventurous journey to India, Borneo and then around the world (1872-1876), undertaken with the confidential task of finding a proper site for a penitential colony (Dal Piaz & Scoth, 2022). Back home from South-America in 1876, Giordano was appointed as head of the Geological Survey and immediately promote field surveys starting in Sicily, Apuane Alps, Elba, Calabria and the Western Alps. Free of family ties, Giordano was devoted full time to the onerous duties of office, carried out both at headquarters and in frequent missions aimed at evaluating the mining and industrial activities in Italy, from the Alps to Sicily, as well as implementing the mapping project and satisfying other requests of Sella by then burdened as he was by his high political role. Other aspects of Giordano's activity and services deserve to be mentioned. Together with Sella, Giordano was among the founders of the Italian Alpine Club (1863) and of the Geological Society (1881). He was also a brave mountaineer, climbing Mont Blanc (1864) and the Matterhorn (1868), the latter after six bivouacs on the wall during an unfortunate personal attempt (1866); this exploit was crowned by an accurate study of the geology of the Matterhorn (Dal Piaz, 1996). Other geotechnical and hydraulic studies were devoted to railway tunnels (Tenda and San Gottardo), artificial lakes, landslides, Tiber flooding and the reclamation of Agro Pontino. These amazing activities were always carried out with the strictness, the technical competence of the engineer-geologist, the curiosity of the scientist and the spirit of service that distinguished his entire life. All that with his unassuming way – belittling difficulties and his successes – that Quintino friendly reproached.

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# The History of geology for a sustainable future of the great Engineering achievements

De Caterini G.*[1-5], Colasanto F.[2], Della Ventura G.[3] & Lucci F.[4]

[1] Engeo Praxis s.r.l., Roma. [2] Regione Lazio, Direzione regionale lavori pubblici, stazione unica appalti, risorse idriche e difesa del suolo, Roma. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [5] Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma.

*Corresponding author e-mail:* giovanni.decaterini@gmail.com

*Keywords:* history of geology, great works of engineering.

Most of the great man-made infrastructures such as roads, dams, bridges, railways in Italy and Europe are between 50 and 100 years old. The collapse of the highway viaduct of the Polcevera and also of other infrastructural works recently pushed the Italian governments to major investments to estimate the state of obsolescence of the italian infrastructural network.

Following the guidelines of the Ministry of Public Works, the definition of the priorities during any intervention must be based on the degree of knowledge of the construction characteristics, the current status and the static/mechanical performances. In modern engineering, the performance of a structure is expressed in statistical terms, by applying the limit state method. According to the accepted standards, a structure is considered as unsafe when it no longer meets the conditions for which it was designed. This criterion is based on rigid and codified technical standards (Eurocodes) introduced in 1991.

In Italy, the application of the new technical standards has become mandatory since 2008 (New Technical Standards of the NTC State 2008) and recently updated in 2018.

A crucial point in this matter, that directly concerns the Earth Science disciplines, is that the infrastructures built in the middle of the last century had no regulations regarding the technology of the used materials (concrete, armor), the seismic zonation and the hydrogeological risk. The evolution of the technical regulations in fact follows, with delay of some years, that of the scientific knowledge and therefore it is evident that the design of the old infrastructure was carried out with a technical acquaintance much inferior with respect the actual state of the art.

For what the geological disciplines are concerned, the systematic application of a geotechnic approach dates back to 1960, while the mechanics of rocks and the systematic mineralogical/petrological study of concretes came into play only after the seventies. The classification of landslides which is nowadays applied is only from the 90s of the last century. Despite these observations the geological models of the past are still valid, in most cases, if the modern designer is aware of the geological culture of his predecessors. Since scientific knowledge was less advanced, the techniques of investigation still little developed: the numerical modelling still non-existent, the designers replaced such short comings with precise reliefs on the ground, described and represented graphically in an impeccable and sometimes artistic manner.

# "In hoc silex vinces": the success of the "sampietrino" in the paving of Roman roads

De Caterini G.*[1-5], Argentieri A.[2-5], Bilotta A.M.[3] & Della Ventura G.[4]

[1] Engeo Praxis s.r.l., Roma. [2] Città Metropolitana di Roma Capitale - Servizio 2 "Geologico, difesa del suolo, rischio idraulico e territoriale" - Dip. IV "Pianificazione, sviluppo e governo del territorio", Roma. [3] I.C., Roma. [4] Dipartimento di Scienze, Università di Roma Tre. [5] Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma.

*Corresponding author e-mail:* giovanni.decaterini@gmail.com

*Keywords:* history of geology, leucititic lava, Gerolamo Lapi.

The "Sampietrino" is a truncate pyramid shaped block of stone, with a square base and a side of 15 cm. It was used to build the paved roads in the city of Rome. The name comes from St. Peter's square, it was the first square (1667) to be paved in the modern age by the Dutch Cornelius Meyer (1640 – 1702) who adopted a technique widely used in Northern Europe by then.

In the Roman slang the Sampietrino is also called "sercio" or "selcio" meaning the typical hard and heavy black stone, which is commonly used for road surfaces, cut into different shapes. The word comes from Latin "silex" meaning cobblestone. According to modern geologists, sercio is a kind of lava constituted by leucitites and tephrites which is really common in the comagmatic provincial areas of Lazio. You can easily find it in our Italian volcanoes but not in the rest of the world.

The history of the Sampietrino bumps into that of Giovanni Gerolamo Lapi (1749 - 1787). He was a geologist and a doctor and he worked at infectious diseases, this is why he is also famous, as a matter of fact he suggested a treatment for smallpox. The Pope Pio VI instructed him to study the problem of the decline in air quality in Rome; he understood that the problem was the water stagnation so he thought to find the solution in the drainage of water thanks to paved roads and hydraulic reclamations.

He also wrote a treaty about that: "*Del Selce romano, ragionamento mineralogico presentato alla Santità di nostro Signore Pio Papa Sesto*". Even if he was the one who first identified the volcanic origins of Albano and Nemi lakes, in this treaty he stated that the sercio is not volcanic like other rocks in Rome. The parallel layers and the presence of limestones keep out the hypothesis that they belong to fiery concretions. He continues stating that they cannot be just like those rocks that "people from the Kingdom of Naples call lava".

Lapi G.G. (1784) - Del Selce Romano, ragionamento mineralogico presentato alla Santità di nostro Signore Pio Papa Sesto. Stamperia Salomoni, Roma

# The geological map of Phlegraean Fields by Bonaventura Montani: the Bagnoli-Agnano reclamation area

Fabbi S.*[1], Console F.[2], Pantaloni M.[1] & Principe C.[3]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Biblioteca, ISPRA, Roma [3] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* simone.fabbi@isprambiente.it

*Keywords:* reclamation, Agnano, Montani.

One of the earlier geological maps of the Phlegraean Fields is the "*Carta geognostica del bacino dei Bagnoli, lago di Agnano e loro dintorni"*, accompanied by a note and four geological cross-sections, realized by Bonaventura Montani in 1856. This map was prepared for the reclamation project of the Agnano Lake area (Montani, 1856), which was necessary as most of the area was unhealthy especially during the summer, due to miasmas (the site was one of the 22 Royal Bourbon properties in the Kingdom of Naples). One of the goals of Montani's mapping project was to detect the origin of such exhalations which were considered as deriving from extensive peat deposits in the subsoil. Montani realized this map indicating the nature of volcanic rocks (tuffs and uncemented conglomerate/lava flows) and the marine deposits of the Bagnoli plain. In addition, he also reconstructed the position of the ancient Bagnoli littoral pond, filled at the beginning of the XIX century to decrease the exhalations. In the explanatory note, Montani described with detail the sea-level oscillations in the area, also recorded in the deposits drilled in seven up to 13 m deep geognostic boreholes. These boreholes proved that no peat deposits were present in the subsoil and so the diffuse gas exhalations in the area had probably a volcanic origin. It is important to note that gaseous emissions, mostly composed of $CO_2$, were not the primary cause of illness for the peasants who worked in the area. Montani inferred that the reason had to be ascribed to the maceration of plants in the stagnant waters of the Agnano Lake (nowadays it is well-known that the puncture of anopheles mosquitos is the real origin of malaria). For the realization of a drainage channel for the Agnano Lake, Montani suggested an ideal trace which allowed to avoid the difficult perforation of trachitic lavas. After the Unification of Italy, with a law issued on May 3, 1865, the new State decided to reclaim the lake by granting a Neapolitan entrepreneur, Domenico Martuscelli, to carry out the work at his own expense, in exchange for ownership of the reclaimed land and surrounding state lands; on September 28th 1870, the channel was completed and the drainage lasted until February 1871. To permanently avoid the reformation of the lake, a still working complex system of tanks and canals was built, allowing to recover 130 hectares of land to agricultural activity. The dried lake revealed for the first time in almost a thousand years a large number of thermal springs, which therapeutic value was known in ancient times.

Montani B. (1856) - Esplorazione Geognostica Del Bacino Dei Bagnoli E Del Lago Di Agnano. Rapporto sulle osservazioni geognostiche del Bacino inferiore dei Bagnoli e sul Lago di Agnano diretto all'Amministratore Generale delle Opere di Bonificazione del Regno Signor Barone Savarese. Litografia dell'Amministrazione delle Bonificazioni, Napoli.

# Arcangelo Scacchi, an Apulian geoscientist in the 19$^{th}$ century

Lippolis E.*, La Perna R. & Tropeano M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* e.lippolis2@studenti.uniba.it

*Keywords:* Arcangelo Scacchi, Gravina in Puglia, molluscs.

Arcangelo Scacchi (Gravina in Puglia, 1810 – Napoli, 1893) was one of the greatest geoscientists of the XIX century. He is well known for his contribution to the fields of mineralogy and volcanology, but his early studies were centered on Recent and fossil malacology. Several new taxa were described by Scacchi, and some species have been dedicated to him, as well as the bivalve genus *Scacchia* Philippi, 1844.

As a paleontologist and malacologist, he published in 1835 "*Notizie intorno alle conchiglie e agli zoofiti fossili delle vicinanze di Gravina in Puglia*", in which many fossils, mostly molluscs, collected in the area of Gravina in Puglia (Apulia, Southern Italy), were reported, along with the first geological description of the area. Among the many molluscs species reported by Scacchi, 13 were described as new. The original Scacchi collection from Gravina in Puglia is housed in the Museum of Paleontology of the University of Naples "Federico II", but some of the original material went lost and only the type material of 9 species described by Scacchi is still present (Cretella et al., 2004).

A modern still on-going study on the fossil molluscs from Gravina in Puglia, based on new material collected in the same area studied by Scacchi, is revealing a remarkably rich fauna, indicative of muddy-sandy shelf bottoms. Its age, traditionally referred to the Pliocene, is Early Pleistocene (Calabrian) instead. Furthermore, this study is allowing some interesting material to be found, such as the bivalves *Microstagon trigonum* (Scacchi, 1835) and *Bathyarca pectunculoides* (Scacchi, 1835), whose original material is no longer present in the Scacchi collection. The new collected material could therefore provide neotypes.

Recently, Gravina in Puglia town as well as the study area of Scacchi have been included in the Murge aspiring UNESCO Global Geopark. Therefore, Scacchi can be considered the first great geoscientist who was born and worked in the aspiring MurGEopark.

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# Torquato Taramelli: the art of Science

Lupi C.*[1], Console F.[2] & Severino F.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* claudia.lupi@unipv.it

*Keywords:* Taramelli, history of geosciences, outreach effort.

The University of Pavia and the Italian Geological Society dedicate the year 2022 to Torquato Taramelli, 100 years after his death.

Torquato Taramelli was born in Bergamo on 15 October 1845. At first, he was educated in the public schools of Bergamo, then Taramelli was admitted at the University of Pavia where attended the geological course held by Antonio Stoppani. The passion for natural sciences and alpinism, as well as shared patriotism, deeply tied the very young Taramelli to Stoppani.

In 1865, he graduated in Natural Sciences and moved to Udine as professor at the Royal Technical Institute. In 1875, Taramelli returned to Pavia as Professor of Mineralogy and Geology at the University, where he was full professor until his retirement in 1920. During his academic career, he was Rector of the university from 1888 to 1891 and he held other academic positions, besides being a member of many Italian and foreign societies. He was the founder of the Friulian Alpine Society in 1874 and President of the Italian Geological Society in 1890 and 1905. In 1891, he was appointed Academician of the Lincei and member of the Lombard Institute of Sciences and Letters.

Taramelli's activity includes over 300 works and 40 geological and geothematic maps. Eclectic scientist, he covered from stratigraphy to paleontology field, from seismology to glacial geomorphology or climatology themes providing the community of his time with tools and perspectives for adequate management and protection of the territory.

During 2022, the University of Pavia and the Italian Geological Society have carried out a series of cultural initiatives aimed at the discovery of an acute geologist, a refined watercolourist, and a curious explorer.

To celebrate the Taramelli's year, the University of Pavia organised an exhibition entitled "Terra Nascosta. Rocce, vulcani e terremoti: dalle scoperte di Taramelli alla Geologia moderna" at the Kosmos Natural History Museum of the University of Pavia, a scientific conference, a series of lectures and activities with schools, teachers and citizens. The aim is to bring society closer to the fundamental themes of geology.

# Giovanni Capellini's Journey to Wallachia (1864): Travel Notes and Early Insights into Petroleum Geology

Macini P.*

Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna.

*Corresponding author e-mail:* paolo.macini@unibo.it

*Keywords:* history of geology, petroleum geology, Capellini Giovanni.

Giovanni Capellini (1833 – 1922) was a prominent professor of the University of Bologna, where he was appointed full professor at the first chair of geology ever established in Italy (1860). He spent all his academic career here, and he was also elected Rector for several terms and, later, Senator of the Italian Kingdom. Co-founder and later president of the Italian Geological Society, Capellini managed to organize in Bologna the 2nd International Geological Congress (1881), also thanks to his extensive network of foreign correspondents. His innate qualities as an active organizer and coordinator were combined with a marked inclination to overcome an exclusively provincial vision of scientific problems. Unlike other national geological Institutes of a predominantly regional nature, he gave the Bologna Institute an international organization and relaunched the whole University that was being built at the end of the nineteenth century with a keen eye on worldwide relationships. It is worth remembering here that 2022 marks the centenary of Giovanni Capellini's death.

Recognized as one of the Italian founders of the modern geological sciences, in his intense academic and public life Capellini also dealt with a number of technical issues relating to petroleum geology and production, a field still in its infancy at the time. He was engaged in this promising industrial activity when he was a young researcher, acting as an academic consultant on behalf of domestic and foreign oil companies. In fact, soon after the Italian unification, petroleum exploration kicked off in many European areas, and in Italy generated the elaboration of technical and statistical reports carried out by the Royal corps of mines and the Royal geological survey, at the time fully engaged in the elaboration of the Italian geological map.

Capellini published some well-known reports and studies dedicated to petroleum geology issues. However, a recent survey of the archival sources in Bologna revealed a travelogue of his journey to Wallachia, a field trip that he organized in 1864 as a consultant to a London oil company. In fact, Romania, together with Italy, was the European Country where hydrocarbons exploration developed the most, immediately after the fortunate North American discoveries of 1859 and the start of the modern and globalized Oil and Gas industry. This travelogue, still in the form of an unpublished manuscript, is kept in the archives of the Geological and Paleontological Museum of the University of Bologna, named after him. Although it contains geomorphological notes, stratigraphic sketches and various geological sections, the typical contents of the surveyor geologist field notebook, it is also an agenda of daily notes, structured in a sort of travel diary, albeit minimal in its narrative structure. More important, it offers a first-hand account of the varied activity of a young researcher and scientist already fully integrated into the European cultural milieu.

# Marianna Paulucci: the "first lady" geologist of the Italian Geological Society

Mazzini I.*[1], Talenti E.[2], Innocenti G.[2] & Cianfanelli S.[2]

[1] Istituto di Geologia Ambientale e Geoingegneria, CNR, Monterotondo (RM). [2] Museo di Storia Naturale "La Specola", Università di Firenze.

*Corresponding author e-mail:* ilaria.mazzini@cnr.it

*Keywords:* women in STEM, museum collections, equitable community.

In the nineteenth century, women in Europe were still practically excluded from the world of science and technical fields. Only a few female intellectuals from the aristocracy contributed to progress and participated in the scientific debates. Marianna Panciatichi Ximenes d'Aragona (3 February 1835 – 7 December 1919) cultivated her interest in natural sciences since her childhood, influenced by her father Fernando Panciatichi, an eclectic man interested in many disciplines, including botany. She was eighteen when she married the amateur botanist Alessandro Anafesto Paulucci. She was active in the collection of naturalistic specimens, maturing over time her skills in scientific research, leading her to be appreciated by the major Italian and European specialists. Initially, she took an essential approach to the collection of naturalistic specimens, but soon she gained enough confidence to participate into some of the major debates of her time: Darwinism and the concept of species. Always showing the utmost prudence and wit in general conclusions and theoretical expositions, she took a firm position with respect to the *Nouvelle École* that saw the French Jules René Bourguignat as its greatest exponent, opposing the unjustified proliferation of the designation of new species. This prudence in recognizing new species can be found already in her first scientific publication concerning the fossil gastropod *Murex veranyi*, for which she had a close correspondence with Joseph Charles Hippolyte Crosse, then director of the most important paleo-malacological journal of the time, before deciding to publish there the article.

In 1882 she joined the Italian Geological Society (SGI) and in the following years she was always the only woman out of an average of 200 male members. Her interests in geological matters began long before she joined the SGI and is testified by her correspondence with Antonio Villa, vice president of the Society of Natural Sciences, on selenite crystals and rounded pebbles found near Volterra (Tuscany). Her interest in molluscs led her to present her collection at the Universal Exposition in Paris in 1878, compiling the first list of species of the Italian non-marine malacofauna. During her travels in Italy and Europe she collected fossils, such as the skull of the saber-toothed tiger (*Homotherium crenatidens*), species published in 1890 by Fabrini in the Bulletin of the Royal Geological Committee. Later she donated her collections to the Royal Museum of Natural Sciences in Florence where they are still kept today. Some specimens of fossil flora from the Valdarno are presently preserved in the Museum National d'Histoire Naturelle in Paris.

# The evolution of Chilean volcanology in the 20th century and the work of Lorenzo Casertano

Musumeci D.*[1-2], Leone G.[3], Branca S.[2-4] & Ingaliso L. [1]

[1] Dipartimento di Scienze Umanistiche, Università di Catania. [2] Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma. [3] Instituto de Investigación en Astronomia y Ciencias Planetarias, Universidad de Atacama, Copiapó (Chile). [4] INGV, Osservatorio Etneo, Catania.

*Corresponding author e-mail:* daniele.musumeci@phd.unict.it

*Keywords:* history of volcanology, Chilean geology, scientific methodology.

Chile is one of the most geologically active countries in the world. About 90 volcanoes in Chile are considered active and more than 400 eruptions have been recorded since the 16th century. Until the 19th and 20th centuries, most of the information on volcanic phenomena came from the accounts of travellers and naturalists, including Charles R. Darwin (1840) and Ignacio Domeyko (1848). At the beginning of the 20th century, the German geologist Juan Brüggen (1887-1953) made a notable contribution. Brüggen is renowned for having studied Chilean geology for forty years and for composing the first general treatise in Spanish, *Fundamentos de la geologia de Chile* (Brüggen, 1950). However, only a small section is devoted specifically to volcanism. A breakthrough came in 1959 with the arrival of the Italian physicist Lorenzo Casertano (1921-2004), who taught the first courses in Volcanology at the Universidad de Chile (Santiago de Chile). His most important contributions concern volcanological studies in Italy, Chile and Costa Rica. Thanks to the presence of Casertano and other foreign scholars, the first Chilean volcanologists working in the area began to gain experience and broaden their knowledge in the following decades. Scientists such as Oscar González-Ferrán (1933-2014), Hugo Moreno, José Antonio Naranjo and others would go on to lead volcanological studies towards an increasingly complex approach, in line with international standards, thanks to the monitoring and research performed by SERNAGEOMIN and the Universities.

Brüggen J. (1950) - Fundamentos de la Geología dé Chile. Instituto Geográfico Militar. Santiago.

## Upper Valsugana: a laboratory for nineteenth-century geological studies

Roghi G.*

Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* guido.roghi@igg.cnr.it

*Keywords:* Valsugana, De Zigno, nineteenth-century.

On 30 September 1849 Achille de Zigno wrote in his fieldbook (Diary B): *"The Valsugana near Borgo village deserves to be studied as there is the conjunction of the Jurassic and Triassic soils as well as the micaschist, the granite, the porphyry and even the tertiary rocks..."*.

The coexistence of different lithologies, a peculiarity well expressed in the words of De Zigno, has made the upper Valsugana, located south of the Dolomites, a very attractive study area for nineteenth century geologists. Hence, the studies conducted in Valsugana by those pioneer scientists are of central interest for the reconstruction of the history of geological sciences. In the first half of the nineteenth century the Valsugana was of particular importance in the debate between Plutonism and Neptunism, that returned to the discussion on primacy and posteriority of primeval "wernerian" rocks. An example is found in the works by Marzari Pencati on the position of the Telve granite but also in the description of one of the first geological maps that included this area, made by von Buch in the 1822. Emilio Cornalia in his *Notizie Geo-mineralogiche sopra alcune valli meridionali del Tirolo* (1848), on the basis of new field observations, added more details to von Buch's map, but a completely different and "modern" map, accompanied by the drawings of many precise geological profiles of the Valsugana area, was presented by Edmund Mojsisovics in Die Dolomitriffe von Südtirol und Venetien (1879). Of this map a hand drawn copy of the lithology of Valsugana area is stored at the library of Geosciences Department of Padua. In the precious diaries of Baron Achille de Zigno (cf. Lonigo & Roghi, 2020) there are numerous notes on the geology of the upper Valsugana, which were written during his endless travels and enriched by his beautiful drawings, with details that still today allow interesting geological discoveries made in localities that would have been otherwise forgotten.

Cornalia E. (1848) - Notizie geomineralogiche sopra alcune valli meridionali del Tirolo. Tip. Guglielmini.

Lonigo A. & Roghi G. (2020) - "I Quaderni di Campagna" del barone Achille De Zigno. Riproduzione digitale degli esemplari manoscritti conservati nell'archivio di famiglia. Editrice Elzeviro, Padova.

Mojsisovics E. (1879) - Die Dolomitriffe von Südtirol und Venetien. Beiträge zur Bildugsgeschichte der Alpen. Ed. Hölder.

von Buch L. (1822) - Esquisse d'une carte Gèologique de la partie meridionale du Tyrol.

# Fossils extraordinary objects: between myth, legend and folklore

Romano M.*

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* marco.romano@uniroma1.it

*Keywords:* history of geology, history of paleontology, geomithology.

Among the various natural productions, fossils have always represented wonderful objects full of mystery, capable of attracting human attention starting as early as the Paleolithic. First written records of a direct interest in the lithified remains of plants and animals are already found in fragments of Thales (636-546 a.C.), Anaximander (615-547 a.C.), Xanto of Sardi (500 a.C.) Herodotus (484-425 a.C.), and Eudossus of Cnidus (circa 366 a.C.). These ancient authors had already attempted an interpretation for such strange natural objects, too similar in general features to currently living organisms (Rudwick, 1972; Romano, 2020). Lithified shells were found in inland deposits very far from the current seas, right up to the tops of the highest mountains, necessarily arousing the human curiosity. However, even before finding a place in the field of naturalistic studies, and several centuries before paleontology emerged as an independent discipline of the Earth Sciences, fossils became a decisive part of the folklore of numerous cultures worldwide. As mysterious and difficult to interpret objects, these lithified remains since the Paleolithic were associated with legends, myths, necromancy, medicinal remedies and alchemy. Furthermore, fossils were a source of inspiration for myths and legends all over the world, some even crystallized in classical and immortal works of antiquity. Legends of dwarves, giants and powerful beings narrated in ancient Greece and Asia Minor, most likely have a direct link to the discovery of fossils of large vertebrates, and ultimately represent a first attempt at an explanation for such unusual finds (Romano & Palombo, 2017; Romano & Avanzini, 2019). Thus, the griffins, the giants killed by Zeus during the rebel climb to Mount Olympus, the Lotophages, the Lestrigons, and again the skeleton of Achilles, Ajax and the cyclops Polyphemus, could actually have a primary paleontological origin.

Romano M. (2020) - I fossili una storia italiana. Il contributo italiano alle prime conquiste della paleontologia. Società Geologica Italiana, Alcione, Lavis, Trento.

Romano M. & Avanzini M. (2019) - The skeletons of Cyclops and Lestrigons: misinterpretation of Quaternary vertebrates as remains of the mythological giants. Hist. Biol., 31(2), 117-139.

Romano M. & Palombo M.R. (2017) - When legend, history and science rhyme: Hannibal's war elephants as an explanation to large vertebrate skeletons found in Italy. Hist. Biol., 29(8), 1106-1124.

Rudwick M.J.S. (1972) - The meaning of fossils. Episodes in the History of Palaeontology. Macdonald: London and American Elsevier Inc. New York.

# Grotta Romanelli (Lecce, southern Italy): the beginning of the systematic and multidisciplinary approach in Quaternary research

Sardella R.*[1], Mecozzi B.[1], Sigari D.[2-3], Tarantini M.[4] & Mazzini I.[5]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Scienze del Patrimonio Culturale, CNR, Montelibretti (RM). [3] CNRS-UMR 5608 Laboratoire TRACES, Tolouse (France). [4] Soprintendenza Archeologia Belle Arti e Paesaggio, Firenze. [5] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* raffaele.sardella@uniroma1.it

*Keywords:* Mediterranean area, geo-archaeology, history.

Grotta Romanelli is a costal site located in the Otranto-Santa Maria di Leuca Coast and Bosco di Tricase regional nature park, in the administrative territory of Castro (Lecce, southern Italy).

The cave has been a reference site for the European stratigraphy of late Quaternary, due to its geomorphological setting and archeological and paleontological content.

The site was discovered during the 1870s by Ulderico Botti, but only in the earlier 1900s Paolo Emilio Stasi coordinated the first excavations. As soon as Stasi published his early discoveries, confirming for the first time the presence of the Upper Palaeolithic period in Italy, a heated debate among scholars began. An important role was played by Luigi Pigorini, who criticized Stasi's interpretation, refusing the presence of Upper Paleolithic in the Grotta Romanelli.

Within this framework, the scientific community started looking for an approach to Palaeolithic studies based on the natural sciences, in order to obtain more reliable contexts.

In this scenario, Gian Alberto Blanc resumed the excavations in the cave, using the utmost methodological rigor in the stratigraphic investigation. Blanc applied an innovative research method which included for example the rigorously distinction by level of provenience of each archaeological find and the use of Cartesian coordinate system to locate the finds and define the borders of the individual levels on plans.

Here, the history of the research at Grotta Romanelli is presented, describing those features at the origin of methodological approach still today used in the archaeological and palaeontological fieldwork activities.

# Quintino Sella mining engineer in Sardinia

Sella M.*

Società Geologica Italiana - Sezione di Storia delle Geoscienze, Roma.

*Corresponding author e-mail:* sellamattia@gmail.com

*Keywords:* Sella Quintino, mining industry, Sardinia.

I would like to remember here Quintino Sella, not as politician, but as scientist and in particular as mining engineer. In 1847 he graduated in Hydraulic Engineering; the same year the Minister of Public Works, Luigi Des Ambrois, sends Sella to the *École des Mines* in Paris. On December 1851 he is nominated "*élève brevété*". In 1852 Sella is named professor of practical geometry at the University of Torino. In 1856 he is unanimously co-opted member of the Royal Academy of Science of Torino. The same year he is nominated "2nd Class Engineer in the *Corpo Reale delle Miniere*. Thus begins his long and successful career at this important institution of the Kingdom. In 1859 he will be promoted 1st Class Chief Engineer and the following year he will become member of the Board of Mines (he will become vice president in 1866). In 1860 he is nominated professor of crystallography at the *Regia Scuola di Applicazione per Ingegneri* of Torino. In 1860 Sella, elected representative of the Council of Cossato (Biella), starts his political career and becomes promoter of Science and Culture. Large scale geological maps are needed for the studies and the realisation of roads, railways, tunnels, mines and in 1861 the project "*Carta Geologica del Regno d'Italia*" was born thanks to Quintino Sella and Felice Giordano. In 1881, together with Giovanni Capellini, Sella organizes the 2nd International Congress of Geology in Bologna. During the event, following his and Capellini's proposal, the Italian Society of Geology is established. In 1869 the Sardinia Island receives a visit from the Committee of Inquiry on the conditions of the Sardinian mining industry. Eugenio Marchese, a 32-year-old mining engineer, and "*ministro Sella*" go on a tour across Sardinia; 18 days by horse to visit the main mining locations. The same year Sella illustrates his "*Condizioni sull'industria mineraria in Sardegna*". The report will be presented to the Chamber on 3 May 1871, a version with new data and cartography. The topographic map of Sardinia, realised by Alberto della Marmora, was attached to the report. In order to study the mines, Sella founds the geological map of Alberto della Marmora (1856) extremely useful, but argues that it is necessary to create a new large-scale map *«entrusted to the engineers of the mines»*. The map was used as a base to localise mineral deposits and active mines and for the creation of the "*Carta mineraria dell'Isola di Sardegna*". An important contribution came from engineer Felice Giordano. In 1852 Giordano had been nominated Second Class Engineer of the Royal Body of Mines and he was sent to Cagliari, where he worked for 7 years. The Mining School, "*Giorgio Asperoni*", funded in Iglesias in 1881, was born following the will of Quintino Sella.

Sella Q. (1871) - Sulle condizioni dell'industria mineraria sarda. Relazione della Commissione Parlamentare d'inchiesta. Reprint by Manconi F., 1999, Ilisso ediz., Nuoro.

# The Fréjus railway tunnel, the first geo-transversal of the Alps

Senesi M.* & Gallo L.M.

Museo Regionale di Scienze Naturali, Torino.

*Corresponding author e-mail:* massimiliano.senesi@regione.piemonte.it

*Keywords:* Frejus, tunnel, Alps.

The Fréjus railway tunnel was built between 1857 and 1870, 12 years ahead of schedule thanks to improvements in Sommellier's compressed air drill. It was the first tunnel dug through the Alpine arc. With a total length of 12234 meters, it runs in a straight line, with the exception of the last section between Bardonecchia (southern entrance) and Modane (northern entrance). It involves the soils of the Calcschists Complex with greenstones ("Complesso del Lago Nero" in Dela Pierre et al., 1999) and the Triassic sediments of the Brianzonese Zone. Designed by the engineers Sebastiano Grandis, Severino Grattoni and Germain Sommeiller, it was an engineering work at the forefront worldwide and followed the route elaborated on the basis of the geological surveys of Angelo Sismonda, who also took care of the preparation of several copies of the lithological collection. The collection, which consisted of 134 samples (mainly carbonaceous schists and argilloschists, calcschists, chlorite-scists, sandstones, limestones and dolomitic limestones, dolomites, anhydrites and gypsums, quartzites and marbles), for a total of 570 specimens, was deposited at the Mineralogical Museum of the University of Turin and was accompanied by a manuscript catalog written by Sismonda himself and included at the end of the *Catalogo della Raccolta Geologica delle Alpi*. Because of the geological importance of the collection as representative of a portion of the Alpine chain, copies of the collection were sent to various Italian and foreign scientific institutions. On the material deposited at the École des Mines in Paris, Élie De Beaumont prepared a printed catalog (*Catalogue des roches rencontrées dans le tunnel des Alpes occidentales*), of which references are also found in the Turin manuscript catalog, called *Catalogo delle rocce attraversate nella scavazione del Tunnel (Galleria) alpino impropriamente detto del Monte Cenisio (Rocce del traforo (tunnel) alpino - Colle Fréjus)*.

Dela Pierre F., Polino R., Borghi A., Carraro F., Fioraso G., Giardino M., Conti A., Gattiglio M., Malusà M. & Mosca P. (1999) - Note illustrative della Carta Geologica d'Italia alla scala 1:50.000, Foglio 132-152-153 Bardonecchia. Regione Piemonte, Direz. Reg. Servizi Tecnici di Prevenzione, Torino.

# S24.

# Geosciences and museums:
# integrated approaches for a sustainable future

*Conveners & Chairpersons*

*Maura Fugazzotto (University of Catania)*

*Rosarosa Manca (University of Firenze)*

*Luca Bellucci (University of Firenze)*

# The resumption of the collection as a protagonist: the Geosciences Museum of IGc-USP

Azevedo M.*

Geosciences Museum, Geosciences Institute, University of São Paulo (Brazil).

*Corresponding author e-mail:* miriamigc@usp.br

*Keywords:* geosciences museum, geosciences collection, geological heritage.

The Geoscience Museum of USP is an university museum whose collection includes minerals, rocks, fossils, and meteorites collected since 1935. The museum was originally a repository of scientific collections for academic purposes and inherited the collection of the Museum of Mineralogy of the Faculty of Philosophy, Sciences and Languages (Azevedo, 2018). Currently it is dedicated to the dissemination of science carried out and researched at the IGc-USP (Azevedo et al., 2020). In 2014, the Museum underwent a self-evaluation process, which included its history, team competencies, strengths, weaknesses and potential. Consequently, a Museological Plan for the Museum was elaborated, allowing for a route orientation that defined its mission, which is “To promote the valorization of ex-situ geological heritage, by bringing Geosciences and society closer together”. The collection was pointed out as the Museum’s main strength, and it was up to the team to carry out a “recovery of the object and collections as the target of current concerns” (Lopes & Barbuy, 2013). From then on, we faced new challenges: 1. revising the language of the exhibition to general public; 2. transforming it into a Geoscience Museum, since the exhibition was predominantly mineralogical, bringing the museum closer to its nomenclature; 3. taking more advantage of the collection. From there, possibilities for action were created, looking at the relationship between the visitor and the object as a center of concern for the museum. Since 2017, new thematic exhibitions have been included, using other geological materials such as fossils, meteorites, sands. In the last five years, the activities of the Museum have shifted from a vision of the institution as central to a vision of the visitors as central, making their practices more sensorial, and using the object as a bridge to their sensitive experience, giving meaning to the visit through educational activities, according to Semedo’s (2004) idea that a museum is a place to establish relationships and communication. For a small museum with a low budget, the social network is a valuable support that cannot be discarded to bring other experiences and public interactions. Even before the Covid-19 Pandemic, the interaction between visitors started through the social network and ended with the visit to the Museum and vice versa. Thus, this paper aims to present in detail the interactions between the public and the Museum from the resumption of the collection as the protagonist.

Azevedo M. (2018) - Acervos que escrevem a história: a trajetória do Museu de Geociências através de suas coleções. Dissertação. Orientadora Dra. Maria M. Lopes. USP, PPGMus.

Azevedo M., Sborja C. & Moitinho de Lima J. (2020) - O Museu de Geociências da USP: esforços para divulgação da ciência além do ambiente acadêmico. Ventilando Acervos, 8(2), 90-110.

Lopes M.M. & Barbuy H. (2013) - Tendências Contemporâneas de Reflexão sobre Museus e Museologia. Introdução. Anais do Museu Paulista, 21, 01.

Semedo A. (2004) - Práticas (I) Materiais Em Museus. Actas do I Seminário de Investigação em Museologia dos países de língua Portuguesa e Espanhola, 1, 62-80.

# Digitisation of the palaeontological collection of the Museum of Geology and Palaeontology of the University of Florence

Bartolini-Lucenti S.[1], Cioppi E.[2], Bellucci L.[2] & Rook L.*[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Museo di Geologia e Paleontologia, Università di Firenze.

*Corresponding author e-mail:* lorenzo.rook@unifi.it

*Keywords:* virtual palaeontology, museum, 3D digitalization.

Virtual palaeontology techniques are becoming more and more common in palaeontological investigation: in the last decades, several independent researchers and research institutions have relied on three-dimensional acquisition technologies – both tomographic and surface scanning – to obtain valuable data for their studies, also thanks to the relative accessibility of the digitisation technologies and the easy-to-use interfaces and tools available today. In the same way, museums have progressively started to exploit the high potential of these technologies for the preservation of fossils in their collections and enrichment of their outreach. In Italy, however, there are still few examples of scientific museums that systematically use these methodologies, and practically none in the field of paleontology. In 2020, thanks to a specific funding provided by the Tuscany regional administration within the framework of the European initiative "POR FSE 2014-2020" a project of digitisation and enhancement of fossils housed at the Museum of Geology and Palaeontology of the University of Florence has started. This Museum is a privileged case for this goal, as it is a national and international reference for its extensive and diversified collections, renowned for their scientific significance since the beginning of the 19$^{th}$ century, particularly for the Neogene and Quaternary mammal remains. The methodologies and results of the digitisation and dissemination project of the Museum's collections are described here, as the first case of systematic digitisation in Italy in a purely palaeontological context.

# Virtual Palaeontology tools for conservation and valorization of geopalaeontological heritage: the case of Cava Monticino Late Miocene Vertebrates

Bartolini-Lucenti S.[1-2], Cirilli O.[2-3], Pandolfi L.[2], Sami M.[4], Dedola G.L.[5] & Rook L.*[2]

[1] Institut Català de Paleontogia «M. Crusafont», Universitat Autònoma de Barcelona (Spain). [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Department of Anatomy, Laboratory of Evolutionary Biology, Howard University, Washington, DC (USA). [4] Museo Civico di Scienze Naturali, Faenza (RA). [5] Struttura Operativa Complessa SOC Radiologia e Struttura Operativa SOS Radiologia San Giovanni di Dio, Firenze.

*Corresponding author e-mail:* lorenzo.rook@unifi.it

*Keywords:* virtual palaeontology, museums, geo-palaeontological heritage.

The ever-increasing development of Virtual Palaeontology is changing the way curators of geo-palaeontological museums handle their collections and exhibits. Numerous practical and theoretical advantages boost this interest: from their non-invasiveness, to the storage of all-around data on the preservation of a specimen; from the engaging 3D visualization in online web pages and apps or in-situ applications, to opportunities of open-science. In the last years, *Paleo[Fab]Lab* (the virtual palaeontology laboratory at the Earth Science Department of the University of Florence) has pioneered the use of a wide array of digital tools (e.g., high-resolution surface and CT-scanners; 3D prints) in different palaeontological museums. Here we report the case of the non-invasive investigation of three ossiferous breccias from the Miocene site of Cava Monticino held at the Natural Science Museum of Faenza, helping their preservation and, contextually, their dissemination to the public. The exhibited specimens are made of slightly different composition: one is a compact clayish-sandy blocks with a bones of a small Miocene hyaenid (*Plioviverrops faventinus*) and two others are argillitic-chalky microconglomerates with numerous bones of carnivorans and herbivores of the diverse association of Cava Monticino included in them. The peculiar composition of the conglomerates makes the blocks particularly fragile and could easily deteriorate. Furthermore, the possibility of finding and identifying bones hidden within the blocks have not been ever investigated by any researchers nor by the museum staff. The use of surface scans generated accurate 3D models of the blocks, with their geometry and texture: should any damages affect them these would grant their possible restoration; moreover, such models could be 3D-printed and made available for the visitor of the Museum of Faenza to be touched, handled, and manipulated, meanwhile keeping the fragile specimens safely in the showcases. The tomographic applications yielded contrasting results: on the one side, the sedimentological-chemical composition of the two microconglomerates made the segmentation hard to be processed for the conspicuous interference and blurriness of components within the two blocks; on the other, the clay-sandy specimen showed a previously unsuspected number of bones hidden in the matrix. The valuable and unexpected results of these digital techniques have sparked the interest of the curators that are planning to include new features (such as digital screens and 3D prints) in the current exhibition to inform visitors of the even greater value of these beautiful specimens preserved and displayed in the Museum.

# DiSSCo Prepare: towards an European Infrastructure for Scientific Collections

Bellucci L.*[1], Bartolozzi L.[1], Biaggini M.[1], Cecchi L.[1], Innocenti G.[1], Manca R.[2-3], Mancinelli M.L.[4], Moggi Cecchi V.[1], Porena M.[5], Presutti V.[5-6], Rossi P.F.[4-7], Rossi De Gasperis S.[1], Veninata C.[4] & Benvenuti M.[1-2-8]

[1] Sistema Museale di Ateneo, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Istituto di Scienze del Patrimonio Culturale, CNR, Napoli. [4] Istituto Centrale per il Catalogo e la Documentazione, Ministero della Cultura, Roma. [5] Istituto di Scienze e Tecnologie della Cognizione, CNR, Roma. [6] Dipartimento di Lingue, Letterature e Culture Moderne, Università di Bologna. [7] Parco archeologico di Ostia antica, Ministero della Cultura, Roma. [8] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* luca.bellucci@unifi.it

*Keywords:* natural sciences collection, research infrastructure, knowledge graph.

European Natural Sciences Collections (NSCs) consist of around 1,5 billion specimens that are crucial for answering fundamental scientific questions about ecological, evolutionary, and geological processes. In the last decades the volume and diversity of information derived from NSCs are exponentially increasing due to the digital transformation and the progressive use of analytical instrumentation, remote sensing and molecular approaches. A holistic approach is therefore required, where cross-linked information effectively underpins the entire research life cycle and provides open access to mass and precise data for researchers. The Distributed System of Scientific Collections (DiSSCo) is a world-class Research Infrastructure (RI) for NSCs currently in its preparatory phase. The DiSSCo RI aims to create a new organisational model for collections that digitally unifies all European natural sciences assets under common access, curation, policies and practices ensuring that all the data are easily Findable, Accessible, Interoperable and Reusable (FAIR principles). DiSSCo thus represents the largest ever formal agreement between natural history museums, botanic gardens and collection-holding universities in the world.

The digitisation of the NSC of the Natural History Museum (NHM) of the University of Florence – one of the largest and most diversified in Italy – is an ongoing, pioneering case study. The NHM of the University of Florence represents in fact the current Italian National Node of the DiSSCo Prepare Project and is playing a key role in establishing innovative relationships between its internal Collection Management System (CMS) and: i) ArCo, i.e., the Knowledge Graph of the Italian Cultural Heritage promoted by the Italian Central Institute for Catalogue and Documentation and the Italian National Research Council (CNR), ii) the General Catalogue of Italian Cultural Heritage web portal created by the ICCD (almost 3 M catalogue records) and, finally iii) the DiSSCo RI. In particular, ArCo ontology network, adopted by Agenzia per l'Italia Digitale (AgID), allows the representation on the semantic web of ICCD standards for natural heritage.

# After the fire: Museum and citizenship at work

Bonaccorsi E.*[1-2-3], Sorbi S.[1-2] & Curzio P.[2]

[1] Museo di Storia Naturale, Università di Pisa. [2] Sportello di Agroecologia, Calci (PI). [3] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* elena.bonaccorsi@unipi.it

*Keywords:* social impact, territory, collaboration.

In 2018, a devastating fire destroyed more than a thousand hectares of forest on Monte Pisano above the Certosa di Calci, a fine monastery dating back to 1366, which houses the Museum of Natural History of the University of Pisa. This catastrophic event inspired the establishment of a collaborative project comprising the "*Sportello di Agroecologia*"- a citizens' association, the Natural History Museum and the Earth Science Department of the University of Pisa, with the aim of highlighting the historical and naturalistic heritage of Monte Pisano. The transformation of a ½ hectare plot of sloping land into an eco-park will serve as a microcosm of the mountain's natural and man-made environment. This involves the restoration and enhancement of its terraced slopes afflicted by the wildfire, respecting the original vegetation and characteristic landscape. Special attention is given to its dry-stone walls (the art of dry-stone walling is UNESCO-recognized intangible cultural heritage since 2018), which are being repaired with some help and guidance of local artisans, thus transmitting a heritage of traditional know-how to the younger generations. Amongst other roles the park will host thematic walks and training courses on the historical, cultural and naturalistic aspects of Monte Pisano, as well as serve as a recreational area for nature lovers.

# In situ Raman analyses of gems and decorative stones of museum collections

Caggiani M.C.*[1], Coccato A.[2], Cavarra M.[1], Manenti A.M.[3] & Barone G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK). [3] Parco Archeologico e Paesaggistico di Siracusa, Eloro, Villa del Tellaro e Akrai, Siracusa.

*Corresponding author e-mail:* mariacristina.caggiani@unict.it

*Keywords:* in situ investigations, Raman spectroscopy, gemstones.

This work aims at validating the suitability of Raman spectroscopy for the investigation of gemstones and decorative stones directly in situ in the museums rooms in which they are kept.

The two case studies involve an archaeological and a mineralogical museum. Following a first explorative analytical campaign at Paolo Orsi Regional Museum (Siracusa, Sicily) (Barone et al., 2016), new investigations were carried out. In detail, we report the results of the in situ Raman study of another corpus of more than 50 loose gemstones and some examples of Hellenistic and Roman jewels. Besides, a collection of 40 minerals and stones was analyzed in the Museum of Mineralogy, Petrography and Volcanology of the Department of Biological, Geological and Environmental Sciences at University of Catania.

The selection of the objects is driven by their questionable classification: this often happens in private collections of miscellaneous materials whose origin cannot be always ascertained, or, as in the case of Catania University Museum, due to several relocations of the collections and loss or exchange of identifying tags. Thus, the final purpose is to integrate, support or discard the macroscopic identification using a noninvasive analytical technique. The identification today reported in the museum catalogues is still often autoptic and can be questioned because mainly based on color and appearance, giving way to misinterpretations not mirroring their real mineralogical or petrographic nature of the materials.

The great part of the gemstones involved in this work belong to two main groups: micro- and crypto-crystalline silica, and garnet. Within the first group, confusion may derive from the complex silica varieties classification: micro- or crypto-crystalline silica is generally called chalcedony and can be divided into fibrous and grainy varieties; jasper is composed of micro-crystalline quartz with moganite, a quartz polymorph. As concerns garnets, their chromatic variety brings sometimes to confusion and to their cataloguing as carnelian.

This work demonstrated that a fast and effective identification of gemological materials can be performed by Raman spectroscopy directly in the museums rooms, with useful results for the complete characterization and the detection of misclassifications. Furthermore, it encouraged the collaboration between geoscientists and museum curators with a fruitful exchange of knowledge and competence.

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Barone G., Mazzoleni P., Raneri S., Jehlička J., Vandenabeele P., Lottici P.P., Lamagna G., Manenti A.M. & Bersani D. (2016) - Raman Investigation of Precious Jewelry Collections Preserved in Paolo Orsi Regional Museum (Siracusa, Sicily) Using Portable Equipment. Appl. Spectrosc., 70(9), 1420-1431.

# Indoor gaseous mercury pollution in the herbaria: risk assessment and potential solutions

Ciani F.*[1], Gianni R.[2], Rimondi V.[1], Costagliola P.[1] & Benvenuti M.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Matematica ed Informatica «Ulisse Dini», Università di Firenze.

*Corresponding author e-mail:* francesco.ciani@unifi.it

*Keywords:* gaseous mercury, risk assessment, herbarium.

Atmospheric pollution in indoor environments like workplaces is a critical topic because it affects workers' health and efficiency.

Herbaria, i.e., the plant collections of natural history museums, are often affected by atmospheric mercury (Hg) pollution resulting from the sample historic treatment with corrosive sublimate, a solution of Hg dichloride. Sublimation of this compound produces over time high levels of gaseous elemental Hg (GEM, $Hg^0$).

In this work, we quantified the $Hg^0$ pollution of two herbaria of the University of Florence (Italy), the *Central Italian Herbarium* (Natural History Museum), and the *Tropical Herbarium Studies Center* (Department of Biology). Gaseous elemental Hg concentrations were recorded for a whole year (once a month from July 2020 to July 2021) in all rooms using a real-time Hg detector (Lumex RA-915M); 48h continuous monitoring (1 measurement/minute) were also done in all seasons. The potential risk to GEM exposure for worker's health has been quantified following the EPA risk analysis model (US EPA, 2009); different scenarios have been evaluated, based on the different exposure times of the employers (all-day or working-hour exposure) and the indoor conditions (herbaria ventilation system on or off) of the exhibition halls.

Hg concentrations inside the herbaria showed a definite seasonal trend, with the highest values reached during summer (up to ~50,000 ng/$m^3$). The risk analysis model showed a potential risk throughout the whole year, and it allowed to establish a threshold Hg concentration (1650 ng/$m^3$) below which the safety for worker's health could be guaranteed. The ventilation of the herbaria rooms, which ensures an air exchange with the outside environment, demonstrated to be very effective in reducing Hg contamination. A mathematical model was set up to predict the Hg concentrations decrease following the ventilation switch on at the observed conditions. More importantly, these data were employed to determine a flow rate ($m^3$/h) and an operating time of the herbaria air ventilation system that could rapidly bring Hg levels below the potential risk threshold.

Long-term monitoring of indoor Hg concentrations in the herbaria of the University of Florence provided potential solutions to reduce the Hg contamination of this workplace. This research could be applied to other worldwide museum collections showing similar contamination problems.

U.S. EPA. (2009) - Risk Assessment Guidance for Superfund, Volume 1, Part F. Office of Emergency and Remedial Response, Washington D.C., EPA/540/1-89/002.

# Behind-the-scenes of MUST (Museo Universitario di Scienze della Terra) between restoration and digitalization

Conti J.*[1-2], Sacco E.[1-2], Sarra A.[1-2], Macrì M.[1-2] & Sardella R.[1-2]

[1] Polo Museale, Sapienza Università di Roma. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* jacopo.conti@uniroma1.it

*Keywords:* earth science museum, 3D models, restoration.

The MUST (Museo Universitario di Scienze della Terra, Sapienza University of Rome), preserves a wealth of historical geological, mineralogical and palaeontological collections acquired during its long history (Manni, 1993; Matteucci, 2012). Established in 2012 as a merger of the three historical earth science museums, it is now in the final stages of structural and exposition renovation before its definitive opening.

During the closing time, several projects have been started, mainly focused on enhancing the collections that will be part of the final exhibition. Among the most noteworthy there is the restoration of large vertebrate fossils and their valorization.

Works started in the second half of 2020. The project consists in five steps: i) the evaluation of the state of conservation of the specimens, ii) the analysis of previous restoration interventions, iii) the acquisition of the three-dimensional pre-restoration models, iv) the new restoration work, v) the 3D digitization of the restored specimen. The preliminary investigation of the assets has shown how the previous interventions were focused on producing an apparently complete specimen, through the abundant use of colors and stuccoes, which did not allow to distinguish the reconstructed parts from the original ones, mystifying some of the diagnostic features of the specimen. The new treatments, aimed to securing the specimens, have highlighted the reconstructed parts, now clearly distinguishing from the authentic ones, overshadowing the "Wunderkammer" effect that was originally perceived in the collections. The entire process has been properly documented with both photographic and video media, while the three-dimensional models have been produced using optical scanners and photogrammetry, to obtain a wide and accessible digital repository. Two different scanners featuring blue light technology were used for the 3D scans, this choice was made to optimise the results according to the size and shape of the analysed specimens.

The aim of this work is to underline the process that led this work and to design museum contents and exhibition which can describe to general audience the backstage of many activities that take place within an earth science museum.

Manni R. (1993) - Il Museo di Paleontologia. I Musei dell'Università "La Sapienza", 46-56.

Matteucci R. (2012) - Cristalli, fossili e marmi antichi della Sapienza. Collezioni storiche dei Musei di Scienze della Terra e Unità d'Italia. Roma, Edizioni Nuova Cultura

# The sulphur crystals collection of Mining School "S. Mottura" in Caltanissetta: 160 years of sulphur mining history

Curcuruto E.*

Istituto Tecnico Industriale Minerario "S.Mottura", Caltanissetta.

*Corresponding author e-mail:* geocurcuruto@gmail.com

*Keywords:* sulphur crystals, sulphur mines, serie gessoso solfifera, earth science.

Sulphur crystals of the "S. Mottura" mineralogical museum, together with gypsum and other evaporitic minerals of the Gessoso Solfifera Formation (Mottura, 1871), form one of the best known minerals collection among mineralogists.

After a reconstruction of history of mineralogical and paleontological collections of the "Sebastiano Mottura" Mining School, the sulphur crystals of the Mottura collection have been analyzed in this paper. They were collected along 160 years of mining school activity in main sulphur mines (Gerbella, 1950), today all abandoned in the territory of Caltanissetta, Enna and Agrigento provinces in Sicily (Curcuruto, 2001). The study puts in evidence the richness and peculiarity of sicilian sulphur crystals.

Since its foundation in 1862 (Baldanza et al., 1990) the collection has been the center for an intensive lab didactic based on Mining and on Earth Science (Curcuruto, 2005). In this paper, it's also exposed museum efforts to conserve and restore what remains of the ancient sulphur mines of central Sicily, which were local most important economic resource.

Baldanza B., Burgio V. & Di Maria V. (1990) - Il Museo Mineralogico, Paleontologico e della Zolfara., Salvatore Sciascia Editore.

Curcuruto M. (2001) - I signori dello zolfo. Ed. Lussografica Caltanissetta.

Curcuruto E. (2005) - Earth Science and educational activities at Mineralogical and Paleontological Museum "Sebastiano Mottura". Quaderni del Museo Geologico Gemmellaro, 8, 115-125.

Gerbella A. (1950) - Arte Mineraria. 1, 2, Hoepli Editore.

Mottura S. (1871) - Sulla Formazione terziaria della zona solfifera siciliana. Mem. R. Comit. Geol. Italia, 1, 49-140.

# The Museo Gemmellaro: a dynamic tool for increasing research and dissemination

D'Arpa C.*[1], Di Patti C.[1] & Di Stefano P.[2]

[1] Museo Geologico «G.G. Gemmellaro», Università di Palermo. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* carolina.darpa@unipa.it

*Keywords:* communication, social inclusion, educational activities, third mission.

The geopalaeontological "Museo Gemmellaro" features a range of exciting events designed for all ages including educational activities, workshops, talks, debates, performances and research projects on the collections.

The museum plays an active role in Geosciences. It took part in the European Union project "GEOschools", supported by the Lifelong Learning Programme, with the aim to "translate" geosciences into a language that can be understood by secondary school students (Fermeli et al, 2015). Using the latest educational practices, the content and layout of the museum's exhibitions have been updated. The six hundred thousand fossils, which the museum preserves, allow to explore the extraordinary geological history of Sicily and enable to reconstruct the original living habitats of fossils (Chiovaro et al., 2020). During the guided tours the visitors can explore the geopalaeontological heritage of Sicily and make unexpected connections with the territory. These links between fossils and outcrops raise awareness among visitors about the safeguarding of these places and more generally about environmental sustainability as a resource for economic development (D'Arpa et al., 2020).

The museum creates and offers cultural learning experiences for all ages and school levels, providing curriculum-focused sessions, visits guided for teachers and classroom resources. The museum is included in the Register of Work-Related Learning Providers (PCTO) of The University of Palermo, and also supports the degree courses in Geological Sciences and Natural Sciences Museology and Museography, etc.

The museum develops the Palermo university 'third mission' combining up-to-date scientific research information with dissemination by taking part in initiatives such as "Notte Europea dei Ricercatori", "Notte dei Musei" and "Settimana del Pianeta Terra". Further support to the museum's accessibility can come by technologies usable by all audiences. Thanks to the funding of 2014/2020 PO FESR Action 6.7.2. project, the Museum is planning to create new virtual reality applications.

Many research projects are carried out on both vertebrate and invertebrate collections in order to review them. In order to increase the online access to the collections, the museum recently joined the cataloging campaign sponsored by the Ministry of Culture, using the web platform SIGECWEB.

The Museo Gemmellaro is a museum constantly evolving, as was demonstrated during the pandemic, when university curricular placements, workshops for secondary schools and dissemination events were designed and implemented entirely online.

Chiovaro V., D'Arpa C., Di Patti C., Di Trapani F. & Ilardi M. (2020) - Il Museo Gemmellaro e l'audience development. Atti del XXIX Congresso ANMS, 202-206.

D'Arpa C., Di Patti C. & Di Stefano P. (2020) - Nuove frontiere per un museo geopalentologico: il Museo "G.G. Gemmellaro" dell'Universita' di Palermo. Atti del XXIX Congresso ANMS, 79-83.

Fermeli G., Meléndez Hevia G., Koutsouveli A., Dermitzakis M., Calonge A., Steininger F., D'Arpa C. & Di Patti C. (2015) - Geoscience Teaching and Student Interest in Secondary Schools-Preliminary Results from an Interest Research in Greece, Spain and Italy. Geoheritage, 7, 13-24. https://doi.org/10.1007/s12371-013-0094-4.

# Born in the Age of Enlightenment – The case of the Targioni-Tozzetti naturalistic collection

Fabrizi L.*[1-2], Moggi Cecchi V.[2] & Benvenuti M.[1-2-3]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Museo di Storia Naturale, Università di Firenze. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* lucilla.fabrizi@unifi.it

*Keywords:* naturalistic collection, Enlightenment, cataloguing.

The collection of Giovanni Targioni Tozzetti (1712-1783), "Father and Master of Italian Naturalists" as defined by Fortis, constitutes a precious historical and scientific document. Giovanni purchased the important naturalistic collection of his master Pier Antonio Micheli (1679-1737) after his death, creating the initial nucleus of his own collection. The collection was expanded during his journey through Tuscany aimed at the naturalistic exploration of this region, with particular regard to the study of rocks. His son Ottaviano (1755-1829) inherited and partially expanded the collection, revising it according with the progress made by science over time (Cipriani & Scarpellini, 2007). The Targioni Tozzetti collection (TTC) was bought by the Natural History Museum of the University of Florence. The TTC in many respects represents one magnificent example of the transition from the old conception of the Wunderkammern towards a "modern"scientific collection (Scarpellini, 2012).

The project aims to study and fully classify the TTC of minerals and rocks and finally create a detailed digital catalogue. The collection, albeit in a fairly good state of conservation, has never been fully catalogued or studied in detail in recent times. The cataloguing studies, carried out in the past, examined the original handwritten analytical catalogue in 12 volumes, but the correspondence between the catalogue entries and the specimens has never been verified.

As a first step, therefore, 150 representative samples have been selected and inventoried by extracting the related information from the TTC catalogues. The original labels report either the name of the element obtained from the mineral (e.g., *Ferrum* for the iron minerals), or the practical use of a raw material (e.g., *Ceramica* for the clay samples). In other cases the terms are ambiguous (e.g., *Magnes*).

The determination of modern mineral and rock species of the specimens has been carried out along with the characterization of other types of materials belonging to TTC (e.g., anthropological artefacts, small statues, pendants, etc.).

This study, although at a preliminary stage, may hopefully spread light on how the first naturalists collected, organized and classified those samples which allowed them to conduct their pioneering studies.

Cipriani C. & Scarpellini A. (2007) - Un contributo alla mineralogia settecentesca: la collezione di Giovanni Targioni Tozzetti. L.S. Olschki, Firenze.

Scarpellini A. (2012) - An 18th Century Litho-mineralogical Collection, in The Museum of Natural History of the University of Florence: the Mineralogical and Lithological Collections. Vol. IV, Firenze University Press.

# Unveiling the Medicean Collection of "Carved Stones"

Fabrizi L.*[1-2], Moggi Cecchi V.[2], Bronconi C.[1], Fantoni L.[2] & Benvenuti M.[1-2-3]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Museo di Storia Naturale, Università di Firenze. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* lucilla.fabrizi@unifi.it

*Keywords:* gems, museum collection, Micro-Raman spectroscopy.

One the most important mission of museums is the study of the collections, in accordance with UNESCO 2015 Recommendation for Museums and Collections. The dissemination of the held results can be an instrument to maintain interest in the collections and to allow a more in-depth knowledge of them to an increasingly wide audience (Barone et al., 2016; Pratesi et. al., 2021).

The project aimed to study from both a scientific and historical point of view *the Medicean Collection of "Pietre Lavorate" (Carved Stones)* develops in this context, with the goal to amplify, and eventually correct, the mineralogical information about the most ancient gems present in the collection. The results involve geology, history of science and scientific dissemination.

The collection is part of the Mineralogy and Lithology collection of the University Museums' System of the University of Florence and counts of about 700 samples: minerals, gems and fine pieces of carved stones. Among them, some artefacts belonged to the personal collection of Lorenzo il Magnifico himself (1449-1492) (Fantoni & Poggi, 2012). The Collection owns a great value concerning the history, the mineralogical variety of the specimens, the preciousness of the workmanship, and represents a journey to the dawn of scientific collecting in the XV cent. AD.

The study focuses on 53 specimens reported in the first official museum Catalogue (1793), which should belong to the pristine most ancient core of the Medicean Collection.

As first step, the mineralogical and any other information written in the several handwritten catalogues (between the XVIII and XX centuries, since the most recent of the 1943/47) are compared. Then, the mineralogical identification of specimens is performed with stereoscopic microscope and μ-Raman spectroscopy. The analyses confirm the presence of emerald, coloured quartz, topaz, and opal, reject the presence of some species reported in the catalogue (i.e., aquamarine, zircon and spinel) and identify the presence of cordierite and garnet. Concluding, the results confirm many inventory information, but reject others, finding interesting corrections on labels (*cangiamenti di etichetta)* occurred with time and raise new open questions as to, for instance, the provenance of peculiar specimens, e.g., the emeralds.

Barone G., Mazzoleni P., Raneri S., Jehlička J., Vandenabeele P., Lottici P.P., Lamagna G., Manenti A.M. & Bersani D. (2016) - Raman Investigation of Precious Jewelry Collections Preserved in Paolo Orsi Regional Museum (Siracusa, Sicily) Using Portable Equipment. Appl Spectrosc., 70, 1420-1431.

Fantoni L. & Poggi L. (2012) - Dal Gabinetto di Mineralogia al Museo di Storia Naturale. In: Pratesi G. Ed., Il Museo di Storia Naturale dell'Università degli Studi di Firenze: le collezioni mineralogiche e litologiche, Firenze University Press, 16-30.

Pratesi G., Franza A., Lascialfari E., Fantoni L. Malesani F. & Hirata A. (2021) - It is hard to be a gem in a rhinestone world: a diamond museum collection between history and science. Geoheritage. 13, 103-118.

# A dip in the Cretaceous reef… of Rocca di Cave

Fabrizi L.[1-2-4], Leone I.[3-4], Graziani V.[4] & Ruggiero L.*[4-5]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Museo di Storia Naturale, Università di Firenze. [3] Centro Universitario Cattolico, Conferenza Episcopale Italiana, Roma. [4] Cultura in Pratica, associazione culturale, Roma. [5] ALES Arte Lavoro e Servizi S.p.A., Roma

*Corresponding author e-mail:* ludovica.ruggiero@beniculturali.it

*Keywords:* geopaleontologic path, Lazio-Abruzzi carbonate platform, family-oriented visiting experience.

The area of the Municipality of Rocca di Cave, on the Prenestini Mountains in the S-E of Rome, hosts a site of community interest: the Cretaceous reef, preserved by "Ardito Desio" Civic Geopaleontologic Museum since 2002. This area is of considerable paleoenvironmental importance, as it is constituted by the rare remains of the western edge of the Lazio-Abruzzi carbonate platform. During the Cenomanian and Turonian, the area was characterised by a very rich fauna with dominant bivalves (rudists and others), gastropods, hexacorals, porifera, rare echinoids and ammonites from pelagic domains, whose fossil remains are magnificently recognizable in the rocks (Carbone & Sirna, 1981). Recently, the discovery of Titanosaur bone fragments further enriched the interest for this area (Del Sasso et al., 2016).

The project PLANET-Rocca di Cave, created by the cultural Association "Cultura in Pratica" (CiP), aims to create a multi-sensorial and accessible experience dedicated to the exploration of the fossiliferous heritage of the area by young visitors and families.

Along the geopaleontologic path, visitors can encounter four main fossiliferous outcrops. In order to provide the autonomous fruition of the path, CiP projected for each outcrop three different levels of contents: a text for the general public, a corresponding audio content, and a story for the children. All the contents are shared by QR codes, available directly in front of each outcrop. The children's contents are easily identifiable by a Titanosaur avatar (Tito) and deals with the story of Tito exploring the reef. This avatar was designed for the project and aims to empathise with children and simultaneously diffuses the knowledge of the important, but also poorly known, scientific discovery of a dinosaur on the Lazial Apennines.

On the other hand, to create a new, family-oriented visiting experience, CiP created an "Explora kit", containing a writing kit, a magnifying glass and an original active book, with games and riddles about the animals living in the Cretaceous reef. The kit, which allows children playing and exploring the outcrops, gives simple inputs and scientific information.

Moreover, to improve the accessibility to the path for those people who can not reach it (due to motoric problems, absence of efficient public transport, etc.) several reconstructions freely available online have been produced. Nine 3D models and a graphic paleo-artistic reconstruction of the ancient reef environment were realised, based on the previously paleontologic research conducted (Carbone & Sirna, 1981).

Carbone F. & Sirna G. (1981) - Upper Cretaceous Reef Models from Rocca di Cave and adjacent area in Latium, Central Italy. SEPM, 30, 427-445.

Del Sasso C., Pierangelini G., Famiani F., Cau A. & Nicosia U. (2016) - First sauropod bones from Italy offer new insights on the radiation of Titanosauria between Africa and Europe. Cretac. Res., 64, 88-109.

# North Eastern Italian decorative stones as museum objects: a non-invasive characterization

Fugazzotto M.*[1] & Coccato A.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK).

*Corresponding author e-mail:* maura.fugazzotto@phd.unict.it

*Keywords:* decorative stones, museum collections, non-invasive characterization.

A sample panel of 48 decorative stones from the North-Eastern part of Italy is on exhibition at the Museum of Mineralogy, Petrography and Volcanology of the University of Catania.

Within the efforts of documentation, scientific cataloguing and digitalization of the museum's heritage, a non-invasive characterization has been carried out on the polished decorative stone samples by means of digital microscopy (Dino-Lite), using visible, infrared and ultraviolet illumination, and portable X-ray fluorescence spectroscopy (Bruker Nano Analytics). For the latter, two settings were adopted, either for the main elements and the traces ($Z > 19$).

The acquisition of high-resolution high magnification images allowed to non-invasively investigate the texture and features of the decorative rocks. On the other hand, chemical data could be easily obtained with two measurements of 60 seconds live-time each, and by a dedicated data-processing.

The vast majority of the samples is a carbonate rock, compatible with the geological settings of the region, where compact fossil-bearing limestones of the Eocene (Chiampo varieties), Jurassic micritic nodular limestones with ammonites (Rosso ammonitico), and Triassic-Jurassic dolomitic limestone with stylolites (Botticino) outcrop (Salvini, 2017; Pieropan, 2018).

The combination of the macroscopic and microscopic observation on the polished surface can support the geological classification of the samples, in addition to the commercial nomenclature. These analytical results could support both researchers and students in their academic pursuit by providing reference data. Moreover, the obtained information on these rock specimens will be integrated in a specific app for the fruition of the museum (Sinitò et al., 2020), in order to widen accessibility to petrographic and mineralogical results to a larger public, who can recognize museum specimens in the real world and vice-versa (Sinitò et al., 2020; De Luca et al., 2021). All the data will be available in a HUB realized thanks to the project DREAMIN (Digital Remote Access of Museum and Infrastructures).

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Pieropan A. (2018) - Proprietà petrofisiche e resistenza al degrado dei calcari utilizzati negli edifici storici dell'italia nord-orientale. PhD thesis, University of Padua.

Salvini S. (2017) - Deterioration of carbonate rocks and vulnerability of cultural heritage in a changing climate. PhD thesis, University of Padua.

Sinitò D., Fugazzotto M., Stroscio A., Coccato A., Allegra D., Barone G., Mazzoleni P. & Stanco F. (2020) - I-PETER (Interactive platform to experience tours and education on the rocks): A virtual system for the understanding and dissemination of mineralogical-petrographic science. Pattern Recognit. Lett., 131, 85-90.

# The Larderello Geothermal Museum: history of a renewable energy invention

Giudetti G.*, Simoni G., Lenzi A., Taccone R., Vecchieschi G. & Clementi R.

Enel Green Power, Pisa.

*Corresponding author e-mail:* geoffrey.giudetti@enel.com

*Keywords:* Larderello, geothermal museum, history, technology.

The Larderello Geothermal Museum is unique in its kind and in the ten rooms, through a rich collection, it describes the phenomenon of geothermal energy in Tuscany from a geological, technological, historical and social point of view. Larderello, in the province of Pisa, is the place where, in 1904, Prince Ginori Conti used, for the first time in the world, the energy of the steam from shallow wells to produce the electric current to light 5 bulbs and, subsequently, in 1913, installed a small 250 kW unit. Today, 37 geothermal units are installed in Tuscany, generating approximately 6 TWh of electricity per year, covering approximately 33% of the regional energy consumption.

The museum is housed in Palazzo De Larderel, near the offices of Enel Green Power Italia. It was conceived in 1956 and updated in 2008 and every year it hosts about 50,000 visitors (2019 data, pre-COVID).

The Museum hosts beautiful specimens of minerals found in the “borax area” such as “Larderellite” and “Sassolite” as well as products for chemical uses extracted in the history of the borax industry: purification baths, cosmetic and pharmaceutical uses.

The visitor learns about the complex geology of the area looking at the stratigraphic sequence and thematic cartography. Examples of the drilled sequence of the Flysch, Tuscan Nappe, metamorphic basement and granites are exhibited. The so-called first reservoir of the geothermal system hosted in the Tuscan successions is exposed in the Biancane area near the municipality of Monterotondo, where steaming and gas leached rocks are visible.

In the rooms different uses of the geothermal resource are described. Starting from the ancient thermal uses, passing through the chemical uses of the Middle Ages, up to 1777 with the discovery of boron in the bubbling pools (Lagoni) and the subsequent technological achievements to extract it. The technological evolution of drilling, started in Larderello as early as 1836, with truly unique pieces of the first models of “rigs” with the relative tools is described, together with models illustrating the boron extraction process and its technological evolution. The museum preserves the “General Regulations” published in 1849 (the first of its kind in Europe) describing the working conditions and the “benefits” for the families of the workers: school, free medical care and medicines, housing and insurance.

In the “famous” book of visits evidence of the passage from Larderello of famous scientists and personalities such as Marie Curie Sklodowska, Enrico Fermi, king Vittorio Emanuele III and Gabriele D’Annunzio are preserved.

The visit can be enriched with the opening of a shallow geothermal well which demonstrates the power of underground steam.

The Larderello museum is one of the few, if not the only, examples of story telling about a natural and renewable resource and of how man has made it available for everyone.

# *Terra Nascosta*: an experiential exhibition to discovery Taramelli and the modern Geology

Lupi C.*[1], Guaschi P.[2] & Guioli S.[3]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Kosmos - Museo di Storia Naturale, Università di Pavia [3] Museo di Scienze Naturali, Voghera (PV).

*Corresponding author e-mail:* claudia.lupi@unipv.it

*Keywords:* experimental exhibition, interactivity, outreach effort.

One hundred years after the death of Torquato Taramelli, the Department of Earth and Environmental Sciences, the Kosmos Museum of Natural History of the University of Pavia and the Museum of Natural Sciences of Voghera present the experiential exhibition "Terra Nascosta. Rocce, vulcani e terremoti: dalle scoperte di Torquato Taramelli alla Geologia moderna". The path is developed on two levels that constantly interact with each other: a historical one with the main stages of Taramelli's scientific career, and a playful-didactic one with interactive stations. From a conceptual point of view, the exhibition aims to discover Geology and the role of the geologist in society. The title "Terra nascosta" wants to underline the ability of the geologist to go beyond the beauty of a landscape, the geologist observes the rocks and in them catches the many clues of the deepest processes of the Earth.

The exhibition is built drawing on the theory of Multiple Intelligences by Howard Gardner and is built thanks to the alternating use of images, concept maps and real objects to be manipulated by varying the methods of treating the individual contents in the attempt to engage heterogeneous audiences and alternatively the intelligence of the visitors.

The exhibition includes 3 big stations: the first dedicated to the lithogenetic cycle and the recognition of rock samples also thanks to digital microscopes; a second station is dedicated to geological maps with a video on the geological survey and the 3D printing of the Foglio Iseo; the third station is dedicated to natural risks with insights into landslides, earthquakes, volcanic eruptions and environmental risk. The visitor is accompanied to discover how much our daily life is linked to the geological nature of the territory in which we live and how much its knowledge is the basis of safe and sustainable development. Many aspects of our daily life, from the water that comes out of the tap to the mobile phone, are connected to Geology and every day this science helps us to face new challenges. The sustainable future of the planet can only be pursued with a deep knowledge of natural processes.

The exhibition was built so that it can be adapted to other exhibition spaces. The tables can be easily disassembled and each station comprehensively represents a basic concept of the Earth Sciences.

The exhibition saw the participation of numerous schools and the family events were always sold out. Evaluation questionnaires of the exhibition path and about the effectiveness of the approach are being collected. Preliminary data show that direct activity on rock samples or carrying out simple experiments positively involves the public and facilitates the acquisition of new content.

# A preliminary activity for the valorization of cultural heritage: the cataloguing of the scientific heritage of the University of Catania

Maci O.[1], Majorana S.[2] & Treffiletti A.*[3]

[1] Area della Terza Missione, Università di Catania. [2] Dipartimento di Scienze Umanistiche, Università di Catania.
[3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* alessandro@treffiletti.it

*Keywords:* cataloguing, scientific heritage.

About 13% of museums in Italy falls into the category of science museums; more than half of them are museums of science and natural history, followed by those of ethno-anthropology, of science and technology, and by botanical gardens (Jalla, 2003). Spread more in the North rather than in the South, dedicated to research and teaching activities and managed mainly by municipalities and Universities, these museums are the exclusive witnesses of a historical-scientific-naturalistic heritage which is fundamental for scientific knowledge. This heritage, however, is not sufficiently valued, mainly due to the inequality of financial and organizational measures between the artistic-museological universe and the scientific one (Dragoni, 1997). To address this problem, in recent years, public and private organizations have promoted a path that has led the national legislation to acknowledge this heritage as a "cultural asset", and to ensure that the scientific and technological heritage was equally protected and promoted, starting from the basic cognitive ability that is cataloguing, which allows to have a general idea about the size of the collections scattered throughout the national territory, through a special standard sheet drawn up by the Central Institute for Catalogue and Documentation (Ferrante, 2018). The University of Catania has undertaken a series of initiatives aimed at improving access and use of the rich heritage of which it is endowed, which tells its centuries-old history, and which is collected in various museums, now incorporated into a single University Museum System – the SiMuA. The cataloguing of naturalistic findings as well as ancient scientific instruments, already under way, is only the preliminary passage for a wider plan, which will promote the findings through digitalization – as already demonstrated by DREAMIN, the digital hub for the remote use of university museum projects, recently launched online (https://dreamin.unict.it/) – and through other means. Moreover, the cataloguing presented in this work – despite the difficulties encountered, such as the lack of information or the condition of disorder in which these findings are – will become an example of best practice to be extended to the collections of other SiMuA museums. Because the first step in benefiting our heritage is knowing the heritage itself and allowing people to access that information must be the primary and fundamental purpose of any museum.

*This work is funded by the project DREAMIN (FISR2020IP_03752; CUP:* E65F20001710001).

Dragoni G. (1997) - Per un dibattito sulla museologia scientifica e naturalistica italiana. La rete dei musei universitari. In: Basso Peressut L. Ed., Stanze della meraviglia. I musei della natura tra storia e progetto, 297-322, CLUEB, Bologna.

Ferrante F. (2018) - Normativa PST- Patrimonio Scientifico e Tecnologico. Versione 4.00. ICCD, Roma.

Jalla D. (2003) - Il Museo contemporaneo. Introduzione al nuovo sistema museale italiano. UTET Libreria, Torino.

# MUST 2.0

Macrì M.* & Sardella R.

Museo Universitario di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* michele.macri@uniroma1.it

*Keywords:* Earth Sciences, museum, dissemination.

Sapienza University of Rome invested in the creation of a modern museum dedicated to the Earth Sciences (MUST - Museo Universitario di Scienze della Terra), by unifying the existing, independent Geology, Mineralogy and Paleontology Museums. The newly established museum will be one of the most important European venues for the number of both exposed and preserved specimens, in the field of Earth Sciences.

The main targets that convinced the Governance of Sapienza to believe in this project are:

– the setup of a modern museum dedicated to the planet Earth, to its history and its relationship with humans, open to the citizens (it is noteworthy that the city of Rome, unlike other European capitals, is so far lacking a natural history museum);
– the reorganization and improvement of the existing museums – already active in the dissemination of scientific culture and in the increase of the geological heritage value – that together preserve the largest Italian collection in the field of Earth Sciences, with specimens among the world's most important ones;
– the research development and methodological innovation through the museum activities, for an efficient dissemination and education on Earth Sciences;
– the promotion of the scientific culture, information and dissemination, both nationally and internationally.

The MUST has a unique entrance, independent of the Department entrance. The signposting and the architecture of the museum will be specifically designed for visitors to improve the accessibility. A specific museographical and museological project has been implemented after the structural works of unification, thus helping the homogenization and connection of museum spaces, along a didactic and aesthetic pathway specifically designed.

The position of the Earth Science Department within the Sapienza Campus implies just minor interventions on the viability in order to allow the accessibility to the museum even during holidays. The entrance to the museum is located on the eastern side of the department building, and it is suitable for disabled visitors. The museum pathway reaches the higher floors, and the exit is located in the bookshop.

Renovation, extension and innovation works implies noticeable efforts by the department staff and the investment of a considerable budget. Scientific and structural surveys and projects have been carried out by a team specifically dedicated to the MUST. A common target defined as "museum for the community" has been defined in order to fill the cultural gap of the city on the scientific-naturalistic cultural heritage.

# IoT for sustainability and efficiency in preventive conservation at the Anthropology and Ethnology Museum of Florence

Manfriani C.*[1], Gualdani G.[2], Roselli M.G.[3], Benvenuti M.[4] & Fioravanti M.[1]

[1] Dipartimento di Scienze e Tecnologie Agrarie, Alimentari, Ambientali e Forestali, Università di Firenze. [2] Painting conservator,San Giovanni Valdarno (AR). [3] Museo di Antropologia e Etnologia, Università di Firenze. [4] Sistema Museale di Ateneo, Università di Firenze.

*Corresponding author e-mail:* chiara.manfriani@unifi.it

*Keywords:* Internet of Things, preventive conservation, climate control.

New technologies are increasingly used to reduce the risks to collections of museums and other cultural institutions. In particular, climate monitoring and control strategies for the interaction between tangible heritage objects and their conservation environments are traditionally based on rigid RH and T values of 50% and 21°C, but a more flexible object-based approach has been adopted in the recent application of the relevant European Standard EN 15757:2010 (Europepan Committee for Standardization, 2010) and the 2019 review of ASHRAE Applications Handbook (ASHRAE, 2019). Furthermore, the contribution of the Internet of Things (IoT) to the implementation of tailored, appropriate climate control systems is becoming increasingly significant due to the progress in sensor and data transmission technologies together with the development of cloud computing.

The present work aims to describe innovative applicative research, based on the use of an affordable and attractive IoT architecture to improve museum and conservation practice. Built on previous research (Manfriani et al., 2021), it proposes an integrated collection of climatic data and conservation information, based on historic climate studies according to international standards, and on the conservation needs of hygroscopic materials.

This approach has been used in the study and the care of a museum collection rich in hygroscopic material, the Anthropology and Ethnology Museum in Florence, part of the Natural History Museum of the University. Four case studies have been chosen and studied from a conservation perspective among the objects preserved in the museum. Moreover, the historic climate in the halls hosting the case studies has been determined based on a monitoring campaign.

The same IoT platform used to collect conservation and climatic data has been used to tailor a climate control system. Real-time remote access to the data was given to the museum staff and conservators, the appropriate alarm logic with immediate feedback to the conservators has been implemented, and active climate control was then introduced and successfully validated.

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European Committee for Standardization (2010) - Conservation of Cultural Heritage - Specifications for Temperature and Relative Humidity to Limit Climate-Induced Mechanical Damage. Standard EN 15757. CEN, Brussels, Belgium.

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# Synopsis of a treasure. A transdisciplinary study of medieval goldworking's biographies

Martiniello S.*[1], Sciuto C.[2], Capitanio A.[2], Lorenzetti G.[3], Legnaioli S.[3], Sala F.[2], Torriti P.[1] & Raneri S.[3]

[1] Dipartimento di Filologia e Critica delle Letterature Antiche e Moderne, Università di Siena. [2] Dipartimento di Civiltà e Forme del Sapere, Università di Pisa. [3] Istituto di Chimica dei Composti Organo-Metallici, CNR, Pisa.

*Corresponding author e-mail:* stefania.martiniello@gmail.com

*Keywords:* gems, museums, Tuscany.

This contribute aims at showing how a transdisciplinary approach can support a better understanding and fruition of precious art objects preserved in Museums. The study focused on four objects of different dating and of great interest in the Tuscan goldsmith scenario, also for their interactions with Byzantine and French world: the *Cintola del Duomo* (Opera del Duomo Museum, Pisa), the *Holy Cross* (Civic Museum, Castiglion Fiorentino, Arezzo), and the Reliquary of the Arm of St. John the Baptist with its case (Siena Cathedral). They are among the most famous objects in the history of goldsmithing, both for their manufacturing exceptional quality and for their devotional value.

For long time, the *Cintola* was considered a fragment of a long garland – adorned with gems, enamel and silver plates – exhibited on the Cathedral's façade in some days of the liturgical calendar. In-depth historical studies suggested that it was lost in the early 1300s; the object nowadays preserved in the Museum is more likely a reconstruction adorned with ancient and modern gems (Novello, 1995). The *Holy Cross* is a reliquary adorned with gems and enamels, dating from the third quarter of the 13$^{th}$ c.; its attribution was greatly disputed by the scholars, debating between a regional or French manufacture (Torriti, 2010). The right arm of St. John the Baptist was donated in 1464 by Pope Pius II to the city of Siena; its manufacture seems to be related to Byzantine world, while the case was made by the goldsmith Francesco d'Antonio di Francesco from Siena (Cioni & Farrorini, 2021). In-situ diagnostic campaigns have been carried out on the precious objects by portable Raman (i-Raman, B&W Tek, excitation source 785 nm) and p-XRF (Elio, Brucker) to reveal the identity of gems, preliminarily investigated by gemological analysis. Moreover, photogrammetric acquisition provided a digital rendering of the *Cintola*, enabling the merging of historical, gemological, and analytical information. The combination of analytical techniques enabled better outlining the multifaceted narrative of the artefacts' history. Regarding the *Cintola*, the analysis provided information on the identity of the gems, opening interesting question on the possible relation with the crown of Henry VII of Luxembourg preserved in the same Museum. The analysis of the *Holy Cross* clarified the nature of the gems, supporting interpretative issues on its provenance. The ongoing research on the Arm of St. John the Baptist are revealing promising results, supporting provenance and manufacture attribution of this unique goldwork.

Overall, the study entails all the aspects linked to the objects' materiality, unveiling the socio-cultural context in which the object has been produced, and supporting their re-contextualization in the Museum, as a symbolic representation of the past.

*The authors acknowledge the Opera del Duomo of Pisa and Siena and the Museum of Castiglion Fiorentino for authorizing the present research.*

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Torriti P. (Ed.) (2010) - Sacra Mirabilia, tesori da Castiglion Fiorentino. Edifir, Firenze.

# The museum of Mineralogy, Petrography and Volcanology of the University of Catania: a multitasking museum

Mazzoleni P.* & Cirrincione R.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* pmazzol@unict.it

*Keywords:* cataloging, research, teaching.

The museum of Mineralogy, Petrography and Volcanology of the University of Catania is an historical museum, born with historical samples collected by famous researchers in Volcanology and then enriched with numerous donations (Patanè & Cristofolini, 2004). Nevertheless, a part for the original cases and furniture, that give to it a charming appearance, it is a modern museum. Indeed, it has been recently renovated in its setting up and it appears as motor of researches and activities, among which new methods of fruitions and dissemination.

Thanks to various projects it was possible to perform non-invasive researchers on the historical samples and on the donated ones, in order to verify their authenticity and their real mineralogical and petrographic attribution; consequently, a digital cataloguing has been started, by following the national standard recommendations both concerning minerals, stones and also the historical instruments preserved in the museum. Due to the high amount of samples exposed, the collections are also considered for creating databases, useful for scientific investigation with ordinary but also innovative analytical techniques, as for example Raman spectroscopy and DRIFT. In the meanwhile, the active collaboration with different Departments, as this of Mathematics and Informatics, gave the opportunity to develop a web-app (Sinitò et al., 2020), that together with a virtual tour, allows to virtually visit the collections, by remote or in museum, customizing the user path according to the interest case by case or to the educational level. From these systems it will be possible furthermore to have access to the scientific data of the collections or to further information collected. Lastly, the museum is open to students' activities in terms of PCTO or dissemination trainings, thus confirming its multitasking skill.

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Sinitò D., Fugazzotto M., Stroscio A., Coccato A., Allegra D., Barone G., Mazzoleni P. & Stanco F. (2020) - I-PETER (Interactive platform to experience tours and education on the rocks): A virtual system for the understanding and dissemination of mineralogical-petrographic science. Pattern Recognit. Lett., 131, 85-90.

# Geoscience in Antarctica, a challenge for a sustainable environment: the example of the Earth Science section of the "Museo Nazionale dell'Antartide"

Palmeri R.[1], Sandroni S.*[1], Olmastroni S.[1] & Cornamusini G.[1-2]

[1] Museo Nazionale dell'Antartide, Università di Siena. [2] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena.

*Corresponding author e-mail:* rosaria.palmeri@unisi.it

*Keywords:* Antarctica, rocks, meteorites.

The Museo Nazionale dell'Antartide (MNA) - Earth Science section of Siena is the national repository for the geological material (rocks, fossils and meteorites) collected during the Italian Antarctic expedition since 1985, and has the aim to acquire, preserve, manage, catalogue and classify all the collection samples and to sort them towards the scientific community; moreover, it also have to promote the knowledge of scientific results achieved by the Italian Antarctic research community. Actually, the collection includes nearly 22,000 rocks and fossils and more than 1,500 meteorites (1,100 recovered during the Italian Antarctic expeditions and 400 from other countries). Both collections are digitalized and available for consultation at the web site of MNA (http://mna.it/collezioni/catalogo-rocce-sede-di-siena for rocks and http://mna.it/collezioni/catalogo-meteoriti-sede-di-siena for meteorites).

The Antarctic rock database can be filtered by locality, lithologic type (i.e., igneous rocks, metamorphic rocks, etc.), lithology, sampler, expedition and sample code. The search results can be exported in an excel table and on a Google Earth map; moreover, details including sample code, locality, longitude and latitude, sampler, area, region, geographic folio, lithology, field description, petrographic classification, photo, bibliographic references, weight, together with thin section, crushed rock and powder rock (if available) are reported for every sample.

Similarly, the Antarctic meteorite database can be filtered by meteorite name, country/place/year of recovery and classification type, and results (which can be limited to approved meteorite names) can be exported to Excels and Google Earth files. For each meteorite, information including fragment/thin section availability, classification data and bibliography are also reported.

The existence of this scientific heritage available for consultation by the scientific community is very important for future geologic research in Antarctica in terms of sustainability, being Antarctica the coldest, windiest, driest, highest, quietest, most remote on Earth, but also the most fragile for the human impact. The existence of samples from already explored areas that can be studied without a novel expedition in the same place contribute to preserve Antarctica as a sustainable continent.

Moreover, the outreach activity in the museum is devoted to promote the polar knowledge to as wide an audience as possible, with special attention dedicated to all-level students and educators. The latter activity allows the visitors to be not only updated with some of the currently more crucial scientific arguments, as the global warming but also to have a major awareness towards the sustainable themes. Antarctica with its unicity and fragility become a model to follow for the Earth care.

# Enhancement of mining heritage of Piemonte, proposals for a didactics and touristic network

Paschetto A.*[1], Bonetto S.[1], Gilli M.[2] & Altomare P.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Regione Piemonte, Torino.

*Corresponding author e-mail:* arianna.paschetto@unito.it

*Keywords:* industrial tourism, geoheritage, geoparks.

Quarries and mines have provided, throughout the ages, natural resources necessary for manufacturing, artistic and industrial development of the society. However, currently, we are not always able to valorize their socio-cultural and historical significance.

The aim of this study is to collect and complete an existing dataset of Piemonte extractive heritage and propose a network of potential sites to be valorized in terms of touristic and didactic uses.

Firstly, abandoned quarry and mine sites was collected and stored using Geographic Information Systems. Was created a database consisting of three databases for mines and a single database for quarries. Based on this data, several criteria were taken into account to select potential sites of interest to create the tuoristic network. The choice of sites was evaluated so as to represent the main materials extracted in Piemonte. Subsequently, using aerial photo and landslide archive, it was possible to consider accessibility of the various areas. Finally quantitative and qualtative rock mass stability investigations were carried out at the sites of greatest interest, based on the characteristics of sites themselves.

Taking these criteria into account, four sites were selected from former mines and four sites were selected from former quarries. For each of them a standard form was created with the aim of collecting information and materials to create a proposal of didactic-tourist itineraries network dedicated to the extractive heritage throughout Piemonte.

# Museum old collections for new science − The case of the Sicilian dwarf elephant housed at the Paleontological Museum of Catania

Rosso A.[1-2], Deias C.[1], Sciuto F.[1] & Sanfilippo R.*[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Museo di Palaeontologia, Università di Catania.

*Corresponding author e-mail:* claudia.deias@phd.unict.it

*Keywords: Palaeoloxodon falconeri*, insular mammals, cultural heritage.

Museums are usually perceived as the elective place for exhibitions and communication of science, but they also represent places where materials are continuously accumulated and preserved for future generations becoming part of local and worldwide cultural heritage.

The Palaeontological Museum of the University of Catania hosts a continuously growing body of collections besides the historical ones many dated back to the 19th and even the 18th centuries. Within materials, vertebrate remains from Plio-Pleistocene Sicilian localities are relevant including a huge collection of bones originating from the Spinagallo Cave near Siracusa, and especially belonging to the iconic Sicilian dwarf elephant *Palaeoloxodon falconeri*. These bones, that were excavated and fist studied in the mid-1990s, continue to attract the interest of public and scholars who have had the opportunity over time to examine them with modern investigation techniques addressing new and challenging questions.

Indeed, the high quantity of bones (especially those from limbs) and their general good preservation state allowed comparison of *P. falconeri* species with further dwarf congeners that populated the Sicilian-Maltese archipelago during the middle-late Pleistocene and to highlight the occurrence of paedomorphic characters in some limb bones in comparison with the ancestral species *P. antiquus* from European continental areas (Scarborough, 2020).

Furthermore, detailed histological examination of some exquisitely preserved bones (including skeletochronology), molars (enamel analysis, plate and crown formation time) and tusks (dentine analysis) of the Catania Paleontological Museum, recently allowed to propose new ideas (Köhler et al., 2021) about the life history of this and other dwarf insular mammal species contrasting with previous hypotheses of an accelerated life-history of *P. falconeri.* Indeed, according to Raia et al. (2003) this species attained sexual maturity at the age of 3-4 years, had a pregnancy period of 189 days and an expected life span of 26 years or slightly more based on estimation of the body mass (Larramendi & Palombo, 2015). In contrast, the new analyses provide evidence that *P. falconeri* grew at very slow rates but over an extended period; it attained maturity and became reproductive at the age of 15 years; and reached a minimum lifespan of 68 years. This last figure exceeds the values inferred through the estimation of the body mass for the same species and those observed in existing elephants.

This shows how the museum exhibits preserve through time valuable information, whose later investigation allow reinterpretations enlivening the scientific debate for advances in knowledge.

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# I-PETER (Interactive Platform to Experience Tours and Education on the Rocks): a new app for the understanding and dissemination of petrographic and mineralogical collections

Stroscio A.*[1], Fugazzotto M.[1], Sinitò D.[2], Allegra D.[2] & Coccato A.[3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Matematica e Informatica, Università di Catania. [3] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK).

*Corresponding author e-mail:* antonio.stroscio@phd.unict.it

*Keywords:* museum, interactive platform, cultural tourism.

Museums of mineralogical and petrographic sciences represent today important resources for the understanding of cultural and natural heritage. There, through the understanding of exploitation of geo-resources and the application of natural stone in architecture, society gets a deeper insight into the economic and social scenario linked to minerals and rocks (Da Milano & Sciacchitano, 2015). Nevertheless, the fruition of the mineralogical and petrographic collections seems to still be reserved to a limited entourage of people. I-Peter (Sinitò et al., 2020) is a Web-App developed to fill the gap between the huge amounts of information and stories linked to the scientific patrimony and the small group of museums' visitors, with the aim to enlarge the cultural accessibility of the collection of the Museum of Mineralogy, Petrography and Volcanology of the University of Catania. The collaboration among earth scientists, conservators and computer scientists led to the implementation of a virtual system that gives to all users, regardless of their educational level, the possibility to actively visit the museum as a main actor. The fundamental principle of our approach is to make the visitor at the center of the visit, letting he/she able to customize the tour and internalize the many fascinating aspects of the geological world.

By using the application, that interacts with a database, the public can choose the modes of exploring the museum's collections: focusing on the rocks as building stones in selected monumental sites or selecting a monument and explore its constituent materials down to the microscale.

The project was further implemented, which represents the advancement of the interactive platform, with the additional possibility to have access to further scientific data linked to the research conducted on the samples exposed in museums, as for example results of non-invasive investigations on monumental sites, which can allow the identification and cataloguing of stones, or on conservation and restoration issues.

Thanks to this pilot project, it will be possible to promote cultural tourism by making it more accessible and appealing to a wider audience, as well as to support scientific research on petrography and mineralogy.

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# Digital enhancement of the paleontological heritage of the Valdemino show cave (Borgio Verezzi, Savona, Italy)

Thun Hohenstein U.*[1], Muttillo B.[1], Zunino M.[1], Pavia M.[2], Isaia M.[3], Delpiano D.[1], Parisi C.[1], Arnetta G.[1], Vaccaro C.[4] & De Curtis O.[1]

[1] Dipartimento di Studi Umanistici, Università di Ferrara. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università di Torino. [4] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara.

*Corresponding author e-mail:* ursula.thun@unife.it

*Keywords:* Valdemino show-cave, 3D digitization, photogrammetry, laser scanner, paleontology.

The Valdemino (or Borgio Verezzi) show cave (Liguria, Italy) represents an attractive site in Italy, visited by an average number of 30,000 visitors per year (Piano et al., 2021). This karst cavity (30 m a.s.l.), discovered in 1933, has been declared a site of speleological and paleontological importance in 1962. The cave is rich in paleontological remains recovered during the excavation (at the end of the 1960s, in 1989, 1990 and 1991) of a vertical gallery filled with Pleistocene sediments, representing the sink-hole of an ancient doline. The faunal assemblages have been dated between the Middle Galerian, in the lowest levels, and the Aurelian Mammal Age, in the upper levels) (e.g., Tozzi, 1969; Fornasiero, 1989; Nocchi & Sala 1997; Sala & Masini 2007; Masini & Sala, 2011). Today the gallery is not accessible to the public and the paleontological remains are stored in different institutions (Civic Museum in Finale Ligure, University of Ferrara, University of Florence) and not exhibited. As part of the ShowCave project (PRIN 2017- Prot. 2017HTXT2R; SHOWCAVE: a multidisciplinary research project to study, classify and mitigate the environmental impact in tourist caves), a three-dimensional processing of the main paleontological remains was performed, in order to promote the accessibility and to increase the research and educational value of this little-known paleontological heritage.

Here we present the 3D digitization of an unpublished macaca jaw stored at the University of Ferrara. The mandible has been digitized processing a high-resolution 3D reconstruction obtained through two different techniques, here compared: digital photogrammetry (using 3D Zephyr software) and 3D laser scanner (Laser scanner HP 3D Scan 5), at the laboratory of digital museology of the University of Ferrara. Other specimens of the main vertebrate species will be digitized in order to prepare an online 3D catalogue, that can be consulted by internet users and cave visitors through the use of QRcode present in the didactic panels.

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# S25.

# Geosciences at School

*Conveners & Chairpersons*

*Francesca Cifelli (Roma Tre University)*

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*Eleonora Paris (University of Camerino)*

*Manuela Pelfini (University of Milano)*

# Urban geo-itineraries as an educational tool for the knowledge of the territory: the example of the city of Rome

Adanti B., Cifelli F.*, Corrado S., Grossi F. & Mattei M.

Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* francesca.cifelli@uniroma3.it

*Keywords:* geoscience, urban geology, geo-itinerary.

Urban geo-itineraries allow keeping alive the 'geological memory' of an area, where urbanization has very often covered the natural landform. The geo-itineraries in the city of Rome have been designed with the aim of intriguing, involving and fascinating students and citizens of the city of Rome, transmitting a different way of observing the territory. The goal is to illustrate the geological resources that the city has been able to benefit from and the geological risks to which it is exposed, in a virtual journey searching for clues in the urban fabric. Urban geo-itineraries therefore offer the opportunity to visit Rome with 'different eye's, to discover the geological reasons that have conditioned its long history and its existence itself.

Among the proposed geo-itineraries, some develop through reserves that still preserve parts of the natural landscape (Parco della Caffarella, Monte Mario Nature Reserve, Decima Reserve), others run through urban routes and allow us understanding how much the geological configuration of the city has influenced the history of Rome (The Capitoline Hill, the Colosseum and the Imperial Forums, the Pantheon). The geo-itinerary in the Basilica of San Paolo 'fuori le Mura' represents an example of how we can approach the knowledge of our rich architectural heritage using the lithotype as a key to understanding, while another geo-itinerary suggests ideas to tell the capital importance of the resource 'for excellence': water.

The geo-itineraries in the city of Rome promote outdoor educational activities, aiming to arouse interest in students and teachers, also thanks to the interdisciplinary links between geology, history and art. In addition, they also represent a tool for 'non-global' tourism, which accompanies the discovery of a different identity of the city, based on the relationship between its geo-naturalistic, historical and artistic treasures.

# Challenges for the extration of raw materials: sustainability and education for transforming mining industry

Alfama V.*[1], Pinto H.[2], Navarro R.[3], Tejado J.J[4], Mutemeri N.[5], Punturo R.[6-7] & Pereira D.[8]

[1] Faculty of Sciences and Technology, University of Cabo Verde, Praia (Cape Verde). [2] Centre for Social Studies, University of Coimbra (Portugal). [3] Minera de Órgiva s.l., Granada (Spain). [4] INTROMAC, Cáceres (Spain). [5] University of Witwatersrand, Johannesburg (South Africa). [6] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.[7] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [8] Department of Geology, Univesity of Salamanca (Spain).

*Corresponding author e-mail:* vera.alfama@docente.unicv.edu.cv

*Keywords:* UNESCO, IGCP, sustainable geoscience.

Natural resources are crucial to advance society, to keep technological advance and satisfy human needs. However, extracting resources is not appreciated by many sectors of society, mainly because of the many negative environmental impacts of the extraction in the past. Education is a possible approach to mitigate this problem modifying the current low social status of mining activities. Most people are aware of the importance of transitioning to clean energy, but very few understand that this implies the use of minerals and relevant metals such as aluminium, cobalt, iron, lead, lithium, manganese, nickel, among others. Most are considered as 'critical raw materials' because the increase of their use is jeopardizing the level of stock around the world. A lot of research is done in Europe and North America, but most resources and reserves are somewhere else (e.g., Asia, Africa, South America). Also, when resources and reserves are found in the so-called developed countries, the public in general is against their extraction. They prefer to keep using commodities that come from peripheral and developing countries, even if the highest benefits from extraction are kept concentrated in the core developed countries. It remains common to hear "not in my backyard" arguments when there is debate about extracting resources in many European countries. At the same time countries in Africa are increasingly pushing for beneficiation and value addition to be done in their countries to optimize the benefits to their own economies.

All these dynamics point to the importance of enriching Earth Sciences study programs at all education levels, with new subjects such as social impact or ethics, including the utilization of good practices in mining and increasing the perception of the importance of artisanal mining. The latter activity is particularly important for sustainability and ethical investments. Including the experience of research from different regions advances good mining practices and contributes to changing the social perceptions regarding resource availability and extraction.

In 2021, UNESCO launched a special topic to their portfolio of funded International Geoscience Program (IGCP) projects that is "Enhancing societal acceptance of the sustainable development of Earth´s geological resources". The project IGCP-736, which falls under this topic will try to align with objectives of this topic by presenting good practices in mining, promoting transparency in the knowledge transfer from science to the quarry and mining industries. The project also intends to highlight the visibility of female researchers working in Earth Sciences to strengthen a gender aspect in policies and practices at all levels of education and working spaces. With its implementation the project expects to contribute to the attainment of different sustainable development goals, connected with challenges to keep citizens and ecosystems safe and healthy around the world by inducing the transformation in the extraction of natural resources.

# Teaching geology, from books to Earth: the contribution of geological maps, a powerful but neglected educational tool

Berra F.*

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* fabrizio.berra@unimi.it

*Keywords:* geological maps, high-school, education.

The most powerful way to store and share geological information is represented by geological maps. Geological maps are not simply coloured maps but are produced by geologists with a shared approach: they explore, walking across the mapped area, and collect in the field information and samples that, after analyses performed in laboratories according to the methods described in textbooks (radiometric dating, paleontological content, chemical and crystallographic analyses, microscope investigations and so on), provide all the data reported in the geological maps. These maps are the base for all the applications of geology: a SGI presentation (https://www.socgeol.it/N956/la-carta-geologica-d-italia-molto-piu-di-un-immagine-a-colori.html) provides the basic elements to understand the evolution, the process of production and the application of geological maps to the everyday life.

Geological maps thus summarize the geological knowledge of a specific area at a certain time: their lecture requires a basic geological knowledge, as that acquired by high-school students. Actually, as for all the thematic maps, to understand the symbolic representation of the geological objects, a basic knowledge of the language of geology and of the approach for the study of processes generating rocks and land morphology are required. Therefore, the lecture of geological maps represents an important exercise to test the understanding of the geological processes and to stimulate the ability to interpret the history of a territory, with implications on the understanding of the role of geology for land management, in terms of resources and risks.

Despite this potential, geological maps are mostly to totally neglected as tools for the education of high-school students, despite they are easily and freely accessible (the institutional web site of ISPRA stores all the 1:100.000 official geological maps of Italy and the updated CARG Project 1:50.000 maps, that are also available on web sites of Regioni and Provincie Autonome). The opportunity to "observe" the geological configuration of any place in Italy represents a fundamental free tool available for teachers to show the geological architecture of a specific area (in the school neighborhood or during open air excursions) and to show the applications of the concepts provided by textbooks: it becomes possible for the students to shift from theory learnt on book to physical objects that they can observe and touch.

The availability of geological maps on the web promotes the digital handling of these data, that can be used with user-friendly tools (such as Google Maps®) to show the relationships between land morphology and geology, in any place on Earth (examples of draping of geological maps in different geological settings can be observed here: https://sites.unimi.it/fberra/didattica-per-insegnanti-in-italiano/), stimulating the curiosity of students toward this fascinating science and the use of digital platforms.

# Tips for new educational experiences in the secondary school based on outdoor activities and 3D modeling of rocky outcrops equipped for climbing

Bollati I.M.*[1], Scandiuzzi C.[2], Tronti G.[1], Ticozzi N.[1], Apuani T.[1], Zucali M.[1] & Pelfini M.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Istituto Comprensivo «Carlo Fontana», Magenta (MI).

*Corresponding author e-mail:* irene.bollati@unimi.it

*Keywords:* geosciences teaching, multimedia, outdoor activities.

During the last years, the search for original approaches to teach scientific disciplines in secondary school is increasing. New strategies start from the already proven assumption that an active involvement of students in learning (i.e., learning by doing) is fundamental, as well as the need of linking the topic to be studied to activities carried out in the everyday-life (Orion, 1993). Moreover, the importance of improving the health and wellness of young generations is well declined in the European Educational Programmes (e.g., ERASMUS+ https://www.erasmusplus.it/) demanding for very active approaches, including outdoor activities. Nevertheless, in these last 2 years, school has undergone a revolutionary approach based inevitably only on digital approaches, from remote, and new plans have been developed by teachers for facing safely the sanitary emergency without renouncing to the educational programme. For about ten years the Earth Sciences Department "A. Desio" of the University of Milan has been involved in activities with schools, and in the specific case, a series of projects have been set to develop innovative educational tools. First the Gekologia Project (e.g., Bollati et al., 2018), and then the UNESCO IGCP 714-3GEO Project (https://en.unesco.org/international-geoscience-programme/projects/714), are examples of project addressed to empowerment of Earth Sciences teaching in secondary school of first level, combining outdoor activities with the use of multimedia products. A selection of rock cliffs equipped for climbing, and located in the Italian Alps, in meaningful geological and geomorphological settings, has been used for preparing and testing activities with schools. These activities have been supported by the use of multimedia videos of rock cliffs located all around the world freely available on YouTube web 2.0 platform, as well as, by the 3D models of rocky cliffs and rock samples realized by researchers and school students at the Earth Sciences Department "A. Desio" posted on the official YouTube channel (https://www.youtube.com/channel/UCvTQMcwmL-9LoiOBL5NIldA). We present some examples of activities at specific sites in the Ossola Valley (Italian Alps), thought for secondary schools on the base of the previous testing experiences, combining geoclimbing and geotrekking, with multimedia material (web-based video of rock cliffs and rocky sample), aimed at proposing, to school teachers, new tools to facilitate students in nicely discovering Earth Sciences.

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# Alternative ideas of the Italian students about the geoscience: a survey

Borghini A.*[1], Pieraccioni F.[1], Bastiani L.[2], Bonaccorsi E.[1] & Gioncada A.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Istituto di Fisiologia Clinica, CNR, Pisa.

*Corresponding author e-mail:* alessandra.borghini@phd.unipi.it

*Keywords:* education, alternative conceptions, survey.

Geology-related issues for our planet – seismic, volcanic, and hydrogeologic risks, climatic changes, and the need for mineral resources – are under the spotlight in Italy and worldwide. To constructively face them, knowledge of the planet and awareness of its problems are essential citizenship competencies, which should be accurately built and monitored during the whole school curriculum. However, in Italy there are several issues related, for example, to the absence of a standard curriculum or to the science teachers' formation, usually lacking an appropriate geological background. In this framework, it becomes useful monitoring the basic geoscience knowledge at the end of schooling, identifying the most common misconceptions. Misconceptions are alternative not-scientific ideas which may persist in students and adult citizens, undermining the comprehension of geology-related issues (Francek, 2013). Here we show the results of a survey carried out in the academic year 2020-21 at the University of Pisa, to 403 students enrolled in the first year of different bachelor courses. The survey used the screening tool IMES2 - Individuation of misconceptions in Earth Sciences 2. This is an implemented follow-up of the survey IMES, presented in Pieraccioni et al. (2019), addressing different geological concepts.

The results discover the presence of several alternative ideas regarding exogenous and endogenous processes (Borghini et al., 2022). For example, 46% of the sample answer that the center of the Earth is made up of liquid material; 55% of the students think that the Earth magnetic field is related to the gravitational one; 78% of students indicate that either the analysis of fossils or carbon dating are suitable methods to know the age of the Earth; 91% answer that clouds are composed by water vapor. Moreover, a close examination of the survey results indicates that the misconception strength (i.e., the proportion of students that choose the misconception reported in literature out of the total number of wrong answers) is not related to the item difficulty, namely, the proportion of students that give the correct answer (Sadler et al., 2009).

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# "When Antarctica was a garden" - A multimodality workshop involving science teachers

Corti V.*[1], Macario M.[2], Olmastroni S.[3], Palmeri R.[3], Sandroni S.[3] & Cornamusini G.[1]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] UNICAMearth group, Liceo Scientifico "N. Copernico", Prato. [3] Museo Nazionale dell'Antartide, Università di Siena.

*Corresponding author e-mail:* valecorti7@gmail.com

*Keywords:* STEM teaching, Inquiry Based Science Education (IBSE), Antarctica.

Through the years, the Museo Nazionale dell'Antartide (MNA) - Earth Science section of Siena, has promoted the dissemination of scientific research and environmental issues, considering the in-service training of teachers as one of the most important keys to spread scientific and environmental awareness among new generations (http://www.mna.it/spes/iniziative-miurmna). However, educational methods are progressively changing, becoming less transmissive and making more use of ICT in everyday school life. In particular, the inquiring approach, Inquiry Based Learning (Bybee et al., 2006; Pedaste et al., 2015) is strongly recommended for European education system (Rocard et al., 2007), as the most effective method to improve STEM disciplines. Our project aims to mix a new teaching/learning approach to science education and teacher training. With a blended course offered by MNA-Siena in the 2021 fall, part in presence and part in e-learning, a group of teachers from secondary school improved their knowledge about the geology of Antarctica and the respective record of data/informations concerning environmental and climate change occurred through the time. The workshop, tutored by researchers of MNA (1,3,4,5,6) and a mentor teacher (2), led participants through a case study based on the reconstruction of paleo-environmental conditions recovered in some sedimentary sequences of Antarctica, thanks to plant fossil remains (pollen, leaves and fossil trunks). During the 2014-15 Italian Antarctic PNRA expedition, researchers from the University of Siena discovered one of the biggest and well-preserved fossil forest in the area of Allan Hills, South Victoria Land. These fossils have been deeply studied to reconstruct the environmental conditions that occurred in Antarctica during the Permo-Triassic transition around 250 My (Cornamusini et al., 2020). The workshop was introduced as an inquiring case study, allowing participants to investigate the fossil remains to reconstruct both the syn- and post-depositional history of the site. The workshop included 3 sessions: in the first one each participant acquired basic knowledge about history and geology of Antarctica, having the opportunity to observe, describe and take note about fossil trunks during an in presence guided visit to the collections of the Museum. In the following two weeks, the teachers performed a self-placed lab activity on their own, consulting on-line material uploaded in Google Classroom. Moreover, they could work at extra labs on dating-methodology, sedimentary rocks or glaciology. After this period, each participant exposed his results during the last session and finally, one of the researchers (1) gave a presentation about the evidence carried out on the fossil trunks. Feedback from participants showed great appreciation for both scientific value and innovative methods used in the workshop, encouraging the MNA - Siena to follow up this kind of format for future training activities for science teachers.

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# Geology for Geography Program - From theory to practice: the teaching scientific collaboration between the "Goffredo Mameli" high school (Rome) and the regional Order of Geologists of Latium (Cambridge course IGCSE-0460)

De Caterini G.[1-5], Pasqua I.[2], Argentieri A.[3-4], Battisti C.[4], Beltramme O.[5], Bianchini G.[6], Bilotta A.M.*[7], Canali P.[8], Ceraudo S.[6], Conte G.[9] & Mingrone S.[2]

[1] Engeo Praxis s.r.l., Roma. [2] Liceo Goffredo Mameli, I.I.S. Tommaso Salvini, Roma. [3] Città metropolitana di Roma Capitale - Servizio 2 "Geologico, difesa del suolo, rischio idraulico e territoriale" - Dip. IV "Pianificazione, sviluppo e governo del territorio", Roma. [4] Città metropolitana di Roma Capitale - Servizio 3 "Aree protette e tutela della biodiversità" - Dip. III "Ambiente e tutela del territorio", Roma. [5] Graduate art historian and archaeologist. [6] Ordine dei Geologi del Lazio, Roma. [7] I.C. Via Santi Savarino, Roma. [8] Roma Servizi per la Mobilità s.r.l., Roma. [9] I.C. Virgilio Ardea II, Ardea (RM).

*Corresponding author e-mail:* a.bilotta@icviasantisavarino.edu.it

*Keywords:* high school course geography, geology lab.

The "Goffredo Mameli" classical high school offers its pupils a Cambridge course of study. This means that during the 5 years of study the pupils have the chance to study a few subjects in English according to the British standard of education. At the end of the 4th year they can take their GCSE exams just like all pupils in the UK do.

As part of the Geography course, pupils usually carry out an experimental field abroad for a week.

Due to the Covid 19 Pandemic, being unable to travel abroad, the school asked the regional Order of Geologists of Latium (OGL) a scientific didactic collaboration.

Professional orders do not usually have didactic purposes, however, one of their goals is the spreading of technical-scientific culture. The OGL has always collaborated with schools of all types and levels by promoting activities on the prevention of geological risk, in addition to this, it has recently established a special Commission, made up of professionals and university professors, to pursue the aim of disseminating the geological culture, at a time when the environmental policy of the whole world is dealing with global warming.

In our modern scientific context, subjects have split up into so numerous branches that the same specialists are sometimes no longer able to understand each other; the Geography course, due to its interdisciplinary connotation, offers the opportunity to pass specialization and to show the geological "world view", that interprets the Earth as a complex superorganism (Praturlon, 2011). It is a culture and point of view necessary to understand nature itself and to plan an harmonious future where the human being is in balance with the natural cycles of the Earth.

The course was developed with the collaboration of various professionals, through some lessons in class and three field trips which aimed to understand the interaction between man and the environment in three different contexts.

The first one was at the park of Villa Ada near the school. This park is a kind of urban garden which offered the opportunity to explore the following topics: wilderness, cartography, physical geography, biodiversity, in relation to the usability of the area in the context of sustainable mobility. It was possible to gain experience in the fields of the prevention of geological risks, e.g., the anthropogenic sink-holes caused by underground cavities.

The second one was at the Basilica of San Paolo Fuori le Mura, an ideal place to evaluate the evolution over time between the anthropic and natural environments starting from the Roman era.

The third one was at the Thyrrhenian seaside area, at the Natural Monument of the swamp of Torre Flavia (a protected area managed by the Metropolitan City of Rome Capital). There it was possible to deal with the topic of the pristine coastal environment and with the problems related to the conservation of nature.

Last but not least, the project also aimed to encourage pupils, after the long pandemic period of physical and psychological confinement, to regain confidence, as a group, with natural environment.

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# Geosciences in school-work alternation proposals: the projects of the Milan State University

Diolaiuti G.A.*[1], Maugeri M.[1], Pelfini M.[2], Lazzati A.[3], Traversa G.[1], Fugazza D.[1], Maragno D.[1], D'agata C.[1], Panizza M.[1] & Senese A.[1]

[1] Dipartimento di Scienze e Politiche Ambientali, Università di Milano. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Istituto Marcelline Tommaseo, Milano.

*Corresponding author e-mail:* guglielmina.diolaiuti@unimi.it

*Keywords:* school-work alternation, geoeducation, climate change.

The School-Work Alternation (SWA) is a teaching methodology that allows students attending upper secondary schools (vocational institutes, technical institutes, high schools) to carry out part of the training path in a company or institution, and together, a tool for combining theoretical classroom study (school preparation) with forms of practical learning carried out in a professional context (assisted experiences in the workplace). The SWA is a tool that allows students to acquire knowledge, skills and competences useful for the development of their professionalism.

Universities can propose School-Work Alternation projects to secondary schools as they fall within the so-called Third Mission that includes activities planned for the transfer to civil society of the results of research and studies conducted and contribute to the cultural growth of the territories where they are located. The proposed activities and projects must include not only a preliminary cultural training of the students but also practical technical activities in the laboratory (under the guidance of tutors and in semi-autonomy) and in the field that allow students to acquire advanced skills and knowledge. The proposed activities can also be useful for students to understand the scope of activities of the various professional figures with high school and university degrees and thus serve to complete the outgoing orientation carried out by the secondary school to which they belong.

The offer of the departments of Environmental Sciences and Policies and of Earth Sciences "A. Desio" of the State University of Milan (UNIMI) for the SWA took the form of projects of 50 hours each, carried out in the presence before the Covid-19 pandemic and remotely during the two years of pandemic restrictions, and aimed at students of classes 3, 4 and 5 of high schools and state and equal technical institutes of the Province of Milan.

The projects, although they are all consistent with each other in terms of objectives and expected results, have been declined in different ways according to the different schools that have adhered to these proposals and the cultural and professional interests of the students involved.

The common thread that unites all the proposed projects is the theme of climate change impacts and of possible mitigation and adaptation strategies. In fact, the two UNIMI departments have long been engaged in studies and research to quantify the intensity of climate change, describe and analyze its environmental and landscape impacts and propose mitigation and adaptation strategies.

In total 8 schools have joined the projects, both public and private, and the total number of students involved is about 250. This contribution illustrates the didactic results obtained from the academic year 2018/2019 and the students' satisfaction with the proposed activities.

# Sedimentary TourInStone: a journey through Italy's sedimentary heritage stones in Turin (Piedmont, Italy)

Franco F.*, Lozar F., D'Atri A. & Borghi A.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* federico.franco523@edu.unito.it

*Keywords:* geosciences education, hands on learning, emotional engagement.

TourInStone is both an app and an open-air activity developed within the "Piano Lauree Scientifiche", a project from MIUR (Italy's Ministry of Education).

The activity is based on the various ornamental stones used in the town of Turin, with the aim to teach students how to describe and classify different rocks. Previous activities dealt with all three rock categories, but here we propose a specific itinerary about sedimentary rocks as seen in the centre of Turin.

In the city centre ornamental stones from all over Italy were used for most of the buildings, the majority coming from the Piedmont region and from the Alps; as such they are mostly igneous or metamorphic, with a few sedimentary exceptions that are endurable enough to be used as ornamental stones. However, most sedimentary rocks are from other Italian regions (Lombardy, Veneto, Liguria, Puglia and Lazio).

The fieldtrip is designed to introduce students to scientific rock observation and classification. The urban setting is more stimulating than a classroom and allows a deeper emotional engagement of the students; it helps connecting with them, who often walk past ornamental stones without "seeing" them and, last but not least, it's easier and cheaper to organise for the schools in Turin.

The itinerary is organised so that different categories of sedimentary rocks can be observed following a common compositional and genetic logical thread.

It starts with orthochemical rocks, then it moves on to terrigenous rocks and terminates with allochemical rocks that contain a variety of fossils.

The activity has the goal to help students understand the varied environments these rocks were formed in both continental and marine rocks are present, and the fossils they contain can help identify different depositional ages and settings, such as water depth and carbonate saturation; a peculiar example is the Ammonitico Rosso, that presents interesting information about its deposition between the aragonite and calcite compensation depths.

Other fossiliferous rocks can help introducing geological time to the students, based on the age of their contained fossils: Jurassic, Cretaceous, Miocene and even relatively recent examples such as Pleistocene.

Rocks observation also helps to introduce the notion of sustainable use of ornamental stones, to show that a correct use of these resources can prevent them from being overexploited, and to avoid the common misconception that they are virtually unlimited.

Interdisciplinarity is a very important part of this activity, as notions about sedimentary rocks can be combined with concepts of physics, chemistry, architecture, technology, history and geography. This allows the activity to be customised for different groups of students and schools.

This activity will be proposed for the first time in the 2022/2023 school year, and it will be evaluated and validated through surveys to both teachers and students, in order to identify possible pitfalls and future improvements.

# Two approaches of Teaching Innovation in Mineralogy in Genova (Italy)

Galliano Y.*[1], Boero M.[2], Garbati P.[2], Romeo F.[2], Torella G.[3], Vercelli V.[2] & Cabella R.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Liceo Scientifico e Liceo Economico Sociale «L. Lanfranconi», Genova. [3] Liceo Statale Classico, Scientifico e Sportivo «M.L. King», Genova.

*Corresponding author e-mail:* yury.galliano@gmail.com

*Keywords:* mineralogy, blended-learning, education.

In traditional geoscience education, learning activities include lectures by teachers, assigned textbook reading, laboratory exercises, and classroom discussion. Geoscience teaching methods commonly use maps, diagrams, and photographs as the primary learning media to illustrate geological concepts.

Senior students and professors from the Courses in Geological Science of University of Genoa took part in teaching and laboratory activities in two high schools located in the City of Genoa (Liguria, Italy). The tutoring sessions were aimed to introduce the students to basic mineralogical and geological concepts. Through the use of several innovative teaching methods, that combined online and in-person interactions, we sought to support the development of the core geoscientific skills necessary to recognise a variety of minerals and their associations. The proposed practical activities enabled the students to get accustomed to the identification of mineral samples through the description of their physical properties and crystal morphologies, and to classify rock samples by means of several diagrams. To guide them through their work, we provided them with flow charts describing how to properly carry out the respective determinations.

At the first school that took part in the collaboration, a *Test-Teach-Test approach* (*TTT*) was used. The students were asked to complete a test at the beginning of each face-to-face lecture and laboratory activity, even if they lacked the background information to carry it out correctly. The questions included in the test allowed them to focus on the key-points of the forthcoming activity. At the end of the sessions, they were asked to go through the same test once more. The comparison of the test results allowed the tutors to assess students' learning and performance.

In the second school, a *Blended Learning* approach and the *World Café* method were adopted. *Blended* (or *Hybrid*) *Learning* consists in the integration of laboratory activities with propedeutic online lectures (Stacey & Gerbic, 2009), and has become a matter of growing importance after the outbreak of Covid-19. The *World Café* method is a simple, effective, and flexible format for hosting small to large group dialogue. It is a creative process for sharing knowledge and creating possibilities for action in groups, while mantaining high engagement through a student-centred approach.

With this methodology we hope to inspire others to take part in geoscience teaching projects, to increase awareness of Earth related topics in high school students and provide them with insights into environmental and sustainability issues.

Stacey E. & Gerbic P. (2009) - Introduction to blended learning practices. In: Stacey E. & Gerbic P. Eds., Effective Blended Learning Practices: Evidence-Based Perspectives in ICT-Facilitated Education, 1-19, IGI Global, Hershey.

# "A Network of Schools for Sustainable Development". The Role of Education in Mitigating Plastic Pollution

Gastaldi M.*, Beccaceci A. & Paris E.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* marco.gastaldi@unicam.it

*Keywords:* STEAM, sustainability, plastic.

In STEAM disciplines (Science, Technology, Engineering, Arts, Mathematics), operational teaching methodologies such as PBL (problem-based learning), peer education, IBSE (Inquiry Based Science Education), combined with open-air learning scenarios, are universally recognized as useful tools to improve the scientific skills of students of all ages. Methods such as learning by discovery and learning by doing, used for teaching paths developed through authentic tasks, are the ideal means to introduce Environmental Sustainability and Agenda 2030 issues. In this project, we decided to use this approach to address the production of waste related to human activities, with a particular focus on plastic waste, which pollutes ocean and land, also contaminating the food chain.

Before proposing the study activities, we administered structured questionnaires to assess the knowledge possessed by 7$^{th}$ grade students of 4 Italian schools about sustainable development, the 4 Rs (reduce, reuse, repair, recycle) and the environmental impact caused by waste in terms of water and $CO_2$ foot-prints. The obtained data represented the baseline acquired through traditional transmissive/theoretical teaching.

Subsequently, we proposed some activities such as: i) webinars, ii) classroom workshops, iii) outdoor learning scenarios. All the activities were interconnected.

In one study group (six 7$^{th}$ grade), we proposed a webinar activity and classroom labs performed by the students (quantification and characterization of the plastic produced by a family of 4 and bio-plastics production).

In another group of the same grade we added an activity of "outdoor learning" carried out on the beach, not a simple "Clean-Up" and "Active Citizenship" initiative, but a real educational activity through a session of collection and analysis of collected sediments, sampling and recognition of various plastic types, based on particle diameter, shape, color, water-relative density. During these activities, therefore, the students observed the different mineral components of the beach sands, and for the plastic fragments found by the students (micro- and meso-plastic), we used the same sampling and classification procedures used in sedimentology for the "natural" particles. We were able to concretely ("hands on") introduce the concept of Anthropocene, to discuss the impact of human activity on the coastal areas and the formation of the "plastic-glomerate rocks" (agglomerates of plastic and mineral particles, too often present in modern beaches). Finally, post-activity questionnaires were administered. We observed, compared to the starting questionnaire, a significant increase in the knowledge about Sustainable Development topics, a greater awareness of the central role that individual citizens play in terms of reducing consumption and waste production, and an optimistic vision for future change.

# T-Learning for geosciences education: a proposal for a sustainable pedagogy

Gerbaudo A.*[1], Tonon M.[1] & Caretto A.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Formazione Primaria, Università di Torino.

*Corresponding author e-mail:* andrea.gerbaudo@unito.it

*Keywords:* geoethics, transformative learning, education for sustainability.

This is a response to Peppoloni & Di Capua's (2021) "Geoethics to start up a Pedagogical and Political path towards Future Sustainable Societies", in which the authors declare that the development of geoethics is at a turning point: the geoethical principles and values must be embodied into a pedagogical project that has to be inclusive, participatory, proactive; it has to be inspired by principles of dignity, freedom and responsibility. As researchers and teachers' trainers, we share the same feeling of an urgent need of renovation in pedagogical practices; in times of ecological crisis, we also agree that these practices must be founded on a set of values that enhances an ethical regeneration of human beings and are consistent with the sustainable development goals.

In this presentation, moving from the call-for-engagement made by Peppoloni & Di Capua, we point out the T-Learning methodologies (where "T" stands for *transformative*, *transgressive* and *transdisciplinary*) as valuable tools to connect science education with the broader concept of Education for Sustainability (Sterling, 2011). After a brief introduction, necessary to give some definitions about T-learning, we focus in particular on art-based methodologies. In accordance to Shelley Sacks' definition of *aesthetics* (Beuys & Sacks, 2004) as the opposite of *an-aesthetic*, a creative approach implies an overcoming of insensitivity and pushes people to responsibility, one of the fundamental principles of geoethics (Marone & Bohle, 2020): art thus is suitable for building a new pedagogical path for geosciences education that is inclusive, participatory, proactive, but also transformative, transgressive and transdisciplinary.

Finally, as an example of educational programs designed with T-learning methods, we describe two workshops that were held as part of an Earth Sciences didactics course for future teachers, in which participants worked with clay and gypsum using an artistic approach.

Beuys J. & Sacks S. (2004) - What is Art? Conversation with Joseph Beuys. Clairview Books, Forest Row, UK.

Marone E. & Bohle M. (2020) - Geoethics for Nudging Human Practices in Times of Pandemics. Sustainability, 12(18), 7271. https://doi.org/10.3390/su12187271.

Peppoloni S. & Di Capua G. (2021) - Geoethics to Start Up a Pedagogical and Political Path towards Future Sustainable Societies. Sustainability, 13(18), 10024. https://doi.org/10.3390/su131810024.

Sterling S. (2011) - Transformative Learning and Sustainability: sketching the conceptual ground. Learn. Teach. High. Educ., 5, 17-33.

# Technominerals, technology under the microscope: design of lectures straddling science and social awareness in the context of secondary school classes

Giai M.*

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* matteo.giai@live.it

*Keywords:* technology, minerals, school content.

What is graphite used for? What is a smartphone made of? What impact does a mine have on the environment and how can this be remedied? But above all: what do minerals have to do with technology?

These are the questions that have been tried to answer, through some lectures dedicated to the classes of the secondary school. In these meetings we have brought palatable topics to the kids, but above all that they were topical and with an ultimate important goal: to convey a greater awareness of what surrounds us and our impact on it, and perhaps provide some points of reflection on the world and on the geopolitical situation of some countries.

This was possible through a presentation by means of PowerPoint, accompanied by some practical experiments and observation of mineral samples in first person, in order to stimulate the touch, the vision and latent knowledge of the students to whom the project was addressed.

With a first brief introduction to the concepts of geology, mineral and georesource, there are two large "families", completely fictitious, of minerals that can be used today: the minerals called "domestic" and the "technological" minerals. At this point we went to analyze some of these mineral species (e.g., talc, graphite, zeolites, gold, REE, etc.) and their uses in everyday life, also presenting some "unusual" uses that not everyone knows. After these more "academic" moments, questions were directed to the listeners, both teachers and students, in order to verify and stimulate their previous and latent knowledge. At the end of this list of minerals were projected some global production data for some of these mineral raw materials.

The second part of the presentation focused on the issues that concern the extraction of these raw materials, which not only lead to environmental damage, but also to the population. And at this juncture we analyzed some aspects little treated as those of "Conflict minerals" and current geopolitical crises (e.g., Afghanistan). Finally, he recalled the approach of the 2030 Agenda and its social and economic objectives, which were proposed globally and how in their small way even the young people involved in the presentation can contribute, through a greater awareness of the world and the concepts of sustainable development. This is to lead not to the creation of a new generation of ecologists, but subjects sensitive to environmental issues and with a greater ability to understand and reason for the political, social and economic phenomena affecting our planet.

At the end of the lesson some molecular models of the mineral species presented during the lesson were presented; to these was proposed an experiment of an electric circuit and some graphite samples, copper, magnetite and graphene to check the degree of conductivity of materials. As an extra material, some samples of fluorescent minerals (e.g., ruby, strontianite, autinite, metatorbernite) were shown, both as an application of some fluorescence physics concepts and as a spectacular artistic effect, much appreciated by the kids.

For about eight years, the Sën Gian Cultural Association has been operating in the territory of Val Pellice in order to promote and transmit the culture, traditions and scientific knowledge that characterize this small but varied territory. Within the numerous events that it presents every year, there is also "MINERALUSERNA", now in its 6$^{th}$ edition, as a mineralogical exhibition focused on the exchange not only of samples of minerals, but also of knowledge and curiosity. And it is here that the project of TECHNOMINERALS is located, as an extension of the MineraLuserna event: born from the idea of bringing academic knowledge in the field of chemistry, mineralogy and petrography even to a less experienced and younger audience than a university student, led to the idea of proposing simple, captivating and fun lessons to children and teenagers in the territory of Val Pellice, assisted by a group of former teachers of the Polytechnic of Turin and students of the Department of Geological Sciences of Turin. This project, later referred to as «MineraLuserna enters schools!» has been going on for four years now and with enthusiasm the schools of the whole Pellice Valley, of the district and from this year also of the *Pinerolese* have joined the initiative, also leading to an update of the staff of teachers and the contents to be proposed, with a continuous renewal of ideas and educational proposals.

# Geology and the city: how to introduce Geosciences to high school pupils

Lozar F.*, Palomba M., Storta E., Borghi A., Stella I. & Franco F.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* francesca.lozar@unito.it

*Keywords:* geoscience education, high schools, Alpine evolution.

The project Piano Lauree Scientifiche of the Italian Ministry for Education (MUR) has involved University and high school pupils and teachers in the last 6 years with the aim of introducing, among other STEM, Earth Science (ES) knowledge to the young generations.

The University of Turin has designed several outdoor activities promoting basic ES principles through hands on activities; among them, a very successful initiative is based on rock observation, classification and interpretation and develops in the city center.

The inspiration arised from the app Tourinstone, published by the DST the first time in 2014, that promotes a self-guided geological tour of Turin through the discovery of its ornamental stones. A further use of the app is to disclose the Alpine arc evolution through the main lithotypes used in the monumental city.

We organized the lab for the high schools as an open air lab, where the students were asked to observe, describe and classify the ornamental stones in the iconic piazza San Carlo and surroundings, as they were in a real fieldtrip studying the outcrops. The final outcome of the lab was to understand the geological origin of the observed lithotypes. During the "field work", they were supervised by university students and professors. Moreover, the lab was integrated at school and in the field with interdisciplinary activities in Architecture or Sustainability.

In order to analyse the efficacy of the lab we proposed both teachers and pupils with a questionnaire before and after the field experience. The aim of the pupil's questionnaire was to test: which basic geoscience knowledge the students had before the experience; if this had improved after the lab, pupil's awareness of the geosciences importance in our everyday life. The teacher's questionnaire provided insights on the lab efficacy to improve the geological curriculum in schools.

We led pupils from three schools in the lab, involving about 250 pupils and their teachers.

The results of questionnaire analysis suggests that the open air activity positively improved the disciplinary knowledge of the pupils, allowing the correct identification of rock components and the classification in the three main rock categories. As for the soft skills, we assessed that the pupils recognized the importance of the geosciences in everyday life, showed high interest in the subject, were happy with the experience and in some cases felt able to lead their peer in the same discovery of Turin ornamental stones as "hidden" information of their city. As for the teachers, indipendently from the didactical period in which the activity was realized, most of them would replicate the experience with future pupils, mostly only lead by experts, but also on their own.

# Earth Sciences teaching experience with high-school students. Case studies from PLS activities

Lustrino M.*

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* michele.lustrino@uniroma1.it

*Keywords:* Earth Sciences, teaching, high-school.

Earth Sciences disciplines are commonly taken into poor consideration in high-school didactic programs because much of the teachers of scientific disciplines have a biological background, with only basic knowledge in geological fields. The Dipartimento di Scienze della Terra of Sapienza University of Rome participates since 2004 to the PLS (Piano Lauree Scientifiche) project of the Italian Ministry of University, collaborating with many tens of high schools. It has served as a boost to increase the number of students enrolled in Geological Sciences Bachelor, which was losing attraction year by year. The aim of the participation to the project is to improve the recognition of the role of geologists in the economy, sustainability and social activities in general, including evaluation of natural risks, assessment of energy resources and mitigation of temperature increase with $CO_2$ geological neutralization and storage.

During the end of 2021, a network including 20 high-schools of Rome and neighbouring districts was defined, aiming to organize a series of seminars and laboratories for IV and V year students. A continuous exchange of ideas was bounced back several time among the teachers and the author to define the arguments of the seminars. During January-February 2022, sixteen seminars (mostly in remote), and four laboratories (all in presence), were held, involving more than 500 students. The arguments treated span wide disciplines, not strictly restricted to geological arguments and include: 1) plate tectonics; 2) magma generation; 3) Earth's origin; 4) geodynamic evolution of Italy; 5) volcanoes; 6) mineral luminescence; 7) radioactivity and radiation; 8) energetic transition. A Google drive folder was created to allow teachers to download in advance the pdf copies of the pptx files presented to the students.

The seminars and laboratory activities lasted from one to two hours, anticipated and followed by a test with 15 questions, each with four answers. A final discussion of the results followed the compilation of the test. Two points were assigned for right answers, zero points to no answers and minus one point to wrong answers.

The results of 471 tests indicate an average pre-seminar score of 8 (over a range of -15 to +30) and an average post-seminar score of 22, with an average increase of 14 points, corresponding to 31% considering 45 points of maximum increase. The standard deviation is between 8 and 9 points for the pre- and post-seminar scores and for the average increase. The main results of this study indicate: 1) the necessity to increase the cooperation with teachers in choosing the arguments of the seminars; 2) the importance to allow teachers to improve their formation, allowing them to consult in advance the didactic material; 3) the utility for the students to check their preparation to specific questions by evaluating the pre- and post-seminar scores; 4) to organize laboratory and hands-on activities.

# "Reading" the rock record: what rocks can tell us of the evolution of our planet – an orientation activity for high school students

Meneghini F.*, Frassi C., Di Rosa M. & Sanità E.

Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* francesca.meneghini@unipi.it

*Keywords:* student orientation, PCTO, geology for high school.

In the frame of the program "Percorsi per le Competenze Trasversali e l'Orientamento" (PCTO, i.e., young apprenticeship and work-related learning programmes), we have proposed a multidisciplinary project to a 3rd year class of the Liceo Scientifico "Ulisse Dini" of Pisa aimed at introducing the students to geological field mapping, and to the study of rocks and their structure at different scales of observations to reconstruct the evolution of an area in the context of plate tectonics.

We started the activity with 2 seminars of 1 h each to introduce the students to the petrogenesis of rocks, rock classification and their main textural characteristics, with special attention to sedimentary rocks. We also introduced the theory of plate tectonics and the process of mountain building, and we focused on the geological setting of the Northern Apennines and the stratigraphic sequence of the metamorphic Tuscan Units exposed on the Monti Pisani, 10 km NE of the town of Pisa.

The next planned activity has been an excursion with the students to the Monte Verruca (Monti Pisani), where extensive outcrops of the continental sequence of the Verrucano *s.l.* are found, with well exposed contacts with the Variscan basement. During the field activity, we introduced the students to the basic of field-scale description of rocks and deformation structures, depositional environment and its meaning, geological mapping and description of geometrical relationships between different rock types.

Back to the Earth Science Department the students visited the Thin Section Laboratory where we showed how to make a thin section from a rock sample. Then, we moved in the Microscopy Lab where the students familiarized with the optical microscope for petrography and how it can be used to describe the petrographic characteristics of rocks and minerals. Finally, we provided to students several thin sections representative of the rocks they saw in the field and we let they make a simple description.

The PCTO activity will be concluded with a final report in the form of a Power Point presentation that the students will prepare in groups back in the class, and that we will evaluate together with their schoolteacher.

# An educational approach to the learn about Construction and Demolition Waste

Messere M.*[1] & Volpintesta F. [2]

[1] ITET «G. Salvemini», Molfetta (BA). [2] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* profmessere@gmail.com

*Keywords:* Construction Demolition Waste, virtual world, sustainability.

The overexploitation of georesources in the construction sector raises important aspects of recycling and reuse in a virtuous process of circular economy (López Ruiz et al., 2020; Zhang et al., 2022). This issue is of great interest in the course of studies dealing with construction technology and the environment.

This work involved students in a second class from the Technical, Economic and Technological Institute of Molfetta (Bari - Italy), specialization in Construction Environment and Territory, in collaboration with the Geology division of University of Camerino, Italy.

The main purpose of the project was to bring students closer to the issues of reuse and recycling of CDW (construction and demolition waste).

The first phase of the project, carried out following the typical steps of the IBL methodology (inquiry-based learning), included an input activity (viewing a documentary on CDWs) and the identification of the issues on which to investigate, deepening the knowledge of some topics through an online meeting with an expert. The expert explained to them in particular: what CDWs are and why they are important, how CDWs are produced and treated, the European and Italian framework on CDW management, bureaucratic issues and the possibilities for recycling CDWs.

The pupils then, distributed in four groups, studied a topic of their choice including the situation of quarries and mines in Italy, statistical analysis on the situation of the CDW and related collection centers in Italy, the recovery of CDWs, the disposal of asbestos. The results of the research work were documented in infographics created with a specific app (Canva).

In the second phase of the project, with a gamification approach, the students created an "escape room" designed and built in a web-based virtual world, Mozilla Hubs, also accessible with virtual reality viewers and smartphones as well as from PC. Students created customized scenarios, enriched with previously created educational content, sources of their research and online quizzes, to be solved by visitors to leave the room.

The activity presented constitutes an example of how, in an attractive and at the same time educational form, digital skills and contents on building sustainability can be transmitted to young people who in the future will be expert professionals in the construction of greener buildings.

López Ruiz L.A., Roca Ramón X. & Gassó Domingo S. (2020) - The circular economy in the construction and demolition waste sector – A review and an integrative model approach. J. Clean. Prod., 248, 119238.

Zhang C., Hu M., Di Maio F., Sprecher B., Yang X. & Tukker A. (2022) - An overview of the waste hierarchy framework for analyzing the circularity in construction and demolition waste management in Europe. Sci. Total Environ., 803, 149892.

# VULCANOPOLY: playing towards a better future

Misiti V.*, Riposati D., Di Laura F., Battelli P. & Crescimbene M.

INGV, Roma.

*Corresponding author e-mail:* valeria.misiti@ingv.it

*Keywords:* geoscience, games, students.

The goal of scientific dissemination is to reach all levels of age and social origin of the population, simplifying scientific concepts and making them appealing to the general public.

A common and understandable language has always been the visual one, for this reason many authors use images as a tool to convey scientific notions and discoveries. From its origins, science has placed images at the center of its communication processes: drawings, diagrams and then, subsequently to scientific discoveries, photographs, films up to satellite images.

In this framework, we emphasize the importance of playful-didactic activity and visual language to facilitate learning and, in particular the development of scientific games.

Our working group has been collaborating for years in the organization of dissemination events with the aim of increasing knowledge on the major geological issues for the protection of the planet.

In this context it is important to highlight the role of scientific dissemination and the different methodologies to be used.

One of the most used and appreciated tools has been the creation of scientific-didactic games: to simplify concepts, the game has in fact proved to be a fundamental tool.

We present VULCANOPOLI, inserted in a series of science games that started with MAREOPOLI and inspired by Hasbro's famous MONOPOLY. The main topic is volcanoes, both from a scientific and a historical point of view. Thanks to this game the historical evolution of some of the most important Italian Volcanoes can be reconstructed.

The rules are those of the original game with some additional questions and concepts to remember, to conquer cities and accumulate points.

The VULCANOPOLY game-board consists of thirty-six spaces containing twenty-one villages and cities on three main italian active volcanoes (Mount Vesuvius, Mount Etna and Stromboli Island) and one quiescent volcano (Colli Albani Volcanic District), four Chance spaces and four Community Chest spaces, a hot water baths space, a geothermal energy space, an underpass space, and the four corner squares: GO, Viewpoint, Magma Chamber and Connecting way.

A deck of thirty-two Chance and Community Chest cards (sixteen each) which players draw when they land on the corresponding squares of the track, and follow the instructions and myths, legends and folklore tales based on real events printed on them.

# Energy and carbon footprint. An education approach for middle school students

Occhioni M.*[1], Di Palma R.[2] & Paris E.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Istituto Comprensivo Nettuno 1, Nettuno (RM).

*Corresponding author e-mail:* michelina.occhioni@unicam.it

*Keywords:* energy, georesources, opensimulator.

A didactic activity was created to be carried on the Opensimulator-based virtual world Techland (Occhioni & Paris, 2021), in a new island focused on sustainability, Ecocity. The aim of this activity was to draw the students' attention to the environmental impact of technology and energy. To approach these themes, the activity introduces the students to the concept of carbon footprint, applied to the production and application of new technologies, spanning from common electronic devices to apparats for renewable energies production.

The activity investigates, for example, the impact of smartphones, both in terms of georesources exploitation and carbon footprint, focusing on the role of rare earth elements in technology. After evaluating their domestic carbon footprint, in term of electricity consumption, the students studied also the impact of renewable energy technology, such as solar panels and horizontal wind turbines on buildings, electric/solar chargers for electric vehicles and so on.

In addition, as part of the course of Civic and Environmental Education, particular emphasis was given to the behaviors that the students should adopt to reduce their personal carbon footprint, such as the use of public transport, domestic savings and responsible purchases.

The activity was carried out with K8 students of the Istituto Comprensivo Nettuno 1, Nettuno (RM). They connected to the Virtual World (VW) as avatars, from their classroom during the school time. While the researcher was online, their teacher, in presence, supported them during their activity, evaluating also the reaction of the students to the new activity and the level of attention during the project hours. The 4-months project (from December 2021 to March 2022), implied meetings twice a month, for a total of about 30 hours.

At the beginning of the activity, students learned how to master movements and communication and get acquainted with the main tools interact/import/build resources in the VW. Then, after choosing the topics for the project, the pupils searched, found and organized information, creating also 3D objects to explain what they learned. The Inquiry-based learning methodology was used, letting students to find answers to driving meaningful questions and discussing together problems and solutions.

Using screen casting, they realized videos to explain all they have done. At the end of the activity their artefacts (3D objects, videos and multimedia presentations) and information have been evaluated in terms of correctness, clarity and originality. The quality of the work and the contents produced revealed a high level of involvement and concentration.

A more general evaluation of the activity was based on questionnaires, demonstrating that students judged positively their experience, improving the use of ICT, and increasing their awareness towards the need of an energy transition to a more sustainable way.

Occhioni M. & Paris E. (2021) - Techland, New Educational Paths Focused on Energy Resources and Sustainability Using Virtual Worlds. In: Panconesi G. & Guida M. Eds., Handbook of Research on Teaching with Virtual Environments and AI, 316-340. IGI GLOBAL.

# The Data Mining Test: an unexpectedly effective tool to promote and recognize soft and hard skills in Earth sciences

Occhipinti S.*

Associazione Nazionale Insegnanti di Scienze Naturali, Aosta.

*Corresponding author e-mail:* susocchip@gmail.com

*Keywords:* data mining test, soft skills.

The purpose of this research is to present the results of a process that has been developed in recent years, as a consequence to the need to use new educational tools imposed by the pandemic.

My personal experience in the teaching- learning process and in the outreach field, with the aim to raise awareness towards Earth sciences prompted me to develop, in particular, easy-to-use, hands-on tools, as they allowed to develop skills "different" from those that students acquired through the use of new technologies.

Manipulation, observation, analysis, reasoning, abstraction, typical steps of a problem solving process, have been developed through the creation of models to be built, touched, verified, with which to simulate phenomena through non-Galilean paths, as they are not repeatable, not reproducible as volcanoes, landslides, earthquakes, meteorological phenomena, climatic variations and related consequences.

Over time, different paths have been tested with overall positive results, always with investigative and problem solving approaches, but using digital tools. Paper and digital maps were compared, as well as the observation on site with aerial photos, finally landslides were studied with the use of all available online resources, but always integrating hands on tools.

The need to use "distance learning", because of the lockdown imposed by the pandemic, has required experimenting with new tools. Moreover, the web offers almost infinite resources, data, maps, cards, virtual 2 and 3D models.

This research, born on the occasion of the national and international Olympiads of Earth sciences, which required to carry out tests using online resources, continued trying to develop a test model, which required students to extract data, then to carry out a Data Mining Test, in compliance with already formalized international standards already applied in particular in ICT and engineering (IFN), while it was not possible to find bibliography in the Earth sciences field.

The aim of the research is to develop models easy to be implemented, which could use digital data of simple and open accessibility, easily analyzed by students, of varying complexity for the different levels of school, but that would prove to be effective tool for recognizing students' skills.

In consideration of the type of test, which already provides data, no knowledge is required, while hard and soft skills are required, recognized and certified.

The student is required to be able to recognize and build relationships, but also to identify useful data and distinguish them from redundant ones, connect the causes of phenomena with their effects, identify significant variables, solve problems, as well as know how to communicate effectively, respect deadlines and even know how work as a team.

Experimentation is underway, but the first data are proving interesting and effective results.

# Learning the Earth Sciences: implementing 3D models in distance education

Pasero F.*, Nerone S., Storta E., Brotto G., Borghi A., Carosi R., d'Atri A., Ferrando S., Groppo C., Iaccarino S., Lozar F., Montomoli C. & Natalicchio M.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* federico.pasero@edu.unito.it

*Keywords:* digital learning, photogrammetry, 3D samples.

As modern digital technology offers many new possibilities, educational methods need to take full advantage. The last two years, affected by the pandemic, required teachers and students to explore new ways of learning. Earth Science education is mostly based on practicals, both in the field and in labs and, as such, has been deeply affected by the restrictions. When in-person activities are limited, three-dimensional (3D) modelling offers incredible educational opportunities, because the obtained realistic objects can support distance learning. In this framework, students and research fellows of the Department of Earth Science of the University of Turin, Italy, started from scratch a project to create 3D models of fossil and rock samples belonging to the didactic collections of the Department. The student contribution was crucial to better understand the most suitable communication tools to reach younger generations. Photogrammetry is at the base of this project, requiring the production of high-resolution photographs of the subjects in sequential rotating order, in at least three different orientations. This ensures that every single spot of the object is recorded in at least three different photos. A 3D imaging software with a photogrammetry specific algorithm has then been employed, and a 3D model was built in 3 steps: point cloud, polygon framework (mesh) and final texture. This process leads to the completion of the virtual 3D model which is then stored in a digital 3D viewing platform (Sketchfab.com) and is ready to be used by students and teachers. The repository currently consists of more than 500 models, including magmatic, metamorphic and sedimentary rocks, as well as fossils, and is freely available on the University of Turin Sketchfab account (/DstUniTo). The 3D models are now extensively used during online lessons, enhancing both teaching and learning experience thanks to the interactive visualization. Also in-person classrooms could benefit from this tool. The main advantages for all school grades are the possibility to access the collection from anywhere and to provide detailed descriptions of all the sample features which can simplify student understanding of Earth Sciences. Depending on the purpose, it can be used as a detailed archive of the Department extensive collections, or as a showcase for curious students. Although hands-on activities are still necessary for a complete understanding of every aspect of geosciences, the integration of traditional teaching methods with modern digital techniques can help students in their learning processes.

# Teacher training and *geoeducation* in Italy: some preliminary remarks

Pelfini M.*[1], Parravicini P.[1], Bonaccorsi E.[2], Cifelli F.[3], Gioncada A.[2], Lupi C.[4] & Paris E.[5]

[1] Dipartimento di Scienze della Terra «A. Desio», Università di Milano. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [5] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* manuela.pelfini@unimi.it

*Keywords:* teacher training, geoeducation.

The latest reform relating to the training of the Italian secondary school teachers provides for the acquisition of 24 academic credits (ECTS) in the anthropo-psycho-pedagogical disciplines and disciplinary didactics. These are compulsory in order to participate in for access to teaching in the every competition classes.

The required 24 ECTS can be obtained in at least 3 of the 4 discipline fields envisaged. The Italian universities have organized useful training courses to obtain the ECTS necessary to participate in the teacher's recruitment phase (PF24).

Among the foreseen teachings there are those of disciplinary didactics and, among these, didactics of the Earth sciences (Pelfini et al., 2019). The content of this teaching was shared among many Italian universities.

In view of the upcoming law changes, we analysed the participation data in the "PF24" courses held in some universities and in particular we analysed the choices made by the participants for what concern disciplinary teaching (4$^{th}$ domain) and in particular Earth Sciences Education courses.

The results collected were discussed considering, among other things, that to be qualified for teaching in class A 50, 12 ECTS must be acquired in the geological disciplines, while for those who qualified for teaching in class A28 they must obtain 6 ECTS in Earth Sciences.

Pelfini M., Parravicini P., Fumagalli P., Graff A., Grieco G., Merlini M., Porta M., Trombino L. & Zucali M. (2019) - New methodologies and technologies in Earth Sciences education: Opportunities and criticisms for future teachers. Rend. Online Soc. Geol. Ital., 49, 4-10.

# A board game meets an App… this is *GeoRisk*!

Piangiamore G.L.*[1], Maraffi S.[2] & Sacerdoti F.M.[3]

[1] INGV, Lerici (SP). [2] Ministero dell'Istruzione, Roma. [3] Università di Napoli "Federico II».

*Corresponding author e-mail:* giovanna.piangiamore@ingv.it

*Keywords:* app, Computer Supported Collaborative Learning Education, natural risk reduction.

*GeoRisk* is a *gamy-learning* experimentation to raise awareness on disaster reduction and risk education enforcing the ability to foster hazards before the occur of extreme events as an amusing way for the last two years of primary school. Our educational tool is within an engagement initiative to ensure effective dissemination and communication and raise public awareness and natural hazard understanding to instill a culture of safety and promote best practice.

A network of schools is involved in our *GeoRisk* research program of *interactive learning* to improve knowledge in Earth Environmental Emergency and Safe Behaviors and we have experienced a Computer Supported Collaborative Learning Education, also testing the efficacy of the *Risk Detective* (Seismic and Hydrogeological Risk paths) table game for class (https://riskdetective.wordpress.com; Piangiamore, 2019) by the *App Save Yourself* (Volcanic, Seismic and the new Hydrogeological Emergencies) (Maraffi & Sacerdoti, 2018a; 2018b). The gaming experiences also accompanies innovation in authentic assessment. Furthermore, we aim to educate to a correct use of technology which can constitute a valid tool of conscious communication for the new generations. Our gamification logic is focused on competition, virtual goods, real-time feedback, storytelling, points, rankings, levels, etc… aiming to develop *emotional intelligence* and *soft skills* and our *on-going*research is developing the modern GeoRisk *gamy-learning* tool enclosing in itself all three types of educational game:

- *Teaching games* (to teach something through the game: the tools are not shown, but discovered by passing tests, solving puzzles, etc... which need an ever deeper understanding of the subject matter);
- *Meaningful games* (to pass a meaningful message to promote change);
- *Purposeful games* (to develop a game path that has some outcome in the real world).

In a few words, a real game path that proposes something not "just for fun", but a game thinking with an environmental educational purpose to sensitize players on the issues of prevention of natural disasters.

Maraffi S. & Sacerdoti F.M. (2018a) - Learning on Gaming. Innovative Teaching with the use of Smartphones and Digital Storytelling. Edizioni Accademiche Italiane.

Maraffi S. & Sacerdoti F.M. (2018b) - The App Save Yourself improves knowledge in earth environmental emergency and safe behaviors. 6th Mediterranean Interdisciplinary Forum on Social Sciences and Humanities, MIFS 2018, Proceedings, 1-5. https://doi.org/10.19044/esj.2018.c5p1.

Piangiamore G.L. (2019) - Metodologie didattiche innovative di educazione dei rischi naturali nei progetti per le scuole del territorio spezzino. In: De Pascale F., Farabollini P. & Lugeri F.R. Eds., Comunicare il rischio, il rischio di comunicare, 113-133. PRISMA IRES Marche.

# Teachers' professional development across the COVID-19 pandemic: EGU Education Field Officer programme in Italy

Realdon G.*[1-2], Beccaceci A.[1], Stacchiotti L.[1], Invernizzi M.C.[1] & Paris E.[1]

[1] UniCamEarth Group, Università di Camerino. [2] European Geosciences Union.

*Corresponding author e-mail:* giulia.realdon@unicam.it

*Keywords:* geoscience education, EGU, EGU Education Field Officers.

The Field Officer (FO) programme was launched by EGU (European Geosciences Union) in 2018 to promote the effective teaching of geosciences in European schools and beyond. Four European and two non-European FOs were appointed, trained, and begun to run teachers' professional development workshops in their respective countries.

FOs prepared materials and built simple equipment needed to perform practical labs during the workshops. They also translated the lab protocols in their languages, so that attending teachers could immediately use them in the classroom. In 2019 the Italian FO (G. Realdon) ran 5 workshops for 80 teachers in 3 regions and 2 teachers' conference presentations. The Italian FO set up workshops addressing the following topics: Earth structure and magnetic field, Fossils and geologic time, Plate tectonics, Rock cycle, Seismology and Volcanism, and collaborated with the UNICAMearth workgroup of the University of Camerino, translating 21 lab protocols into Italian and publishing 3 original activities.

The outbreak of the COVID-19 pandemic in early 2020 halted all face-to-face school activities, including prearranged teachers' trainings. This has heavily affected the FO programme in all the 6 countries where the programme has been started and prevented the training of 7 new FOs that had already been appointed in other new countries. Since the beginning of the programme, and during the forced interruption, the FOs regularly met online to reflect on past activities, leading to the publication of two papers on the assessment of the programme's outcomes (Correia et al., 2020; Realdon et al., 2020) and of an educational article in a teachers' journal (Realdon et al., 2021).

Between early 2020 and fall 2021, FOs switched to remote teachers' training activities at national and international level. In Italy, 3 online workshops and 5 webinar presentation were run during the periods of restrictions. Once face-to-face teaching resumed across Europe, new workshops were organised. Since fall 2021, 5 workshops were run in Italy in Puglia, Lazio and Veneto regions, cumulatively attended by 93 teachers.

All the face-to-face workshops before and after the restrictions were evaluated using a questionnaire administered in the host nation language. In this conference we are presenting the data emerged from the Italian participants, which provide an encouraging picture and useful suggestions for the future development of the FOs programme.

Correia G., Realdon G., Coupechoux G., Juan X., Baskar R., Burgeoini Y. & King C. (2020) - Geoscience Education Field Officer international programme: The first year of activity (May 2019 – April 2020). ASE Internat., 10, 11-21.

Realdon G., Coupechoux G., Correia G.P., Juan X., Baskar R., Bourgeoini Y. & King C. (2020) - EGU (European Geosciences Union) Education Field Officer programme: teachers' appreciation, perceptions and needs. Eur. Geologist J., 50,10-14.

Realdon G., Correia G.P., Juan X., Coupechoux G., Baskar R., Bourgeoini Y. & King, C. (2021) - Watery world – hands-on experiments from Earthlearningidea. Sci. School, 54.

# A Tribute to Chris King

Realdon G.*[1-2]

[1] UniCamEarth Group, Università di Camerino. [2] European Geosciences Union.

*Corresponding author e-mail:* giulia.realdon@unicam.it

*Keywords:* Chris King, Earthlearningidea, EGU.

I first knew about Chris King indirectly, through his *Earthlearningideas*, hands-on teaching activities on geoscience topics both simple in appearance and rich in pedagogical and scientific content. Then, in 2014, I witnessed Chris King with his colleagues Peter Kennet and Elizabeth Devon performing their inspiring workshops for geoscience teachers. Observing him in person made me discover a new way of teaching, which I further experienced at EGU - European Geosciences Union, during GIFT Workshops in Vienna, and then practicing as a EGU Education Field Officer for Italy, under the guidance of Chris King himself as the Chair of the EGU Committee on Education.

Chris King was skilled and inspiring, while remaining always friendly and helpful. Before becoming a world-renowned expert in geoscience education, he had a long and diverse life experience. After starting his career as a geologist in diamond prospecting, he became a schoolteacher and joined the UK Earth Science Teachers Association, where he was an active member for 41 years, and acted as chairman too. He then joined Keele University (1996-2015), where he directed the Earth Science Education Unit. He contributed to training about 37,000 teachers and student teachers, indirectly influencing the learning of several million students in UK and beyond.

Chris King did not limit his activities to the UK but played a role on a global scale. In 2000, he was a founding member and became the first chairman of the International Geoscience Education Organisation (IGEO). At EGU he also inspired new initiatives including the EGU Higher Education Teaching Grants and Higher Education Geoscience Teaching Workshops, to name but a few. He wrote countless articles and books, among which an innovative online open access textbook for high schools.

During his career, Chris King was honoured by the Geological Society's Distinguished Service Award, the RH Worth Prize, the Halstead Medal and the international Geoethics Medal. He gained a reputation for being an incredible educator, an inspiring master and role model.

Prematurely stolen from this life by an unforgiving illness, he faced this extreme challenge with courage and grace, finding the energy to say one last farewell to friends, colleagues and students.

I salute him with the words of Ravi Shankar of IGEO India: "*Above all, Chris was an amazing gentleman and a pleasure to work with. He respected, supported and cheered everyone. He treated all with vast amounts of dignity, support and understanding. Chris brought a special kind of light into the room; his gentle, wry smile and dry humour was always a delight! With such exemplary attributes he touched the hearts of all. He was an example of a great human being and a great geoscientist, who devoted his entire life to Earth science education. His vast legacy should be continued in the future*".

*Information on Chris King's biography kindly provided by Peter Kennet and by EGU Committee on Education*

# "An ocean of science" project: a journey to the seabed

Ricca M.[1], Albanese M.P.[1], Donato A.[1], Ruffolo S.A.[1], Bruno F.[2], Randazzo L.*[3] & La Russa M.F.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Ingegneria Meccanica, Energetica e Gestionale Università della Calabria, Rende (CS). [3] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* luciana.randazzo@unipa.it

*Keywords:* underwater cultural heritage, cultural identity, innovative educational paths.

The protection of underwater cultural heritage, as an integral part of the cultural heritage of Humanity, is exercised according to the same general principles envisaged for the underground archaeological heritage. These principles are reaffirmed and extended in a fundamental international legal instrument, the Convention on the Protection of the Underwater Cultural Heritage, adopted in Paris on 2 November, 2001 by the General Conference of UNESCO Member States. Archaeological materials coming from underwater environments are of great relevance in order to study technologies, origin and progressive evolution of ancient civilizations and for a better understanding of historic events (Sacco et al., 2015; Canoro, 2021; Ricca et al., 2021). Underwater sites are highly dynamic environments and undergo the influence of the marine system; they are also of considerable interest for their natural, geomorphic, physical, biochemical characteristics, with particular regard to marine flora and fauna as well as for their scientific, ecological, cultural, educational and economic importance. Being the umpteenth testimony of the vast cultural that enriches our territory, the submerged heritage bears witness to our cultural identity. Undermining the beauty of the hidden treasures protected by our waters, in addition to the well-known illegal trafficking activities, contributes and aggravates the environmental damage and, consequently, the conservation of the submerged cultural heritage.

The project "An Ocean of Science" (CUP H23D21002060001), promotes effective interventions and innovative educational paths to support the growth of knowledge and skills in schools, helping the relevant institutions to ensure more inclusive cohesion policies with a high cultural and scientific impact. The project is aimed at high school students with the aim of raising awareness of the enhancement and enjoyment of the finds and evidence of the past culture that lie on the seabed and also to study the pollution of the seas, as one of the major threats to the marine ecosystem. The results will be aimed at increasing students' knowledge and awareness of their own cultural identity and at promoting the enhancement of the national submerged cultural heritage, also acquiring awareness of its environmental importance.

Canoro C. (2021) - Patrimonio Culturale Sommerso. Passaporto per il futuro. Dive in the past, Editoriale scientifica.

Ricca M., Camara B., Fort R., De Buergo M.A., Randazzo L., Davidde Petriaggi B. & La Russa M.F. (2021) - Definition of analytical cleaning procedures for archaeological pottery from underwater environments: The case study of samples from Baia (Naples, South Italy). Mater. Design, 197, 1-12.

Sacco F., Cevoli T., Vignola L. & Putrella D. (2015) - L'arte sotto il mare. Legambiente, 5-11.

# Geosciences teaching experiences during Covid-19 emergency

Scacchetti M.*

AMI - Associazione Micromineralogica Italiana.

*Corresponding author e-mail:* mauscacchetti@alice.it

*Keywords:* Google classroom, authentic task, skills.

The last two school years were influenced by the Covid-19 pandemic spread throughout the world and consequently by the use of distance learning, that is simply defined as the process of transferring knowledge to learners who are separated from the instructor by time or physical distance. Although many teachers, educators and families prefer traditional didactic approaches rather than distance learning, the use of the last one during Covid-19 pandemic spread, forced the teacher teams to employ some interesting didactic tools and methods. My first distance learning experience in a 3rd classroom of a 1st grade secondary school in Reggio Emilia (Italy) related to Geosciences. The students in this school were already able to use "Google Classroom", a widespread online course platform used by my language colleague to distribute assignments and resources in class. Learning units about Geosciences were Volcanoes and earthquakes, Geomorphic processes, Plate tectonics, Fossils and Earth geologic time, Climate changes. For every unit I developed the following steps: (1) editing of a PPT with images, relative captions and short explanations; every presentation included the request of an authentic task as homework; (2) loading of a multimedia file, by Screen cast-o-matic program, focused on the slideshow presentation; (3) preparation of homemade students' notes on the base of the multimedia file; (4) preparation of the authentic task by every student, with problem-based learning, and its return to the teacher by Google Classroom; (5) oral discussion about the homemade notes and the authentic task during the following Meet virtual lesson with every student. Students' assessment was performed by testing several skills (comprehension of the question, communicating, correct writing, use of scientific terms, digital competences) during the oral interviews, the administration of tests, the correction of the homemade notes and the authentic tasks. In spite of initial difficulties about Meet connections and the new didactic approaches, I positively consider this experience for the following reasons: (1) implementation of my digital competences, (2) testing of several cross-curricular European key competences like digital competences, learning to learn, sense of initiative and entrepreneurship, cultural awareness and expression in my students (Herrington et al., 2006; OECD, 2021).

Herrington J., Reeves T.C. & Oliver R. (2006) - Authentic Tasks Online: A synergy among learner, task, and technology. Distance Education, 27(2), 233-247.

OECD (2021) - 21st-Century Readers: Developing Literacy Skills in a Digital World, PISA. OECD Publishing, Paris.

# An italian user-friendly tool to increase awareness about causes and impacts of climate change

Senese A.*, Lombardo L., Manara V., Diolaiuti G.A. & Maugeri M.

Dipartimento di Scienze e Politiche Ambientali, Università di Milano.

*Corresponding author e-mail:* antonella.senese@unimi.it

*Keywords:* carbon footprint, climate change, geoeducation.

In recent decades, increasing attention has been paid to the issue of global warming and then the concept of carbon footprint has become common. Following Pandey et al. (2011) and Wiedmann & Minx (2008) the carbon footprint can be defined as the quantity of greenhouse gases (GHGs) expressed in terms of $CO_2$ equivalent ($CO_{2\text{-eq}}$), that are directly and indirectly emitted into the atmosphere by an individual, organization, company, process, product (including goods and services), or event within a specified boundary. Approaches based on comprehensive environmental life-cycle assessment methods are available to track total emissions across the entire supply chain. However, because consumers can influence the carbon footprints of goods and services through their purchase decisions, beside to methods that allow accurately assessing the carbon footprint of companies, organizations and cities, it is also important to develop methods that allow people estimating their own individual carbon footprint. In this case, the approach must be a user-friendly online questionnaire that can be filled in within a short time. Moreover, the questions should be easy to answer without asking for information that most would not be able to provide.

Within this context, in collaboration with Vaillant Italia Spa (the Italian office of Vaillant Group, a German company mainly dedicated to the heating, ventilation and air-conditioning) we developed an online tool for quantifying the carbon footprint that is directly and indirectly caused by an individual over a year (https://latuaimpronta.vaillant.it/). Specifically, we focused on the main and easiest to quantify sources of direct $CO_{2\text{-eq}}$ emissions: gas and electricity consumption (due to heating, illumination and use of domestic appliances), transport, food and waste. By compiling the questionnaire, people can immediately observe how results change modifying their habits. In this way, our carbon footprint calculator shows in which sector people have the greatest impact, stimulating them to emit less by adopting more virtuous and more sustainable behaviors.

During these last years, we proposed our tool to several levels of students at middle school, high school and university. In addition, we compared the results obtained by middle school students with the questionnaires compiled by their parents in order to better evaluate the individual awareness.

Our online questionnaire can be considered an evaluable tool for geoeducation, since it can be linked to earth sciences, physics, chemistry, mathematics. In addition, Civics is now required at all education levels and as a cross-cutting theme; therefore, increasing the individual awareness by means of our tool can be also considered of didactic utility.

Pandey D., Agrawal M. & Pandey J.S. (2011) - Carbon footprint: current methods of estimation. Environ. Monit. Assess., 178(1-4), 135-160.

Wiedmann T. & Minx J. (2008) - A Definition of 'Carbon Footprint'. In: Pertsova C.C. Ed., Ecological Economics Research Trends, 1-11. Nova Science Publishers.

# Geoeducation and immersive experience: from researcher projects to student opinions

Senese A.[1], Panizza M.[1], Porta M.[2], Maugeri M.[1], Ambrosini R.[1], Traversa G.[1], Fugazza D.[1], Azzoni R.S.[3], Bollati I.M.[3] & Diolaiuti G.A.*[1]

[1] Dipartimento di Scienze e Politiche Ambientali, Università di di Milano. [2] Istituto comprensivo «Guido Galli», Milano. [3] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* guglielmina.diolaiuti@unimi.it

*Keywords:* immersive experience, geoeducation, climate change.

Laboratory and outdoor activities (e.g., field work and field trips) are considered crucial in geoeducation. Nevertheless, they are conditioned by many factors: the teachers' attitude in organizing outdoor activities, normative and costs, sanitary emergences like the recent Covid-19, etc. Moreover, some morphoclimatic environments are less approachable than others: for instance, the high mountain and glacierized areas where field trips can only be planned from May to September (a period not very compatible with the time window exploitable for scholastic field trips), and needing a more than one day schedule. Video clips can help in presenting such fascinating environments; nevertheless, only an immersive vision allows an experience comparable with the one possible in the real world. An immersive experience is a virtual tour based on 360° contents, i.e., a video you can "explore". This is possible thanks to 3DoF (Degrees of Freedom) experiences: standing at a fixed point, the virtual tourers can look in any direction turning their head left or right, tilting it up or down, or pivoting left and right. The University of Milan developed a virtual tour on the Forni Glacier, the widest valley glacier of the Italian Alps, using 360° contents obtained by means of an 8-sensor video camera that shoots in all directions of space (Diolaiuti et al., 2022). In order to increase the fruition of this innovative experience, we make the multimedia products usable everywhere via smartphone or tablet or by means of VR (Virtual Reality) headsets by the link https://video.unimi.it/video/forni_glacier_360/.

The 360° videos of Forni Glacier were also developed to be offered at the Italian Pavilion of EXPO Dubai 2021 and at the 2021 International Science Festival organized by La Sorbonne University of Paris by framing the QR code with always positive feedbacks.

We have been tested this innovative teaching methodology by providing the virtual experience to students of the secondary schools of first and second level and the last two years of the primary school. To these students we also proposed an online questionnaire to evaluate both their satisfaction and the effectiveness in conveying concepts and information in the field of Earth sciences. Tests represent not renounceable instruments to verify the educational and disseminative efficacy of any technology.

Here we present the results from the questionnaire and the opportunity to replicate such experience on other contexts to increase understanding and knowledge of Earth sciences.

Diolaiuti G.A., Maugeri M., Senese A., Panizza M., Ambrosini R., Ficetola G.F., Parolini M., Fugazza D., Traversa G., Scaccia D., Franceschini M., Citron L. & Pelfini M. (2022) - Immersive and virtual tools to see and understand climate change impacts on glaciers: a new challenge for scientific dissemination and inclusive education. Geogr. Fis. Dinam. Quat., 44, 83-93.

# S26.

# Climate change and the fossil record

*Conveners & Chairpersons*

*Massimo Bernardi (MUSE - Science Museum, Trento)*

*Daniele Scarponi (University of Bologna)*

# Nannoplankton assemblages over the last 25 kyr: paleoproductivity and surface ocean dynamics from IODP sites U1385 and U1313

Argenio C.*[1], Flores J.A.[2], Fuertes M.A.[3], Balestra B.[4-5-6] & Amore F.O.[1]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Department of Geology, Universidad de Salamanca (Spain). [3] Department of Didactics of Mathematics and Experimental Sciences, Universidad de Salamanca (Spain). [4] Environmental Science Department, American University, Washington, DC (USA). [5] Smithsonian, Paleobiology Department, National Museum of Natural History, Washington, DC (USA). [6] Institute of Marine Sciences, University of California, Santa Cruz, CA (USA).

*Corresponding author e-mail:* argenio@unisannio.it

*Keywords:* calcareous nannofossils, Last Glacial Maximum, North Atlantic.

Many marine sedimentary sequences of the Atlantic Ocean provide evidence of dramatic climate transitions that took place on Earth starting from the Last Glacial Maximum (LGM). The coccolith record in sedimentary sequences is an indicator of primary productivity conditions and useful to decipher upwelling strength variations. This work is carried out through calcareous nannoplankton paleo-assemblages retrieved at the Integrated Ocean Drilling Program (IODP) sites U1385 and U1313, located respectively along the Western Iberian Margin and in the North Atlantic Ocean, during the last 25 kyr.

Through the comparison between coccolith paleoproductivity proxies, calcification and dissolution/preservation signals, the paleoceanographic reconstruction of sea-surface dynamics is provided. Coccolith absolute abundances (coccoliths per gram of sediment) and accumulation rates (coccoliths $cm^{-2}$ $ka^{-1}$) are estimated following Flores & Sierro (1997). A quantitative estimation of carbonate dissolution on calcareous nannoplankton paleo-assemblages is also provided through the CEX' dissolution index (Boeckel & Baumann, 2004) and the preservation is qualitatively evaluated following Flores et al. (2003). Lastly, the coccolith thicknesses are calculated through the C-Calcita software (Fuertes et al., 2014) to check variations occurrence in response to environmental factors affecting the calcification process.

The data show that main differences concerning productivity and calcification/dissolution between the two latitudes affect the Heinrich Stadials (HS), the LGM and the Bølling-Allerød (B/A). During both the Younger Dryas (YD) and the Holocene intervals size-normalised thicknesses of the different species show a constant pattern at both sites. The HS events register a higher productivity at Site U1313. The two sites are placed in different oceanographic and sedimentary scenarios. Dissimilarities recorded are mainly due to the different position of the sites in relation to the Subtropical gyre and to their distance from continental shelves.

Boeckel B. & Baumann K.H. (2004) - Distribution of coccoliths in surface sediments of the south eastern South Atlantic Ocean: Ecology, preservation and carbonate contribution. Mar. Micropaleontol., 51, 301-320.

Flores J.A. & Sierro F.J. (1997) - Revised technique for calculation of calcareous nannofossil accumulation rates. Micropaleontol., 43, 321-324.

Flores J.A., Marino M., Sierro F.J., Hodell D.A. & Charles C.D. (2003) - Calcareous plankton dissolution pattern and coccolithophore assemblages during the last 600 kyr at ODP Site 1089 (Cape Basin, South Atlantic): Paleoceanographic implications. Palaeogeogr. Palaeoclimatol. Palaeoecol., 196, 409-426.

Fuertes M.Á., Flores J.A. & Sierro F.J. (2014) - The use of circularly polarized light for biometry, identification and estimation of mass of coccoliths. Mar. Micropaleontol., 113, 44-55.

# *Helicosphaera carteri* during the Marine Isotope Stage 5: how its abundance and distribution can contribute to natural carbon capture and storage

Bianco S.*[1-2], Bordiga M.[3], Di Giulio A.[2] & Lupi C.[2]

[1] Istituto Universitario di Studi Superiori, Pavia. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* stefania.bianco@iusspavia.it

*Keywords:* MIS 5, calcareous nannofossils, *Helicosphaera carteri*.

The Marine Isotope Stage (MIS) 5 (130-70 kyr) is the last major interglacial interval of the Earth's history and it can be considered as an analogue of the current situation because of its high sea level and temperature, its reduced ice sheets, and atmospheric carbon dioxide ($CO_2$) concentration of 290 ppm corresponding to pre-industrial level. Hence, its comparison with the current time could be helpful to predict the future developments and to understand the effects of related-environmental changes on biota.

Coccolithophores are a group of calcifying marine phytoplankton and could be a good tool to reconstruct the past climate variations and their effects on calcifying primary producers.

In this project, their fossil remains (i.e., nannofossils) from the IODP Site U1501C (South China Sea) were analysed to provide an overview of their responses during the MIS 5. Particular attention was dedicated to *Helicosphaera carteri*, an important species in terms of calcium carbonate production because of its big size and heavily calcified coccoliths if compared to other species. To reconstruct the behaviour of this peculiar species during the MIS 5 and clarify its ecological preferences, the *H. carteri* abundance variations and $CaCO_3$ production in South China Sea were compared with those from 9 sites of different oceanographic settings (Pacific Ocean, Atlantic Ocean, Southern Ocean, Mediterranean Sea). The comparison highlighted the occurrence of a peak in the relative abundance of this species during the MIS 5e in most of the areas: N Atlantic (<0,5%), NW Pacific (4%), SW Pacific (2%), Southern Ocean (~40%), Mediterranean Sea (~ 8%), South China Sea (<1%).

For some of these sites, the data on bulk and coccolith-derived $CaCO_3$ (wt%) are also available, and by comparing them with *H. carteri* peaks, this species could be considered one of the main contributors to the coccolith-derived $CaCO_3$ in the bulk together with other heavily calcified species such as *Calcidiscus leptoporus* and *Coccolithus pelagicus*. Despite the low abundances of these species compared to very abundant but smaller, lightly calcifying ones (e.g., *Emiliania huxleyi*, *Gephyrocapsa* small), the bigger size and sturdy calcified morphology allow these species to constitute the main contributors to the carbon sequestration and $CaCO_3$ storage into the deep-sea sediments. Regarding the specifics on *H. carteri*, its increase in abundance during the MIS 5e in the studied sites is related to an increase in $CaCO_3$ production although it is often less than the 4% of the entire assemblages. These findings highlight *H. carteri* ability to fix and store carbon under high $CO_2$ concentration levels. Moreover, its peaks during MIS 5e in many sites distributed in both open oceanic and coastal areas confirm *H. carteri* as a tolerant species, easily adaptable to different oceanographic contexts and with a good resilience that has allowed it to inhabit the surface waters of the oceans for millions of years.

## Coralligenous build-ups of the CRESCIBLUREEF project: a Mediterranean geobiological archive

Bracchi V.A.*[1-2], Sanfilippo S.[2-3], Bazzicalupo P.[1], Bertolino M.[4], Bruno F.[5], Costa G.[1], Donato G.[3], Fallati L.[1], Gallo A.[5], Guido A.[6], Leonardi R.[3], Muzzupappa M.[5], Negri M.P.[1], Rosso A.[2-3], Savini A.[1-2], Sciuto F.[2-3], Serio D.[2-3], Varzi A.G.[1], Viola A.[3] & Basso D.[1-2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [4] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [5] Dipartimento di Ingegneria Meccanica, Energetica e Gestionale, Università della Calabria, Rende (CS). [6] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* valentina.bracchi@unimib.it

*Keywords:* coralligenous, geobiology, conservation paleobiology.

Several mesophotic bioconstructions have been developing on the Mediterranean continental shelf since the Holocene. They are important carbonate frameworks shaping the submarine geomorphology, and geobiological archives of environmental changes of the recent past, recorded in the skeletons of the biological components that determined their accretion. Unlike their tropical counterparts, these temperate reefs are deeper and not yet adequately described. Among them, Coralligenous is the most monumental bioconstruction, developed along the circalittoral zone, mostly produced by the overlapping of several generations of crustose coralline algae through time, with a variable contribution of other taxa such as bryozoans, sponges and serpulids.

The project FISR_04543 "CRESCIBLUREEF - Grown in the blue: new technologies for knowledge and conservation of Mediterranean reefs" focuses on Coralligenous bioconstructions (algal reefs), and on their variability in terms of structure and composition along a depth gradient (20-100 m) off Marzamemi (Ionian Sea, Sicily).

The project is aimed at understanding the inception and development of the Coralligenous, and the type of its accretionary structures and growth rate, also in connection with the Holocene climate fluctuations recorded by geobiological and geochemical proxies. Tackling the structure and framework of the Coralligenous helps to recognize the role of successive generations of builders over time, and is complementary to the biological approach, which is aimed at assessing exclusively the biodiversity and ecological functioning of the surface living layer. Moreover, in order to develop appropriate measures for management and conservation of this unique habitat, the nature of the substrate should be univocally defined and considered.

Preliminary results include a detailed cartography of Coralligenous in the study area, its geomorphological classification and the quantification of its distribution also in terms of carbonate production. Evidence from the first samples collected at 36 m of water depth revealed that both surface and internal structures are dominated by calcareous red algae, with a minor contribute of some other taxa. Among the latter, sponges seem to play an important role in bioconstruction, with the presence of several species intermingled with the algal thalli. A high biodiversity has been highlighted by The occurrence of different species of serpulids and bryozoans result in a high biodiversity, although they show a subordinate contribution to the volume of the bioconstruction. The study of any internal variation of these coralligenous concretions is ongoing. In addition, the list of all identified taxa is being refined, some of which for the first time found associated with this peculiar habitat.

# Changes in floral composition and landscape setting during a Wuchiapingian sea-level shift in the tropics

Branz R.*[1], Kustatscher E.[1-2-3], Heynck M.[2], Nowak H.[1], Roghi G.[4], Forte G.[1] & Franz M.[5]

[1] Museo di Scienze Naturali dell'Alto Adige, Bolzano. [2] Department für Geo- und Umweltwissenschaften, Paläontologie und Geobiologie, Ludwig-Maximilians-Universität, München (Germany). [3] Bayerische Staatssammlung für Paläontologie und Geobiologie, München (Germany). [4] Istituto di Geoscienze e Georisorse, CNR, Padova. [5] Abteilung Angewandte Geologie, Georg-August-Universität Göttingen (Germany).

*Corresponding author e-mail:* branz.roberta@gmail.com

*Keywords:* paleoenvironmental reconstruction, plant communities, Lopingian.

The Wuchiapingian is characterized by aridisation and substantial sea-level changes, which affected strongly the local composition of ecosystems and the preservation potential for terrestrial biota. The well-known succession exposed in the Bletterbach Gorge (Dolomites, N-Italy) yielded one of the best-preserved and most diverse vertebrate ichnoassociations and plant assemblages of the Wuchiapingian worldwide. These features, as well as the rare co-occurrence of plant fossils, tetrapod footprints and plant-animal interactions make the Bletterbach Gorge a crucial site for the understanding of late Permian terrestrial ecosystems in Euramerica. Most plant remains and tetrapod footprints come from the Gröden/Val Gardena Formation, a succession dominated by mainly coarse- to medium-grained sandstones, primarily red in colour. Particularly fossil-rich levels are located about 70 metres above the base of the formation, close to the so-called Cephalopod Bank, which corresponds to the maximum flooding surface of a marine transgression. Sedimentological, palaeobotanical, palynological and geochemical analyses around the Cephalopod Bank enable the reconstruction of environmental changes during the late transgression, highstand and initial phase of regression in a primarily near-coastal setting. During the sea-level lowstand, the landscape corresponded to a near-coastal floodplain under an arid climate. The conditions were not favourable for the preservation of plant macrofossils, but palynomorphs reflect a conifer-dominated zonal vegetation spread out on the floodplain and an intrazonal vegetation on the river margins dominated by conifers, with few ginkophytes and seed ferns, as well as Czekanowskiales, horsetails, ferns and/or lycophytes. During the following sea-level rise, the area turned into a wave-dominated estuary bay with a consequently higher water table. A rich and diverse intrazonal vegetation developed in the locally (azonal) humid environments. The vegetation around standing or running water bodies of the estuary bay was dominated by conifers and ginkgophytes, with other groups (Czekanowskiales, putative cycadophytes, seed ferns, sphenophytes) being rare. During the sea-level highstand, the section lay at the position of a barrier complex that had formed in the estuary and corresponds to the Cephalopod Bank. The fossil content illustrates a marginal marine fauna with nautiloids, bivalves, and *Skolithos* burrows. During the following regression, the area was part of a coastal plain close to the estuary bay. Here, conifers dominated, while xerophytic seed ferns were secondary elements in the flora. Relatively rare were Czekanowskiales and putative cycadophytes. This flora reflects an azonal vegetation.

# The Bolca Lagerstätten of northern Italy: A window into tropical marine life in early Eocene of Tethys

Carnevale G.*

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* giorgio.carnevale@unito.it

*Keywords:* Konservat-Lagerstätten, Ypresian, western Tethys.

The Eocene limestones exposed around the village of Bolca, NE Italy, comprise a series of localities yielding a unique picture of life in a warm, shallow marine setting in the early Cenozoic, roughly 50 million years ago. Deposited within an archipelago near the western end of the Tethys Ocean, the major localities of Bolca collectively yield over 500 species of marine and terrestrial vertebrates, invertebrates, and plants.

The outstanding relevance of Bolca is evident especially for fishes and derives from four main features: the excellent preservation of fossils, its early Eocene age, its unique environmental setting and its paleogeographic location. Fossils from Bolca are often exceptionally well-preserved, commonly known as part and counterpart with traces of pigmentation and phosphatized soft tissues. With respect to age, the Bolca fauna postdates the Cretaceous-Paleogene (K-Pg) mass extinction by roughly 15 million years, providing a glimpse into mature ecosystem postdating an interval of evolutionary recovery. As far as concerns the environmental setting, Bolca falls near the dawn of modern reef ecosystems and its reefal association results in substantially higher species richness of fishes, representing the earliest modern reef fish assemblage known in the record. With respect to paleogeography, Bolca is ideally located for capturing a high-diversity marine assemblage of Eocene age. High species diversity of benthic foraminiferans, corals and molluscs in the late Eocene of the western Tethys suggest this region was an ancient biodiversity hotspot, comparable to the present Indo-West Pacific.

The fossil fishes of Bolca are particularly significant in documenting the spectacular rise of acanthomorphs, the dominant group of marine teleosts, as well as providing critical clues to the early assembly of modern tropical reef ecosystems. More than 250 species of fishes have been described to date, making that of Bolca as the most diverse fossil vertebrate assemblage known worldwide. Although they are often overshadowed by the fishes, a wide range of marine invertebrates, aquatic plants and algae, and remains of terrestrial plants and insects are also known from Bolca. The transitional to continental sites of Bolca remain poorly examined, and their relationship to the well-known localities remains unclear.

# Cold-adapted birds show greater changes in range size than temperate birds during past climatic oscillations

Carrera L.*[1], Pavia M.[2] & Varela S.[3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Departamento de Ecoloxía e Bioloxía Animal, Universidade de Vigo (Spain).

*Corresponding author e-mail:* lisa.carrera3@unibo.it

*Keywords:* birds, fossils, Last Glacial Maximum.

Investigation of ecological responses of species to past climate oscillations provides crucial information to understand the effects of global warming. In this work, we investigated how past climate changes affected the distribution of six bird species with different climatic requirements and migratory behaviours in the Western Palearctic and in Africa. Species Distribution Models and Marine Isotopic Stage (MIS) 2 fossil occurrences of selected species were employed to evaluate the relation between changes in range size and species climatic tolerances. The Last Glacial Maximum (LGM) range predictions, generally well supported by the MIS 2 fossil occurrences, suggest that cold-dwelling species considerably expanded their distribution in the LGM, experiencing more pronounced net changes in range size compared to temperate species. Overall, the thermal niche proves to be a key ecological trait for explaining the impact of climate change in species distributions. Thermal niche is linked to range size variations due to climatic oscillations, with cold-adapted species currently suffering a more striking range reduction compared to temperate species. This work also supports the persistence of Afro-Palearctic migrations during the LGM due to the presence of climatically suitable wintering areas in Africa even during glacial maxima.

# Environmental influence on calcification of the bivalve *Chamelea gallina* on a millennial temporal scale, in the Northern Adriatic Sea

Cheli A.*[1-2], Mancuso A.[1-2], Falini G.[2-3], Goffredo S.[1-2] & Scarponi D.[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Fano Marine Center, Laboratorio congiunto di ricerca per lo studio della biodiversità, le risorse e le biotecnologie marine, Fano (PU). [3] Dipartimento di Chimica «Giacomo Ciamician», Università di Bologna.

*Corresponding author e-mail:* alessandro.cheli2@unibo.it

*Keywords:* Holocene, climate change, bivalves.

The bivalve *Chamelea gallina* is a valuable economic species expected to be impacted by several anthropogenic stressors that threaten the biological and economic sustainability of its fishery. Understanding species 'long term adaptive response to climate change is crucial to define proper conservation and management strategies. In this light, the latest Quaternary fossil record allows to investigate past ecological responses to climate-driven environmental transitions (e.g., Cheli et al., 2021; Scarponi et al., 2022). Here, skeletal parameters (micro-density and apparent porosity) and growth parameters (bulk density, linear extension, and net calcification rates) of *C. gallina* are investigated. Four shoreface deposits rich in *C. gallina* are being evaluated: two from the present-day Adriatic coastal settings and two from Adriatic cored shoreface successions of the Middle Holocene, when regional temperatures were higher than today, thus giving insights on the ecological response of this species in the face of global warming. Specifically, we aim to determine: the life span of selected specimen using three independent ageing methods (shell surface growth rings, shell internal bands and stable isotope composition); shell skeletal and growth parameters for each assemblage investigated. Preliminary results indicate that *C. gallina* from shoreface deposits of the Holocene Climatic Optimum have a denser exoskeleton than modern specimens. The net calcification rates on the contrary are higher in modern specimens from shoreface environments, as a result of a significant increase in linear extension rates. Modern specimens seem to promote faster growth rate, at the expense of a less dense shell. The observed differences in shell density could depend on different mineralization rates driven by temperature. Warmer water masses reduce the thermodynamic work requested to deposit calcium carbonate, enabling an increase in calcification rates, which in turn can be reflected in a denser shell. This study contributes to the reconstruction of *C. gallina* natural range of variability on timescales well beyond the ecological monitoring or small-scale experiments and offer insights on the adaptive capacities of *C. gallina* facing near-future anthropogenic warming.

Cheli A., Mancuso A., Azzarone M., Fermani S., Kandorp J., Frederic M., Montroni D., Polishchuk I., Prada F., Stagioni M., Valdré G., Boaz P., Falini F., Goffredo S. & Scarponi D. (2021) - Climate variation during the Holocene influenced the skeletal properties of *Chamelea gallina* shells in the North Adriatic Sea (Italy). PLoS ONE, 16(3), e0247590.

Scarponi D., Nawrot R., Azzarone M., Pellegrini C., Gamberi F., Trincardi F. & Kowalewski M. (2022) - Resilient biotic response to long-term climate change in the Adriatic Sea. Global Change Biology, 00, 1-13. https://doi.org/10.1111/gcb.16168.

# Paleoenvironmental changes across Permo-Triassic Boundary: Palynology and Paleobotany of Beacon Supergroup (Antarctica)

Corti V.*[1], Spina A.[2], Cornamusini G.[1] & Gulbranson E.[3]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Dipartimento di Fisica e Geologia, Università di Perugia. [3] Gustavus Adolphus College, Saint Peter, MN (USA).

*Corresponding author e-mail:* valecorti7@gmail.com

*Keywords:* palynology, Antarctica, Permo-Triassic Boundary.

The sedimentary sequence deposited during the Permian and Triassic time could reveals precious information about the changing of the landscape during the bigger mass extinction. This study presents one of the most complete palynostratigraphic sequence of Permo-Triassic deposits from Antarctica. The continuity in the sedimentation between the Permian Weller Coal Measures Formation and the Triassic Feather Sandstone and Lashly Formation sampled during the XXX Italian Antarctic Expedition at Allan Hills (South Victoria Land), allow to reconstruct the microfloristic trend across one of the most crucial time in the history of the Earth. The sedimentary and palynological study of this formations yields a bio-stratigraphical data that consent the attribution of time-span for each formations and the correlation with coaeval formation across the Transantarctic Mountains (TAM) and other area of the Gondwana. In the Weller Coal Measures Formation the sporomorphs assemblage suggests a late Permian age, with the presence, in the upper part of a palynofacies mainly composed by long-shape inertinite, proxy data of a paleo-fire, probably linked with EPE (end-Permian Extinction), moreover the successive *Protohaploxypinus microcorpus* zone, could be assigned to the late Permian (due to the provincialism) or to the Early Triassic (as in Sydney Basin with the recent calibration). Through the sporomorphs assemblage, supported also by the paleobotany remains, a deep change affecting the flora between the Permian and Triassic time has been observed. The floristic turnover, also noted in many areas of Gondwana, is strictly linked to the deep change of paleoenvironmental conditions between the Permian and Triassic widespread all over the world due to a general greenhouse. Following a non-fossiliferous sandstone succession deposited during Induan and Olenekian time interval, the flora returned flourishing in the Middle Triassic in the member A of Lashly Fm. From the succession deposited in the Middle Triassic, four different associations of palynomorphs were recovered and has been possible to establish the different environmental conditions that affected the sedimentary sequence, with an alternation of stable and instable landscapes. The stable landscape, that dominated during the deposition of members A and C, was characterized by developed soil, testified also by the presence of hypogeum fungal spores; while the instable landscape dominated during the deposition of member B of Lashly Fm., highly characterized by coarse sandstones linked with massive fluvial flows that also caused the transport and deposition of the "Allan Hills Fossil Forest". This area is characterized by the presence of more than 300 fossil trunks, they have been studied by a multi-analytical approach to reconstruct the syn and post depositional events and the paleoenvironmental conditions that occurred during the Middle Triassic time.

# A sclerochronological approach to test brachiopod shells as archives of seasonality

Crippa G.*[1], Harper E.M.[2], Leng M.J.[3-4], Zanchi M.[5] & Angiolini L.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Department of Earth Sciences, University of Cambridge (UK). [3] NERC Isotope Geosciences Facilities, British Geological Survey, Nottingham (UK). [4] Centre for Environmental Geochemistry, University of Nottingham (UK). [5] Centro per la Complessità e i Biosistemi , Università di Milano.

*Corresponding author e-mail:* gaia.crippa@unimi.it

*Keywords:* brachiopod, stable isotope, sclerochronology.

Brachiopods are not abundant in modern seas and oceans, where they are mainly represented by taxa of the Order Terebratulida and Rhynchonellida, but they dominated the benthic communities during the Palaeozoic, when many orders were present and when they reached their maximum morphological and chemico-structural diversification. They are benthic, sessile, and low-metabolism physiologically unbuffered organisms, affected by environmental changes that they record in their diagenesis-resistant, low-Mg calcite shells. For these reasons, fossil and recent brachiopod shells have been successfully used as high resolution biomineral archives for (palaeo)environmental and (palaeo)climatic reconstructions in the near and deep time.

Recent brachiopods have been analysed to test the equilibrium of their shell stable isotope composition with that of seawater (Butler et al., 2015; Rollion-Bard et al., 2019). However, there is no study focused on how the different shell microstructures (i.e., fibrous vs. columnar layer) record the seasonal signal.

Here, we examined specimens belonging to three extant terebratulid brachiopod species (*Liothyrella neozelanica*, *Liothyrella uva* and *Gryphus vitreus*) coming from different latitudes and depths and with a different shell layer succession (two-layer vs. three-layer shells); we analyzed the stable isotope composition of the shell along the growth direction applying a high resolution sclerochronological approach and transforming length into ages based on the Brody-Bertalanffy equation and the position of annual growth lines. We aim to test the fidelity of the fibrous and columnar microstructures in recording the seasonal signal, in order to devise an approach to reconstruct the seasonality to be used not only in recent specimens, but also in fossil ones. Indeed, seasonality is a fundamental component of the climate system and has a strong influence on biotic distribution and evolution. Resolving seasonality changes, using fossil brachiopod shells as palaeoclimatic archives during intervals of climate change in the recent and distant past, has thus important implications for understanding and predicting long-term transformations of the climate system.

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Rollion-Bard C., Milner Garcia S., Burckel P., Angiolini L., Jurikovac H., Tomašových A. & Henkel D. (2019) - Assessing the biomineralization processes in the shell layers of modern brachiopods from oxygen isotopic composition and elemental ratios: Implications for their use as paleoenvironmental proxies. Chem. Geol., 524, 49-66.

# Paleoenvironmental changes and Biotic resilience across the Middle Eocene Climatic Optimum (MECO): Foraminiferal and Calcareous Nannofossil record from the Neo-Tethyan Baskil Section (Eastern Turkey)

D'Onofrio R.*[1], Zaky A.S.[2-3], Frontalini F.[4], Luciani V.[1], Catanzariti R.[5], Francescangeli F.[6], Giorgioni M.[7], Coccioni R.[4], Özcan E.[8] & Jovane L.[9]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Institute of Geological Sciences, Oeschger Centre for Climate Change Research, University of Bern (Switzerland). [3] Geology Department, Faculty of Science, Menoufia University, Shebin El-Kom (Egypt). [4] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [5] Istituto di Geoscienze e Georisorse CNR, Pisa. [6] Department of Geosciences, University of Fribourg (Switzerland). [7] Instituto de Geociências da Universidade de Brasília, Brasília (Brazil). [8] Department of Geological Engineering, Faculty of Mines, Istanbul Technical University (Turkey). [9] Instituto Oceanográfico da Universidade de São Paulo, Praça do Oceanográfico, São Paulo (Brazil).

*Corresponding author e-mail:* dnfrrt@unife.it

*Keywords:* MECO, foraminifera, calcareous nannofossils.

The climate-induced stress ($CO_2$ emissions, warming, ocean acidification, eutrophication, anoxia) affects the stability of modern ecosystems. The paleontological archive allows us to evaluate the climate changes impact on biotic communities on a greater temporal perspective with respect to the present observations. Indeed, exploring extreme climatic events from our geological past has become an urgent issue for the scientific communities. The middle Eocene Climatic Optimum (MECO, ~40 Ma) is one of the major Paleogene global warming events, representing thus a valuable past climatic analogue. The MECO was characterized by highly stressed environmental conditions including a ~3–6°C warming and shifts in the global carbon cycle, such as rise in atmospheric $pCO_2$ and ocean acidification. Nonetheless, the biotic response is still poorly detailed.

Here we provide new results of an integrated benthic foraminiferal and calcareous plankton high-resolution (~100 m/My) record across the MECO from the Baskil section (Turkey), in the Neo-Tethys, which offers a complete magneto-biostratigraphic and geochemical framework. The statistical approach adopted to combine our biotic record with geochemical variations outlined five environmental scenarios across the studied event. Specifically, the PRE-MECO was characterized by a well-stratified oligotrophic water column. These conditions are inferred by abundant oligotrophic nannofossil indices, occurrence of surface (mainly *Acarinina*) and thermocline planktic foraminifera, and low abundance of bi-triserial benthic foraminifers. Across the INITIAL MECO and MECO $\delta^{13}C$ NEGATIVE EXCURSION, changes in all the groups suggest a progressive increase in temperature and carbonate dissolution. A shift towards meso-eutrophic conditions is recorded in this phase, possibly due to accelerated hydrological cycle. Benthic foraminifera suggest less oxygen availability at the seafloor. The MECO WARMING PEAK marks the most striking biotic changes that indicate extreme warming and eutrophication, as testified by peaks in abundance of the warm and eutrophic nannofossils indices. The virtual disappearance of the oligotrophic planktic foraminifera, large *Acarinina* and *Morozovelloides,* and the peak in eutrophic deep-dweller *Subbotina* support this scenario. This phase also records a peak in carbonate dissolution that may have amplified the original planktic foraminiferal response. Benthic foraminifera suggest a decrease in the exported organic matter to the seafloor though with high quality. Finally, the POST-MECO interval documents the recovery to the pre-event conditions. In conclusions, the calcareous nannofossils and benthic foraminifers proved to be resilient to the perturbations induced by the MECO through the recorded assemblage variations. However, planktic foraminifera experienced a permanent change as large *Acarinina* and *Morozovelloides* did not restore, possibly due to the POST-MECO cooling.

# *Schizosphaerella* size and abundance variations across the Toarcian Oceanic Anoxic Event in the Sogno Core (Lombardy Basin, Southern Alps)

Erba E.*, Faucher G., Visentin S. & Gambacorta G.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* elisabetta.erba@unimi.it

*Keywords:* T-OAE, nannofossils, morphometry.

Abundance and size variations of nannofossil *Schizosphaerella punctulata* were quantified in the uppermost Pliensbachian–Lower Toarcian succession recovered with the Sogno Core (Lombardy Basin, Northern Italy). High-resolution nannofossil biostratigraphy and C-isotopic chemostratigraphy identified the Jenkyns Event within the Toarcian oceanic anoxic event (T-OAE) interval. Absolute abundances and morphometric changes of "small *S. punctulata*" (< 7 µm), *S. punctulata* (7-10 µm; 10-14 µm; > 14 µm) and "encrusted *S. punctulata*" (specimens with a fringing crust) show large fluctuations across the negative C-isotopic Jenkyns Event. The *Schizosphaerella* crisis is further characterized by a decrease in average valve size in the early–middle Jenkyns Event. The abundance fall was caused by the failure of *S. punctulata* specimens > 7 µm and "encrusted *S. punctulata*" that along with the increased relative abundance of small specimens, produced the reduction of average dimensions also documented in the Lusitanian and Paris Basins, although with a diachronous inception. The average valve size from the Lombardy Basin is ~2 µm smaller. Hyperthermal conditions associated with excess $CO_2$ and ocean acidification possibly forced the drastic reduction of *S. punctulata* abundance/size. In the pelagic succession of the Sogno Core there is a strong positive correlation between the *S. punctulata* (> 7 µm) absolute abundance/size and the $CaCO_3$ content, with a negligible contribution by "small *S. punctulata*". Encrusted specimens testify selective neomorphic processes: the diagenetic crust seems diagnostic to separate *S. punctulata* from *S. astraea.*

# Stable-isotope paleoecology of dextrally and sinistrally coiled *Morozovella* and *Acarinina* at the Early Eocene Climatic Optimum (ca 53-49 Ma) from the Pacific Ocean (Sites 1209-1210): evidence of resilience strategies to global warming?

Filippi G.[1], Sigismondi S.*[1], D'Onofrio R.[1], Westerhold T.[2], Wade B.S.[3], Dickens G.R.[4] & Luciani V.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Center for Marine Environmental Sciences, University of Bremen (Germany). [3] Department of Earth Sciences, University College, London (UK). [4] Department of Geology, Trinity College, Dublin (Ireland).

*Corresponding author e-mail:* silvia.sigismondi@edu.unife.it

*Keywords:* paleoecology, planktic foraminifera, EECO.

The knowledge of Eocene global warming impact on the environment and related biota strategies are essential for paleoclimate reconstructions, particularly in light of the ongoing climate change.

In this respect, the EECO (ca 53-49 Ma) is a key interval of time to examine the repercussions on marine biota of extreme climate events considering that, during this interval, Earth temperatures and $pCO_2$ reached the peak of the entire Cenozoic Era. The unicellular planktic foraminifera (PF) are a major group of open-marine calcifiers largely adopted in paleoceanographic reconstructions as extremely sensitive to environmental and climatic variations.

Here we present new insights on planktic foraminiferal response to the EECO global warming from the tropical Pacific Ocean ODP Sites 1209-1210 (Shatsky Rise).

Our study shows a marked and definitive decline in the abundance and diversity of the symbiont-bearing genus *Morozovella* at the EECO beginning (J Event) paralleled by a permanent increase of abundance and diversity of the genus *Acarinina*.

Moreover, the genus *Morozovella* switched its coiling direction (capability of growing chambers in clock or counterclockwise) from dominantly dextral (DX) to dominantly sinistral (SN) within 400 kyr after the K/X event. The morozovellids crisis might be therefore recognized as the DX morphotypes crisis. Interestingly, our data are in good agreement with the record from the Atlantic Ocean. Quantitative studies performed at Sites 1209-1210 on the coiling direction of *Acarinina coalingensis* and *A. soldadoensis* (the most abundant forms), show that the two morphotypes of these species, differently from *Morozovella*, retained rather equal proportion below and across the EECO.

Searching for the driving factors leading to the recorded foraminiferal response we generated oxygen and carbon stable isotopes on DX and SN morphotypes (or cryptic species) on six *Morozovella* species, *A. coalingensis,* and *A. soldadoensis*. We selected levels below and above the drop in abundance and coiling direction changes.

Our results record generally lower stable carbon isotope signatures for SN morozovellids, thus suggesting reduced dependence on symbiotic relationships and/or slightly deeper habitat. The recorded paleoecology may have enabled SN forms to sustain the EECO stressors. Conversely, acarininids display values that suggest major ecological flexibility that possibly enabled them to proliferate.

Our quantitative abundance analysis and derived stable isotope data allow us to infer new insights on the paleoecology and resilience strategies of PF under the striking global warming conditions of EECO.

# Chronostratigraphic distribution of great white shark teeth in the Plio-Pleistocene Mediterranean Basin

Freschi A.[1] & Cau S.*[2]

[1] Ricercatore indipendente, Piacenza. [2] Ricercatore indipendente, Parma.

*Corresponding author e-mail:* cau.simone2@gmail.com

*Keywords: Carcharodon carcharias*, paleobiology, climate-change.

The presence of *Carcharodon carcharias* (Linnaeus, 1758) teeth in the Plio-Pleistocene fossil record of the Mediterranean Basin is dated from the early Zanclean. However, what the earliest stages of *C. carcharias* Mediterranean colonization were has not yet been clarified because teeth from Zanclean deposits are rare, whereas in the Piacenzian successions the remains are more abundant and widespread. Recent molecular analyses have inferred the formation of the Mediterranean *C. carcharias* population around 3.2 Ma, confirming this scenario (Leone et al., 2020). To improve the understanding of white shark distribution in the Mediterranean, we processed data from 241 fossil teeth collected from a large sample of Mediterranean sites. Based on the most recent and accurate stratigraphic framework of the Plio-Pleistocene, we improved the chronostratigraphic interpretation of these sites and, where possible, we obtained more accurate age dating of white shark occurrences. The largest number of specimens were collected from the Italian peninsula: 42% from Tuscany, 24% from Emilia Romagna, and 11% from Calabria regions. Sites containing white shark teeth appear significantly concentrated in Piacenzian deposits. A decrease in fossil frequency is recorded across the Pliocene-Pleistocene transition. This chronostratigraphic distribution appears similar to that recognized for the mediterranean cetofauna (Dominici et al., 2018; Freschi et al., 2019). The chronostratigraphic distribution of *C. carcharias* suggests a complete paleofaunal turnover with *Otodus megalodon*, a Neogene predator extinct at 3.6 Ma and preferential to warm waters. Currently the white shark shows a preferential distribution in temperate waters and in the Mediterranean the increase dated at 3.2 - 3.0 Ma may be related to Pliocene climate deterioration.

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# The Low-C27r event: a turning point in carbonate cycle dynamics following the Cretaceous/ Paleogene boundary disruption

Galeotti S.[1], Mannucci A.*[1], Reghellin D.[1], Coxall H.[2], Monechi S.[3], Petrizzo M.R.[4], Raffi I.[5] & Skinner L.[6]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Department of Geological Sciences, Stockholm University (Sweden). [3] Dipartimento di Scienze della Terra, Università di Firenze. [4] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [5] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [6] Department of Earth Sciences, University of Cambridge (UK).

*Corresponding author e-mail:* a.mannucci@campus.uniurb.it

*Keywords:* LC27r, global carbon cycle, biological pump.

The mass extinction at the Cretaceous/Paleogene boundary (K/Pg) profoundly altered the global carbon cycle and marine ecosystems, which both took several million years to fully recover. One step of this recovery process is an hyperthermal-like event, coined LC27r, described in the lower part of magnetochron C27r of Atlantic, Pacific and Tethys Ocean sedimentary successions. Here we show that the LC27r was a turning point in the setting of marine planktonic communities, which globally impacted the carbon cycling and climate, by comparing published sedimentary records from Ocean Drilling Program (ODP) Sites 1209 and 1262 and from the Bottaccione section. The LC27r marks the onset of a long-term increase in bulk d$^{13}$C, which in turn increased the surface-benthic Dd$^{13}$C, and benthic foraminifera d$^{18}$O. In addition, sedimentation rates and $CaCO_3$ mass accumulation rates increased, while the proportion of foraminifera over nannofossils preserved in sediments decreased. To reconcile these observations, a major increase in the productivity and relative contribution to sediment of calcareous nannofossils is required. The change to a plankton community more dominated by autotroph nannoplankton at the LC27r strengthen the biological pump and decreased the ratio between particulate inorganic/organic matter fluxes. This may have increased the biological pump efficiency, enhancing atmospheric $CO_2$ drawdown and triggering a long-term climate cooling, at the same time explaining the widening of Dd$^{13}$C.

# High climatic suitability led to prolonged persistence of amphibians in the Italian biogeographic province

Macaluso L.*[1], Carnevale G.[1] & Delfino M.[1-2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Institut Català de Paleontologia «Miquel Crusafont», Universitat Autònoma de Barcelona (Spain).

*Corresponding author e-mail:* loredana.macaluso@unito.it

*Keywords:* extirpation, Neogene, climate change.

It is generally assumed that the three major Mediterranean peninsulas of Europe, the Iberian, the Italian, and the Balkan Peninsula (as well as the adjoining Anatolian Peninsula) played a significant role as biodiversity refugia during the Plio-Pleistocene coolings, but comparative analyses among these three units are far from being exhaustive. The Italian biogeographic province currently has the most diversified amphibian fauna of the Mediterranean Region and hosts the highest number of endemic taxa: the presence of three endemic genera of amphibians (salamanders) is of exceptional relevance. Such high rate of endemization contrasts with the particularly low rate of endemic reptiles, which have no endemic genera. Looking at the fossil record, most reptiles show a pattern of progressive extirpation from the Italian province, whereas this area seemed to have acted as a selective refugium for several amphibian taxa. In fact, Italy hosts the last fossil occurrence in Europe of the giant frog *Latonia*, which went extirpated before the end of the Pliocene in the whole Europe but survived until the Early Pleistocene in central Italy, and of the allocaudate *Albanerpeton*, representative of a salamander-like clade of amphibians that was thought to go extinct in the Late Pliocene, but was found in an Early Pleistocene locality in northern Italy. Moreover, two of the extant endemic amphibian genera (*Salamandrina* and *Speleomantes*) showed a wider distribution in the past – that at least for the former extended from Iberia to Balkans – and are now only present within the limits of the Italian province. The modern occurrences of these genera were herein combined with current climatic data and used to reconstruct their climatic niche through Ecological Niche Modelling methods. Projecting these data on past climatic scenarios (from Late Pliocene to Late Pleistocene), climate was proved as the possible driver leading to extirpation of these genera from most of Europe and to their persistence in the Italian province. This work proves that the Italian peninsula had the potential to act as selective refugium for amphibians, thanks to its suitable climate during the past geological time.

# Evidence for the Carnian Pluvial Episode in Turan Domain, Iran: New insights into depositional and climate evolution of the Aghdarband Basin

Mazaheri-Johari M.*[1], Roghi G.[2], Caggiati M.[1], Kustatscher E.[3-4] & Gianolla P.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Istituto di Geoscienze e Georisorse, CNR, Padova. [3] Department of Earth and Environmental Sciences, Paleontology & Geobiology, Ludwig-Maximilians-Universität München (Germany). [4] SNSB-Bayerische Staatssammlung für Paläontologie und Geologie, München (Germany).

*Corresponding author e-mail:* mzhmni@unife.it

*Keywords:* Aghdarband Basin, Carnian Pluvial Episode, palynology.

Global climate change is still, arguably, the most critical issue facing the world today. Evidence for climate and environmental changes is preserved in a wide range of geological settings from continental to marine environments and is deduced from any natural archive over all timescales. Plant fossils and palynomorph records, as natural archives, are one of the most useful indicators of climate change through time when they are combined with different geological proxy records. The current study discusses plant fossils and palynomorphs recovered from the Upper Triassic successions of the Turan Domain (Aghdarband Basin, NE Iran) and provides novel insights into the depositional and climate evolution of the basin by combining the results of palynology, paleobotany, stratigraphy, and sedimentology. A succession with alluvial facies developed in the early Late Triassic times on volcanoclastic materials in the Aghdarband Basin. It forms the lowermost part of the so-called Miankuhi Formation that lies unconformably upon volcanoclastic sediments of the Sina Formation. Palynological studies revealed diverse components of plant assemblages (sphenophytes, ginkgophytes, conifers, and *incertae sedis*) from the base of the Miankuhi Formation, along with a new macroplant assemblage dominated by roots and vegetative organs of *Neocalamites iranensis*. A rich and diverse palynoflora document wetlands covered with lush vegetation, referring to a warm and rather wet environment. Based on the stratigraphic distribution of the various species, two main sporomorph assemblages are defined for the studied interval, indicating a late Ladinian to Carnian (Julian-Tuvalian) age for the upper Sina and the lowermost Miankuhi formations, respectively. The quantitative composition varies noticeably between the two main palynological assemblages, with a clear shift toward hygrophytic elements in the lowermost part of the Miankuhi Formation (Carnian). The general dominance of hygrophytic elements is also reported from coeval Tethyan successions at the same latitudinal belt and correlates this part of the succession with a record of the Carnian Pluvial Episode (CPE). The evolutionary pattern of the studied successions shows a transition from a deep marine environment to a delta setting in the upper Sina Formation, then an unconformity enhanced by an interval of fluvial deposits with histosol levels in the basal Miankuhi Formation, associated with the hygrophytic palynological assemblages. According to the sedimentary evolution, the unconformity between the Sina and the Miankuhi formations is interpreted as a result of a relative sea-level fall: noteworthy, a significant sea-level drop during the CPE is documented worldwide, and an enhanced erosion can be favoured by fluvial incision of rivers related to the wet climate.

# Enhanced continental weathering in western Tethys during the end-Triassic mass extinction

Onoue T.*[1], Rigo M.[2-3], Jadoul F.[4], Michalík J.[5], Yamashita K.[6], Namiki K.[6], Shirozu H.[7], Yamashita M.[6], Kusaka S.[7] & Soda K.[8]

[1] Department of Earth and Planetary Sciences, Kyushu University, Fukuoka (Japan). [2] Dipartmento di Geoscienze, Università di Padova. [3] Istituto di Geoscienze e Georisorse, CNR, Padova. [4] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [5] Earth Science Institute, Slovak Academy of Sciences, Bratislava (Slovakia). [6] Department of Earth and Environmental Sciences, Kumamoto University (Japan). [7] Graduate School of Natural Science and Technology, Okayama University (Japan). [8] School of Marine Science and Technology, Tokai University, Shizuoka (Japan). [9] Center for Advanced Marine Core Research, Kochi University (Japan).

*Corresponding author e-mail:* onoue.tetsuji.464@m.kyushu-u.ac.jp

*Keywords:* Sr isotopes, C isotopes, Triassic-Jurassic boundary.

Widespread eruptions of flood basalts in the Central Atlantic Magmatic Province (CAMP) are thought to have triggered the end-Triassic mass extinction (ETE). Although previous studies of shallow marine deposits from western Tethys suggest that deforestation and catastrophic soil loss occurred during the CAMP volcanism and ETE interval, the intensity and timing of continental weathering in the western Tethys Ocean remain unclear. Here we present strontium and carbon isotope data, as well as principal component analysis (PCA) of major element contents, for the Rhaetian limestone successions in Slovakia and Italy, to develop a continental weathering record in the western Tethys during the ETE event. The studied section in the Western Carpathians, Slovakia consists of a shallow marine carbonate sequence of the Rhaetian Fatra Formation and overlying Hettangian Kopieniec Formation (Michalík et al., 2010). The Rhaetian-Hattangian succession of the Bergamasc Alps (western Southern Alps, Italy) comprises the Calcari di Zu Formation and the unconformably overlying Malanotte Formation (Zaffani et al., 2018).

Two negative carbon isotope excursions (NCIEs) occur in the uppermost Fatra Formation in Slovakia. These two NCIEs can be correlated with the "precursor" and "initial" NCIEs reported for the Calcari di Zu Formation during the latest Rhaetian (Zaffani et al., 2018). Strontium isotope analysis of the limestones revealed an abrupt increase in Sr isotope ratios between the precursor and initial NCIEs, which indicates that continental weathering of the hinterland increased rapidly in the latest Rhaetian. PCA of the major element compositions of limestone samples also revealed that intense chemical weathering of the hinterland was accelerated after the precursor NCIE, the timing of which overlaps with the emplacement of the CAMP. The release of volcanic and contact metamorphism-related thermogenic C ($CO_2$) and/or volcanic $SO_2$ emissions from the CAMP may have triggered the extreme continental weathering between the precursor and initial NCIEs. Our geochemical data and PCA also suggest that the marine environments in European basins may have developed an oxygen minimum zone during the increase in continental weathering during the latest Rhaetian, and these environmental changes may have had an important role in the marine ETE event.

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# Biodiversity patterns of Neotethys shallow-water communities (larger foraminifera and scleractinian corals) during the climate fluctuations of Paleocene and Eocene

Papazzoni C.A.*, Benedetti A. & Bosellini F.R.

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* papazzoni@unimore.it

*Keywords:* Paleogene, biodiversity, climate changes.

We performed a biodiversity analysis on two large databases obtained by means of a comprehensive revision of the literature regarding two groups of shallow-water organisms, namely larger foraminifera (LF) and scleractinian reef corals (SC), in order to test the response of these organisms to major global climate changes. The selected time interval covers the Paleocene and the Eocene, because for those epochs the available literature for LF and SC is abundant and allows to work at both genus and species level.

The temporal resolution of collected data for LF allows to distinguish different parts of the same stage, whereas for SC we can use only the stages as minimum time unit.

The results for LF show that, following the crisis at the K/Pg boundary, a rapid evolutionary radiation occurred at the genus rank during the late Danian, involving mainly rotallids, miscellaneids, and soritids. Then, another major change corresponds to the PETM event, involving a sudden species diversification of alveolinids and nummulitids. The maximum of 180-200 species roughly corresponding to the EECO event is reconsidered, because by normalizing data per Ma we can observe a real decrease in diversity in the same period. A similar pattern is observed for the MECO as well. Moreover, after these events a new increase in diversity is recorded, as highlighted by the post-PETM biozone SBZ 5 and the post EECO SBZ 12.

As regards SC, at first it seems that there is an increasing diversity from the Paleocene up to the Ypresian. However, after normalization for Ma, we can observe a real increase from Danian to Thanetian, followed by a general decline of biodiversity during Ypresian and Lutetian, and eventually a new increase in species up to the Priabonian.

The general pattern is therefore surprisingly similar for LF and SC, even if their skeletons with different mineralogical composition (calcitic for LF and aragonitic for SC) should suggest they do not react in the same way to the climatic variations. The parallel changes in the $CO_2$ content of the atmosphere and hence the acidification of the oceans apparently acted with similar (negative) effects both on calcitic and aragonitic frameworks.

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# The Early Pliocene birds of prey from Langebaanweg, south-western Cape Province, South Africa

Pavia M.*[1], Delfino M.[1-2], Govender R.[3], Haarhoff P.[4], Matthiews T.[3] & Cohen B.[5]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Institut Català de Paleontologia «Miquel Crusafont», Universitat Autònoma de Barcelona (Spain). [3] Iziko South African Museum, Cape Town (South Africa). [4] West Coast Fossil Park, Langebaanweg (South Africa). [5] The National Museum, Bloemfontein (South Africa).

*Corresponding author e-mail:* marco.pavia@unito.it

*Keywords:* birds, Pliocene, South Africa.

The fossiliferous Upper Varswater Formation at Langebaanweg (South Africa) produced one of the largest pre-Pleistocene bird bone accumulations worldwide, which is still insufficiently known despite the numerous studies reported by Manegold and cohautors. According to latest estimates, more than 35 bird families with around 100 species have been recorded, mostly representing the earliest family records for the African continent. The study of the nocturnal birds of prey (Strigiformes) revealed the presence of five species including the two extinct species *Tyto richae* and *Athene inexpectata*, the latter representing the oldest record of the genus worldwide and the first evidence of the genus south of the Sahara. The analysis of the diurnal bird of prey (Accipitriformes and Falconiformes) shows the presence of a vulture (*Aegypius varswaterensis*), two species of eagle (*Aquila*), two species of hawk (*Accipiter*), one species of kite (*Milvus*) and two species of falcon (*Falco*), all of them representing taxa new for the science and still to be described. This analysis allows to know in detail the composition of the guilds of the birds of prey, nocturnal and diurnal, which are relatively diverse and shed new light on the palaeoenvironment and palaeoecology of the site. From the palaeobiogeographical point of view, we confirm that the Early Pliocene African avifauna is characterized by extinct forms of Palaearctic affinities, as none of the taxa detected at Langebaanweg so far belong to African endemic lineages.

In addition, these results confirm the great importance of Langebaanweg as an archive to understand the palaeobiodiversity of South Africa during the Early Pliocene, just before the beginning of the hominin evolution in this part of the African continent.

# Mediterranean calcareous red algae as seawater pH recorders

Piazza G.*[1-2], Paredes E.[2], Bracchi V.A.[1], Pena L. D.[2], Hall-Spencer J.[3], Ferrara C.[4], Cacho I.[2] & Basso D.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra e Consorzio Nazionale Interuniversitario per le Scienze del Mare, Università di Milano-Bicocca. [2] Department of Earth and Ocean Dynamics, University of Barcelona (Spain).
[3] School of Biological and Marine Sciences, University of Plymouth (UK).
[4] Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca.

*Corresponding author e-mail:* g.piazza15@campus.unimib.it

*Keywords:* boron isotopes, coralline algae, paleoclimate.

Calcareous red algae have calcified cell walls constituted by high-Mg calcite or aragonite. They are considered suitable paleoclimate archives due to their worldwide distribution and their longevity through indeterminate growth (Kamenos et al., 2008). Boron isotopes ($\delta^{11}B$) measured in their calcified thallus are considered a pH proxy (Hemming & Hanson, 1992). In seawater, boron occurs as boric acid and borate ion. Both species are enriched in $^{11}B$ as pH increases, with boric acid characterized by an enrichment factor of 27‰ compared to borate (Dickson, 1990). According to the B-pH proxy theory, borate is exclusively incorporated in the mineral lattice. Therefore, if we measure $\delta^{11}B$ in carbonates, we can derive the seawater pH at the time of precipitation (Hemming & Hanson, 1992). Literature data on $\delta^{11}B$ in calcareous red algae are sparse, and the mechanisms of boron incorporation are still poorly known (Piazza et al., 2022).

We measured boron isotopes on a broad collection of Mediterranean calcareous red algal species collected across the Basin by the Research Group in Paleontology and Geobiology of the University of Milano-Bicocca (Italy), including hydrothermal sites in Ischia (Italy) and Methana (Greece). Environmental data characterizing the seawater during the algal growth were extracted from CMEMS products (Marine Copernicus Service Information), or provided by literature (Baggini et al., 2014; Foo et al., 2018). Analyses were performed by MC-ICP-MS at the CCiTUB (Scientific and Technological Centres of the University of Barcelona, Spain) and pH reconstructions derived from $\delta^{11}B$ were achieved by applying species-specific calibrations available in literature (Hönisch et al., 2019).

Boron isotopes ranged from 20.07 ± 0.51‰ to 27.92 ± 0.86‰ over a natural pH range from 6.80 ± 0.43 to 8.13 ± 0.07 units. Results suggest a mineralogical control over $\delta^{11}B$, with calcitic species more enriched in $^{11}B$ compared to aragonite. Differences among species grown in the same environment also suggest a specific boron incorporation, actively controlled by the algae. Reconstructions of seawater pH from $\delta^{11}B$ in algae collected in naturally acidified environments, near hydrothermal vents, revealed data within the standard deviations of the actual pH values measured in the sites. Particularly, a multispecies calibration based on data collected from cultured corallines from literature allowed the best accordance in pH between reconstructions and real values.

We obtained a significant dataset of $\delta^{11}B$ data in Mediterranean calcareous red algae, enhancing the knowledge of boron incorporation in this taxonomic group. Moreover, we produced encouraging results for the application of calcareous red algae in pH reconstructions. The proposed calculations for multispecies calibration could potentially be applied in the future to infer the paleo-pH using fossil species.

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# What happened at the end of the Messinian salinity crisis? A high resolution multiproxy approach to the Miocene-Pliocene transition in the Northern Mediterranean

Pilade F.*[1], Dela Pierre F.[1], Natalicchio M.[1], VasilievI.[2], Birgel D.[3], Mancini A.M.[1], Lozar F.[1] & Gennari R.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Senckenberg Biodiversity and Climate Research Centre, Frankfurt am Main (Germany). [3] Institut für Geologie, Centrum für Erdsystemforschung und Nachhaltigkeit, Universität Hamburg (Germany).

*Corresponding author e-mail:* francesco.pilade@unito.it

*Keywords:* Miocene-Pliocene transition, molecular fossils, Messinian Salinity Crisis.

The Miocene-Pliocene transition (MPT) in the Mediterranean area represents one of the unsolved geological riddles of the Neogene. The MPT coincides with the end of the Messinian salinity crisis (MSC), an event that led to the deposition of a huge volume of evaporite on the Mediterranean seafloor. The final stage of the MSC started at ~5.53 Ma and corresponds to the "Lago-Mare ʻʻ phase, characterised by the occurrence of brackish shallow water ostracods of Parathethyan origin. The "Lago-Mare ʻʻ deposits are sharply overlain by Zanclean (earliest Pliocene) marine sediments, the base of which is astrocronologically dated at 5.33 Ma.

The interpretation of the rapid transition from shallow water brackish conditions in the Messinian to open marine environments in the Pliocene is debated and two scenarios were proposed: a) the catastrophic flooding of the Mediterranean sub-basins, previously disconnected from the Atlantic Ocean and one from each other. b) The gradual refilling of the Mediterranean started during the Lago-Mare phase and continued in the early Zanclean.

To reconstruct what happened at the end of the MSC, we analysed six sections along a west-east transect from the Northern Apennine foredeep, using an integrated approach that merge the traditional palaeontological, stratigraphic, geochemical, and petrographic data with the analysis of molecular fossils (lipid biomarkers).

The top of the Messinian is marked by a bioturbated dark layer in all the studied sections. The presence at its top of glauconite and of firm ground burrows of the Glossifungites ichnofacies filled with Zanclean sediments, suggest starved sedimentary conditions with consequent partial lithification of the sea floor during the earliest Zanclean. In addition, benthic foraminifera indicate initial dysoxic conditions followed by an increase of bottom oxygen content from the basal Pliocene.

The biomarkers inventory suggests a sharp environmental change across the MPT. The presence of the pentacyclic triterpenoid tetrahymanol only in the Miocene sediments reflect the intense stratification of the water column during the Lago Mare phase and its sudden disruption at the base of the Pliocene; the early Zanclean deposits are characterised by high contents of long chain n-alkanes (LCalk) sourced by terrestrial higher plants and by the scarcity of Glycerol Dialkyl Glycerol Tetraethers (GDGTs) of both marine and terrestrial origin. Moreover, evaluation of the Alkenone unsaturation indices (Uk37) from the Maccarone section allowed the reconstruction of Sea surface temperature across the MPT.

Additional compound-specific isotope analyses on 2H and 13C on Alkenones, GDGTs and LCalk are planned in the near future, especially for the reconstruction of the still enigmatic Lago Mare paleoenvironmental conditions. Finally, this study highlights that a multiproxy approach is absolutely needed to unravel the complex and ultra-rapid environmental changes that took place at the MPT.

# Biotic extinction at the Norian/Rhaetian boundary (Upper Triassic): geochemical and isotope evidence of a previously unrecognised global event

Rigo M.*[1], Onoue T.[2], Sato H.[1-2], Tomimatsu Y.[2], Soda K.[3], Godfrey L.[4], Katz M.[5], Campbell H.[6], Tackett L.[7], Golding M.[8], Lei J.[9], Husson J.[9], Maron M.[10], Satolli S.[10], Zaffani M.[11], Concheri G.[11], Bertinelli A.[12], Chiari M.[13] & Tanner L.[14]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Department of Earth and Planetary Sciences, Kyushu University, Fukuoka (Japan). [3] Center for Advanced Marine Core Research, Kochi University, Nankoku (Japan). [4] Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ (USA). [5] Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY (USA). [6] GNS Science, Wellington (New Zealand). [7] Department of Geosciences, North Dakota State University, Fargo, ND (USA). [8] Geological Survey of Canada, Vancouver (Canada). [9] School of Earth and Ocean Sciences, University of Victoria (Canada). [10] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [11] Dipartimento di Agronomia, Animali, Alimenti, Risorse naturali e Ambiente, Università di Padova. [12] Diparitmento di Fisica e Geologia, Università di Perugia. [13] Istituto di Geoscienze e Georisorse, CNR, Padova. [14] Department of Biological and Environmental Sciences, Le Moyne College, Syracuse, NY (USA).

*Corresponding author e-mail:* manuel.rigo@unipd.it

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The latest Triassic was an interval of prolonged biotic turnovers culminating in the so-called End-Triassic Extinction. We attribute onset of this interval of declining diversity to unusually high volcanic activity at the Norian/Rhaetian boundary (NRB) that may have initiated the stepwise extinctions of the Late Triassic (Rigo et al., 2020). We correlate the initiation of a rapid decline in $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$ seawater values (Callegaro et al., 2012; Nozaki et al., 2019) to a negative organic carbon isotope shift, which we attribute to volcanogenic $CO_2$ outgassing to the ocean-atmosphere system by the Angayucham large igneous province (LIP). By studying the geochemical and isotope composition of bulk rocks from different sections located at different latitudes, sides of the Pangea continent and Hemispheres, we documented an accelerated chemical weathering due to global warming by elevated $CO_2$, which enhanced nutrient discharge to the oceans and thus greatly increased biological productivity; higher export production and oxidation of organic matter led to oceanic dysoxia to anoxia at the NRB. Biotic consequences of these climatic and environmental changes include severe extinctions of several fossil groups, such as ammonoids, bivalves and radiolarians, as has been documented worldwide (Rigo et al., 2020).

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# The Plio-Pleistocene section of Baia Massolivieri (Syracuse, South-Eastern Sicily): palaeclimatic and paleoenvironmental insights

Sanfilippo R.*[1-2], Reitano A.[3-4], Insacco G.[3], Rosso A.[1-2] & Minniti G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Museo Civico di Storia Naturale, Comiso (RG). [4] Collaboratore con Museo di Paleontologia, Università di Catania.

*Corresponding author e-mail:* sanfiros@unict.it

*Keywords:* Boreal guests, Hyblean plateau, Neogene.

Highly fossiliferous Plio-Pleistocene sediments rich in paleoclimatic proxies fill a graben delimited by sin-sedimentary faults at Baia Massolivieri, Peninsula of Maddalena (south-eastern Sicily). The sedimentary succession is ca. 7 m thick and comprises basal Pliocene whitish marls rich in planktonic foraminifers, containing sparse joined valves of oysters (*Neopycnodonte cochlear*) and brachiopods (*Terebratula terebratula*), followed by a 20 cm-thick layer of highly fossiliferous Gelasian yellow silts, with *in situ* shells of *Amusium cristatum*, *T. terebratula* and *T. scillae*, bones of the pygmy right whale *Caperea marginata,* plus more than thirty species among bryozoans, bivalves, serpulids, echinoids, gastropods, crustaceans among which *Coronula*. Teeth of Osteichthyes together with teeth and vertebrae of *Carcharodon carcharias* also occur with the last species here first recorded from Gelasian sediments of Sicily. A 10 cm thick, tightly cemented sandy layer with abundant *A. islandica* moulds (Calabrian) follows upwards. Over 1.5 meters of biogenic sands with *Ophiomorpha* traces and invertebrate remains among which bryozoans (*Hormera frondiculata, Idmidronea triforis* and *Reteporella* spp.) and serpulids (with abundant *Ditrupa arietina*) follow upwards. The succession ends with 2.5 m thick calcarenites rich in free calcareous algae (maerl facies), bivalves (*Pecten jacobaeus*, *Glycymeris* sp.) and bryozoans.

Apart from the Pliocene marls indicative of deep-sea settings, fossils and sedimentological features of the Pleistocene succession suggest mid-shelf paleoenvironments. Particularly, the yellow silts and the *Arctica*-bearing layer denote lower hydrodynamic conditions compared to the overlaying sands containing a Coastal Detritic paleobiocenosis.

A cold paleoclimate is suggested by the presence of the Boreal Guest *A. islandica* and other cold-taxa like the dwarf whale *C. marginata* (Tsai et al., 2017), as well as giant cold ecophenotype of the serpulid *Spirobranchus triqueter*.

The finding of small-sized teeth of the extinct shark *Otodus megalodon* from Pliocene sediments close to the studied section, leads to hypothesize a reduction in size of this apical predator as a response of selective spatial and ecological pressures and climatic deterioration in the Pliocene Mediterranean before its extinction. This opens new research on interspecific competition between the Megatooth survivor and the white shark conditioned by the events that occurred in a key interval of the history of the Mediterranean Sea, that is around the turning point between warm Pliocene and cold Pleistocene.

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# Changes in terrestrial ecosystems and mammalian communities during the Pleistocene of Italy

Sardella R.*[1], Conti J.[2], Iannucci A.[1], Iurino D.A.[1], Mecozzi B.[1], Moscarella A.[1] & Strani F.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Polo Museale, Sapienza Università di Roma.

*Corresponding author e-mail:* raffaele.sardella@uniroma1.it

*Keywords:* Quaternary, Europe, large mammals.

The Italian Peninsula, thanks to its natural position as a biogeographic crossroad and rich fossil record, represents a crucial area for investigating the response of Pleistocene ecosystems to recurrent climatic and environmental changes occurred during this period, in turn providing perspective on how biotas could respond to ongoing and future perturbations. Mammalian faunas are especially important because they are often the closest proxy to the "human scale" of perception of these dynamics, which is relevant for forecasting future scenarios as well as for providing insights into the paleoecological context in which *Homo* lived. Each mammal species can differently respond to ecological changing (e.g., shifts in geographic distribution, extinction, evolution, ecomorphological adaptations), but there are certain (bio-)events that epitomize time of substantial faunal turnover, related to important environmental changes. The giant hyena *Pachycrocuta brevirostris* disappeared from Europe ~0.8 Ma, apparently not able to cope with the mutated environmental instability connected to the Early–Middle Pleistocene Transition (EMPT), while other more adaptable species arrived (Iannucci et al., 2021). The increase in the cyclicity of glacial-integlacial oscillations occurred with the EMPT had indeed a profound impact on mammalian faunas. The consolidation of climate cycles with an almost-100 kyr periodicity is marked by the Mid-Brunhes Event at the MIS 12-MIS 11 transition, roughly concurrent with different significant bioevents, including the appearance of the wolf, *Canis lupus*, in Europe (Iurino et al., 2022).

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Iurino D.A., Mecozzi B., Iannucci A., Moscarella A., Strani F., Bona F., Gaeta M. & Sardella R. (2022) - A Middle Pleistocene wolf from central Italy provides insights on the first occurrence of *Canis lupus* in Europe. Sci. Rep., 12, 2882.

# Palaeoenvironmental evolution of the late Middle-Late Pleistocene Marano Equo Basin (Latium, central Apennines)

Scaccia D.*[1], Molin P.[1], Soligo M.[1], Cosentino D.[1], Esu D.[2] & Gliozzi E.[1]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* david.scaccia@uniroma3.it

*Keywords:* ostracods, molluscs, springs.

In the central Apennines, the intermontane basins have been studied not only to reveal the evolution of the chain, but also to obtain data on paleoenvironment and on climatic variability. In this respect, the Marano Equo depression in the Aniene River valley (Latium, central Italy) is a good example. Here the bedrock is made up of Meso-Cenozoic limestones, Miocene marls, and syn-orogenic pelitic-arenaceous rocks (Upper Miocene).

The Marano Equo depression is filled by a sedimentary succession more than 150 m thick. The sediments and the paleontological content of the cores of eight continuous boreholes were analysed. The results indicate that the core sediments can be referred to braided plain deposits and calcareous tufa. The fluvial deposits (conglomerates, sands, silts, and clays) point to varying fluvial energy, whereas the calcareous tufa locally record the presence of springs.

Five samples of calcareous tufa and sand have been dated by the disequilibrium method in the Uranium series. The results, ranging from 109±3 kyr to >350 kyr, allow to refer the sediments to at least the Middle-Upper Pleistocene.

On three sediment cores, molluscs and ostracods were studied. Among the molluscs, the most abundant were terrestrial species, adapted to dry or humid open environments (*Vallonia pulchella*, *Vertigo pygmaea*, *Vitrea contracta*, *Vertigo angustior*, *Carychium minimum* and *Oxyloma elegans*). The few freshwater species (*Galba truncatula*, *Pisidium personatum*) point to marshy grasslands or ephemeral ponds.

Among ostracods, eighteen species were identified. The first group (*Eucypris pigra*, *Herpetocypris brevicaudata*, *Heterocypris reptans*, *Ilyocypris bradyi*, *Ilyocypris inermis*, *Potamocypris zschokkei*, *Psychrodromus olivaceous* and *Scottia pseudobrowniana*) inhabits spring habitats of different kind. The second group (*Candonopsis scourfieldi*, *Darwinula stevensoni*, *Heterocypris incongruens*, *Neglecandona neglecta*, and *Pseudocandona albicans*) typically lives in ponds, lakes, and springs. The third group (*Cyclocypris laevis*, *Cypria ophtalmica*, and *Limnocythere inopinata*) tolerates a wide range of environmental conditions (stagnant and flowing waterbodies). The fourth group (*Candonopsis kingsleii* and *Dolerocypris fasciata*) lives in the littoral zone of lakes, in ponds and swamps.

The application of the multivariate analysis (Cluster Analysis and Principal Component Analysis) on the ostracod assemblages indicates that the Marano Equo braided plain was partially occupied by ponds fed by groundwater, floods, and springs.

The MOTR analysis performed on ostracods indicates an air temperature range similar to the present day. However, in one core two samples suggest climatic conditions cooler than today. In addition, the discovery of several terrestrial molluscs indicates the momentarily lack of water, confirmed by the absence of ostracods.

Finally, the ostracod assemblages recovered at Marano Equo represent one of the few fossil records of cold spring paleocommunity.

# Ecological resilience documented in the Adriatic fossil record

Scarponi D.*[1], Nawrot R.[2], Azzarone M.[1], Pellegrini C.[3], Gamberi F.[3], Trincardi F.[3] & Kowalewski M.[4]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Department of Palaeontology, University of Vienna (Austria). [3] Istituto di Scienze Marine, CNR, Bologna. [4] Florida Museum of Natural History, University of Florida, Gainesville, FL (USA).

*Corresponding author e-mail:* daniele.scarponi@unibo.it

*Keywords:* climate change, paleobiology, Mediterranean.

Climate changes present increasing threats to marine ecosystems and the ecological consequences of these changes remain poorly understood despite their biological and economic importance (Hoegh-Guldberg & Bruno 2010). Recent sedimentary successions are crucial for acquiring a historical perspective on species dynamics and/or community assembly of modern ecosystems that have been shaped by past climatic oscillations (e.g., Cheli et al., 2021; Huntley & Scarponi, 2021). This research represents the first long term ($10^5$ yr) study on biotic dynamics (based on macrobenthic invertebrates) in the Mediterranean Basin. It documents responses of nearshore mollusk assemblages to long-term climate shifts (glacial-interglacial) and sea-level changes by using 223 samples (approximately 71,300 specimens) retrieved from latest Quaternary sediment cores of the Adriatic coastal systems. The results of comparative quantitative analyses reveal a remarkably resilient (over persistent or stochastic) behavior of nearshore mollusk assemblages to major climate fluctuations that took place in the Adriatic Sea over the last 125 thousand years. Marine ecosystems of the last interglacial reassembled again in the Holocene (with near-perfect accuracy) after the last glacial phase, a period of time characterized by substantially different nearshore mollusk associations. These shifts point to a climate-driven habitat filtering modulated by dispersal processes. The resilient response of the mollusk assemblages to past climate changes suggests that Adriatic nearshore benthic ecosystem may be buffered, to some extent, against future global environmental changes. Over the last century, however, pollution, eutrophication, trawling, and invasive species have been affecting coastal ecosystems and are shifting coastal ecosystems into novel system states far outside the range of natural variability archived in the fossil record.

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# Paleoceanographic dynamics in the "41 ka world" off Southern Iberia (IODP Site U1387) based on coccolithophore assemblages

Trotta S.*[1], Marino M.[1], Voelker A.[2-3], Rodrigues T.[2-3], Flores J.A.[4], Maiorano P.[1], Girone A.[1], Addante M.[1] & Balestra B.[5-6]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Instituto Português do Mar e da Atmosfera, Divisão de Geologia e Georecursos Marinhos, Alges (Portugal). [3] Centro de Ciências do Mar, Universidade do Algarve, Faro (Portugal). [4] Department of Geology, Universidad de Salamanca (Spain). [5] American University. Environmental Science Department, Washington, DC (USA). [6] National Museum of Natural History. Smithsonian, Paleobiology Department. Washington, DC (USA).

*Corresponding author e-mail:* samanta.trotta@uniba.it

*Keywords:* Early Pleistocene, coccolithophores, Gulf of Cadiz.

To better understand the paleoceanographic frame in the Early Pleistocene interval ("41 ka world"), high temporal resolution analyses (300 years) on coccolithophore assemblages through MIS 48-45 were carried out at IODP Site U1387, recovered in the Gulf of Cadiz (GC). The abundance fluctuations of key taxa, such as *Gephyrocapsa caribbeanica*, *Coccolithus pelagicus* ssp. *pelagicus*, warm water taxa, and large *Gephyrocapsa* (> 5.5 µm), allowed the recognition of glacial (MIS 48-46) and interglacial (MIS 47-45) phases, in agreement with $\delta^{18}O_{G.bulloides}$ curve pattern at the study site, reflecting the southward/northward migration of the Portugal current/Iberian Poleward Currents, respectively. Temperature and productivity were the environmental factors influencing the taxonomic composition of coccolithophore assemblages through the studied interval. Short-term increases of *C. pel. pelagicus* during glacial phases pointed out to the arrival of polar meltwater also evidencing a millennial-scale climatic variability during the Early Pleistocene. The productivity increases during glacial phases were related to enhanced northerly wind intensity, leading to surface water mixing and improved nutrient availability, while productivity increases during interglacial phases occurred during insolation maxima/precession minima, which promoted an increase in rainfall and river run-off, and favored enhanced riverine nutrient supply. This last environmental condition co-occurred with sapropel deposition in the eastern Mediterranean Sea supporting the orbitally-controlled higher precipitation and similar climatic conditions at the west and east of Gibraltar Strait during the Early Pleistocene, as already observed in the Middle Pleistocene intervals (Voelker et al., 2015). The correlation between the insolation curve at the same latitude of IODP Site U1387 (36° N) and coccolithophore productivity revealed that the latter followed seasonal and regional insolation forcing, increasing when insolation maxima occurred in spring/summer or autumn during interglacial phases, and in summer or autumn during glacial phases, in agreement with modern conditions in the GC (Lévy et al., 2005).

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# Brachiopods from the Upper Permian of Central Iran: shell microstructure and isotopic signature as archives of global changes in the geological past

Viaretti M.*, Crippa G. & Angiolini L.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* marco.viaretti@unimi.it

*Keywords:* biotic change, microstructure, brachiopods.

Studies on recent brachiopods indicate that they respond to environmental perturbations modifying calcification and growth. This was observed also in specific time intervals of the geological past, characterized by extreme environmental perturbations, as the latest Permian (Garbelli et al., 2017). During this interval, Siberian Traps $CO_2$ and $CH_4$ volcanic emissions caused global warming and oceanic acidification leading to the severest mass extinction of the Phanerozoic (e.g., Dal Corso et al., 2022). The Late Permian thus represents a natural laboratory to understand the responses of benthic species to extreme warming and acidification in the long term (4 m.y.).

In this contribution, we focus on shell microstructural variations of brachiopods prior to the mass extinction, presenting microstructural data and the oxygen and carbon isotope composition of brachiopod shells coming from the Permian-Triassic section of Abadeh, central Iran (Viaretti et al., 2021). The brachiopods were collected from the Wuchiapingian Hambast Formation, from 17 fossiliferous levels. The preservation of brachiopod specimens is generally poor; however, some shells still preserve pristine portions. We selected specimens belonging to the orders Productida and Athyridida to compare taxa with laminar and fibrous secondary layer, besides the columnar tertiary layer. Among taxa with a laminar secondary layer, *Araxilevis intermedius*, *Leptodus nobilis*, *Spinomarginifera iranica* and *Spinomarginifera* sp. were analyzed. For those with a fibrous secondary layer, *Araxathyris bruntoni*, ?*Rectambitus* sp., *Transcaucasathyris araxensis*, *T. kandevani* and *T. lata* were examined. The shell microstructure of the selected taxa was analyzed using SEM; cathodoluminescence microscopy was performed to assess the shell preservation before undertaking stable isotope analyses.

This study, besides providing data on the different alteration patterns of the brachiopod shell microstructural types, allows to constrain the background conditions that anticipate the end-Permian mass extinction.

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# S27.

# Earth's carbon cycle in active magmatic-tectonic systems and in the mantle: from production to transport, fixation and outgassing


*Conveners & Chairpersons*

*Rosario Esposito (University of Milano - Bicocca)*

*Chiara Groppo (University of Torino)*

*Andrea Rizzo (INGV)*

*Andres Sandoval-Velasquez (University of Palermo)*

*Azzurra Zucchini (University of Perugia)*

# Emissions of carbon dioxide, methane and heat in the geothermal area of Monterotondo Marittimo (Italy)

Ariano A.*[1], Frondini F.[1], Cardellini C.[1], Chiodini G.[2], Ricci L.[1], Vetuschi Zuccolini M.[3] & Virgili G.[4]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] INGV, Bologna. [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [4] Thearen s.r.l., Torino

*Corresponding author e-mail:* arianoalessandra.95@gmail.com

*Keywords:* geothermal system, carbon dioxide, geothermics.

This work is part of a larger study aimed at investigating the relationships between carbon emissions ($CO_2$ and $CH_4$) and heat from geothermal systems in the Larderello-Travale area. The study area, which roughly corresponds to the Biancane Geopark, one km north from Monterotondo Marittimo, is located in the southernmost part of the Larderello-Travale system (Tuscany, Italy), a large-scale steam dominated geothermal system with reservoir temperatures that can exceed 350°C (Bellani et al., 2004). The specific objective of this study is to analyze the distributions of carbon dioxide and methane soil fluxes and the distribution of soil temperatures of the area. More than three hundred $CO_2$ and $CH_4$ flux measurements have been performed using the accumulation chamber method. The soil temperature was also measured at each measuring station. $CO_2$ fluxes range from 0.1 g $m^2$ $d^{-1}$ to about 20000 g $m^2$ $d^{-1}$ , while $CH_4$ fluxes vary between 0 and 637 g $m^2$ $d^{-1}$. Both variables follow a bimodal distribution with (i) a background population characterised by an average $CO_2$ fluxes of 14 g $m^2$ $d^{-1}$ and methane fluxes often below the detection limit, and (ii) an anomalous population with an average $CO_2$ flux of about 1200 g $m^2$ $d^{-1}$ and an average $CH_4$ fluxes of 87 g $m^2$ $d^{-1}$. The areas, characterised by the presence of anomalous carbon dioxide and methane fluxes, show also a strong soil temperature anomaly (reaching values close to 100°C), suggesting that soil degassing is accompanied by a significant process of steam condensation. In the anomalous areas, the $CO_2/CH_4$ ratios by weight vary between 4.3 x $10^{-4}$ to 9.3 x $10^{-2}$ and fall in the range of variation observed for the geothermal fluids of the Larderello-Travale region (Truesdell & Nehring, 1978; Chiodini et al., 1991; Chiodini & Marini, 1998).

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# Anthropogenic-scale $CO_2$ emissions from the Central Atlantic Magmatic Province behind the end-Triassic crisis

Capriolo M.*[1], Mills B.J.W.[2], Newton R.J.[2], Dal Corso J.[3], Dunhill A.M.[2], Wignall P.B.[2] & Marzoli A.[4]

[1] Centre for Earth Evolution and Dynamics, University of Oslo (Norway). [2] School of Earth and Environment, University of Leeds (UK). [3] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan (China). [4] Dipartimento di Territorio e sistemi agro-forestali, Università di Padova.

*Corresponding author e-mail:* manfredo.capriolo@geo.uio.no

*Keywords:* $CO_2$, CAMP, palaeoclimatic modelling.

The Central Atlantic Magmatic Province (CAMP) is among the most voluminous Large Igneous Provinces and its activity was synchronous with the end-Triassic mass extinction. The investigation of melt and fluid inclusions within both effusive and intrusive CAMP rocks revealed the emission of abundant C volatiles, especially $CO_2$ from volcanic degassing and $CH_4$ from magma–sediment interaction (Capriolo et al., 2020; 2021). Whereas the $CH_4$ emissions may be poorly constrained during the long-lived intrusive activity of CAMP, the $CO_2$ emissions may be well constrained to the short-lived pulses of the different volcanic phases of CAMP. The first and main volcanic phase of CAMP (201.6-201.5 Ma), synchronous with the onset of the main extinction phase, was employed in a biogeochemical box model for C cycle to reconstruct the effects of rapid and massive $CO_2$ emissions from CAMP volcanism (Capriolo et al., 2022). The geological constraints on time and volumes for the reconstructed pulses of the first volcanic phase of CAMP highlighted a clear similarity with the current anthropogenic emissions, in the timeframe of 100s years. Positive feedback phenomena may be invoked to explain the observed C isotope excursions at the end-Triassic. However, this palaeoclimatic model revealed that the intense and pulsed volcanic activity of CAMP alone may have caused repeated temperature increases up to 5°C (i.e., global warming) and pH drops of about 0.2 log units (i.e., ocean acidification), implying a severe impact on biota. Brief and massive volcanic $CO_2$ emissions from CAMP affected the end-Triassic climate and environment at a global scale, and the similarity between a single CAMP pulse and total anthropogenic emissions hints new scenarios for the interpretation of climatic and environmental changes, especially for Earth's evolution.

Capriolo M., Marzoli A., Aradi L.E., Ackerson M.R., Bartoli O., Callegaro S., Dal Corso J., Ernesto M., Gouvêa Vasconcellos E.M., De Min A., Newton R.J. & Szabó Cs. (2021) - Massive methane fluxing from magma-sediment interaction in the end-Triassic Central Atlantic Magmatic Province. Nat. Commun., 12, 5534.

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# $CO_2$ storage and migration in the sub-continental lithospheric mantle: clues from Antarctica ultramafic xenoliths

Casetta F.*[1], Faccini B.[2], Ntaflos T.[1], Abart R.[1], Lanzafame G.[3], Faccincani L.[2], Mancini L.[4-5], Giacomoni P.P.[2] & Coltorti M.[2-6]

[1] Department of Lithospheric Research, University of Vienna (Austria). [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [4] Elettra-Sincrotrone Trieste. [5] Lund Institute for advanced Neutron and X-ray Science, Lund (Sweden). [6] INGV, Palermo.

*Corresponding author e-mail:* federico.casetta@univie.ac.at

*Keywords:* $CO_2$ storage, lithospheric mantle, Antarctica mantle xenoliths.

The volatiles cycle in between the Earth's surface and its deep portions is both trigger and effect of the main geodynamic events. In the last years, many studies modelled the amount of volatiles, mainly C-O-H species, sulphur and halogens, that can be stored in the lithosphere and asthenosphere. However, the extent and modality by which these elements can be retained or migrate through the mantle, and the likely links to partial melting and metasomatic/refertilization processes, are still poorly constrained. In order to understand how, where and when $CO_2$ is stored or migrate through the mantle, we investigated ultramafic xenoliths from northern Victoria Land (Antarctica) by combining "conventional" petrology with the measurements of $CO_2$ trapped in bulk rock- and mineral-hosted fluid inclusions (FI), and 3D textural and volumetric characterization of intra- and inter-granular microstructures.

Our results showed that prior to xenoliths entrainment by the host basalt, fluids were stored in the Antarctica sub-continental lithospheric mantle (SCLM) as FI trails inside minerals and/or inter-granular fluids, making up <1.2 vol.% of the mantle. The amount of $CO_2$ stored in FI is intimately related to the mineral phase and the degree of fertility of the rocks, and varies from 0.1 μg($CO_2$)/g(sample) in olivine from the anhydrous harzburgites, up to 187.3 μg/g in orthopyroxene from the highly metasomatized lherzolites. According to modal percentage of mantle minerals the bulk $CO_2$ storage in the SCLM ranges from 0.3 to 57.2 μg/g. Combining these results with mineral chemistry, thermo- and oxy-barometric models, we linked the volatile contents to the processes that affected the Antarctica SCLM, from the infiltration of $CO_2$-poor tholeiitic melts in the Jurassic to the massive mobilization of $CO_2$ right before the alkaline metasomatism associated with the Cenozoic rift-related magmatic event. In all lithotypes, the partitioning of $CO_2$ is favoured in orthopyroxene and clinopyroxene-hosted FI with respect to olivine-hosted FI. Interestingly, if we compare the $CO_2$ contents of FI to the $H_2O$ amount retained in pyroxene lattices, we obtain $H_2O/(H_2O+CO_2)$ molar ratios from $0.72 \pm 0.17$ to $0.97 \pm 0.03$, well comparable to the values measured in olivine-hosted melt inclusions from Antarctic primary lavas and assumed as representative of the partition of volatiles at the local mantle conditions.

# *sp*$^2$ to *sp*$^3$ transition in amorphous carbonate glass: Implications for the storage of primordial carbon in the deep Earth

Cerantola V.*[1-2], Sahle J.S.[3], Petitgirard S.[4], Wu M.[5], Checchia S.[3], Weis C.[6], Di Michiel M.[3], Vaughan G.[3], Collings I.[3], Arató R.[7], Wilke M.[8], Jones A.P.[9], Hanfland M.[3] & Tse J.[10]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca, [2] European XFEL, Schenefeld (Germany). [3] ESRF, Grenoble (France). [4] Department of Earth Sciences, Institute of Geochemistry and Petrology, Zurich (Switzerland). [5] College of Materials Science & Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang (China). [6] Fakultät Physik/DELTA, Technische Universität Dortmund (Germany). [7] Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Debrecen (Hungary). [8] Institut für Geowissenschaften, Universität Potsdam (Germany). [9] Earth Sciences, University College, London (UK). [10] Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon (Canada).

*Corresponding author e-mail:* valerio.cerantola@gmail.com

*Keywords:* phase transition, high pressure, deep carbon cycle.

Most of Earth's carbon may have been stripped away from the mantle during core formation. However, at deep magma ocean conditions it becomes less siderophile and thus large amounts of the Earth's primordial carbon may be stranded instead in the deep mantle. Here, we investigate the structure and compaction mechanisms of a carbonate glass to deep mantle pressure. Our results demonstrate a pressure-induced change in hybridization of carbon from *sp*$^2$ to *sp*$^3$ starting at 40 GPa, due to the conversion of $^{[3]}CO_3^{2-}$ groups into $^{[4]}CO_4^{4-}$ units, which is completed at ~112 GPa. The pressure-induced increase of carbon coordination number from three to four increases possibilities for carbon-oxygen interactions with lower mantle silicates and increased compatibility. Tetracarbonate melts provide a mechanism for changing the presumed siderophile nature of deep carbon and instead imply storage of carbon in the deep mantle as a possible source for carbon-rich emissions registered at the surface in intra-plate and near-ridge hot spots.

# The volatile evolution of mafic melts associated with magmas of the Mt. Somma-Vesuvius volcano

Esposito R.*[1], Redi D.[2], Danyushevsky L.V.[3], Gurenko A.[4], De Vivo B.[5], Manning C.E.[6], Bodnar R.J.[7], Steele-MacInnis M.[8] & Frezzotti M.L.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Mazzeschi s.r.l., Colle Val d'Elsa (SI). [3] CODE, Univeristy of Tasmania, Hobart (Australia). [4] Centre de Recherches Pétrographiques et Géochimiques, Paris (France). [5] Università Telematica «Pegaso», Napoli. [6] Earth, Planetary and Space Sciences, University of California, Los Angeles, CA (USA). [7] Department of Geosciences, Virginia Tech, Blacksburg, VA (USA). [8] Earth and Atmospheric Sciences, University of Alberta (Canada).

*Corresponding author e-mail:* rosario.esposito@unimib.it

*Keywords:* Vesuvius, $CO_2$, melt inclusions.

Vesuvius is a dormant strato-volcano to the east of the city of Naples in southern Italy. Eruptions at Mt. Somma-Vesuvius (SV) have been highly explosive, such as the one of Pompeii (AD 79) that killed many people after a long period of quiescence. Because of its current dormant state, and its close proximity to a major urban center, the mechanism that triggers explosive eruptions at SV needs to be better understood. Despite SV having been extensively investigated, many geological questions remain open. For instance, correlations between pre-eruptive volatile contents and the explosivity of past eruptions is still debated. Also, correlation between the volatiles exsolving from mafic magmas in the lower crust and the volatiles degassed at the surface are still not fully understood.

In this study, we reheated melt inclusions (MI) hosted in olivine and analyzed the pre-eruptive concentrations of volatiles in the glass. We corrected these concentrations for the volatile contents of the bubble of the same MI previously published (Esposito et al., 2016). Our results first suggest that the volatile content of mafic melts associated to SV does not correlate with the explosivity and age of eruptions. Instead, two group of MI can be recognized: one group of MI is volatile-rich and consists of MI hosted in Fo-rich olivine; the other group is volatile-poor and consists of MI hosted in Fo-poor olivine. The volatile contents of these two groups of MI suggest that the magma evolved and crystallized under volatile-saturated conditions, and that the vapor phase exsolved from the melt was $CO_2$-rich but contained significant amounts of $H_2O$ and S. Secondly, we calculated a $CO_2$ flux of 517 t/d based on the $CO_2$ contents of the most mafic melts (MI hosted in $Fo_{90}$ olivine), which is almost double the $CO_2$ flux at the surface today (301 t/d). It is important to note that the $CO_2$ flux corresponds to 1100 t/d (0.4 Mt/y) if magma ascends to ~1 km prior to eruption from depths comparable to that of the Moho. In addition, we estimate based on these results that the thickness of the carbonate platform is around ~10 km based on the gap of pressures (depths) between the two groups of MI estimated from the compositions of MI. These findings suggest that, at SV, the volatile contents of MI do not show any geochemical trends to understand or predict the future behavior of this volcanic system. Thus, in addition, our findings suggest that forecasting the style of eruptions cannot be based on the amount of the $CO_2$ fluxing at the surface. Also, the $CO_2$ fraction of the flux originated from decarbonation should not significantly change from dormant stage to active stage SV.

Esposito R., Lamadrid H.M., Redi D., Steele-MacInnis M., Bodnar R.J., Manning C.E., De Vivo B., Cannatelli C. & Lima A. (2016) - Detection of liquid $H_2O$ in vapor bubbles in reheated melt inclusions: Implications for magmatic fluid composition and volatile budgets of magmas? Am. Min., 101(7), 1691-1695.

# Carbon fluxes in the lithospheric mantle recorded by fluid inclusions

Frezzotti M.L.*

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* maria.frezzotti@unimib.it

*Keywords:* Earth Carbon Cycle.

The role of the lithospheric mantle as a significant carbon reservoir is a poorly constrained variable that could play a critical role in the deep carbon cycle. It is known that the lithospheric mantle can store substantial amounts of carbon resulting from progressive metasomatic enrichment. Carbon fluxes by fluids and melts can be induced by active tectonics and might result in massive carbon degassing at the surface. Here, I present fluid and melt inclusions data from peridotites, providing a framework for interpreting mantle carbon-bearing fluids' and melts' chemical and physical properties in different tectonic settings. Data show that in the lithospheric mantle, at depths below about 60 km, the dominant fluid phase is $CO_2$ ± brines, changing to alkali-carbonate-rich (silicate) melts at higher pressures. Major solutes in aqueous fluids are chlorides, sulfates, silica and alkalis (saline melts; > 50 wt.% NaCl eq.). Fluid inclusions in peridotites record $CO_2$ fluxing from reacting metasomatic carbonate-rich melts at high pressures and suggest significant upper-mantle carbon outgassing over time. Mantle derived $CO_2$ (±brines) may eventually reach crustal levels, including the atmosphere, independent from and additional to magma degassing from active volcanoes.

# Towards the quantification of geological $CO_2$ outgassing of the Alps

Frondini F.*[1], Donnini M.[2], Cardellini D.[1], Melelli L.[1], Ricci L.[1], Ariano A.[1], Chiodini G.[3] & Vetuschi Zuccolini M.[4]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Perugia. [3] INGV, Bologna. [4] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* francesco.frondini@unipg.it

*Keywords:* Alps, carbon dioxide, degassing.

In the study of the geological carbon cycle, a question that is still open concerns the role of large orogens, i.e., whether they act as sources or sinks for atmospheric carbon on the geological time scale. Carbon dioxide outgassing from collisional orogens is a potentially significant mechanism of carbon transfer from the solid Earth to the atmosphere (Groppo et al., 2022), but large mountain ranges are also regions where chemical weathering acts significantly as a sink, sequestering large amounts of $CO_2$ through silicate alteration (Donnini et al., 2016). In this work, we present the preliminary results of a study aimed at estimating the total outgassing of the entire orogen of the Alps. The study is based on chemical and isotopic analyses and on hydrogeological data from more than 3000 springs. The concept behind our work is that since much of the $CO_2$ that rises from the deep is dissolved by groundwater it is possible to estimate deep $CO_2$ flux from the mass and isotopic balance of dissolved carbon in regional aquifers (Chiodini et al., 2000). Carbon isotopic data were used to distinguish surface carbon sources from deep sources related to metamorphic and/or mantle outgassing. Carbon budget results from individual springs were regionalized using the geostatistical technique of sequential Gaussian simulations (sGs) over an area of about 200000 $km^2$ including western alpine peripheral zone, Swiss's Molasse and the Eastern Alps. The computation of stochastic simulation at finer tile resolution to obtain estimates and a cumulative distribution probability function at a coarser one, lead to an estimation of the variability expressed by a median of $CO_2$ transported by groundwater of 1.9 Mmol/year per square kilometre and a range of variation between 1 and 25 Mmol/year per square kilometre. Preliminary results of the carbon isotope balance indicate that almost 50% of this $CO_2$ transported by groundwater derives from a deep outgassing process.

Chiodini G., Frondini F., Cardellini C., Parello F. & Peruzzi L. (2000) - Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: The case of central Apennine, Italy. J. Geophys. Res. Solid Earth, 105, 8423-8434.

Donnini M., Frondini F., Probst J.L., Probst A., Cardellini C., Marchesini I. & Guzzetti F. (2016) - Chemical weathering and consumption of atmospheric carbon dioxide in the Alpine region. Glob. Planet. Change, 136, 65-81.

Groppo C., Rolfo F. & Frezzotti M.L. (2022) - $CO_2$ outgassing during collisional orogeny is facilitated by the generation of immiscible fluids. Commun. Earth Environ., 3, 13.

# Crustal fluids in the Nepal Himalaya: spatial organization and sensitivity to the earthquake cycle

Girault F.*[1], France-Lanord C.[2], Adhikari L.B.[3], Upreti B.N.[4], Paudyal K.R.[5], Gajurel A.P.[5], Agrinier P.[1], Losno R.[1], Groppo C.[6-7], Rolfo F.[6-7], Thapa S.[1], Tamang S.[1-6] & Perrier F.[1]

[1] Institut de Physique du Globe de Paris, CNRS-Université de Paris (France). [2] Centre de Recherches Pétrographiques et Géochimiques, Université de Nancy, Vandoeuvre-lès-Nancy (France). [3] Department of Mines and Geology, National Seismological Centre, Lainchaur, Kathmandu (Nepal). [4] Nepal Academy of Science and Technology, Kathmandu (Nepal). [5] Central Department of Geology, Tribhuvan University, Kathmandu (Nepal). [6] Dipartimento di Scienze della Terra, Università di Torino. [7] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* girault@ipgp.fr

*Keywords:* hydrothermal system, carbon dioxide, Himalaya.

Over its 800 km strike, the Nepal Himalaya exhibits numerous geothermal zones located in the vicinity of the major thrust fault systems. Characterised by high thermal gradient, the hydrothermal sites show various surface manifestations: thermal springs, travertine deposits, hydrothermal alteration, 'tectonic' fumaroles and diffuse degassing structures. Gas released is dominated by carbon dioxide ($CO_2$), with steam and trace gases (hydrogen sulphide, radon, helium). Isotopic signature suggests that $CO_2$ is produced at pluri-kilometric depth by metamorphic activity, percolates toward the surface along fault and fracture networks, and can mix with infiltrated meteoric waters and degas at shallow depths before reaching the surface. The hydrothermal activity depicts a large-scale spatial organisation related to the seismic segmentation of the chain. Catastrophic events such as large earthquakes influence the temporal variations of the hydrothermal activity. The hydrothermal systems appear as precious assets for the study of past, present and future Himalayan orogenic activity, and a unique probe of active metamorphic and alteration processes.

# $CO_2$ degassing in collisional orogenic settings is enhanced by fluid immiscibility at depth

Groppo C.*[1-2], Rolfo F.[1-2] & Frezzotti M.L.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.
[3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* chiara.groppo@unito.it

*Keywords:* fluid immiscibility, $CO_2$ outgassing, thermodynamic modelling.

Metamorphism of crustal rocks in collisional orogens produces carbon-bearing fluids over geologic time scales, primarily through decarbonation reactions, potentially contributing to the global Earth's carbon cycle. However, the relevance of such a contribution is still debated. The efficiency of metamorphic $CO_2$ degassing in orogenic settings is primarily controlled by the ease at which the $CO_2$-bearing aqueous fluids produced at depth are transported upward without interacting with the host rocks. If fluid-rock interactions occur during retrograde metamorphism, leading to carbon re-precipitation in the form of carbonates or graphite, collisional orogens' contribution to the global Earth's $CO_2$ degassing would be minimal. Conversely, if metamorphic $CO_2$-bearing fluids do not react with the host rocks, orogenic decarbonation would represent an important source of $CO_2$ at the global scale. Recent research balancing estimates of decarbonation rates from deeply exhumed rocks and $CO_2$ fluxes measured at the surface, support the second hypothesis. However, neither were the physical and chemical characteristics of the released metamorphic fluids studied in detail nor was the transport path of deep $CO_2$ fully elucidated.

Here, we use thermodynamic modeling to investigate the decarbonation of sediments metamorphosed under high geothermal gradients. We present petrological evidence that most dehydration and decarbonation reactions in these lithologies occur at P-T conditions in the two-phase field of the $H_2O$- $CO_2$-salt ternary fluid systems, generating immiscible $CO_2$-rich vapors and hydrosaline brines. Our results demonstrate a crucial role of fluid immiscibility in driving $CO_2$ transport from the deep crust, explaining how and why significant amounts of $CO_2$ could be effectively degassed at the surface from orogenic belts (Groppo et al., 2022). This study reconciles geophysical and geochemical observations from active collisional orogens such as the Himalaya, where intense $CO_2$ degassing is currently measured at the surface. Results further highlight the role of hydrosaline brines as metasomatizing and/or granulitizing agents in the lower crust.

Groppo C., Rolfo F. & Frezzotti M.L. (2022) - $CO_2$ outgassing during collisional orogeny is facilitated by the generation of immiscible fluids. Comm. Earth Environ., 3, 13.

# Three occurrences of kalsilite bearing-rocks in central Italy – a first comparison

Innocenzi F.[1], Ronca S.[1], Agostini S.[2], Pistocchi L.[1], Foley S.[3] & Lustrino M.*[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Geoscienze e Georisorse, CNR, Roma. [3] Department of Earth and Planetary Sciences, Macquarie University, Sydney (Australia).

*Corresponding author e-mail:* michele.lustrino@uniroma1.it

*Keywords:* kalsilite, kamafugite, potassic.

Kalsilite ($KAlSiO_4$) rarely occurs as a primary phase in strongly ultrabasic ($SiO_2$ ~30-40 wt.%) mildly alkaline rocks and in ultrapotassic not-so-strongly ultrabasic-basic ($SiO_2$ ~40-48 wt.%) compositions. Three main variants of kalsilite-bearing igneous rocks (katungite, mafurite and ugandite) were originally identified in the western branch of the East Africa Rift (Toro Ankole and Virunga), and grouped under the acronym KaMafUgite (Sahama, 1974). Later, kamafugites have been identified in the Intra-Apennine Province (San Venanzo and Cupaello) and in the Alto Paranaiba Igneous Province and Goiás Alkaline Province (Brazil). We report for the first time the occurrence of kalsilite also in the groundmass of melilititic lavas of Montefiascone volcanic complex (Vulsini Mts.). This mineral has been previously reported only in crystalline ejecta (Di Battistini et al., 2001).

A comparison based on petrographic, mineral chemical, geochemical and isotopic (Sr-Nd-Pb) data on selected samples from San Venanzo, Cupaello and Montefiascone, highlights variable $SiO_2$ depletion, from strongly ultrabasic to basic ($SiO_2$ = 37.4-46.8 wt.%), all ultrapotassic ($K_2O$ = 5.2-8.5 wt.%; $K_2O/Na_2O$ = 4-34) and with variable $CaO/Al_2O_3$ ratios (0.4-2.0). Samples show high Th, U and Pb, low content of selected HFSE (Nb, Ta and Ti), and relatively high REE budget. These features, clue of a former subduction, are reflected in the strongly fractionated patterns of the primitive mantle-normalized diagrams. In absence of plagioclase fractionation, the Eu negative anomalies (Eu/Eu* = 0.68-0.73) of Italian magmas can be considered as a further hint of the interaction of the mantle sources with subducted lithologies (e.g., terrigenous sediments). The strongly radiogenic $^{87}Sr/^{86}Sr$ (0.7104-0.7112) and the low $^{143}Nd/^{144}Nd$ (0.51200-0.51219) ratios are compatible with a derivation from a subduction-modified source. Lead isotopes span in a much smaller range, approaching average upper crustal values ($^{206}Pb/^{204}Pb$ = 18.73-18.78; $^{207}Pb/^{204}Pb$ = 15.56-15.68).

The major oxide and trace element content, as well as the Sr-Nd-Pb isotopic ratios of the Italian kalsilite-bearing magmas is completely different from the two other localities where this mineral has been reported as primary phase (Brazil and Uganda). This speaks for different petrogenetic processes, with basic to ultrabasic and ultrapotassic melts generated in Italy by partial melting of a carbonate-phlogopite peridotite mantle sources, probably related to recycling of sedimentary lithologies during previous subduction processes and possibly contaminated by marly and/or limestone assimilation during upwelling through the continental crust.

Di Battistini G., Montanini A., Vernia L., Venturelli G. & Tonarini S. (2001) - Petrology of melilite-bearing rocks from the Montefiascone Volcanic complex (Roman Magmatic Province): new insights into the ultrapotassic volcanism of Central Italy. Lithos, 59, 1-24.

Sahama T.G. (1974) - Potassium-rich alkali rocks. In: Sørensen H. Ed., The Alkaline Rocks, 96-109. Wiley.

# Impact of geogenic degassing on C-isotopic composition of dissolved carbon in karst systems of Greece

Li Vigni L.*[1], Cardellini C.[2-3], Chiodini G.[3], D'Alessandro W.[4], Daskalopoulou K.[5-6], Calabrese S[1-4], Brugnone F.[1] & Parello F.[1]

[1] Dipartimento delle Scienze della Terra e del Mare, Università di Palermo. [2] Dipartimento di Fisica e Geologia, Università di Perugia. [3] INGV, Bologna. [4] INGV, Palermo. [5] Institute of Geosciences, University of Potsdam, Potsdam-Golm (Germany). [6] German Research Centre for Geosciences, Potsdam (Germany).

*Corresponding author e-mail:* livignilorenza@gmail.com

*Keywords:* Earth C-cycle, $CO_2$ degassing, karst systems.

The Earth C-cycle is complex, where endogenic and exogenic sources are interconnected, operating in a multiple spatial and temporal scale (Lee et al., 2019). Non-volcanic $CO_2$ degassing from active tectonic structures is one of the less defined components of this cycle (Frondini et al., 2019).

Carbon mass-balance (Chiodini et al., 2000) is a useful tool to quantify the geogenic carbon output from regional karst hydrosystems. This approach has been demonstrated for central Italy and may be valid also for Greece, due to the similar geodynamic settings. Deep degassing in Greece has been ascertained mainly at hydrothermal and volcanic areas, but the impact of geogenic $CO_2$ released by active tectonic areas has not yet been quantified.

The main aim of this research is to investigate the possible deep degassing through the big karst aquifers of Greece. Since 2016, 156 karst springs were sampled along most of the Greek territory. To discriminate the sources of carbon, the analysis of the isotopic composition of carbon was carried out. $\delta^{13}C_{TDIC}$ values vary from -16.61 to -0.91‰ and can be subdivided into two groups characterized by (a) low $\delta^{13}C_{TDIC}$, and (b) intermediate to high $\delta^{13}C_{TDIC}$ with a threshold value of -6.55‰. The composition of the first group can be related to the mixing of organic-derived $CO_2$ and the dissolution of marine carbonates. Springs of the second group, mostly located close to Quaternary volcanic areas, are linked to possible carbon input from deep sources.

Chiodini G., Frondini F., Cardellini C., Parello F. & Peruzzi L. (2000) - Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: The case of central Apennine, Italy. J. Geophys. Res., 105(B4), 8423-8434.

Frondini F., Cardellini C., Caliro S., Beddini G., Rosiello A. & Chiodini G. (2019) - Measuring and interpreting $CO_2$ fluxes at regional scale: the case of the Apennines, Italy. J. Geol. Soc., 176, 408-416.

Lee C.A., Jiang H., Dasgupta R. & Torres M. (2019) - A framework for understanding whole-Earth Carbon cycling. In: Orcutt B.N., Daniel I. & Dasgupta R. Eds., Deep Carbon: Past to Present, 313-357. Cambridge University Press.

# Carbon and Sulphur speciation in subarc subduction-zone fluids calculated with electrolytic-fluid thermodynamic modelling of a UHP marble as a function of P-T-$fO_2$

Maffeis A.*[1], Connolly J.A.D.[2], Frezzotti M.L.[3], Castelli D.[1] & Ferrando S.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Department of Earth Sciences, ETH Zürich (Switzerland).
[3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* andrea.maffeis@unito.it

*Keywords:* carbon & sulphur, redox, subduction fluids.

Element speciation in subduction fluids controls the transport efficiency of elements from the down-going slab to the overlying mantle wedge. P-T-X-$fO_2$ and bulk-rock composition (i.e., rock-buffered) control the elemental speciation in such mobile phases. Elements like C and S, being characterised by a wide range of possible valance states, are crucial in regulating the redox state of the arc mantle and the associated volcanism. However, dominant carbonate sediments (representing ~70% of the total subducted carbon; Clift, 2017) are only marginally considered in the modelled subduction processes, mostly because of the lack of relevant decarbonation reactions at HP-UHP conditions. Similarly, because S is considered to be primarily subducted at UHP conditions as sulphides or sulphates within the altered oceanic crust (e.g., Walters et al., 2020), the S input from dominant carbonate sediments has been rarely considered.

To address the role of dominant carbonate sediments on the C and S long term cycles, we conducted electrolytic-fluid thermodynamic modelling of the fluid phase in equilibrium with a UHP impure marble from the Dora-Maira Massif (Western Alps). This marble experienced multiple carbonated dissolution-precipitation events during active subduction at HP-UHP conditions. The study of this natural sample allows linking the thermodynamically modelled HP-UHP evolution, of both rock and fluid, to the HP-UHP mineral assemblages and related fluid inclusions (Maffeis et al., 2021). Using the bulk composition of the studied marble, we modelled the chemical evolution of the fluid along the prograde P-T path (from ~490°C-1.5 GPa to ~730°C-4.3 GPa) and of at different $fO_2$ (between +2 and -2 from the FMQ buffer). At changing P-T-$fO_2$ conditions, C and S speciation and concentration in the fluid are different. At reduced conditions, C is additionally speciated as carboxylic compounds and hydrocarbons, while S is speciated as $H_2S$ and $HS^-$. At oxidized conditions, C and S are speciated as $HCO_3^-$ and $SO_4^{2-}$, respectively. The dissolution of carbonate dominated sediments is an effective process for the mobilisation of both C and S, with C being more easily released at reduced conditions and S at oxidised conditions instead. Thus, dissolution is a more effective process than decarbonation and desulphurisation reactions in releasing C and S during subduction at sub-arc depths.

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# Implications of the December 2020 Milan earthquake for the carbon emission budget of non-volcanic collisional settings

Malusà M.G.*[1], Brandmayr E.[2], Panza G.F.[2], Romanelli F.[3], Ferrando S.[4] & Frezzotti M.L.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Accademia Nazionale dei Lincei, Roma. [3] Dipartimento di Matematica e Geoscienze, Università di Trieste. [4] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* marco.malusa@unimib.it

*Keywords:* carbon outgassing, cold subduction, European Alps.

Recent studies integrating petrological modeling and geophysical imaging of the Earth mantle of the Alpine region have revealed the importance of long-term carbon sequestration into the mantle wedge located above the subducted European slab (Malusà et al., 2018). A prominent shear-wave low-velocity anomaly, likely generated by extraction of carbonate-rich melts from the asthenosphere, is observed in surface-wave tomography models at depths greater than 180 km. Processes taking place in cold subduction settings provide a viable explanation for this observation: (i) low paleogeothermal gradients allow for the preservation of subducted carbonates and hydrous minerals to asthenospheric depths; (ii) their breakdown produces carbonate-rich hydrous melts that infiltrate the overlying mantle wedge inducing peridotite partial melting; (iii) the resulting melt network is frozen when the mantle geotherm crosses the carbonated hydrous peridotite solidus. This scenario produces extensive peridotite carbonation and the formation of a long-term carbon reservoir in the asthenospheric and/or lithospheric upper mantle, which is potentially released after millions of years during the breakup of continental plates. However, the seismic event that occurred beneath Milan on the 17$^{th}$ of December 2020 at 15:59:22 UTC provides an invaluable opportunity to investigate the possibility that carbon sequestered beneath the Po Plain can be locally remobilized on shorter-term time scales and released to the atmosphere. Here we demonstrate that the source moment tensor of the Milan earthquake includes a major explosive component. This is interpreted as the effect of rapid release of carbon dioxide when carbon-rich melts migrate along upper-mantle shear zones and exit the carbonate stability field (Malusà et al., 2022). Melting of carbonated peridotite occurs within shear zones in the asthenospheric mantle at depths around 180-100 km. Carbon-rich melts ascend to depths less than 100 km along shear zones due to buoyancy and very low viscosity. The associated carbon dioxide output towards Earth's surface is greater than the daily emissions of top-ranking most actively degassing volcanoes such as Nyiragongo and Etna (e.g., Aiuppa et al., 2019), which underlines the importance of carbon-rich melts for the emission budget of non-volcanic collisional settings located along former cold-subduction zones.

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# A structural and mineralogical study of the magnesite deposit in the ultramafic rocks of Gerakini (NE Greece)

Marescotti P.*[1], Grieco G.[2], Tzamos E.[3], Comodi P.[4], Zucchini A.[4], Bussolesi M.[5], Giordan V.[1], Ghiorzo S.[1] & Crispini L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [3] Laboratory of Chemical and Environmental Technology, Aristotle University of Thessaloniki (Greece). [4] Dipartimento di Fisica e Geologia, Università di Perugia. [5] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* pietro.marescotti@unige.it

*Keywords:* magnesite, carbonation, Gerakini.

The study area is located within the Gerakini magnesite mining district in the Chalkidiki peninsula (NE Greece). The magnesite ore is located in the Mesozoic Gerakini-Ormylia ophiolite complex that represents part of the supra-subduction zone (SSZ) ophiolite complex of west Chalkidiki Peninsula, dated Middle to Upper Jurassic. The ophiolite consists of massive dunite, minor harzburgites, serpentinized peridotite, layered pyroxenites and gabbros, which host magnesite veins and stockworks. To the NE of Gerakini, ophiolitic complex is bounded by diorite and quartz diorite as well as metamorphic rocks from the continental crust.

The aim of this work is to characterize the poorly studied Gerakini magnesite deposit for understanding the geologic history of the area along with its magnesite ore deposits as well as the fluid-rock interactions processes driving the carbonation of the host ultramafic rocks. Here we present the preliminary results of a multiscalar structural and mineralogical investigation. This includes: i) a detailed fieldwork for definition of the tectonic setting and the deformation structures-mineralisation relationships; ii) a mineralogical, crystallochemical and microstructural study of the host rocks and veins performed by optical, SEM-, FESEM-microscopy, XRPD, EDXRF, and Raman spectroscopy.

Various types of magnesite mineralisations have been identified occurring in massive veins, syntectonic extensional veins, sheared veins and slickenfibers in fault zones. Magnesite is cryptocrystalline to microcrystalline and, at the sample scale, it appears as either massive or nodular, with "cauliflower-like", "porcelanous" (with conchoidal fracture), fibrous, and lamellar structures. At places, the host rocks are either carbonated and silicified or oxidised at various degrees. On the basis of their structural and mineralogical features, veins can be grouped in three main sets: 1) magnesite large veins, 1-2 m wide, mainly filled with cryptocrystalline to fibrous magnesite. The contact with the host rock is generally sharp with mm to cm-scale alteration haloes of green fibrous minerals. 2) magnesite veins in stockwork with variable thickness (up to 20 cm) and sharp contacts with the host rock. The filling magnesite is cryptocrystalline with either granular or fibrous texture. 3) composite magnesite ± talc ± calcite veins (15 to 40 cm) with green alteration halos. Filling minerals show from massive to "cauliflower-like" and fibrous structures. The stockwork mineralisations are more common in the shallower level of the mined area, whereas thicker veins occur mainly in the deeper levels.

Our results allow the definition of a preliminary geologic evolutionary model which links tectonics, mineralisation and host rock alteration. The knowledge of these magnesite mineralised systems is of outstanding importance not only for the mining industry, as they represent the main source of magnesia, but also for the understanding of geological processes linked to carbon-cycle in active tectonic settings.

# The dynamic of magmas associated to the Agnano-Monte Spina eruption: new insights from melt inclusions hosted in clinopiroxenes

Pingitore F*., Frezzotti M.L. & Esposito R.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* pingifede32@gmail.com

*Keywords:* Campi Flegrei, melt inclusions, $CO_2$.

Campi Flegrei caldera (CFc) is an active volcanic system in southern Italy and represents one of the most monitored volcanoes in the national territories. In fact, CFc past activity have produced super eruptions and it has been undergoing through an unrest crisis consisting of a ~93 cm uplift of the central part of the caldera. The high urbanization of CFc and the proximity to the city of Naples makes the volcanic risk very high. The Agnano-Monte Spina (A-MS) eruption is the highest explosive event since the last epoch of CFc activity (5.5 - 3.5 ka), and it is a reference scenario for assessing the volcanic risk for future high-VEI eruptions.

In this study, we first selected 100 clinopyroxenes from an air fall deposit of the A-MS and analyzed their major element compositions using an electron-microprobe. Secondly, we analyzed the petrography of melt and fluid inclusions (MI) hosted in these crystals. Finally, we analyzed the volatile contents of the bubble of MI observed in the selected samples. Based on the petrographic and geochemical analyses, the pyroxenes were divided in two groups. The MgO-rich group is classified as diopsidic pyroxene (MgO = 16-18 wt.%), show a light green colour, and presents resorbed margins. The MI hosted in the first group were mostly crystallized, but in some cases is possible to observe a vapour bubble. The MgO-poor group is classified as salitic pyroxene, showing a dark green colour. The crystals of this group had a lower content of MgO than the diopsidic ones (12-14 wt.%). The crystals were larger than the diopsidic clinopyroxenes. MI hosted in the MgO-poor crystals are mostly glassy or bubble-bearing. The bubbles of MI in MgO-poor clinopiroxene show always shrinkage bubbles, but those in MgO-rich crystals were trapped heterogeneously together with the melt, suggesting two different magmatic stages. The bubbles hosted in the MIs of salitic pyroxene did not show any Raman signals of volatile species, while those hosted in the MIs of Mg-rich clinopyroxene showed $CO_2$, carbonate, and $H_2S$ (only one) Raman signals.

Our results suggest that a magma mush of relatively less evolved composition interacted with a deeper and more evolved magma before the A-MS eruption. This interpretation corroborates previous funding relative to the A-MS (e.g, Arienzo et al., 2010). Also, we suggested that the magmatic fluids of the less evolved magma were $CO_2$ and $H_2S$(?) saturated, while the more evolved magma did not present evidence of volatile saturation. Other evidences of $H_2S$ in other bubbles could lead to important implications in understanding the vapor phases conditions before volcanic events at CFc and volcanic forcing on climate change.

Arienzo I., Moretti R., Civetta L., Orsi G. & Papale P. (2010) - The feeding system of Agnano–Monte Spina eruption (Campi Flegrei, Italy): Dragging the past into present activity and future scenarios. Chem. Geol., 270(1-4), 135-147.

# An experimental determination of the liquidus and a thermodynamic melt model in the $CaCO_3$-$MgCO_3$ binary: modelling carbonated mantle melting

Poli S.*[1], Zhao S.[2], Schmidt M.W.[3], Rinaldi M.[1-4] & Tumiati S.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Institute of Geophysics & Geomatics, China University of Geosciences, Wuhan (China). [3] Department of Earth Sciences, ETH Zürich (Switzerland). [4] School of Earth & Environmental Sciences, University of St. Andrews (UK).

*Corresponding author e-mail:* stefano.poli@unimi.it

*Keywords:* carbonatite, mantle, thermodynamics.

The system $CaCO_3$-$MgCO_3$ has been used since the '60s for reconstructing the petrogenesis of carbonated lithologies, notably of carbonatite magmas possibly generated in the Earth's mantle. We experimentally determined the melting of aragonite and magnesite to pressures of 12 GPa, and of calcite-magnesite mixtures at 3 and 4.5 GPa, at variable Ca/(Mg+Ca) ($X_{Ca}$). The melting curves of aragonite, and magnesite have similar slopes, the latter melting ≈ 30°C higher than aragonite. In the Ca-Mg binary, the minimum of the liquidus surface situates at an $X_{Ca}$ of 0.65-0.60, at 1200°C - 3 GPa, and 1275°C - 4.5 GPa. Together with available data at 1 and 6 GPa, the minimum liquid composition remains approximately constant with pressure. All available experimental data are then fit by the first thermodynamic model for $CaCO_3$-$MgCO_3$ liquids. Surprisingly, although carbonate liquids should behave as relatively simple molten salts, the liquids display large non-ideality and a three-component, pressure dependent, asymmetric liquid solution model is required to model the liquidus surface. Attempts to use only the two end-member components fail, invariably generating a very wide magnesite-liquid loop in disagreement with the experimental evidence.

The liquid model is then used to evaluate results of experimentally determined phase relationships for carbonated peridotites in $CaO$-$MgO$-$SiO_2$-$CO_2$ (CMS-$CO_2$), and $CaO$-$MgO$-$Al_2O_3$-$SiO_2$-$CO_2$ (CMAS-$CO_2$). Computations highlight that the liquid composition in the CMS-$CO_2$ and CMAS-$CO_2$ and in more complex systems do not represent «minimum melts» but are more magnesian at high pressure. The pressure-temperature position of the solidus, as well as its *dP/dT* slope, including the appearance or absence of the "carbonatite ledge", depend on bulk composition, unless truly invariant assemblages occur.

# Dolomite-and magnesite-bearing lithologies from the Upper Lesser Himalayan Sequences: A petrological perspective in the framework of $CO_2$ degassing during collisional orogeny

Tamang S.*[1], Groppo C.[1-2], Rolfo F.[1-2], Girault F.[3] & Perrier F.[3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino. [3] Institut de Physique du Globe de Paris, Université Paris Cité (France).

*Corresponding author e-mail:* shashi.tamang@unito.it

*Keywords:* collisional orogeny, decarbonation, P/T-$XCO_2$ pseudosections.

The Lesser Himalayan Sequence (LHS) is a thick Proterozoic sedimentary sequence originally deposited on the northern margin of the Indian plate, metamorphosed during the Himalayan orogeny. Abundant carbonatic lithologies occur in the Upper-LHS, in the Dhading Dolomite and Benighat Slates Formations. The lithostratigraphic features of these formations are relatively well-known; however, these lithologies have been rarely investigated from a petrologic point of view, and their metamorphic reaction history is fundamentally unknown.

Here we present the results of a detailed petrologic study on different carbonatic lithologies from the Upper-LHS, whose protoliths can be grouped in: (1) a dolomitic series (dolostones, dolomitic marls, dolomitic pelites), and (2) a magnesitic series (sparry magnesite ores, magnesitic pelites). In the dolomitic series: (a) impure dolomitic marbles contain variable amounts of quartz, phlogopite, and/or muscovite; (b) calcschists derived from dolomitic marls consist of carbonates (dolomite ± calcite), phlogopite, quartz and variable types of silicates among which hornblende or kyanite; (c) schists derived from dolomitic pelites show mineral assemblages similar to those of normal metapelites, but with significant amounts of Ca-rich minerals (e.g., plagioclase) and with biotite anomalously enriched in Mg. In the magnesitic series: (a) magnesite-rich rocks consist of coarse-grained magnesite partially replaced by talc + Mg-chlorite; (b) schists derived from magnesitic pelites are characterized by uncommon assemblages, such as orthoamphibole + kyanite + garnet + phlogopite.

Thermodynamic forward modelling (P/T-X($CO_2$) pseudosections) applied to selected samples from each series allowed to: (1) understand the nature of the main decarbonation reactions; (2) constrain the P-T conditions at which these reactions occurred, and (3) estimate the amounts of carbonates consumed during prograde metamorphism, and the correspondent amounts of released $CO_2$.

The results of this study suggest that carbonatic lithologies from the Upper-LHS: (1) could have produced relevant amounts of $CO_2$ in the past, through metamorphic decarbonation reactions, and (2) they can still be an efficient source of $CO_2$, thus contributing to the diffuse Himalayan $CO_2$ degassing observed at present along the most important tectonic discontinuities.

# Characterization of graphitic schist occurrences in the Nepal Himalaya

Thapa S.*[1], Girault F.[1], Deldicque D.[2], France-Lanord C.[3], Groppo G.[4-5], Rolfo F.[4-5], Adhikari L.B.[6], Bhattarai M.[6], Paudyal K.R.[7], Losno R.[1] & Perrier F.[1]

[1] Institut de Physique du Globe de Paris, Université Paris Cité (France). [2] École Normale Supérieure, CNRS-Université Paris Sciences & Lettres (France). [3] Centre de Recherches Pétrographiques et Géochimiques, Université de Nancy, CNRS, Vandoeuvre-lès-Nancy (France). [4] Dipartimento di Scienze della Terra, Università di Torino. [5] Istituto di Geoscienze e Georisorse, CNR, Torino. [6] Department of Mines and Geology, National Earthquake Monitoring and Research Centre, Lainchaur, Kathmandu (Nepal). [7] Central Department of Geology, Tribhuvan University, Kathmandu (Nepal).

*Corresponding author e-mail:* sandeepthapa.geo@gmail.com

*Keywords:* Himalaya, MCT, graphite.

While elementary carbon, in the form of diamond or coal, dominates economic resources, graphite is an intriguing signature of orogenic processes. In the Nepal Himalaya, graphitic schist is ubiquitously observed in the upper Lesser Himalayan Sequence in the footwall of the Main Central Thrust (MCT), the ductile shear zone separating rocks from the Lesser Himalaya from those from the Greater Himalaya to the north. Here, we carried out a systematic investigation of these graphitic schists for the first time at high resolution and at various spatial scales collected from five different outcrops in the upper Trisuli valley, Central Nepal. Total organic carbon content and Raman properties including peak metamorphic temperature were determined on a total of 74 samples from this valley. Additionally, 63 samples from other valley of Nepal were analyzed. Most samples are metamorphosed from organic content represented by d$^{13}$C mean value of -26.3±0.1 ‰. Both the total organic carbon content and peak metamorphic temperature were found relatively homogeneous from sample to outcrop scales, and at the scale of the entire geological Unit over the Nepal Himalaya ($n$ = 137), demonstrating that black schists consistently represent large-scale metamorphic processes. Possibly, an along strike W-to-E increase in peak metamorphic temperature is observed. This study provides the first quantitative estimate of the amount of carbon stored as graphite within the black schists exposed all along the MCT from Western to Eastern Nepal, and constrains its thermal metamorphic evolution.

# Experimental devolatilization of carbonaceous material at warm subduction conditions (550°C, 1 GPa): assessing the reactivity of carbon forms and their contribution to COH fluid production

Toffolo L.*, Tumiati S., Amalfa A., Villa A. & Fumagalli P.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* luca.toffolo@unimi.it

*Keywords:* COH fluids, carbonaceous material, carbon cycle.

Subducted carbon has a key role on fluid and magma generation underneath volcanic arcs and can be ultimately responsible for long period oscillations in Earth's climate. An estimated 20% of the presently subducted carbon has an organic origin, i.e., it is hosted in rocks as carbonaceous material (CM). The behavior of CM throughout the subduction factory is a matter of debate, in that very little is known about the magnitude of its devolatilization and graphitization, its reactivity and solubility, its contribution to COH fluid production and volcanic arc gaseous emissions. In particular, it has to be remarked that CM in subduction environments is present as a spectrum of forms, reflecting the diversity of organic precursors and the variable maturation paths, but rarely as graphite, whose formation is restricted to higher-grade conditions. This potentially causes profound deviations from thermodynamically predicted carbon mobility models, which consider carbon as graphite.

To investigate the reactivity of CM we carried out a set of experiments at 550°C and 1 GPa on five commercially available synthetic carbon forms, i.e., glassy carbon, graphite, graphite oxide, mesoporous carbon and Vulcan® carbon. Experiments were performed by means of a rocking end-loaded piston cylinder apparatus and buffering the redox state at various $fO_2$ using the double capsule technique. Both the starting materials and the solids retrieved from the capsules after the experiments were thoroughly characterized by Raman spectroscopy, transmission electron microscopy and X-ray photoelectric spectroscopy. Fluids produced at the end of every run were extracted and analyzed by quadrupole mass spectrometry.

Our results show that no noticeable nanostructural reorganization of the CM types occurs after 1 hour runs, meaning that no graphitization is occurring. However, the different carbon forms can experience substantially diverse degree of devolatilization: glassy carbon, Vulcan® carbon and graphite oxide produce significant amounts of $CO_2$ in a wide range of redox conditions; graphite and mesoporous carbon do devolatilize at quite oxidizing states (hematite-magnetite and nickel-nickel oxide buffers) but the amount of $CO_2$ is one to two orders of magnitude smaller compared to that produced by the other carbon forms; methane forms in appreciable quantities at most reducing conditions ($H_2$ buffer) from Vulcan® and glassy carbon and at intermediate redox states (ferrosilite-magnetite-quartz and wustite magnetite buffers) from graphite oxide.

To a first approximation, the observed reactivity seems to be proportional to the percentage of oxygen heteroatoms contained in the starting carbon form, while the crystallinity and the degree of $sp^2$ and $sp^3$ hybridization of carbon appear to be of secondary importance. Hence, immature CM could play a major role on COH fluid production, especially when considering shallower subduction environments.

# Nyerereite: a possible new guest in the deep C cycle

Zucchini A.*[1], Gavryushkin P.N.[2-3], Golovin A.V.[2], Bolotina N.D.[4], Stabile P.[5], Carroll M.R.[5], Comodi P.[1], Frondini F.[1], Morgavi D.[1], Perugini D.[1], Arzilli F.[6], Cherin M.[1], Kazimoto E.[7], Kokh K.[2-3-8], Kuznetsov A.[2] & Medrish I.V.[9]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, Novosibirsk (Russia). [3] Department of Mechanics and Mathematics, Novosibirsk State University (Russia). [4] Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow (Russia). [5] Scuola di Scienze e Tecnologie, Università di Camerino. [6] School of Earth and Environmental Sciences, University of Manchester (UK). [7] Department of Geosciences, School of Mines and Geosciences, University of Dar es Salaam (Tanzania). [8] Kemerovo State University (Russia). [9] Samara Center for Theoretical Material Science, Samara State Technical University (Russia).

*Corresponding author e-mail:* azzurra.zucchini@unipg.it

*Keywords:* nyerereite, X-ray diffraction, structure refinement.

The last decade has witnessed a great deal of interest in the mineral physics of alkali carbonates at non ambient conditions. Indeed, besides their occurrence in natrocarbonatite magmas, alkali carbonates were identified in multiphase solid inclusions in diamonds and kimberlite groundmass (e.g., Golovin et al., 2017). Nyerereite [approx. $(Na_{1.64}K_{0.36})Ca(CO_3)_2$] is one of the most interesting alkaline carbonates and the main rock-forming mineral of natrocarbonatites, together with gregoryite $[(NaCa_xK)_{2-x}CO_3]$. The aim of the present project is to study K-free synthetic nyerereite samples by a multimethodological approach coupling scanning electron microscopy, energy dispersive spectroscopy, Raman spectroscopy and single crystal X-ray diffraction.

Different attempts on refining the crystal structure of nyerereite have been made in synthetic hydrothermal K-free samples and it was refined as a three-component twinned structure in the centrosymmetric *Pbca* space group, with the ratio of the three twinning components 0.221(3):0.287(3):0.492(3).

A topological analysis was performed and results indicate that there are no strict analogies between the crystal structure of nyerereite and other carbonates except for the structure with similar composition $K_2Ca(CO_3)_2$ (fairchildite). However, an interesting comparison between the crystal structure of the centrosymmetric *Pbca* nyerereite structure and that of aragonite ($CaCO_3$, *Pmcn* space group) can be proposed. In particular, the *Pbca* nyerereite structure might undergo crystal-chemical modifications towards a 9-fold coordinated Na and Ca sites resembling that of aragonite at elevated P, laying the foundation to extend the stability field of $Na_2Ca(CO_3)_2$ nyerereite to deep mantle conditions. These considerations have raised the interest in the high-pressure (HP) behavior of nyerereite and allow speculating about the possibility for its crystal structure to be stable at mantle conditions. Synchrotron single crystal X-ray diffraction data collected at non ambient conditions, devoted to study the behavior of nyerereite at HP and high to low temperatures, are being processed. Hence, nyerereite may be transported within carbonatitic melts from the lower mantle to the surface and the stability/decomposition reactions occurring during decompression can be fundamental constraints for the $CO_2$ release from mantle-derived magma, which can be expected to influence magma viscosity and eruption explosivity (Allison et al., 2021).

Allison C.M., Roggensack K. & Clarke A.B. (2021) - Highly explosive basaltic eruptions driven by $CO_2$ exsolution. Nat. Commun., 12, 217.

Golovin A.V., Sharygin I.S. & Korsakov A.V (2017) - Origin of alkaline carbonates in kimberlites of the Siberian craton: Evidence from melt inclusions in mantle olivine of the Udachnaya-East pipe. Chem. Geol., 455, 357-375.

# S28.

# A journey into Earth's upper mantle: spotlights on its composition, structure and dynamics


*Conveners and Chairpersons*

*Luca Faccincani (University of Ferrara)*

*Federico Casetta (University of Vienna)*

*Barbara Faccini (University of Ferrara)*

*Cristina Perinelli (University of Roma - Sapienza)*

*Luca Ziberna (University of Trieste)*

# Formation of wehrlite in the shallow lithosphere beneath intra-continental rifts and basins, and its link to the volatile cycle

Aulbach S.*[1], Lin A.[2], Stagno V.[3] & Caracausi A.[4]

[1] Institute for Geosciences, Goethe University Frankfurt (Germany). [2] State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an (China). [3] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [4] INGV, Palermo.

*Corresponding author e-mail:* s.aulbach@em.uni-frankfurt.de

*Keywords:* continental mantle, $CO_2$ degassing, xenolith.

The subcontinental lithospheric mantle (SCLM) formed via extraction of a melt volume large enough to confer buoyancy and viscosity via FeO- and $H_2O$-depletion, accompanied by reduction due to preferential extraction of ferric iron (e.g., Foley & Fischer, 2017). Below the SCLM, small-volume, variably carbonated melts (SVCM) from the carbonatite-basanite spectrum form, depending on lithosphere thickness, and on temperature, oxygen fugacity ($fO_2$) and composition of the underlying mantle volume. As $CO_2$ is highly incompatible and can be generated from reduced carbon via redox melting (e.g., Stagno et al., 2013), the mantle sources of SVCM need not be unusually volatile-rich or carbonate-bearing. Melts and fluids infiltrating the originally refractory and reduced continental mantle over time caused local re-enrichment and re-oxidation. Combined with the predicted increase of $fO_2$ in peridotite mantle with decreasing depth, this allows SVCM to stabilise in the shallow lithosphere. We will underpin this qualitative concept with thermodynamic modelling tracing the temperature-$fO_2$ evolution of the SCLM through time.

It has long been recognised that interaction of SVCM with depleted peridotite leads to formation of wehrlite in the shallow SCLM, particularly in rifts and basins, and also that mantle-$CO_2$ passively degasses in extensional settings. Using wehrlite-bearing xenolith suites, these two strands of evidence for carbon mobility through and out of the mantle were recently combined, linking the liberation of mantle-$CO_2$ in rifts to a concrete petrologic process at depth (Aulbach et al., 2020). The mass of $CO_2$ liberated to the atmosphere due to decarbonation was estimated from wehrlite-bearing xenolith suites. Here, we will use a global compilation of the flux of mantle-$CO_2$ in extensional settings to estimate the thickness of a hypothetical wehrlite layer at depth formed as result of the reaction between peridotite and SVCM with variable $CO_2$ content. We are also compiling literature data from wehrlite xenoliths to constrain whether $fO_2$ correlates with the volume of the SVCM inferred from the wehrlites' chemical composition. Because wehrlite xenoliths are clinopyroxene-rich and frequently amphibole and/or phlogopite-bearing, this opens the prospect to detect such layers seismically in extinct rifts, and link these to past episodes of mantle-$CO_2$ degassing.

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# Trace element re-distribution in clinopyroxene via reactive melt infiltration of mantle peridotite: an experimental study at 1-2 GPa

Borghini G.*[1], Fumagalli P.[1], Arrigoni F.[1], Klemme S.[2], Rampone E.[3] & Tiepolo M.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Westfalische Wilhelms Universitat Munster (Germany). [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* giulio.borghini@unimi.it

*Keywords:* melt-rock reaction, mantle heterogeneity, trace elements.

Porous flow is the main mechanism of melts transport in the deep hot mantle and within the thermal boundary layer. Reaction between mantle minerals and transient melts may strongly affect the mineralogy and chemistry of the upper mantle. Chemical changes in terms of major and trace element phase composition are function of temperature, pressure and melt amount and composition. However, to which extent the chemical exchange can reset the trace element (e.g., REEs) and, over time, isotopic composition of pristine minerals (above all clinopyroxene), has been so far poorly constrained. This work aims at investigating the role of melt-peridotite reaction by piston cylinder experiments on mixture of natural MORB-like mantle clinopyroxene and San Carlos olivine ($Fo_{90}$), used to model the peridotite matrix, and a moderately evolved oceanic basalt ($X_{Mg}$ = 0.60, ($Na_2O+K_2O$) = 4.29 wt.%) with Enriched-MORB signature ($La_N/Yb_N$ = 5.49). Crystallization experiments on the selected basaltic melt revealed that clinopyroxene is the liquidus phase followed by olivine at 1 GPa or garnet at 1.5-2 GPa. Reaction experiments have been performed at 1200-1350°C, at 1, 1.5 and 2.0 GPa, on basalt:clinopyroxene:olivine mixtures in proportions 2:1:1 and 1:1:1. All runs (1-2 GPa) produced chemical and textural evidence of dissolution and reprecipitation according to the reaction: $glass_1 + cpx_1 + ol_1 = glass_2 + cpx_2 + ol_2$. The new olivine is chemically homogeneous and shows slightly lower $X_{Mg}$ and higher Ca content with respect to San Carlos olivine. Clinopyroxene consists of large relicts, preserving the initial major element composition, and newly crystallized grains. They occur as rather large (80-150 µm) rims around cpx relics or new crystals and display lower $X_{Mg}$, Cr, Ca and higher Al, Na contents relative to the initial clinopyroxenes. The replacement of initial clinopyroxene by the new one is mostly promoted by temperature and run durations. New clinopyroxenes show REE patterns with increasing LREE/MREE and lower HREE abundances with respect to the initial clinopyroxene. The interaction with EMORB generates clinopyroxene with lower $Sm_N/Nd_N$ and $Lu_N/Hf_N$ ratios. The most incompatible element content increases in clinopyroxene as a function of initial melt amount and through high crystallization rate in melt-consuming reaction experiment. Notably, few clinopyroxene relicts preserve initial trace element composition whereas most of them record higher LREE and lower MREE-HREE suggesting that diffusion also plays a role during the melt-cpx reaction. Reacted glasses have high $X_{Mg}$ and low CaO, $Al_2O_3$, $Na_2O$ and REE contents, suggesting olivine (and minor cpx) dissolution. $D_{REE}^{cpx/liq}$ measured in the longest runs approach those derived from our crystallization experiments and literature. These experimental data indicate that melt-peridotite interaction induces a rapid redistribution of trace elements in mantle clinopyroxene, even at the timescale of experiments.

# Constraining the mantle sources of Italian magmatism through high field strength elements and $^{176}Hf/^{177}Hf$

Bragagni A.*[1-2], Mastroianni F.[1], Münker C.[2], Avanzinelli R.[1] & Conticelli S.[1-3]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Institut für Geologie und Mineralogie, Universität Köln (Germany). [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* alessandro.bragagni@unifi.it

*Keywords:* Italian magmatism, HFSE, Etna.

High Field Strength Elements (HFSE) are a powerful proxy to investigate specific processes occurring in complex magmatic settings. Being only limited released by slab derived fluids/melts, HFSE are not easily overprinted by subduction processes and are also sensitive to peculiar metasomatic processes such as those involving carbonatite melts. In this study, we report high-precision HFSE isotope dilution concentration and $^{176}Hf/^{177}Hf$ data from representative magmas of the Neogene to Quaternary Italian volcanism (i.e., Vesuvius and other Central Neogene to Quaternary volcanoes, Tyrrhenian seafloor, Etna, and Pantelleria).

Etna and Vulture volcanic rocks show Nb/Ta ratios much higher than any OIB and MORB. The high Nb/Ta cannot be explained by an influence of the Ionian subduction and may reflect carbonatite metasomatism in the mantle similarly to that of the Hyblean volcanism. A C-rich metasomatic event explains the large $CO_2$ degassing of Etna and it is consistent with a mantle flow that erodes the bottom portions of the SCLM.

Other Italian volcanoes do not show such an anomalously high Nb/Ta with the exception of some leucite-bearing rocks from Mid Latin Valley (Central Italy). Hafnium isotopes are partially decoupled from Nd isotopes. Vulture, Vesuvius, and some subduction related Central Italian leucite-free magmas show significant variations in $^{143}Nd/^{144}Nd$, but a rather constant $^{176}Hf/^{177}Hf$. Given the lower mobility of Hf (with respect to Nd), during subduction processes, the constant $^{176}Hf/^{177}Hf$ could reflect a common asthenopheric component. Since the Tyrrhenian seafloor and intraplate volcanoes of the region (e.g., Pantelleria and Etna) show more radiogenic Hf, the signature of Vesuvius, Vulture, and the leucite-free products of the Mid Latin Valley volcanic field could reflect a less depleted asthenospheric source for these magmas.

# Spatial and temporal variation of magmatism in the East Africa Rift System: implications for rates of extension and interaction between different mantle domains

Braschi E.*[1], Tommasini S.[2], Bragagni A.[2], Corti G.[1] & Orlando A.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Firenze. [2] Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* eleonora.braschi@igg.cnr.it

*Keywords:* East African Rift, Afar plume, sub-continental litosphere.

The East African Rift System (EARS) is the classic example of an active continental rift associated with extension, deformation, lithosphere thinning, and generation of magmas from different mantle domains and depths. Magmatism and tectonics have always been closely linked and their mutual relationships concern many processes such as the kinematics and rates of extension, the passive versus active role of mantle upwelling and magma genesis. In addition, the spatial and temporal variations of the geochemical signature of magmas varies in response to different mantle domains contributing to their genesis (subcontinental lithosphere, asthenosphere and deeper mantle sources).

In this study we carefully screened an exhaustive geochemical database of basalts (including authors' unpublished data) emplaced in the EARS to decipher the possible connection between different mantle domains, and the evolution and tectonic characteristics of the EARS. The geochemical data were subdivided according to spatial and temporal criteria: from a spatial point of view, the samples were ascribed to five groups, namely Afar, Ethiopia, Turkana depression, Kenya and Tanzania. From a temporal point of view, the magmatic activity of the EARS was subdivided into three main temporal sequences: 45-25 Ma, 25-10 Ma and 10-0 Ma.

The geochemical signature and radiogenic isotopes (Sr, Nd, Pb) of the selected basalts reveal significant spatial and temporal variations and permits to place important constraints on the contribution of subcontinental lithosphere, asthenosphere, and lower mantle in magma genesis.

# Petrology of ultramafic xenoliths and host lavas of Ngaoundéré (Adamawa Plateau, Cameroon Volcanic Line)

Buian A.*[1], Tucker R.D.[2], Francalanci L.[1], Melluso L.[3] & Conticelli S.[1-4]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Bureau de Recherches Géologiques et Minières, Service Géologique National (France). [3] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [4] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* andrea.buian@unifi.it

*Keywords:* Cameroon Volcanic Line, petrology, sub-continental lithospheric mantle.

The Cameroon Volcanic Line is a NE-SW intraplate alkaline volcanic alignment extended for more than 1,700 km. It lies, for about 700 km, on oceanic lithosphere of the Gulf of Guinea (ca. 80-120 Ma), and for about 1,000 km on the continental African plate extending to the Lake Chad. The present study focused on the Adamawa Plateau, an asymmetric N70°E horst located in the area at North of the Ngaoundéré Plateau and bordered at North and South by the Adamawa and Djérem-Mbéré fault systems, respectively. Peridotitic xenoliths revealed hints on the nature of subcontinental African lithospheric mantle and the origin of their host lavas. Lherzolite and olivine-websterite are found among the peridotite xenoliths. Lherzolites are divided in two distinct groups equilibrated within different P-T conditions: a first group equilibrated in the ranges of 1.2-1.3 GPa and 913-979°C of P and T, respectively, whilst the other one in the ranges of 1.6-1.8 GPa and 996-1079°C. Olivin-websterite equilibrated within P-T conditions intermediate between the two lherzolitic groups, estimated at 1.4 GPa of P and 997°C of T. Chemical data on minerals from the peridotite xenoliths suggested the possible occurrence of at least one mantle metasomatism event overprinting a highly heterogeneous sub-continental lithospheric upper mantle. Geochemical and petrological data on host alkaline basalts suggested a clear OIB signature showing consistently high contents in Nb and Ta (46-89 ppm, 2.8-5.3 ppm, respectively) with a strong primitive character that suffered no crustal contamination during ascent to the surface. On the basis of incompatible trace element ratios, a magma genesis of the host lavas from low degree of partial melting (< 2 vol.%) of an asthenospheric upper mantle, equilibrated within the garnet stability field (8-9 vol.%) and characterised by the presence of an EM I component, is argued.

# Mantle-derived cargo or phenocrystic phases? Linking the texture and composition of olivine and phlogopite to the liquid line of descent of the Udachnaya kimberlite and the sub-cratonic mantle structure

Casetta F.*[1], Asenbaum R.[1], Ashchepkov I.[2], Ageeva O.[1], Ntaflos T.[1] & Abart R.[1]

[1] Department of Lithospheric Research, University of Vienna (Austria). [2] Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences. Novosibirsk (Russian).

*Corresponding author e-mail:* federico.casetta@univie.ac.at

*Keywords:* Udachnaya kimberlite, olivine xenocrysts, sub-cratonic mantle.

Kimberlites and the entrained mantle-derived xenoliths and diamonds bear witness to the processes occurring in the deepest realms of the Earth lithosphere. However, reconstructing the structure and composition of the sub-cratonic lithosphere and the physico-chemical properties of the melts/fluids raised through it is extremely difficult, as their original features are obliterated by the mutual interactions between kimberlite melts and xenoliths. This because: i) the "mantle assimilation" is a process that is intimately related to the genesis of kimberlite melts themselves, and is thought to be the main trigger for their fast ascent; and ii) the kimberlite melt-related metasomatic phenomena are widespread in the sub-cratonic lithospheric mantle. Furthermore, due to the intense hydrothermal alteration that typically affects kimberlites worldwide, most of the textural and compositional information in both the mantle xenoliths and the kimberlite host rocks are obscured. Here, a detailed textural and compositional study of olivine and phlogopite in fresh samples of the Udachnaya East kimberlite (Siberia, Russia) was put forward to model the evolution of kimberlite melts along ascent through the sub-cratonic lithosphere. Routine and high-precision electron microprobe analyses were used to:

- discriminate the mantle-derived cargo from the phenocrystic phases;
- reconstruct the P-T-X-$fO_2$ engraved in the mineral phases of the kimberlite;
- model the interactions between kimberlite-related fluid/melts and the sub-cratonic lithosphere.

Results showed that phlogopite in Udachnaya kimberlite is mostly phenocrystic, even though rare mantle-derived xenocrystic fragments can occur, while olivine cores are mostly xenocrystic. Based on their major and trace element concentration, olivine xenocrystic cores were thought to represent specific portions of the sub-cratonic lithospheric mantle, while the overgrowths were ascribed to the various evolutive stages of the kimberlite liquid line of descent.

# Petrology of ultramafic xenoliths from the Massif d'Ambre (Madagascar) combined with volatiles measurements in fluid inclusions: implications for the metasomatizing agent

Da Val E.*[1], Faccini B.[1], Faccincani L.[1], Rizzo A.L.[2] & Coltorti M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] INGV, Milano.

*Corresponding author e-mail:* elena.daval@edu.unife.it

*Keywords:* mantle xenoliths, metasomatism, Massif d'Ambre.

The Massif d'Ambre is a Cenozoic stratovolcano that was originated upon intense volcanic activity in northern Madagascar (12.1±0.1 Ma - 0.85 Ma), together with the Bobaomby volcanic field, the Nosy Be Archipelago and the intrusion of the Ampasindava Peninsula (e.g., Cucciniello et al., 2011). This area is characterized by the widespread occurrence of mantle xenoliths, mostly, but not restricted to, spinel lherzolites and subordinately pyroxenites, which are hosted in mafic volcanic rocks.

In this work, we investigated a suite of ultramafic peridotite xenoliths from the Massif d'Ambre by integrating petrography, mineral and glass chemistry and the concentrations of volatiles [$CO_2$ and noble gases (He, Ne and Ar)] in fluid inclusions (FI) hosted in olivine (Ol), orthopyroxene (Opx) and clinopyroxene (Cpx).

The suite of mantle xenoliths comprises 18 lherzolites, 11 harzburgites, 2 dunites, 3 wehrlites and 1 Ol-clinopyroxenite. Based on their petrographic features, the suite was divided into five distinct groups: group 1A is characterized by protogranular to porphyroclastic textures and includes the largest number of xenoliths; group 1B is characterized by large and porphyroclastic olivines; group 2 xenoliths include infiltrated dunites and wehrlites; group 3 includes cumulate-textured wehrlites, each with a different degree of wehrlitization; and group 4 with the Ol-clinopyroxenite xenolith.

From the mineral chemistry, a clear separation can be observed between Ol in groups 1A and 1B, having highly forsteritic olivine (Fo 88.4 - 93.2) and groups 3 and 4, having a lower and larger forsterite range of olivine (Fo 78.7 - 89.1). The distinction between groups 1A-1B and groups 3-4 is even more evident from the Mg# of orthopyroxenes (89.5 - 93.2 vs. 82.7 - 87.3, respectively) and clinopyroxene (90.9 - 95.2 vs. 81.4 - 89.9, respectively). This provides further confirmation on the distinct origin of the groups, with xenoliths belonging to 1A-1B having the most refractory character, while groups 3-4 xenoliths reflecting metasomatism/refertilization event/s. Based on glass analyses, we propose that a carbonatitic fluid may have interacted with some portion of the source mantle, in agreement with Coltorti et al. (2000). The noble gases in FI hosted in Ol, Opx and Cpx exhibit $^3He/^4He$ ratio corrected for air contamination (Rc/Ra values) ranging from 5.90 Ra to 7.05 Ra, which is well below the typical MORB-like upper-mantle value (8±1 Ra). Furthermore, the great majority of the xenoliths exhibits $^4He/^{40}Ar^*$ ratios between ca. 0.2 to ca. 0.8.

The major element distribution in mineral phases together with the systematic variations in FI composition will be used to place constraints on the origin and evolution (in terms of melting and metasomatism) of this portion of the mantle below the Massif d'Ambre.

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# First in-situ oxygen fugacity determination of an inclusion pair still trapped within its host diamond (Udachnaya kimberlite): implications for diamond formation and for the redox state evolution of the Siberian craton

Faccincani L.*[1], Cerantola V.[2], Nestola F.[3], Nimis P.[3], Ziberna L.[4-5], Pasqualetto L.[3], Chumakov A.I.[6], Harris J.W.[7] & Coltorti M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] European XFEL, Schenefeld (Germany). [3] Dipartimento di Geoscienze, Università di Padova. [4] Dipartimento di Matematica e Geoscienze, Università di Trieste. [5] Bayerisches Geoinstitut, University of Bayreuth (Germany). [6] ESRF, Grenoble (France). [7] School of Geographical and Earth Sciences, University of Glasgow (UK).

*Corresponding author e-mail:* luca.faccincani@unife.it

*Keywords:* inclusions in diamond, oxygen fugacity, Siberian craton.

Diamonds and their mineral inclusions are among the most intriguing natural samples on Earth as they provide unique snapshots of the otherwise inaccessible deep regions of our planet. Thanks to the physical strength and chemically inert nature of diamond, inclusions in this mineral may remain exceptionally preserved from alteration processes and chemical exchanges with surrounding minerals, fluids, and/or melts since diamond formation, therefore providing uncorrupted geological samples. Cr-bearing spinels, although volumetrically scarce in typical mantle peridotites, are among the most common inclusions found in peridotitic diamonds. The oxygen fugacity ($fO_2$) determined from their chemical composition is considered to reflect the redox state of their source mantle rocks.

In this study, a magnesiochromite-olivine touching pair hosted in a diamond from the Udachnaya kimberlite (Siberia, Russia) was investigated by in-situ Single-crystal X-ray Diffraction (SCXRD) and Energy-Domain Synchrotron Mössbauer Spectroscopy (SMS), aiming to constrain the physical-chemical conditions of diamond formation and to explore the redox state of this portion of the Siberian craton when the diamond was formed. Thermo-oxy-barometric analyses indicate the P-T-$fO_2$ conditions of the inclusion pair at the time of entrapment to be respectively ~ 5.7(0.4) GPa, ~ 1015(50)°C and $\Delta$log $fO_2$ = -1.4(0.8) relative to the fayalite-magnetite-quartz (FMQ) buffer. The determined $fO_2$ value falls near the enstatite-magnesite-olivine-diamond (EMOD) buffer, which marks the upper limit for diamond stability, and is very similar to those of xenoliths from Udachnaya originating from the approximately the same depth. However, while xenoliths last equilibrated with the surrounding mantle just before their entrainment in the kimberlite at ~ 360 Ma, the inclusion retains the signature of a mantle as old as 3.5-3.1 Ga or ~ 2 Ga, i.e., the time at which the magnesiochromite-olivine pair got trapped in its host diamond, and allows the earlier redox state of the source mantle to be evaluated. Based on the similarity between xenoliths and inclusion $fO_2$'s, we propose that the modern redox state of at least this portion of the Siberian lithosphere was attained relatively early after its formation and persisted for billions of years after diamond formation. Our $fO_2$ estimate for the inclusion pair also provides the first direct evidence for diamond formation under relatively oxidizing conditions ($\Delta$FMQ between about -1 to -2). These conditions are consistent with recent models of diamond formation suggesting relatively oxidized, water-rich CHO fluids as the most likely parents for lithospheric diamonds (Luth & Stachel, 2014).

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# Geochemistry and volatile contents of olivine-hosted melt inclusions from Mt. Etna tholeiitic and alkaline magmatism

Giacomoni P.P.*[1], Masotta M.[1], Delpech G.[2], Lanzafame G.[3], Ferlito C.[3], Villeneuve J.[4] & Coltorti M.[5]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Department of Geological Sciences, University of Paris-Saclay (France). [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [4] Centre de Recherches Pétrographiques et Géochimiques, CNRS, Nancy (France). [5] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* pierpaolo.giacomoni@unipi.it

*Keywords:* mantle melting, volatile elements, primary magmatism.

Geochemistry and volatile contents of high pressure/high temperature re-homogenized olivine-hosted melt inclusions (MIs) provide new insights on the composition of parental magmas from Mt. Etna. The concentrations of $H_2O$, $CO_2$, F, Cl and S were determined by Secondary Ion Mass Spectrometry (SIMS) in MIs trapped in $Fo_{88\text{-}67}$ olivines, with the aim to investigate the volatile compositional variations and degassing of the volatile phase through the whole, vertical-extended feeding system. The MIs composition varies significantly in terms of major elements (36.64-45.84 wt.% $SiO_2$; 3.39-7.98 wt.% $Na_2O+K_2O$). Despite the still well-documented trend towards more $K_2O$-rich magmas in recent products, both sodic and potassic melts co-exists in MIs from the alkaline period. A rhyolite MELTs fractionation modelling was conducted and is able to reproduce most of the observed geochemical differences by means of polybaric crystallization along the Ol+Sp/Mt+Cpx+Plg liquid line of descent under a variable $fO_2$ regime (DFMQ varying from +1.5 to +3). The studied MIs also present variable volatile contents (2.14-5.27 wt.% $H_2O$; 282-8151 ppm $CO_2$; 132-640 ppm F; 213-1400 ppm Cl and 15-1359 ppm S). From early tholeiites to the recent 2015 alkaline products, a slight decrease in the molar $H_2O/(H_2O+CO_2)$ ratio is observed with time, allowing to estimate a minimum 10600 ppm $CO_2$ and maximum of 5.2 wt.% $H_2O$ in primary melts of the current activity. The solubility modelling suggests that most of MIs underwent significant degassing, mostly under open-conduit regime or in closed-system with up to 25% in excess of fluid phase. The possible causes of the observed changes in $H_2O/(H_2O+CO_2)$ molar ratio can be reconciled with small changes in the eutectic proportions of amph+phlog during partial melting of a spinel fertile lherzolite.

# Gas geochemistry at Gran Comore and Mayotte Islands, Indian ocean: first results

Liuzzo M.*[1-2], Di Muro A.[3-4], Rizzo A.L.[1-5], Caracausi A.[1], Grassa F.[1], Boudoire G.[1-6] & Coltorti M.[1-2]

[1] INGV, Palermo. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [3] Institut de physique du globe de Paris, CNRS, Université de Paris (France). [4] Observatoire volcanologique du Piton de la Fournaise, Institut de physique du globe de Paris, La Plaine des Cafres (France). [5] INGV, Milano. [6] Laboratoire Magmas et Volcans, Université Clermont Auvergne, CNRS, IRD, OPGC, Clermont-Ferrand (France).

*Corresponding author e-mail:* marco.liuzzo@ingv.it

*Keywords:* He-Ne_Ar, $CO_2$ & isotopic-signature.

Located within the Mozambique Channel, Comoros archipelago is situated within a complex geodynamic system of great interest owing to recent and ongoing volcanic and seismic activity. While knowledge of the region in terms of petrography and geophysics is well-developed, very little research has been conducted regarding gas geochemistry. Two particular islands of the archipelago, Grande Comore and Mayotte, show significant evidence of active volcanism. Situated on Grande Comore is Karthala volcano, a basaltic shield volcano that has erupted regularly over the last century. It is the most active volcano in the western Indian Ocean after Piton de la Fournaise in La Reunion. In contrast, Mayotte, the oldest island in the archipelago, has witnessed no eruptions since that documented around 2050 BC ± 500; volcanic activity associated with Mayotte is still very much present, however, in the form of a large area of subaerial and underwater degassing on the small island of Petite Terre, just off the north-east coast. This island was recently (2018) affected by an important seismic crisis that lasted several months, and was accompanied by the formation of the largest submarine volcano in recent centuries.

This work presents the first findings of pilot geochemical surveys undertaken in the above locations between 2018 and 2020, and provides results regarding the main components and isotopic characteristics of sampled gas emissions. Our results reveal helium isotopic ratios in the range of $\sim 6 \leq Rc/Ra \leq \sim 7.5$ at Petite Terre, and $\sim 4.6 \leq Rc/Ra \leq \sim 5.8$ at Karthala (Liuzzo et al., 2021). While both of these ranges are comparable to existing data in values found in fluid inclusions of Karthala lavas (Class et al., 2005), they are markedly different to OIB volcanoes where a lower mantle component is clearly present. Thus, the hypothesis of a deep plume interacting with the oceanic lithosphere characterised by a low-He signature (Class et al., 2009) remains a matter of debate. An alternative conjecture of a possible mixing between a homogeneous deep plume source (EM1 component), plus a variable contribution of the shallower heterogeneous and old metasomatised oceanic lithosphere finds a better match with our results. A further output of our results is the evaluation of the temporal variations recorded in the Rc/Ra ratio at Petite Terre. In detail, the increased $^3He/^4He$ ratios between 2008 and 2018-19, may be ascribed to a magma input from the mantle that lead to the recent submarine volcano activity offshore Petite Terre. The findings of this research address an existing gap in current knowledge of the gas geochemistry of the Comoros archipelago, not only allowing a correlation between the gas emissions measured at the surface and the related deep source connected to a potential SCLM mantle component, but also improving the understanding of the present state of magmato-volcano activity.

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# Origin of dunites adjacent to the mantle peridotite massif of Balmuccia (Ivrea-Verbano Zone, Italian Alps)

Mariani D.*[1], Tribuzio R.[1-2] & Zanetti A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.
[2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* davide.mariani01@universitadipavia.it

*Keywords:* lower continental crust, mantle-crust transition zone.

The Balmuccia mantle massif is enclosed in a deep sector of the Mafic Complex of the Ivrea-Verbano Zone (Southern Alps), gabbronorite-diorite batholith intruding the lower continental crust during the post-Variscan transtensional tectonics. The massif was interpreted as a mantle fragment tectonically-emplaced into the lower continental crust before the intrusion of the Mafic Complex (Quick et al., 1995). Here, new petrological and geochemical data are presented for two dunite lenses exposed at about 100 m east of the Balmuccia mantle massif, at a higher stratigraphic position, with the main purpose of providing new information about the formation of the Mafic Complex.

The two dunite lenses are some tens of meters thick, and about 1 km apart. They are both mantled by a pyroxenite reaction ring, similar to that enclosing the Balmuccia mantle massif (Quick et al., 1995), and share similar micro-structural and compositional characteristics. The dunite olivine has 85 mol% forsterite and is associated with spinel including irregular Cr-magnetite blebs and rims. The dunites also comprise accessory amounts of clinopyroxene, amphibole (pargasite) and sulfides (troilite and minor pentlandite). The chondrite-normalized Rare Earth Element (REE) patterns of both the clinopyroxene and the amphibole are characterized by slight enrichment of heavy REE over middle REE, and variable light REE fractionation compared to middle REE.

We propose that the two dunite lenses originally formed a single body, dismembered by the formation of the gabbronorites of the Mafic Complex. The dunites most likely record a process of reaction with infiltrating melts migrating through porous flow, which crystallized clinopyroxene, amphibole and sulfides, and led to formation of Cr-magnetite blebs and rims in spinel. We speculate that this process preceded the formation of the pyroxenite reaction ring. Two major hypotheses may be formulated for the origin of the studied dunites. In the first, the dunites have a cumulus origin, namely they represent the early crystallization products of chemically primitive melts intruding the lower continental crust during the early growth stages of the Mafic Complex. In the alternative scenario, the dunites originally were in physical continuity with the Balmuccia mantle massif, to represent an ancient mantle-crust transition zone.

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# EntraPT: an online platform for host-inclusion elastic thermobarometry

Mazzucchelli M.L.*[1], Angel R.J.[2] & Alvaro M.[3]

[1] Mainz Institute of Multiscale Modeling & Institute of Geosciences, Johannes Gutenberg University, Mainz (Germany).
[2] Istituto di Geoscienze e Georisorse, CNR, Padova.
[3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* mmazzucc@uni-mainz.de

*Keywords:* thermobarometry, elastic barometry.

Information on the evolution of the lithospheric mantle through time can be obtained by investigating exposed mantle rocks and diamonds. To this aim, correct estimates of their pressures and temperatures (P-T) history are often necessary. The elastic interaction between mineral inclusions and their host minerals provides a method of geobarometry independent of the achievement of chemical equilibrium. Remnant strains in an inclusion trapped inside a host mineral are developed because the inclusion and the host have different thermoelastic properties, and the inclusion does not expand in response to P and T as would a free crystal. When rocks are exhumed to the surface of the Earth, residual strains may be still preserved in mineral inclusions and can be quantified with micro-Raman spectroscopy and/or X-ray diffraction while the inclusion is still contained in its host. If measured and interpreted correctly, they give us information on the pressures experienced by rocks and diamonds in their history.

EntraPT is an online platform that provides an easy-to-use tool to calculate the entrapment conditions of inclusions, with error propagation, from the residual strain measured in mineral inclusions. EntraPT establishes a workflow to import and analyse the measured residual strains, calculate the mean stress in the inclusions, compute the entrapment isomekes with uncertainty estimation, and visualize all the results in relevant graphs. It enables the user to avoid the many possible errors that can arise from manual handling of the data and from the numerous steps required in geobarometry calculations. The elastic calculations are based on a consistent dataset of validated Equations of State (EoS) and elastic stiffness tenors, that is expanded in time as properties of further minerals become available. This allows barometric calculations to be performed on both quasi-isotropic and anisotropic minerals. For all the calculations involving EoS, EntraPT relies on Eosfit7, a stable and efficient Fortran code that has been validated over many years. All of the data, parameters and settings are stored in a consistent format and can be exported as project files and spreadsheets, and imported back to EntraPT for further analysis. This allows researchers to store and/or share their data easily, making the checking and the comparison of data and results reliable. We will show how EntraPT can be used to carry out detailed analyses of the residual strains measured in inclusions and to calculate the entrapment isomekes with their uncertainties.

EntraPT is accessible at http://www.mineralogylab.com/software/.

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# Amphibole formation in ultramafic rocks: settings, processes and thermometry

Moutzouris D.*[1], Kostopoulos D.[1], Pomonis P.[1] & Moulas E.[2]

[1] Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens (Greece). [2] Institut für Geowissenschaften, Johannes Gutenberg-Universität Mainz (Germany).

*Corresponding author e-mail:* dimmoutz@geol.uoa.gr

*Keywords:* amphibole, mantle, geothermometry.

Amphibole is a secondary phase commonly found in ultramafic lithologies (mantle xenoliths, Alpine-type and ophiolitic peridotites) occurring in diverse environments such as magmatic arcs, plate interiors, transform faults, rifts and collision zones. Its formation has mainly been attributed to fluid-melt/rock interaction (reactive amphibole) or direct crystallisation from melts/fluids (precipitative amphibole). We compiled an extensive database using published major-element analyses of natural amphiboles in ultramafic rocks from various geotectonic settings but also from a wide spectrum of experiments on mafic to felsic compositions. Our approach enables discriminate between different types of amphibole and the processes involved in their formation. Type-I amphiboles (enriched in Na and Ti but depleted in Cr) are the products of direct crystallisation from basaltic, basanitic, andesitic and dacitic melts and are mostly found in continental arcs (e.g., Kharchinsky volcano, Kamchatka, Russia), within-plate settings (e.g., West Eifel, Germany) and oceanic transform faults (e.g., 15°20΄N Fracture Zone, Mid-Atlantic Ridge). Type-II amphiboles are Cr-rich, contain variable amounts of Ti and alkalis, and form via reaction between the aforementioned melts and primary mantle phases (mostly clinopyroxene and spinel). They are usually found in within-plate magmatic centers (e.g., Massif Central, France) and several localities in continental arcs (e.g., Ichino-megata, Japan). Amphiboles belonging to type-III reflect hydrous fluid/melt-rock interactions above subduction zones (hydrothermal amphiboles are included here). Type-III amphiboles are predominantly encountered in oceanic arcs (e.g., TUBAF seamount, PNG) and ophiolites (e.g., Lycian Ophiolite, Turkey) but occasionally they also occur in continental-arc settings (e.g., Avacha volcano, Kamchatka, Russia). Interestingly, ophiolitic amphiboles from more depleted mantle peridotites show higher Cr contents. Our methodology is in essence an inversion technique that sheds ample light on the mode of formation of amphibole in mantle rocks based solely on the major-element composition of the mineral when any other piece of information is unavailable. We have furthermore calibrated a new FeMg exchange thermometer between amphibole and clinopyroxene based on existing experimental data on ultramafic compositions with an error of ±46°C in the pressure range 0.5-3.7 GPa. Peridotite xenoliths that display good evidence of textural and chemical equilibration among their constituent minerals (e.g., Dish Hill, California, USA; West Eifel, Germany; Eastern Transylvanian Basin, Romania; Injibara, Ethiopia) yield amphibole temperatures comparable to those predicted from two-pyroxene FeMg exchange thermometry. Our thermometer can be used to quantify amphibole residence in the mantle at ambient temperatures for time periods long enough so as to diffusionally equilibrate with primary phases.

# The initial differentiation stages of the Middle Triassic magmas in the Southern Alps as recorded by clinopyroxenitic xenoliths from the Latemar area (Dolomites)

Nardini N.*[1], Ntaflos T.[2], Zanetti A.[3] & Coltorti M.[1-4]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Department of Lithospheric Research, University of Vienna (Austria). [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] INGV, Palermo.

*Corresponding author e-mail:* nrdncl@unife.it

*Keywords:* clinopyroxene, Middle Trias, cumulates.

The lack of effusive products with primitive composition makes the reconstruction of the early liquid line of descent of Mid-Triassic transitional magmatism in the Southern Alps challenging. In this study, we present a detailed compositional study of clinopyroxenitic xenoliths entrained in lamprophyric dykes cutting lava sequence north of Predazzo (Dolomites, Southern Alps). These xenoliths have a cumulitic texture, with well-preserved clinopyroxene crystals with sizes from 0.2 to 2 mm. The dominant phase is diopsidic clinopyroxene (Mg# = 90-92, Wo = 48-49, CaO ~24 wt.%), with $TiO_2$, $Cr_2O_3$, $Al_2O_3$ and $Na_2O$ contents in the range 0.05-0.2 wt.%, 0.15-0.4 wt.%, 0.7-1.4 wt.% and 0.1-0.5 wt.%, respectively. Sometimes, clinopyroxene crystals enclose small (~60 μm), resorbed olivine grains with $Fo_{85}$ and a NiO content up to 0.15 wt.%. Some clinopyroxenites are infiltrated by veins and their clinopyroxene crystals are diopsides with less primitive composition (Mg# = 83-84, Wo = 47-48, CaO ~23 wt.%) and zoning patterns in some individuals, having a more evolved rim (Mg# = 75-77) with $TiO_2$ and $Al_2O_3$ contents of 0.4-0.7 wt.% and 4.5-6.0 wt.% respectively. This compositional range is compositionally similar to the diopsidic bands (Mg# = 79-91; Wo = 44-47) of the clinopyroxene phenocrysts in the Mid-Triassic volcanic products from Predazzo, Mt. Monzoni, Cima Pape, and Sciliar. These diopsidic bands mostly occur between augitic cores and rims, and likely represent episodes of mafic recharge from a deep magma reservoir into the feeding systems of Mid-Triassic eruptive centers (e.g., Nardini et al., 2022). Hence, the crystals from clinopyroxenites in the Latemar area could represent the first cumulitic products of the Middle Triassic trachy-basaltic event in the Southern Alps, and the primitive compositional end-member of the diopsidic domain among clinopyroxene crystals in lavas. The reconstruction of the first stages of the liquid line of descent of these magmas could also be promoted by the olivine hosted in clinopyroxene crystals, whose compositions confirm the magmatic nature of the nodules.

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# Petrology and textures of mantle-wedge xenoliths from the Northern Andes (Mercaderes area, Colombia)

Notini L.*[1], Rampone E.[1], Scambelluri M.[1], Tommasi A.[2], Zanetti A.[3], Ferri F.[4-5] & Rodríguez-Vargas A.[6]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Géosciences Montpellier, Université de Montpellier (France). [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] Dipartimento di Geoscienze, Università di Padova. [5] EIT Raw Materials, South Innovation Hub, Roma. [6] Minerlab, Bogotà (Colombia).

*Corresponding author e-mail:* luca.notini@edu.unige.it

*Keywords:* xenoliths, mantle, Colombia.

Mantle xenoliths of the Granatifera Tuff pleistocenic body (Mercaderes - Rio Mayo area of Southern Colombia) offer a direct view of the supra-subduction mantle underneath the Northern Andes (Weber, 1998; Rodríguez-Vargas et al., 2005; Bloch et al., 2017). They range from subordinated garnet peridotite to dominant garnet websterite, ortho- and clinopyroxenites. Granular structures (evident in garnet pyroxenite) are shown by a few xenoliths that retain evidence of melt-rock interaction (e.g., anhedral interstitial garnet, orthopyroxene overgrowing and overgrown by coarse, anhedral pyroxene grains). Most xenoliths show porphyroclastic textures, with coarse porphyroclasts (ortho-, clinopyroxene and garnet) embedded in a fine-grained recrystallized matrix composed by orthopyroxene ± clinopyroxene ± olivine. The Mg-value of most mantle minerals lies between 88 and 92 associated with relatively low amounts of incompatible elements (Na contents in clinopyroxene between 0.70-1.60 wt.%). The major and trace element mineral compositions are very homogeneous within a single xenolith, without core-to-rim or porphyroclast-to-matrix variations. REE concentrations in clinopyroxene and garnet follow the Mg# distribution, with higher amounts of incompatible elements associated to the more fertile (i.e., with lower Mg-value) xenoliths. Pressure-temperature estimates (performed using two pyroxene and garnet-pyroxene calibrations) range between 24-40 kbar and 1000-1250°C. Modes, textures and the deformation state of all xenoliths have been studied through EBSD analysis resulting in the discrimination between granular, undeformed mantle rocks retaining evidence of pristine melt-rock interaction and variably deformed up to mylonitic samples, some of which carries evidence of fluid-rock interaction. These new data suggest that the Mercaderes xenoliths derive from a heterogeneous deformed mantle-wedge domain that only slightly interacted with subduction-related melts and fluids.

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# The composition of noble gas and $CO_2$ in the European subcontinental lithospheric mantle

Rizzo A.L.*[1-2] & Coltorti M.[2-3]

[1] INGV, Palermo. [2] INGV, Milano. [3] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* andrea.rizzo@ingv.it

*Keywords:* noble gases, $CO_2$, mantle.

The investigation of mantle-derived products coming from Sub Continental Lithospheric Mantle (SCLM) is crucial for constraining its geochemical features and evolution, the mantle-crust interaction, the volatiles recycling, and for better evaluating the information arising from the study and monitoring of volcanic gases. A significant contribution in the comprehension of the mantle features may come from the study of noble gases and $CO_2$ trapped as fluid inclusions (FI) hosted in ultramafic xenoliths, coupled with the petrography and chemistry of the minerals.

Here, we report a reappraisal of the knowledge recently developed on the European SCLM, based on the study of distinct suites of mantle xenoliths representative of the mantle beneath Lower Silesia (19-21 Ma; Eger Rift in SW Poland), Persani Mts. (0.6-1.2 Ma; Eastern Transylvanian Basin, Romania), Eifel (0.01-0.5 Ma) and Siebengebirge (6-30 Ma; Germany).

The chemistry of FI (He-Ne-Ar-$N_2$-$CO_2$ systematics) reveal that: i) FI are $CO_2$-dominated with variable amounts of $N_2$; ii) there seems to be a systematic different partition of volatiles between olivine and pyroxene, which probably reflect either crystallographic features or the distinct behaviour of the minerals during mantle recrystallization in sub-solidus conditions.

In detail, the mantle below Lower Silesia and Siebengebirge was depleted by variable extents of partial melting, with the overprinting in Lower Silesia of at least one metasomatic event by carbonated hydrous silicate melt related to Cenozoic volcanism. This process resulted in entrapment of $CO_2$-rich inclusions whose chemical and isotope composition resembles that of a metasomatizing melt with MORB-like signature. Instead, the mantle beneath Eifel reflect multiple metasomatism/refertilisation events by $CO_2$-rich melts that took place in the regional SCLM between ~6 and ~0.5 Ma. In Lower Silesia, however, the $CO_2$ isotopic composition indicates for the first time clear evidences of a recycled crustal carbon by old subducted altered oceanic crust and/or oceanic lithosphere. Finally, the mantle beneath Persani Mts. was strongly refertilized by a calc-alkaline subduction-related melt, which reflects the different geodynamics that characterizes this portion of the European mantle.

The $^3He/^4He$ ratio of the European mantle varies in the range 5.5-6.9 Ra, indicating a widespread recycling of crustal material related to fossil subduction(s) and confirms the complex geodynamics that characterized this continent. A more careful observation reveals that the $^3He/^4He$ values are the lowest in Persani Mts., where a subduction is still active, while are the highest where the SCLM was metasomatized or refertilized by astenospheric MORB-like melts.

# The radiogenic nature of the lithospheric mantle beneath Lanzarote (Canary Islands)

Sandoval-Velasquez A.*[1], Rizzo A.L.[2-3], Aiuppa A.[1] & Coltorti M.[4]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] INGV, Palermo. [3] INGV, Milano.
[4] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* andreslibardo.sandovalvelasquez@community.unipa.it

*Keywords:* Canary Islands, mantle xenoliths, stable isotopes.

In this study, the carbon (of $CO_2$) and noble gas isotope signatures of fluid inclusions hosted in Lanzarote mantle xenoliths were investigated. The analyzed samples come from Quaternary alkali basic lavas belonging to cycles III and IV of Fuster et al. (1968), which are recognized as the most recent volcanic deposits on the island. In this study, 7 mantle xenoliths were investigated: 6 spinel harzburgites and 1 dunite. We find 4He/20Ne and $^{40}Ar/^{36}Ar$ ratios comparable to those measured in xenoliths from El Hierro islands (Sandoval-Velasquez et al., 2021), suggesting the presence of an atmosphere-derived component (possibly inherited from paleo-subduction events) in the lithospheric mantle beneath Lanzarote. In most of the samples, the $^{4}He/^{40}Ar^{*}$ ratios decrease from olivine (Ol) to orthopyroxene (Opx) at increasing Mg# with values lower than in xenoliths from El Hierro. This behavior is compatible with variable degrees of partial melting, which supports the residual character of the spinel harzburgites and dunite studied here. Rc/Ra values ($^{3}He/^{4}He$ ratios corrected for atmospheric contamination) indicate a more radiogenic mantle signature (5.97±0.44 Ra; 2σ, n = 13) than in El Hierro (7.45±0.26 Ra; 2σ, n = 14) and other Canary Islands (Sandoval-Velasquez et al., 2021). This evidence reinforces earlier findings of a systematic west to east decrease in $^{3}He/^{4}He$ ratios along the Canary Islands (from La Palma-El Hierro to Lanzarote). Considering that fluid inclusions in mantle xenoliths better preserve (than surface gases or lavas) the isotopic composition of the local mantle, these results point to source heterogeneity, and identify the presence of an enriched mantle (EM) component beneath eastern islands coming from the African subcontinental lithospheric mantle (SCLM). Finally, the first $\delta^{13}C$ values reported for Lanzarote show a heavier isotopic signature ($-2.25‰ < \delta^{13}C < +0.8‰$) than classical MORB-like upper mantle ($-8‰ < \delta^{13}C < -4‰$), as recently found in El Hierro xenoliths. This supports that recycled crustal carbon is presumably a regional characteristic of the upper mantle located beneath the Canary Islands.

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# Variable depletion signatures in the oceanic upper mantle

Sani C.*[1-2], Sanfilippo A.[1-3], Peyve A.A.[4], Genske F.[2] & Stracke A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Institut für Mineralogie, Westfälische Wilhelms-Universität, Münster (Germany). [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] Geological Institute, Russian Academy of Sciences, Moscow (Russia).

*Corresponding author e-mail:* camilla.sani01@universitadipavia.it

*Keywords:* mantle, isotopic heterogeneity.

The time-integrated effect of melt depletion is inferred from radiogenic signatures of mantle peridotites. For instance, Sm/Nd and Lu/Hf increase dramatically with the extent of melt extracted, and residual peridotites thus develop extremely high Hf and Nd isotope ratios over geologic time periods ($10^8$-$10^9$ years). Such 'ultra-depleted' Hf and Nd isotope ratios, however, are extremely rare amongst mantle peridotites (e.g., Stracke et al., 2011), although they should be general characteristics of the depleted upper mantle (Byerly & Lassiter, 2014; Sanfilippo et al., 2019). With this contribution, we reveal that 'ultra-depleted' hafnium isotope signatures are preserved in abyssal peridotites exposed in the Equatorial portion of the Mid Atlantic Ridge, where they are closely associated with peridotites characterized by moderate hafnium-neodymium isotope ratios. Combining major and trace elements (Sani et al., 2020) and Nd-Hf isotopic data we show that peridotites preserving highly radiogenic Hf values ($\varepsilon$Hf up to 101) have reacted with traversing melts, shown by their high Na contents and flat LREE in Cpx, and MORB-like Nd isotope ratios ($\varepsilon$Nd up to 12). These features reflect partial resetting of ancient highly depleted mantle by recent melt-rock reaction at the MAR axis. On the other hand, peridotites having Nd-Hf isotope ratios similar to the local MORB ($\varepsilon$Nd = 7-12 and $\varepsilon$Hf =12-19) reveal a purely residual character, such as very depleted incompatible element compositions. These features reflect a mantle parcel that developed with only modest incompatible element depletion until recent melting at the Mid Atlantic ridge axis, when it melted again, but did not react with migrating melts, and thus acquired its strongly residual character. The kilometer-scale association of such isotopically heterogeneous domains suggests that the upper mantle exposed in this portion of Atlantic formed by a combination of ancient and recent partial melting and ancient melt-rock reactions. The Earth mantle's isotopic record of prior melt extraction can thereby be moderated by past reaction with migrating melts, therefore limiting the overall incompatible element depletion of the Earth's mantle.

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# Textural and chemical characterization of glass-bearing mantle xenoliths from Fernando de Noronha, Brasil

Venier M.*[1], Ziberna L.[1], Mancini L.[2-3], Petrelli M.[4], Velicogna M.[5], Beltrame M.[1], De Min A.[1] & Lenaz D.[1]

[1] Dipartimento di Matematica e Geoscienze, Università di Trieste. [2] Elettra-Sincrotrone Trieste. [3] Lund Institute for Advanced Neutron and X-ray Science, Lund (Sweden). [4] Dipartimento di Fisica e Geologia, Università di Perugia. [5] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* marco.venier@phd.units.it

*Keywords:* xenoliths, metasomatism, Fernando de Noronha.

The Fernando de Noronha (FN) archipelago is located in the Atlantic Ocean, 350 km off the coast of NE Brazil. Its volcanism is characterized by multiple eruptions of different ages that have been triggered by intermittent melting of an enriched mantle source. This process is considered to be generated by the FN asthenospheric plume (Lopes & Ulbrich, 2015). The products of the magmatism are three main formations: Remédios, with a potassic and a sodic series, that shows an age ($^{40}Ar/^{39}Ar$) between 12.5±0.1 and 9.4±0.2 Ma, Sao José formation (9.5±0.4 and 9.0±0.1 Ma), which is the only one hosting mantle xenoliths, and finally Quixaba formation, characterized by nephelinites erupted between 6.2±0.1 and 1.3±0.1 Ma.

Many authors focused on mantle xenoliths from this locality, tentatively searching pieces of evidence of the FN mantle plume on the lithosphere. Rivalenti et al. (2000) reported that FN xenoliths show evidence of modal variation induced by reaction with percolating melts. The isotopic analysis performed on their clinopyroxenes were compatible with an EMII type source of metasomatism, same signature as the one of Remédios formation. Kogarko et al. (2001) reported the evidence of carbonate metasomatism. Their model invokes various degrees of partial melting, followed by the percolation of carbonate melts in the depleted mantle. The last model was proposed by Liu et al. (2019), which theorized infiltration of asthenospheric melts inside the lithosphere, followed by reactive percolation of the main magmatism that formed the islands.

In this contribute, we present the direct evidence of mantle metasomatism occurred in Fernando de Noronha archipelago. We performed both textural (optical microscopy and 3D X-ray microtomography imaging) and chemical analysis (EMPA and LA-ICP-MS) on K-rich glasses inside the xenoliths to understand the nature, dynamics, and composition of FN mantle section, to test the previous hypothesis and to give new insights on the formation and evolution of potassic rich melts within the lithosphere.

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# The nature of the mantle beneath La Grille volcano (Grande Comore Island, western Indian Ocean) as revealed by mineral chemistry, noble gas geochemistry and $CO_2$ abundance in ultramafic mantle xenoliths

Ventura Bordenca C.[1], Faccini B.*[2], Coltorti M.[2-3], Di Muro A.[4-5], Caracausi A.[3], Rizzo A.L.[3-6], Liuzzo M.[2-3], Aiuppa A.[1] & Pik R.[7]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [3] INGV, Palermo. [4] Institut de Physique du Globe de Paris, CNRS, Université de Paris (France). [5] Observatoire Volcanologique du Piton de la Fournaise, Institut de Physique du Globe de Paris (France). [6] INGV, Milano. [7] CNRS-CRPG, Université de Lorraine, Vandoeuvre-les-Nancy (France).

*Corresponding author e-mail:* claudio.ventura@hotmail.it

*Keywords:* mantle xenoliths, fluid inclusions, Grande Comore.

Petrology and fluid inclusions (FI) geochemistry are increasingly used in tandem to constrain the compositional features and evolution of the lithospheric mantle. In this study, we combine petrography and mineral chemistry with the first analyses of noble gases (He, Ne and Ar) and $CO_2$ concentrations in olivine-, opx- and cpx-hosted FI from ultramafic xenoliths collected at La Grille volcano in Grande Comore Island, in the attempt to better characterize one of the most controversial portions of the western Indian Ocean lithospheric mantle. Xenoliths have been divided in three groups on the basis of their textural features: Group 1 (Opx-bearing), characterized by protogranular to porphyroclastic texture overprinted by metasomatic reactions; Group 2 (Opx-free), with ad-cumulitic, infiltrated characteristics, and Group 3 (Cumulate), showing ortho-cumulitic texture. Petrographic observations and mineral phase compositions indicate that the sampled lithospheric portion experienced variable degrees of melting (from 5% to 35%), recorded by Group 1 most refractory harzburgites and lherzolites, as well as modal metasomatic processes as evidenced by the severe recrystallization of cpx at the expenses of opx in Group 1 fertile lherzolites and wehrlite and by Group 2 xenoliths. Crystallization of oversaturated basic silicate melts seems also to have occurred, as shown by Group 3 xenolith. The calculated equilibration temperatures range from 930°C to 1180°C with oxygen fugacity values between −0.93 and +0.71 $\Delta\log fO_2$ [FMQ]. A positive trend between temperature and $fO_2$ can be envisaged, with Group 2 and 3 xenoliths testifying for hotter and more oxidised conditions than Group 1. The variability of the He/Ar ratio (0.005-0.42), significantly below typical values of a fertile mantle (He/Ar = 1-5), can be explained by the variable degrees of partial melting coupled to metasomatism enrichment that may account for increasing He/Ar, as also indicated by the mineral composition. He-Ar-$CO_2$ relationships support the presence of a metasomatic process post-dating the melt extraction and affecting their relative abundances, as suggested by Coltorti et al. (1999). The $^3He/^4He$ isotopic signature corrected for air contamination (6.30 to 7.36 Ra) are intermediate between the lower limit of MORB mantle signature (8±1Ra) and the higher values of SCLM (6.1±0.9Ra). The Ne and Ar isotopic signatures are consistent with a mixing between an air-derived component and a MORB-like mantle, supporting the hypothesis for a lithospheric origin of the Comoros magmas. This is also corroborated by combining Ne with He isotopes, showing that La Grille ultramafic xenoliths are far from the typical plume-type compositions.

Coltorti M., Bonadiman C., Hinton R.W., Siena F. & Upton B. (1999) - Carbonatite metasomatism of the oceanic upper mantle: evidence from clinopyroxenes and glasses in ultramafic xenoliths of Grande Comore, Indian Ocean. J. Petrol., 40, 133-165.

# Reassessment of the geodynamic evolution of the mantle massifs of the Ivrea-Verbano Zone (Southern Alps) based on new petrochemical and geochronological data

Zanetti A.*[1], Decarlis A.[2], Ogunyele A.C.[3-1], Bonazzi M.[3-1] & Sanfilippo A.[3-1]

[1] Istituto di Geoscienze e Georisorse, CNR, Pavia, [2] Earth Sciences Department, Khalifa University of Science and Technology, Abu Dhabi (United Arab Emirates). [3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* zanetti@crystal.unipv.it

*Keywords:* lithospheric mantle, Southern Alps, magmatism.

The Ivrea-Verbano Zone (IVZ) is the westernmost sector of the Southern Alps. It is constituted by granulite-to-amphibolite-facies lower continental crust rocks that form the basement of the Adria plate (or Southern Adria).

Its present-day position, which exposes the former sub-horizontal succession tilted at the surface, results from a complex and still not a wholly-established sequence of deformation events, which took place from the post-collisional setting of the Variscan orogeny to the rifting and collisional stages of the Alpine orogenic cycle.

The IVZ (metasediments, metavolcanites, intrusive bodies) contain a wealth of mantle peridotite slivers.

The largest and best known orogenic mantle peridotites (from south to north, the Baldissero, Balmuccia, Premosello and Finero) are aligned along the Insubric Line at the lowest stratigraphic units of the IVZ, in contact with units of mafic-ultramafic crustal intrusives.

The constant association of the IVZ mantle peridotites with High-T shear zones suggests that none of them was emplaced into the crust by mantle diapirism. Alternative hypotheses involve emplacement at the crustal level at the onset of the Mesozoic extensional regime or tectonic addition to accretionary wedges of Paleozoic subduction zones. Recent gravimetric data and seismic experimental campaigns converge in indicating that high-density rocks compatible with the mantle materials are very close to the surface in the Ivrea-Verbano Zone near the Insubric Line, thus supporting the possibility that the large peridotite mantle massifs exposed to the surface are a direct expression of the underlying subcontinental mantle.

This contribution focuses on the new field, petrographic, geochemical and geochronological data, indicating that most of these peridotite massifs underwent a tectonic-magmatic evolution at conditions compatible with mantle environments up to the Mesozoic and that the associated mafic complexes have peculiar geochemical and structural characteristics.

These data will be discussed with a redefinition of the geodynamic evolution of mantle bodies, which could produce important new understandings on the evolution of mantle-crust systems at the Europe Africa margin. In particular, the compositional differences of the lithospheric mantle can have strongly affected the rifting process of the Adria margin in Jurassic times.

# S29.

# Stressed minerals and microstructures: a link between grain-scale processes and lithosphere dynamics


*CONVENERS & CHAIRPERSONS*

*Nicola Campomenosi (University of Hamburg)*

*Mattia Gilio (University of Pavia)*

*Mattia L. Mazzucchelli (University of Mainz)*

*Alberto Ceccato (University of Bologna)*

*Francesco Giuntoli (University of Bologna)*

*Barbara Marchesini (University of Roma - Sapienza)*

# Garnet Equations of State for interpreting inclusion stress states

Angel R.J.*

Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* rossjohnangel@gmail.com

*Keywords:* garnet, EoS, inclusions.

To interpret the remanent pressures, stresses and strains in inclusion phases in garnets as their entrapment conditions by the methods of elastic geobarometry accurate EoS are required. However, differences between published EoS even for the end-member garnets often prevent meaningful or reliable geological information to be obtained from the stress states of inclusions trapped within them.

We have used experimentally-measured heat capacities to calculate the thermal pressure in order to determine the consistency of all published volume and elasticity data for the garnet end members grossular, pyrope, almandine and spessartine. All of the consistent data, both for elasticity and volume, was then simultaneously fitted by least-squares to determine the parameters of Mie-Grüneisen-Debye thermal-pressure EoS in combination with 3rd-order Birch-Murnaghan EoS to describe the isothermal compression at 298 K. For grossular and pyrope garnets there is sufficient data to determine that the value of $q$ used to define the volume dependence of the thermal Grueneisen parameter g as $q$ = d(ln g)/d(ln V) has a value of $q$ = 0.8(2). For other garnets, the data do not constrain the value of $q$ so we used a $q$-compromise version of the Mie-Grüneisen-Debye EoS in which both g/V and the Debye temperature are held constant at all P and T. For pyrope and grossular the two versions of the Mie-Grüneisen-Debye EoS predict indistinguishable properties over the metamorphic pressure and temperature range, and the same properties as the EoS based on experimental heat capacities. Final refined parameters are listed in the order $V_0$, $K_{0T}$, K', Debye temperature and $g_0$:

Pyrope : 113.13 cm$^3$/mol, 169.3(3) GPa, 4.55(5), 771(28) K, 1.185(12)
Almandine: 115.25 cm$^3$/mol, 174.6(4) GPa, 5.41(13), 862(22) K, 1.16
Spessartine: 117.92 cm$^3$/mol, 177.57(6) GPa, 4.6(3), 860(35) K, 1.18(3)
Grossular: 125.35 cm$^3$/mol, 167.0(2) GPa, 5.07(8), 750(13) K, 1.156(6)

Files containing these EoS for use in the EosFit7 are available at www.rossangel.net and in the EntraPT software for elastic barometry calculations at www.mineralogylab.com.

The biggest change from previously-published EoS is for almandine for which the new EoS predicts geologically reasonable entrapment conditions for zircon inclusions in almandine-rich garnets.

# Raman spectroscopic study of omphacite at variable pressures

Baratelli L.*[1], Cámara F.[1] & Mihailova B.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Department of Earth Sciences, University of Hamburg (Germany).

*Corresponding author e-mail:* lisa.baratelli@unimi.it

*Keywords:* omphacites, Raman spectroscopy, elastic geobarometry.

Omphacitic clinopyroxenes ((Ca,Na)(Mg,Al)$Si_2O_6$) made up of a solid solution of jadeite, augite and aegirine are among the principal constituents of eclogites and can be found in blueschist facies or ultra-high-pressure rocks. They can be also recovered in the Earth's upper mantle and in the subducted oceanic crust. Natural omphacites have two distinct polymorphs, a low-temperature phase with a space group *P*2/*n*, which shows splitting of the octahedral sites and the relative cation ordering, and a high-temperature chemically disordered phase with space group *C*2/*c*.

Raman scattering of a mineral is very sensitive to structural deformations developed while heating or under external stresses, a phenomenon that is the basis of Raman elastic geobarometry. This novel method is based on the contrast in elastic properties between the host and the inclusion, and allows estimating pressure and temperature of entrapment of an inclusion, to the condition of knowing the elastic properties of both the host and the inclusion and the residual strain of the latter, allowing estimating the conditions attained during metamorphic processes (Angel et al., 2018). Therefore, the application of this methodology to omphacites requires an accurate knowledge of their elastic behaviour, for which several data are available (for example Pandolfo et al., 2012) and its response to stresses accounted through Raman spectroscopy, which has never been systematically applied for studying omphacites under variable pressure conditions. This technique has already been used to investigate the order-disorder phenomenon in the octahedral sites of omphacites (Katerinopoulou et al., 2008) and it has been shown how the position and width of some Raman peaks depends on the ordering state. Therefore, this study would permit to calculate the entrapment pressure of omphacite inclusions and would potentially allow calibrating which Raman peaks are insensitive to changes in cation ordering.

Here we report the results from in situ high-pressure Raman spectroscopy on omphacites crystals from Münchberg Massif (Bavaria, Germany) formed at metamorphic-peak conditions of 2.5 GPa/600-700°C (O'Brien, 1993).

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Pandolfo F., Nestola F., Cámara F. & Domeneghetti M.C. (2012) - New thermoelastic parameters of natural C2/c omphacite. Phys. Chem. Minerals, 39, 295-304.

# In-lab rheology of host-inclusion systems and implications for elastic geothermobarometry

Campomenosi N.*[1], Angel R.J.[2], Alvaro M.[3] & Mihailova B.[1]

[1] Department of Earth Sciences, University of Hamburg (Germany). [2] Istituto di Geoscienze e Georisorse, CNR, Padova. [3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* nicola.campomenosi@uni-hamburg.de

*Keywords:* host-inclusion rheology, zircon, Raman spectroscopy.

Elastic thermobarometry constrains the pressure (P) and temperature (T) of metamorphic processes by using the contrast in the thermoelastic properties between host minerals and inclusions trapped within them. Since confined inclusions cannot expand as a free crystal, they develop a residual pressure $P_{inc}$, which is usually measured via Raman spectroscopy. For a given $P_{inc}$ there is a P-T line along which no confinement effects exist. This is the isomeke and it represents the possible conditions of inclusion entrapment. Away from the isomeke, the inclusion exhibits elastic compression or tension with respect to a free crystal at the same external P and T (e.g., Angel et al., 2015). Elastic thermobarometry then gives correct entrapment conditions provided no plastic deformation of the host occurred during its post-entrapment metamorphic history. Until now, the effects of visco-plastic processes have been investigated only via numerical models (e.g., Zhong et al., 2020).

We have investigated both the elastic and non-elastic behaviour of host-inclusion systems by in situ Raman spectroscopy of zircon inclusions in garnets during heating at ambient P. We find that upon heating, plastic relaxation takes place immediately after the zircon inclusions develop tensile strains with respect to a free crystal at the same T. When the system is subsequently cooled a stress gradient in the host and a $P_{inc}$ in the inclusion is again developed that reflect the maximum T reached. This suggests that the resistance to plastic deformation of garnet decreases considerably under tensile stress. Therefore, we conclude that ZiG systems are more reliable when applied to low-P high-T rocks where the exhumation path goes quickly into the compression domain of the inclusion. On the other hand, plastic relaxation and consequent ZiG resetting will easily occur in high-P rocks where quasi-isothermal exhumation paths will have brought the inclusion into a tensile state at high-T and low-P, where it will be reset. This explains why ZiG systems from some UHP rocks exhibit $P_{inc}$ that correspond to conditions during exhumation and not entrapment.

Angel R.J., Nimis P., Mazzucchelli M.L., Alvaro M. & Nestola F. (2015) - How large are departures from lithostatic pressure? Constraints from host-inclusion elasticity. J. Metam. Geol., 33(8), 801-813.

Zhong X., Moulas E. & Tajčmanová L. (2020) - Post-entrapment modification of residual inclusion pressure and its implications for Raman elastic thermobarometry. Solid Earth, 11(1), 223-240.

# myflow2.0 – a practical Matlab toolbox for rheological modelling of mylonites

Casini L.*[1] & Maino M.[2]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* casini@uniss.it

*Keywords:* shear zone, crustal strength, paleopiezometry.

Mylonites form in a wide range of metamorphic conditions in mid- to lower-crustal shear zones and provide fundamental constraints to develop integrated Pressure-Temperature-Deformation paths. The grain size of a recrystallized monomineralic aggregate deformed by dislocation creep is inversely correlated with differential stress according to piezometric equations, thus mylonitic rocks could be potentially used to assess the rheology of ductile shear zones (Twiss, 1977). Yet, mylonites are commonly composite rocks made of two or more mineral phases characterized by different physical properties. The compositional heterogeneity of mylonites limits the applicability of piezometric relationships, posing significant limitation for evaluating the strength of the ductile crust. Besides, each mineral in the composite accommodates strain by variable grain size-stress- and temperature-dependent deformation mechanisms, making the rheological analysis of composite mylonites a challenging task. In this contribution, we analyze the microstructure of composite mylonites using myflow 2.0, a Matlab-derived software package that includes several piezometric calibrations derived for the main mineral phases and evaluate, for each phase, the active deformation mechanism in stress-strain rate-temperature-grain size space. The code implements also several mixture models based on different mechanical constraints that allow to model the rheological behavior of composite rocks with heterogeneous grain size distribution. The code is demonstratively used to evaluate the rheology of selected mylonite samples collected from three amphibolite to granulite facies shear zones from the Variscan crust of Sardinia, the Western Alps, and the Mid-Atlantic ridge.

Twiss R.J. (1977) - Theory and applicability of a recrystallized grain size paleopiezometer. Pure Appl. Geophys., 115, 227-244.

# Mineral reactions during earthquakes

Di Toro G.*[1-2], Aretusini S.[2], Chinello M.[2], Cornelio C.[1], Del Rio L.[1], Feng W.[1], Gomila R.[1], Masoch S.[1], Nielsen S.[3], Pennacchioni G.[1], Spagnuolo E.[2] & Tesei T.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] INGV, Sezione di Sismologia e Tettonofisica, Roma. [3] Department of Earth Sciences, Durham University (UK).

*Corresponding author e-mail:* giulio.ditoro@unipd.it

*Keywords:* earthquakes, minerals, rock friction.

In the upper crust, the seismic versus aseismic behavior of natural faults is driven by on-fault and off-fault physical and chemical processes fueled by the release of elastic strain energy stored in the wall rocks (Scholz, 2019). Though our understanding of earthquake mechanics and of the seismic cycle increased considerably in the last decades, basic questions critical also for seismic hazard assessment still remain without answer. For instance, why most seismic ruptures propagate for some meters whereas very few for tens of kilometers becoming large-in-magnitude damaging earthquakes? How fault zones and their wall rocks heal and seal during the seismic cycle allowing the storage of new elastic strain energy after a mainshock?

The mineral assemblages of the fault and wall rock, their interaction with pore fluids, their spatial distribution, and evolution with time, play a key role in the ability of a fault network to nucleate, propagate and arrest seismic ruptures. In particular, during seismic faulting, given the large slip rates (about 1 m/s), displacements (up to tens of meters for large-in-magnitude earthquakes) and effective stresses (tens of MPa), a large amount of frictional work (0.1-100 MJ/$m^2$) and work rate (1-100 MW/$m^2$) is dissipated within mm- to cmthick fault slipping zones. These deformation conditions result in intense rock fragmentation and possibly abrupt temperature increase which trigger pore fluid phase transitions, mineral breakdown and release of volatiles, formation of new minerals and of amorphous and highly reactive materials which control – or are associated with – the activation of a plethora of co-seismic fault weakening mechanisms. Depending on the ambient conditions (temperature, pressure, presence and composition of the pore fluids, etc.) these peculiar "co-seismic" rock products contribute to the type and on the magnitude of the post-seismic fault healing.

Here we will discuss recent microanalytical observations of natural and experimental fault products, the latter also obtained with newly-conceived machines and devices, aimed at the investigation of mineral reactions & fluid-rock interaction occurring during seismic slip and post-seismic fault healing. Some of the experimental datasets yielded quite surprising results (e.g., under hydrothermal conditions, "negative" post-seismic fault healing rates have been found) which are currently under investigation.

Mineral reactions activated during earthquakes are difficult to study because of challenging experimental, microanalytical and modeling/computational techniques, but also because their investigation and application to the seismic cycle requires a knowledge on the borderline between mineralogy, geology, geochemistry, experimental rock deformation and geophysics. However, these multidisciplinary studies may yield a new vision of earthquakes and the seismic cycle.

Scholz C.H. (2019) - The mechanics of earthquakes and faulting, 3rd Ed. Cambridge University Press.

# Microstructures of olivine gabbros from the Atlantis Bank OCC (SWIR): Role of compaction in melt extraction and accumulation at a slow spreading center

Ferrando C.*[1], Basch V.[2], Ildefonse B.[3], Deans J.[4], Sanfilippo A.[1-2], Barou F.[3] & France L.[5]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] Géosciences Montpellier, CNRS-Université de Montpellier (France). [4] School of Biological, Environmental, and Earth Sciences, University of Southern Mississippi, Hattiesburg, MS (USA). [5] Université de Lorraine, CNRS, CRPG, Nancy (France).

*Corresponding author e-mail:* ottaferrando@gmail.com

*Keywords:* plagioclase crystallographic preferred orientation, magmatic fabrics, melt migration.

The exposure of gabbroic sequences at Oceanic Core Complexes (OCC) along ultraslow- to slow-spreading ridges permits the study of the processes forming the lower oceanic crust. On top of the Atlantis Bank OCC along the ultraslow-spreading Southwest Indian Ridge, IODP Expedition 360 drilled Hole U1473A, mainly composed of primitive olivine gabbros interspersed with more evolved Ti-Fe oxide-bearing gabbros. These rocks record a complex history of protracted magmatism during continuous uplift and deformation of the gabbroic sequence. Extensive crystal-plastic deformation is dominantly recorded in the shallower sections of the drillhole, whereas the deeper sections better preserve primary magmatic features. We focus on microstructures, including intra-crystalline deformation of rock-forming minerals, and plagioclase crystallographic preferred orientations of olivine gabbros lacking evidence for exhumation-related crystal plastic deformation, to gain insights on the relationship between compaction, melt migration and melt accumulation during the early magmatic history of this section of lower oceanic crust. Olivine gabbros are characterized by ubiquitous grain-size variations, from coarse- to fine-grained intervals. Minerals in coarse-grained intervals show intra-crystalline deformation, while fine-grained crystals lack internal strain. Bent coarse-grained plagioclase associated with weak magmatic foliation and lack of lineation suggest that the coarse-grained intervals were deformed under weak compaction. On the other hand, crystallographic preferred orientations of undeformed fine-grained plagioclase show weak lineations, likely indicative of non-coaxial strain. We thereby infer that the coarse-grained intervals underwent ongoing weak compaction from the stage of olivine + plagioclase ± clinopyroxene crystal mush to the melt-poor stage, and that this process likely aided melt extraction and accumulation in discrete melt-rich zones where crystals orientated in the direction of magmatic flow. Crystallization of melts in the melt-rich zones ultimately formed the fine-grained intervals at different depths in Hole U1473A. This indicates that processes of compaction can lead to local chemical and grain-size heterogeneities in a lower crustal section, while had a minor role in the melt movement at larger scales (e.g., the whole crystal mush) within the oceanic crust.

# Coupled elastic and intracrystalline geothermobarometers to constrain PT conditions of lower arc crust granulites

Gilio M.*[1], Cesare B.[2], Gianola O.[2], Ferri F.[2], Murri M.[3], Barbaro A.[1-2] & Alvaro M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Geoscienze, Università di Padova. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* mattia.gilio@gmail.com

*Keywords:* elastic geothermobarometry, QuiG.

In metamorphic petrology, element-exchange geothermobarometry allows us to retrieve the pressure and temperature (PT) conditions of equilibration of a mineral assemblage. However, their interpretation is particularly challenging in (U-)HT rocks due to chemical re-equilibration during cooling. Here we try to overcome the abovementioned problems of determining the UHT conditions of peak metamorphism or of mineral growth by proposing an alternative and viable method. We present and discuss the estimates of equilibration P-T conditions of a crustal garnet-pyroxenite xenolith from the Granatifera tuff, located in the Mercaderes-Rio Mayo area of the southern Colombian Andes, obtained using multiple geothermobarometric methods. This xenolith formed as a residue after extraction of granitic melt, and consists of garnet, clinopyroxene ($X_{Mg}$ 0.73, $Jd_{16}$), plagioclase ($Ab_{72}An_{26}Or_3$), minor pargasitic amphibole ($X_{Mg}$ 0.87) and accessory rutile and apatite. Garnet is chemically homogeneous ($Alm_{42-43}Pyr_{38-41}Grs_{16-20}Sps_1$) and often contains inclusions of quartz and zircon within the same crystals, as well as primary melt inclusions. Quartz is present only as inclusion in garnet. The sample has a well-equilibrated granoblastic texture, without evidence of reaction rims pointing to interaction with the host lava during entrapment and magma ascent.

We estimated the pressure and temperature of equilibration using a multi-methodological approach involving intracrystalline geothermometry, elastic geothermobarometry and classical Fe-Mg exchange between garnet and clinopyroxene. The equilibration temperatures obtained on clinopyroxenes using the intracrystalline geothermometer by Brizi et al. (2000) are around 1150-1250°C. This estimate is consistent with results of elastic geothermobarometry: the isomekes for quartz- and zircon-in-garnet indicate equilibration conditions of 1150-1200°C and 1.7-2.1 GPa. Instead, geothermometry based on Fe-Mg exchange between garnet and clinopyroxene (Nakamura, 2009) gives lower equilibration temperatures of 950-1000°C, suggesting a re-equilibration during regional cooling at the roots of the magmatic arc. Our results have important implications for the reliability of element-exchange geothermobarometry in UHT rocks. Elastic geothermobarometry gives reliable and independent P-T estimates and it is virtually unaffected by the diffusion-induced reset during retrogression typical of cation-exchange geothermometry. This new approach solves the long-standing issue of estimating pressure and temperature conditions in HT and UHT rocks and appears to be robust and reliable to temperatures as high as 1200°C.

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Nakamura D. (2009) - A new formulation of garnet-clinopyroxene geothermometer based on accumulation and statistical analysis of a large experimental data set. J. Metam. Geol., 27, 495-508.

# Hydrothermal fault healing evolution of tonalite, granodiorite and their fault-related products

Gomila R.*[1], Feng W.[1] & Di Toro G.[1-2]

[1] Dipartimento di Geoscienze, Università di Padova. [2] INGV, Roma.

*Corresponding author e-mail:* r.gomilaolmosdeaguilera@unipd.it

*Keywords:* fault healing rate, fluid-rock interactions, seismic cycle under hydrothermal conditions.

Understanding the mechanical and geochemical processes of fault rock development is a key clue into the understanding of fault healing rates. Fault healing rate $\beta$ – the change of the static friction coefficient ($\Delta\mu$) with log time ($\beta=\Delta\mu/\Delta log\ t_{hold}$) – is a significant parameter in the seismic cycle, controlling the storage of the elastic strain energy in the fault wall rocks and allowing earthquakes to repeatedly occur in pre-existing faults.

Fault healing is investigated by means of slide-hold-slide (SHS) experiments aimed at reproducing the seismic cycle. However, most of these experiments have been conducted, in the past years, under room conditions, while the ambient conditions for natural earthquakes nucleation is at temperatures T > 150°C and in presence of pressurized fluids. Under these conditions, fluid-rock interaction (reaction kinetics, pressure-solution transfer, sub-critical crack growth, etc.) may impact severely on *b* and on the magnitude of $\Delta\mu$ .

In this preliminary study, SHS experiments were performed in RoSA, a rotary shear apparatus equipped with HYDROS, a dedicated hydrothermal vessel, to investigate the healing behavior of gouge-bearing faults made of tonalite, granodiorite and their natural fault related products (chlorite- and epidote-rich gouges) and to explore how the mechanical properties and healing rates evolve with fault maturity due to changes in fault displacement and fault-products composition.

For each gouge type (grain size < 75 µm), two experiment of SHS were conducted, with run-in durations of 500s and 5000s each. The gouges were slid for ca. 15 mm and 60 mm respectively, at a slip rate of 10 µm/s and under an effective normal stress ($\sigma_n^{eff}$) of 10 MPa, a fixed temperature T of 300°C and a constant pore fluid pressure $P_f$ of 25 MPa. Hold periods between slip events ranged from 3s to 10000s, to investigate the dependence of $\beta$ with both cumulative slip and duration of the experiment.

Under this hydrothermal conditions ($P_f$ = 25 MPa and T = 300°C; liquid condition for water) preliminary data shows that for granodiorite gouges $\beta$ increased linearly with holding time ($\beta$ = $1.199\times10^{-2}\pm7.539\times10^{-4}$ and $\beta$ = $1.023\times10^{-2}\pm7.681\times10^{-5}$ , for run-in of 500s and 5000s respectively) until they switched to negative values of $\beta$ = $-3.768\times10^{-2}$ and $\beta$ = $-2.351\times10^{-2}\pm2.045\times10^{-4}$ , for run-in of 500s and 5000s, and hold times of 3000s and 1000s respectively.

This suggest that under hydrothermal conditions, the total displacement and duration of the interaction between the fluids and the host minerals play a key role in enhancing mineral reactions that promotes negative healing (*b* < 0) in faults during the seismic cycle. Further microstructural and geochemical/mineralogical analyses of the experimental fault products will provide us with better tools to understand the underlying processes of fluid-rock interaction responsible for this change in faults behavior from *b* > 0 to *b* < 0 under hydrothermal conditions.

# Quartz-in-zircon elastic thermobarometry: methods and a first application

Gonzalez J.P.*[1], Morana M.[2], Alabarse F.G.[3] & Angel R.J.[4]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Chimica, Università di Pavia. [3] Elettra-Sincrotrone Trieste. [4] Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* joseph.gonzalez@unipv.it

*Keywords:* zircon, quartz, elasticity.

Zircon is frequently used for petrologic studies because it can be used for both geochronology and thermometry. However, there are few methods for determining the depths of zircon crystallization. To this aim, we have recently developed an elastic model for quartz inclusions in zircon hosts (QuiZ) that accounts for the host-inclusion orientation and can be used to calculate the anisotropic strains developed in the inclusion upon exhumation. This elastic model can be inverted to constrain the P-T conditions of host-inclusion elastic equilibration. However, QuiZ elastic thermobarometry not yet been applied because measurements of quartz inclusion strains via Raman spectroscopy is challenging because of the high-absorbance of the zircon host. In this study, we used single in-situ crystal X-ray diffraction (XRD) to measure quartz-in-zircon inclusion strains which allows us to overcome this analytical limitation. Zircon crystals from the Grenville age Woodland Gneiss near a shear zone in Georgia, USA were selected based on their abundance of large isolated quartz inclusions. Previous petrologic observations suggest that the zircons were metamorphosed at amphibolite facies conditions during shear zone deformation at mid-crustal depths. XRD measurements performed at the Xpress beamline of the Elettra synchrotron facility were used to determine the host-inclusion orientations and strained unit cell parameters of the inclusions. Strains of the inclusions were calculating from the difference in the unit cell parameters between the inclusion and a free quartz crystal measured during the same analytical session. The measured strains in the inclusions at ambient P-T conditions are slightly positive indicating that the inclusions are under tensile strains. Both isotropic and anisotropic elastic models were used to calculate entrapment isomekes that constrain the potential entrapment conditions. QuiZ isomekes calculated using the isotropic elastic model are consistent between individual zircon crystals and with the previously estimated regional metamorphic conditions. For the anisotropic elastic model we calculated the axial isomekes and their average. In principle, the intersection point of the axial isomekes should indicate the P-T condition of elastic equilibration. The average of the axial isomekes is consistent with previously proposed metamorphic conditions. However, the axial isomekes generally intersect at geologically unreasonably low pressures and temperatures. Further work is underway to understand the significance of the axial isomeke intersection and the associated uncertainties. Despite this, we conclude that this analytical method using XRD for the measurement of quartz inclusion strains in zircon hosts is reliable and can be used for thermobarometry.

# Crystal alignment and clustering during crystallisation of experimental basalt under strain

Griffiths A.T.*[1], Musu A.[2], Habler G.[1], Peres S.[1], Petrelli M.[3] & Caricchi L.[2]

[1] Department of Lithospheric Research, University of Vienna (Austria). [2] Department of Earth Sciences, University of Geneva (Switzerland). [3] Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* th.griffiths@univie.ac.at

*Keywords:* experimental petrology, electron backscatter diffraction, crystal clustering.

Crystallisation in volcanic systems rarely occurs in static conditions. The effects of melt flow on crystal shape, size, orientation, and clustering behaviour may have important consequences for rheology and melt-crystal separation. Experiments carried out in the Petro-Volcanology Research Group lab of the University of Perugia allow observation of the effect of strain on shape preferred orientation (SPO), crystallographic preferred orientation (CPO), and clustering behaviour during igneous crystallisation. A basaltic starting glass synthesised from lava from the 2002/3 eruption of Mt. Etna was placed in a 37 mm diameter crucible in a high temperature furnace. After heating above the liquidus (at room pressure in air), a central spindle was rotated to constantly stir the melt. The strain rate was fixed at $1s^{-1}$ at the spindle rim. The sample was cooled to 1170°C (~30°C undercooling), then subjected to sub-liquidus temperature oscillations to create chemical zoning, before air-quenching after 8 hours.

The sample contains mostly glass, subhedral plagioclase (Pl) and clinopyroxene (Cpx), with some skeletal magnetite (Mt). Electron backscatter diffraction (EBSD) mapping was carried out for two domains, one near to and one far from the spindle. Near the spindle, Pl exhibits a strong SPO subparallel to the shear direction and a weak CPO, with Pl (010) normals oriented subperpendicular to the shear plane. Cpx shows only a very weak SPO subparallel to the shear direction, and a very weak CPO characterised by Cpx [001] axes lying preferentially in the shear plane. Far from the spindle, the Pl SPO and CPO weaken considerably, the Cpx SPO disappears, the median Cpx grain length is 3x higher, and the area fraction of glass is 7% higher.

Near the spindle, touching Pl-Cpx and Cpx-Cpx grain pairs show preferential crystallographic alignments. Plotting crystal orientations with respect to their neighbours reveals a $\{110\}_{Pl}\|\{010\}_{Cpx}$ rotational statistical crystallographic orientation relationship (COR) for Pl-Cpx grain pairs, while Cpx-Cpx grain pairs follow a dispersional statistical COR ($\{110\}_{Cpx}\sim\|\{110\}_{Cpx}$ and $\{001\}_{Cpx}\sim\|\{001\}_{Cpx}$). Far from the spindle, very few boundary segments follow these statistical CORs. The CORs are thus inferred to indicate strain-induced alignment and clustering of crystals in the melt (synneusis). Heterogeneous nucleation is unlikely as individual grain pairs deviate from fixed (specific) CORs, and heterogeneous nucleation of Cpx on Cpx is energetically unfavourable vs. growth.

In conclusion, even where a strong SPO is present, CPO is weak. Therefore, detecting crystallisation under strain using anisotropy-based geophysical methods may be difficult. Statistical CORs resulting from crystal alignment and attachment are observed even where both SPO and CPO are weak, suggesting CORs may provide a more reliable indicator of crystallisation in flowing magma than SPO or CPO alone.

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# Fluid-rock interactions in nature and in the laboratory: through time and space using X-ray Computed Tomography

Macente A.*[1], Fusseis F.[2], Butler I.B.[2], John T.[3], Menegon L.[4], Tudisco E.[5], Hall S.[5], Andò E.[6] & Vanorio T.[7]

[1] Civil and Environmental Department, University of Strathclyde, Glasgow (UK). [2] School of Geosciences, University of Edinburgh (UK). [3] Department of Earth Sciences, Freie Universität Berlin (Germany). [4] Department of Geosciences, University of Oslo (Norway). [5] Department of Construction Sciences, Lund University (Sweden). [6] Center for Imaging, École polytechnique fédérale de Lausanne (Switzerland). [7] Department of Geological Sciences, Stanford University, Stanford, CA (USA).

*Corresponding author e-mail:* alice.macente@gmail.com

*Keywords:* X-ray computed tomography, fluid-rock interactions, pressure-solution creep.

Fluid-rock interaction represents a common deformation process that causes substantial local scale petrophysical and geochemical changes, affecting porosity and permeability properties of the rock. Understanding how fluid-rock interactions occur is critical to quantify how these local microscale dynamics affect the macroscale behaviour of the lithosphere. We used novel imaging techniques (X-ray Computed Tomography - XCT) to map the evolution of deformation microfabrics in 3D in natural samples, showing a chemical transformation from pristine olivine gabbros to omphacite-garnet bearing eclogites, as a result of strain localisation and fluid-rock interaction (Macente et al., 2017). The findings suggest that garnet coronas were mechanically disintegrated during strain localisation, and rearranged into individual clusters. With the advances in imaging techniques, we can also reproduce processes in the laboratory, and image their microstructural evolution as it happens in "real" time. We performed pressure-solution creep experiments, a common type of fluid-rock interaction deformation mechanism in the upper crust, that critically affects the hydraulic properties of rocks (Macente et al., 2018, 2019). Saturated NaCl powder samples were loaded uniaxially to a constant load. Different sample mixtures were tested to understand the effects of phyllosilicates (biotite) on the process. We imaged and quantified the evolution of NaCl grains over time during ongoing compaction and the distribution of the evolving porosity. The evolution of strain localisation in the samples was quantified through Digital Volume Correlation, while the evolution of permeability during ongoing deformation was measured with Lattice-Boltzmann Modelling. The results show that biotite induces a marked reduction in porosity and pore connectivity and contribute to an increase in the local strain rates by an order of magnitude over pure NaCl samples. Pressure solution creep causes the formation of a compaction band perpendicular to the direction of loading, forming a barrier for permeability. Biotite flakes create an enhanced porosity decrease leading to compaction and reduction of pore connectivity. This reduction in porosity affects local stresses and local contact areas, reducing over time the driving force. According to positive feedback between texture and porosity distribution, the reduction in porosity causes salt ions to dissolve in the marginal salt and precipitate within the biotite-bearing layer, where the bulk volume of salt grains increases over time. These results extend the current understanding of the effect of pressure-solution creep on the mechanical and hydraulic properties of rocks. We show the potential of using XCT in combination with other methods to quantify the evolution of microfabrics, porosity, permeability and strain localization through time and space during fluid-rock interaction processes, to map the deforming lithosphere at the microscale.

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Macente A., Fusseis F., Menegon L., Xianghui X. & John T. (2017) - The strain-dependent spatial evolution of garnet in a high-P ductile shear zone from the Western Gneiss Region (Norway): a synchrotron X-ray microtomography study. J. Metam. Geol., 35, 565-583.

Macente A., Vanorio T., Miller K.J., Fusseis F. & Butler I.B. (2019) - Dynamic Evolution of Permeability in Response to Chemo-Mechanical Compaction. J. Geophys. Res. Solid Earth, 124, 11204-11217.

# Subseismic strain rates at high-temperature (> 900°C) conditions driven by melt-enhanced grain-boundary sliding: inferences from 16.5° N, Mid-Atlantic Ridge

Maino M.*[1-2], Casini L.[3], Sanfilippo A.[1-2], Ildefonse B. [4] & Dick H.J.B.[5]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [4] Géosciences Montpellier, Université de Montpellier, CNRS, Université des Antilles, Montpellier (France). [5] Woods Hole Oceanographic Institution, Woods Hole, MA (USA).

*Corresponding author e-mail:* Alessio.Sanfilippo@unipv.it

*Keywords:* strain localization, grain boundary sliding, HT shear zone.

EBSD-based microstructural analyses were performed on variably deformed troctolites from the Mid Atlantic Ridge 16.5°N OCC (Casini et al., 2021). The deformation gradient is positively correlated with increasing temperature from ~900°C in the proto-mylonite to ~1100°C toward the mylonite-ultra-mylonite boundary. The deformation mechanisms operative in the decimetre-scale shear zone have been investigated using high-resolution EBSD analyses, plagioclase and olivine grain size piezometry and 1D rheological modelling. Deformation in proto-mylonite and mylonite is mainly accommodated by combined subgrain-rotation and grain boundary migration. Diffusion creep-accommodated grain boundary sliding is instead dominant in the ultra-mylonite band, as testified by a dramatic reduction of grain size (< 10 μm), substantial increase of the phase mixing, associated with weakening of the plagioclase CPO but enhanced shape preferred orientation and CPO intensity of amphibole. We argue that the deformation mechanism switch has resulted into a dramatic decrease of strength in the ultra-mylonite, providing the necessary softening for shear localization at high temperature conditions close to the solidus of troctolite. Weakening was promoted by the presence of amphibole and melt, which acted as microstructural lubricant that facilitated grain boundary sliding localizing deformation in a narrow shear zone. Rheological modelling indicates that the mylonite/ultra-mylonite transition corresponds to a local increase of both strain rate, from $1\times10^{-9}$ to $5\times10^{-7}$ $s^{-1}$, and differential stress, from about 60 to 200 MPa. This implies that the switch from dislocation creep to a grain-size sensitive mechanism approached the frequencies of slow slip earthquakes. This study highlights the importance of hydrated magmatic phases (amphibole) to promote the onset of detachment faulting still at very high-temperature (> 900°C) condition in Oceanic Core Complexes (OCC).

Casini L., Maino M., Sanfilippo A., Ildefonse B. & Dick H.J. (2021) - High-Temperature Strain Localization and the Nucleation of Oceanic Core Complexes (16.5° N, Mid-Atlantic Ridge). J. Geophys. Res. Solid Earth, 126(9), e2021JB022215.

# A journey towards the forbidden zone: a new, cold, UHP unit in the Dora-Maira Massif (Western Alps)

Manzotti P.*[1], Schiavi F.[2], Nosenzo F.[1], Pitra P.[3-4] & Ballèvre M.[3]

[1] Department of Geological Sciences, Stockholm University (Sweden). [2] Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, Clermont-Ferrand (France). [3] Université Rennes, CNRS, Géosciences Rennes (France). [4] Czech Geological Survey, Prague (Czech Republic).

*Corresponding author e-mail:* paola.manzotti@geo.su.se

*Keywords:* coesite, chloritoid, Dora-Maira.

The distribution of ultrahigh-pressure metamorphism (UHP) at the scale of a mountain belt is of prime importance for deciphering its past subduction history. In the Western Alps, coesite has been recognized in the southern Dora-Maira massif, in the lens-shaped Brossasco-Isasca Unit, but has not been found up to now in the other parts of the massif. We report the discovery of a new UHP unit in the northern Dora-Maira Massif (Western Alps), named Chasteiran Unit. It is only a few tens of metres thick and consists of garnet-chloritoid micaschists. Garnet inclusions (chloritoid, rutile) and its growth zoning allow to precisely model the P-T evolution. Coesite crystals, which are pristine or partially transformed to palisade quartz occur as inclusions in the garnet outer cores. According to thermodynamic modelling, garnet displays a continuous record of growth during the prograde increase in P and T (25-27 kbar 470-500°C) (stage 1), up to the coesite stability field (27-28 kbar 520-530°C) (stage 2), as well as sub-isothermal decompression of about 10 kbar (down to 15 kbar 500-515°C) (stage 3). The main regional, composite, foliation, marked by chloritoid and rutile, began to develop during this stage, and was then overprinted by chlorite-ilmenite (stage 4). The Chasteiran Unit is discontinuously exposed in the immediate hangingwall of the Pinerolo Unit, and it is located far away from, and without physical links to the classic UHP Brossasco-Isasca Unit. Moreover, it records a different, much colder, P-T evolution, showing that different slices were detached from the downgoing subduction slab. The Chasteiran Unit is the fourth and the coldest Alpine UHP unit known so far in the entire Alpine belt. Its P-T conditions are comparable to the ones of the Tian Shan coesite-chloritoid-bearing rocks.

# Deformation and fabric evolution in carbonate rocks during pluton emplacement: a tool to decipher competing magmatic and tectonic processes

Meneghini F.*[1], Vezzoni S.[2], Pandolfi L.[1], Marroni M.[1], Rocchi S.[1] & Dini A.[2]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* francesca.meneghini@unipi.it

*Keywords:* contact metamorphism, marble microfabric, Botro ai Marmi intrusive body.

The emplacement of intrusive bodies in the upper crust represents one of the best examples of the interplay between tectonic, metamorphic and magmatic processes: an intruding granitic pluton determines a thermal perturbation of the surrounding host rock leading not only to a progressive evolution in space and time of the temperature profile but also to a progressive variation in the rheological behaviour and strain accommodation of the host rocks, that is usually recorded by complex polyphased tectonometamorphic histories.

We have analysed at different scales the evolution of fabrics developed in marble during granite pluton emplacement, to show how large- to small-scale deformation structures can be used to describe the competition between tectonic, contact metamorphic and magmatic processes.

The selected area of Campiglia Marittima belongs to a portion of the Northern Apennine where post-collisional extensional tectonics led to the emplacement of several plutonic bodies. We have performed a geological-structural mapping of two quarries exploiting the marble host of one of these intrusions, and a microfabric study of marble sampled at different structural distances from the pluton.

A temperature-dependent polyphased deformation history was reconstructed, schematized in a "ductile phase", related to the peak of temperature reached during the waxing stage of contact metamorphism, and a "brittle phase" developed during the waning stage when temperature decreased, all obliterating the previous, collision-related deformation. The microstructural analysis of marble fabrics allowed to detail different evolution steps: the proposed model features a phase of pluton-related heating and high thermal gradient that allowed marble development through calcite static recrystallization, and ductile flow of the rheologically weakened marbles. As temperature decreased, deformation was accommodated in localized shear zones where static fabric was obliterated by dynamic recrystallization. Then, the "brittle phase" evolved through systems of joints and faults as well as by emplacement of porphyritic dykes and skarn-ore bodies.

# Quartz and zircon in garnet elastic geobarometry of HP rocks from the Sesia Zone

Mingardi G.*[1], Gilio M.[1], Giuntoli F.[2], Musiyachenko K.[3] & Alvaro M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [3] Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver (Canada).

*Corresponding author e-mail:* giulia.mingardi02@universitadipavia.it

*Keywords:* Sesia zone, elastic geobarometry, host-inclusion system.

The Sesia zone is a rifted portion of the Adriatic Margin that subducted to high-pressure conditions during the Alpine Orogeny. It consists of two main complexes: the Internal Complex (IC) and the External Complex (EC). The IC is made up of polymetamorphic micaschists, eclogites, and ortho-gneisses equilibrated at eclogite facies conditions; the EC consists of alpine monometamorphic orthogneiss with minor paragneiss and quartzites metamorphosed at epidote blueschist facies conditions and intensely retrogressed at greenschist facies conditions. The question is therefore to understand if we can trace the Alpine metamorphic history through methods that do not rely only on chemical equilibration.

To tackle this objective, we used elastic geobarometry to derive pressure and temperature (P-T) conditions reached by three micaschists from the IC and one garnet-orthogneiss from the EC. Entrapment P obtained for the quartz inclusions in garnet in the IC range from 1.5-2 GPa at 600-650°C, in agreement with the P-T estimates determined through thermodynamic modelling. Coupled quartz and zircon in garnet geobarometry in the garnet-orthogneiss from the EC also display P-T conditions of 1.8 GPa and 650°C. These estimates disagree with the greenschist facies mineral assemblage of the rock (Ttn + Grt + Phg + Chl) and with the results of thermodynamic modelling (0.6-0.8 GPa and 500°C). The misfit in P-T estimates between elastic geobarometry and thermodynamic modelling might be due to an elastic reset of the quartz and zircon host-inclusion pairs at HP conditions. The use of coupled elastic geobarometry and thermodynamic modelling can help to unravel complex tectonometamorphic histories.

# Measuring Strains and Stresses in minerals by spectroscopy

Morana M.*[1], Gonzalez J.P.[2], Barbaro A.[2], Mingardi G.[2], Albarse F.G.[3] & Angel R.J. [4]

[1] Dipartimento di Chimica, Università di Pavia. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Elettra-Sincrotrone Trieste. [4] Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* marta.morana@unipv.it

*Keywords:* mineral inclusions, XRD, Raman spectroscopy.

Elastic geobarometric calculations allow the conditions of pressure and temperature of the entrapment to be calculated for host-inclusion systems from the strain in the inclusion and the equations of state of both minerals. Raman spectroscopy is a popular technique for characterising mineral inclusions, since it is quick and allows small portions of the sample to be probed. It is observed that the Raman peak positions of inclusions are different from those of a free crystal of the same mineral. These changes Dw in the wave-numbers, w, of the vibrational modes (phonons) of crystals depend only upon the strains applied to the crystal, whether such strains are generated by stress, pressure or temperature (Ziman, 1960). This relationship is described by the second-rank phonon-mode Grueneisen tensor: Dw/w = giei. The determination of the values of the tensor components by spectroscopic measurements is challenging as homogeneous deviatoric strain states must be precisely induced in a crystal. Thus, the use of Grueneisen tensors determined from DFT simulations has been proposed (Angel et. al, 2019). Calculations under different strains to show that, provided the crystal symmetry is not broken, the phonon wavenumbers shift linearly with strains up to several percent strain. Fitting these data yields the values of the components of the Grueneisen tensor for each phonon mode that correctly predict the measured Raman shifts under pressure. This methodology can potentially provide suitable data for elastic barometry calculations from Raman spectroscopy that could be employed as a quick and easy way to determine and map the strains in minerals. However, inclusions are under non-hydrostatic stress so the method must also be validated against experimental data. Since X-ray diffraction (XRD) allows to directly determine the strains from the change in the unit cell parameters of the included mineral with respect to a free crystal, also with good precision, it is the technique of choice to cross-check the strains obtained from Raman shifts. In this study, we used synchrotron XRD at the Xpress beamline, Elettra Sincrotrone, to characterize in situ various host-inclusion systems. We then compared the resulting strains with those determined from Raman Spectroscopy. In general, the strain in inclusions calculated using the Grueneisen tensor agree within their uncertainties with the strains measured directly by XRD, thus validating the approach.

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# The base of the Silvretta Nappe: a youngest generation of pseudotachylytes contributes to the understanding of the deformation at the base of the upper plate

Pittarello L.*[1], Levi N.[2-3], Wegner W.[1] & Stehlik H.[4]

[1] Naturhistorisches Museum, Wien (Austria). [2] Institut für Geologie, Universitaet Wien (Austria). [3] NiMBUC Geoscience OG, Wien (Austria). [4] Engineer, Wien (Austria).

*Corresponding author e-mail:* lidia.pittarello@nhm-wien.ac.at

*Keywords:* pseudotachylytes, Silvretta, subduction.

At the base of the Austroalpine Silvretta Nappe, multiple generations of pseudotachylytes can be observed. The occurrence of pseudotachylytes associated with ultramylonites in the area is known and has been interpreted as formed during the Eoalpine (mid-Cretaceous) collisional phase (Koch & Masch, 1992). These pseudotachylytes were subsequently recrystallized, deformed under viscous-plastic conditions, consistent with greenschist metamorphic facies, and finally pervasively epidotized.

A new study on samples collected in the Jamtal, Tyrol (Austria), revealed the presence of a younger generation of pseudotachylytes, which overprint the previously described pseudotachylytes and mylonites. These youngest pseudotachylytes did not experience extensive recrystallization and deformation under viscous-plastic conditions, nor epidotization, suggesting a more recent and possibly shallower formation than those of the “older” generation. The most likely scenario is formation during the final subduction of the Penninic Unit of the Engadine Window in the Paleogene (Pittarello et al., 2022 and reference therein), in agreement with K-Ar dating of some pseudotachylytes from the area (Thöni, 1988).

The localization of (brittle) deformation at the base of the upper plate, the so-called “basal erosion” (Agard, 2021) is attributed to fragments of continental crust in the subducting units. In this case, the subducting units included rigid fragments of crystalline basement from the Austroalpine (and likely also from the Briançonnais microcontinent) mixed with softer Penninic carbonates and serpentinites. The proposed interpretation is supported by other occurrences of pseudotachylytes in the Alpine domain localized at the base of the upper plate.

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Pittarello L., Levi N., Wegner W. & Stehlik H. (2022) - The pseudotachylytes at the base of the Silvretta Nappe: A newly discovered recent generation and the tectonomometamophic evolution of the Nappe. Tectonophysics, 822, 229185.

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# Investigation of microscale fracture opening in host inclusion systems

Puhan B.*[1], Mazzucchelli M.L.[2], Reali A.[3] & Alvaro M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Mainz Institute of Multiscale Modeling and Institute of Geosciences, Johannes Gutenberg Universität Mainz (Germany). [3] Dipartimento di Ingegneria Civile e Architettura, Università di Pavia.

*Corresponding author e-mail:* biswabhanu.puhan01@universitadipavia.it

*Keywords:* fracture nucleation, earthquake.

Due to weak rheology and high confining pressure, the proper mechanism for nucleation of Earthquakes in the lower crust remained an open question for the past 70 years. The main mechanisms proposed so far require either the presence of hydrous minerals or pre-existing ductile shear zones. However, many studies on pseudotachylytes from Norway and Australia provided evidence for paleo Earthquakes where neither the pre-requisites were satisfied (Dunkel et al., 2020; Hawemann et al., 2018).

In this work, we explore the hypothesis for a new mechanism for earthquake nucleation triggered by the mechanical instability of host inclusion pairs. Upon changes in external pressure and temperature conditions, a host-inclusion system can develop considerably large deviatoric strains which in turn create a significant non-hydrostatic stress that could be responsible for nucleation of fractures and their subsequent propagation in the host. Cracks developed from two or more inclusions can interact and coalesce to form a macro crack, that can ultimately result in a fault.

In order to assess this possibility, we performed numerical simulations on host-inclusion system using the extended finite element method present in the code ABAQUS. To mimic the material properties in the lower crust, a Traction Separation Law (TSL) was introduced to enable modelling the quasi-brittle behaviour for the material by introducing a linear softening between two crack planes.

Our results demonstrated that (1) we could successfully trigger fracture nucleation; (2) fractures nucleated between two inclusions can coalesce to form a macro crack which seems to support our initial hypothesis for fracture nucleation without large external deviatoric stresses.

Dunkel K.G., Zhong X., Arnestad P.F., Valen L.V. & Jamtveit B. (2020) - High transient stress in the lower crust: evidence from dry pseudotachylytes in granulites, Lofoten Archipelago, Northern Norway. Geology, 49, 135-139.

Hawemann F., Mancktelow N.S., Wex S., Camacho A., Pennacchioni G. (2018) - Pseudotachylyte as field evidence for lower-crustal Earthquakes during the intracontinental Petermann Orogeny (Musgrave Block, Central Australia). Solid Earth, 9, 629-648.

# Disorientation control on trace element segregation in fluid-affected low-angle boundaries in olivine

Tacchetto T.*[1-2], Reddy S.[1-2], Saxey D.[2], Fougerouse D.[1-2], Rickard W.[2] & Clark C.[1]

[1] School of Earth and Planetary Sciences, Curtin University, Perth (Australia). [2] Geoscience Atom Probe Facility, Curtin University, Perth (Australia).

*Corresponding author e-mail:* tommaso.tacchetto@postgrad.curtin.edu.au

*Keywords:* olivine, deformation microstructures, Atom Probe Tomography.

The geometry and composition of deformation-related low-angle boundaries in naturally-deformed olivine were characterized by electron backscattered diffraction (EBSD) and atom probe tomography (APT). EBSD data show the presence of discrete low-angle tilt boundaries, which formed by sub-grain rotation recrystallisation associated with the (100)[001] slip system during fluid-catalysed metamorphism and deformation. APT analyses of these interfaces show the preferential segregation of olivine-derived trace elements (Ca, Al, Ti, P, Mn, Na and Co) to the low-angle boundaries. Boundaries with < 2° show marked enrichment associated with the presence of multiple, non-parallel dislocation types. However, at larger disorientation angles (> 2°), the interfaces become more ordered and linear enrichment of trace elements coincides with the orientation of dislocations inferred from the EBSD data. These boundaries show a systematic increase of trace element concentration with disorientation angle. Olivine-derived trace elements segregated to the low-angle boundaries are interpreted to be captured and travel with dislocation as they migrate to the sub-grain boundary interfaces. However, the presence of exotic trace elements Cl and H, also enriched in the low-angle boundaries, likely reflect the contribution of an external fluid source during the fluid-present deformation. The observed compositional segregation of trace elements has significant implications for the deformation and transformation of olivine at mantle depth, the interpretation of geophysical data and the redistribution of elements deep in the Earth. The observation that similar features are widely recognised in manufactured materials, indicates that the segregation of trace elements to mineral interfaces is likely to be widespread.

# Squishing and breaking amphibolites along a major thrust: the example of the Ben Hope Sill, Moine Supergroup, NW Scotland

Tesei T.*, Pozzi G., Schorn S. & Holdsworth R.E.

Dipartimento di Geoscienze, Universitá di Padova.

*Corresponding author e-mail:* telemaco.tesei@unipd.it

*Keywords:* shear zone, amphibolite, faults.

Amphibolites, despite their abundance in the lower crust, have a somewhant underinvestigated rheology, especially compared to better-known quartzo-feldspathic and phyllosilicate-rich rocks. We studied the deformation of amphibolites (Ben Hope Sill) along the Ben Hope thrust (NW Scotland), one of the major faults of the Caledonian orogen.

The Ben Hope Sill is a metamorphosed mafic body embedded within the Moine metasediments. During Caledonian thrusting, it experienced top-to-the-WNW transport associated to mylonitization and tight-to-isoclinal sheath folding. At the outcrop scale, the sill(s) are strain localization horizons displaying progressive strain localization, from almost undeformed lenses to pervasively mylonitized horizons. The undeformed lenses are characterized by massive, coarse-grained amphibolites (hbl+qtz+plg+grt) in which static growth of poikiloblastic hornblende and almandine garnet, hosts a fabric of an earlier (D1) event. D2 (Caledonian) thrusting produce mylonitic amphibolites by progressive pressure-solution of quartz, plagioclase and amphibole demonstrated by: i) the decrease in modal abundance of plg and qtz and increase/recrystallization of hbl; ii) the precipitation of hbl in pressure shadows and iii) the growth of Ca-rich rims of porphyroblastic garnet. Moreover, pockets of (locally sourced) overpressured fluids are represented by 1-30 cm veins of quartz (±Plg±Cal) that cross cut the shear bands and are locally highly strained into sheath folds. Thin horizons, typically observed at the edge of the deformed sill, show enrichment in biotite at the expense of the amphiboles and progressive brittle fragmentation of garnets.

Collectively, these observations suggest that initial D2 strain softening and localization within the amphibolites is guided by pressure solution. However, pressure solution proceeds only until the hornblend load-bearing framework is left. The resulting amphiboles-dominated mylonites then deform by brittle failure, accompanied by local fluid overpressure and ingress of metasomatic fluids. We emphasize the importance of fluids in supplying and removing chemical species during deformation, leading to complex brittle-viscous deformation cycles in amphibolitic rocks under middle crustal conditions.

# S30.

# A petrographic and mineralogical journey through the extraterrestrial bodies: from differentiated to undifferentiated materials

*Convener & Chairpersons*

*Mara Murri (University of Milano - Bicocca)*

*Jacopo Nava (University of Padova)*

*Anna Barbaro (University of Pavia)*

# Shock origin of diamond in ureilites: the important role of Fe-Ni compounds in diamond growth

Barbaro A.*[1], Nestola F.[1] & Domeneghetti M.C.[2]

[1] Dipartimento di Geoscienze, Università di Padova.
[2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* barbaroanna08@gmail.com

*Keywords:* ureilites, carbon phases, impact event(s).

The origin of carbon phases in meteorites is still a debated issue within the scientific community of planetary geology, with significant implications for the sizes of early Solar System bodies. Carbon phases occur in different kinds of meteorites, spanning from differentiated to undifferentiated ones. In particular, among the differentiated meteorites carbon is present in iron meteorites and in ureilites. Our study was focused on the investigation of carbon in ureilites meteorites (achondrites), which consist of ultramafic rocks, mainly composed of olivine, pigeonite, and minor carbon (graphite and diamond) and Fe-Ni compounds (Goodrich et al., 1992).

The main expected outcome of this study was to have further insights into the origin and relationships among carbon phases in ureilites with the final aim to definitively clarify the diamond formation processes occurring for these achondrites. To this purpose, we used Scanning Electron Microscopy (SEM), Micro-Raman Spectroscopy, Micro-X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM) on different ureilitic fragments (from Almahata Sitta, NWA 7389, Y-74123 and Kenna) focusing on their characterization, determination of their crystallite size and on the temperature recorded by graphite using the geothermometer by Cody et al. (2008).

Our results, which are reported in Nestola et al. (2020) and Barbaro et al. (2021) and references therein, demonstrate that the mineral association of nano-, micro-diamonds and nano graphite in ureilites was produced in an impact event with the help of catalysis of Fe-Ni compounds. The observation that the graphite in all these ureilites is nanometric suggests that it records shock conditions that occurred during the impact events involving the ureilite parent body. The temperature measured on graphite, which ranges from 1180 to 1314°C (±120°C), could represent the temperature related to the shock event.

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# Meteorite 6A: chemical, physical and petrological characterizations

Bonadiman C.[1], Curetti N.*[2], Lugari C.[3], Pavese A.[2] & Vaccaro C.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Laboratorio Ricerca e Sviluppo, Saint-Gobain Italia S.p.A., Milano.

*Corresponding author e-mail:* nadia.curetti@unito.it

*Keywords:* H-type chondrite, mesostasis, K-feldspar.

The meteorite 6A is a H-type chondrite found in the valley of the Draa river (Sahara desert, SW Morocco); the label follows the field-recovery grid scheme. It is spheroidal in shape (3x5x6 $cm^3$) and wrapped by a melting crust (0.5 cm thick). Chondrules are well defined and form the 80% of the rock (Bonadiman et al., 2018). They are mainly composed of olivine, pyroxene, plagioclase, chromites, Fe-Ni metal, sulfides, and micro to crypto-crystalline mesostasis. The mesostasis and the homogeneity of feldspar suggest the petrological type 3-4. Fine grain matrix mainly consists of FeNi alloys, locally transformed in goethite as terrestrial product (weathering degree: W4). The chondrules have variable size, 200-600 µm on average, up to 1 mm; the great majority shows lower degree of weathering (W1-2).

EDS maps show that olivines and pyroxenes have variable size in different chondrules; they range from micro- to single-crystals of about 500 µm, by defining porphyritic olivine-pyroxene (POP), and radial pyroxene (RP) as most common textural types. An orthogonal distribution of bar olivine forms an unusual BO chondrula (Scott & Krot, 2014). The chemical composition of olivines is uniform in all grains and the average formula is $(Mg_{1.61}Fe_{0.37}Mn_{0.01}Ca_{0.01})SiO_4$. A single grain of Fe-rich olivine $(Fe_{1.52}Mg_{0.46}Ca_{0.12}Ni_{0.03}Cr_{0.01})[Si_{0.90}Al_{0.05}]O_4$, appearing as porphiric relict, was found as core of an enstatite bars series.

Likewise, ortho-pyroxenes have homogeneous enstatic contents, with small variations in the amounts of Ca, Mn, Cr, Al, Ti; the average formula is $(Mg_{1.62}Fe_{0.35}Mn_{0.02}Ca_{0.02}Ti_{0.02}Cr_{0.02})[Si_{1.97}Al_{0.03}]O_6$. Some pyroxene-bars show Ca enrichment in the core, until $(Mg_{0.93}Ca_{0.80}Fe_{0.11}Al_{0.05}Cr_{0.04})[Si_{2.02}]O_6$.

In all chondrules occur feldspathic mesostases, with on average high K content (Ab 73-85%, An 10-23% and Or 4-11%). The crypto-crystalline mesostases are a mixture of two distinct feldspars, albite and K-feldspar, both with small content of Ca. Anorthites has not been found. Compositional maps of mesostasis evidenced K-rich microzones (< 10 mm); point-analyses returned a composition corresponding to a K-feldspar: $(K_{0.80}Na_{0.09}Ca_{0.12})[Si_{2.91}Al_{1.07})O_8$. Porosity is important in meteorites and asteroids because affects density. The real density of this sample measured with He pycnometer is 3.56(1) g $cm^{-3}$, while the average intrinsic density estimated on the base of the occurring phases (X-ray microtomography) is 4.18 g $cm^{-3}$; the difference is related to the oxidation of Fe alloys with formation of goethite (7.9 and 4.3 g $cm^{-3}$ for kamacite and goethite, respectively).

Primary porosity is estimated 10% by volume with average pore sizes of ≈300 µm. The observed dissolution of mesostasis glass with the formation of micro K-rich feldspars may be related to the porosity that facilitates the transport of fluid during aqueous alteration and metasomatism, accompaning thermal metamorphism of the parental body (Kovach & Jones, 2010; Lewis et al., 2018).

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# Tin isotopes in chondrites and Earth: mass independent isotope fractionation and radiogenic $^{115}Sn$

Bragagni A.*[1-2], Wombacher F.[2], Kirchenbaur M.[2-3], Braukmüller N.[2-4] & Münker C.[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Institut für Geologie und Mineralogie, Universität Köln (Germany). [3] Institut für Mineralogie, Leibniz Universität Hannover (Germany). [4] Institut für Geologische Wissenschaften, Freie Universität Berlin (Germany).

*Corresponding author e-mail:* alessandro.bragagni@unifi.it

*Keywords:* tin, nucleosynthetic anomalies, mass independent isotope fractionation.

The occurrence of nucleosynthetic isotope anomalies in meteorites reveals an incomplete homogenization of the material that formed the solar system. So far, nucleosynthetic isotope anomalies have been observed for many refractory elements, but only few studies focused on moderately-volatile elements (MVE) (e.g., Toth et al., 2020). Since isotope anomalies in MVE are not expected to survive strong heating events, they provide constrains on the thermic conditions and physical processes occurring in the early stages of the solar system.

The identification of nucleosynthetic anomalies has been questioned for same elements because mass dependent and mass-independent isotope fractionation processes can produce similar isotope patterns (Fujii et al., 2006). Owing to the large number of stable isotopes, Sn provides the opportunity to discriminate nucleosynthetic anomalies from mass-dependent and mass-independent isotope fractionation. In addition, $^{115}Sn$ is produced by the radioactive decay of $^{115}In$ and thus can be used to trace processes that fractionated Sn from In.

We present a novel method for the Sn chemical separation and the MC-ICP-MS measurements. High precision Sn isotope measurements on terrestrial rocks and chondrites display patterns consistent with two mass independent isotope fractionation processes: the nuclear volume and the magnetic isotope effects. A sample preparation induced fractionation seems unlikely as different groups of chondrites show systematic patterns. Thus, the origin of the isotope fractionation is unclear but point towards unknown natural geo/cosmochemical processes. After considering mass-independent and mass-dependent effects, there is no evidence of nucleosynthetic anomalies, as observed for other MVE (e.g., Toth et al., 2020).

Most chondrites show a deficit in $^{115}Sn/^{120}Sn$ (around 200 ppm) relative to terrestrial samples, with the exception of one ordinary chondrite that displays an excess of about 250 ppm. The $^{115}Sn/^{120}Sn$ data correlate with In/Sn content, being consistent with $^{115}In$ decay over the age of the solar system. This represents the first evidence of the $^{115}In$-$^{115}Sn$ decay system in natural samples. The radiogenic $^{115}Sn$ signature of mantle derived magmas likely reflects the preferential partitioning of Sn into the Earth's core.

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# Reflectance spectroscopy of ol-bearing ungrouped achondrite meteorites

Bruschini E.[1], Carli C.*[1], Cuppone T.[2] & Pratesi G.[2]

[1] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma. [2] Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* enrico.bruschini@inaf.it

*Keywords:* meteorites, reflectance spectroscopy, mineralogy.

We report here a reflectance spectroscopy investigation of a set of achondrite meteorites with variable mineralogical and chemical composition. The samples were analyzed in the VNIR (350 - 22500 nm) and MidIR (6000 - 15000nm) spectral ranges on both powders (grain sizes < 100 μm) and slabs. The chemistry and mineralogy of the samples were investigated in the University of Florence by a combination of SEM and EPMA. In the VNIR spectral range, we observe a quite clear spectroscopic distinction between samples with high olivine content with respect to samples with high pyroxene content. The high-olivine group is dominated by the spectral features of olivine with a broad and asymmetric band centered at about 1100 nm. A deep and quite symmetric band around 900 nm and a smaller but broader band at about 1900 nm characterize the high pyroxene group. The FTIR investigation confirms the VNIR results but also reveals the peculiar spectroscopic features of sample Asuka 881548 whose Reststrahlen bands differ significantly from the other members of the high pyroxene group. From a quantitative comparison between slabs and powders we observe only minor variations of the spectral features while, as expected, spectral contrast is highly enhanced in powders for the VNIR measurements and in slabs for MidIR spectra. We compare the VNIR spectra of our samples with earth based spectroscopic observations in order to highlight ad quantify similarities between spectral features of achondrites and possible parental bodies.

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# The formation of coesite in impact rocks

Campanale F.*[1], Mugnaioli E.[2], Folco L.[2] & Gemmi M.[3]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Center for Materials Interfaces, Istituto Italiano di Tecnologia, Pontedera (PI).

*Corresponding author e-mail:* fabrizio.campanale@unimib.it

*Keywords:* coesite, shock metamorphism, impact cratering.

Coesite, a high-pressure silica polymorph, is a diagnostic indicator of impact cratering in quartz-bearing target rocks. The mechanism formation of coesite is still debate since its discovery in 1960s therefore it remains the subject of numerous studies aiming to better understand how silica polymorphs react under sudden and extreme P-T increases. Here, I show evidence documenting the coesite formation through direct quartz-to-coesite transformation in subsolidus conditions studying two different impact events: Kamil crater (Egypt), a small-scale simple crater of 45 m in diameter, and the large-scale Australasian tektite/microtektite strewn field.

In Kamil crater, coesite occurs as individual and spheroidal single-crystal grains (Campanale et al., 2021) that represent the first crystallization seeds of coesite. In the Australasian samples, coesite occurs as individual grains or aggregate, either with subrounded or subhedral shape. In both Kamil crater and Australasian tektite strewn field, quartz and coesite, when in direct contact, show a recurrent reciprocal orientation, with the {10-11} or {-1011} plane families of quartz almost parallel with the plane (010) of coesite. This suggests a genetic relation between the recurrent {10-11} orientation for planar features in shocked quartz, including planar deformation features (PDFs) and the twinning of impact coesite along (010) composition planes. A possible way to transform quartz into coesite would be through a topotactic transformation. The presence of pre- and post-shock discontinuities in the target rock may facilitate the quartz-to-coesite transformation, in which the shock-wave reverberation provides the P-T-t conditions for coesite formation.

This work is also a good test-case for showing the potential of the TEM-based techniques, i.e., three dimensional electron diffraction (3D ED) and precession-assisted crystal orientation mapping (PACOM), in integrating well-established analytical methods like SEM, conventional TEM, and Raman micro-spectroscopy. Such combination can push forward the structure characterization of nanoscale materials, shock metamorphic features and their defective nature in the impact rocks. TEM and ED allow to address outstanding open questions in shock metamorphism and impact cratering studies, such as the high-pressure polymorph transformation mechanisms induced by the passage of shock waves in impact scenarios.

Campanale F., Mugnaioli E., Gemmi M. & Folco L. (2021) - The formation of impact coesite. Sci. Rep., 11, 16011. https://doi.org/10.1038/s41598-021-95432-6.

# Investigating VNIR spectral properties of Mercury, what we can learn about composition from remote sensing and laboratory analogues

Carli C.*[1], Zambon F.[1], Giacomini L.[1], Bruschini E.[1], Morlok A.[2], Ferrari S.[3], Mari N.[4], Galiano A.[1], Alvaro M.[4], Pratesi G.[5], Klemme S.[6], Renglli C.[6] & Capaccioni F.[1]

[1] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma. [2] Institut für Planetologie, Munster University (Germany). [3] Dipartimento di Geoscienze, Università di Padova. [4] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [5] Dipartimento di Scienze della Terra, Università di Firenze. [6] Institut für Mineralogie, Munster University (Germany).

*Corresponding author e-mail:* cristian.carli@inaf.it

*Keywords:* Kuiper Quadrangle, Mercury planet, reflectance spectroscopy.

The MESSENGER mission provides new constrains on the Mercury surface and its geological history. In particular, we have knowledge of peculiar geological features and new insight of the reflectance spectral properties in the VNIR, and lower spatial scales elementary composition. The volcanic material on Mercury shows, in general, low Fe/Si (i.e., < 1wt.% FeO) and variable Al/Si, Mg/Si and Ca/Si ratios; moreover, K/Si, Na/Si and K/Th ratios are higher than expected. The abundance of S and C is unexpected high, suggesting an anomalous large contribution of volatiles, which correlates with the presence of large pyroclastic deposits, hollows which are features associated to degassing, and dark, blue terrains (e.g., Rothery et al., 2020). Reflectance highlights the heterogeneity of the surface, showing a large spectral variety among the terrains and, in particular, pyroclastic deposits, hollows and potential C-rich regions with specific spectral characteristics that permit to differentiate them.

In this work, we studied the spectral properties from MDIS camera color filters mosaics of the Kuiper quadrangles, recently studied from a geological point of view by Giacomini et al. (2021). We investigate the Kuiper quadrangle at different spatial resolution (and coverage) to show the relationship between the different geological units and to obtain the spectral characteristics of local features at the highest possible resolution. In particular, we show how spectral properties similar to the hollows in Dominici Crater (see Rothery et al., 2020 and reference therein) are present in different bright features, either recognized as hollows or not. Hollows show some spectral properties that seems to be different from other geological features, although some small secondary fresh craters looks like spectrally similar to those features. Another interesting aspect of this quadrangle is the presence of different craters with pyroclastic deposits and vents, some of which are associated with hollows. Pyroclastic deposits and vents appear similar (with the vents that are often brighter), but distinct from the hollows. Moreover, spectral properties within some vents indicate similarities with the hollows (e.g., Mistral Crater),which however do not have morphological counterparts.

Finally, here we discuss also the spectral characteristics of potential analogues from the compositional or spectral point of view, as iron pure achondrites (i.e., aubrites), Mercury-like analogues glasses, and mineral mixtures of igneous rocks with graphite or sulphides. Our aim is extrapolate indication that could help in mineralogical interpretation from MESSENGER data and, in particular, the future BepiColombo measurements.

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# OIBODIEs: advancement on mineralogical and geochemical analysis on ungrouped achondrites

Cuppone T.*[1], Casalini M.[1], Carli C.[2] & Pratesi G.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma.

*Corresponding author e-mail:* tiberio.cuppone@unifi.it

*Keywords:* cosmochemistry, ungrouped achondrites, mineral chemistry, Cr isotopes.

Meteorites, together with return mission samples, represent the unique material to investigate Solar System bodies. Among meteorites, ungrouped achondrites represent natural sampling of ancient, from fairly to highly, differentiated bodies and provide fundamental information about their genesis and the processes associated with the origin of our Solar System. These extra-terrestrial bodies (i.e., asteroids and comets) are usually investigated through indirect analytical methods allowing the characterisation of many of them but without achieving the high-precision level provided by direct analysis.

Within the scope of the "Olivine-bearing ungrouped achondrites and their parent bodies in the Solar System" (OlBODIEs, ASI-INAF) Project, we selected several ungrouped achondrites aiming to highlight the most prominent aspects related to their classification, combining multidisciplinary mineralogical-petrographic-geochemical-isotopic-spectroscopical approaches.

We present preliminary results based on mineralogical, petrographic, geochemical and isotopic characterisation of achondrite meteorites to provide a detailed characterisation of the samples. We selected a set of ungrouped achondrites with brachinites affinity, bearing variable amount of olivine and other mineralogical phases (e.g., pyroxene, graphite, spinel). Eight samples (Al Huwaysah 010, the paired MIL 090206-090405, the paired NWA 5363-5400-6077-6292, and NWA 6112) were investigated through Scanning Electron Microscope and Electron Microprobe (EMPA) to determine the mineral chemistry of major (olivine, pyroxene and plagioclase) and minor phases (Fe-Ni alloys, oxides, sulphides, phosphates), while EBSD analyses are planned to investigate olivine petrofabric. The presence of secondary phosphates in all NWA 5400 paired samples (Cl-apatite replaced by Fe-phosphates) points to Fe-rich fluid circulation on their parent body, while the Fe-sulphide + Fe-Ni + orthopyroxene fine-grained assemblage in olivine rims resembling ureilite reduction rims in the other 4 samples (and absent in the 5400 group) is probably due to reduction of iron in olivine according to the reaction $Mg_2SiO_4 + Fe_2SiO_4 + C = 2(MgSiO_3) + 2Fe + CO_2$. These two different paragenesis mark a strong dichotomy within this brachinite-like meteorite group. We combine mineralogical and petrographic determinations along with geochemical (by ICP-MS) and isotopic analyses (by TIMS) performed on bulk samples and, as a future application, to specific mineralogical phases. In this light, we are also developing a high-precision measurement procedure for Cr isotope compositions (i.e., $e^{53}Cr$ and $e^{54}Cr$). These will be coupled with other methods (e.g., reflectance spectroscopy, oxygen isotopes) to infer about the parent body nature (if a single compositionally heterogeneous source or multiple sources) and to reinforce the confidence of association of the studied samples with their parent body family.

# IUGS classification of extra-terrestrial igneous rocks

Day J.M.D.*[1], Lustrino M.[2] & the IUGS Subcommission on the Systematics of Igneous Rocks

[1] Scripps Institution of Oceanography, University of California, San Diego, CA (USA). [2] Dipartimento di Scienze della Terra, Sapienza Universitá di Roma.

*Corresponding author e-mail:* jmdday@ucsd.edu

*Keywords:* IUGS, classification, extra-terrestrial.

Concerted efforts supported by the International Union of Geological Sciences (IUGS) have led to a systematic classification of igneous rocks that has been widely adopted by the Earth Science community (Le Maitre et al., 1989; 2002). The IUGS classification of igneous rocks provides a descriptive approach to terrestrial rocks free from association to specific tectonic settings or petrogenetic linkage. Although most extraterrestrial rocks are igneous in origin, to date they have been omitted from the IUGS classification scheme. A new IUGS task group is currently working with updating igneous rock nomenclature, including extra-terrestrial rocks for the first time. Rock classifications of extra-terrestrial materials include meteorites in addition to samples collected during manned and robotic missions to planetary bodies (e.g., Apollo, Luna, Chang'E 5, Hayabusa 2). Foundations already exist for extra-terrestrial rock classification, with basic definitions and groups such as primitive chondrites, partially melted achondrites, iron and stony iron meteorites and achondrites from differentiated planetary bodies including Mars and the Moon (e.g., Weisberg et al., 2006). A fundamental difference exists in the evolutionary approach developed by planetary geologists versus the IUGS approach, which is based on petrography, modal mineralogy, mineral composition and, if available, bulk-rock chemistry. The IUGS intends to link terminology used for terrestrial rocks to some extra-terrestrial materials with terms classically accepted by the meteoritical community (e.g., olivine shergottite = picrite; eucrite = basalt, etc.). The goal is to enable petrologists dealing with terrestrial or extra-terrestrial rocks to recognize similarities in materials with which they are dealing in terms of similar mineral paragenesis, petrographic features and approximate bulk-rock composition. An additional complication to address is the affiliation of extraterrestrial rocks based on stellar-nucleosynthetic (e.g., $e^{54}Cr$, $e^{50}Ti$) isotopic characteristics or CO photodissociation ($D^{17}O$). Addressing general terminology, aided by more detailed isotopic considerations, will ideally help non-experts to better understand petrogenetic processes occurring on other planetary bodies or in the original primitive carbonaceous and non-carbonaceous materials from which they derived (Warren, 2011). In this contribution, we will discuss the proposed outline for extra-terrestrial igneous rock classification and some of the distinctive challenges that arise in folding these materials into the IUGS classification of igneous rocks.

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# The reflectance spectra of $NH_4^+$-bearing minerals: the effects of temperature, granulometry and viewing geometry

Fastelli M.*[1], Comodi P.[1], Schmitt B.[2], Beck P.[2], Poch O.[2] & Zucchini A.[1]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Université Grenoble Alpes, CNRS, IPAG, Grenoble (France).

*Corresponding author e-mail:* maximiliano.fastelli@gmail.com

*Keywords:* icy bodies, ammonium-bearing minerals, reflectance.

Some icy bodies are characterized by the possible presence of subsurface oceans beneath their icy surface, composed of different minerals. On Ceres dwarf planet, data collected by the *Dawn* mission suggested the presence of ammonium bicarbonate and/or ammonium chlorides as a residual of the recent ascent of deep brine (De Sanctis et al., 2016). On Pluto, data from the Linear Etalon Imaging Spectral Array (LEISA) installed in the *New Horizons* mission show absorption bands located in the 2.15-2.17 µm possibly explained by ammonium minerals such as $NH_4Cl$ and $(NH_4)_2CO_3$ (Cruikshank et al., 2019). In this work, we measured a set of natural terrestrial and synthetic analogues of $NH_4^+$-bearings minerals interesting for planetary science. Data were collected in the spectral range from 1 to 4.8 µm down to 90 K with three different grains sizes in the 150-36 µm range. We also studied the effect of different viewing geometry for mascagnite and salammonic samples, considering a set of 3 incidence angles (*i*) and 8 emergence angles (*e*) between -70° and 70° at room temperature (T). For the reflectance measurements we used the experimental setups of the Cold Surface Spectroscopy Facility (CSS) located at the IPAG: (1) SHADOWS spectro-gonio radiometer; (2) CarboN-IR cryogenic environmental cell to collect spectra at low T (https://cold-spectro.sshade.eu). Reflectance spectra of anhydrous samples show defined absorption features at ~ 1.06, 1.3, 1.56, 2.02, and 2.2 µm due to $NH_4^+$ group overtones and combinations and could be useful to discriminate these salts. Water-rich samples show $H_2O$ fundamental absorption bands strongly overlapping the $NH_4^+$ bands, flattening the spectra over 3 µm. The parameters area, depth and width of several absorption bands change in relation to the low T and changing geometries. The low T spectra reveal fine structure compared to the room T ones displaying more detailed and defined absorption bands. Some of the collected minerals are characterized by low T phase transitions and showed clear and interesting spectral bands variations during cooling, indicating that a phase transition occurred. For example, $(NH_4)_2SO_4$ has a phase transition at 223 K changing from space group *Pnam* at room T to $Pna2_1$ at low T. The different granulometries mainly affect the bands parameters area and depth, that usually increase as the grain size becomes larger. Furthermore, different *i* angles have a greater influence on the shape, area and width of the bands than the *e* angles. The detection of $NH_4^+$ salts on the surface of icy bodies can give information about their internal composition/dynamics and potential habitability.

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# *Ab initio* thermodynamics of $MgSiO_3$ protoenstatite at high temperatures and implications for planetary processes

La Fortezza M.*[1], Menescardi F.[1] & Belmonte D.[1-2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Museo Nazionale dell'Antartide, Università di Genova.

*Corresponding author e-mail:* mattia.lafortezza@edu.unige.it

*Keywords:* thermodynamics, ab initio, protoenstatite.

Protoenstatite (PEn) is one of the high temperature forms of $MgSiO_3$ pyroxenes, having stability range from 1200 to 1600 K at ambient pressure. Its importance has been recognized by many authors, in fact PEn is regarded as a precursor phase of low-clinoenstatite (LP-CEn)/orthoenstatite (OEn) intergrowths in some cometary samples (Schmitz & Brenker, 2008) and in calcium-aluminum-rich inclusions (CAIs) from CV3 chondrites (Che & Brearley, 2021). The presence of a high temperature PEn precursor in planetary materials implies that its formation must have occurred close to solar nebula conditions by equilibrium condensation via a reaction between forsterite and gaseous SiO (Nagahara, 2018) or, alternatively, as a result of reheating process after primary condensation (Che & Brearley, 2021). Despite its role as a precursor mineral phase in the solar system, very little is known about the thermodynamics and phase relations of PEn with other $MgSiO_3$ polymorphs. This is due for the most part to its unquenchable nature, meaning that even if PEn can be synthetized at high temperature conditions, it doesn't preserve as a metastable phase at ambient conditions since it very rapidly reverts either to OEn or LP-CEn (Smyth, 1974). The impossibility to perform measurements on samples of PEn prevents to obtain information on its thermodynamic properties, which are in turn fundamental for the investigation of phase equilibria. In that sense, *ab initio* calculations based on quantum-mechanical theory are one of the most reliable methods available to obtain information on thermodynamics and phase relations of minerals at planetary conditions.

We present a DFT based *ab initio* B3LYP computational study on $MgSiO_3$ protoenstatite thermodynamics. All the relevant thermophysical and thermodynamic properties of PEn (e.g., heat capacity, vibrational entropy, thermal expansion, EoS) have been calculated in the framework of the quasi-harmonic approximation (QHA) by a full phonon dispersion calculation. This allowed to obtain original insights into protoenstatite thermodynamics and enabled to retrieve a complete set of physically consistent thermodynamic properties, that are in excellent agreement with the very few experimental data currently available.

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# Martian mantle heterogeneities inferred from in situ analyses of shergottites

Mingardi G.*[1], Im S.[2], Park J.W.[2-3], Langone A.[4] & Mari N.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] School of Earth and Environmental Sciences, Seoul National University (South Korea). [3] Research Institute of Oceanography, Seoul National University (South Korea). [4] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* giulia.mingardi02@universitadipavia.it

*Keywords:* Martian shergottites, magmatic process, melt inclusion.

Isotopic and trace element studies on shergottites indicate that the Martian mantle formed during the early stages of planetary differentiation, crystallizing from Martian magma ocean (Moriwaki et al., 2020). This differentiation resulted in at least two different sources for basaltic shergottites: an enriched and a depleted mantle.

We studied the chemical and isotopic compositions of two olivine-phyric shergottites, DaG 670 and NWA 4222, to determine their mantle source and geochemical evolution. We measured in situ the Pb isotopic composition of 15 melt inclusions in olivine for each shergottite. Lead isotopic ratios of NWA 4222 cluster while DaG 670 data are spread along the 4.55 Ga Geochron. This distribution suggests that the two samples originated from different mantle sources. Lead isotope ratios of NWA 4222 suggest that its source was very similar to the terrestrial depleted mantle, whereas the geochemical heterogeneities shown in DaG 670 may be accounted for a mixing between depleted and enriched end-members.

Trace element compositions of pyroxenes in the matrix revealed significant Eu and Sr anomalies. Similar patterns have been observed in terrestrial clinopyroxene of low-crust gabbroic rocks in the Ivrea Verbano Zone and interpreted as the result of the mixing between the magma intrusion and the plagioclase cumulates present in the crust (Mazzucchelli et al., 1992). In this light, it can be foreseen that a similar process might have occurred during the formation of the studied shergottites.

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# Space weathering simulation of silicate surfaces in water

Murri M.*[1], Capitani G.C.[1], Fasoli M.[2], Monguzzi A.[2], Calloni A.[3], Bussetti G.[3], Malaspina N.[1] & Campione M.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca. [3] Dipartimento di Fisica, Politecnico di Milano.

*Corresponding author e-mail:* mara.murri@unimib.it

*Keywords:* pulsed laser ablation, space weathering, olivine.

Dust grains populate various astrophysical environments with silicates as the most common species (Escatllar et al., 2019). They are subjected to a strong structural and chemical modification during their lifetime due to events such as grain-grain collisions and irradiation (Carrez et al., 2002; Saunders & Plane, 2011). However, the origin together with the structural and chemical changes of these grains are still poorly understood and intensively debated (Escatllar et al., 2019).

Therefore, we carried out liquid-phase nanosecond pulsed laser ablation experiments on olivine single crystals followed by a multiple technique characterization to (i) simulate space weathering in a water environment (e.g., hydrous or volatile-rich bodies) and (ii) study the chemical and structural evolution of both the target surface and the ablated material. In particular, optical spectroscopy has been performed on the ablated material and correlated with high-resolution transmission electron microscopy analyses; whereas, chemical variations of the ablated target surface have been determined by X-ray photoelectron spectroscopy.

Our results showed that the target material was enriched in Fe and depleted in Mg after the ablation process with the formation of magnetite on the sample surface. This phenomenon could be ascribed to the effect of the water environment which triggered the oxidation of $Fe^{2+}$ into $Fe^{3+}$ in a region confined at the solid-liquid interface (Broadhead & Tibbetts, 2020) and thus promoting the formation of magnetite on the sample surface. On the other hand, no metallic iron nanoparticles have been detected in the ablated material which was mainly made by olivine crystalline fragments with shock features and Mg-rich crystalline nanoparticles. Our laboratory simulation of space weathering in water environment revealed structural and chemical changes which are expected to produce distinctive features in the reflectance spectra when compared to those from airless bodies of the inner Solar System.

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# Cryovolcanic laboratory experiments on carbonaceous chondrites - Formation of alkanes via outburst and sublimation

Nava J.*[1], Massironi M.[1], Maturilli A.[2], Pizzini S.[3], Ferretti P.[3], Alemanno G.[2], Folco L.[4], Perosa A.[5], Genovesi S.[6] & Helbert J.[2]

[1] Dipartimento di Geoscienze, Università di Padova. [2] German Aerospace Center, Institute of Planetary Research, Berlin (Germany). [3] Dipartimento di Scienze Ambientali, Informatica e Statistica, Università «Ca' Foscari», Venezia. [4] Dipartimento di Scienze della Terra, Università di Pisa. [5] Dipartimento di Scienze Molecolari e Nanosistemi, Università «Ca' Foscari», Venezia. [6] Università di Bologna.

*Corresponding author e-mail:* jacopo.nava@unipd.it

*Keywords:* cryovolcanism, organics, chondrites.

Organic matter is a major component of comets and icy-asteroids and is thought to be a remnant of the Solar Nebula or pre-Solar in origin (Raponi et al., 2020). The occurrence of organic compounds on cryovolcanic regions of icy-asteroids (Ruesch et al., 2016) and on sublimation dominated cometary nuclei (Raponi et al., 2020), however, suggests that cryovolcanism and solar irradiation might play a role on their evolution. Sublimation and outbursting are among the most evident processes induced by both cryovolcanism and solar irradiation (Ruesch et al., 2016; Vincent et al., 2016) and, in order to investigate their association with organic matter, we recreated these processes in laboratory by heating in vacuum frozen powders of carbonaceous chondrites mixed with water. Reflectance spectra and Gas Chromatography-Mass Spectrometry revealed that new aliphatic hydrocarbons are formed in the lag and ejected powders after sublimation and outbursting. We conclude that organic matter is not only a remnant of the Solar Nebula or pre-Solar in origin, but can also be newly formed material created by cometary activity.

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# Stony achondrite meteorites: just normal rocks!

Pittarello L.*[1], Chernonozhkin S.M.[2], Ferrière L.[1], Roszjar J.[1], Goderis S.[3] & Rider-Stokes B.[4]

[1] Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum Wien (Austria). [2] Lehrstuhl für Allgemeine und Analytische Chemie, Montanuniversität Leoben (Austria). [3] Analytical-, Environmental-, and Geo-Chemistry AMGC, Vrije Universiteit Brussels (Belgium). [4] School of Physical Sciences, Open University, Milton Keynes (UK).

*Corresponding author e-mail:* lidia.pittarello@nhm-wien.ac.at

*Keywords:* stony achondrites, petrology, geochemistry.

Stony achondrites represent the result of partial to complete differentiation in their respective parent bodies. Except for the primitive achondrites, the silicate-rich achondrite can be considered equivalent to terrestrial igneous rocks. Thus, to unravel their formation condition and evolution, they can be investigated using the same petrographic, geochemical, and isotopic methods developed and calibrated for terrestrial rocks. In this work, current studies on a selection of stony achondrites are presented.

Acapulcoites and lodranites are primitive achondrites, showing evidence of high degree thermal metamorphism and early partial melting, followed by slow cooling. This allowed equilibration between phases and annealing of the silicates. These meteorites have potentially retained information on the early stages of planetary differentiation.

Ureilites are also considered "primitive" by some authors, due to their non-equilibrated isotopic and element compositions, inherited from the nebular stage. This process is recorded in the isotopic zoning of some elements across olivine grains and preserved from the subsequent chemical reduction and shock metamorphism. An unusual sample, not fitting in the general picture, might pose new questions on the early evolution of the ureilite parent body.

Angrites are amongst the oldest basaltic achondrites in the Solar System, and some of them display a unique texture with large olivine xenocrysts embedded in a fine-grained matrix. These olivine xenocrysts can be investigated for microstructural deformation, and chemical and isotopic zoning, to constrain the evolution and deformation in the lithospheric mantle of their parent body.

Diogenites belong to the Howardite-Eucrite-Diogenite (HED) clan, which likely originated from the asteroid 4 Vesta and the Vestoids. Diogenites represent the lower crust of the differentiated asteroid and mostly consist of magnesian pyroxene. The occurrence of a vesiculated layer in an anomalous diogenite contributes to our understanding of the related magmatic processes.

Eucrites, also belonging to the HED clan, represent the upper basaltic crust of the differentiated asteroid Vesta. In some samples, high abundance of metallic iron has been reported. This recalls the occurrence of native iron in basalt in a limited number of localities on Earth. A comparative study could help to explain a not yet fully understood formation process.

In conclusion, unshocked stony achondrites preserve evidence of their magmatic history and, due to their similarities with terrestrial igneous rocks, can be studied with same analytical approach, even though some adjustments are necessary. In addition, the extraterrestrial environment can be seen as a kind of simplified analog of the terrestrial processes, with a rather limited number of variables, allowing the simulation and a better understanding of the evolution of the early Earth, for which the pristine features have been obliterated by subsequent processes.

# Preliminary data on the geochemical characterisation and Cr isotope composition of Libyan Desert Glasses and ordinary chondrites

Shehaj X., Casalini M.*, Tommasini S., Avanzinelli R. & Pratesi G.

Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* martina.casalini@unifi.it

*Keywords:* cosmochemistry, Libyan Desert Glasses, Cr isotopes.

Libyan Desert Glasses (LDG) are an enigmatic type of natural silicate glasses, which occur in well-defined geographic area in the western part of the Great Sand Sea (between Egypt and Libya, North Africa). These materials have gained the attention of many researchers through the last century (early 1930s) but, despite the large number of published studies (> 80) committed to this argument, their origin (terrestrial vs. extra-terrestrial) is still debated. The hypothesis that links their origin to meteoritic impact seems the more likely due to the lack of correlation with the geochemical compositions of the local sand or sandstone analysed from various locations in the common region of recovery. On the other hand, there are some differences with respect to classical impact glasses (i.e., the occurrence of peculiar high-T mineral phases or the presence of an impact crater). According to several authors the strongest indication for the presence of a meteoritic component could be retained in the dark streaks of layers presented by some glass samples.

Chromium isotopes systematic can be used to discriminate between terrestrial vs. extra-terrestrial material and to investigate meteorite characteristics. Cr isotope isotopic compositions ($^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$) can discriminate different meteorite type by the presence of the heterogeneously distributed $^{54}Cr$ nucleosynthetic anomalies and similar $^{53}Cr$ excess. Terrestrial rocks on the other hand are not expected to show any variation in Cr isotope composition.

This systematic has thus the big advantage, compared to other geochemical systematics such as Os isotopes and PGE abundance, of being selective regarding the terrestrial vs. extraterrestrial origin of the Cr source, and also regarding the meteorite type. Indeed, this method is able to provide at the same time evidence for the presence of extraterrestrial component in impactites, and information about the type of projectiles.

We present the preliminary compositional data of Cr isotopes and high-precision trace elements on six ordinary chondrites, which are classified but not yet fully characterised for their geochemical features, used to test the reproducibility of the analytical methods. Two samples of LDG were analysed along with the meteorite samples with the aim of shed light on the origin of these exotic materials. Would be this the solution to the enigma?

# Protosolar hydrogen source for water in the Moon and the Early Earth: insights from nominally anhydrous minerals

Stephant A.*[1-2], Anand M.[2-3], Zhao X.[2] & Franchi I.A.[2]

[1] Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Roma. [2] School of Physical Sciences, Open University, Milton Keynes (UK). [3] Department of Earth Sciences, Natural History Museum, London (UK).

*Corresponding author e-mail:* alice.stephant@inaf.it

*Keywords:* hydrogen, isotopes, Moon.

The origin of endogenous water in the Moon has been a matter of long-standing debate, because of the hydrogen isotopic heterogeneities recorded by lunar samples (i.e., dD ~ -300‰ to ~ +300‰) (e.g., Barnes et al., 2014; Hui et al., 2017). Given the binary nature of the Earth-Moon system, the current assumption is that Moon's water originated mainly from the early Earth. To estimate the hydrogen isotopic composition and water concentration of the lunar mantle, various hygrometer phases are used with in-situ measurements, mostly performed by secondary ion mass spectrometer (SIMS). As such, lunar volcanic glasses (e.g., Saal et al., 2013), apatite (e.g., Barnes et al., 2014), melt inclusions (MIs)(e.g., Stephant et al., 2020) and nominally anhydrous minerals (NAMs) (Hui et al., 2017) have been studied to ascertain the $H_2O$ and dD composition of the lunar interior. Apatite has been the mineral of choice for the past ten years on account of its widespread occurrence across almost all lunar lithologies and its relatively $H_2O$-rich nature. However, apatite is a late-formed mineral, and is often influenced by late magmatic and secondary processes. With recent improvements in SIMS protocols, it has become possible to target less-water-rich but more primitive phases in lunar samples, i.e., MIs and NAMs. We have measured the hydrogen isotopic composition of NAMs from Apollo samples representing all major lunar lithologies. Our results suggest that lunar hydrogen isotopic composition heterogeneities can be reconciled in the context of a global-scale degassing of the lunar magma ocean and a light hydrogen isotopic composition for the proto-Moon is estimated (-444±46‰). Our favoured interpretation is that the light hydrogen isotopic composition of the proto-Moon also fingerprints the hydrogen isotopic signature of the early Earth. This hydrogen isotopic composition for the proto-Moon and the Early Earth is lighter than the chondritic hydrogen isotopic ratio, arguing for incorporation of D-poor nebular hydrogen in the building blocks of terrestrial planets in the early stage of the Solar System formation.

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# S31.

# Towards modern concepts in seismotectonic-model definition and imaging: multidisciplinary and multiscale approaches in different tectonic settings

*Conveners & Chairpersons*

*Rita de Nardis (University of Chieti, CRUST)*

*Fabio Luca Bonali (University of Milano - Bicocca, CRUST)*

*Federica Ferrarini (University of Chieti, CRUST)*

*Valeria Paoletti (University of Napoli - Federico II, CRUST)*

*Debora Presti (University of Messina, CRUST)*

# A recent, low-magnitude seismic sequence in the epicentral area of Ms 6.9, 1980 Irpinia earthquake

Adinolfi G.M.*[1-3], Bello S.[2-3], Garofalo A.[2] & Lavecchia G.[2-3]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [3] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* gmadinolfi@unisannio.it

*Keywords:* seismotectonics, 1980 Irpinia earthquake, seismogenic sources.

The 1980 Irpinia earthquake was the most destructive, instrumental earthquake of Southern Apennines, occurred along NW-SE trending normal faults. A complex rupture process involved multiple fault segments according to (at least) three different nucleation episodes producing ~ 3000 fatalities, ~ 9000 injured, and up to 280,000 displaced people. Several models, characterized by different number, geometries and locations of activated fault segments, have been proposed by different authors to explain the complex rupture that originated the Irpinia earthquake (Bernard and Zollo, 1989 and references therein). 42 years later, some questions about the number and the location of seismogenic sources of the region are still open within the scientific community, despite recent studies have been published (Adinolfi et al., 2020; Festa et al., 2021; Bello et al., 2021).

This work proposes a detailed study of a small seismic sequence ($M_L$ 3.7 mainshock) that occurred in March 2012 in the proximity of a specially interesting zone, the so called "Sele Gap", which remained inactive during the Irpinia 1980 earthquake. Despite the limited number of small magnitude events, the analyzed micro-seismic sequence was highly space-time clustered and can be a powerful tool to investigate the activated fault segment in terms of geometry, kinematics or depth extension within the seismogenic layer of the Irpinia area. Our preliminary results, based on the earthquake re-locations and focal mechanisms, show the activation, during the 2012 sequence, of a fault located near the Marzano-Cervialto normal fault segments, which have been interpreted as two strong asperities, activated during the 1980 Irpinia earthquake and separated by the low-strength zone, Sele ("relaxation") barrier (Bernard and Zollo, 1989).

Our analysis contributes to further studying the Irpinia, low-magnitude instrumental seismicity, and to better define the fault segmentation pattern of the seismogenic structures of the area.

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# A useful tool to estimate the uncertainty of micro-earthquake focal mechanism solutions

Adinolfi G.M.[1-3-*], De Matteis R.[1], de Nardis R.[2-3] & Zollo A.[4]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [3] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [4] Dipartimento di Fisica, Università di Napoli "Federico II".

*Corresponding author e-mail:* gmadinolfi@unisannio.it

*Keywords:* seismotectonics, focal mechanism, 1980 Irpinia earthquake.

Improving the knowledge of seismogenic faults requires the integration of geological, seismological, and geophysical information. A multidisciplinary approach led to depict the structures blind or buried inside the seismogenic layer, capable of producing earthquakes, whose existence is unknown or questioned. Among several analyses, the estimation of fault plane solutions provides the orientation and the geometry of individual faults, whose data are essential to define the stress field of a region. Even though the existing techniques operates in different magnitude ranges, both in the time and frequency domain, reliable focal mechanism solutions are not straightforward to achieve, especially when small magnitude earthquakes occur. In fact, several factors severely affect the uncertainty of micro-seismic fault plane solutions such as the limited number of stations that record small events, higher noise level or the inadequate description of the medium response at the wavelengths at which microearthquakes radiate.

In this work, we propose a valid tool, as described in Adinolfi et al. (2022): 1) to test the performance of local seismic networks to recover fault plane solutions and 2) to estimate the uncertainty of focal mechanism solutions when it is unavailable or not provided by other techniques. Using a Bayesian approach that jointly inverts the long-period spectral-level P/S ratios and the P polarities, as input data (De Matteis et al., 2016), we explore the reliability of focal mechanism solution as a function of magnitude, location, and kinematics of seismic source from a theoretical point of view.

As case study, we explore the capability of the Irpinia Seismic Network (ISNet), in terms of number and geographical distribution of seismic stations, to constrain the fault plane solution of earthquakes assessing their solution uncertainties or parameter errors. ISNet is a local seismic network operating in the Campania-Lucania Apennines (Southern Italy) aimed to monitor the complex normal fault system activated during the Ms 6.9, 1980 earthquake. We prove the effectiveness of the proposed tool which can be easily customized for other case studies or network geometries.

Adinolfi G. M., De Matteis R., de Nardis R. & Zollo A. (2022) - A functional tool to explore the reliability of micro-earthquake focal mechanism solutions for seismotectonic purposes. Solid Earth, 13, 65-83. https://doi.org/10.5194/se-13-65-2022.

De Matteis R., Convertito V. & Zollo A. (2016) - BISTROP: Bayesian inversion of spectral-level ratios and P- wave polarities for focal mechanism determination. Seismol. Res. Lett., 87, 944-954. https://doi.org/10.1785/0220150259.

# A reappraisal of macroseismic data with statistical analysis for the strongest Calabrian earthquakes of the XVIII to XX centuries (southern Italy)

Andrenacci C.*[1-3], Bello S.[1-3], Barbano M.S.[2-3-4], Carducci A.[1-3], Pirrotta C.[2], Pietrolungo F.[1-3] & Lavecchia G.[1-3]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [3] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [4] INGV, Catania.

*Corresponding author e-mail:* carlo.andrenacci@unich.it

*Keywords:* macroseismic fields, historical Calabrian earthquakes.

This study deals with some of the earthquakes that occurred in Calabria from 1783 to 1908. Although they have been largely studied, robust and commonly accepted seismic sources are still missing. Starting from the studies reported in the CFTI5Med catalogue (Guidoboni et al., 2018), we reanalysed historical reports and reassessed the intensity of the shocks by using the European macroseismic scale 98 (EMS), which classifies damage according to its level and vulnerability class of buildings. We revised the 1783 seismic sequence, the 1791 Central Calabria, the 1894 southern Calabria, the 1907 Aspromonte and the 1908 Messina Straits earthquakes. The results obtained are used to compute new source parameters and some statistical analyses.

In particular, we used the new compilation of Intensity Data Points (IDP) to carry out a quantitative analysis of the macroseismic intensities distribution, computing the attenuation curves (e.g., Gasperini, 2001) which describe the propagation of the earthquakes in the near and far field and obtaining the main components of the macroseismic intensity for each IDP: isotropic component ($I_I$) and anisotropic component ($I_A$).

Considering the anisotropic component ($I_A$) we analyzed the local amplification and attenuation (e.g., De Rubeis et al., 2016) to compare with lithoseismic classes properties of the localities struck by the earthquakes considered. We used approaches adopted in the literature (Sbarra et al., 2019) to determine the approximate hypocenters' depths and calculated the seismogenic layer by using instrumental data. These analyses allowed a quantitative characterization of the studied historical earthquakes in terms of magnitude, size of the seismogenic sources and allowed us to attribute a seismotectonic domain to the nine earthquakes studied.

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# Atmo-stress cloud service: an open-source tool to reconstruct stress trajectories

Bressan S.*[1], Gounari O.[2], Ntouskos V.[2], Corti N.[1], Bonali F.L.[1-3], Karantzalos K.[4] & Tibaldi A.[1-3]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] National and Kapodistrian University of Athens (Greece). [3] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di MIlano-Bicocca. [4] Athena - Research and Innovation Center, Marousi (Greece).

*Corresponding author e-mail:* sofia.bressan@unimib.it

*Keywords:* structural geology, stress trajectory mapping, cloud-based service.

We present the Atmo-stress service, an open-source cloud service designed to reconstruct the stress trajectories in plan view for a given area, considering a specific stress component (e.g., σHmax or σHmin) as main input data. It has been developed in the framework of the NEANIAS (Novel EOSC Services for Emerging Atmosphere, Underwater & Space Challenges) project https://www.neanias.eu/. The software is available at https://atmo-stress.neanias.eu/.

Our service represents an improved version of the approach presented by Lee and Angelier (1994), including i) a newest user-friendly interface; ii) output data compatible with both Google Earth and GIS software; iii) setting menus to select the interpolation method (Polynomial and Distance Weighting) and to define the processing area scale (from Global to Local); iv) automatic or manual setting of all parameters used during the interpolation.

Regarding the input data, they can be uploaded in Excel or ASCII text file format, listing the following mandatory data: the azimuth value of the stress, the angular error, and the corresponding coordinates in a metric grid (e.g., UTM or local coordinate system) for each record of the dataset. Data for the selected stress can originate from different sources such as focal mechanism solutions, field data, GPS or in-situ geotechnical measures.

The service aims to reconstruct the present-day stress field and the paleo-stress trajectories of an active tectonic area to study: *i)* the evolution of its tectonic regime, *ii)* to assess seismic and volcanic hazards, and *iii)* to provide information about the fluid path on the shallow crust. Due to its purposes, the service could be used in different research fields, like geology, seismology, and volcanology but also in the oil and gas industry sector and by national institutions such as Civil Protection for the natural hazard prevention and management planning.

We also showcase two different case studies with different types of input dataset:

The Icelandic dataset includes in-situ data collected by the Structural Geology UNIMIB research group and they are presented in Corti et al. (2021). Field data belonging to the North Volcanic Zone (NVZ) are coming from Theistareykir (1634 data) and Krafla Fissure swarms (1378 data).

The Caucasus dataset contains 128 GPS data distributed within the Greater Caucasus (Azerbaijan, Georgia and Russia) and Transcaucasian depression (Tibaldi et al., 2021).

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Tibaldi A., Babayev G., Bonali F.L., Pasquaré Mariotto F., Russo E., Tsereteli N. & Corti N. (2021) - Active Kinematics of the Greater Caucasus from Seismological and GPS Data: A Review. In: Building Knowledge for Geohazard Assessment and Management in the Caucasus and other Orogenic Regions, NATO-Springer Series, 33-57.

# Building a new generation of seismotectonic models (northern Apennines, Italy): the ongoing PRIN projects NASA4SHA

Caputo R.* & NASA4SHA Working Group

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* rcaputo@unife.it

*Keywords:* earthquake geology, seismic hazard, fault segmentation.

Accretionary wedges, especially during their late continental stages, consist of numerous reverse faults, mainly with a low-angle setting and a common vergence. Although single shear zones and slip surfaces could have a relatively simple geometry, the crustal volumes affected by such contractional features are characterized by overstepping and/or overlapping structures, curved geometries (both along strike and downdip), and complex kinematic patterns (either in terms of rake or amount of displacement). During the last million years, the area that now corresponds to northern Italy was affected by a complex geodynamic 'engine' that led to stress concentrations/shadows and variable stress rates both in space and time at different scales. As a consequence, the identification of the seismogenic sources affecting the external sectors of the N. Apennines and S. Alps is particularly complex, and it represents a challenge for more realistic SHA, not only for northern Italy, but also for all similar tectonic settings.

From the geologic/structural point of view, segment boundaries within major fault zones might influence the start and stop of earthquake ruptures, thus controlling the magnitude and rupture propagation patterns during sequences. They correspond to structural discontinuities such as relay zones and large step-overs, pronounced bends, or branch faults and large cross-faults, and changes in rheology. Many of these geologic features are interpreted as higher strength rock volumes/fault zones, able to stop the propagation of coseismic ruptures (geometric and structural barriers), but also to nucleate ruptures.

The Po and Veneto-Friuli plains, including their contiguous foothills, are affected by two opposite verging thrust systems. Arc-shaped geometries of different sizes and curvatures have developed in both orogens, generating a complex system of minor-order structures with different dimensions and seismogenic potential. Although for both thrust belts several seismotectonic investigations have been carried out, the segment boundaries within major seismogenic sources, and especially their possible impact in terms of partial reactivations of the whole structure and maximum credible magnitude that could be released has been not sufficiently treated.

The main objective of the NASA4SHA Project is to address specific challenges in seismotectonic characterization in contractional systems mainly consisting of blind structures, though local evidence of surface ruptures also occurs, by investigating different space and time scales aiming at a substantial progress in the knowledge and 3D structural representation of large sectors of Northern Apennines and Southern Alps, with focus on their segmentation and the consequent seismogenic behaviour.

# Seismicity clustering and tectonic structures: inferences from seismological and statistical indexes in central Italy's high seismic hazard area

Carbone L.*[1], Vuan A.[3], Romano M.A.[3] & Lavecchia G.[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* luca.carbone@unich.it

*Keywords:* seismic swarm, template matching, seismotectonics.

After L'Aquila 2009 seismic sequence (Central Apennines, $M_W$ 6.3), southward of the fault causative of this earthquake (e.g., Paganica fault), a general increase in the seismicity rate is observed at the hanging wall of the internal west-dipping normal fault alignment (Salto Valley, Fucino basin and Sangro Valley) and the east-dipping extensional detachment (Latium-Abruzzi Etrurian Fault System as in Lavecchia et al., 2017).

This area is characterized by a low level of background seismicity that increased fivefold from 2009 to 2020 and culminated with an event that occurred on 16 February 2013 ($M_L \sim 4.8$), near Sora town that represents the most energetic event of the last 20 years.

We studied the seismicity that preceded the Sora event in two steps. The first aims to produce an enhanced catalog, detecting seismic clusters occurring between 2009 and 2013 before the Sora earthquake and analyzing their possible association with the active fault systems of the study area. The second is focused on the investigation of the relationships between the occurrence of the observed seismic activity and (1) the distribution of the static and dynamic triggering caused by the L'Aquila earthquake, (2) the transient (i.e., the fluid role) or tectonic phenomena.

The enhanced catalog was retrieved using the open-source seismological package PyMPA (Vuan et al., 2018), which detects microseismicity from cross-correlation of continuous data and templates. The final dataset of ~11000 seismic events ($-2.3 \leq M_L \leq 4.8$) was used for the cluster analysis. We detected 7 clusters close to the 2013 seismic sequence. For each one, we computed the (1) the interevent times and covariance of interevent times, (2) the evolution of seismic moment, (3) the along-strike and along-dip migration velocities, and (4) the temporal evolution of the effective stress-drop. The analyses of these indexes jointly with the static and dynamic triggering observations suggest that the clustering of mixed foreshocks and swarm-like sequences is likely a consequence of static stress transfer.

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Vuan A., Sugan M., Amati G. & Kato A. (2018) - Improving the Detection of Low-Magnitude Seismicity Preceding the Mw 6.3 L'Aquila Earthquake: Development of a Scalable Code Based on the Cross-Correlation of Template Earthquakes. Bulletin of the Seismological Society of America, 108, 471-480.

# The role of lithology distribution and tectonic structures in controlling coseismic surface deformation inferred by geological and DInSAR data

Carboni F.[1-2], Porreca M.*[1-2], Cenci G.[1], Valerio E.[3], Manzo M.[3], De Luca C.[3], Ercoli M.[1-2], Occhipinti M.[1] & Barchi M.R.[1-2]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di Perugia. [3] Istituto per il Rilevamento Elettromagnetico dell'Ambiente, CNR, Napoli.

*Corresponding author e-mail:* massimiliano.porreca@unipg.it

*Keywords:* ground deformation, DInSAR, earthquake.

In the last three decades, remote sensing techniques, such as Differential Synthetic Aperture Radar Interferometry (DInSAR), have been exploited for investigating, with high accuracy, ground displacement phenomena. Large seismic events ($M_w > 5.5$) can trigger deformations at the surface, which are controlled by the active faults and the intercepted lithologies characterizing the struck area.

In 2016-2017, a long earthquake sequence struck the Apennines in central Italy, producing impressive surface ruptures attributed to the 24 August Mw 6.0 and 30 October Mw 6.5 mainshocks. These ruptures were investigated and mapped by field geologists soon after the earthquakes, and during the following years also by remote sensing data.

We present detailed maps of the surface deformation pattern produced by the M. Vettore Fault System (VFS) during the October 2016 earthquakes. The DInSAR analysis has been retrieved from ALOS-2 SAR data, via the Parallel Small BAseline Subsets (P-SBAS) algorithm. On these maps, we trace a set of 5 geological cross-sections to inspect a possible link between the coseismic vertical displacement, the lithology distribution and the tectonic structures of the area (i.e., thrusts, normal faults). On these sections, we also project the seismicity distribution recorded during October 2016.

The integration of such datasets allows the recognition of an important lithological control in the overall distribution of the deformation, which shows respectively, maximum values in correspondence of the carbonatic multilayer, whilst minimum values within the clastic succession. The deformation field gradually reduces northwards, where the VFS is at its tip and where marly lithologies crop out.

In addition, we observe that further deformation is localized at the footwall of the VFS, mainly in the surroundings of the Mt. Bove, corresponding to the hangingwall block of an important thrust fault, where shallow seismicity was also recorded. Here, we observe that the coseismic deformation tends to decrease toward the outcropping thrust. In the south sector, instead, we do not observe a control of thrusts acting as a barrier to the deformation.

The results of this work demonstrate that the integration of surface geology, remote sensing data and seismicity, can lead to a better understanding of the influence of geological structures on the distribution of the surface deformation associated with earthquakes.

# A combined seismologic-kinematic approach for 3D *b*-value zonation in Southern California

Carducci A.*[1-2], Andrenacci C.[1-2] & Lavecchia G.[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* andrea.carducci@unich.it

*Keywords:* seismotectonics, earthquake-size distribution, faulting styles.

We propose a two-step method for a three-dimensional seismotectonic zonation of the Southern California Authoritative Region. This approach consists of:

1. quantification of stress field and Anderson's faulting style, called $A_\lambda$, to create a stress and kinematic 3D model for well-distinguished crustal volumes buffering each of the Quaternary fault segments of the area at depths <20 km;
2. quantification of the 3D *b*-values variability for the individual crustal volumes and the overall crustal system.

We use an input dataset of focal mechanisms, combined with relocated coordinates from an earthquake catalog for better spatial adherence to the seismogenic structures: the merged earthquakes-focal mechanisms (MEFM) comprise ~56700 seismic events over the 1981-2019 time window, with magnitudes in the 0-7.3 range. The MEFM dataset is interpolated over a 3D grid structure, to identify volumes featuring homogeneous stress levels and kinematic styles. These seismological homogeneous crustal structures are determined starting from the 3D nonplanar fault structures of the Southern California Community Fault Model and assuming for each fault and, in some cases fault alignment, an earthquake buffer zones. The perpendicular-to-surface size of the buffer zone is defined based on the estimated spatial uncertainties associated with the input data and the seismogenic structures. A density-based cluster identification algorithm is used to discretize the buffer volumes into kinematic homogeneous granular sub-volumes, that we call syn-kin clusters. The syn-kin clusters form the basis of the here proposed 3D-seismotectonic zonation approach. They are used as sampling input data for frequency-magnitude evaluation and 3D representation *b*-values spatial variability.

The *b*-values from the Gutenberg-Richter equation and Magnitude of Completeness levels are computed and plotted as 3D distributions within the identified syn-kin clusters, considering statistics from magnitudes of both the relocated earthquakes and the MEFM dataset. Subsequently, the relationship between *b*-values and $A_\lambda$ kinematic classes in the syn-kin clusters model is evaluated through a weighted average method, which considers the seismic energies released by the events comprised in each cluster.

The developed seismotectonic approach to the computation and analysis of *b*-values is a methodological alternative to the purely seismologic method of the "mobile windows", commonly used in spatial frequency-size statistical analyses. The corresponding 3D zonation gives some insights into the potentialities and limitations of the combined use of relocation solutions and kinematic features for statistical seismology and demonstrates the flexibility of a hybrid seismotectonic-seismological approach.

# 3D fault model building and seismic potential in the Pollino area (Calabria–Basilicata, southern Italy)

Cirillo D.*[1-2], Totaro C.[2-3], Lavecchia G.[1-2], Orecchio B.[2-3], de Nardis R.[1-2], Presti D.[2-3], Ferrarini F.[1-2], Bello S.[1-2] & Brozzetti F.[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.

*Corresponding author e-mail:* d.cirillo@unich.it

*Keywords:* 3D fault model building, Pollino seismic activity, Quaternary extensional tectonic.

We reconstructed the 3D geometries and kinematics of the interconnected fault pattern responsible for the moderate-magnitude earthquakes, which were recently affected by the 2010-2014 seismic activity of the Pollino area (Calabrian-Lucanian boundary). The 3D Faults Model of the Pollino area was reconstructed by integrating the structural-geological and seismological data. We constrained the model at the surface with fault-slip data and by using selected relocated hypocenters' distributions at depth.

Geological and seismological data allowed us to highlight an asymmetric active extensional fault system characterized by an E to NNE-dipping low-angle detachment with high-angle synthetic splays and SW- to WSW-dipping, high-angle antithetic faults.

Hypocenters and the time-space evolution of the events suggest that two main sub-parallel WSW-dipping seismogenic sources, the Rotonda-Campotenese and Morano-Piano di Ruggio faults, are responsible for the strongest events of the 2010-2014 seismic activity (Brozzetti et al., 2017; Ercoli et al., 2021; Cirillo et al., 2022).

We calculated the area of the seismogenic patches obtained by projecting the hypocenters of the early aftershocks on the 3D fault planes is consistent with the observed magnitude of the strongest events of October 2012 and May 2012 (Mw=5.2 and Mw=4.3).

Since earthquake-scaling relationships provide maximum expected magnitudes of Mw=6.4 for the Rotonda-Campotenese and Mw=6.2 for the Morano-Piano di Ruggio faults, we may suppose that during the 2010-2014 seismic activity, the two structures did not release their seismic potential entirely.

The reconstructed 3D faults model also points out the relationships between the activated fault system and the western segment of the Pollino Fault. This latter was not involved in the recent seismic activity but could have acted as a barrier to the southern propagation of the seismogenic faults, limiting their dimensions and the magnitude of the generated earthquakes.

Brozzetti F., Cirillo D., de Nardis R., Cardinali M., Lavecchia G., Orecchio B., Presti D. & Totaro C. (2017) - Newly identified active faults in the Pollino seismic gap, southern Italy, and their seismotectonic significance. J. Struct. Geol., 94, 13-31. https://doi.org/10.1016/j.jsg.2016.10.005.

Cirillo D., Totaro C., Lavecchia G., Orecchio B., de Nardis R., Presti D., Ferrarini F., Bello S. & Brozzetti F. (2022) - Structural complexities and tectonic barriers controlling recent seismic activity in the Pollino area (Calabria-Lucania, southern Italy)-constraints from stress inversion and 3D fault model building". Solid Earth, 13(1), 205-228. https://doi.org/10.5194/se-13-205-2022.

Ercoli M., Cirillo D., Pauselli C., Jol H.M. & Brozzetti F. (2021) - Ground-penetrating radar signature of Quaternary faulting: A study from the Mt. Pollino region, southern Apennines, Italy. Solid Earth, 12(11), 2573-2596. https://doi.org/10.5194/se-12-2573-2021.

# Multiscale approach to reconstruct the tectono-stratigraphic architecture of the Squillace Basin (Offshore Calabria, Italy) from Late Miocene to Recent time

Corradino M.*[1-2], Morelli D.[3], Ceramicola S.[4], Scarfì L.[5], Barberi G.[5], Monaco C.[1-5-6] & Pepe F.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Scienze della Terra e d el Mare, Università di Palermo. [3] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [4] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS). [5] INGV, Osservatorio Etneo, Catania. [6] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di Catania.

*Corresponding author e-mail:* marta.corradino@unipa.it

*Keywords:* active tectonics, Calabrian Arc, multiscale analysis.

Offshore, active faults are usually inferred by detecting seafloor scarps in bathymetry and identifying the offset of the Upper Quaternary deposits in seismic profiles. Although the active faults deform a significant seafloor region, they could be secondary features formed in response to local stresses, and not associated with large earthquakes.

In this work, we have reconstructed the tectono-stratigraphic architecture of the Squillace Basin (Ionian offshore of the Calabria region) from the Late Miocene to Recent, and distinguished between shallow, non-seismogenic, active faults (second-order structures), and deep blind faults (first-order structures), capable of producing large earthquakes. We have used a multiscale approach based on the interpretation of seismic reflection profiles with different penetration/resolution, calibrated with well-log data and integrated with bathymetric data, and the distribution of instrumental earthquakes.

Our results highlight the occurrence of three main tectonic events. The first extensional/transtensional phase occurred during the Late Miocene. This event led to the formation of roughly W-E oriented horst and half-graben structures and a WNW-ESE transtensional fault located in the central sector of the basin. During the Pliocene, the extensional/transtensional tectonics continued to be dominant. From the Early Pleistocene (Calabrian), the extensional tectonics was interrupted by a left-lateral transpressional phase. This last event caused the positive inversion of some deep (> 3 km) extensional faults inherited from the previous event and the formation of NW-SE to WNW-ESE transpressional/thrust faults and related anticlines. The latter deform the seafloor of the northern and western basin, forming NW-SE to WNW-ESE oriented ridges. These transpressional structures can be considered the offshore prolongation of the transpressional faults formed in the left-lateral shear zones documented in the northern Calabrian Arc.

At the culmination of anticlines related to the deep transpressional faults, shallow (<3 km) high-angle normal faults offset the younger deposits. Some of the faults propagate upwards reaching the seafloor and forming well-developed seabed scarps. These morphological features indicate the recent fault activity. The orientation of the shallow normal faults is parallel to the elongated axis of the ridges. Based on their depth and direction, we interpret these faults as secondary structures due to tensional stress that occurred in the extrados of the anticlines associated with the transpressional structures.

Our findings are supported by seismological data. The earthquake location highlights several alignments that reveal active structures affecting the Ionian offshore, oriented around NW-SE. Events are mainly located in the northern sector of the Squillace Basin, with a depth range between 0 and 30 km. Focal mechanisms of earthquakes with M> 3 indicate mainly strike-slip or transpressive movements.

# Earthquake catalogue enhancement through template matching: an application to the Southern Apennines (Italy)

Diaferia G.*[1], Valoroso L.[1], Improta L.[1] & Piccinini D.[2]

[1] INGV, Roma. [2] INGV, Pisa.

*Corresponding author e-mail:* giovanni.diaferia@ingv.it

*Keywords:* seismicity, template-matching, high-resolution catalogue.

Improving the capability of seismic networks to detect small-magnitude seismicity, commonly near or below the detectability threshold, is the prerequisite to characterize the seismotectonics of an area in terms of fault geometry, kinematics and mechanics, thus leading to an improved comprehension on the physical mechanisms that generate small and large earthquakes.

In this work, we apply template-matching, a cross-correlation based technique for the detection of hidden earthquakes, at the scale of the Southern Apennines (Italy). Here, the ongoing extension of the Mio-Pliocene Apennine thrust-belt poses a major seismic risk, as testified by several Mw~7 earthquakes that struck this area in the past 300 years. No clear consensus exists on the seismotectonic models related to such events, particularly in terms of characterization of the fault structure and crustal rheology that can thus largely benefit from the application of template-matching.

As template events, we use ~9000 earthquakes occurring between 2009 and 2015, recorded by 181 stations from the INGV National Seismic Network. Six years-long (2009-2015) continuous recordings are scanned by the template-matching algorithm. Of about 3 million new detections, around 3% (~88.000 events) comply with the minimum quality thresholds we set (at least four P and S picks, recorded at least at five stations). For determining earthquake locations we used the fully-probabilistic non-linear code NonLinLoc, with an ad-hoc 1D velocity model and corrections for station residuals.

By accounting for the quality of the hypocenter location, the final catalog comprises ~50.000 new seismic events with a mean horizontal and vertical error of 1.4 and 2.5 km, respectively, and a mean RMS of 0.13 s, parameters that are similar to those of the template catalog.

Given the small magnitude (Mw<1) of the majority of the newly detected events, the new catalog shows a decrease in magnitude of completeness from 2.5 to 1.9, assessed through the Lilliefors' goodness-of-fit test.

The spatial and temporal pattern of seismicity unravelled by the enhanced catalog provide new insights especially for those seismogenic structures that are poorly known. For the main seismic sequences that occurred in the analyzed period (i.e., Pollino and Matese Mw 5+ sequences) the aftershocks as well as the foreshock phases appear particularly enriched. Main NW-SE trending seismogenic structures of the axial zone of chain are illuminated by abundant microseismicity, with evident gaps delineating the boundary of such structures. In addition, the new catalog unravels distinct E-W oriented clusters in the external zone of the seismic belt, likely related to shear zones developed in the deeper crystalline crust of the Adria plate.

# Enhancing fault patterns on the deep seismic reflection line CROP-04 through data pre-conditioning and seismic attributes

Ercoli M.*[1-2], Carboni F.[1-2], Akimbekova A.[1-2], Carbonell R.[3] & Barchi M.R [1-2]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di Perugia. [3] GEO3BCN, CSIC-Geosciences Barcelona (Spain).

*Corresponding author e-mail:* maurizio.ercoli@unipg.it

*Keywords:* reflection seismic, earthquakes, seismic attributes.

Seismotectonic studies are critical in linking the active faults traces mapped at surface with the hypocentral earthquake source. The seismic reflection method is the most powerful tool to constrain the geometry and kinematics of faults at depth, and commercial data are often re-used for these purposes. Across the Italian peninsula, deep reflection seismic profile like the "CROP" also aided to shed light on the deep subsurface structures. However, legacy data are frequently characterized by random noise hampering the seismic interpretation. The CROP-04 "Agropoli-Barletta" was acquired from the Tyrrhenian to the Adriatic Sea (Mazzotti et al., 2007) across the Southern Apennines fold-and-thrust belt and the foreland system. This profile crosses the Irpinia fault, source of the destructive 1980 Mw 6.9 earthquake (Pantosti & Valensise, 1990). Different geological interpretations were derived from such data and, aiming to reduce this uncertainty, we set up a customized workflow based on a pre-conditioning strategy and on seismic attributes, to attenuate the random noise and extract additional information (Ercoli et al., 2020). Combination of filters and co-rendered seismic attributes, applied for the first time on such deep seismic data, considerably enhanced the reflection patterns and the overall interpretability, contributing to the understanding of a complex geological area of the Southern Apennines. Our results do unveil complex sets of normal faults, depicting subsurface features invisible in the original CROP-04 and partially at the surface (Bello et al., 2021). The improved data also clearly display low-angle W-dipping thrusts as well as deep regional features. Our approach revealed efficient to revive legacy CROP-like data, which are unique and nowadays (possibly) not repeatable. Their reinterpretation may provide new important insights in seismotectonic studies across seismically active areas, not only by extending the interpretation of outcropping faults to depth, but also by tracing unknown faults for driving surface mapping field work.

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# 3D crustal structure of the Irpinia region (Southern Apennines): constraints from the integration of subsurface data and local earthquake tomography

Feriozzi F.*[1], Improta L.[2], Maesano F.E.[2], De Gori P.[2] & Basili R.[2]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INGV, Roma.

*Corresponding author e-mail:* fabio.feriozzi1996@gmail.com

*Keywords:* seismic reflection profiles, Apulian carbonate platform, seismicity relocation.

The Irpinia region in the Southern Apennines is one of the areas with the highest seismic hazard in Italy, as also testified by several recent and historical earthquakes ranging between Mw 6.6-6.9 (1694, 1732, 1930, 1980). The shallow crust structural setting of this area is characterized by multiple deformational stages, which caused the tectonic stacking of sedimentary sequences deposited in different paleogeographic domains. The overall structure of the chain is still contended between the thin-skinned model and the thick-skinned model.

In this framework, we built a 3D geological model of key stratigraphic and tectonic elements based on the analysis of 2D seismic reflection profiles from confidential (ENI), public (ViDEPI), and CROP-04 datasets, integrated with well data and surface geology information (CARG project). We also computed a 3D velocity model of the upper crust (Vp and Vp/Vs) through a local earthquake tomography to provide inferences on the structure and rock properties of the deep Apulian tectonic stack, especially where this is poorly imaged by seismic reflection imaging. In addition, we propose an integrated interpretation of the deep structure based on the analysis of the CROP-04 deep seismic profile. Our results highlight the presence of a regional thrust separating a shallow domain, characterized by relatively low angle thrust surfaces (Allochthonous domain), from a deeper domain by high-angle buried thrusts that affect the Apulian carbonate platform succession.

The Plio-Pleistocene Apulian compressional architecture seems to control the seismotectonic of the area. The background seismicity of the last decade re-located in the 3D tomographic model follows the Apulian structural trends, and most of the earthquakes occur within high-Vp Triassic-Jurassic carbonates. From a methodological point of view, our 3D geological model is suitable for future earthquake relocations based on a data-driven velocity model reconstruction that considers the 3D geological complexities.

# Linking long-term- to seismogenic deformation in tectonically-active settings: methods and results coming across recent (1997-2016) Italian normal-fault seismic sequences

Ferrarini F.*[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* f.ferrarini@unich.it

*Keywords:* Multi-scale deformation, normal-fault earthquakes, central Italy.

The Apennines extensional belt of central Italy represents an excellent setting to investigate active deformation through space and time. Evident exposition of normal fault scarps and recent major seismic sequences (from 1997 to 2016) provide case studies suitable for seismic hazard assessment, given the relevant availability of field- and geophysical data (e.g., structural- and remote sensing data, well-relocated seismicity, etc.).

Moving across time and consequently-improved tools and dataset resolution, I will show examples of integrated methodological approaches dealing with the seismotectonic contexts of the Colfiorito 1997 (Mw 6.0), L'Aquila 2009 (Mw 6.1) and Norcia 2016 (Mw 6.5) earthquakes. Comparisons between the long-term- and (instantaneous) seismogenic deformation affecting the normal faults activated by the earthquakes, will be detailed and discussed. In particular:

- in the 1997 and 2009 epicentral areas, stress-field analyses comparing independent sets of structural data and focal mechanisms allowed to support evidence of a long-lasting and common field (least horizontal stress axis oriented NE-SW) acting along the Colfiorito and L'Aquila fault systems. This reflects in both the geometry and kinematics of the Plio-Quaternary E-to-NE- and SW-dipping normal faults which crop out in central Italy, and the nucleation and development of the recent seismicity. The slip on inherited- as well as hidden seismogenic sources (i.e., Annifo and Ocre during 1997 and 2009 sequences, respectively) also concur to the overall deformation, locally or along the east-dipping detachment, as favourably oriented to the regional stress field;
- the Norcia 2016 earthquake provided the scientific community with huge collections of measured coseismic offsets as well as geophysical constraints (e.g., remote sensing techniques and well-relocated hypocenters) on the in-depth geometry of seismogenic sources and their activation through time. The comparison of structural-kinematic data with (along-distance) co-seismic- and topographic throws, pointed out again a clear correlation between the short- and long-term deformation along the Mt Vettore-Mt Bove fault system. In addition, and unexpectedly, the analysis of the spatial distribution of the seismicity during a wider time window (2016-2018), integrated with morphotectonic analysis of offset paleosurfaces, 3D earthquake-fault association and Coulomb stress-transfer calculations, pointed out the existence of the up-to-date unknown immature (but potentially active) Pievebovigliana fault, along the northern tip of the fault system.

In all the cases, the comparison through integrated approaches of different time-scale evidence of deformation helped to confirm, refine, and improve the knowledge of the fault systems' geometry, and their activation through Quaternary and recent times; thus contributing to the seismic hazard assessment in central Italy.

# Faults and fluids interaction during the Emilia 2012 seismic sequence

Fonzetti R.*[1-2], Valoroso L.[1], De Gori P.[1] & Chiarabba C.[1]

[1] INGV, Roma. [2] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* rossella.fonzetti@uniroma3.it

*Keywords:* Emilia seismic sequence, double-difference tomography, hydraulic properties of fault zones.

In this study, we used cross-correlation (Schaff & Waldhauser, 2005; Waldhauser & Schaff, 2008) and double-difference methods (Waldhauser, 2001; Zhang & Thurber, 2003) to relocate the aftershocks of the 2012 Emilia seismic sequence and to compute new crustal velocity models of the area. During the sequence, two mainshocks, $M_L$ = 5.9 on 20th May and a $M_L$ 5.8 on May 29th, activated two adjacent thrust segments.

Soon after the occurrence of the seismic sequence, the attention focused on the possibility that the exploitation at the Cavone oil field influenced the mainshocks occurrence. Previous studies reported that the large distance between the oil field, the first shock and the lack of hydraulic connectivity between the two faults were evidence to exclude the anthropic contribution to the spatiotemporal evolution of the seismic sequence. Other analyses explained the triggering of the second mainshock with a high pore pressure pulse at the base of the carbonate multilayer (Pezzo et al., 2018). Anyway, there is still no information on the possible alteration before the first shock or triggering mechanism by fluids.

To investigate in more detail the relationships between the two thrusts involved in the seismic sequence, we use the TomoDD source code (Zhang & Thurber, 2003) to simultaneously compute aftershock relative locations and P- and S- waves velocity models. The accurate relocations, highlight a complex system with small-scale fault-segments coalescing in the Mirandola and Ferrara thrusts. We observe a broad high Vp/Vs anomaly at seismogenic depth suggesting a possible hydraulic connection between the thrusts. The close look at seismicity indicates a simultaneous activation of the entire thrust system. Furthermore, the crustal velocity model suggests that the two mainshocks and the larger magnitude aftershocks occurred in an area characterized by high fluid pressure (i.e, high Vp/Vs), suggesting hydraulic connectivity along the fault system.

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# A multidisciplinary analysis for a 3D modelling application in seismotectonic: The case study of Quaternary Faults in southern Calabria

Giuffrida S.*[1], Brighenti F.[1-2], Cannavò F.[3], Carnemolla F.[1-2], De Guidi G.[1-2], Barreca G.[1-2] & Monaco C.[1-2-3]

[1] Dipartimento di Scienze Biologiche Geologiche e Ambientali, Università di Catania. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Catania. [3] INGV, Osservatorio Etneo, Catania.

*Corresponding author e-mail:* salvatore.giuffrida@phd.unict.it

*Keywords:* active tectonic, seismogenic faults, 3D modelling.

Active normal faulting and uplifting dominate the Quaternary tectonics of the southern Calabria, consistent with WNW-ESE oriented extensional dynamics. The main fault structures of this sector of the Calabrian Arc (e.g., Serre, Cittanova, S. Eufemia and Scilla faults) are considered responsible for the 1783 seismic sequence (M 6.5-7; Jacques et al., 2001). A multidisciplinary approach was applied to define, through a 3D analytical model, the geometry, kinematics and dynamics of the Cittanova and Serre fault planes. Their geometry was defined using the distribution of crustal seismicity projected on a schematic geological section, reconstructed through the interpretation of CROP seismic profiles and morpho-structural investigations. Modelling is performed in MOVE software through the Faults Response Modelling module which use the TDE (Triangular Dislocation Elements) analytical method (Meade, 2007). The geometric, seismological and kinematic features of the modelled faults have been validated by comparing them with empirical models (e.g., Wells & Coppersmith, 1994). A first attempt to invert the available GNSS data is carried out to constrain an analytical Okada model (Cannavò, 2019 and references therein) of the studied faults. The models obtained from the different approaches will be compared to improve our knowledge of the considered area. The study methodology applied in this paper, may represent a guideline that can be used to modelling other quaternary seismogenic structures in the Calabrian Arc.

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# Overtime tectonic, dynamic and rheological control on destructive MUltiple Seismic Events. Special faults & earthquakes in southern Italy: PRIN Project MUSE 4D

Lavecchia G.*[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* glavecchia@unich.it

*Keywords:* 3D fault model building, earthquakes, southern Italy.

MUSE 4D is aimed at studying and constraining the geometric, kinematic and dynamic setting of the Quaternary, active and seismogenic fault systems of the southern Campania-Lucania-Calabria extensional belt and at the unrevealing the tectonic control on multiple magnitude 7-class earthquakes. The project focus on four destructive Special EarthQuakes (SEQs): Reggio Calabria-Messina 1908 ($M_w$7.1), Irpinia 1980 ($M_w$6.9), Basilicata 1857 ($M_w$7.1), South Calabria 1783 ($M_w$7.1). These events released similar cumulate magnitudes in a time-lapses variable from instantaneous (1908) to few seconds (1980), few minutes (1857), few days, and few months (1783).

The Project has been organized in six Research Units with expertise in structural geology, seismology, and geophysics. Five Research Units (RUs) belong to CRUST, an Inter-University Italian Center for Research on 3D Seismotectonics, and one RU belongs to INGV.

In particular, the research has been aimed at developing:

- a new unified 3D geometric and kinematic fault model of the southern Campania-Lucania and southern Calabria seismogenic systems, within the seismotectonic context of the overall southern Apennines of Italy;
- a 4D seismotectonic model of the SEQs structural/rheological and seismological complexities and their interconnection in time and 3D space with a special focus on the possible presence of time transitory barriers to the deformation propagation (i.e., Earthquake Gates);
- analogue dynamic models that schematically reproduce the SEQS complexities and highlight fault parameters most influent on surface deformation/rupture patterns;
- an overall new understanding of overtime tectonics and earthquake dynamics in southern Italy.
- The methodological strategy has been based on two main points:
- adopting a multi-scale interdisciplinary approach (geology, seismology, geophysics) with continuous exchanges among researchers with different backgrounds and expertise;
- reconstructing the active and potentially seismogenic deformation pattern in a long-term tectonic perspective (overall Quaternary time, last 2.5 My) and at different scales (from outcrop to regional).

A number of unified, complete, and original databases on fault traces, fault/slip data, deformation rates, high-quality hypocentral locations and focal mechanisms, earthquake source models, and crustal parameters ($V_s$, $V_p$, density) plus parametrized nonplanar mesh surfaces have been developed, along with uncertainties analysis. The slip tendency and Coulomb stress transfer scenarios and a conceptually innovative 4D Seismotectonic Model have been developed for the four SEQS, also advancing new possible seismotectonic interpretations and reconstructing new seismogenic scenarios.

Analogue dynamic models that schematically reproduce the SEQS complexities and highlight fault parameters most influential on surface deformation/rupture patterns are still in progress.

# QUaternary fault strain INdicators database - QUIN 1.0 - first release from the Apennines of central Italy

Lavecchia G.[1-2], Bello S.*[1-2], Andrenacci C.[1-2], Cirillo D.[1-2], Ferrarini F.[1-2], de Nardis R.[1-2], Roberts G.[3] & Brozzetti F.[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] Department of Earth and Planetary Sciences, University of London, Birkbeck (UK).

*Corresponding author e-mail:* simone.bello@unich.it

*Keywords:* Quaternary faulting, strain/stress, fault-striation pairs.

Open-access databases of present-day stress patterns, at regional to local scale, are available for most of the world (generally represented as horizontal stress orientations) but are mostly defined by indicators such as focal mechanisms, borehole breakouts, and overcoring data, while geological fault data are subordinate. This global under-utilization of geological data in active stress databases may be partly attributed to the limited number of well-exposed faults recognized as Late Quaternary (last 0.126 my) in age and to a lack of systematic collaboration amongst the geological community. We consider that in areas, such as Italy, where, according to several authors, the regional stress field has remained unchanged over the last few million years, the analysis of structural data relevant for seismogenic purposes can be extended at least to the overall Quaternary time interval (last 2.58 my). This assumption makes long-term surface fault-slip data valuable to better and more extensively constrain the present deformation pattern and the corresponding crustal state of stress.

In such a context, we present QUIN, a "QUaternary fault strain INdicators database", designed to integrate and unify published and new local-scale geological information and derive deformation and strain parameters for seismotectonic analysis. QUIN provides data on 3339 Fault Striation Pairs (FSPs; fault plane and slickenline), distributed within 455 survey sites exposed along the intra-Apennine Quaternary extensional faults of Central Italy. The area covers an extent of ~550 km in an average NW-SE direction. QUIN gives information on FSP location, attitude and kinematics, and deformation axes.

Together with QUIN, we also provide an original shapefile of the faults hosting the FSP. Making available a regional compilation of detailed fault traces and structural data is fundamental to constraining the geometry and kinematics of the intra-Apennine potentially seismogenic faults, also performing detailed studies on kinematic partitioning and rupture segmentation, both with classical methodologies and with new technologies. Our data help to clarify and implement the contemporary geometric and kinematic deformation pattern of Central Italy that appears scattered and incomplete whenever exclusively derived from earthquake data. Each Structural Site with a sufficient and kinematically homogeneous fault population, represented as pseudo-focal mechanism, can be compared with seismological focal mechanisms, and used for formal stress field inversion.

QUIN is useful to refine and locally extend the surface boundary of the Italian extensional seismogenic province, with relevance for hazard assessment evaluation, especially in areas that have not yet released earthquakes since historical times.

The database will be extended to southern peninsular Italy, with data recovered from the literature ad newly acquired within the frame of the MUSE-4D PRIN2017 project.

# Multi-scale conceptual database for 3D SEIsmic Source characterization in Compressional environment - SEISC 1.0 - first release from eastern Central Italy

Lavecchia G.[1-2], Pandolfi C.*[1-2], Carducci C.[1-2] & Akinci A. [3]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] INGV, Roma.

*Corresponding author e-mail:* glavecchia@unich.it

*Keywords:* 3D seismotectonics, fold-and-thrust multi-scale database, central Eastern Italy.

We present SEISC-3D, an ArcGIS geodatabase for 3D SEIsmic Source Characterization, that integrates multi-scale and multi-depth geological and seismological information in a Compressional tectonic environment. It contains a detailed regional-scale, geometric and kinematic, 3D curvilinear fault model, relevant for seismotectonic, geodynamic modeling and seismic hazard studies. This first release focuses on the late Pliocene-to-Quaternary arcuate and eastward convex fold-and-thrust belt still active along the Outer front of the Italian Apennines in eastern Central Italy. The near-surfaces, onshore and offshore, thrust faults represent the hanging-wall structures of a potentially seismogenic crust-scale shear zone, known as Adriatic Basal Thrust. Three hierarchic levels of structural maps are provided with decreasing details moving from fold-and-thrusts traces, enveloping thrusts, and regional thrust alignment traces. Different geographic datasets (points, lines, surfaces) are unified, compiled, and held in a common ARC GIS file system folder and linked on the base of relational models.

SEISC is composed of the following datasets:

1- fold hinges traces;
2- individual fold-related thrusts;
3- enveloping thrusts organized in hierarchic orders;
4- interconnected nonplanar fault surfaces built along the down-dip projection of the enveloping thrusts;
5- gridded structural dataset with geometric and kinematic data (attitude, dip-angle, slip-vector, rake, sense of movement) for the triangulated mesh of each fault surface.

The SEISC database is compiled from 20 local and regional structural maps, about 100 geological sections and transects from literature, and a large number of hypocentral sections drawn with different directions and semi-widths across the arcuate belt. Ad hoc developed Matlab codes allow extracting point data within chosen rock volume buffering the fault surfaces.

A crucial point when dealing with compressional structures is the difficulty of adopting segmentation criteria suitable for a realistic earthquake-fault association. In our methodological approach, the along-strike segmentation is strongly driven by the en-echelon distribution of the fold-related thrusts and by sharp variation in strikes and bending of the enveloping thrusts. The down-dip segmentation is controlled by the crustal mechanical layering derived from earthquake distributions and mechanical stratigraphy.

# Seismic and geodetic monitoring of the Gargano promontory (Southern Italy)

Miccolis S.*[1], Carafa M.M.C.[2], Filippucci M.[1], Merryman Boncori J.P.[3] & Tallarico A.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] INGV, Sezione di Sismologia e Tettonofisica, Roma. [3] Space Institute, Technical University of Denmark, Lyngby (Denmark).

*Corresponding author e-mail:* simona.miccolis@uniba.it

*Keywords:* monitoring, seismicity, Persistent Scatterer Interferometry (PSI).

Recent advances in active-processes monitoring have proven to be successful in properly determining the seismic hazard of a region. However, some areas are still underinvestigated or require further investigations. This is the case of the Gargano Promontory (hereafter GP), in Southern Italy.

Much geological information has been achieved over time; it has been recognized that the GP belongs to the Adriatic plate and consists of a carbonate-dolomitic succession. It was also observed that this area was affected by strong historical earthquakes and that a non-marginal seismic activity interests the GP crust. However, the link between surface faults traces and historical earthquakes (or instrumental seismicity) is debated if not obscure. For this reason, we have studied the microseismicity and surface deformation of GP to constrain its seismotectonics.

First, all the events recorded since 2013 were re-analyzed, providing a new seismic database of 635 microearthquakes used to retrieve focal mechanisms and the actual stress field of the GP. These data have been recorded using the OTRIONS local seismic network (Tallarico, 2013), installed by the University of Bari "Aldo Moro" in cooperation with INGV. Then, to overcome the limitation related to the seismic approach, we integrated this study with the Persistent Scatterers InSAR analysis (Ferretti et al., 2001), performed in collaboration with the Technical University of Denmark.

According to the data, the frictional part of the GP extends up to 40 km with a maximum earthquake frequency in the 14-37 km depth range, mainly with compressive and transpressive kinematics. Furthermore, seismicity highlights a deep surface trending SW-NE and dipping towards NNW which is considered the most likely responsible for the observed seismicity (Miccolis et al., 2021). In addition, the integrated use of geodetic survey allows observing a large subsiding area south of the GP and a general uplift with low to very-low rates along the whole area. The absence of localized displacements suggests that the deformation is spread in the whole frictional part of the crust. Short-term and anthropic signals affect PS data, and they largely overwhelm the tectonic one, not allowing for a coherent assessment of the interseismic trends of the deformation.

A preliminary rheological profile is proposed to explore the geodynamic implications of a thick frictional layer in the GP crust.

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# Geological, seismological and geodetic evidence of recent deformation along the Alfeo-Etna Fault System (western Ionian Sea)

Monaco C.*[1-2-3], Barreca G.[1-2], Bruno V.[3], De Guidi G.[1-2], Ferlito C.[1-3], Gambino S.[1], Gutscher M.-A.[4], Gross F.[5-6], Mattia M.[3] & Scarfì L.[3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] INGV, Osservatorio Etneo, Catania. [4] Geo-Ocean, Univ Brest, CNRS, Ifremer, Plouzané (France). [5] Institute of Geosciences, Kiel University (Germany). [6] Center for Ocean and Society, Kiel University (Germany).

*Corresponding author e-mail:* cmonaco@unict.it

*Keywords:* earthquakes and faulting, seismic reflection data, GPS data.

Morpho-structural and seismological data, seismic profiles and bathymetric maps suggest that the Alfeo-Etna Fault System (western Ionian Sea) is active. This is a large shear zone that connects the southeastern slope of Mt. Etna with the Alfeo sea mount (Polonia et al., 2016; the North Alfeo Fault, Gutscher et al., 2016). In particular, the NW-SE trending dextral shear zone of the Alfeo-Etna Fault System turns to N-S direction near the Ionian coastline, where the extensional Timpe Fault System is located. In turn, NW-SE trending right-lateral strike-slip faults connect the Timpe Fault System with the upper slope of the volcano, where the eruptive activity mainly occurs along N-S to NE-SW trending fissures. Morpho-structural analysis, together with geodetic and seismological data, suggest that similar transtensional features characterize the shear zone both on the eastern flank of the volcano and in the Ionian offshore (Barreca et al., 2018; Gambino et al., 2022). Offshore deformation is related to ~NNW–SSE horizontal P-axes and local ~E-W trending T-axes and caused seismic events mostly characterized by magnitude between 1 and 4 and hypocentral depth between 10 and 25 km. This is confirmed by the sequence that has affected this sector of Ionian Sea since November 2021, culminated on 15 April 2022 with a M=4.2 earthquake, located about 39 km of distance off the coast between Catania and Siracusa, at a depth of 30 km. The occurrence of this earthquake suggests the necessity of a better evaluation of the seismic hazard of the area.

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Gambino S., Barreca G., Bruno V., De Guidi G., Ferlito C., Gross F., Mattia M., Scarfì L. & Monaco C. (2022) - Transtension at the Northern Termination of the Alfeo-Etna Fault System (Western Ionian Sea, Italy): Seismotectonic Implications and Relation with Mt. Etna Volcanism. Geosciences, 12, 128. https://doi.org/10.3390/geosciences12030128.

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# Seismic deformation styles of the Calabrian subduction zone (South Italy) inferred from waveform inversion focal mechanism

Orecchio B., Presti D., Scolaro S.* & Totaro C.

Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina.

*Corresponding author e-mail:* silscolaro@unime.it

*Keywords:* focal mechanisms, subduction interface, Calabrian Arc region.

By analyzing waveform inversion focal mechanisms of earthquakes that occurred in the last decades in the Calabrian Arc region, we propose the first attempt to distinguish between the earthquakes and related styles of deformation occurring in the upper plate (i.e., overriding tectonic unit located above the subduction interface) and those in the lower plate (i.e., the shallower portion of the subducting plate, below the subduction interface). The Calabrian Arc region is the most seismic area of Italy according to historical catalogs, with nine earthquakes of magnitude larger than 6.5 occurred since 1600, and the only where active subduction can be still found along the Nubia-Eurasia convergent margin. We focused our analysis on earthquakes shallower than 40 km and, in order to reduce the effects of very local scale processes, with magnitude 4.0 and larger. Hypocenters of the individual earthquakes with their uncertainties have been compared with location and geometry of the Calabrian Subduction Interface (CSI) reconstructed by previous investigators on the basis of seismic reflection lines, seismicity and tomographies, with the purpose of associating the individual earthquakes focal mechanisms to the shallower part of the Ionian subducting plate (lower plate) or to the Tyrrhenian overriding plate (upper plate). By integrating focal mechanisms available from literature and catalogs with those properly estimated in this study we obtained a dataset of 31 focal mechanism solutions. Considering the focal depth of each earthquake and the CSI depth in the relative epicentral area, 30 FMs show an evident separation between the western earthquakes of the Tyrrhenian Sea and mainland Calabria occurring in the upper plate domain (17 earthquakes), and the eastern ones of the Calabria Ionian shore and relative offshore occurring in the lower plate domain (13 earthquakes). Only one of the selected earthquakes could not be univocally associated to one of the two domains (lower or upper plate). The focal mechanism distribution highlights clear extension in the Tyrrhenian overriding plate with opening direction trending roughly perpendicular to the Calabrian Arc mountain chain, while seismic faulting detected in the lower plate indicates marked heterogeneity with prevailing compressional features. The different faulting regimes described by our data, including the ones of the most heterogeneous sector, well correlate with the complex local kinematics depicted by GPS velocity field and strain-rate reported in the literature.

# Earthquake Rate Model from a Spatially Smoothed Seismicity of a New High-Detailed Catalog for PSHA purposes in central Eastern Italy

Pandolfi C.*[1-2], Taroni M.[3], de Nardis R.[1-2], Lavecchia G.[1-2] & Akinci A.[3]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] INGV, Roma.

*Corresponding author e-mail:* claudia.pandolfi@unich.it

*Keywords:* PSHA, smoothed seismicity, central Eastern Italy.

In any probabilistic seismic hazard analysis (PSHA), the computation of earthquake forecasting models is a fundamental step. A widely used approach is the smoothed seismicity, which uses seismic catalogs to produce earthquake forecasts in time, space, and magnitude. Early smoothed seismicity models, called fixed smoothing, used spatially uniform smoothing parameters, such that the kernels were invariant to spatial variations in seismicity rate. However, recently developed adaptive smoothing methods spatially adapt the smoothing parameters according to the earthquake density. A new approach described by Taroni & Akinci (2021) gives the possibility of using a complete (i.e., not declustered) catalog to include aftershocks and foreshocks in the spatial smoothing. This study implemented the fixed and adaptive approach using a declustered catalog and a complete one. The added value of our work is the kinematic division of the catalog to determine the contribution of both the extensional and the compressional domains of central Eastern Italy in the smoothing approach individually. For an accurate selection of seismicity, we used a new high detailed catalog collected by ReSIICO (Rete Sismometrica Integrata dell'Italia Centro-Orientale). This database contains events for the time window 2009–2017 and covers the area of central Eastern Italy. It was used to perform a detailed analysis of multi-layered crust-scale seismogenic deformation thanks to its quality in location. In the first step, we used seven SW-NE striking crustal serial sections with a 20-km-semi-width to select with high-detail the seismicity related to the extensional seismogenic layer and the seismicity related to the compressional one. In this way, we created two catalogs, one for the extensional domain with 167381 events with ML from 0 to 5.8 and another for compression with 5406 events from 0 to 4.8 ML. We then analyzed the magnitude of completeness, Mc, of both catalogs, removing the events below the Mc, and declustered the catalogs by evaluating both the Reasenberg and the Gardner & Knopoff approach. Finally, we performed the fixed and adaptive smoothed approaches with a spatial regular grid of 0.1°x0.1° adopting both fixed and variable sigma of the Gaussian kernel. We repeated all the processes with complete catalogs to incorporate aftershocks and foreshocks in the computation following the new approach proposed in Taroni and Akinci (2021). We also presented these forecasting models in the multipoint model of Openquake, generating the final PSHA maps in central Eastern Italy for 2% and 10% of probability in 50 years.

Taroni M. & Akinci A. (2021) - A New Smoothed Seismicity Approach to Include Aftershocks and Foreshocks in Spatial Earthquake Forecasting: Application to the Global Mw ≥ 5.5 Seismicity. Appl. Sci., 11, 10899.

# Geophysical Modeling in Seismotectonic Analysis

Paoletti V.*[1], Fedi M.[1], Florio G.[1], Bruno P.P.G.[1], Nappi R.[2] & Cella F.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] INGV, Osservatorio Vesuviano, Napoli. [3] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* paoletti@unina.it

*Keywords:* gravity imaging, multiscale derivative analysis.

The integration of surface geological investigations with geophysical techniques is useful to characterize systems of active faults, whose deep anatomy is often complex. Geophysical methods can yield important information on the underground geometry of rupture planes.

We give an overview of how an integrated analysis of geo-structural, seismological and gravimetric data can allow the identification and geometrical description of faults with associated density contrast both at the surface and at depth. At the surface, we accomplish this task by a Multiscale Derivative Analysis (MDA) of the Bouguer anomaly map and by the integration of the MDA maps with the epicentral distribution and all the available geological information. The characterization of fault structures at depth is instead performed by the combination of the Depth from Extreme Points (DEXP) gravity imaging method with the hypocentral sections. Further structural insights can be derived by integrating the information from gravity data and active seismic experiments, with the latter filling possible gaps related to gravity data resolution.

We applied our multi-parametric approaches to different seismically active regions, such as the areas of Paganica hit in 2009 and Amatrice-Visso-Norcia hit in 2016-2017 (Central Apennines), and the area of San Giuliano di Puglia (Southern Italy), struck by a moderate earthquake in October 2002.

# A multi-scale approach to the potential recent activity of the Stradella fault (Emilia Arc, northern Italy)

Pedicini M.*[1], Tibaldi A.[1-2], De Nardis R.[3-2], Torrese P.[4-2], Bressan S.[1], Talone D.[3-2], Bonali F.L.[1-2], Corti N.[1], Russo E.[1-2] & Lavecchia G.[3-2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali. [3] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [4] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* m.pedicini@campus.unimib.it

*Keywords:* recent faulting, Emilia Arc, structural-geophysical surveys.

The frontal thrusts and folds of the Northern Apennines -Italy- are mostly covered by the thick pile of Plio-Pleistocene deposits of the Po Plain. Some of these structures, mainly active during the Pliocene, show evidence of Quaternary activity, thus posing the need for an accurate seismic hazard reassessment due to the widespread presence of house settlements, industries and lifeline infrastructures. Here we propose a multidisciplinary study of a fault with poor evidence despite its importance for the seismogenic potential. The Broni-Sarmato structure is an 18 km-long outcropping section of the north-verging Stradella Thrust, located 50 km south of Milan, along the pede-Apennine thrust front (PTF) of the Emilia Arc (Boccaletti et al., 1985).

We performed morphostructural, geophysical and seismological analyses to evaluate the recent activity of the Broni-Sarmato Fault and to assess its compatibility with the Emilia Arc deformation field. Morphostructural mapping was performed through the analysis of aerial photos, field surveys, GPS and Unmanned Aerial Vehicles (UAVs) surveys. Three Electrical Resistivity Tomography (ERT) profiles were acquired in a direction orthogonal to the Broni-Sarmato fault scarp. Seismotectonic and earthquake data analyses were performed for the whole Emilia Arc, integrating geological and seismological data from literature with new focal mechanisms.

Detailed field surveys highlight the presence of an 18 km-long E-W scarp, with cumulative surface throws between 6 and 23 m, locally characterized by the presence of a minor 0.55-3.85 m scarp at its feet. Both scarps offset Pleistocene-Holocene terraces and present a rectilinear trace in plan view, with some left- and right-stepping geometries, along with the presence of hanging valleys and triangular facets. ERT surveys suggest the presence of a wide zone of shallow deformation along the Broni-Sarmato scarp, which represents a preferential flow path for deep saline waters towards the surface. Horizontal interruption and vertical dislocation of a shallow high-resistivity layer suggest that the Broni-Sarmato fault produced shallow deformation. The instrumental seismicity evaluated in the 1985-2020 time interval, is characterized by small-to-moderate-sized earthquakes ($0.1 \leq ML \leq 4.9$) and a low seismicity rate. Earthquakes distribution identifies two distinct and independent seismogenic compressional volumes, both coherent with a NNE direction of regional compression.

Our study confirms the tectonic origin of the Broni-Sarmato scarp and possible faulting events of late Quaternary age. The investigated regional earthquakes distribution identifies two distinct and independent seismogenic compressional volumes: an uppermost one associable with the Stradella-Salsomaggiore thrust at depths between 5 and 12 km, and a lowermost one at depths between 20 and 30 km associable with the down-dip prosecution of the Emilia Basal Thrust, all coherent with a regional NNE-directed compression.

Boccaletti M., Coli M., Eva C., Ferrari G., Giglia G., Lazzarotto A., Merlanti F., Nicolich R., Papani G. & Postpischl D. (1985) - Considerations on the seismotectonics of the Northern Apennines. Tectonophysics, 117, 7-38.

# Enhanced microseismicity catalogue in the Southern Abruzzi area (Central Apennine, Italy) and seismotectonic implications

Romano M.A.*[1], Carbone L.[2], Cipressi G.M.[2], de Nardis R.[2-3], Vuan A.[1], Lavecchia G.[2-3], Peruzza L.[1] & Priolo E.[1]

[1] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS). [2] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [3] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* aromano@ogs.it

*Keywords:* microseismicity, Southern Abruzzi, active faults.

Southern Abruzzi is one of the Italian regions characterized by the highest seismic hazard, struck by four damaging earthquakes during the last 300 years (1706, $M_w$ 6.8; 1915, $M_w$ 7.0; 1933 $M_w$ 6.0; 1984, $M_w$ 5.9). A low level of background seismic activity and clustering characterize this area.

For about 30 months (from 27/5/2009 to 22/11/2011), the study area was monitored by a local and temporary seismic network (Romano et al., 2013), deployed soon after the 2009 L'Aquila earthquake, which occurred on the NW prolongation of the active normal fault system here existing.

The temporary network recorded continuous seismic data that were adequately integrated with those from permanent stations, and provided a catalogue of earthquakes the best constrained of which were used as templates to feed the matching phase algorithm PyMPA (Vuan et al., 2018). This technique sharply enhanced the starting catalogue completeness magnitude, detecting ten times the number of microearthquakes in the area.

All the new detected microearthquakes with $M_L \geq 0.2$ were manually analyzed and, whenever possible, relocated with the 1D velocity model computed for the study area by Romano et al. (2013).

Such an approach allowed to 1) enlighten some strengths and weaknesses of automatic and manual techniques of seismological data analysis, 2) associate the identified microearthquake clusters to well-known and outcropping normal faults, but also hypothesize the existence of active tectonic structures not yet recognized as seismogenic.

Romano M.A., de Nardis R., Garbin M., Peruzza L., Priolo E., Lavecchia G. & Romanelli M. (2013) - Temporary seismic monitoring of the Sulmona area (Abruzzo, Italy): quality study of microearthquake locations. Nat. Hazard Earth Sys, 13, 2727-2744.

Vuan A., Sugan M., Amati G. & Kato A. (2018) - Improving the Detection of Low-Magnitude Seismicity Preceding the Mw 6.3 L'Aquila Earthquake: Development of a Scalable Code Based on the Cross-Correlation of Template Earthquakes. BSSA, 108, 471-480.

# New seismic tomographic images in eastern Abruzzi (central Italy): inferences on the structural style of the Outer Thrust System

Talone D.*[1-2], de Nardis R.[1-2], Lavecchia G.[1-2] & De Siena L.[3]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti. [3] Institute of Geoscience, Johannes Gutenberg University, Mainz (Germany).

*Corresponding author e-mail:* donato.talone@unich.it

*Keywords:* seismic tomography, Central Italy.

The segment of the Outer Thrust System (OTS) that runs along the coastal area of the Abruzzi region in Italy is a matter of scientific debate due to its geometry, seismic activity, and deformation style. The low level of seismicity, the blind thrusting, and the poor quality of seismic lines do not lead to a consistent seismotectonic model. Here, a novel local-earthquake tomography integrated with geological cross-sections, seismicity patterns, and focal mechanisms allows us to infer, for the first time, the characteristics of the deformation style of the OTS. We used the code FMTOMO (Rawlinson & Sambridge, 2006) to invert 42176 P e 29045 S wave arrival times from 5712 earthquakes (2.0The P- (Vp) and S- (Vs) velocity models show broad low-velocity anomalies (Vp<5 km/s) in the upper crust, within the intra-Apennines extensional domain and, subordinately, at the hanging wall of the buried Abruzzi Basal Thrust. The middle-lower crust is dominated by a significant Vp inversion recognizable along several cross-sections having different orientations. The 3D Vp inversions correlate with the mapped trace of the Abruzzi thrust, constrained with morphotectonic data, geological maps, and cross-sections (Ferrarini et al., 2021). This result, verified by using specific spike tests, has important implications for the crust-scale geometry and deformation style. In fact, the tomographic images and the geological data highlight a crustal doubling of the Abruzzi thrust and allow us to reconstruct a regional 3D fault model in an area where seismological data and seismic lines do not permit identifying deep potentially-seismogenic structures. Moreover, these results provide valuable constraints on the structural style of the overall OTS, supporting a thick-skinned interpretation for the most external compressive front.

Ferrarini F., Arrowsmith J.R., Brozzetti F., de Nardis R., Cirillo D., Whipple K.X. & Lavecchia G. (2021) - Late Quaternary Tectonics along the Peri-Adriatic Sector of the Apenninic Chain (Central-Southern Italy): Inspecting Active Shortening through Topographic Relief and Fluvial Network Analyses. Lithosphere, 2021(1), 7866617.

Rawlinson N. & Sambridge M. (2006) - Seismic wavefront tracking in 3D heterogeneous media: applications with multiple data classes. Explt. Geophys., 37, 322-330.

# Frictional control on the base of the seismogenic zone: insights from the Apenninic basement, Central Italy

Volpe G.*[1], Pozzi G.[2], Carminati E.[1], Barchi M.R.[3], Scuderi M.M.[1], Tinti E.[1], Aldega L.[1], Marone C.[1-4] & Collettini C.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] INGV, Roma. [3] Dipartimento di Fisica e Geologia, Università di Perugia. [4] Department of Geoscience, Pennsylvania State University, University Park, PA (USA).

*Corresponding author e-mail:* giuseppe.volpe@uniroma1.it

*Keywords:* structural heterogeneities, basement, seismogenic regime.

Crustal seismicity is in general confined within the seismogenic layer, which is bounded, at depth, by processes related to the brittle-ductile transition (BDT) and in the shallow region by fault zone consolidation state. In the last 10-15 years, high resolution seismological and geodetic data have shown that faulting within the seismogenic layer occurs in a large variety of slip modes. Frictional and structural heterogeneities have been invoked to explain such differences in fault slip mode and behaviour. However, an integrated and comprehensive picture remains extremely challenging because of difficulties to properly characterize fault rocks at seismogenic depths. This is not the case of the active region of central-northern Apennines, where the integration of deep-borehole stratigraphy and seismic reflection profiles with high resolution seismological data show that the strongest seismic sequences are limited within the sedimentary cover (depth < 9-10 km), suggesting that the underlaying basement plays a key-role in dictating the lower boundary of the seismogenic zone.

Here we integrate structural data on exhumed outcrops of basement rocks with laboratory friction data to shed light on the mechanics of the Apenninic basement. Structural data highlight heterogeneous and pervasive deformation where foliated and phyllosilicate-rich rocks surround more competent quartz-rich lenses up to hundreds of meters in thickness. Phyllosilicate horizons deform predominantly by folding and foliation-parallel frictional sliding whereas quartz-rich lenses are characterized by brittle signatures represented by extensive fracturing and minor faulting. Laboratory experiments revealed that quartz-rich lithologies have relatively high friction, m ~ 0.51, velocity-strengthening to neutral behaviour, and elevated healing rates. On the contrary, phyllosilicate-rich (muscovite and chlorite) lithologies show low friction, 0.23 < m < 0.31, a marked velocity strengthening behaviour that increases with increasing sliding velocity and negligible rates of frictional healing.

Our integrated approach suggests that in the Apenninic basement, deformation occurs along shear zones distributed on thickness up-to several kilometers, where the frictionally stable, foliated, and phyllosilicate-rich horizons favour aseismic deformation and therefore confine the depth of major earthquake ruptures and the seismogenic zone. In the basement, continued aseismic deformation, can concentrate stress within and around the strong and potentially unstable quartz lenses, which may lead to minor earthquake, in particular following increment of shear strain rates.

# How details of faulting affect large scale properties of seismicity and tectonics

Zaccagnino D.*[1], Telesca L.[2] & Doglioni C.[1-3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ). [3] INGV, Roma.

*Corresponding author e-mail:* davide.zaccagnino@uniroma1.it

*Keywords:* scaling properties of seismicity, tectonic settings, earthquake triggering.

Since the dawn of the modern science of earthquakes, a clear split has risen among theoretical and statistical seismology and tectonics. Classical seismology explains what happens during a few seconds of fault slip following rock breakdown, with the consequent radiation of seismic waves, while statistical seismology describes how seismicity occurs in space and time. Even though they investigate the same subject, differences are so deep that a relationship among them can be drawn not without significant effort. Statistical seismology is mainly grounded on two fundamental laws, i.e., the Gutenberg–Richter law and the Omori–Utsu law, both characterized by a scaling behavior. In our model (Zaccagnino et al., 2022), we suggest that the brittle crust abides by a simple principle of optimization of the energy needed to achieve more stable configurations. This paradigm, ruling almost all the natural processes, can be used to put into contact coseismic dynamics with large-scale seismic processes and tectonics so far treated separately despite a flurry of evidence suggests the opposite (e.g., Schorlemmer et al., 2005; Leonard, 2010). Each perturbation within a fault interface has a probability of growing an earthquake or not, depending on disorder within the fault zone and the energy accumulated in the adjoining volumes, mainly controlling the evolution of seismic sequences. Moreover, it implies that a relationship between fracturing regimes, "efficiency" of the seismic process, duration of the seismic sequences and geodynamic setting exists, with outstanding potential impact on seismic hazard. Our model also suggests that the parameter describing how the number of earthquakes decreases after a major seismic event, p, is positively correlated to the exponent of the frequency-size distribution of seismicity, b, according to the formula $p \approx 0.6 + 0.65\ b$, which is compatible with observations.

Leonard M. (2010) - Earthquake fault scaling: Self-consistent relating of rupture length, width, average displacement, and moment release. Bulletin of the Seismological Society of America, 100(5A), 1971-1988.

Schorlemmer D., Wiemer S. & Wyss M. (2005) - Variations in earthquake-size distribution across different stress regimes. Nature, 437(7058), 539-542.

Zaccagnino D., Telesca L. & Doglioni C. (2022) - Scaling properties of seismicity and faulting. Earth and Planetary Science Letters, 584, 117511.

# S32.

# From Source to Sink - the history of sediments inferred from the geological record


*Conveners & Chairpersons*

*Luigi Bruno (University of Modena and Reggio Emilia)*

*Bruno Campo (University of Bologna)*

*Claudio Pellegrini (ISMAR-CNR Bologna)*

*Cristina Stefani (University of Padova)*

*Marcello Tropeano (University of Bari)*

# The evolution of the southern Po delta between the Roman period and Late Antiquity in light of new geoarchaeological data

Abballe M.[1-2-3], Bortoluzzi D.[4], Cavalazzi M.[5-6], Dinelli E.[7] & Marabini S.*[4]

[1] Department of Archaeology, Ghent University (Belgium). [2] Dipartimento Culture e Civiltà, Università di Verona. [3] Istituto di Scienze dell'Atmosfera e del Clima, CNR, Roma. [4] Independent researcher. [5] Dipartimento di Storia Culture Civiltà, Università di Bologna. [6] Department of Classics, University of Michigan, Ann Arbor, MI (USA). [7] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* stemarabini@libero.it

*Keywords:* stratigraphy, geoarchaeology, geochemistry.

Numerous studies have attempted to reconstruct the palaeogeographic evolution of the southern Po delta in the Late Holocene, thanks to a combination of various methods, including geology, geoarchaeology and remote sensing (Bruno et al., 2017; Greggio et al., 2018). At the same time, it is much more complex to reconstruct the relationship of the Apennine rivers with the Po River, mainly because of the thick alluvial sedimentation connected with the reclamation of large parts of the Romagna plain.

About this, an integrated approach between geology and archaeology can be extremely helpful to investigate this crucial area, important from both a historical and archaeological point of view due to the presence of the city of Ravenna, located in the southernmost part of the delta. This city had a central role already in Roman times when it hosted the Adriatic fleet in the nearby Classe and then became even more important in the Mediterranean scene from 402 CE, firstly as the capital of the Western Roman Empire and later of the Byzantine Exarchate.

Indeed, although it is currently impossible to prove a direct physical relationship between the river Po and the city of Ravenna in Roman times, the connection was certainly ensured through the Fossa Augusta reported by Pliny the Elder, a probable artificial canal resulting from the arrangement of endo lagoon routes. Later one, the Badareno/Padoreno, a new and more easterly channel, most likely replaced the Fossa between Late Antiquity and the 8th century (Bortoluzzi & Cavalazzi, 2022). This new watercourse was likely a way to adapt to the new, more southerly course of the Po known as Primaro. Its existence caused coastal progression and sedimentary accretion, physically interrupting and/or determining the silting up of the Augustan canal.

In this regard, two cores carried out respectively near the archaeological site of Butrium, to the north of Ravenna, and within the so-called centuriation of Bagnacavallo, in association with targeted absolute dating and geochemical analyses, seem to shed some light on the transformations that occurred in the southern Po delta between the Roman period and Late Antiquity. Firstly, they bear witness to a crucial palaeogeographical change in the area to the north of Ravenna as early as the 2nd-4th centuries CE, so previously compared to what is thought today. Secondly, they attest to consistent sedimentary growth inland before the 5th-6th centuries CE. Together, these data open up the possibility of better detailing the peculiar palaeogeographical evolution of this portion of the Po plain and its function as a crucial catchment area for the sediments of the Po and the Apennine rivers during historical times.

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Bruno L., Bohacs K.M., Campo B., Drexler T.M., Rossi V., Sammartino I, Scarponi D., Hong W. & Amorosi A. (2017) - Early Holocene Transgressive Palaeogeography in the Po Coastal Plain (Northern Italy). Sedimentology, 64(7), 1792-1816.

Greggio N, Giambastiani B.M.S., Campo B., Dinelli E. & Amorosi A. (2018) - Sediment Composition, Provenance, and Holocene Paleoenvironmental Evolution of the Southern Po River Coastal Plain (Italy). Geological Journal, 53(3), 914-28. https://doi.org/10.1002/gj.2934.

# Sediment routing systems and their stratigraphic record

Amorosi A.*

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* alessandro.amorosi@unibo.it

*Keywords:* source-to-sink, sequence stratigraphy, Quaternary.

Linking onshore and offshore segments, from river catchments via coastal plain and shelves to the deep oceans, is essential to the evaluation of sediment routing systems (SRSs). The fate of sediment from source to sink is reconstructed through quantification of sediment generation, transfer, storage, and redistribution on a variety of timescales, with input from experimental, numerical, and field studies.

Quantitative geomorphology is an effective approach to assess autogenic control on upstream catchment physiography and to evaluate the interplay between tectonics and climate change. In proximal segments of SRSs, source-to-sink analysis aims to quantify the rates of bedrock weathering, soil production and sediment transport through characterization of landslide sediment supply to river channels and estimation of channel/hillslope processes. Fluxes and fate of river-derived sediments to the deep sea are controlled by a variety of processes that take place in the transfer zone, including modification of sediment fluxes in distributary channel networks, patterns of delta upbuilding, relations between longshore vs cross-shelf transport, and shelf margin wedge accretion.

Linking terrestrial denudation to marine deposition is especially effective for the last sea-level cycle and, in particular, for Holocene SRSs, where antecedent catchment is preserved and quantitative sequence-stratigraphic analysis can confidently be assessed. On the other hand, modern sediment yield, especially in watersheds that have undergone substantial anthropogenic modifications, can be a poor indicator of long-term delivery rates. Reconstructing the Earth's sediment cycle during the Anthropocene requires additional evaluation of human drivers of environmental change and terrestrial flux, such as increasing population, energy consumption and productivity.

All these notions will be illustrated through examples from the Po-Adriatic SRS and elsewhere. A basin-scale model of provenance and sediment flux will be shown based on compositional fingerprints of 50 fluvial systems and their comparison to coastal, shelf and deep-marine sediments. The geochemical signature of Adriatic shelf muds reflects the cumulative contribution of unique catchment lithologies from multiple source regions (Alps, Apennines, Dinarides) that provide onshore to offshore tracers. Geochemical signals can be traced downstream as long as 1000 km, from the Alpine zone of sediment production to the area of final deposition, offshore Apulia. Sediment yield calculations and compositional features at entry points reveal prevailing longitudinal dispersion linked to the general cyclonic, counter-clockwise Adriatic circulation associated with conspicuous detrital input from transversal pathways.

# Coralligenous carbonate production through a multiscale approach: the case study of the CRESCIBLUREEF project (Ionian Sea, Italy)

Bracchi V.A.*[1-2], Varzi A.G.[1], Savini A.[1-2], Bazzicalupo P.[1], Fallati L.[1], Rosso A.[2-3], Sanfilippo R.[2-3], Guido A.[4], Leonardi R.[3], Negri M.P.[1] & Basso D.[1-2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [4] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* valentina.bracchi@unimib.it

*Keywords:* coralligenous, carbonate production, temperate.

In the Mediterranean Sea, crustose red algae form endemic reefs known as Coralligenous (C). These reefs modify the submarine environment by affecting the evolution of the submerged landforms, although their role is still far from being defined. C contributes to the increase of carbonate volume along the whole temperate shelf, acting as an autochthonous process of sediment production and accumulation, halfway between siliciclastic-carbonate mixed and pure-carbonate realm in temperate shelf.

In the framework of the FISR project CRESCIBLUREEF, which aims at exploring the components, growth-rate and accretion style of the Mediterranean C bioconstructions, we collected remote and direct data in an area offshore Marzamemi (Ionian Sea, Italy) covering about 17 km$^2$ of the seafloor between 20 and 100 m of water depth (wd).

We approached the quantification of C bioconstructions following a multi-scale approach.

Remote dataset includes bathymetric, backscattering and shallow seismo-stratigraphic data. These data were used to produce a high-resolution morpho-bathymetric map of the study area. We performed geomorphometric analyses to classify different C habitats, calculate their extents, and identify discrete C build-ups whether possible, together with their main morphometric features.

Direct data include ROV videos, which were used to ground-truth the acoustic dataset and to evaluate C abundance when mosaicked with other habitats; direct sampling (two build-ups) have been used for fine scale quantification of the components *via* photogrammetry and computed tomography (CT).

C forms hybrid banks (C *sensu stricto*) between 36 and 42 m wd, covering an area of 0.91 km$^2$. At shallower depth (30-36 m wd), C build-ups are mosaicked with *Posidonia oceanica*, covering a total area of 0.81 km$^2$. Below 42 m wd, C still forms discrete build-ups but sparse on detritic bottom (42-80 m wd, 0.77 km$^2$), and further on muddy bottom (80-100 m wd, 365 m$^2$).

Photogrammetry investigation of the two build-ups confirms that C is mostly made up by crustose coralline algae on its surface, whereas CT shows that the inner structure is made by coralline algae (70%) together with autochthonous micrite that strengthen the primary framework due to its syndepositional cementation (10% of the volume).

C as hybrid banks have a mean height of 0.73 m, an area of 0.91 km$^2$ and a volume of 664 m$^3$, which means 465 m$^3$ of carbonate by coralline algae.

C on muddy bottom is characterized by discrete build-ups, a mean height of 1.29 m and a cover of 365 m$^2$. Thus, the calculated volume is about 471 m$^3$, among which 329 of carbonate made by crustose algae.

These results increase the knowledge of the carbonate production along temperate shelves, giving important insights for past environments, as well as quantify a threatened habitat for a sustainable management of present-day offshore biotic resources.

# Tectono-stratigraphic evolution and transpressive tectonics of the Apulian foreland (Northern Ionian Sea) between two converging orogens

Chizzini N.*[1], Artoni A.[1], Torelli L.[1], Basso J.[1], Polonia A.[2] & Gasperini L.[2]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Istituto di Scienze Marine, CNR, Bologna.

*Corresponding author e-mail:* nicolo.chizzini@unipr.it

*Keywords:* Apulian foreland, calabrian accretionary wedge, transpressive tectonics.

In the Northern Ionian Sea, the Calabrian Accretionary Wedge (CAW) is facing directly the westward subducting Apula Plate, a continental microplate covered by about 8 kms of Mesozoic and Tertiary carbonates (Nicolai & Gambini, 2007; Del Ben et al., 2010; Volpi et al., 2017; Mila et al., 2017). Deformation patterns of this microplate, inferred from analysis of geological/geophysical data include: 1) flexure/bending, under the load of CAW; 2) buckling, in response to compression of the surrounding orogens (southern Apennines, Hellenides); and 3) slab roll-back and eastward retreat. In this work, a reprocessed dataset of five seismic reflection profiles is used to determine the interplay between these processes during the progressive advancement of the CAWsince Pliocene times and the tectonic-sedimentary evolution of this study area, characterized by the lack of exploration wells. Seismic interpretation allows to identify four main domains: the highly tectonized CAW; the Bradano foredeep basin filled by a Upper Pliocene-Holocene subhorizontal succession; the massive carbonate succession of the Apulian Platform showing reef and carbonate platform margin facies; the layered succession of the Apulian Platform characterized by ‘‘intra-platform’’ facies in the easternmost portion of the area. Three main regional unconformities were recognized: i) the Messinian unconformity, related to a regional erosion process on the exposed Mesozoic Apulian Platform, cut by normal faults in the foreland and by thrust in the CAW; ii) the angular and erosive middle Pliocene Unconformity truncates the Lower Pliocene reflectors and is affected by normal faults in the foreland and by compressive tectonics in the CAW; iii) a Jurassic/Cretaceous unconformity in the foreland is marked by Cretaceous reflectors clearly onlapping the Jurassic carbonate platform. The CAW is characterized by compressive tectonics with several fore-thrusts forming a leading imbricate fan system. Whereas the Apulian platform, affected by active extensional tectonics driven by flexural bending since Lower Pliocene (Calamita et al., 2003; Volpi et al., 2017; Maesano et al., 2020; Cicala et al., 2021) that probably reactivated old normal faults related to the Permian-Triassic rifting stage, results to be affected by transpressive and positive inversion tectonics which suggest that the Apulia Plate is already part of the Southern Apennines/Calabrian/Hellenic belts. According to these observations, compressive tectonics affecting the Apulia Plate is interpreted as related to shortening processes and oblique convergence of both the CAW and Hellenic wedges whose interference plays an important role in 1) defining the Tertiary to recent tectonic-stratigraphic evolution of the Apulia Plate and 2) the occurrence of transpressive tectonics inside the Apulia Plate.

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# New integrated geochemical and petrographic constraints to paleo-thermal and paleo-environmental reconstructions from organic matter dispersed in the Early Toarcian organic-rich shales of the Paris Basin (France)

Corrado S.*[1], Vergara Sassarini N.A.[1-2-3], Schito A.[4], Michel P.[2] & Gasparrini M.[2-5]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] IFP Energies nouvelles, Paris (France). [3] Sorbonne Université. [4] School of Geosciences, University of Aberdeen (UK). [5] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* sveva.corrado@uniroma3.it

*Keywords:* Paris basin, Toarcian black shales, thermal maturity.

An original geochemical and petrographic dataset on organic matter dispersed in the Lower Toarcian of the Paris Basin is presented to characterize its composition, HC potential and thermal maturity through Rock-Eval 6 and vitrinite reflectance investigation. The aim of the work is to provide new constraints to the paleo-thermal and paleo-environmental evolution of the basin. Data derive from the analysis of forty-six specimen from eight wells aligned along a regional E-W transect across the basin, moving from the main depocenter to its eastern margin.

Kerogen type ranges between II along the eastern basin margin, to III and mixed II-III moving toward the main depocenter (west), showing slight differences along the transect (109<HI<719 and 9<OI<47) and Tmax between 415°C and 438°C, indicating immature to middle mature stages of HC generation, moving from the basin margin to the main depocenter. Data along the present-day basin margin support the occurrence of moderate exhumation (minimum 1.5 km), with the geological contacts between the Mesozoic basin fill and the Ardennes Massif corresponding to an erosional contact in agreement with reconstructions from recently performed burial history and thermo-chronological datasets. Data from two wells, located about 50 km to the East of the basin margin, show thermal maturity compatible with higher exhumation amount (minimum 1 km) compared with recent models. In conclusion, the new dataset confirms, at a regional scale, recent 3D sedimentological and burial-thermal models, but provides further constraints to detail the regional models in future reconstructions for such a widely explored area.

# Sedimentary features of Quaternary gravelly beachface deposits in the Metaponto area (southern Italy)

De Giorgio V.*, Sabato L. & Tropeano M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* vincenzo.degiorgio@uniba.it

*Keywords:* gravelly beachface deposits.

The hinterland of the Taranto Gulf in Basilicata (southern Italy) is mainly characterized by the middle and upper Quaternary marine terraced deposits of the Metaponto area. These wedge-shaped bodies comprise coarse-grained coastal deposits (Massari & Parea, 1988), developed with complex cyclical architectures in response to the interference between uplift and sea-level changes of different orders. These deposits spark a twofold interest: on the one hand, they represent one of the best exposed examples of depositional marine terraces in the world; on the other hand, they offer a unique opportunity to study coarse-grained coastal deposits both along dip and strike.

This abstract deals with the last topic, and in particular the description of beachface deposits, well represented in the area by an alternance of up to 20 cm-thick gravelly and sandy lenses organized in up to 1 m-thick sigmoidal gravelly bodies. Gravel shows a good clasts selection in both shape and size; slope-angle of clinoforms passes from 5° in the upper beachface (close to the rollover point) up to 30° along the lower beachface. As in the facies analysis performed by Bluck (1967), four main facies characterize the observed deposits: discoidal cobbles (*large-disc zone* of Bluck), representing the high-storm berm in the landward upper beachface; imbricated discoidal pebbles (*imbricate-disc zone* of Bluck), representing ordinary berms and cusps in the seaward upper beachface; matrix-supported and clast-supported gravels made up of spherical or subspherical pebbles lacking sedimentary structures (*infill zone* of Bluck), representing the lower beachface; laminated sandy lenses (*sand run* of Bluck), which mark the transition from the *imbricate-disc zone* to the *infill zone*.

Facies features and their arrangement are the result of physical processes triggered by wave motion. Discoidal clasts tend to be transported preferentially in suspension and resettled in the upper portion of the beach; spheroidal clasts tend to avalanche along slope accumulating at the foot of the beachface, High energy processes characterizing the beachface allow the removal of finer material consisting of small gravel and sand, sometimes leaving a well-cleaned deposit. However, as the transport takes place on a gravelly surface that acts as a sieve, this finer material is often trapped between pebbles and cobbles.

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# Composition of core sands from the central Po Plain (northern Italy). Implication for sediment provenance

Demurtas L. *, Bruno L., Fontana D. & Lugli S.

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* luca.demurtas@unimore.it

*Keywords:* fluvial-sand composition, sediment provenance, Pleistocene-Holocene.

The Po River, flowing from the Western Alps to the Adriatic Sea, interacts with a dense network of transverse tributaries draining catchments with distinct lithotypes. The northern tributaries drain the Central and Southern Alps with extensive outcrops of carbonate (limestone and dolostone), plutonic-volcanic, and metamorphic rocks. The Southern tributaries drain a sector of the Northern Apennines dominated by limestones and mudstone. Based on stratigraphic, sedimentological and petrographic analyses of two cores drilled along the Po River (core SBP) and 20 km southward (core MDL), we reconstructed the evolution of the fluvial network of the central Po Plain during the Mid-Late Pleistocene and Holocene.

The cored succession has been subdivided in three stratigraphic intervals composed of fluvial-channel sands and subordinated overbank muds. In the lower interval, observed only in core MDL and dated to ca. 500-250 ky BP, sand bodies are up to 13 m-thick and include etherolithic pebbles and cobbles. Fluvial-channel bodies of the intermediate interval, dated to ca. 250-10 ky BP, are thicker than 9 m and mainly composed of coarse sand. The upper interval, observed only in core MDL and $^{14}C$ dated to the Holocene, has a relatively higher percentage of mud with fluvial-channel bodies, 3-5 m thick, composed of fine-medium sand.

Sands from these stratigraphic intervals correspond to three petrofacies, which we compared with the composition of modern river sands. Petrofacies 1, characterized by high content in limestone and dolostone grains, frequent volcanic lithics and low content in metamorphic lithics, shows affinity to Mincio and Adige rivers draining the Central-Southern Alps; Petrofacies 2, characterized by very high content of quartz-feldspar and metamorphic lithics, and low content of carbonates, shows affinity with the modern Po-River close to the confluence with Oglio and Mincio rivers; Petrofacies 3 displays high content in sedimentary lithics, and low content in quartz and feldspar, compositional characters typical of Apennine rivers Secchia and Panaro. These variations in sand composition are interpreted to reflect significant reorganizations of the channel network during the last 500 ky. Between ca 500 and 250 ky BP, the Po River flowed south of core MDL (more than 20 km south of its modern location). After 250 ky BP, the Po River shifted northward and wandered in a 20 km-wide area south of its present position. A further northward shifting is recorded during the Holocene, when Apennine rivers flowed through the area of core MDL. Overall, the Mid-Late Pleistocene and Holocene succession of the central Po Plain records a progressive northward migration of the Po River.

# Multiparametric calibration of the Erosion Potential Method on petrographic, mineralogical and geochemical parameters

Dominici R.[1], Donato P.[1], Imbrogno G.[2], Lirer S.[3], Tenuta M.*[3] & De Rosa R.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] E3 (Environment, Earth, Engineering), s.c. - spin-off Università della Calabria, Rende (CS). [3] Dipartimento di Scienze Ingegneristiche, Università «Guglielmo Marconi», Roma.

*Corresponding author e-mail:* mariano.tenuta@gmail.com

*Keywords:* EPM model, Ofanto river, multiparametric calibration.

The Erosion Potential Method (EPM model) estimates the average soil loss through the integration of multiple weather-climatic, erodibility and physical processes, but without taking into account the characteristics of the products, the sediments, which represent the final result of the interaction of the variables. On the contrary, the provenance studies are based on the characteristics of the products trying to identify the rock that was the source without however quantifying the processes that regulated its generation, transport and dispersion.

These aspects are even more pronounced in the Ofanto basin where, in samples of river sand, the volcanic component is significantly overestimated compared to the sedimentary and carbonate components.

For these reasons, the work proposes an innovative approach in the calibration of the Erosion Potential Method and in particular of the Y coefficient (coefficients of rock and soil resistance to erosion), based on the products and obtained through the integration between the EPM model and the petrographic, mineralogical and geochemical characteristics of sediments.

The "squared cell" method made it possible to obtain the spatial distribution of the solid volume (W - $m^3$ / year) produced annually by the basin. With the same approach, sediment productions were estimated for each lithology and for each drainage sub-basins .

Using a probabilistic approach, the combinations of values of attribute Y were identified which would allow to obtain the same ratios between the volumes produced by the lithologies and the results of the modal analysis carried out on sand samples taken in the same drainage sub-basins.

The lithologies capable of producing two components (e.g., sedimentary and volcanic), were considered individually, while the fine sedimentary component (clays, marls, silt, ...) was, after calibration, multiplied by a factor of reduction, depending on the presence of clays, marls, silts, etc. in the sand samples analyzed.

Finally, by means of the weighted average between the different Y values obtained for the different subbasins, the final Y value was obtained.

The isotopic study, on the other hand, made it possible to discriminate a double volcanic source in the sands of the Ofanto river: a first of a Campanian nature and a second of a Vulturian nature.

The calibration process obtained from the comparison with the petrographic - mineralogical and geochemical composition of the sand transported by the Ofanto river made it possible to draw up a map on the areas with the highest production of sand and gravel in the basin. These areas are of strategic importance as the sediments produced at the hydrographic basin scale represent the main source of sediment for a coastal physiographic unit.

# Time-scale implementation of the EPM model: Implications in the Ofanto basin and in the physiographic unit connected to it

Dominici R.[1], Donato P.[1], Imbrogno G.[2], Lirer S.[3], Tenuta M.*[3] & De Rosa R.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] E3 (Environment, Earth, Engineering), s.c. - spin-off Università della Calabria, Rende (CS). [3] Dipartimento di Scienze Ingegneristiche, Università «Guglielmo Marconi», Roma.

*Corresponding author e-mail:* mariano.tenuta@gmail.com

*Keywords:* EPM model, Ofanto river, dams.

The Erosion Potential Method (EPM model) is a model for qualifying the erosion severity and estimating the total annual sediment yield of a catchment. In this work we propose a further implementation of the EPM model on a time scale in order to be able to reconstruct the production of sediment in a specific time range. The results will be compared with the evolution of the correlated physiographic unit and over the same time period. The aim will be to identify the main causes of a possible sediment deficit.

The coefficient of land use (X-factor) represents the factor with the greatest influence in the temporal evolution of the model. In the first phase of the work, the data relating to the Corine Land Cover database (COoRdinate INformation on the Environment) for the years 1990, 2000, 2006, 2012 and 2018 were recovered. In addition, data for the same time span were obtained, also for the meteo-climatic (h and T) and morphological (γ) parameters.

The analysis of the temporal evolution of sediment production rates generally shows an increase in production between 1990 and 2018. The causes are linked to a low rate of anthropization of the basin and a simultaneous increase in the cultivated areas and those used for the cultivation of orchards, especially olive trees, and vineyards. These areas are characterized by a greater capacity to produce sediment than other areas such as those used for woodland or used for grazing.

However, the trend is in contrast with the evolution of the line of the stretch of coast influenced by the Ofanto basin. The physiographic unit in question is in fact affected, in various sections, by a progressive and constant retreat. The process is even more evident just near the mouth of the Ofanto river where the coast has had a retreat of over 300 m in about 30 years. For this reason, in the second phase of the study, the main dams present in the Ofanto basin were analyzed.

For each dam have been identified: (i) the starting year of commissioning, (ii) the area of the basin involved and (iii) an estimate of the potential impact on the production of total sediment, coarse sediment and on the specific particle size fraction capable of influencing the physiographic unit. The start-up of the San Pietro dam at the end of the 1950s and of the Locon and Conza dams at the beginning of the 1990s are matched by a strong increase in the erosion process along the entire physiographic unit.

Although the impacts of dams on sediment production and transport have been known for some time, the use of the EPM model implemented with the YES plug-in and further calibrated with petrographic and particle size observations would allow to estimate the areas of greatest impact on the production of sediment and consequently define the most suitable areas for the construction of a dam. The Epm model and its implementations also find potential in the implementation of VIA studies (environmental impact assessment) for the ability to assess the actual impact of the dam on the environment.

# Oligocene-Miocene ice volume variations in the Ross Sea, Antarctica: insight from a provenance study on core DSDP270 empowered by U-Pb dating, apatite geochemical signature and fission-track data

Olivetti V*.[1], Balestrieri M.L.[2], Zurli L.[3], Perotti M.[3], Pace D.[3], Chew D.[4], Cornamusini G.[3] & Zattin M.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze [3] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [4] Trinity College, Dublin (Ireland).

*Corresponding author e-mail:* valerio.olivetti@unipd.it

*Keywords:* provenance, UPb-AFT dating, Antarctica.

Provenance study of glaciomarine sediments in the Antarctica continental shelf provides key information on the evolution of the ice sheets through time, pivotal to any paleoclimatic reconstruction at regional and global scale. Provenance analyses have been mostly used to reconstruct Last Glacial Maximum ice volume (Licht & Hemming, 2017; Perotti et al., 2017), whereas its application to older sedimentary records in Antarctica is less common (e.g., Marschalek et al., 2021)

Here we present a multidisciplinary provenance study of the Oligocene to Miocene glaciomarine sediments drilled by the DSDP project in the 1970s (Leg 28, Site 270) in the Central High of Ross Sea. The study is based on U-Pb dating of detrital apatites and zircons, coupled with fission track dating and trace element and REE composition of apatite grains. We applied a recently conceived approach based on the geochemical composition of apatite and the categorization by a machine learning method to find indications on the lithology of the bedrock source, thus, helping to better discriminate the possible source areas.

A thick diamictite horizon is present in the uppermost Oligocene strata and it is interpreted as being deposited by a proximal grounded glacier. Our study points to a far source for the sediments composing the diamictite strata, likely located in southern West Antarctica. This implies that a well-developed continental-based Ice Sheet was already existing in the latest Oligocene. It was enlarged enough to carry sediments from southern West Antarctica into a shallow Central Ross Sea, till a latitude proximal to the Site 270.

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# On depositional processes governing fine-grained deposits: unlocking the Little Ice Age parasequence on the Adriatic shelf

Pellegrini C.*[1], Sammartino I.[1], Schieber J.[2], Rossi V.[3], Tesi T.[4], Paladini F.[1], Chiggiato J.[1], Schroeder K.[1], Asioli A.[1], Trincardi F.[5] & Amorosi A.[3]

[1] Istituto di Scienze Marine, CNR, Bologna. [2] Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, IN (USA). [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [4] Istituto di Scienze Polari, CNR, Venezia. [5] Dipartimento di Scienze del Sistema Terra e Tecnologie per l'Ambiente, CNR, Roma.

*Corresponding author e-mail:* claudio.pellegrini@bo.ismar.cnr.it

*Keywords:* river delta, depositional processes, organic carbon.

In source-to-sink systems, river-dominated coastal deposits accumulate large amounts of sediment (including land-derived Organic Carbon, OC) on the shelf because of their proximity to terrestrial catchments. The depositional processes recorded by shelf deposits, however, vary widely largely depending on the mode of delivery and deposition of organic and inorganic material to the sedimentary basin. We used seismic, sedimentological, paleontological, and geochemical data to investigate how the different depositional processes are recorded in terms of sedimentary structures, OC nature, sediment provenance, and benthic fauna assemblages (foraminifera and ostracods) along the 600-km-long Adriatic mud-wedge (Italy). We considered the modern Adriatic oceanographic regime to validate processes reconstructed from the sedimentary archive. In particular, we focused on the Little Ice Age parasequence (AD 1500-1850), which contains a continuum of genetically related fine-grained beds from river mouths to the deeper shelf that, at a first glance, may appear quite homogenous.

Our results reveal that strata within the LIA parasequence host km-wide beds that reflect the interplay between event-dominated river supply, energetic meteo-ocean conditions, and alongshore dispersion. The multidisciplinary approach applied at different scales of observations helped in: i) differentiating three main driving processes that controlled the deposition of crypto hyperpycnites, tempestites, and drift-related beds; and ii) understanding the relative timing of sediment transport before final burial that strongly promoted the loss of carbon by microbial degradation and oxygen exposure.

Overall, the depositional processes reconstructed acted as main drivers of the lateral heterogeneity of preserved sedimentary structures, faunal associations, and the ultimate nature of OC. Our findings imply that fine-grained systems characterized by high sedimentation rates do not necessarily reflect high terrestrial OC burial sites and a continuous record of the geological time, even at bedset scale, when sediments are redistributed by the oceanographic regime. The results have implications on the forcing conditions that ultimately control the location and nature of fine-grained beds in both modern and ancient systems.

# Messinian mudrocks of the Calcare di Base Formation (Catanzaro Basin, Calabria): implications for source-area provenance and palaeoweathering conditions

Perri F.*, Cipriani M., Guido A., Cianflone G. & Dominici R.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* francesco.perri@unical.it

*Keywords:* Calcare di Base, composition, weathering.

During the late Miocene, the Mediterranean region was affected by the Messinian Salinity Crisis (MSC) characterized by combination of tectonic processes (causing a reduction in the exchange of water between the Atlantic Ocean and the Mediterranean Sea) and paleoclimate conditions (a regional dry and warm/humid climate). The geochemistry and bulk mineralogy of mudrock samples of the Calcare di Base Formation (Catanzaro Basin, Calabria) were studied using X-Ray Florescence and X-Ray Diffraction techniques. The mineralogy was found to be essentially calcite and phyllosilicates, quartz and minor/trace feldspars, hematite and gypsum. The geochemistry reveals that the order of abundance of major oxides is Si>Fe>Al≥Ca>Mg>K>Ti≥Na>Mn≥P. Only two samples show higher values of Ca than the other oxides. The low kaolinite and feldspar amounts may indicate low-moderate degree of weathering processes. The variations of the chemical weathering processes were determined by several chemical indices (e.g., Chemical index of Alteration) characterized by low-medium values and thus suggesting weak-moderate source area(s) weathering conditions. The studied samples are derived from an environment in which non-steady-state weathering conditions prevailed and active tectonism allows erosion of all zones within weathering profiles (e.g., Perri et al., 2015). This trend indicates a paleoclimate characterized by persistent dry and warm/arid conditions alternating with relatively wet conditions. The Al-Zr-Ti plot suggests that the samples likely record a recycling effect from their basement rocks that are characterized by mainly felsic source such as the rocks composed the Sila Massif.

Perri F., Dominici R. & Critelli S. (2015) - Stratigraphy, composition and provenance of argillaceous marls from the Calcare di Base Formation, Rossano Basin (northeastern Calabria). Geological Magazine, 152, 193-209.

# Stratigraphic architecture of a late Quaternary incised-valley along the Adriatic coast (Chienti River, Marche Region, Italy)

Pierini M.*[1], Di Celma C.[1], Pierantoni P.P.[1], Negri A.[2], Amorosi A.[3], Di Martino A.[3] & Leoni M.[4]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [4] Agenzia Regionale per la Protezione Ambientale, Macerata.

*Corresponding author e-mail:* michela.pierini@unicam.it

*Keywords:* Quaternary, incised valley, Chienti River.

Late Quaternary incised valleys of Apennine rivers represent important transfer zones of the Po Plain–Adriatic sediment routing system (Amorosi et al., 2016) and their deposits contain valuable information about regional depositional processes and both climatic and sea-level changes. In order to understand the impact of late Quaternary sea-level changes along the southern coast of the Marche Region (eastern central Italy), we reconstructed the stratigraphic architecture of the Chienti River valley fill.

The study area extends for 5 km from the modern coastline, between the municipalities of Civitanova Marche and Porto Sant'Elpidio, and is classified as a polluted site of regional interest since 2001. The available dataset consists of about 500 well logs and recently acquired continuous cores that range in depth between 23 and 36 m, providing extremely high-density subsurface stratigraphic information beneath the modern alluvial and coastal plains of the Chienti River. The valley was incised into Calabrian clays (the marine Argille Azzurre formation) in response to the last glacial sea-level fall, when the river was an Apennine tributary of the Po River, and was infilled during the Last Glacial Maximum and the succeeding post-glacial sea-level rise by a sediment wedge up to about 25 m thick comprising a variety of alluvial and paludal deposits. A series of detailed transverse and longitudinal stratigraphic panels highlights the three-dimensional facies architecture of the valley fill and indicates that amalgamated fluvial-channel and floodplain facies associations dominate at proximal locations, whereas alternating fluvial-channel, floodplain, swamp, and beach deposits occur distally.

Improving our understanding of the subsurface stratigraphic architecture of the Chienti River incised-valley fill is important to achieve an evaluation of possible environmental response of this area to future climate-change scenarios and thus predict social and environmental consequences of future changes, and is a crucial requirement toward a successful three-dimensional representation of the aquifer systems of this contaminated site for successful environmental remediation.

Amorosi A., Maselli V. & Trincardi F. (2016) - Onshore to offshore anatomy of a late Quaternary source-to-sink system (Po Plain–Adriatic Sea, Italy). Earth-Science Reviews, 153, 212-237.

# The Middle Pleistocene fluvio-deltaic systems preserved at the margin of the Northern Apennines between Parma and Enza rivers (Po Valley – Northern Italy): a tectonically-controlled sink zone

Pinardi R.*[1], Artoni A.[1], Tinterri R.[1], Petrella E.[1] & Fornaciari A.[2]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma.
[2] Studio Geotech, Parma.

*Corresponding author e-mail:* riccardo.pinardi@studenti.unipr.it

*Keywords:* physical stratigraphy, Pleistocene fluvio-deltaic systems, tectonics and sedimentation.

During the last decades the growing demand for water in the Po Valley in Northern Italy has dictated the construction of many water wells for industrial and agricultural purposes. These wells provide basic stratigraphic information on the Quaternary units of the Po Plain and foothills of the Northern Appennines. Based on 95 of these wells, derived from public and private databases, drilled in an area of ~40 $km^2$ located SE of Parma, between the Parma and Enza rivers, this work aims to provide a renewed and detailed stratigraphic setting of the Pleistocene-Holocene synthems known in the study area as CMZ , AEI, AES. The physical distribution and the (likely) depositional environment of the sedimentary bodies, belonging to these synthems, were characterized accurately; thus, the dynamic development of the alluvial systems and the major tectonic structures present in the study area could be defined.

The available dataset allowed to reconstruct: 1) nine surface-subsurface stratigraphic-cross sections showing lateral and vertical distribution of Pleistocene-Holocene units; 2) two contour maps, one representing the base of CMZ synthem and one the base of AEI synthem; 3) four isopach/(facies) maps showing thicknesses of the four alluvial bodies recognized within the CMZ synthem. These reconstructions allow to identify a series of laterally shifting alluvial fans and fan delta that can be tentatively attributed to the Middle Pleistocene sinking zone of the (paleo-)Parma, (paleo-)Enza fluvial systems. Then, the above reconstructions revealed that the major tectonic lineaments known in the area (Pedeapenninic Thrust Front or Pieghe Emiliane) are here complicated by minor, 3-4 km long and arcuate anticlines-synclines pairs that still strongly control the sedimentation, depocenters and evolution of the alluvial fans and fan deltas recognized.

This work shows that, taking advantage of a well dataset for water supplies continuously updated, the characterization and geological record of a sink area can be progressively refined. Furthermore, considering that in this sink zone the conglomeratic and arenaceous bodies correspond to the aquifer horizons exploited for water supplies, the progressive refinements of the distribution and geometry of the alluvial fans and delta fans assume a practical and applicative value strictly linked to research and optimal use of water resources in the Po Valley.

# The fate of the Volturno delta (northern Campania, Italy) among geological history and human influence

Ruberti D.*, Buffardi C. & Vigliotti M.

Dipartimento di Ingegneria, Università della Campania "Luigi Vanvitelli", Aversa (CE).

*Corresponding author e-mail:* daniela.ruberti@unicampania.it

*Keywords:* Volturno delta plain, recent coastal evolution, Holocene stratigraphy.

The present geomorphology of the Volturno River delta system (northern Campania, southern Italy) is largely a product of complex, long-lived relationships between geological evolution and human impacts. This presentation describes the evolution of the alluvial and coastal plain from the Holocene to the present time. The study was based on stratigraphic well log data analysis, cartographic sources from the last 150 years, bathymetric data acquired in 1887 and in 1987 and compared to extract seafloor changes in the delta offshore (Ruberti et al., 2022). The basis for the Holocene reconstruction was provided by the top of the Campania Grey Tuff (CGT) relief map, which evidences the incised valley excavation following the LGM sea level drop. The CGT is the product of a huge pyroclastic eruption of the Campi Flegrei volcanic district, occurred 39 ky BP, and thus represents both a major marker for the reconstruction of the subsurface stratigraphic record and a sturdy morphologic substrate engraved by river incision associated with the sea level fall that accompanied the last glacial period. The lowstand, transgressive and aggradation/highstand stacking of the Holocene facies were displayed. The present landscape appears largely inherited by the past MIS5 and LGM landscapes. A progressive increment of anthropic forcing took place after 2000 yr BP but the strongest modifications of the landscape occurred since the end of the XVII century. Until that time the landscape was largely covered by marshes and ponds. Human interventions started during the Spanish vice-Kingdom, at the end of the XVI century, when reclamation works were carried out with the aim to drain most of the marshy areas. The availability of reclaimed lands resulted in an intensive land transformation and the loss of most coastal wetland coupled with coastal erosion. Progradation of the delta ended during the early-middle XIX century. A peak of major alterations of the deltaic environment, and retreat of the coastline was attained between the 1960s and the 1990s. It is evident that the transformations of the landscape that have taken place over the last millennium are largely caused by anthropogenic impacts (i.e., reclamation, development of drainage network, land use changes). The sediment input of the river to the Tyrrhenian Sea sharply decreased, thus resulting in a dramatic change of the deltaic morphology and significant coastal land loss. The coastal zone, considered as a dissipative-type shoreline, evolved to an irreversible non-dissipative inshore profile characterized by mean erosional rates of 5 m/yr along the beaches and 24 m/yr on the delta mouth. The river delta changed from a cuspate, wave-dominate delta to arcuate and eventually delta-estuary type.

Ruberti D., Buffardi C., Sacchi M. & Vigliotti M. (2022) - The late Pleistocene-Holocene changing morphology of the Volturno delta and coast (northern Campania, Italy): Geological architecture and human influence. Quat. Int., 625, 14-28. https://doi.org/10.1016/j.quaint.2022.03.023.

# Sediment provenance and environmental changes during the Last Deglaciation in the Adriatic Sea

Sammartino I.*[1], Amorosi A.[2], Tesi T.[3], Langone L.[3], Pambianco C.[4], Asioli A.[1], Trincardi F.[5] & Pellegrini C.[1]

[1] Istituto di Scienze Marine, CNR, Roma. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [3] Istituto di Scienze Polari, CNR, Venezia. [4] Dipartimento di Scienze Ambientali, Informatica e Statistica, Università «Ca' Foscari», Venezia. [5] Dipartimento di Scienze del Sistema Terra e Tecnologie per l'Ambiente, CNR, Roma.

*Corresponding author e-mail:* irene.sammartino@bo.ismar.cnr.it

*Keywords:* sediment provenance, environmental changes, Last Deglaciation.

The last sea-level lowstand combined with the large extent of the continental glaciers led to the funneling of the Italian continental runoff, resulting in the ancestral river system draining the Adriatic shelf (Mediterranean Sea). Since the last deglaciation, Alpine and Apennines glaciers were connected to the Middle Adriatic Depression (MAD) in the Adriatic Sea, making this basin a suitable location to investigate changes in river input and related paleoenvironmental conditions. The MAD provides an example where inherited bathymetry convolved with changes in base level and oscillations in sediment supply influenced the stacking patterns and geometry of clinoforms that accumulated in the last 15 kyr. Sediment cores were collected along a dip-oriented profile. X-ray fluorescence (XRF) data from discrete samples of sediment cores were analyzed to assess the provenance of the sediment deposited in the MAD. Sediment composition was compared with main modern catchment domains whose geochemical signature had been defined by means of XRF analyses from > 450 samples acquired along river trunks and mouths. The amount of sediment deposited in the basin was measured as clinothem volume. Finally, we combined the use of organic carbon stable isotopes, high-resolution XRF core scanner, alkenone, and biomarkers to trace changes in marine productivity, river runoff, and sea surface temperature. Our results show that the last deglaciation records an overall progressive increase in surface temperature and freshwater, and a parallel decrease of terrestrial input into the basin, along with changes in vegetation on land (increase in C24 plants). Changes in sediment provenance from Alpine to Apennine source promoted a centripetal infill of the MAD. From a stratigraphic perspective, the Marine Regression Surface best approximates the inflection point that records changes in those parameters. In addition, the overall trend is punctuated by abrupt changes in marine productivity/organic matter preservation in the basin. Overall, our results document the MAD as a sink that hosts a potential archive for the reconstruction of regional-scale sediment provenance and environmental changes related to global climate.

# Compositional, micromorphological and geotechnical characterization of Holocene Tiber floodplain deposits (Rome, Italy) and stratigraphic implications

Tentori D.[1]*, Mancini M.[1], Milli S.[1-2], Stigliano F.[1], Tancredi S.[2] & Moscatelli M.[1]

[1] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* tentori.daniel@gmail.com

*Keywords:* micromorphology, paleosoils, floodlplain.

We report a high-resolution micromorphological characterization of floodplain deposits to investigate the relationships among compositional, textural and geotechnical data, and integrate soil micromorphology with sequence stratigraphy. Compositional and textural characterization of facies associations and soil features show that depositional features and post-depositional modifications are intrinsically associated with geotechnical parameters (e.g., cone resistance, sleeve friction, and friction ratio). Petrographic and micromorphological features from a borehole advanced 60 m into the Tiber channel belt and floodplain, document incipient pedogenetic modifications across stratigraphic markers evidenced by faunal and plant activity, accumulation of peat, and typified by precipitation of heavy metals, iron oxides and secondary carbonates. All these features developed in correspondence with surfaces of sequence stratigraphic significance, herein named "alluvial flooding surfaces", that can be correlated with non-marine and marine flooding surfaces recognized in the transgressive and highstand coastal and lagoonal deposits of the Tiber Depositional Sequence. These observations tell us about a specific history case of incipient soils formation in an alluvial sector of the Tiber Depositional Sequence but may serve as a model to reconstruct the sequence-stratigraphic evolution of ancient relict soils. Nevertheless, additional criteria (for example, their stratigraphic position and correlative surfaces) are necessary to adequately interpret the genesis of such low-rank stratigraphic surfaces. This work demonstrates that a combination between sedimentological and stratigraphic observations and soil micromorphology can be critical to supplement field observations and determine the relative effect of pedogenic and depositional processes on the organization, composition and texture, and geotechnical properties of floodplain in urban areas.

# Tracing sediment provenance in the Shaotanghe River (southwest China)

Usman M.*, Garzanti E. & Vezzoli G.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* m.usman1@campus.unimib.it

*Keywords:* bulk petrography, heavy minerals, sediment provenance.

The present work describes the diagnostic petrographic and mineralogical signatures of fluvial detritus derived from the Shaotanghe River (right bank tributary of the Minjiang River). The river length is 71 $km^2$ and its drainage area is 1730 $km^2$. Six bed-load sediment samples were collected from different tributaries of the Shaotanghe based on the lithological variations. On each sample, high-resolution petrographic analysis was carried out according to Gazzi-Dickinson method (Ingersoll et al., 1984). Sand was classified based on three main compositional components quartz (Q), feldspars (F) and lithic fragments (L), considering their exceeding 10%QFL (Garzanti, 2019). Average rank of rock fragments in each sample was expressed by the Metamorphic Indices MI and MI* (Garzanti & Vezzoli, 2003). Heavy-mineral analyses were carried out on a 4 φ-wide size window (32–500 µm) obtained by wet sieving. Heavy mineral concentrations (HMC and tHMC) have been calculated in volume percentage of the total and transparent heavy minerals from sediments (Garzanti & Andó, 2019). The results show that Shaotanghe River has complex sediment composition from Quartzo-lithic sands, quartzo-lithic metamorphiclastic sands and litho-quartzo-feldspathic with low- to high-rank metabasite with different metamorphic index (MI* ≈ MI ≈ 270-370). Shaotanghe River has extremely poor to rich tHM suite that include apatite, tourmaline, titanite, epidote, zircon, with amphibole (mainly blue/green hornblende and anthophyllite). This tracing study demonstrates that sediment composition is influenced by the source rocks that occupy minor portion of the whole catchment.

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# Automatic organic facies identification using Raman spectra on dispersed organic matter by means of Unsupervised Learning techniques (Paris Basin – France)

Vergara N.A.*[1-2-3], Schito A.[4], Corrado S.[1], Michel P.[3] & Gasparrini M.[5]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Sorbonne Université, ED 398 - GRNE, Paris (France). [3] IFP Energies nouvelles, Paris (France). [4] Department of Geology and Petroleum Geology, University of Aberdeen (UK). [5] Dipartimento di Scienze della Terra «A. Desio», Università di Milano.

*Corresponding author e-mail:* sassarini@gmail.com

*Keywords:* organic matter, Raman Spectroscopy, machine learning.

In recent years, Raman spectroscopy has been widely used as a tool for organic matter thermal maturity assessment in catagenesis and metagenesis with good success. This technique has shown to be a good candidate to replace the most used optical and geochemical tools (i.e., vitrinite reflectance, Rock-Eval pyrolysis) even if at low diagenetic conditions (liquid hydrocarbon generation) the high heterogeneity of organic facies may lead to an erroneous assessment of thermal maturity. In this work, we show, for the first time, how clustering analysis on Raman spectra can be a powerful and reliable tool for the automatic identification and classification of organic facies. Raman analyses were performed on a set of 27 organic-rich samples from the Lower Toarcian source rock interval (*Schistes Carton*) of the Paris Basin (France), characterized by three main organic facies: Amorphous Organic Matter (AOM), translucid and opaque phytoclasts. A total of 1365 Raman spectra were obtained, and Principal Component Analysis (PCA) was applied in order to reduce the dimensionality of the dataset into a 2-D array. Unsupervised clustering was then performed on Raman spectra principal components. Three different clustering algorithms were used: k-means, Gaussian Mixture Models (GMM), and Density-Based Spatial Clustering for Applications with Noise (DBSCAN). These algorithms were tested on their ability to correctly assign the number of clusters, their size, orientation and distribution. Results showed the best performances were obtained through the application of GMM clustering in terms of its ability to successfully determine cluster geometry and the optimal number of clusters by integrating a Bayesian Information Criteria (BIC). In addition, the GMM algorithm showed the best prediction performance among the three analyzed algorithms, being able to correctly identify each organic class with an accuracy >70%, and >80% for the opaque phytoclast class which represents the target group for thermal maturity assessment.

This is a first example of the use of unsupervised learning techniques coupled with Raman spectroscopy for organic matter content characterization, showing promising future applications for Earth and planetary sciences.

# S33.

# Taphonomy and diagenesis of marine biogenic sediments in ancient and modern depositional environments

*Conveners & Chairpersons*

*Luca Pellegrino (University of Torino)*

*Alan Maria Mancini (University of Torino)*

*Karen Gariboldi (University of Pisa)*

*Giulia Bosio (University of Milano-Bicocca)*

*Manuela Bordiga (OGS-Trieste)*

# Preliminary results on coccolith assemblages sedimented inside coralligenous build-ups (Marzamemi, Sicily)

Bazzicalupo P.*[1], Malinverno E.[1], Bracchi V. A.[1-2], Varzi A. G.[1], Savini A.[1-2], Fallati L.[1], Guido A.[3], Rosso A.[2-4], Sanfilippo R.[2-4], Leonardi R.[4], Negri M.P.[1], Cipriani M.[3] & Basso D.[1-2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [4] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* pietro.bazzicalupo@unimib.it

*Keywords:* coralligenous, coccolithophores, Mediterranean reefs.

Coralligenous, made up of crustose coralline algae, is one of the main components of the Mediterranean mesophotic reefs and a major hotspot for biodiversity, with the algal skeletal structure, characterized by holes and crevices, that supports many different dwellers. The porosity of this bioconstruction acts as a sediment trap, potentially storing important climatic and/or hydrological information. Although previous studies have focused on the sediment composition inside the coralligenous structure, an analysis on the calcareous nannofossil assemblages (i.e., coccoliths) has been largely overlooked. In this contribution we present some preliminary analyses on the coccoliths assemblages found in two coralligenous build-ups, collected during the project FISR 04543 "CRESCIBLUREEF - Grown in the blue: new technologies for knowledge and conservation of Mediterranean reefs" (https://crescibluereef.unimib.it/), at 36 and 37 m wd, respectively. We found reworked coccolith taxa, likely transported during river runoff/land erosion, as reflected by the age of these taxa, in accordance with the stratigraphy on land. Additionally, several samples have been identified as extant taxa. The known stratigraphical distribution and relatively good preservation of the samples suggest nannoplankton sedimentation from the upper water column during the development of the build-ups, thus indicating the coralligenous as potential "trap" for coccolith snow throughout its life. The study on these assemblages, coupled with the coralligenous stratigraphy, could help highlight the ecological preferences of some coccolithophore species, and clarify their role as proxies of turbidity, river discharge, nutrient arrival, water mixing, etc. In this sense, the comparison of coccolith assemblages with other biogenic components and terrigenous sediments inside the coralligenous could be a powerful tool for unravelling local/regional hydrological and climatic changes.

# Il buono, il brutto, o il cattivo? The role of diagenetic alteration of coccolith-rich rocks in constraining the palaeoceanographic setting

Bojanowski M.J.*[1], Ciurej A.[2], Dubicka Z.[3], Minoletti F.[4] & Olszewska-Nejbert D.[3]

[1] Institute of Geological Sciences, Polish Academy of Sciences, Warsaw (Poland). [2] Institute of Geography, Pedagogical University of Cracow (Poland). [3] Faculty of Geology, University of Warsaw (Poland). [4] Institut des Sciences de la Terre - UMR 7193 ISTeP, CNRS, Sorbonne Université, Paris (France).

*Corresponding author e-mail:* mbojan@twarda.pan.pl

*Keywords:* coccolith ooze, palaeoceanography, diagenesis.

Coccolith ooze is a valuable archive of past climatic and environmental conditions. One of the major concerns potentially limiting their applicability in such research is the post-depositional alteration, which can overprint all kinds of proxies, including biotic, sedimentological, isotopic, elemental, and organic. It is therefore vital to asses the effects of these alterations in order to verify the usefulness of the coccolith ooze as a palaeoceanographic archive. Here we present results of a multiproxy research from several studies performed on coccolith-rich rocks from Poland (Bojanowski et al., 2017; 2018; Ciurej et al., 2020; Dubicka et al., 2021) spanning a wide range of lithologies, paleoenvironmental settings, climatic conditions, depositional ages, and diagenetic histories. These are

- marls, chalks, and carbonate laminites
- deposited in either shallow epicontinental, open marine, or deep brackish basins
- during various global environmental perturbations, such as an oceanic anoxic event, hyperthermal conditions, biotic crisis, or glacial period
- between mid-Cretaceous and Oligocene,
- which were affected by insignificant diagenesis to deep burial and exhumation.

It is observed that the diverse diagenetic alterations imposed very different effects on the palaeoceanographic proxies examined depending on the timing and conditions of alteration, which we analyze in detail. We demonstrate that even if the post-depositional modifications are significant, it may still be possible in some instances to constrain the past conditions in the marine basin. Moreover, diagenetic modifications, when properly identified and analyzed, can even provide additional data concerning syn-sedimentary or early-diagenetic processes taking place at or below the basin floor. Although we appreciate this generally positive and optimistic conclusion, we need to stress that obtaining the paleoenvironmental data from diagenetically altered coccolith-rich rocks requires an investment in time-consuming analytical procedures and statistically significant, large datasets.

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# Autochthonous *vs* allochthonous micrite in Mediterranean coralligenous: ecological and depositional implications

Cipriani M.*[1], Basso D.[2-3], Bazzicalupo P.[2], Bertolino M.[4], Bracchi V.A.[2-3], Bruno F.[5], Costa G.[2-4], Dominici R.[1], Muzzupappa M.[5], Rosso A.[3-6], Sanfilippo R.[3-6], Sciuto F.[3-6] & Guido A.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [4] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [5] Dipartimento di Ingegneria Meccanica, Energetica e Gestionale, Università della Calabria, Rende (CS). [6] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* mara.cipriani@unical.it

*Keywords:* coralligenous, micrite, biomineralization.

Two coralligenous bioconstructions, along the Mediterranean shelf in front of the Marzamemi village (Sicily, Italy), have been collected in the frame of the project FISR 04543 "CRESCIBLUREEF - Grown in the blue: new technologies for knowledge and conservation of Mediterranean reefs". They allow to study the main builders of the biostructures and to investigate the role of the non-skeletal organisms in their morphology and depositional geometry. The primary framework is mainly built by crustose coralline algae, which in turn create the substrate for a high-diversified epi- and infaunal community. Sponge colonizes widely the internal crevices and together with soft algae, they represent the main organisms of the external surface. Fine micritic sediments represent subordinate components. Optical microscopy, UV-epifluorescence and Scanning Electron Microscopy (SEM) were applied to figure out whether these fine sediments can be a direct marker of biological activity or not. Two types of micrite were recognized: allochthonous and autochthonous micrite. The first type derives from physical processes, notably erosion, transport and deposition; it shows dense texture and is composed of sub-euhedral low-magnesium calcite minerals. Under UV-excitation, this micrite does not display epifluorescence. The lithification rate of this type of micrite is generally low and may take place over time after the primary framework is formed. The second type, high-magnesium calcite in composition, is made of very fine and amorphous crystals. It engulfs sponge spicules and organic matter remains, which under UV-excitation attribute a bright epifluorescence to this micrite. The autochthonous micrite could derive from induced biomineralization, mediated by microbial metabolic activity, or influenced biomineralization, mediated by organic matter decay (Perry et al., 2007; Dupraz et al., 2009; Görgen et al., 2020). The occurrence of this component allows hypothesizing a possible contribution of non-skeletal carbonate in the strengthening of the primary framework due to its syndepositional cementation. The strict connection of the autochthonous micrite with sponge spicules suggests organomineralization phenomena of sponge 'tissue' but further micromorphological and biogeochemical analyses will allow to depict the mineralization process involved in its deposition.

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# When was the Mediterranean water body born? What the Nd isotope record of Miocene phosphatic hardgrounds is telling us

Cornacchia I.*[1], Brandano M.[2-3], Agostini S.[1] & Munnecke A.[4]

[1] Istituto di Geoscienze e Georisorse, CNR, Pisa. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [4] GeoZentrum Nordbayern, Fachgruppe Paläoumwelt, Friedrich-Alexander-Universität, Erlangen (Germany).

*Corresponding author e-mail:* irene.cornacchia@igg.cnr.it

*Keywords:* Mediterranean, Miocene, paleoceanography.

Phosphate-rich hardgrounds are key surfaces for paleoenvironmental and paleoceanographic reconstructions because their occurrence is strictly linked to changes in the phosphorous and carbon cycles. Furthermore, in shallow water carbonate successions, phosphatic hardgrounds are associated with severe changes in the biota, platform drownings and depositional hiatuses. Phosphate-rich hardgrounds frequently occur in the Miocene carbonate successions of the Mediterranean area and they have been significantly studied to tackle their link to climate changes and carbon cycle perturbations. However, the identification of the water masses that formed them has been poorly reported in literature so far. Nd isotopes are a reliable proxy of water masses movements and paleoceanographic changes. In this study, we investigated the $^{143}Nd/^{144}Nd$ ratios of fossil shark teeth belonging to three Miocene hardgrounds of the central Mediterranean to identify the source of the water masses forming these peculiar deposits, framing them within the complex oceanographic evolution of the Mediterranean basin. As a Rare Earth Element, Neodymium is incorporated into apatite at or near the sediment-water interface, making $^{143}Nd/^{144}Nd$ ratios in shark teeth a proxy for deep water masses. The Nd isotope record of the investigated hardgrounds show values spanning from $\varepsilon_{Nd}$ -7.5 to -7.1. Thus, not only the $^{143}Nd/^{144}Nd$ ratios of the same hardground are consistent, but also the three hardgrounds (whose ages span from early Middle to Late Miocene) show a persistent Nd isotope signature, very similar to the present deep eastern Mediterranean water mass. Thus, the distinct Nd isotopic fingerprint of the hardgrounds testifies for an eastern provenance of the deep waters that formed them. Therefore, this dataset attests the onset of locally evolved deep waters in the eastern Mediterranean, influenced by local runoff. The closure of the Indo-Pacific connection (~18 Ma), in fact, affected the Mediterranean circulation, leading to a longer residence time of waters and limited exchanges with the Atlantic Ocean. Lastly, the Nd isotope signature of the analysed hardgrounds supports their origin through upwelling of deep water. The onset of the upwelling is related to global climatic changes that affected the Mediterranean area. The deep water ascended to the eastern side of the Mediterranean carbonate ramps via upwelling before returning to the Atlantic, triggering the increase of primary productivity and the development of phosphatic hardgrounds.

# LGM – Holocene West Antarctic Ice Sheet evolution by multidisciplinary analysis of five gravity cores collected in the Glomar Challenger (Eastern Ross Sea, Antarctica)

Geniram A.*[1], Colizza E.[1], Melis R.[1], Torricella F.[1], Tesi T.[2], Pambianco G.[3], Miserocchi S.[2], Gallerani A.[4] & Colleoni F.[5]

[1] Dipartimento di Matematica e Geoscienze, Università di Trieste. [2] Istituto di Scienze Polari, CNR, Bologna. [3] Università «Ca' Foscari», Venezia. [4] Istituto di Scienze Marine, CNR, Bologna. [5] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* ANDREA.GENIRAM@phd.units.it

*Keywords:* Ross Sea, Glomar Challenger Basin, multi-proxy analyses.

The history of the Western Antarctic Ice Sheet (WAIS) during the Last Glacial Maximum (LGM) – Holocene transition is still debated. The most accepted interpretation is that the WAIS was grounded near the shelf break during the LGM (e.g., Halberstadt et al., 2016; Anderson et al., 2018; Gales et al., 2021). An alternative hypothesis was proposed by Bart & Owolana (2012): the ice sheet was grounded in the middle shelf during the LGM and morphologies identified at the shelf break were formed during previous glacial cycles. Timing and mechanisms of the last glacial retreat are still under investigation.

Here we present the preliminary results of a transect of five gravity cores collected in the Glomar Challenger Basin (Eastern Ross Sea, ERS), from the inner continental shelf to the shelf break, in the framework of several PNRA expeditions. The reconstruction of sedimentary dynamics and paleoenvironmental evolution is based on a multidisciplinary approach: sedimentological, geochemical (XRF), micropaleontological and biomarker ($IPSO_{25}$) analyses and physical properties. Accelerator Mass Spectrometry (AMS) is used to date the gravity cores using organic matter. Three phases have been identified, representing the evolution of the Glomar Challenger since the LGM: a glacial phase represented by subglacial diamicton (heterogeneous and over-compacted sediments), a glacial-marine phase represented by sub-ice shelf ice rafted debris-rich sediments and the Holocene characterized by muddy sediments.

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# A mud-mound like carbonate build-up from the messinian terminal carbonate complex of the Salento peninsula (Southern Italy)

Guido A.*[1] & Vescogni A.[2]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* aguido@unical.it

*Keywords:* mud-mound, microbialites, Messinian.

A late Messinian shallow-water succession composed of bioclastic/microbialitic carbonate deposits has been described in the Salento Peninsula (Vescogni et al., 2022) and has been considered as a central Mediterranean equivalent of the Terminal Carbonate Complex (TCC), up to now mainly known from the Western Mediterranean (Bourillot et al., 2020).

The changes forced by the Messinian Salinity Crisis on the Mediterranean marine environments, particularly on shallow-water carbonate factories, allowed the development of microbial communities which metabolic processes induced microbialite deposition, mostly under shallow-water and normal marine salinity conditions during warm climatic phases. Among the various microbialite texture described by Vescogni et al. (2022), massive dendrolite/thrombolite (MDT) form a mound-like carbonate build-up, which extend for 26 m and show a maximum thickness of 3.2 m. Here we present a micromorphological and biogeochemical approach integrating optical and electron microscopy analyses with UV-Epifluorescence observations, EDS microanalyses and Raman Spectroscopy, in order to investigate the processes involved in the deposition MDT facies of the build-up. Two different wave-resistant fabric have been recognized at meso- and microscale observations: a) dendritic, shrub-like mesofabric made of short, digitate ramifications; b) thrombolitic growth forms made of thin, upward oriented branches. Preliminary data of UV-Epifluorescence and Raman spectroscopy suggest the presence of organic matter remains trapped among the fine crystals of the microbialite textures, suggesting biomediated processes involved in their precipitation. Among the bioclastic/microbialite facies of the Salento TCC carbonate, the MDT are the only characterized by a very reduced amount of skeletal grains. This difference could be due to peculiar environmental conditions limiting the development of metazoans and allowing the proliferation of microbial communities or to periodical high hydrodynamic conditions able to remove carbonate particles and hampering gravitative sedimentation as well as trapping and binding.

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# Coccoliths acidification: an experimental approach to constrain the preservation degree of nannofossil assemblage in sediment samples

Isella E.*, Lozar F. & Mancini A.M.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* erik.isella@edu.unito.it

*Keywords:* coccolithophorids, paleoenvironmental reconstruction, acidification.

Coccolithophores are unicellular planktic algae, which are coated by calcite plates called coccoliths. Coccolithophores have an important fossil record, from their first appearance around 225 Ma to extant specis. Their fossil record has proved to be a fundamental tool for reconstructing past environmental conditions. This is possible by comparing the distribution of living coccolithophores and the assemblages preserved in the fossil record. However, the coccolith fossil record is affected by various preservation degrees that could hamper the reliability of the paleoenvironmental information stored. Indeed, not all the coccolithophores taxa thriving in the water column have the same fossilization potential. Among the factors that contributing to alter the fossil assemblage; the acidification of seawater, that also interacts with other processes. What still needs to be understood is what effects and intensities these processes have on different taxa, and which species are more resistant to these effects, in order to improve the reliability of data obtained from the fossil assemblages. We present the first experimental attempt to constrain the degree of preservation of the calcareous nannofossil assemblages that could ultimately improve the reliability of the micropaleontological data for the paleoenvironmental reconstruction purposes. Messinian sediment samples, from the Sorbas Basin, were experimentally treated with 1 molar acetic acid, in order to simulate the alteration that can occur either during coccolith settlement to the sea floor or during diagenesis. Samples were prepared with standard micropaleontological procedure (i.e., smear slide) from the acid-treated and untreated solutions for the observation under a light microscope. Alterations of coccoliths of the species *Coccolithus pelagicus* and *Pontosphaera multipora* were considered by comparing the acid-treated sample with the untreated one. For the evaluation of the preservation, we established two parameters: the dissolution (which is a chemical alteration) and the fracturation (which is a mechanical alteration). We defined four classes with increasing degrees of dissolution and fracturing observing the specimens at 1250X. Thirty specimens per taxon, both in untreated and treated samples, were classified according to the four preservation classes defined. For the degree of dissolution, an increase in classes 2 and 3 and the reduction in classes 0 and 1 of both taxa were noted. For the degree of fracturing, a reduction in class 3 was noted for both species. This could be explained by the difficulty to taxonomically recognize coccoliths with high degree of fracturing; therefore, we think that the fracturing is not a good indicator of alteration on these taxa. Conversely, the dissolution proves to be an excellent indicator of the degree of preservation. Our experiment also shows that, of the two species, *P. multipora* is the most resistant to alteration.

# Dolomite layers in the Miocene diatomaceous sediments of the Pisco Formation (East Pisco Basin, Peru)

Malinverno E.[1], Bosio G.*[1], Gioncada A.[2], Cimò R.[3], Andò S.[1], Mariani L.[1], Coletti G.[1], Boschi C.[4], Gariboldi K.[2], Galimberti L.[1], Bianucci G.[2], Urbina M.[5] & Di Celma C.[6]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Istituto Comprensivo Statale «San Giovanni Bosco», Cremeno (LC). [4] Istituto di Geoscienze e Georisorse, CNR, Pisa. [5] Departamento de Paleontología de Vertebrados, Museo de Historia Natural, Universidad Nacional Mayor de San Marcos, Lima (Peru).

*Corresponding author e-mail:* giulia.bosio@unimib.it

*Keywords:* carbonate concretions, early diagenesis, dolomite.

Low temperature and early diagenetic dolomite formation in marine environments has been related to microbial processes occurring within organic-rich and oxygen-depleted sediments (e.g., Vasconcelos et al., 1995). In both extant and past settings, sedimentary successions from upwelling zones exhibit dolomite concretions and less frequent laterally continuous layers, such as in the Peruvian offshore (Meister et al., 2007).

Along the Peruvian coast, the East Pisco Basin is a forearc basin that was active between the Eocene and the Pliocene. Nowadays, its sedimentary succession is exposed in the Ica Desert, where the Miocene Pisco Formation crops out. At Cerro los Quesos, laterally continuous dolomite layers characterize the diatomaceous sediments of the P2 sequence, where a large number of marine vertebrates are exceptionally preserved, many enclosed in dolomite nodules (Gariboldi et al., 2015). At this locality, cemented layers were described and sampled for further investigations through optical and electron microscopy, XRD, XRF, Raman spectroscopy, and stable isotope ratio determination. Dolomite layers are 10 to 50 cm in thickness and well cemented. The underlying sediments usually exhibit sparse dolomite crystals and abundant Mn- and Fe-oxides. The composition of the sediment varies from biogenic, terrigenous, volcanoclastic, to phosphate. Two generations of cement can be recognized: a cryptocrystalline one, from the very early diagenesis, and a sparry one, which fills the cavities in a later stage. In most samples, dolomite also replaced calcite shells, such as foraminifera, and filled the inner spaces of diatom areolae replicating their finest ultrastructure. $\delta^{18}O$ and $\delta^{13}C$ values from two layers are in agreement with those reported for the Peru margin (Meister et al., 2007) and fall in both the fields of sulphate-reduction and methanogenesis.

All the data point to a dolomite precipitation associated with low-temperature early diagenesis that typically occurs in upwelling settings, where high productivity in surface waters is responsible for high rates of organic carbon flux to the sea bottom and for the development of an oxygen minimum zone (OMZ) and related oxygen depletion in the shallow sub-bottom.

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# Reconstructing paleoenvironment and taphonomic processes from Messinian diatomaceous sediments of the Lower Chelif basin (NW Algeria)

Mansour B.*[1], Bachiri N.[1], Mennad S.[1] & Saint Martin J.P.[2]

[1] Laboratoire de Paléontologie Stratigraphique, Université d'Oran 2 (Algeria). [2] Muséum National d'Histoire Naturelle, Paris (France).

*Corresponding author e-mail:* bouhameur@gmail.com

*Keywords:* Messinian, diatomites, taphonomy, Algeria.

During the Messinian, the Mediterranean region experienced a dramatic intensification of the biosiliceous deposition, whose deep causes are still debated. Northern Algeria represents a key area for elucidating the processes that governed the Messinian biosiliceous event, due to the abundant and well-exposed diatomite-bearing sedimentary successions. We present the preliminary results of the first detailed sedimentological study of Messinian diatomites and associated deposits of the Lower Chelif Basin (NW Algeria), aimed at reconstruct paleoenvironmental and taphonomic processes responsible for their formation.

Five main lithofacies have been distinguished and further characterized by scanning electron microscopy (SEM): i) diatom-bearing laminated marl; ii) finely laminated diatomite; iii) massive diatomite (often bioturbated); iv) diatomaceous laminite, made up of whitish lenses of elliptical and/or rounded shape, flattened, aligned along the bedding plane, locally forming more or less continuous laminae; v) black marls (sapropels).

Diatom-bearing laminated marls contain fragmented and dissolved remains of centric and pennate diatoms, suggesting a turbulent sedimentary environment.

Laminated diatomites are typified by two types of diatom-rich laminae: one lamina type is dominated by *Actinocyclus curvatulus* or *Coscinodiscus marginatus*, while the other by *Thalassionema nitzschioides*. These laminae can be interpreted as reflecting seasonal blooms. The arrangement of the frustules and their good preservation suggest deposition in a quiet, deep environment where lamination would result from the absence of bioturbation and therefore from anoxic conditions.

The massive diatomite is made up of poorly preserved frustules, very fragmented and randomly arranged, pointing to a rather turbulent sedimentary environment.

The examination of the whitish lenses in diatomaceous laminite revealed a high concentration of fragmented diatom remains, pointing to their inclusion in fecal pellets after grazing.

Sapropel analysis highlighted abundant tests of radiolarians (Spumellaria), planktic diatoms, silicoflagellates and demosponge spicules aligned parallel to the bedding plane and deposited under bottom oxygen depletion.

The taphonomic processes occurred in the sedimentary environment, especially those resulting in the fragmentation or dissolution of diatom remains, could seriously distort the original microfossil record of this type of deposits.

# Tracers of the lost seagrass: the bias introduced by diagenesis on foraminiferal assemblages indicative of palaeo-seagrass meadows

Mariani L.*[1], Coletti G.[1], Mateu-Vicens G.[2], Bosio G.[1], Collareta A.[3], Khokhlova A.[2], Di Cencio A.[4], Casati S.[4] & Malinverno E.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Interdisciplinary Ecology Group, Universitat de les Illes Balears, Palma de Mallorca (Spain). [3] Dipartimento di Scienze della Terra, Università di Pisa. [4] Gruppo Avis Mineralogia e Paleontologia, Scandicci (FI).

*Corresponding author e-mail:* l.mariani35@campus.unimib.it

*Keywords:* benthic foraminifera, *Posidonia oceanica*, Pleistocene.

Seagrass meadows, worldwide, represent trove of biodiversity and *Posidonia* meadows in particular are one of the most ecologically-relevant marine coastal-habitats of the Mediterranean Sea. While seagrass meadows have a key role in the shallow sea, their geological record is relatively scarce, as these plants have a limited preservation potential. Therefore, most of the paleontological research on fossil seagrasses is based on indirect indicators, such as carbonate-producing organisms associated with the meadow (Reich et al., 2015). Among them, benthic foraminifera are one of the most common and relevant group. Even though foraminifera, being characterized by a calcium carbonate test, display a higher preservation potential in comparison to seagrasses, they are not immune to diagenesis. This research investigates the foraminifera assemblages associated with well-preserved remains of an early-Pleistocene-aged *Posidonia oceanica* meadow cropping out at Fauglia, Tuscany (Italy) (Bosio et al., 2021). The detailed analysis of the foraminiferal assemblage clearly indicates how several taxa of miliolids, whose presence is usually considered suggestive of a seagrass meadow, only occur in certain layers, characterized by the exquisite preservation of both aragonitic shells and organic matter remains. In the remaining layers of the successions miliolids are almost absent, greatly hindering the potential of the foraminiferal assemblage as indirect seagrass indicator. Our analysis also tests different indexes used for investigating modern seagrass meadows using foraminiferal assemblages: the modified Foraminifera Index (FI'), the "long vs. short life-span index" ($I_{LS}$), and the abundance of permanently attached, encrusting foraminifera (Mateu-Vicens et al., 2014). New indexes, devised to overcome the bias introduced by diagenesis, were also tested, namely the above-mentioned indexes calculated without considering miliolids abundance, and the $K/R_{EXT}$ ratio, consisting of the ratio between keeled *Elphidium* and the sum of rounded elphidiids and other related genera that display a rounded periphery (e.g., *Astrononion*, *Haynesina*). High-values of the $K/R_{EXT}$ ratio in association with the presence of permanently attached foraminifera revealed to be the most reliable palaeo-seagrass indicators, suggesting that this combination could be very useful also settings where the diagenesis altered the foraminiferal association.

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# Reverse Weathering: Past, Present and Future

Michalopoulos P.*

Hellenic Centre for Marine Research, Athens (Greece).

*Corresponding author e-mail:* pmichalo@hcmr.gr

*Keywords:* reverse weathering, authigenic clay minerals.

Reverse weathering reactions refer to the formation of authigenic clay minerals from the reaction of cation poor aluminosilicates or biogenic silica with dissolved seawater cations. The Reverse Weathering concept was introduced by Mackenzie & Garrels in 1966 in an attempt to reach a balance between cations, anions and alkalinity in seawater. Initially Reverse Weathering was shown to play a significant role as a sink for cations (K, Mg) and reactive silica in deltaic systems (Amazon, Mississippi). More recently it was shown that major and trace elements are involved in marine RW reactions, and authigenic clay mineral formation and they are important sinks for Li, Ge, F and alkalinity. They also appear to promote climatic stability (e.g., $CO_2$ source) and regulate variations in elemental cycling over long time scales.

A new hypothesis of microbial mediation in early diagenesis of silica and reverse weathering was recently tested against the dominant concept of abiotic diagenetic silica cycling and will be presented. Incubation experiments using archived sediments from the Congo Deep Sea fan and fresh sediments from the Mississippi River plume revealed the importance of microbially-mediated net silica sequestration compared to lower sequestration rates under abiotic conditions. In fresh Mississippi River plume sediments, a radiotracer (32Si) enabled the quantification of underlying silica cycling processes such as particle adsorption, abiotic precipitation, and microbially-mediated silica neoformation. The microbially-mediated silica precipitation is shown to be ~3.2x the abiotic precipitation under average experimental solid -solution ratios, and ~3.8x at simulated surface pore water diagenetic conditions (porosity 90%).

Finally, studies in Mississippi and Danube delta sediments indicate strong linkages between reactive silica and organic matter cycling and storage in these sediments. It is highly probable that the formation of reverse weathering products may facilitate organic matter preservation in deltaic sediments.

# High-resolution investigation of a pre-evaporitic Messinian precessional cycle in the Pecetto di Valenza section (NW Italy): from sapropel to diatomite deposition as revealed by stable isotope and morphometric analyses on planktic and benthic foraminifera

Nallino E.*, Gennari R., Mancini A.M., Pellegrino L., Pilade F. & Lozar F.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* enrico.nallino@unito.it

*Keywords:* stable isotopes, foraminifera, *Neogloboquadrina*.

Sapropels are the sedimentary expression of remarkable perturbations of the carbon cycle. During the late Miocene, the Mediterranean basin experienced a progressive restriction, during which a significant increase of the sapropelitic deposition occurred. The triggers responsible for the deposition of pre-evaporitic Messinian sapropels are still debated. Two interpretations regarding the trigger for the sapropel deposition were proposed: the first invokes a weakening/stop of the thermohaline circulation that provides oxygen to the sea floor; the second recognises productivity and organic matter export as responsible for bottom oxygen consumption.

Our attempt to solve sapropel deposition riddle relies on the well-preserved foraminifer record of the Pecetto di Valenza section, at the northernmost offshoot of the Mediterranean, in which the sapropelitic deposition is associated with diagenetic processing involving Mn oxides. Mn-rich sediment are uncommon in the sedimentary record of the Messinian Mediterranean Sea, and the mechanisms behind this diagenetic process is still unclear. Through the analysis of carbon and oxygen stable isotopes on benthic infaunal, epifaunal, and two planktic foraminifera taxa, we reconstructed the variability of the chemical and physical conditions of the water column, developing a depositional model. Moreover, the reconstruction of the water column geochemistry could bring some useful evidence to untangle the causes behind Mn diagenetic enrichment. Additional morphometrical analysis were performed on the genus *Neogloboquadrina* in order to characterize the late Miocene morphotypes, and to test their relation with oceanographic and environmental conditions.

Stable isotopes highlight a prominent continental freshwater influence during sapropel deposition, preceded by an increase in surface water productivity, pointing towards a complex interaction between thermohaline circulation intensity and organic matter export pattern to the seafloor. The diatomite deposited after the sapropel is instead characterized by generally homogeneous marine conditions of the water column. Regarding morphometric analyses, we observed that, more than the Neogloboquadrinid morphotypes relative abundance, test parameters within each morphotype respond to variations of paleoceanographic conditions. Our high-resolution study allows to better understand the complex dynamic behind sapropel deposition, adding details to the previous model. Moreover, our study let us remark the importance of the comprehension of the different ecological driver interplay, in the establishment of anoxic condition at the seafloor and organic matter preservation in sediments.

# Deciphering early and late diagenetic history in Triassic reef to slope facies (Southern Alps, Lombardy, and Southern Apennine, Sicily)

Randazzo V.*[1], Berra F.[1], Todaro S.[2] & Di Stefano P.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* vincenzo.randazzo@unimi.it

*Keywords:* carbonates, diagenesis, Triassic.

Cementation represents the most important diagenetic process transforming carbonate sediments in the massive limestone and dolostone bodies that we recognize in outcrop and subsurface. Cement precipitation occurs at syndepositional and at different post-depositional stages, leading to the subsequent gradual reduction of the original porosity. Cementation produces carbonate cements that can differ in texture, size, and geochemical composition, and may alternate with dissolution and/or the development of fractures, filled in turn by new generations of cements.

In order to characterize the diverse stages of cement precipitation, two Triassic carbonate platforms were selected for a detailed study performed with the integration of cathodoluminescence, optical, and geochemical (stable O and C isotopes) analyses. The same analytical approach was applied, in order to characterize different generations of cements in different carbonate systems and to provide the critical elements for (i) deciphering the different syndepositional, postdepositional, and late diagenetic conditions, for (ii) separating the early marine cementation from the later stages, and for (iii) reconstructing the processes influencing porosity and permeability over time. Coarse reef-to-slope breccias characterized by abundant cements related to diverse events have been observed in the Esino (Ladinian, Southern Alps, Lombardy) and in the Billiemi limestones (Norian-Rhaetian, Southern Apennine, Sicily). Despite comparable facies, the Esino and the Billiemi limestones have different tectonic and diagenetic histories and belong to different paleogeographic domains. Both the studied facies are characterized by depositional breccias and boundstones, with a high depositional porosity (up to 35-40%) rapidly filled by abundant fibrous radiaxial isopachous marine cements, black under CL. The diverse generations of late cements, with specific signatures in the two platforms, record a different burial history and a gradual decrease of the porosity remaining after the deposition of the marine cements in the two studied platforms. No clear evidence of dissolution is recorded; diverse sets of fractures filled by cements or by internal sediments are responsible for an increase of secondary porosity at different diagenetic stages. The characterization of the diverse generations of cements indicates a comparable syndepositional to early diagenetic history for the two studied platforms, stressing the major role of marine cement precipitation during and immediately after the deposition. The later cementation events, whose role is critical for the definition of the petrophysical properties of carbonate bodies, are instead strongly related to the conditions existing during the burial and the tectonic events affecting the carbonate platforms from deposition up to exhumation.

# The stratigraphic expression of the Middle Eocene Climatic Optimum (MECO) in a mixed siliciclastic carbonate system: the Capo Mortola section (Ligurian Alps, Italy)

Ruscitto V.*[1], Tomassetti L.[2], Cornacchia I.[3], Lirer F.[1], Cascella A.[4], Aldega L.[1], Catanzariti R.[3], Trapasso F.[5] & Brandano M.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] Istituto di Geoscienze e Georisorse, CNR, Pisa. [4] INGV, Pisa. [5] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* valeria.ruscitto@uniroma1.it

*Keywords:* Calcare Nummulitico, Bartonian, chemiostratigraphy.

The Middle Eocene Climatic Optimum (MECO) was one of the most intense short-term global climate perturbations of the Cenozoic, characterized by a 4-6°C global temperature increase that lasted between 400 and 500 kyr. This warming event is marked by a distinct negative shift in $\delta^{18}$Obenthic values of deep-sea cores of the Southern Ocean (Bohaty & Zachos, 2003; Westerhold et al., 2020). The MECO is "enigmatic" since it is characterized by the absence of a negative $\delta^{13}$C excursion at the onset of the event (Bohaty et al., 2009), suggesting that it was not related to volcanic $CO_2$ or methane release. Classically the MECO has been investigated in deep-sea records, while only few data from the shallow water records are available. This work aims to identify the impact of MECO on a shallow water environment through biostratigraphy, facies and multiproxy geochemical analyses, and X-ray diffraction of clay minerals.

We measured and sampled a 45 m thick stratigraphic section exposed on the Capo Mortola promontory (Western Ligurian Alps, Liguria, Northern Italy). The sedimentary succession, belonging to the Calcare Nummulitico Formation, identifies a mixed siliciclastic carbonate ramp developed between the Lutetian and Bartonian in the Alpine foreland. Three main lithozones can be recognized from bottom to the top: the lower portion consists of a nummulite-dominated lithozone followed by marly deposits with isolated corals, bivalves and nummulites evolving in the upper part to discocyclinid-rich marly limestones. The upper lithozone is represented by bioclastic calcarenites with nummulites.

On the basis of benthic foraminifera and calcareous nannofossil assemblages, it was possible to ascribe the section to the Bartonian stage. Facies and biostratigraphic analyses coupled with Magnetic Susceptibility (MS), trace elements and clay mineral variations, allowed us to reconstruct the paleoweathering conditions across the MECO. Preliminary results show an overall increase of the terrigenous input during the warming phase, coinciding with major spikes of MS, and a general increase of lithogenic trace elements, consistent with continent-derived sediment pulses.

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# First taphonomic insight on a coralligenous build-up off Marzamemi (SE Sicily)

Sanfilippo R.*[1-2], Basso D.[3-2], Bazzicalupo P.[3], Bertolino M.[4], Bracchi V.A.[3-2], Cipriani M.[5], Costa G.[2], Dominici R.[5], Donato G.[1], Rosso A.[1-2], Sciuto F.[1-2] & Guido A.[5]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Consorzio Nazionale Interuniversitario per le Scienze del Mare, Roma. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [4] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [5] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* sanfiros@unict.it

*Keywords:* crustose algae, invertebrates, early diagenesis.

A discrete build-up located 33.5 m depth in an area with high coralligenous cover located off the Marzamemi village (south-eastern Sicily), has been studied in the frame of the project FISR 04543 "CRESCIBLUREEF - Grown in the blue: new technologies for knowledge and conservation of Mediterranean reefs".

The relationships among the components of the framework were examined, including the encrusting calcareous red algae representing the main builder, and the secondary builders mainly consisting of serpulids, bryozoans, foraminifera and molluscs, all having carbonate exoskeletons cementing to each other. The role of large sponges and sediments trapped inside some cavities was also investigated.

Two scraped samples were examined, one from the bottom half (sample CBR2_5_35_Gb) of the build-up and one from the top half (sample CBR2_5_32_Gt), which is more densely covered by soft algae and peyssonneliaceans.

On the top half, builders show more frequent life interactions than in the bottom one, with numerous overgrowths between encrusting calcareous red algae, serpulids and bryozoans pointing to a more active growth. Among dwellers serpulids, bryozoans and foraminifera are dominant. Sponges occupy interspaces between superimposed laminar thalli and engulf crevices between superimposed metazoans and voids inside skeletons, like the lumina of large empty serpulid tubes. The bottom half is made of mostly dead coralline algae. Cavities within laminar convolutions are colonized by numerous sciaphilic small dwellers like encrusting bryozoans, serpulids, brachiopods and foraminifera, and are often darkened by Fe-Mg oxides coatings.

Numerous cm- to mm-sized cavities inside the fruticulose framework are obvious, some empty but other partly or entirely filled with sediments. The larger ones may contain allochthonous sand and gravel including free-living coralline algae (maerl), small gastropods and shell debris deriving from organisms associated with the bioconstruction or transported from the surrounding soft bottoms. The smaller cavities can trap finer sediments. These are whitish allochthonous micrites with shell debris, or fine autochthonous micrites incorporating sponge spicules and remains of organic matter. On the bottom half, micrites from the innermost cavities at discrete distance from the surface appear locally lithified. Analogously, neighbouring calcite thalli show evidence of early diagenesis and recrystallization. The decay of the sponges would seem to enhance the inception of these taphonomic processes indirectly contributing to strengthen the primary structure. The presence of organic matter deriving from decayed sponges in some micrite sediments suggests phenomena of organomineralization of the sponge tissues and opens up future investigations on the still poorly understood mineralization processes involved in the coralligenous formation, stabilisations and preservation.

# Taphonomy and sedimentary context remarks from Cenozoic siliceous microfossils deposition: how paleoenvironmental and paleoceanographic changes can affect sedimentary series preserved on Antarctic continental margins

Tolotti R.*[1-2], Donda F.[1], Sauli C.[1], de Santis L.[1], Caburlotto A.[1], Corradi N.[2], Colizza E.[3], Crosta X.[4] & Leventer A.[5]

[1] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS). [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [3] Dipartimento di Matematica e Geoscienze, Università di Trieste. [4] UMRCNRS 5805 EPOC, Université de Bordeaux (France). [5] Department of Geology, Colgate University, Hamilton, NY (USA).

*Corresponding author e-mail:* raffaella.tolotti@virgilio.it

*Keywords:* Antarctica, continental margins, Cenozoic climate changes, biosiliceous micropaleontology.

Antarctic continental margins are extremely challenging environment for paleoenvironmental and paleoclimatic reconstructions. Qualitative and quantitative analyses on siliceous microfossils may greatly help as biostratigraphic, paleoceanographic and paleoclimatic tools, when inserted in the proper sedimentary, taphonomic and diagenetic context and compared with other geo-astronomic and age diagnostic tools and paleoceanographic inferences (Rebesco et al., 2014; Tolotti et al., 2014, 2017, 2021). We here present some general sedimentary remarks and problems linked to taphonomic processes of biosiliceous microfossils and assemblages turnover. The shown examples have been chosen from some marine cores from the East Antarctic margin (North Western Ross Sea sector, Wilkes Land and Sabrina Coast) during the last 800 kyr climatic cycles and, at a more large scale, from the ocean basinal environment in the Southern Indian Ocean (DSDP Leg 119, Kerguelen Plateau) during the opening of the Drake Passage, matching with some of the most important Cenozoic climatic events.

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# S34.

# The Sediment Routing System as a tool to the understanding of fossil depositional systems and the preservation of modern ones

*Conveners & Chairpersons*

*Francesca Micheletti (University of Bari)*

*Emilia Le Pera (Università of Calabria)*

*Stefania Lisco (University of Bari)*

# Sandstone diagenesis and petrophysics of San Mauro formation (Cilento group), Southern Apennines, Italy

Civitelli M.*, Criniti S., Borrelli M. & Critelli S.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* massimo.civitelli@unical.it

*Keywords:* Cilento Group, composition, diagenesis, burial history.

The Cilento Group (Langhian-to-Tortonian) is an upward thickening and coarsening turbiditic mega-sequence (1200-2500 m) of the Southern Apennines foreland region that unconformably overlain the Lucanian oceanic terranes. In the studied stratigraphic section (Monte della Stella), we focus the post-depositional history of the upper portions of the Cilento Group, the San Mauro Formation (SMF).

The lower portion of the SMF, 300–500 m in thickness, consists of thin bedded sandstone and thick mudstone and marls of the fan fringe and basin plain turbidite facies associations. Several intrabasinal carbonaticlastic turbidites and a coarse grained volcaniclastic layer are interbedded with distal fan turbidites. An impressive intrabasinal carbonate turbidite megabed, of 65 m in thickness, separates the lower and the upper portions. The upper portion of SMF, about 1100-1200 m in thickness, consist of sandstone lobe turbidites and thin fan-fringe facies to channel-mouth and channelized turbidite sandstone and conglomerate for over 700 m in thickness, passing upward to, 400–500 m in thickness, coarse-grained sandstone and conglomerate turbidite beds of the channel mouth and channelized facies association. A second impressive intrabasinal carbonate megaturbidite bed, 35 m in thickness, is interbedded within inner channelized turbidite facies (Critelli et al., 2011).

Sandstones are quartzolithic, volcanolithic and quartzofeldspathic, whereas hybrid arenites and calcarenites characterize the carbonate megabeds.

Several diagenetic processes reducing porosity and permeability, such as compaction and cementation, occurred within the SMF. Framework grains are generally compacted, as testified by the common deformation of ductile grains (mainly micas) and detrital matrix. Authigenic minerals occur as both pore-filling cements or replacement on detrital grains. The main cements are: 1) carbonate, such as calcite and less dolomite, occurring mainly as replacement and also as pore-filling cement; 2) small amount of authigenic quartz represented by little overgrowths or mosaic quartz; 3) phyllosilicates, mainly developing in the upper part of SMF as pore filling chlorite cement or as small and incomplete illite coatings on skeletal grains; 4) Fe-oxides occurring as patchy or pore-filling cements.

The pore system consists of inter-intra-granular pores with a small pore radius and fractures. The porosity and permeability values are highly variable, and are on average higher in the lower SMF.

The relationship between the compactional porosity loss (COPL) and the cementational porosity loss (CEPL) testifies that compaction is the main reduction porosity process for both upper and lower SMF sandstones. Burial analysis (Corrado et al., 2019) suggests two phases of intense subsidence, interpreted as the result of syn-orogenic extension at shallow crustal levels intermitted by periods of low sedimentation rates, linked to gravitational instability of a vertically growing orogen.

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# A reliable geochronological method for Quaternary gravelly marine terraces covers: luminescence Rock Surface Dating performed on Cala Mosca and Cala Viola areas (Sardinia, Italy)

Cossu G.*[1], Sechi D.[1], Pascucci V.[1] & Andreucci S.[2]

[1] Dipartimento di Architettura, Design e Urbanistica, Università di Sassari. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* gicss1987@gmail.com

*Keywords:* marine surfaces, geochronology.

Unravelling the dynamics of past rocky shorelines and associated pocket-beach systems represents a key tool to proxy past sea-level position and clarify geodynamic evolutions. The high energy of such beach systems results in erosive features as tidal notches or wave cut platforms and associated sedimentary covers composed of gravelly or mixed sandy-gravelly marine sequences. A major issue is usually constraining the age of such systems because of the common lacking of suitable materials for traditional dating methods (e.g., fossils in life position for U/Th or quartz k-feldspar grains for luminescence dating).

Recently, a new branch of luminescence dating methods, named Rock Surface Dating (RSD) has been developed. It is based on the ability of light to penetrate into the rock until a certain depth and to reset the luminescence signal stored by minerals (quartz and k-feldspars). During the subsequent burial period, the signal can be rebuilt and stored toward a certain intensity. Measuring the variation of luminescence signal with depth allows determining the time elapsed since the last light exposure and, indirectly, the burial time (e.g., Souza et al., 2021).

Two mixed sandy-gravelly beach deposits mantling the Last Interglacial (MIS 5e, 126-117 ka) marine terraces of Cala Mosca and Cala Viola bays (Sardinia) were investigated and selected cobbles dated using RSD method. Burial ages of cobbles were determined, resulting in 131 ± 8 ka for Cala Mosca and 126 ± 9 ka for Cala Viola. These are consistent with previous results and stratigraphic reconstruction, confirming that RSD is a powerful method for dating shallow marine gravelly deposits and open new opportunities in Quaternary rocky coastal studies.

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# Composition and provenance of Late Carboniferous to Permian sandstones within the Circum-Mediterranean region

Criniti S.*[1], Critelli S.[1], Costamagna L.G.[2], Di Stefano P.[3] & Sulli A.[3]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [3] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* sara.criniti@unical.it

*Keywords:* Late Carboniferous-Permian sandstones, Circum-Mediterranean region, provenance analysis.

Late Carboniferous to Permian sandstone suites within the Circum-Mediterranean region occur both in subsurface (Puglia 1 well) and are exposed in Sardinia and Sicily. These clastic wedges record the most critical and dramatic restocking of Pangaea supercontinent. In this contest, the circum-Mediterranean region was experiencing particular tectonic and climatic environment, imprinted in siliciclastic strata.

Here are discussed compositional data of Permian strata of the Apulia Unit, the Permian San Calogero Formation in Sicily, the Late Carboniferous-early Permian Rio Su Luda Formation and the Permian Mulargia Formation in central Sardinia.

The Apulia Unit is crucial in the Mediterranean paleogeographical contest because, for its position, it received a great Permian sedimentary load. These strata are intersected in Puglia 1 well, between 7070 m to 6110 m in depth, for 960 m in thickness, with sandstone, mudstone and breccia strata. The Permian succession in Sicily is strongly tectonized (Lercara complex), outcropping around the Roccapalumba-Lercara area and the Sosio Valley (Northwestern Sicily). It consists of rock packages of different facies among which deep-water turbidites. Also, Carboniferous-to Permian sandstones (Gerrei basin, Central Sardinia) of the Rio Su Luda and Mulargia formations display a quite succession made of conglomerate, sandstone, mudrock and episodically interbedded volcaniclastic breccia and sandstones.

Sandstones of the Puglia 1 Well are quartzolithic, with abundant quartz and metasedimentary lithic fragments (mainly phyllite and schist), while feldspars are minor.

Sandstones of the Lercara complex are variable in composition and suffer the marine imprinting. Here, quartz-rich sandstones, hybrid arenites and calclithite include abundant extrabasinal carbonate fragments, metasedimentary lithic fragments, and intrabasinal carbonate grains. Primary volcanic and volcaniclastic layers are interbedded with sandstone.

Sandstones of the Rio Su Luda and Mulargia formations display a more variable composition range, from quartzolithic to lithic with diverse amount of volcanic and metamorphic lithic fragments. Metasedimentary lithic fragments are abundant and derived from schist and phyllite basement rocks occurred in Sardinia and Corsica, whereas abundant volcanic lithic fragments are mainly derived from active Late Paleozoic volcanism widespread in Sardinia.

Permian sandstone detrital modes of the three key areas within the central Mediterranean region, are typical of quartzolithic to lithic, hybrid arenite and calclithite, that should be related to the erosion of the recycled orogenic section of Cambrian-Carboniferous rocks, with most of metasedimentary and sedimentary rocks occurring in Calabria-Peloritani, southern Alps, Sardinia-Corsica and in internal domains of the Circum-Mediterranean orogens. Furthermore, volcanic signature in the Sardinian basins demonstrate an active volcanic activity during late early Permian.

# Interpreting provenance relations from detrital modes of Circum-Mediterranean sandstones in relation to tectonic setting

Critelli S.*

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* salvatore.critelli@unical.it

*Keywords:* Circum-Mediterranean Orogens, provenance analysis, paleogeography and paleotectonics.

The composition and stratigraphic relations of clastic strata in diverse sedimentary basins of the circum-Mediterranean region reflect a complete record of provenance relations since break-up of Pangaea, neo-Tethyan rifting, and subsequent plate convergence between the two major plates of Europe and Africa, and other related microplates of Iberia, Adria and Mesomediterranean microplate (Critelli, 2018).

Since plate reorganization after the breakup of Pangea, at the end of Paleozoic-earliest Mesozoic, clastic wedges filled sedimentary basins within geodynamic settings evolving from continental rifts, rifted-continental margins, protoceanic basins, arc-trench systems, remnant ocean basins, proforeland basin systems and back-arc basins within the circum-Mediterranean region (Critelli, 2018).

The changing nature of clastic particles in these clastic wedges reflect the provenance relations from different source rocks within the spatial and temporal evolving geo-puzzle terranes, including relations between ophiolite-bearing, uplifted continental crust (both shallow to deep crust terranes), volcanic and sedimentary (particularly carbonate strata) source rocks. Typical sand(stone) suites are quartzose, derived from flexured cratonal area, followed by quartzolithic and quartzofeldspathic derived from the growth fold-thrust belt (Critelli & Criniti, 2021). Mixed siliciclastic and carbonate shallow- to deep-marine clastic wedges are diffuse in many filled basin systems along the Circum-Mediterranean region (Critelli et al., 2007), as such as volcaniclastic sand(stone) may also occur interbedded with typical quartzolithic suites, in both remnant ocean basins and foreland basins.

The variable mosaic of source terranes within the Circum-Mediterranean region, because of elegant examples of proforeland sandstone suites, offered the possibility to investigate provenance relations in sandstones with a new plane of precision and sophistication, discriminating grain particles in clastic wedges using spatial (extrabasinal versus intrabasinal), and temporal (coeval versus noncoeval) distinction of detrital signals (Critelli & Criniti, 2021). The spatial/temporal approach in deciphering particles in clastic rocks has been widely used to detail the basinal dispersal pathways in different geotectonic settings, wherever mixed silicate and carbonate terranes act as the major source rocks, from rifted-continental margins to collisional orogens.

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# Sedimentological study of the worm reef along the Adriatic coasts

de Luca A.*[1], Lisco S.[1], Corriero G.[2] & Moretti M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Biologia, Università di Bari «Aldo Moro».

*Corresponding author e-mail:* alessia.deluca@uniba.it

*Keywords: Sabellaria spinulosa*, sedimentology, worm reef.

Reefs are more or less cohesive sedimentary bodies and can consist of a large number of species of organisms capable of directly forming a rigid structure through the production of calcium carbonate or through the aggregation of particles already present in the sedimentary environment.

The polychaetes of the genus *Sabellaria* are among the most common organisms capable of creating large bioconstructions in shallow marine environment called worm reefs.

In the Mediterranean sea the species *Sabellaria spinulosa* (Leukart, 1849) and *Sabellaria alveolata* (Linnaeus, 1767) are amply distributed and the presence of reefs formed by them is well documented also in Italy.

The importance of worm reefs consist of the dual role that they play: i) they are authentic natural breakwaters, ii) they create an ideal habitat for many species in environments characterized by low specific variability, increasing biodiversity.

In this work, we investigate the sedimentological and morphological features of different Sabellarian bioconstructions along the Apulian coasts. In particular, we compare textural and petrographic characteristics of the sands trapped into the structure with the sediments of the beaches. The methodological approach allows to analyse the structure at different observation scales to quantify the interaction between physical and biological processes which define the evolution of the bioconstructions. The textural and compositional analyses of sands trapped in the structure performed both directly and indirectly methods (by means of image analysis) improve the definition of the variability of the structure with high temporal resolution.

The investigations carried out allow us to observe the evolution over the time of the bioconstructions and to quantify the impact of the presence of these structures on the sandy beach environment. Defining the evolution and the morphology (at macro-, meso- and microscale) of these structures also allows us to understand how a complex system currently so widespread on all latitudes is still so little known today in the fossil record documentation. Finally, the study highlights the connection between the ecosystems and the coastal environments.

# Serravallian-Tortonian buried stratigraphy of Crotone basin: sedimentary and compositional evolution

Falsetta E.*, Criniti S., Civitelli M., Pugliese E. & Borrelli M.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* ettore.falsetta@unical.it

*Keywords:* Stratigraphic reconstruction, provenance and diagenetic analysis, basin modeling.

The starting phase of the Crotone Basin infill is recorded by a siliciclastic Serravallian–Tortonian cycle, reliable both on outcrop and in the subsurface. In this study, a total of 16 well logs, located both onshore and offshore, were analysed to evaluate the stratigraphical and sedimentological variations along transects of 60 km (N-S) and 27 km (W-E), which entirely cover the area of Crotone Basin with more than 3.700 m in depth.

The studied Serravallian-Tortonian cycle starts with the San Nicola dell'Alto Fm., dominantly composed of arenites and conglomerates, testifying an alluvional to coastal depositional environment. In the studied wells, the San Nicola dell'Alto Fm. is commonly found at depth spanning from 897 m to 2.976 m, in the diverse wells, and shows a constant thickness of ca. 300 m in average, with a maximum of 468 m in the southernmost portion of the basin and a minimum of 32 m in its central part. The San Nicola dell'Alto Fm. passes upward to the Ponda Fm. (detectable between 780-2.570 m in the diverse wells), dominantly characterized by claystones, marly mudstones and secondly by sandstone levels, indicating a deep marine pelagic depositional environment interested by frequent turbiditic sedimentation. The Ponda Fm. shows extreme variation in thickness, with a maximum of ca. 1.147 m in the northernmost part of the Crotone Basin and a minimum of 37 m in its southernmost part. The allochthonous Cariati Nappe, that cut the upper part of this sedimentary cycle, is not fully intersected by the studied well logs unless its siliciclastic turbiditic portions.

The sandstone levels both found in the recovered cores were analysed through a sandstone modal analysis in order to evaluate their composition and to correlate them with their outcrop counterparts. The base of the basin shares a quartzolithic input that becomes quartzofelspathic upward (Cariati Nappe). Sandstone addressable to San Nicola dell'Alto and Ponda formations reveal quartzofeldspathic suites. In particular quartzolithic sandstone (Q52 F5 L42) has abundance of extrabasinal carbonate grains, argillite and low metamorphic fragments. While moving to quartzofeldspathic sandstone (Q50 F40 L10), lithic variability types are still kept, but lower than feldspar and quartz input that increase rapidly upward.

Diagenetic features of San Nicola dell'Alto and Ponda formations do not share a deep compaction and cementation, unless some samples that show early carbonate cementation, and rarely replacement and dissolution. Samples were all stained and coloured to well appreciate porosity that suffer a reduction with depth. These data are processed with a digital method for a next implementation in GIS environment to create a 3D model of compositional and diagenetic variation along the basin.

# Provenance of repurposed building stones in the historical town of Rende (Cosenza, Italy)

Fiorenza E.*[1], Criniti S.[2] & Le Pera E.[2]

[1] Dipartimento di Culture, Educazione e Società, Università della Calabria, Rende (CS). [2] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* elia.fiorenza@unical.it

*Keywords:* Architectural stones, provenance, palaeochristian age.

Archeological proofs of the paleochristian age in modern Calabria are very few. Painting, goldworking and bronze artifacts are very few. This dearth of artifacts is related to the high historical seismicity of the southern Italy and to a depletion controlled by conflicts that led to worse life conditions. The first evidence of paleochristian art in Calabria is represented by damaged items such as silver and bronze rings belonging to the Marquis Gallo of Castrovillari (Lipinsky, 1966), currently missing. In the historical churches of Rende town (Cosenza) some stony sherds are attributable to the early Christian age. Specifically, these are represented by an arcade made up of calcarenite, a gravestone of early middle age, and some marbled tombstones belonging to the local aristocracy. This research is an attempt to reconstruct the provenance and use of these architectural stones.

Lipinsky A. (1966) - Oreficeria e minuterie paleocristiane ed Italo Bizantine in Calabria. In: Atti del IV Congresso Storico Calabrese, 321 pp.

# Grain size control on mineralogy and geochemistry in quartz-rich sandstones

Fornelli A.* & Micheletti F.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* annamaria.fornelli@uniba.it

*Keywords:* quartzarenites, grain size control, industrial use.

Numidian quartz-rich sandstones collected from a reconstructed section along the Apennine chain of Southern Italy (Pietragalla Village, near Potenza), have been studied for their textural, petrographic and geochemical characteristics to test their potential industrial use. The sandstones are sub-arkoses and quartzarenites and the petrographic features point to a high compositional maturity, whereas the abundant matrix, irregular contour of the grains and poor sorting point to an immature texture. Whole rock chemistry is characterized by high $SiO_2$ values (94 wt% in average) and low amounts of contaminant elements such as CaO (0.1 wt%), MgO (0.08 wt%), $Fe_2O_3$ (0.75 wt%), $TiO_2$ (0.2 wt%), Y (5-2 ppm) and Zr (180-66 ppm) due to the absence of carbonate components (cement and lithics) and scarce presence of clay-ferruginous cement and heavy minerals. These sandstones show a good potential vocation to be used in the glass industry. However, the coloring element contents are too high for clear or optical glass production (reference values in Fornelli & Micheletti, 2021). They are suitable as raw material for colored glass, insulating fibres, foundry molds or air Crete. With the aim of assessing the possible improvement of chemical characters, four granulometric fractions (A< 63 µm, B 63-125 µm, C 125-250 µm and D >250µm) from six samples were analyzed for their major chemical elements. Fractions C and D show enrichment in $SiO_2$ (about 95.5 wt%) and low contaminant contents ($Fe_2O_3$=0.68-0.35%, $Al_2O_3$=2.56-1%, MgO=0.09-0.02%, CaO=0.1-0.03%), they are the most suitable for a vitrifiable mixture (coloured glass).

Fractions A and B result less suitable in glass industry for their chemical characteristics having low silica contents ($SiO_2$=93.5–84%) and high contaminants ($Fe_2O_3$=2-0.6%, MgO=0.4-0.1%, CaO=0.8-0.1%, Y=37-5 ppm and Zr=1550-180 ppm). In order to use all the fractions, a mixing in appropriate proportions of A and B fractions previously cleaned from clays, heavy minerals and iron hydroxides, could be used as raw material for the paint industry. These data clearly confirm the grain size control on mineralogy and geochemistry in studied quartz-rich sandstones. In the bulk samples, the element concentration is controlled mainly by the matrix of the sample, in particular the weight % of fraction A. The granulometric partitioning analysis point out the role of particle size in the enriching of some trace elements. Finest fraction (A) registers highest concentrations of Rb, Sr, Y, Nb and, in particular, Zr (with enrichment up to 6-15 times) with respect to sand-dominant fractions.

The obtained results prospect a complete exploitation of the sandstones in the manufacturing industry, reducing waste materials and enhancing the economic value of these lithic resources from southern regions of Italy.

Fornelli A. & Micheletti F. (2021) - Evaluation of Numidian quartz sandstones from southern Italy for industrial applications. Acta Geodyn. Geomater., 18(4), 473-485. https://doi.org/10.13168/AGG.2021.0034.

# Late Paleogene trench-slope syn-sedimentary volcaniclastic turbidites of the Candela Stream (Southern Italy). New constrains for the geodynamics of the Southern Apennine in the Central Mediterranean

Gallicchio S.*, Cerone D., Fornelli A., Maiorano P. & Micheletti F.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* salvatore.gallicchio@uniba.it

*Keywords:* volcaniclastic turbidites, U-Pb zircon ages, late Paleogene.

Stratigraphy, sedimentology and petrography of deep-sea turbidite deposits are classical tools used to investigate timing and evolution of the Southern Apennine Orogen (e.g., Critelli et al., 2018 and r.t.). In the last decades several geodynamic models have been provided, nevertheless some questions are still unsolved: i) beginning of the westward Apennine subduction; ii) type of syn-orogenic basin system and iii) timing and distribution of calc-alkaline volcanic activity in the Central Mediterranean (e.g., Guerrera et al., 2019 and r.t.). A lithostratigraphy and facies re-examination of the most representative succession of the Tufiti di Tusa along the Calabria-Basilicata boundary (Cerone et al., 2017) added new depositional details on one of the inner turbidite succession of the Southern Apennines, and promoted new petrographic, bio- and chronostratigraphic studies which have yielded crucial information on the sedimentation age, sediment pathway and paleogeography.

The study section crops out along the Candela Stream (south of Rotondella Village, S. Italy) and represents an excellent field example of eastward-migrating ponded basin developed in front of the westward subducting oceanic/transitional Ligurian Tethys lithosphere (Adria Plate). The source area was represented by Hercynian and Alpine basements, Mesozoic sedimentary covers and Late Paleogene calc-alkaline volcanic centres. U-Pb spot ages detected on detrital and euhedral zircons from syn-sedimentary volcaniclastic sandstones is about 33±1 Ma (Fornelli et al., 2020); moreover, new calcareous nannofossils biostratigraphic data allowed to refer the study succession to the late Eocene–early Oligocene. These results allow to correlate the study succession with other volcaniclastic turbidite successions of the Northern Apennine (Val d'Aveto, Petrignaccola and Ranzano formations), and to suggest the presence of an eastward-migrating trench-slope system in front of a volcanic arc, discontinuously developed from south to north in the late Paleogene central Mediterranean region.

Cerone D., Gallicchio S., Moretti M. & Tinterri R. (2017) - Vertical facies evolution of the Tufiti di Tusa Formation cropping out in the Lucanian Apennines (Southern Italy). Jour. of Med. Ear. Sc., Spec. Sect. of XIII Geosed Cong., 9, 109-112.

Critelli S. (2018) - Provenance of Mesozoic to Cenozoic circum-Mediterranean sandstones in relation to tectonic setting. Earth Sci. Rev., 185, 624-48.

Fornelli A., Gallicchio S., Micheletti F. & Langone A. (2020) - Preliminary U-Pb detrital zircon ages from Tufiti di Tusa Formation (Lucanian Apennines, Southern Italy): Evidence of Rupelian volcaniclastic supply. Minerals, 10(9), 1-24.

Guerrera F., Martín-Martín M. & Tramontana M. (2019) - Evolutionary geological models of the central-western peri-Mediterranean chains: A review. Int. Geol. Rev., 1-22.

# Provenance of the Lower-Middle Jurassic successions of the Prerif foreland basin (Rif chain, Morocco)

Kairouani H.*[1], Fornelli A.[2], Micheletti F.[2], Abbassi A.[1-3], Zaghloul M.N.[1], Critelli S.[4] & EL Mourabet M.[5]

[1] Research Team in Natural Risks, Abdelmalek Essaadi University, Tetouan (Morocco). [2] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [3] Dipartimento di Scienze, Università di Roma Tre. [4] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [5] Laboratory of LR3G, Abdelmalek Essaadi University, Tetouan (Morocco).

*Corresponding author e-mail:* annamaria.fornelli@uniba.it

*Keywords:* provenance of sediments, Rif Chain, Morocco.

This study deals with the petrographic and chemical features of the Lower-Middle Jurassic sedimentary successions of the Prerif Foreland basin forming a part of the external Domain of the Rif chain. The collected data provide new insights on provenance and sorting/recycling processes, contributing to define the geodynamic setting. Four sandstones and fifteen marl/clay samples were collected from Jbel Zerhoune, Dhar Nsour I and II, and Jbel Outita stratigraphic sections. Chemical analysis of sandstones and mudrocks were performed using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and X-Ray Fluorescent (XRF).

The Lower-Middle Jurassic sandstones are feldspathic litharenite, litharenite and lithic arkose. The petrographic characters reveal a provenance from medium to high-grade metamorphic rocks located on Transitional Continental block or recycled orogen.

The chemical composition indicates that they are relatively close to the composition of Post-Archean Australian Shales (PAAS) except for MnO, $Na_2O$, Zr, Hf, and REEs showing a degree of depletion while CaO and Sr are enriched.

Many discriminant diagrams (e.g., Cr/V vs. Y/Ni, Cr/Th vs. Th/Sc, La/Sc, Th/Sc, Th/Co, Th/Cr, Cr/Th ratios) were used to indicate the provenance of sediments, the mechanical sorting, the sediment's maturity and the geodynamic setting.

Th/Sc vs Zr/Sc and $Al_2O_3$-Zr-$TiO_2$ diagrams together with the relatively high values of the compositional variability index (ICV) suggest a weak recycling and poor mechanical sorting of sediments indicating that the deposits are related to first-cycle immature sediments formed by un-weathered detrital minerals.

The main results reveal that the Lower-Middle Jurassic sediments derived from felsic rocks located in the western Meseta promontory in the hinterland belt (El Hadi et al., 2014; El Haibi et al., 2021) and, probably, also, from exhumed gabbroic rocks of the Mesorif dated at 200–192 Ma (Gimeno-Vives et al., 2019, Haissen et al., 2021).

The geodynamic setting of the sedimentation basin in which the Lower-Middle Jurassic sediments were deposed could be located in correspondence of a passive margin along the northern African margin's affected by rifting/drifting tectonism.

El Hadi H., Tahiri A., Simancas F., Lodeiro F.G., Azor A. & Poyatos D.M. (2014) - Pillow Lavas of Rabat (Northwestern Moroccan Meseta): Transitional Geochemical Signature of Magmas set up in an Early Ordovician Extending Platform. European Journal of Scientific Research, 122(1), 45-57.

El Haïbi H., El Hadi H., Pesquera A., Tahiri A., Poyatos D.M., Zahour G., Mehdioui S. & Tahiri. M. (2021) - Geochemical and Sr–Nd isotopic constraints on the petrogenesis of the Tiflet granitoids (Northwestern Moroccan Meseta): geological implications. Journal of Iberian Geology. https://doi.org/10.1007/s41513-020-00156-7.

Gimeno-Vives O., Mohn G., Bosse V., Haissen F., Zaghloul M.N., Atouabat A. & Frizon de Lamotte D. (2019) - The Mesozoic margin of the Maghrebian Tethys in the Rif Belt (Morocco): Evidence for polyphase rifting and related magmatic activity. Tectonics, 38. https://doi.org/10.1029/2019TC005508.

Haissen F., Zaghloul M.N., Dilek Y., Gimeno-Vives O., Mohn G., Cambeses A., Frizon de Lamotte D. & Bosse V. (2021) - Geochemistry and Petrogenesis of Lower Jurassic Mafic Rock Suites in the External Rif Belt, and Chemical Geodynamics of the Central Atlantic Magmatic Province (CAMP) in Northwest Morocco. Journal of Geology, 129(5). https://doi.org/10.1086/716499.

# A possible "green house" to "ice house" paleoclimate transition during Middle-Late Jurassic in the northern African margin (Prerif–Mesorif sub-domain, external Rif, Morocco): preliminary results from elemental geochemistry

Kairouani H.[1], Fornelli A.[2], Micheletti F.[2], Abbassi A.[1-3], Zaghloul M.N.[1] & Critelli S.*[4]

[1] Research Team in Natural Risks, Abdelmalek Essaadi University, Tetouan (Morocco). [2] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [3] Dipartimento di Scienze, Università di Roma Tre. [4] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* salvatore.critelli@unical.it

*Keywords:* geochemistry, paleoweathering, paleoclimate, Prerif, Mesorif Rif Chain, Morocco.

This work deals with the foreland basins Jurassic siliciclastic and hybrid deposits belonging to the Prerif and Mesorif sub-domains of the external Rif Chain. We used major geochemical elemental proxies using X-Ray Fluorescent (XRF) on mudrock and marl suites to assess paleoclimate in the northern African margin during Early-Late Jurassic and to reconstruct the paleoweathering, paleo-precipitations, and paleotemperatures conditions in the source area. These samples have been examined for geochemical analysis of the fine-grained from Domerian-Bajocian and Bathonian-Oxfordian of the Prerif and Mesorif successions, respectively.

The Prerif and Mesorif marls/mudrocks are enriched in $Al_2O_3$, $Fe_2O_3$, CaO, and $SiO_2$. The Chemical index of alteration CIA values ranges between 49% to 77% for Prerif and 44 to 91% for Mesorif.

Different climofunctions to assess paleorainfall (Mean Annual Precipitation: MAP1, MAP2, and MAP3), paleotemperatures, and paleohumidity (Sheldon, 2002; Nordt & Driese, 2010) were used to reconstruct the source area(s) paleoclimate conditions.

The obtained MAP clusters vary between 887, 809, and 841 mm/year for the Domerian–Toarcian, Toarcian-Bajocian, and Bathonian-Oxfordian, respectively. The Main Annual Temperatures (MAT) clusters (Sheldon, 2002) evolve from 12.7°C to 13°C for the Domerian-Toarcian, and Toarcian-Bajocian. They vary from 13,8°, 11,9° to 14.45° for the Bathonian, Callovian, and Oxfordian.

The CALMAG weathering index (Nordt & Driese, 2010) used here to assess paleorainfall and soil moisture regimes; indicates Ustic- Udic soil moisture regime (57 to 68) for Domerian-Aalenian and turn to Ustic conditions in the Bajocian (50 averagely). The Bathonian-Callovian and Oxfordian samples display Udic conditions (63.6 averagely). The moisture regime of the Middle to Late Jurassic indicates Ustic and Udic paleosols developed under moderate to high humidity conditions.

These results are compatible with the warming Toarcian Oceanic Anoxic Event (TOAE) starting from the Domerian and match the global sea-level rise (Haq, 2017). It may correspond to a greenhouse climate state (Holz, 2015) triggered by the onset of global seafloor spreading and related volcanic activity since the Middle Jurassic, which may have increased the $CO_2$ degassing. The Bajocian–Bathonian transition (around 168 Ma) may correspond to a severe onset of a major "cooling event" reaching the "Callovian Ice Age" explained by downthrows in $CO_2$ concentrations and known as the "Icehouse" event (see Bodin et al., 2020) before to rewarm again since the late Oxfordian synchronously with an evident global rise of the sea level until the Late Jurassic (Tithonian).

Bodin S., Mau M., Sadki D. & Danisch J. (2020) - Transient and secular changes in global carbon cycling during the early Bajocian event: Evidence for Jurassic cool climate episodes, Global and Planetary Change. https://doi.org/10.1016/j.gloplacha.2020.103287.

Haq B.U. (2017) - Jurassic Sea-Level Variations: A Reappraisal. GSA Today, no. 1.1.

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Nordt L.C. & Driese S.D. (2010) - New weathering index improves paleorainfall estimates from Vertisols. Geological Society of America Bull. 38, 407-410.

Sheldon, N., Retallack, G., and Tanaka, S., 2002, Geochemical climofunctions from North American soils and application to paleosols across the Eocene-Oligocene boundary in Oregon: Journal of Geology, 110, 687-696.

# Sand provenance of Le Dune and Torre Guaceto beach (Southern Italy)

Lapietra I.*[1], Lisco S.[2], Milli S.[2] & Moretti M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* isabella.lapietra@uniba.it

*Keywords:* sand provenance, sedimentary dynamics, pocket beach.

The sandy littoral sectors of the Apulia Region (Southern Italy) show a large textural and compositional variability of the beach sands characterizing the different sedimentary dynamics of the Ionian and Adriatic coastal areas.

The study areas include two Apulian pocket beaches (Torre Guaceto and Le Dune beach) which are representative of the coastal dynamics of a large sector of the central/northern Mediterranean Sea involving southern Adriatic Sea and northern Ionian Sea.

Torre Guaceto beach is a 1 km littoral stretch located on the Adriatic Sea. Beach sediments range between coarse and fine sands and they include siliciclastic minerals and carbonate granules. Le Dune beach is located along the Ionian Seaside and develops for about 800 m. Beach sediments range from very coarse to medium-fine sands and they are mainly made up of bioclast fragments. Both study areas are part of marine protected reserves which includes 15 different habitats of the typical Mediterranean submerged populations and the presence of Posidonia oceanica meadows.

Sedimentological, compositional and ecological investigations allowed describing the textural and petrographic characteristics of the beach sands by interpreting their sand provenance. The physical/biological interactions led us to analyse the beach sedimetary dynamics which is fundamental for pocket beach conservation. The sand compositional study highlighted the presence of mixed hybrid sands (terrigenous and bioclastic) and a longshore significant composition variability at Torre Guaceto beach, whereas the carbonate component (bioclasts more than 90% and lithics) represents the main element of Le Dune beach.

# Heavy minerals provenance in modern beach and fluvial sands of the Betic Cordillera (Spain)

Le Pera E.*[1], De Luca R.[1], Miriello D.[1], Pugliese E.[1] & Tangari A.C.[2]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* emilia.lepera@unical.it

*Keywords:* sand provenance, heavy detrital minerals, Betic Cordillera.

The Betic Cordillera is an uplifted thrust belt, consisting of several thrust units with several source rock types: metamorphic (low- to high-grade), mantle-exhumed rocks, sedimentary (carbonate, siliciclastic, and evaporite), and volcanic rocks. These rocks supply large amounts of detritus to the coastal and deep-marine environments of the Alboran Sea, a tectonically active collisional basin, located in the deformation region that marks the modern African and European plate boundary. The Betic Cordillera provides a natural laboratory for the examination of the effects of source lithotypes, climate, weathering, transport, and depositional environments on the composition of modern sands. Critelli et al. (2003) studied the main mineralogy of river and beach sands collected along the Mediterranean side of the Betic thrust belt between Almeria and Cadiz, recognizing three petrologic provinces, corresponding with the physiographic provinces of the Sierra de los Filabres, Sierra Nevada, and Malaga Mountains, and named:

1. Petrofacies A or Almeria–Malaga Province;
2. Petrofacies B or Marbella Province, and
3. Petrofacies C or Algeciras–Cadiz Province.

Only one sand sample is volcaniclastic (Cabo de Gata–Carboneras petrofacies), and it has been described without formal definition of petrographic province. Raman spectroscopy, combined with the polarizing microscope, allowed identification of different heavy minerals suites. The Petrofacies A is characterized by a heavy minerals suite including graphite+almandine, the Petrofacies B olivine+forsterite+chromite+diopside and the volcaniclastic petrofacies buergerite+hypersthene+almandine. Heavy mineral grains compositions, determined by Raman spectroscopy, provided additional information in separating the three petrological provinces. This tool conveyed identification of the clastic supply from minor source rocks, or with low Sand Generation Index (e.g., Palomares & Arribas, 1993), otherwise diluted and/or unrecognizable using only the $Q_mFL_t$ approach.

Critelli S., Arribas J., Le Pera E., Tortosa A., Marsaglia K.M. & Latter K.L. (2003) - The recycled orogenic sand provenance from an uplifted thrust belt, Betic Cordillera, southern Spain. Journal of Sedimentary Research, 73, 72-81.

Palomares M. & Arribas J. (1993) - Modern stream sands from compound crystalline sources: Composition and sand generation index. In: Johnsson, M.J. & Basu A., eds., Processes Controlling the Composition of Clastic Sediments: Geological Society of America, Special Paper, 284, 313-322.

# Textural and compositional evolution analysis of coastal sands (Lazio, Italy) as fundamental tool to plan a sustainable nourishment

Lisco S.*, Fornelli A., Micheletti F. & Moretti M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* stefania.lisco@uniba.it

*Keywords:* sand, textural analysis, compositional analysis.

The Tyrrhenian coast of Lazio (central Italy) is characterized by sandy beaches with a high compositional variability. This sector suffer from coastal erosion, partly linked to the reduction of the contribution of river sediments and has already been the subject of some nourishment works. Furthermore, this coastal sector is characterized by the widespread presence of bioconstructions built by the polychaete *Sabellaria alveolata*, which traps the sands already present in the environment. Such structures can play the role of sand reservoirs and interfere with the dynamics of the beaches. In general, reef worms defend the coast by decreasing the intensity of storm waves, offering a hard and more stable substrate to the beach and providing coarse and cohesive sedimentary material. Sabellaria seems to select sediments on the basis of their size, morphology and density.

This work shows the results of sedimentological and petrographic analyses of three different sites along this stretch of coast (both of the incoherent current beach sands and of those trapped in the worm reefs) and aims to define the relationships that regulate the distribution of these sediments in the environment of beach and along the entire coastal sector.

Selected sites are (from S to N): Sabaudia Seafront (SA, Latina), Lido dei Pini (LP, Anzio, Rome) and Torre Flavia (TF, Ladispoli, Rome).

The textural and sedimentological analyses were carried out both with standard procedures and through image analysis by specific software. The analyses contribute to understanding the sediment source areas that contribute to the dynamics of the beaches and the distribution of these sediments. In particular, the petrographic study define the sediment sources currently available in this area and compare them with the sands trapped and selected by the worms to build the bioconstruction.

The final segment of the Tevere (~80 km) crosses the volcanic rocks of the Roman Comagmatic Province and debris-alluvial rocks. Tevere introduces large quantities of debris into the Tyrrhenian Sea and the detritus is pushed along the Tyrrhenian coasts by superficial sea currents directed mainly towards the north (towards the Ligurian Sea).

SA sands are essentially characterized by clastic carbonate material and seem to be affected only minimally by the Tevere supply. LP sands are still affected by the local redistribution of Tevere debris, even if carbonatic detritus becomes more abundant. For TF sands the fundamental detrital contribution due to supplying of Tevere is evidenced by the abundance of alkaline volcanic rock fragments and their typical minerals (clinopyroxene, brown hornblende and leucite).

The definition of the sedimentary dynamics and the understanding of the sediment distribution from S to N between the different sites allows both to define the evolution status of the beach and to plan possible nourishment actions that protect both the beach environment and the ecosystem.

# Petrography and Geochemistry of post-Cretaceous Bauxite from Murge Area (Apulia, southern Italy): A Provenance Tool

Micheletti F.*, Festa V., Fornelli A., Tursi F. & Spalluto L.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* francesca.micheletti@uniba.it

*Keywords:* bauxite, mixed detrital supply, Apulia.

Petrographic and geochemical features of a post-Cretaceous bauxite deposit from the Murge area of Apulia (southern Italy) are presented and discussed with the aim of assessing the nature of its source material. Sampling derives from a geosite (Geosite CGP0043: "Vuotano Santiquando", Alta Murgia National Park) hosting a temporary pond in a depression at the bottom of an erosive dry valley. Samples were taken from a few-m thick stratigraphic succession showing unaltered limestones – calcite concretions - pisolithes - terra rossa soils.

The carbonate bedrock corresponds to the lower part of the "Calcare di Altamura" Fm, late Cretaceous in age, made up of limestones deposited in inner-shelf environments.

The alteration products are related to fractured bed-rock with more or less fibrous calcite concretions, and to non-cemented authigenic nodules (pisolithes) having 0.5-4.0 cm in size while the latest alteration products are represented by terra rossa soils.

Petrography, whole rock chemistry (major and some trace elements, XRF), semiquantitative mineral chemistry and micro-textural images (SEM) were collected from all samples.

Unaltered limestones consist of bioclastic wackestones and packstones made up of abundant rudist fragments, benthic foraminifers and calcareous algae. The fibrous concretions display red-coloured columnar calcite in which some crystals of silicate minerals can be observed. Nodules show a concentric growth with fibrous calcite in a ferruginous matrix containing detrital silicate grains as quartz, feldspar, zircon and monazite and some lithic fragments in which porphiric textures can be recognized. The terra rossa soils consist of extra fine red-brown grains.

A progressive enrichment in $TiO_2$ (0.00 - 0.25%), $Fe_2O_3$ (0.02 - 1.80%), $Al_2O_3$ (from 0.07 to 4.19%) and $SiO_2$ (from 0.12 to 6.52%) can be observed from unaltered limestone to pisolithes. The highest contents of these elements have been measured in terra rossa soils in which $TiO_2$ (1.36%), $Fe_2O_3$ (8.70%), $Al_2O_3$ (23%) and $SiO_2$ (50%) reach appreciable levels for an industrial use assessment. In particular the contents of $Al_2O_3$ are significant for the extraction capacity. The Zr contents (406 ppm) are quite high indicating high zircon concentration, known to contain high HREE amounts.

These preliminary data indicate that during the alteration process of limestones, under subaerial conditions, igneous and clastic materials were mixed with the residual products of calcareous dissolution. These petrographic evidences are consistent with the deductions of Mongelli et al. (2014, 2016) and Sinisi (2018) for other residual Apulia deposits (N to S: San Giovanni Rotondo, Spinazzola, Otranto). These authors on the basis of REE distribution, suggest that the parental material for the bauxite deposits was derived from a combination of clastic and magmatic materials coming from continental margin (northern Africa), and Carpatho-Balkan orogenic belt, respectively.

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# Provenance of Modern Sands from Baja California Rivers (Mexico)

Tangari A.C.*[1], Andò S.[2], Marinangeli L.[1], Riber L.[3] & Le Pera E.[4]

[1] Dipartimento di Scienze Psicologiche Umanistiche della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [3] Department of Geosciences, University of Oslo (Norway). [4] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* a.tangari@unich.it

*Keywords:* volcaniclastic sand, Baja California, heavy minerals.

Modern streams sand-sized sediments within a geodynamic context of a dissected magmatic arc, produced large volumes of volcaniclastic detritus in two basins of the Rosario segment in the Alisitos arc (Peninsular Ranges, Baja California Mexico) (e.g., Marsaglia et al., 2016). We investigate sandy sediment of the El Rosario, San Vicente, and San Fernando rivers, which lies in the central part of the Alisitos arc using high-resolution sand petrography, integrating light and heavy minerals compositional. These rivers are chiefly fed from erosion of a magmatic arc consist of minor feldspatho-lithic (Fl) to quartzo-litho-feldspathic (qFL) sand and dominant quartzo-feldspatho-lithic (qLF) and litho-feldspatho-quartzose (lQF) sand. Increasing degree of dissection is indicated by progressive increase in quartz, K-feldspar, sedimentary and metamorphic, and decreasing of volcanic lithic fragments. Sand, within the Lv field, microlitic (Lvmi), contains felsitic (Lvf), and lathwork (Lvl) types, and trace amounts of vitric grains (Lvv), such as pumice particles. Andesitic volcanic province of the Alisitos arc shed quartz-poor sand containing mainly microlitic lithic fragments and plagioclase, sand derived from more felsic rhyolites and rhyodacitic and trachyandesitic products contains largely felsitic volcanic lithics whereas minor lathwork lithics are mainly derived from subordinate basalts. The abundance of igneous rock fragments and volcanic and sedimentary lithics of the three studied rivers sand faithfully represents the relative abundance of a heterogeneous [volcanic+plutonic+sedimentary] bedrock exposure in each drainage basin. In the medium to fine sand of the drainage systems, the transparent heavy minerals suite includes mainly amphibole, pyroxene, epidote, titanite, zircon, and minor amount of staurolite, rutile, actinolite, tourmaline, garnet, and apatite. The main difference in composition is showed by San Fernando, river sand where minor andalusite, as well as sillimanite and kyanite, are also present. Specifically, San Fernando and San Vicente rivers are enriched in magmatic hornblende compared to the El Rosario river sands where an enrichment in metamorphic hornblende occur. Unstable heavy minerals such as hornblende and pyroxene show mainly from corroded to etched morphologies due to the diagenetic dissolution and semi-arid climate. Specifically, etched morphology characterizes mainly the pyroxene more than the amphibole. Zircon are mainly subrounded with some grains rounded observed in the San Fernando river sand suggesting sedimentary recycling. Therefore, sand composition typified by the heavy minerals reflect a mixed provenance characterized mainly from magmatic source rocks. Specifically, San Fernando and San Vincente river abundance and weathering textures match predominant volcanic bedrock lithologies and El Rosario sedimentary and metasedimentary source rocks.

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# S35.

# Field mapping and stratigraphy: significant insights from the geologic record


*Conveners and Chairpersons*

*Angelo Cipriani (Servizio Geologico d'Italia - ISPRA)*

*Simone Fabbi (Servizio Geologico d'Italia - ISPRA)*

*Chiara Zuffetti (University of Milano - La Statale)*

# Geological map of the Mt. Soratte ridge (central Apeninnes, Latium, Italy)

Artegiani F.*[1] & Fagioli G.[2]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* federico.artegiani@gmail.com

*Keywords:* geological mapping, Umbria-Marche-Sabina succession, Mt. Soratte.

The geological map here presented is the first detailed contribution to the Mt. Soratte area since the publication of the Geological Map of Italy at the scale of 1:100.000 (Sheet no. 144 "Palombara Sabina"). The Mt. Soratte ridge extends for about 5 km in the Tiber Valley with a NW-SE trend and is characterized by Meso-Cenozoic rocks of the Umbria-Marche-Sabina sedimentary succession. It represents the only relief between Sabini and Sabatini mts and has an altitude of 691 m a.s.l. These sectors of the Tethys Ocean were affected by the Hettangian/Sinemurian extensional phase, which dismembered a peritidal shallow-water carbonate platform (Calcare Massiccio Fm). This normal faulting led to the structuring of a complex seafloor architecture, made of horsts and grabens connected to each other by submarine escarpments (Centamore et al., 1971; Santantonio, 1994), and characterized by different sedimentation rates (Fabbi & Santantonio, 2012). In the late Tithonian these paleotopographic differences were smoothed out by the Maiolica Fm, despite with local exceptions. A geological mapping project covering the Mt. Soratte area and performed at a 1: 5000 scale allowed to collect a fresh dataset of tectono-stratigraphic information, revealing the presence of a Jurassic structural high in the village of Sant'Oreste, surrounded by basinal deposits; the latter onlap the Hettangian/Sinemurian escarpments. Further evidence for a Cretaceous post-rift extensional phases was identified in the study area, as testified by the unconformable stratigraphic contact of the Scaglia Rossa Fm. (preserved in discontinuous patches) on the Lower Jurassic deposits (Calcare Massiccio B member). The tectonic phase that allowed the latter stratigraphic relationship has also been recognized in the Mt. Cosce sector (Narni Mts.), around 20 km NW of Mt. Soratte (Cipriani & Bottini, 2019).

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# Mapping sedimentary and low-grade metasedimentary rocks: the Geologic Event approach

Barale L.[1], Bertok C.[2], d'Atri A.[2], Martire L.[2], Mosca P.[1] & Piana F.*[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* fabrizio.piana@cnr.it

*Keywords:* Geologic Event, sedimentary successions, metamorphism.

Sedimentary successions record the evolution of palaeogeographic domains and orogenic systems, which can be described referring to a sequence of Geologic Events (GeoEvents). The GeoEvents are preserved in the stratigraphic record in different ways, such as, unconformities, distinctive lithofacies, chronostratigraphic gaps, condensed successions, hardgrounds, paleoescarpments etc. The recognition of the GeoEvents gives a chance to correlate tectonic and paleoenvironmental processes at large regional scale across sedimentary basins and coeval orogenic belts (Piana et al., 2017; Mantovani et al., 2020). The GeoEvent concept is one of the main cornerstones of the Geologic Feature classification in the IUGS GeoSciML and INSPIRE (Data Specification on Geology) standard for geology, so it should drive the organization of the Map Legend and the design of the DataBase structure of the modern digital geological maps. The GeoEvent class has a specified geologic age and may have specified environments and processes. Even though the GeoEvent age can represent an instant in time and/or an interval of time, the GeoEvent approach can allow correlation between rock units of different geological domains, even if they were subjected to different, post-depositional, tectono-metamorphic conditions. Some examples of geologic correlation across the successions of syn-orogenic sedimentary basins and those scattered in coeval, adjacent orogenic belts are given, and a discussion on the scientific consistency of this approach is proposed.

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# Early to middle Eocene tectono-sedimentary evolution of the External Ligurian accretionary wedge (Northern Apennines): constraints from the geological mapping of different types of chaotic rock units

Barbero E.*[1], Festa A.[2], Catanzariti R.[3] & Fioraso G.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* edoardo.barbero@igg.cnr.it

*Keywords:* chaotic rock unit, geological mapping, tectono-sedimentary evolution.

Chaotic rock units are significant components of many exhumed subduction complexes around the world, representing mappable bodies at 1:25,000 or smaller scale, with a block-in-matrix fabric. Non-metamorphic chaotic rock units may form through tectonic, sedimentary, and diapiric processes or their interaction and superposition during distinct phases of the tectono-sedimentary evolution of subduction complexes. Observations on chaotic rock units around the world have documented different map-scale features and internal structural-stratigraphic architectures of the chaotic rock units in relation to both the processes and the tectonic setting of their formation. Consequently, detailed mapping and stratigraphic-structural analysis of chaotic rock units in exhumed subduction complexes are essential to reconstruct their tectono-sedimentary evolution. We present the results of geological mapping and multiscale structural and stratigraphic studies on the External Ligurian accretionary wedge in the north-western sector of the Northern Apennines (from the Monferrato to the Voghera sector, Italy), which consists of the tectonic and/or stratigraphic superposition of different types of chaotic rock units. The latter resulted from the interaction and superposition of both tectonic and sedimentary (mass wasting) processes that occurred and alternated during the early to mid- Eocene Ligurian Tectonic Phase. The timing of this deformation is well constrained by the unconformable deposition of the middle- to late Eocene – Miocene wedge-top Epiligurian succession, which is commonly bounded at the bottom by a regional-scale heterogeneous mass transport body with a block-in-matrix texture.

The geological mapping and the application of specific criteria (Festa et al., 2019 and references therein) to differentiate among different types of chaotic rock units with different block-in-matrix fabrics, and the relationships between tectonic deformation and stratigraphic unconformities, allow us to constrain the time and space tectono-stratigraphic evolution of the Ligurian accretionary wedge and the alternating of processes that characterized the Ligurian Tectonic Phase. Our findings demonstrate that the distinction of different types of chaotic units following diagnostic criteria is fundamental during the geological mapping, also with significant implications for the 1:50.000 scale CARG mapping project.

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# Balanced Cross-sections and 3D Geological Model of the Monte Fema area, Umbria-Marche Apennines (Italy)

Basilici M.*[1], Jablonská D.[1], Pedini M.[1], Spinaci A.[1], Pierantoni P.P.[1], Mazzoli S.[1] & Capotorti F.[2]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* matteo.basilici@gmail.com

*Keywords:* Apennines, balanced cross-section, 3D model.

The Monte Fema area is located within the 1:50,000 scale Sheet 325 "Visso" of the Italian Geological Map (CARG Project), in the Umbria-Marche Apennines. The fold and thrust belt in this area is crosscut by steep, dominantly extensional faults of various and debated origin, ranging from Jurassic to Neogene-Quaternary age (Mazzoli et al., 2005; Di Bucci et al., 2021; Santini et al., 2021). Normal faults may include both pre-thrusting (i.e., Mesozoic rift-related and Neogene forebulge/foreland flexure-related) and post-thrusting structures/ reactivations.

In this study we produced the first 3D geological model of the Monte Fema area in order to shed new light on the tectonic setting of this sector of the Apennine fold and thrust belt. The 3D model was built using Move software (Petroleum Experts) that allows to produce 3D surfaces by applying spline interpolation between a series of balanced geological cross-sections. The used dataset consisted in: (i) a high resolution stratigraphic and structural survey of the study area based on a topographic map 'CTR – 1:10,000', (ii) a 10 m cell size digital elevation model (DEM), (iii) seismic interpretation, and (iv) the hypocentre location and focal mechanisms of instrumental seismicity since 1985 (available from ISIDe and RCMT catalogues, INGV).

The balanced cross-sections and 3D structural model allowed us to show in a high-resolution visualization the articulated tectonic setting of the Monte Fema area. It permits to study the relation between thrust faults and normal faults of different generations (pre- and post-thrusting), thus providing useful insights into the tectonic setting of the entire Apennine fold and thrust belt.

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# A new record of Trubi Fm. from Trabia (North-western Sicily) and its significance

Bova P.[2], Contino A.[1-2], Esposito G.*[1-2] & Greco G. [3]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] Accademia Mediterranea Euracea di Scienze, Lettere e Arti, Palermo. [3] Freelancer Geologist, Palermo.

*Corresponding author e-mail:* espositogsp@gmail.com

*Keywords:* Trubi Fm, Lower Pliocene, North-western Sicily.

An unpublished Lower Pliocene outcrop (Trubi Fm), located in the village of Trabia (north-western Sicily) has been discovered. In early 2010, storm surges partially exhumed the sea cliff of Castello Lanza for a height of ca. 3-5 m. Sea storms have exposed, just above the sea level, for a maximum height of ca. 70 cm, white marl and marly limestone bearing calcareous plankton (Trubi Fm). The abundant planktic assemblage is characterized by the occurrence of *Globorotalia margaritae* and *Gt. puncticulata* (MPl3 Zone - Cita, 1975 emended by Sprovieri, 1992). The Trubi contain an abundant clastic fraction of quartz, sourced by the quartzarenites of the Numidian Flysch (Upper Oligocene-Lower Miocene, outcropping in the nearby localities of S. Rosalia and Calvario). Trubi chalks are truncated at the top by an unconformable sub-horizontal surface, covered with polymictic conglomerates and siliceous arenites (Upper Pleistocene, Barcarello Synthem - see Di Maggio et al., 2017). This important outcrop is completely missing in the previously published official cartography (CARG project, see Catalano et al., 2011). The study of the old photos (early 20$^{th}$ century) of the site proved to be an investigative tool of primary importance that allowed a precise reconstruction of the geometry and lateral continuity of the chalk outcrop and its relationship with the stratigraphically overlying Upper Pleistocene deposits. The hitherto unknown Pliocene outcrop of Trabia constitutes a new element to reconstruct the urban geology of this village. Moreover, it is a further important tessera that is added to the complex mosaic of the Pliocene outcrops that border the coastal sector of the Gulf of Termini Imerese.

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# The Sciliar formation and its subunits: a tricky matter for mapping geology

Caggiati M.*, Gianolla P. & Riva A.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* marcello.caggiati@unife.it

*Keywords:* Sciliar, Southern Alps, middle Triassic.

The Sciliar dolomite (Schlerndolomit) is one of the most known stratigraphic units of the Mesozoic sedimentary cover of the Southern Alps. It was identified and described for the first time by von Richthofen in 1860 in the Dolomites and since then, it has been thoroughly studied both in the XIX and XX centuries.

The name of the lithostratigraphic unit in cartography has changed several times up to the last decades, when the use of "Sciliar formation" has been adopted in official geological maps. The unit is related to Middle Triassic high-relief carbonate platforms and is mainly composed by dolostones, even if it can also consist of limestones and dolomitic limestones in some confined zones of the Dolomites (mapped sometimes as Calcare della Marmolada). Two main lithofacies characterize the unit: well-bedded inner carbonate platform, peritidal facies and massive to clinostratified, platform margin to slope facies. In several places of the western Dolomites this repartition is clearly visible, such as in the Sciliar/Schlern, Catinaccio/Rosengarten and Latemar massifs.

In the Italian Geologic Map - 1:50000 scale CARG Project, the Sciliar formation has been officially reported at first in areas west to the Adige Valley, where it basically consists of horizontally, well-bedded dolostones. This led to consider the main unit as composed by inner platform facies, and to include massive and slope facies in a secondary lithofacies. However, this classification contrasts with what can be seen in the Dolomites, where inner platform facies are very few in terms of total volume of the formation and map coverage, and it wasn't applied in the Geological Sheet 029 "Cortina".

Furthermore, since the 90's it has been outlined that the Sciliar formation can be subdivided in a pre-volcanic and a sin/post-volcanic portion: this distinction, not present up to now in the official map, is easy to apply where volcanic and volcanoclastic products related to the late Ladinian magmatic paroxysm are common, while it is more difficult in other places, where platform bodies seem often vertically merged. However, it can be still applied based on etheropic relationships with basinal formations and on peculiar sedimentological patterns of carbonates.

With the publication of the new Geological Sheet 046 "Longarone", a revision of the hierarchization of the sub-units and lithofacies of the Sciliar formation has been proposed, aiming to solve these issues and to become a standard in new geological maps. The single lithofacies (inner platform and slope) represent two sub-categories of the main unit, that should be used only when tectonization and dolomitization prevent the distinction of facies. When recognizable, the syn/post-volcanic portion of the formation must constitute a member of the main unit. Additionally, a peculiar lithofacies has been described, as constituted by sediments deposited in a restricted, intra-platform basin.

# Tectono-sedimentary evolution of Central-Northern Apennines in the geologic record of 348 "Antrodoco" and 337 "Norcia" Sheets

Capotorti F.*, Marino M. & Muraro C.

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* maurizio.marino@isprambiente.it

*Keywords:* Apennines, geological mapping, synsedimentary tectonics.

The Geological Survey of Italy carried out the mapping of the sheets 348 "Antrodoco" and 337 "Norcia" of the Italian Geological Map (CARG Project). The geological mapping associated with multidisciplinary analysis, including biostratigraphy, sedimentology and structural geology, allowed new constrains and insights for a better reconstruction of the tectono-sedimentary evolution of a wide part of the Central-Northern Apennines.

Emphasis is on the role of detailed stratigraphy in identifying and defining the characteristics and timing of several synsedimentary faults related to six extensional tectonic phases (Early Jurassic, Bajocian, Turonian-Coniacian, late Paleocene, late Eocene and Late Miocene) before the Late Miocene-Pliocene p.p. orogenic compression and the following -Quaternary extension.

These tectonic phases are linked to different geodynamic regimes involving contiguous paleogeographic domains (carbonate platforms and pelagic basins) well identified in the studied areas. Paleotectonics is currently recognized on the basis of repeated drowning of parts of the Apenninic carbonate platform as well as back-stepping of its margins, and by variations of the platform-derived detrital supply in adjacent basins.

The well-known Early Jurassic Tethyan rifting caused the drowning of a part of a huge carbonate platform, generating the long-lasting Latium-Abruzzi Platform and the Umbria-Marche-Sabina and Gran Sasso basins, hosting pelagic carbonate platforms (PCPs) identified by condensed Jurassic p.p. successions. The Bajocian tectonics probably represents a far-field effect of the onset of spreading in the Piedmont-Liguria Ocean. In the NW sector of the L-A platform the M. Giano PCP was created, newly catch up by Tithonian shallow water facies. The Late Cretaceous and Paleogene tectonic phases were probably related to the opening of the southern Atlantic Ocean. They caused, along with eustatic and biological factors, the final drowning of the NW portion of the L-A Platform and the creation of a complex paleotopography, with the previous margin and inner carbonate platform draped by "condensed scaglia" and onlapped by typical basinal "scaglia". The Late Miocene extensional tectonics, related to the peripheral bulge flexuration, often produced the maximum throws, and is mainly documented by anomalous contacts within the carbonate succession. During this phase also confined foredeep basins (e.g., Antrodoco basin) were created, evidenced by the relationships between the siliciclastic deposits and the previous carbonate units.

During the Late Miocene-Early Pliocene compression, the preceding extensional faults were variously translated, rotated, segmented or positively inverted.

Finally, the Pliocene-Quaternary extensional tectonics could reactivate inherited faults.

The identification of synsedimentary tectonic phases and related faults and of their timing and throws allows to separate and correctly evaluate deformation and dislocation due to the orogenic and to the post-orogenic evolution.

# The continental Quaternary of the 337 Norcia and 348 Antrodoco Geological Sheets: new insights and cartographic implications

Chiarini E.* & Papasodaro F.

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* edi.chiarini@isprambiente.it

*Keywords:* intermontane basins, stratigraphic units, Central Apennines.

The complex interaction between climatic changes acting on a global scale, effects of regional uplift, setting and evolution of hydrographic network, and more local factors, first of all, the activity of border faults imply that Quaternary sedimentary successions cropping out in intermontane basins record distinctive evolutionary histories that make each basin unique and different from all the others.

Stratigraphic studies suggest many basins originally experienced endorheic and lacustrine conditions. In some case, the endorheic-exorheic transition, related to the balance between sedimentation rate and basin subsidence induced by border-fault activity, had been yielding a progressive connection along drainage lines or valleys parallel to the strike of the main faults, as in the case of the intermontane basins of the Aterno river valley. Consequently, part of the sedimentary records has been eroded giving rise to several significant stratigraphic unconformities. In extreme case, a deep downcutting of the basin-fill deposits exposed the whole sedimentary succession. In contrast, other basins experienced a long period of sedimentation and still remain substantially undissected or preserve endorheic conditions. The occurrence of these deferred in time events has created stratigraphic architectures that change from basin to basin, sometimes indecipherable without planning geognostic surveys, due to critical outcrop conditions.

In the first Geological Sheets of the CARG Project carried out in Central Italy, published more than 15 years ago, where cartographic synthesis criteria prevailed, the continental stratigraphic sequences of the lower and middle Pleistocene were often referred to few main unconformity-bounded stratigraphic units extended to vast territories, and to several sedimentary basins delimited by regionally extensive discontinuities.

However, the improvement of the knowledge framework achieved by scientific research through the survey of new sheets of the Geological Map has led to more accurate stratigraphic reconstructions and has required more refined distinctions within the main units.

In this perspective, with the support of subsoil data, radiometric datings, paleomagnetic, palynological, and tephrostratigraphic studies, the detailed surveys carried out for the 337-Norcia and 348-Antrodoco Geological Sheets have provided new chronological constraints on the Quaternary sedimentary sequences, have allowed to define the main steps of the Quaternary basin evolution and partially to overcome the lack of stratigraphic markers, but have led to the definition of unit successions that are different from basin to basin.

Some examples taken from the wide series of case studies contained in the two Geological Sheets, relating to intermontane basins in distinctive evolutionary stages, will be illustrated and compared, with the aim of providing useful insights and discussion topics for the purposes of the new Geological Cartography Project.

# Closing the "Monte delle Fate" and "il Casone" tectonic windows: new insights from the CARG project 364-Bracciano

Cipollari P.*, Abbassi A. & Cosentino D.

Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* domenico.cosentino@uniroma3.it

*Keywords:* geological mapping, stratigraphy, olistostrome.

According to different authors (Fazzini et al., 1972; Funiciello & Parotto, 1989), some Meso-Cenozoic carbonate rocks, with Tuscan affinities, crop out in tectonic windows of the overlying allochthonous "Flysch della Tolfa" (External Ligurian Unit), to NE of Santa Severa (RM). These carbonate rocks are mainly referable to the Calcare Massiccio, Calcari selciferi, and Scaglia Toscana. A different interpretation on the relationship of these carbonate rocks with the overlying succession ("Flysch della Tolfa") was previously suggested by Bertini et al. (1971). These authors indicated that the Calcare Massiccio and the Calcari selciferi cropping out in Bagni, il Casone, and Monte delle Fate are the substratum of the "Flysch della Tolfa", which transgressively overlies the Meso-Cenozoic formations with Tuscan affinities.

Recently, field work for the geological survey of the CARG Project 364-Bracciano, carried out in the area between Monte delle Fate and Bagni (Pian della Carlotta, Cerveteri, RM), provided new insights into the relationships among the Meso-Cenozoic carbonate rocks and the "Flysch della Tolfa". In the "il Casone" and "Monte delle Fate" areas, the stratigraphical and geometrical evidence observed in the field, enhanced by drone high-resolution images, point to different and disordered blocks of carbonates, mainly made of Calcari selciferi and Scaglia Toscana, within a highly deformed argillaceous matrix. The Calcari selciferi from "il Casone" consist of different-sized blocks of grey limestones, with both oolitic and micritic textures, containing large spicules of sponges, bivalves, gastropods, and ammonite embryos. In a different area of "il Casone", disordered blocks of limestones and marly limestones are mainly from Upper Cretaceous and Upper Paleocene-Lower Eocene Scaglia Toscana Fm. In addition, calcareous nannofossils assemblages from the highly deformed argillaceous matrix show the occurrence of *Reticulofenestra umbilicus*, pointing to an age not older than 43 Ma (Lutetian, Middle Eocene).

In conclusion, field work, high-resolution images by drone, and analyses on the calcareous nannofossils assemblages point to interpret the disordered blocks of Calcari selciferi and Scaglia Toscana within a highly deformed argillaceous matrix as a part of a huge Middle Eocene sedimentary mélange (olistostrome) in the stratigraphy of the External Ligurian sedimentary basin.

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# Geology of the high Tenna Valley (Sibillini Mts): Mesozoic paleotectonics and its control on the orogenic deformations

Cipriani A.*[1] & Curzi M.[2]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

*Corresponding author e-mail:* angelo.cipriani@isprambiente.it

*Keywords:* Tethyan rifting, Jurassic inheritances, rheological contrasts.

The high Tenna Valley (Marche) offers the possibility for an in-depth reconstruction of (i) the Meso-Cenozoic tectono-sedimentary evolution of central-northern Apennines and (ii) the role played by stratigraphic and paleotectonic inheritances on the development of orogenic thrusts. Here, Jurassic to Miocene rocks of the Umbria-Marche-Sabina succession are spectacularly exposed at the hanging wall of the Sibillini Mts Thrust. A Jurassic rift-related pelagic carbonate platform (PCP; Santantonio, 1994) characterizes the Sibilla-Priora mts area (Pierantoni et al., 2013). This horst-block was tilted towards the north (in present-day coordinates), as testified by the angular unconformity between the pre-rift Calcare Massiccio and the overlying Jurassic *p.p.* drowning/condensed succession. The PCP-top succession also hosts Middle Jurassic (?tectonically-triggered) gravity deposits.

Three Jurassic submarine scarps bound the Sibilla-Priora PCP, producing a triangular geometry in plant-view. The northern apex of the PCP coincides with a "ship's keel" geometry defined by antithetic fault-related scarps (respectively, ENE- and W-dipping). The southern, S-dipping escarpment of the PCP also crops out in the study area. All these unconformity surfaces are onlapped by Sinemurian-Tithonian cherty pelagites and are pervasively silicified. Locally, stepped morphologies led to the formation of perched basins, on which discontinuous condensed successions accumulated. Clinoforms of Calcare Massiccio and epi-escarpment condensed deposits occur along the margins.

A km-scale, concave-northeastward scalloped morphology carved along the eastern escarpment was mapped. The result of the dismantling is recorded in its basin-margin onlap succession, where Calcare Massiccio megablocks are embedded in basinal pelagites.

During the Late Miocene orogenesis, the rheological contrasts associated with the aforementioned Jurassic paleogeographic inheritance, coupled with lithological heterogeneities, played a key role into the development of i) a box-shaped hanging wall anticline, reflecting the attitude of bedding of the PCP and its onlapping and overlying pelagic deposits, ii) tight and disharmonic folds within pelagites onlapping the olistoliths, and iii) localized shear planes and cataclasites within the olistoliths. Therefore, the latter represented rigid rheological barriers which promoted buttressing processes and steered the localization of shear planes.

Pierantoni P.P., Deiana G. & Galdenzi S. (2013) - Stratigraphic and structural features of the Sibillini mountains (Umbria-Marche Apennines, Italy). Italian Journal of Geosciences, 132(3), 497-520.

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# Deciphering the tectono-stratigraphic evolution of the East Pisco Basin (southern Peru): new insights from the geological mapping of its central portion

Di Celma C.[1], Pierantoni P.P.[1], Volatili T.*[1], Molli G.[2], Mazzoli S.[1], Sarti G.[2], Ciattoni S.[3], Bosio G.[4], Malinverno E.[4], Collareta A.[2], Gariboldi K.[2], Gioncada A.[2], Jablonska D.[1], Landini W.[2] & Bianucci G.[2]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [4] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* tiziano.volatili@unicam.it

*Keywords:* East Pisco Basin, basin inversion, forearc basin.

The Cenozoic fill of the East Pisco Basin (EPB) preserves the sedimentary record of several episodes of deformation of the forearc crust along the Peruvian margin. The 1:50,000 scale geological map presented here covers an area of about 1,000 km$^2$ lying astride the Ica River and, by establishing a first-order tectono-stratigraphic frame for the exposed mid-Eocene–upper Miocene succession, contributes to our understanding of the timing and mode of basin filling and deformation.

In the study area, deposition initiated onto the PaE0 nonconformity during the middle Eocene time and continued under an extensional regime until early Oligocene time, with a break in deposition recorded by the OE0 unconformity separating the Paracas and Otuma sequences (megasequence P). During this time interval, a single forearc Pisco Basin extended between an offshore outer forearc high and the Western Cordillera. An Oligocene relative sea-level fall, probably resulting from a combination of tectonic inversion and multiple events of eustatic lowstand, led the Pisco Basin to become subaerially exposed. Evidence for this phase of deformation is recorded by the conspicuous CE0 angular unconformity interposed between megasequences P and N.

The oldest normal fault populations documented here consist of NNW- and ENE-trending faults largely predating the CE0 erosional hiatus. This widespread extensional faulting was accompanied by the exhumation of the Outer Shelf High-Coastal Cordillera, which segmented the earlier, Paleogene Pisco Basin into the present-day inner EPB and outer West Pisco Basin. Different tectonic processes have been invoked to explain the Oligocene uplift of the extensional Peruvian forearc basins and formation of the Outer Shelf High, including crustal thickening by underplating at an erosive margin or inversion by propagation of basement-rooted, west-verging thrust faults.

By earliest Miocene time, uplift ceased and subduction erosion and thinning of the overriding plate resulted in renewed subsidence, rise in relative sea level, and marine transgression over the CE0 unconformity with deposition of the lower Miocene Chilcatay and middle to upper Miocene Pisco composite sequences (megasequence N). The early Miocene phase of extension and associated subsidence was followed by a late Miocene contractional tectonic event, with shortening being accommodated by: (i) oblique-slip (reverse plus dextral) reactivation of inherited NE-trending extensional faults, and development of associated fault-parallel hanging-wall anticlines; and (ii) renewal tectonic uplift of the southwestern basin margin, as suggested by the fanning geometry of the northeast-dipping strata of the Pisco composite sequence and their progressive onlap on top of the basement towards the northeastern, internal margin of the basin.

# The Monti Ernici Miocene-Quaternary stratigraphy: An attempt for the definition of new stratigraphic units in the sheet 377 "Trasacco"

Fabbi S.*[1], Cipriani A.[1] & Consorti L.[2]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Istituto di Scienze Marine, CNR, Trieste.

*Corresponding author e-mail:* simone.fabbi@isprambiente.it

*Keywords:* CARG Project, Quaternary, Clastic sedimentation.

A portion of the sheet 377 "Trasacco", in the Simbruini-Ernici Ridge, has been mapped in the frame of the CARG Project. Here we describe the uppermost Miocene to Quaternary siliciclastic deposits covering the Meso-Cenozoic carbonate succession (Latium-Abruzzi Carbonate Platform).

The *conglomerati di Monte Prato* (PTY) consist of polygenic heterometric conglomerates bearing exotic clasts such as «*pietra paesina*», pelagites, metamorphic and granitoid rocks. Clayey intervals with freshwater gastropods and ostracods crop out locally. PTY records latest Miocene-Early Pliocene thrust top sedimentation in coastal, deltaic environments (Cosentino & Cipollari, 2012). Maximum thickness is >250 m.

The Plio-Quaternary continental deposits have been grouped in UBSUs. Two synthems characterize the Tiber/Aniene basin:

i) the *sintema della Val Granara* (VGR), cropping out upslope of Filettino. VGR is bounded at the base by an erosional surface carved on the pre/syn-orogenic units. Within the VGR, two subsynthems, *subsintema di Vaglie* ($VGR_1$) and *subsintema di Pezze della Macchia* ($VGR_2$), are separated by an erosional unconformity. Both represent a gravel-dominated alluvial systems. Compositional differences ($VGR_2$ bears clasts of PTY) and morphological clues, prove that $VGR_2$ refers to a younger drainage system comparable to the Recent one. The age is Early ($VGR_1$) to Middle ($VGR_2$) Pleistocene (Delchiaro et al., 2021). Total thickness is >150 m;

ii) the *Sintema Fiume Tevere* (SFT), developed above the last glacial lowstand erosional surface. It includes the *subsintema dei Monti Simbruini* ($SFT_1$), which groups all the glacial and periglacial deposits related to the Aniene basin such as >30-40 m thick moraines. Locally, glacial derived plurimetric erratic boulders occur. Backwards of the moraines, flat morphologies suggest sedimentation in small barrage basins.

Two synthems characterize also the Liri/Sacco Basin:

i) the *sintema di Guarcino* (GUR), consisting of ?Upper Pliocene polygenic breccias and conglomerates made up of heterometric carbonate clasts, siliciclastics and PTY boulders. Development of GUR is related with the extensional activity of the Guarcino fault;

ii) the *Sintema di Isoletta* (ISL), developed above the last glacial lowstand erosional surface. It includes the *subsintema dei Monti Ernici* ($ISL_1$) which groups all the glacial and periglacial deposits related to the Sacco basin, i.e., disorganized heterometric angular carbonate clasts related to the reworking of moraines through debris-flows, alluvial transport, and avalanches. Maximum thickness is a few tens of meters.

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# The Cansiglio South-Western Escarpment: an Alpine transfer zone developed on a Dinaric thrust

Fioraso M.*[1], Bondesan A.[2], Preto N.[3] & Massironi M.[3]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Dipartimento di Scienze Storiche, Geografiche e dell'Antichità, Università di Padova. [3] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* m.fioraso@student.unisi.it

*Keywords:* geological mapping, tectonic evolution, foreland basin.

The Cansiglio Plateau is the north-western tip of the Adriatic Carbonate Platform (AdCP) representing an important structural high at the boundary between different palaeogeographical domains. The Mesozoic transition between AdCP and Belluno Basin, and the present boundary between high-relief limestone plateau and low-relief foothills (molasse succession), are located on the south-western escarpment of the Cansiglio Plateau.

A new geological and geomorphological survey was conducted in this area, focusing on the structural setting, using field-work and remote sensing to obtain ground-proof and quantitative observations on the Oligo-Miocene Venetian Basin, a polyphase tectonics foreland basin (e.g., Mellere et al., 2000). Landscape analysis, based on the interpretation of morphotectonic markers, was done with a twofold purpose: to find out evidence of active tectonics and to understand the geometrical relationship between tear faults, minor thrusts and possible precursors of Alpine structures.

The Montaner Fault, a seismogenic Alpine transpressive fault, is the main tectonic line on the escarpment that produces a visible displacement, detected by markers and slope deformations, representing the main boundary between Mesozoic platform limestones and the Cenozoic flysch-molasse sequence.

Combining information from a large number of outcrops, the entire escarpment appears to be the southernmost Dinaric anticline in this foredeep, whose tectonic deformation was active up to the Langhian. The anticline was then cut by southern-alpine-trending faults. A new interpretation of the geological evolution of the area takes into account a Dinaric thrust and an Alpine transfer zone during the molasse deposition, modifying the geometry of the basin at a local scale. The existence of a dinaric fault should be considered when reconstructing lateral and vertical transitions between Cenozoic facies up to Langhian times.

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# New geological data on the eastern termination of the Mt. Kumeta-Alcantara Line (NE Sicily)

Foti A.*[1], Catalano S.[1-2], Pavano F.[3], Tortorici G.[1] & Romagnoli G.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [3] Department of Earth and Environmental Sciences, Lehigh University, Betlehem, PA (USA).

*Corresponding author e-mail:* alessandro.foti@phd.unict.it

*Keywords:* Peloritani sole-thrust, Mt. Kumeta-Alcantara Line, orogenic system.

We present a new 1:10.000 scale geological map of the eastern termination of the Mt. Kumeta-Alcantara Line (KAL), the impressive E-W tectonic lineament, controlling the entire axial zone of northern Sicily, from the Trapanese area to the Peloritani region (Ghisetti & Vezzani, 1982). In the analysed region, the KAL intersects the southwestern border of the *Nebrodi-Peloritani Transition* Zone (NE Sicily) (Pavano et al., 2018), where the SW-verging Peloritani sole-thrust (Catalano et al., 2018) causes the tectonic superposition of the Kabilo-Calabride Chain (European margin) on the Apenninic-Maghrebian Chain (African margin). The region is also affected by a NW-SE oriented narrow belt characterized by Plio-Pleistocene, NW-trending, dextral strike-slip faults that developed at the southern margin of the SE-ward migrating Calabrian Arc. The study gives the opportunity to explore the kinematic relation between the arc migration and the Sicily tectonic evolution, both originated during the Nubia-Eurasia collision (Ghisetti & Vezzani, 1982; Dewey et al., 1989). The geological map, which was realized using ESRI ArcGis and CorelDraw software, extends for about 58 $km^2$ and pictures the Peloritani sole-thrust and the NW-SE dextral faults displaced at the footwall of the KAL. According to the new data, the KAL represents the youngest tectonic lineament of the region, that was active after the emplacement of the allochthonous nappes and the displacements along the NW-SE strike-slip faults. This evidence provide new insights to better constrain the regional scale models of NE Sicily.

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# The origin and the significance of the extensive detrital production along the western margin of the Hyblean Plateau (SE Sicily)

Foti A.*[1], Catalano S.[1-2], Tortorici G.[1] & Salerno A.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* alessandro.foti@phd.unict.it

*Keywords:* SE Sicily, Hyblean Plateau, broken formation.

The extensive geological mapping of the western margin of the carbonate Hyblean Plateau (SE Sicily), promoted in the frame of the CARG Project for the realization of the Sheet 648 "Ragusa" of the Geological Map of Italy at 1:50,000 scale, evidenced the possible origin of the local anomalously high detrital production, in a region generally affected by karst evolution and long-lasting preservation of the landforms. This margin is the tectonic border between the foreland and the foredeep domains of south-eastern Sicily. It originated from the Quaternary normal faulting along the prominent arc-shaped, west-facing fault arrays of the Comiso-Chiaramonte System (Salerno et al., 2022), along which the Meso-Cenozoic carbonate successions of the foreland collapsed to form the depression, now hosting the Vittoria Plain. Huge volumes of Quaternary coarse-grained heterometric sediments were distributed along the margin to form slope deposits and several alluvial fans at the hangingwall of the Comiso-Chiaramonte fault system.

The nature of blocks suggests a provenance from the Oligo-Miocene carbonate horizons of the Ragusa Fm., consisting of a monotonous alternation of fine-grained limestones alternated with marls levels, at the base, capped by prevalent calcarenitic deposits, at the top. Particularly, the lithology and the size of blocks forming the Quaternary coarse-grained deposits are consistent with the thickness of the strata and the spacing of the joint systems we recognized within the lower portion of the formation. Along the margin, deformed levels of this interval show the effects of severe stratal disruption, due to almost three distinct mechanisms whose effects are well exposed. Generally, the fragmentation of strata and the dislocation of blocks is closely related to the injections of fluids through the spaced intrastratal joints within the limestone beds that have been enlarged by a remobilized matrix, which squeezed out from the interleaved overpressured marly-clay levels. At places, the stratal disruption occurred also in dry conditions, by a rotation of the blocks isolated by the joints, due to the motion along discrete low angle detachment surfaces. Finally, chaotic block-in-matrix deposits, form vertical intruded bodies confined between high-angle contacts within younger hosting rock-levels.

The new field data evidence that the distribution of the Oligo-Miocene disrupted levels is almost independent from the orientation of the high-angle normal faults of the Comiso-Chiaramonte System that seems to have only controlled the redistribution of the coarse-grained materials along the Quaternary topography. The mode of deformation and the possible relation of the stratal disruption with a transient fluid overpressure, coupled with evidence of the remobilization of low-angle detachments and diapirism, strongly suggest a generalized contractional deformation that affected the foreland area before the final exhumation of the Oligo-Miocene succession due to the normal faulting.

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# Traditional geological mapping with non-traditional 3D survey methods: A Case study from "Le Cute", Sibillini Mts., Central Italy

Galdenzi S.*[1], Jablonská D.[1], Volatili T.[1], Pierantoni P.P.[1] & Capotorti F.[2]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* danica.jablonska@unicam.it

*Keywords:* platform and pelagic carbonates, karst.

We present an integrated geological mapping survey of the southern area of "Le Cute" - Croce di Mt. Rotondo (Sibillini Mts. - Umbria-Marche Apennines), as a part of the sheet 325 – Visso of the Geological Map of Italy 1: 50,000 (CARG project). The field mapping revealed geological and geomorphological features, some of which were previously reported, but their geometrical relationships or origin were not fully understood. In this study, the traditional field mapping was supported by a drone survey of less accessible areas.

The studied area of Le Cute represents a steep slope on Jurassic platform carbonates (Calcare Massiccio Fm.) unconformably overlain towards the south by Jurassic pelagic carbonates (Bugarone group, Marne a Posidonia, Calcari Diasprigni, and Maiolica). Large, pronounced rills incise downslope the surface of the escarpment. These structures were described first by Lippi Boncampi (1948) as karren produced by karst erosion, however, in a later study, Bice & Stewart (1990) considered them Lower Jurassic erosional grooves carved on the paleoescarpment. Our surveys showed basinal carbonates directly onlapping the platform carbonates on top of the slope. In the eastern termination of the escarpment, slope-to-basinal carbonates also lie on the stratigraphically middle portion of the paleoescarpment. In the lower part of the outcrop, on the western side, Pliensbachian Bugarone facies fill shallow, concave channel-like features or Neptunian dikes. At certain locations, the rills are filled with Quaternary breccias. The drone survey unveiled the presence of several cave entrances aligned along the uppermost termination of the platform facies. The "structural high" is westward confined by a normal fault putting in contact Jurassic platform and Cretaceous pelagic carbonates (Pierantoni et al., 2013). This fault shows evidence of recent reactivation through the free face exposure, which corresponds to one of the northernmost expressions of the 2016 seismic sequence of the Mt. Vettore Fault. 3D outcrop reconstruction of drone-obtained photographs was a good additional tool to the traditional field mapping and enabled us to reconstruct the geometrical relationships of the observed features.

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# Tectonic evolution of the eastern coastal area of the Hyblean region

Gambino S.*[1], Barreca G.[1-2], Pagano M.[1], Carbone S.[1] & Monaco C.[1-2-3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università di Catania. [3] INGV, Osservatorio Etneo, Catania.

*Corresponding author e-mail:* salvatore.gambino@unict.it

*Keywords:* Hyblean Plateau, field-survey, tectonic evolution.

The Hyblean region is a portion of the Africa foreland constituting, along with the Siculo-Maghrebian chain and the Gela-Catania Foredeep, one of the main structural domains of the eastern Sicily. It culminates in a SW-NE oriented structural high (the Hyblean Plateau) bounded by Plio-Pleistocene normal fault systems. As regards the stratigraphy, the Hyblean Plateau is constituted by a mainly carbonate Mesozoic-Cenozoic thick succession with intercalations of several interval of basaltic volcanic products, diffused until the Early Pleistocene. The Messinian sea level fall at the onset of the Mediterranean desiccation caused the early emersion of the plateau and the triggering of the exogenous processes that caused the moulding of the area, characterised by tabular morphology with deeply entrenched valleys. Plio-Pleistocene deposits occur on the tectonic lowered sectors of the eastern coastal area, where the deposition was controlled by the activity of coeval normal faults, mostly WSW-ENE and NW-SE oriented. In this coastal area, large Pleistocene marine terraces indicate a regional tectonic uplift partially resulting from the Quaternary activity of offshore fault systems. The morphological analysis of the several orders of Middle-Upper Pleistocene marine terraces occurring along the coast allowed us to estimate tectonic uplift rates ranging from 0.2 mm/yr to 0.4 mm/yr (Bianca et al., 1999; Meschis et al., 2020) from north to south, even though INSAR (Anzidei et al., 2021; Henriquet et al., 2022) data show a current slight subsidence of the entire coastal area. Quaternary climatic changes and tectonic uplift, together with stratigraphic and structural features, have also controlled the diffused karstic morphogenesis in the Hyblean region, which started during the Pliocene emersion.

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# Anisian tectonics ruling sedimentation in the Eastern Southern Alps: evidence from CARG geological mapping

Gianolla P.*, Caggiati M. & Riva A.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* piero.gianolla@unife.it

*Keywords:* stratigraphy, Triassic, Dolomites.

The recent investigations as part of the new sheet "Longarone – 046" of the Italian Geological Map, 1:50000 scale (CARG project), pointed out an important role of Anisian tectonics in the stratigraphic evolution of the study area, and more generally of the eastern Southern Alps.

Polyphased Anisian tectonics was characterized by mainly extensional and transtensional faults, nearly always reactivated by Alpine tectonics during the Cenozoic. The structures are not always easily recognizable, but several adjacent blocks with different Anisian successions have been identified.

A first pulse in the Bithynian allowed the dissection of the almost flattened early Anisian paleotopography, creating depocenter zones in the eastern part of the investigated area. Enhanced by interactions with relative sea-level oscillations, the differential subsidence became more pronounced in the early Pelsonian, when structural paleo-high conditions were set in the western part of the investigated area, where alluvial sedimentation took place in places. On the other hand, persisting fast subsidence in the eastern and southern sectors favoured basinal sedimentation and allowed the nucleation and aggradation of microbial carbonate platforms, up to 200 m- thick. One of the tectonic margins between zones with contrasting subsidence rates is recognizable northeast to the Agordo town: here, the interfingering of alluvial sediments and shallow carbonates with pelagic siliciclastics is documented for most of the Anisian.

While the paleoenvironmental differentiation is easily decipherable in the relatively low deformed portions of the Dolomites, things get messy close to the Valsugana Fault System, where the original paleotectonic pattern has been obscured by the interference between mesoalpine ("Dinaric") and neoalpine tectonic phases. Adjacent tectonic lithons bearing different Anisian successions were originally located several kilometers away, and were displaced toward SW by the Mesoalpine phase, then included in neoalpine interference structures with SE-directed transport. As an example, the succession cropping out at Sotto le Rive locality has been interpreted as developed on a paleo-high persisted until the late Pelsonian, and subsequently drowned in the Illyrian: this paleo-high is now representing a single lithon, with its boundaries reactivated as compressional and transpressive faults.

The understanding of the Anisian series in the Longarone sheet allowed us to better differentiate and understand the tectonic deformation and transport close to the Valsugana Fault system, outlining the high geological complexity of this area.

# From Jurassic rifting to early Miocene shortening: polyphase history of the Longobucco/Paludi welded basins (northern Calabria)

Innamorati G.*[1], Aldega L.[1], Fabbi S.[2] & Santantonio M.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* giulia.innamorati@uniroma1.it

*Keywords:* rift basin, peripheral bulge, poliphase deformation.

The northern slopes of Sila Greca (Northern Calabria), facing the Ionian Sea, host two superimposed basins of contrasting nature, the Jurassic/earliest Cretaceous Longobucco Basin and the Paleogene Paludi Basin, separated by an ~75 Myr-long unconformity. Field mapping reveals the extensional architecture of the Longobucco rift basin, evidenced by preserved basin-margin tracts, up to >20 km long, where the extended Paleozoic basement (granitoid rocks and low-grade metamorphites) is onlapped by deep-water deposits via interposed fringing carbonate bodies developed on the rift shoulders. Basin-margin deposits along mappable synsedimentary fault zones include spectacular wedges of mass-transport deposits, with megaclasts of basement rock and of the pre-rift (Rhaetian-Sinemurian) units. Conversely, the submerged footwall-block tops and flanks hosted thin condensed pelagic deposits, known as the Caloveto Group.

In the early Eocene (Ypresian) the area was uplifted as it found itself at the periphery of the Alpine foreland. This would be a "retro-foreland", should one accept the notion that subduction was "East-dipping" at the time. Bulging was accompanied by block faulting, which locally involved the reactivation of Early Jurassic faults, all this accounting for the widespread unconformable nature of the base of the Paludi Fm., erosion of post-earliest Cretaceous deposits, and re-utilization of the inherited rift-basin margins as the physical boundaries of the Eocene retro-foredeep/bulge depositional system. Footwall blocks in the peripheral bulge, along with the foreland, hosted mixed carbonate/siliciclastic factories of the "heterozoan" type. These sourced the gravity flow deposits, rich in benthic macroforaminifera, which are found interbedded with the hemipelagites in adjacent hangingwall blocks. At sites of active extensional faulting, the progressive dismantling of the bulge, including the inherited Jurassic highs, occurred through repeated collapses. This is documented by thick clastic wedges made of basement rocks and of units belonging to the Caloveto Group.

The two welded basins are now shortened by north-verging thrusts. The age of these thrusts is constrained at the Oligocene-Aquitanian boundary, by means of biostratigraphic and geochronological analyses and 1D thermal modeling constrained by mixed-layers illite-smectite.

This orogenic phase ("Balearic" phase) is linked with the rotation of the Sardinia-Corsica blocks, to which the Calabrian terrane was welded.

# The Tachrift Project: combining field mapping and detailed stratigraphic measurements to reconstruct the sedimentary architecture of channel-levée systems (late Tortonian, Tachrift Turbidite System, NE Morocco)

Invernizzi D.*[1], Felletti F.[1], Marini M.[1], El Kati I.[2], Pantopoulos G.[1], Reguzzi S.[1] & Zuffetti C.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Natural Resources and Environment laboratory, Sidi Mohamed Ben Abdellah University, Taza (Morocco).

*Corresponding author e-mail:* daniele.invernizzi@unimi.it

*Keywords:* turbidite, Morocco, sedimentary basin.

The Taza-Guercif Basin is one of the several basins of North-Eastern Morocco that represent remnants of an ancient seaway, the Rifian Corridor (Late Miocene), connecting the Atlantic Ocean to the paleo-Mediterranean Sea. The Rifian Corridor is a key area for the understanding of the Upper Miocene stratigraphy of the Mediterranean domain, because of its closure is directly related with the onset of the Messinian salinity crisis.

The Tachrift Project focuses on the sedimentary architecture of the Tachrift Turbidite System belonging to the late Tortonian Melloulou Fm. (Bernini et al., 2000). This turbidite system spectacularly crops out in the South-Eastern Taza-Guercif Basin, showing several levéed turbidite channel complexes, which are up to few tens of metres-thick and intercalated with hemipelagic marlstones, totalling a stratigraphic thickness of ca. 800 m.

This sedimentary succession was initially studied during 1960s by Benzaquen (1965), who provided the first geological map of the area (1:100.000 scale). Later, Bernini et al. (2000) published a more detailed geological map (1:50.000 scale) highlighting the Tachrift Turbidite System outcropping to the East of the Zobzit river. Felletti et al. (2020) recently published a high-resolution geological map (1:5.000 scale) of the Tachrift Turbite System, dividing it into nine superimposed channel-levée complexes, identifying the main architectural elements.

Looking at the different maps in literature, it is clear how a detailed field mapping can improve the knowledge about the stratigraphy of a sedimentary basin. The existing geological map provides the basis to deepen sedimentological investigations upon the channel-levée complexes of the Tachrift Turbidite System.

This contribute demonstrates how an extremely detailed geological map is crucial to: i) accurately locate the measured logs and to plan next field activities, ii) build and interpret 2D and 3D cross-sectional profiles, iii) identify, hierarchize and characterize channelized elements, and iv) reconstruct the channels latero-vertical evolution over space and time.

Benzaquen M. (1965) - Etude stratigraphique preliminaire des formations du bassin de Guercif. Direction des Mines et de la Geologie, Service de la Carte Geologique, Bureau d'Etudes des Bassins Sedimentaires, Rabat, 73 pp.

Bernini M., Boccaletti M., Moratti G. & Papani G. (2000) - Structural development of the Taza-Guercif basin as a constraint for the Middle Atlas shear Zone tectonic evolution. Marine and Petroleum Geology, 17(3), 391-408.

Felletti F., Marini M., El Kati I. & Tabyaoui H. (2020) - The Tachrift channel-levée turbidite complexes (Tortonian) of the Taza-Guercif basin (South Rifian Corridor, NE Morocco). Journal of Maps, 16(2), 902-917.

# Geological map of Valenza-Montecastello area: new field constraints for the Oligocene-Quaternary tectono-stratigraphic evolution of the eastern Monferrato (NW Italy)

Irace A.*[1], Catanzariti R.[2], Fioraso G.[1], Da Prato S.[2], Barbero E.[1], Bonadeo L.[3], Livio F.[1-4], Ferrario F.[4], Scaramuzzo E.[4] & Zerboni A.[5]

[1] Istituto di Geoscienze e Georisorse, CNR, Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Pisa. [3] INGV, Roma. [4] Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Como. [5] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* andrea.irace@cnr.it

*Keywords:* geological mapping, Eastern Monferrato, tectono-stratigraphic setting.

We present the preliminary version of a new geological map of the eastern termination of the Monferrato (NW Italy). It covers an area of 45 km$^2$ encompassing the hills-Po Plain transition, in the hanging-wall of the buried, NE-vergent Padane outer thrust front (PTF). This area is of current interest, as it includes the NW corner of the Sheet 177 Tortona of the Geological Map of Italy at 1:50,000 scale, in progress, and the junction with the adjacent sheets (158 Casale Monferrato, 159 Garlasco and 176 Alessandria), still to be started. Detailed field mapping, integrated with biostratigraphic analyses and subsurface data interpretation, allow us to decipher the complex tectono-stratigraphic relations among the External Ligurian Units of the N-Apennines, the Tertiary Piemonte Basin (TPB) and Pliocene-lower Pleistocene successions, giving helpful constraints to interpret the late Oligocene to early Pleistocene evolution of the area. The early Cretaceous-early Eocene Ligurian Units and Rupelian part of the TPB successions show complex tectonic relationships along a NNW-striking fault zone, and they are unconformably sealed by lower Langhian-upper Tortonian outer shelf to slope formations of the TPB. This tectono-stratigraphic assemblage suggests the syn-sedimentary, Chattian to Tortonian tectonic uplift of a submarine relief, associated with the activity of the Monferrato NNW-striking high angle fault systems. The succession continues with Messinian marls and euxinic shales (deep-water equivalent of the primary evaporites) then followed by post-evaporitic deltaic/shelfal deposits through the intra-Messinian unconformity, marking the uplift and partial emersion of the area. This event was likely controlled by a renewed tectonic activity along NW-striking high angle strike-slip and reverse fault zones, which is consistent with the NW propagation of the PTF. The occurrence of fan-delta/shelf deposits at the base of the Pliocene succession points to residual topographic highs during the earliest Zanclean. Slope deposits follow upward, reflecting a phase of subsidence and temporary submersion. The mapped contractional tectonic structures were reactivated during the Pliocene, involving the successions along major NW-striking thrusts and fault zones and ENE- to WNW-directed folds. Pliocene tectonics likely led to a significant NE movement of the compressive PTF that overthrust the Monferrato onto the Po Plain foredeep. This favored shallowing and creation of new submarine reliefs during Piacenzian. In the north foothills, the N-ward tilted Gelasian unconformity between the Mio-Pliocene successions and lower Pleistocene fluvial/marginal marine deposits marks the continued early Pleistocene uplift of the E-Monferrato and NW-SE directed folding of the pre-Quaternary stratigraphy. In conclusion, new stratigraphic-structural data and interpretations are illustrated in the map, representing a reference geological base for the ongoing CARG mapping Project and future research.

# Geological mapping and 3D geological Model of the Pieve Torina - Visso Synclinorium, Sibillini Mts. (Central Italy). Application for Geofluid reservoirs

Jablonská D.*, Zambrano M., Volatili T., Pierantoni P.P., Mazzoli S. & Materazzi M.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* danica.jablonska@unicam.it

*Keywords:* deformed carbonates, geofluid reservoirs.

The geofluids reservoirs confined between two thrust faults, in pelagic carbonates with various clay content, bring many challenges in recognizing the large-scale preferential flow pathways and the total volume estimation of the present fluids. The presence of later extensional faults may produce further complex heterogeneities for the fluid flow. Structural discontinuities, such as thrusts and normal faults within the same carbonate reservoir may act simultaneously as barriers, baffles, and conduits (Volatili et al., 2019) depending on the deformation style.

The Pieve Torina – Visso Synclinorium is located in the inner part of the fold and thrust belt of the Umbria-Marche Apennines. Field mapping of structures involving pelagic carbonates was conducted at 1: 10,000 scale which enabled the construction of six transversal and five longitudinal detailed balanced geological cross-sections. The horizons of balanced geological cross-sections were used to build a 3D geological model of the studied area using Move software (Petroleum Experts). The visualization of the surfaces and later corrections helped to better characterize the fault and fold geometries and their interactions in the areas where the lack of outcrops hindered interpretations. The main large-scale structural features were characterized according to their hydraulic behavior, putting in contact different stratigraphic units with dissimilar fluid-flow properties. Confirmation and calibration of the model were accompanied by the integration of geophysical surveys, such as electrical resistivity tomography, and passive and active seismic velocity profiling.

Volatili T., Zambrano M., Cilona A., Huisman B.A.H., Rustichelli A., Giorgioni M., Vittori S. & Tondi E. (2019) - From fracture analysis to flow simulations in fractured carbonates: The case study of the Roman Valley Quarry (Majella Mountain, Italy), Marine and Petroleum Geology, 100, 95-110.

# Introduction to the IGCP 710 Project: Western Tethys meets Eastern Tethys

Krobicki M.* & co-leaders and members of the IGCP 710

Department of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków (Poland).

*Corresponding author e-mail:* krobicki@agh.edu.pl

*Keywords:* Eurasia, plate tectonics.

The geological history of Tethys Ocean is broadly established. Yet many details are still unknown and many major questions remain, related to geotectonics, paleogeography, paleoceanography and paleobiogeography. There is little or no agreement about the number or size of separate basins neither on their space-time relationships. Moreover, there is no consensus on the number and location of former micro-continents and on their incorporation into the present-day Eurasian-Mountain Belt. Correlation between Western and Eastern Tethys is difficult not only because of the large distances involved but also because they are separated by the area of the huge Himalayan collision within which much of the pre-Paleogene tectonostratigraphic information has been lost. The aim of this IGCP project is to bring together geologists from the western and eastern parts of the former Tethys (Morocco/Iberia–SE Asia) for establishing a common framework and a common tectonostratigraphical concept.

The supercontinent Pangea was formed during the Carboniferous as the result of the Hercynian orogeny. However, separation of the Cimmerian Continent from the Gondwanan part of Pangea started during the latest Carboniferous–earliest Permian times in the eastern Tethys and from the latest Permian onwards in the western Tethys by rifting and drifting event originated the Neotethys Ocean. Northwards migration of Cimmerian Continent took place during Permian-Triassic times causing wide opening of the Neotethys and closing of the Paleotethys Ocean. From Asian perspective, during the latest Permian and earliest Triassic fast rifting of this ocean and drifting of several Gondwana-derived blocks caused the Indosinian orogeny during Late Triassic.

The IGCP 710 Project focus on the comparison between the Western and Eastern part of the Tethys during the latest Paleozoic–Mesozoic times (Carboniferous–Cretaceous), mainly on Permian-Jurassic, in three main fields of our expertise: (i) geodynamic reconstruction of the Tethys Realm (tectonostratigraphic scheme(s)); (ii) reconstruction of paleoceanographic conditions between Western and Eastern Tethys and changes of oceanic circulations (mainly with "sedimentological" events) after geodynamic revolutions (including Pangea break-up); (iii) paleobiogeographic patterns of distribution/migration of fauna and flora.

From these points of view, the development of the Tethyan Realm is such a complicated problem that it remains far from being clarified. Execution of successive IGCP projects (224, 321, 411, 516 and 589) targeting mainly at geological evolution of South-East Asia and other related researches have contributed much in working out more constraints on the evolution of the Tethys. The investigation into the complicated problems related to the geological evolution of Tethys between Europe and Asia could continue with a new look from wider, near-global perspective.

# Volcano-sedimentary sequences of the Western Tethys (Ukrainian Carpathians; Early Cretaceous and Italian Dolomites; Middle Triassic) – comparative sedimentological studies and their geodynamic significance

Krobicki M.*[1], Di Capua A.[2-3], Feldman-Olszewska A.[4], Hnylko O.[5] & Iwańczuk J.[4]

[1] AGH University of Science and Technology, Kraków (Poland). [2] Dipartimento di Scienza ed Alta Tecnologia, Università dell'Insubria, Como. [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Milano. [4] Polish Geological Institute, National Research Institute, Warsaw (Poland). [5] Institute of Geology and Geochemistry of Combustible Minerals, National Academy of Science, Lviv (Ukraine).

*Corresponding author e-mail:* krobicki@agh.edu.pl

*Keywords:* volcano-sedimentary sequences, Tethys.

The geological record of the Alpine belt preserves the whole Permian-Mesozoic history of the Tethys Ocean and constitutes the base for palaeogeographic/geodynamic reconstruction of this ocean. The Ukrainian Carpathians, as prolongation of the Alpine system of western Europe, form a connecting link between the Western and Eastern Carpathians. Outer Carpathian flysch is divided into inner and outer flysch nappes. Inner flysch nappes of the Outer Eastern Carpathians (Fore-Marmarosh flysch prism) were formed in the front of Tisza-Dacia terrane during the Cretaceous-Paleogene times. The Transcarpathian Ukraine tectonostratigraphic units (Kamyanyi/Kaminnyi Potik, Rakhiv and Burkut) were developed in the frontal part of the Marmarosh basement nappes (Crystalline Massif) of the Central East Carpathians and correspond to the Outer Dacides-Severinides (Romania). Volcano-sedimentary complex of the Kamyanyi Potik Unit (Chyvchynian Mountains), equivalent of the so-called Black Flysch in Romanian part of the Carpathians (Marmarosh Mountains), is represented by basalts (including pillow lavas), peperites, debris-flows and volcanic breccias, and thin-bedded micritic limestones with cherts interbedded by coarse and fine-grained volcanogenic turbidites with calcareous accidental fragments. The flow of massive basaltic pillow lavas is the first episode originating the volcano-sedimentary sequence in our reconstruction. Then, different kinds of volcanogenic facies as continuous transition from proximal (debris-flows) to distal (turbiditic-type) turbiditic facies have been accumulated. These lithological associations were formed on the presumable oceanic crust of the Carpathian basins floor during Early Cretaceous (Berriasian) time, according to biostratigraphical data. On the other hand, the Triassic units in Dolomite Mountains (Italy) are tripartite – from Werfen-type clastic-carbonate Early Triassic units, through Mid-Triassic carbonate platforms with volcanogenic-carbonate deposits up to Late Triassic prograding and aggrading carbonate platforms. The middle part of this sequence represents the Late Anisian–Ladinian Magmatic Cycle in Dolomites, which had produced large amounts of volcano-sedimentary sequences. This magmatic event is well-documented in the geodynamic history of the Dolomites, consisting of submarine volcanic effusive sequences (e.g., basaltic pillow lavas) and numerous volcanogenic deposits (conglomerates interpreted as debris flows, sandstones/mudstones, either accumulated by hyperpycnal flows or fallout events). Our comparative studies between Carpathians and Dolomites shows that the volcano-sedimentary sequences are almost identical in terms of facies and sedimentary architectures, representing a break-through in the investigation of how such kind of sequences formed during the development of the Tethys Ocean.

# The tectono-stratigraphic evolution of the alpine Ligurian margin: new insights from the marine Quaternary deposits (Albenga and Genova sheets - CARG project)

Locatelli M.*, Morelli D., Crispini L., Corradi N., Federico L., Cianfarra P. & Brandolini P.

Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* michele.locatelli@edu.unige.it

*Keywords:* Alpine Ligurian margin, tectono-stratigraphic evolution, CARG.

The structural architecture of the alpine Ligurian margin, located at the junction between the SW-termination of the Western Alps and the Ligurian Basin, is still partly unknown. It involves several tectonic units, characterized by a complex and polyphasic geological evolution.

Within the framework of the CARG Project (Genova and Albenga sheets) we used and integrated multiple sets of data collected since the 80's on the Ligurian continental shelf to unravel the Pleistocene geological evolution of the Alpine Ligurian margin. These data, merged within a single, GIS-based software (Geosuite AllWorks®), comprise digitalized scans of paper-back maps and seismic lines, stratigraphic logs from vibracore sampling, catalogues of natural seismicity and a dense grid of recent chirp and sparker seismic lines.

Main outcomes can be summarised as follows:

– for the Albenga area, the identification of high-amplitude acoustic facies, coupled with the analyses of the identified paleo-morphologies, allowed the mapping of (at least) four paleo-coastal strips along the shelf. These gravelly and sandy littoral spits, with high lateral continuity are developed at constant depth. Their retrogradiational geometry and "terraced" distributions likely indicate a sequence of episodic, stepwise retreats of Late Quaternary coastal system (last 18-8 Ka).
– In the Genova area the Late Quaternary transgressive coastal system shows a more complex arrangement, likely linked to the local platform paleomorphologies. Here, the erosion of the bedrock during the Messinian saline crisis carved the Polcevera and Bisagno canyons, which are separated by a structural high bounded by steeply dipping, N/NW-S/SE-trending faults. A second order, W/NW-E/SE-trending fault system defines a semi-graben nearly parallel to those occurring in the Genova inland. The analyses of the acoustic facies of the Plio-Pleistocene sediments infilling the submerged paleo-valleys shows progradational geometries connected to erosional surfaces, often articulated in narrow fluvial incisions flanked by massive and coarse accumulation, typical of high-energy, sediments-rich depositional systems (paleo-fluvial channels and delta-conoids/underwater canyons).

Here we present a detailed 3D reconstruction (obtained by modelling on Qgis® and Surfer® software) of the distribution and structures of late Quaternary transgressive deposits of the continental shelf in front of Genova and Albenga areas. This provides a new contribution to unravel the Pleistocene geological evolution of the Alpine Ligurian margin under the combined effect of the glacio-eustatic variations and the recent tectonic uplift.

# The New Subsurface Geological Map of the Torino metropolitan Area (Western Po Plain): from database and 3D model construction to the map graphic representation

Marcelli I.*, Irace A. & Fioraso G.

Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* marcelli.igor@gmail.com

*Keywords:* subsurface geological map, GIS geodatabase, 3D modeling.

Subsurface geological maps derived from 3D models and related geo-databases are becoming increasingly important scientific instruments for academic researche and technical tools for improving management and protection of geo-resources. In this respect, we present a new subsurface geological map of the Torino metropolitan area. The map relies on an original geological database and is aimed at tying the 2D map representation to the 3D model of the Pliocene-lower Pleistocene, marine to continental successions and tectonic structures that are buried in the western part of Po Plain subsurface (i.e., beneath the middle Pleistocene-Holocene, terraced alluvial deposits). To design the GIS geodatabase architecture and to ensure greater accessibility and sharing of data, we used the Open-Source platform QGIS (version 3.4_Madeira). An innovative dataset structure, founded on an explicit conceptual model, was designed to ensure i) a reliable representation of the distribution of well and boreholes data along x, y and z axes, as well as their integration with surface geology and ii) the accurate georeferencing and the in-depth projection of the stratigraphic contacts. The geological 3D model was undertaken using the GMS ("Groundwater Modeling System") software by AQUAVEO and was based on a detailed, dense network of cross-sections. Stratigraphic log correlations along triangle meshes allowed careful mapping of the sedimentary units and interpolation of geological contacts below the base of the alluvial plain sequence, according to the trend of main regional scale folds. Due to software limitations, faults modeling was not possible, nevertheless they were ultimately represented in the map based on recently published seismic interpretations, as well as inconsistent stratigraphic situations. The new map represents an improvement of the state of knowledge on the tectono-stratigraphic architecture of the Torino subsurface (Balestro et al., 2009) and provides an updated geologic classification through the distinction of lithostratigraphic units according to the legend of the GeoPiemonte map at a scale 1:250.000 (Piana et al., 2017). The methodical and orderly organization is potentially ready for loading on a dedicated WebGIS WMS System, providing a service for the society and a tool for territorial and resource planning. Future work should focus on: i) study and modeling of adjoining sectors, and ii) data model adjustment to the INSPIRE international standards.

Balestro G., Cadoppi P., Piccardo G.B., Polino R., Spagnolo G., Tallone S., Fioraso G., Lucchesi S. & Forno M.G. (2009) - Carta Geologica d'Italia alla scala 1:50:000, Foglio 155 Torino Ovest. - ISPRA, Istituto Superiore per la Protezione e la Ricerca Ambientale, Roma.

Piana F., Barale B., Compagnoni R., D'atri A., Fioraso G., Irace A., Mosca P., Tallone S., Monegato G., Morelli M. (2017) - Geological Map of Piemonte Region at 1:250,000 scale. - Explanatory Notes. Acc. Sc. Torino, Memorie Sc. Fis. 41, 3-143.

# 3D stratigraphic architecture of the Permian-to-Cenozoic succession of the Po Basin

Marino M.* & D'Ambrogi C.

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* maurizio.marino@isprambiente.it

*Keywords:* Po Basin, 3D stratigraphic architecture, synsedimentary tectonics.

The EU-funded HotLime project has modeled 4 regional-wide stratigraphic horizons in the Middle Triassic-Quaternary succession throughout the Po Basin (from Piemonte to the Adriatic coastline) together with synsedimentary Mesozoic extensional faults and Paleogene to Neogene thrust-systems (Diepolder & HotLime Team, 2021). This 3D geological model was based on an integrated analysis of a wide dataset of boreholes and 2D seismic reflection profiles kindly provided by ENI.

Successively, within the same dataset, attention has been focused on the Late Paleozoic-Early Cenozoic part of the sedimentary succession.

As in the field-mapping practice, stratigraphic study has been associated with facies analysis on the borehole logs (i.e., 117 boreholes) to identify main facies changes, recording the principal steps of the paleogeographic evolution of the Adria plate, in particular during the early Mesozoic transtensional and rifting phases.

For such analysis, the well-established lithostratigraphy and paleogeography of the Southern Alps and Northern Apennines have been considered as a reference, together with paleogeographic reconstructions in restricted sectors where the same successions crop out. The main facies changes have been associated with stratigraphic horizons through well-log-correlation panels. The investigated horizons correspond to the top of the Permian volcanites, the base of Ladinian euxinic deposits, the unconformities at the base (Carnian unconformity) and the top of the Upper Triassic carbonate platforms, the top of the Lower Jurassic carbonate platforms, the top of Maiolica and top of carbonate units.

They recorded the changes of the topography, the thickness variability, and the lateral variations throughout the basin in different time intervals.

Finally, the 3D model of these horizons has been built, taking to account the 3D geometries of the faults established during the HotLime Project.

Finally, a novelty results in the 3D stratigraphic setting of the Permian-Paleogene p.p. succession throughout the subsurface of the Po Basin. The 3D model allows to highlight strong lateral variations: to the west, the whole interval has been reconstructed but horizons are discontinuous, in particular in the Jurassic part of the succession, confirming the presence of different unconformities on top of Mesozoic ridges typical of the western Southalpine area (e.g Lugano ridge). To the east, the Permian-Early Triassic horizons have been not yet modeled, but the upper ones are generally continuous, throughout super-regional-extended paleogeographic structures (e.g., Trento Plateau).

The model allows to observe in 3D the stratigraphic architecture and its relation with synsedimentary tectonics of the Po Basin overcoming the generally proposed 2D view along regional transects

Diepolder G.W. & HotLime Team (2021) - Atlas of Carbonate Rock Geothermal Reservoirs Across Europe. https://repository.europe-geology.eu/egdidocs/hotlime/hotlime_geothermal_atlas.pdf

# Depositional age models in lacustrine systems from zircon and carbonate U-Pb geochronology

Montano D.*[1-2-3-4], Gasparrini M.[5], Rohais S.[1], Albert R.[2-3] & Gerdes A.[2-3]

[1] IFP Energies nouvelles, Rueil-Malmaison (France). [2] Institut für Geowissenschaften, Goethe University, Frankfurt (Germany). [3] Frankfurt Isotope and Element Research Center, Goethe University, Frankfurt (Germany). [4] Sorbonne Université, Paris (France). [5] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* damaris.montano89@gmail.com

*Keywords:* U-Pb geochronology, lacustrine carbonates, depositional age model.

The Yacoraite Fm. (Salta rift, Argentina) consists of Maastrichtian-Danian lacustrine carbonate and siliciclastic deposits with interbedded volcanic ash layers, organized in four, third-order, stratigraphic sequences. It offers the exceptional opportunity to jointly apply in situ zircon and carbonate U-Pb (LA-ICPMS) geochronology that resulted in two distinct depositional age depth models. Ages of the youngest zircon population from ash layers were linearly interpolated to derive a zircon depositional age (ZDA) depth model. A carbonate depositional age (CDA) depth model was instead obtained from dated carbonate phases including microbialites, ooids, oncoids of calcitic and dolomitic mineralogy as well as early lacustrine calcite cements. Mean ages were defined from different carbonate phases belonging to the same layer and then linearly interpolated. Sedimentation rates were calculated from both depth models, by using pairs of dated samples. The rates allowed to estimate the age of the sequence boundaries, as well as the duration of the four stratigraphic sequences. The ZDA and CDA depth models agree with biostratigraphic constraints and exhibit excellent consistency. The onset and end of sedimentation were estimated at 68.2 ± 0.9 Ma and 62.3 ± 0.6 Ma (duration ~5.7 Ma) via zircon geochronology and at 67.9 ± 1.7 Ma and 61.9 ± 1.3 Ma (duration ~6.0 Ma) via carbonate geochronology. The results of this study show that suitable samples and a newly implemented working strategy, make in situ U-Pb dating of depositional and early diagenetic carbonates a valuable chronostratigraphic tool, for estimating sedimentation rate and duration in poorly time-framed depositional systems.

# The Glossary 3.0 of the CARG Project: An updated web-based controlled vocabulary of terms related to geological maps

Muraro C.*[1], Vita L.[1], Cipriani A.[1], Consorti L.[1-2], Battaglini L.[1], Fiorentino A.[1], Fiorenza D.[1], Martarelli L.[1], Orefice S.[1], Pieruccioni D.[1], Silvestri S.[1] & Troccoli A.[1]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Istituto di Scienze Marine, CNR, Venezia.

*Corresponding author e-mail:* cristina.muraro@isprambiente.it

*Keywords:* semantics, harmonization, geological maps.

The wide experience gained during the first phase of the CARG Project (realization of the 1: 50,000 scale Geological Map of Italy), along with its new funding in 2019, has evidenced the need for a new expanded Glossary. Despite it is not so exhaustive to cover all fields of Geology, it aims to provide a shared and univocal semantics for the CARG Project products (Geological Sheet, Explanatory Notes, Database). The Glossary 3.0 is intimately related with the Geological Database of the CARG Project (GDB), which is in turn based on the terms used for geological mapping. It implements and updates previous versions included in the guidelines of the CARG Project (Servizio Geologico Nazionale, 1992, 2009a,b). The revision of the inherited terms was performed by referring to the most recent and accredited bibliography (note the bibliographic references in the descriptions). The Glossary contains terms occurring in the GDB as well as other terms useful to describe more specific items. Related concepts and synonyms are mutually connected through hyperlinks, creating a semantically harmonized and technically interoperable geo-dataset. The terms contain the broadest description possible, including different meanings adopted in the multidisciplinary fields of Geosciences, when necessary. In some cases, the general description of terms is complemented by their specific meanings in the GDB. For each GDB occurrence, the names and domain codes of the fields and tables of the GDB are also provided. Several terms are linked to the INSPIRE terminology, according to the EU directive requirements (INSPIRE), or to the semantically-controlled vocabulary of IUGS (i.e., GeoSciML) if they are not listed in INSPIRE. This choice has had the purpose to: i) refer to the European vocabulary, ii) compare the latter with the CARG terminology, which is often different, and iii) remark that the complexity of the Italian geological context requires a plethora of specific terms adopted in this Glossary.

The Glossary 3.0 is available online and periodically updated. It is designed as a useful and flexible tool for a wider audience (i.e., geoscientists, students, teachers, etc.), and in particular for those working within the CARG Project. In fact, the Glossary must be taken as the reference for the vocabulary of terms occurring in the Legend, the side-elements of the Geological Sheet, and the related Explanatory Notes, as well as in the GDB. The Glossary 3.0 entirely replaces the previous versions.

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Servizio Geologico Nazionale (2009b) - Carta Geologica d'Italia – 1:50.000 Progetto CARG: Modifiche ed Integrazioni al Quaderno n. 1/1992. Quaderni, serie III, 12(3), pp. 54.

# Geology of the Ligurian units in the Calvana and Morello mountains (Northern Apennines of Italy)

Nirta G.*

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* giuseppe.nirta@isprambiente.it

*Keywords:* External Ligurian units, chaotic units, ophiolite.

The Morello unit is the most extended tectonic unit among the External Ligurian units (EL) exposed in the Tuscan Apennine. It overthrusts on the Sub-Ligurian units and the foredeep deposits of the Adria plate on the Tyrrhenian side of the chain whereas, on the Adriatic side, it gradually tapers out and is only recognizable as metric to km-sized blocks within the Sestola Vidiciatico unit (SVU). The latter is defined as a tectonic mélange forming the shear zone between the Ligurian wedge and the foredeep deposits of the Adria plate (Vannucchi et al., 2008). Toward the Umbrian-Marchean sector of the chain, the SVU is no more recognizable and the Morello Unit is unconformably covered by the late Eocene-Oligocene Epiligurian units. In its turn, the Morello Unit is overthrust by the more internal Ligurian thrust sheets both pertaining to the EL (Castelnuovo Val di Cecina unit; Nirta et al., 2005) and the Internal Ligurian units (IL, Gottero unit; Cerrina Feroni et al., 2017). The Calvana and Morello mountain ridges (a few tens of km NW of Florence) represent the type locality for the Morello unit succession (Bortolotti, 1964). Here, the detailed mapping (1:10.000 scale) and the new biostratigraphic data collected in the Morello unit allowed a reconstruction of the complex stratigraphy of the Cretaceous-early Eocene shale-dominated "basal complex" (i.e., Sillano Fm.) and the early-middle Eocene marly-calcareous turbiditic unit (i.e., the Monte Morello and Pescina formations). The structural analysis permitted to unravel the deformation history of this portion of the Ligurian wedge from the middle Eocene to the present. Our investigations clarified the relationships among the km-sized ophiolitic slivers and the ophiolite-bearing sedimentary chaotic units exposed in the western part of the study area.

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Vannucchi P., Remitti F. & Bettelli G. (2008) - Geological record of fluid flow and seismogenesis along an erosive subducting plate boundary. Nature, 451, 699-703.

# Processes of ophiolite incorporation at shallow structural levels of subduction complexes: field constraints from the External Ligurian Units (Northern Apennines, Italy)

Nirta G.*[1], Barbero E.[2], Festa A.[3] & Remitti F.[4]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Istituto di Geoscienze e Georisorse, CNR, Torino. [3] Dipartimento di Scienze della Terra, Università di Torino. [4] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* giuseppe.nirta@isprambiente.it

*Keywords:* ophiolites, accretionary wedge, sedimentary mélange.

Ophiolite emplacement is a long-debated argument since the advent of plate tectonics. The reconstruction of processes responsible for the incorporation of oceanic slices into the accretionary wedge, their sedimentary routing as rock fragments, and their eventual metamorphism and exhumation have clear implications for the reconstruction of the tectono-sedimentary scenario of a convergent margin. Field study of ancient accretionary wedges, embedding slices of ophiolite, offers the opportunity to fill the gap with their modern analogues in which direct observations are not possible. Throughout detailed geological mapping and stratigraphic-structural observations of the Morello Unit, the lowermost unit of the Ligurian accretionary wedge in the Northern Apennines, we document two kinds of ophiolite occurrences derived from the dismemberment of a non-metamorphosed succession and consisting of portions of oceanic igneous rocks (serpentinite and gabbro) and its related pelagic volcano-sedimentary cover: (i) large slide blocks embedded in clastic sedimentary deposits and, (ii) km-sized tectonic slivers. Field analyses of these ophiolite occurrences shed some light on the geodynamic scenario for the transport and emplacement of large ophiolitic slide blocks, and the conditions under which portions of the oceanic substratum are incorporated into a subduction complex at shallow structural levels. We suggest that oceanic reliefs and sea-floor heterogeneities can be considered as the source of the ophiolite slide blocks and ophiolite-bearing mass-transport deposits, and influenced the deep-sea clastic sedimentation.

# Geological map and stratigraphic subdivision of the Marnoso-Arencea Formation, biostratigraphic and petrographic constraints: Umbrian Apennines (Italy)

Pasqualone L.*[1], Brozzetti F.[2], Mirabella F.[1], Patacchiola E.[1] & Barchi M.R.[1]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* luca.pasqualone@studenti.unipg.it

*Keywords:* Umbria-Romagna foredeep, biostratigraphy, Marnoso-Arenacea foredeep basin.

In the Umbrian pre-Apennines, the CARG Project financed the survey of the "Gubbio" and "Nocera Umbra", 1:50,000 scale Geological Sheets, both characterized by extensive outcrops of turbidite foredeep successions. Their mapping represents a unique opportunity to reconstruct the Miocene Umbrian foreland basin system based on modern facies analysis and biostratigraphy.

In this sector of the Apennines, the tectono-stratigraphic history of the Miocene turbidite succession is still under debate. The timing of deformation is roughly defined, except for some restricted areas.

Here we present the preliminary results of the in-progress survey of the Sheet no. 312 "Nocera Umbra", whose western sector is dominated by outcrops of the Marnoso Arenacea Formation.

We performed geological-structural mapping at a 1:10,000 scale integrated by photo-interpretation aimed at morphostructural analysis. Fieldwork was carried out using both traditional and digital methods (FieldMove Pro, Petroleum Experts Limited) and was accompanied by elaboration of composite LOGs, obtained by correlating several stratigraphic sections. The latter were constrained by petrographic and micropaleontological analyses. We have completed the revision of the stratigraphy at present and we are about to conclude the Geological Map and the related Gis-based Database.

The main element of interest is the formalization of new lithostratigraphic units (members, lithofacies, and key-beds) of which we defined age, sandstone/mudstone ratio, and petrographic composition.

The mapped area is suitable for the study of transversal-supplied turbidites and of the "Colombina-type" bioclastic calcarenites of southern provenance, which are particularly abundant and show considerable thicknesses.

The identification of the Contessa mega-bed has not been confirmed with certainty, as petrographic determinations on a >6 m-thick hybrid arenite, comparable with the Contessa relying on age and stratigraphic position, are still pending.

The reconstruction of a detailed stratigraphy and the recognition of potentially mappable layers at regional scale, is the basis to attempt an overall synthesis aimed at correlating the studied succession with those characterizing the northern Valtiberina and Romagna areas.

# Tectono-stratigraphic reconstruction of the Pietra di Finale (Ligurian Alps, Italy): new insights from the discovery of soft-sediment deformation structures

Perozzo M.*[1], Tamburelli S.[1], Mueller P.[1], Menegoni N.[1], Maino M.[1], Crispini L.[2] & Seno S.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* michele.perozzo01@universitadipavia.it

*Keywords:* field mapping, soft sediment deformation, Ligurian Alps.

We present new field-based data derived from geological mapping of the Finale Ligure area (Ligurian Alps), where post-collisional Miocene deposits of the "Pietra di Finale Formation" and its "Basal Complex" occur. The fieldwork has been performed during the 1:10,000 scale mapping of the Sheet 245 "Albenga" in the framework of the Italian Geological Survey Project (CARG). The Langhian-Serravallian carbonate-siliciclastic coastal wedge of the "Pietra di Finale Formation" (Boni et al., 1968; Brandano et al., 2015) unconformably overlays the deformed Mesozoic carbonate sequence belonging to the inner Briançonnais units (Vanossi et al., 1984). Between them, the heterogeneous uppermost Oligocene- early Miocene terrigenous sequence (conglomerates, sandstones, and marls) of the "Basal Complex" locally occurs.

Traditionally, all the post-collisional sediments are considered as a low strain region due to the lack of any deformation evidence, suggesting a Miocene tectonic quiescence in the southernmost part of the Alps (Brandano et al., 2015).

Our new data show that the boundary between the "Basal Complex" and the "Pietra di Finale Formation" displays a uniquely well-exposed assemblage of Soft Sediment Deformation (SSD) features. These features include (i) vertical sediment expulsions recognizable by gross changes in granulometry compared to the hosting sediments, (ii) carbonatic fluid-expulsion veins, (iii) lateral continuity of SSD-prone layers and (iv) sequential vertical and lateral organization of SSDs. The main clues suggest that these structures were originated from a (syn-sedimentary) seismic event.

The main goal of this study is to unravel the origin of atypically large coarse-clastic injections into the hosting calcarenites, distinguishing seismically from diagenetically induced sediment disturbances. The recognition of seismically-induced deformation shed a new light on the geodynamic evolution of the studied alpine sector. The role of anticlockwise rotation of the Corse-Sardinia block during the Oligo-Miocene time needs to be considered. The Ligurian sector did not experience significant deformation, but only rigid body type rotation (Vanossi et al., 1994). This event may have triggered, both directly or indirectly, the genesis of the mapped SSD structures during the Miocene.

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# Geological mapping as a tool for understanding the historical landscape evolution of an Alpine valley: the Piuro case study (Bregaglia Valley, SO)

Pigazzi E.*, Apuani T. & Bersezio R.

Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* enrico.pigazzi@unimi.it

*Keywords:* palimpsest landscape, Alpine valley stratigraphy, Piuro 1618 landslide.

Mountain valleys are characterized by an intense geological and geomorphological activity, representing territories in continuous evolution. In the Alps, this evolution is tightly connected with the human exploitation that has to coexist with the natural processes. Geological mapping of these territories hence covers a fundamental role for the understanding of the active geological processes and the assessment of hydrogeological risk, but it is also the key tool to interpret their palimpsest landscape evolution. The case study here presented is located in the area of Piuro, a small village of the Italian Bregaglia Valley (Central Alps) famous for the catastrophic landslide that in 1618 erased the entire ancient town. Within the Interreg project A.M.AL.PI.18 (Interreg V-A IT-CH 2014-2020 Cooperation Program – Axis 2 "Cultural and natural enhancement", Id 594274 - A.M.AL. PI.18 "Alpi in Movimento, Movimento nelle Alpi. Piuro 1618-2018") we realized a 1:10.000 geological map and two boreholes (S1: 76 m b.g.s.; S2: 25 m b.g.s.) (Pigazzi et al., 2022) with a stratigraphic, structural and geomorphological approach, principally aimed to the reconstruction of the extent of the landslide deposits and of the source area. Coupling these data with field and remote geomorphological analyses performed on a high resolution 0.50 m DTM (Marotta et al., 2021), radiocarbon age determinations from borehole samples and archaeological and historical observations we constrained the relative depositional chronology of the lithosomes that compose the valley bottom. We then proceeded with the sub-surface interpretation of the single sedimentary bodies that were progressively subtracted from the actual topographic surface to obtain a 3D reconstruction of the interpreted pre- and immediately post-1618 event topographic surfaces. We also proposed a plausible interpretation of the chronological evolution of the valley bottom of Piuro from the post-Last Glacial Maximum to present, that shows how the evolution of this section of the valley has been predominantly dominated by gravitational and torrential related processes for the last ca 10.000 years.

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# Sedimentary evolution of the Quaternary cover and its relationships with buried structures: insights from subsurface 3D modelling of the CARG - 185 Ferrara Sheet

Riva A., Caggiati M.* & Caputo R.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* marcello.caggiati@unife.it

*Keywords:* CARG, geological mapping, 3D modeling.

A large amount of subsurface datasets is available in the Po plain, derived from both wells and seismic profiles carried out for hydrocarbon exploration, and from direct and indirect tests used in applied and environmental geology (e.g., core drilling and cone penetration tests). This information, collected in a large spatial database during the development of the Sheet 185 "Ferrara" of Italian Geological Map (CARG Project), allows to obtain reliable 3D models of the structure and architecture of the Late Quaternary sedimentary succession. Furtherly, the techniques used in the mapping project provide clues on the subsidence rate and on the behavior of Quaternary depositional systems. 3D surfaces, based on these datasets, have been modelled for better understanding the sedimentary evolution.

Within the investigated area, the major tectonic structures belong to the broader Ferrara Arc and form a large anticlinal ramp-fold system with a ESE-WSW hinge axis. This structure affects the whole Mesozoic and Tertiary succession, but its persistent activity clearly controls and deforms the Pleistocene sedimentary cover up to the post-Last Glacial Maximum deposits. The latter mainly consist of fluvial sandstones (Po and Adige rivers affinity) in the central and northern part of the mapped area, and of a mixed succession of muddy sediments with fluvial sand lenses (Apennine rivers affinity) in the southern part of the mapped area. The subsurface anticline is characterized by relatively steep flanks, with a backthrust in the backlimb, and the uplift, localized along the crest, strongly controls the hydrographic network causing rivers diversions.

Stratigraphic information, joined with historical and archaeological data, suggest that younger sediments are characterized by an approximately W to E increase in relative subsidence rates. This variation could be possibly associated to the occurrence of a likely NNE-SSW-trending fault inherited from the Mesozoic break-up phase. Its role in the present-day tectonics should be further investigated.

# The eastern margin of the Trento Platform in the Dolomiti Bellunesi area (NE-Italy): evidence from CARG geological mapping

Riva A., Gianolla P.* & Caggiati M.

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* piero.gianolla@unife.it

*Keywords:* Jurassic, carbonate platform margin, carbonate platform demise.

The recent investigations as part of the new Sheet 046 "Longarone" of the Geological Map of Italy (CARG Project) at 1:50,000 scale, contributed to improve the knowledge on the evolution of the eastern margin of the Early Jurassic Trento Platform and to understand its relationships with the adjacent basin.

The evolution of the eastern margin of the Trento platform has been matter of debate, due to poor stratigraphic characterization and difficult accessibility of the outcrops.

The Jurassic succession east of the Cismon creek is characterized at the base by bituminous dolomites overlying the Upper Triassic Dolomia Principale, representing a signal of the birth of the nearby Belluno Basin. The area roughly between the Cismon and Cordevole creeks, however, remained in shallow water conditions until the Pliensbachian, when a backstepping phase occurred.

The Calcari Grigi Group succession in this area is different from the classical one of the Asiago Plateau, described by many authors. The first unit, the Monte Zugna Fm, is heavily affected by dolomitization ("Dolomia del Nusieda" Auct.) and is about 500 m thick. The top of the Monte Zugna Fm is regionally marked by a deepening trend dated to the Early Sinemurian. It is outlined by the transition from peritidal environments towards relatively deeper settings, where the deposition of ooidal and peloidal shoals (e.g., Loppio Oolite in Asiago) occurred. The post-Early Sinemurian succession of the Dolomiti Bellunesi is then represented by a thick succession (400-500 m) of ooidal and peloidal grainstones, often showing cross laminations, fading towards the margin of the platform: this implies that is extremely difficult to identify the exact topographic location of the margin, as it is made by ooidal sands aggrading and prograding towards the basin. In the very last phase of evolution of this shoal system, the shedding in the basin was increased, creating a tongue of calcarenites (Soffranco mb.) within the basinal succession, extending several kilometres from the edge of the platform. The marginal succession resembles, in some ways, the Massone Oolite of the western margin of the Trento Platform and is, in fact, age equivalent, spanning from Early Sinemurian to Pliensbachian.

In the Late Pliensbachian, a strong backstepping of the platform margin occurred, with partial drowning: in the areas close to the Valsugana Fault System (Monte Celo), the Fanes Encrinites are recording this phase on the platform top, while some encrinites were also shed into the nearby basin (Val degli Erbandoli lithofacies of the Igne Fm). The same encrinites have been recorded east of the geological sheet, in the Piani Eterni area, that probably represented a long-lasting horst of the platform, where the peloidal/ooidal carbonate factory was located.

The final drowning of the Trento Platform occurred in the latest Pliensbachian/Early Toarcian and is documented in the basin by the disappearance of resedimented shallow water products.

# Geological and structural lineaments of Chiaramonte Gulfi area (Hyblean Plateau)

Salerno A.*[1], Foti A.[1], Tortorici G.[1] & Catalano S.[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingeneria, CNR, Roma.

*Corresponding author e-mail:* salerno.alberto92@gmail.com

*Keywords:* Hyblean Plateau, Ragusa Formation, Comiso-Chiaramonte fault system.

We performed a detailed (1:10,000 scale) geological and structural field survey in the Chiaramonte Gulfi area, located in the northwestern margin of the Hyblean Plateau (eastern Sicily). In the study area, Late Oligocene-Middle Miocene carbonate "Ragusa Formation" (Rigo & Barberi, 1959; Grasso et al., 2000) extensively crops out. This is constituted at the base by the ~100 m thick marly limestones of Leonardo member (Upper Oligocene) and on top by Irminio member (Aquitanian-Langhian), represented by a lower portion constituted of well-cemented packstone beds, separated by thin marly-sandy interlayers, passing upward to an alternation of calcarenites and marls for a total thickness of about 150 m. Observed lithostratigraphic units and tectonic lineaments have been displayed in a geological map by means of a GIS software (ArcGIS). The field analysis was integrated, on the GIS platform, with a detailed (2x2 m) Digital Elevation Model, 1:10,000 scale regional topographic maps, and orthophotos.

In the study area, a set of N-S oriented normal faults (Chiaramonte System) splaying from a major N60 left-lateral fault (Comiso fault) separate three sectors characterized by different lithological successions. In the western sector, bordered by the Chiaramonte System to the East, and the Comiso Fault to the Southeast, a chaotic brecciated formation, here named "Monte Raci" succession, extensively crops out. The brecciated lithofacies (Foti et al., 2022), made of cm-to m-sized blocks immersed in a chaotic matrix, derives from the complete stratal disruption of an alternation of limestones and marls. They represent the top of the Ragusa Fm, directly covering the lower stratigraphic horizons of the same formation (Leonardo member). We interpreted these deposits as the product of the compression recorded along low-angle detachments that produced the fluid overpressure needed to favor the fluid injection and the stratal disruption. In the central sector, across the Chiaramonte Fault System, a monotonous alternation of basinal limestones and marls forms the entire succession of the Ragusa Formation, here named "Chiaramonte" succession. In the eastern sector, the succession named "Ragusa", is characterized by the occurrence of type-succession, made up of the lower Leonardo member and overlaying Irminio member. The new field evidence strongly suggests that the area of the modern western margin of the hyblean Plateau suffered high mobility during the Oligo-Miocene, that controlled the facies distribution of the Ragusa Formation and the early deformation in a general contractional context.

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# Subsurface geological data analysis of the Hyblean region (SE Sicily): implications in the tectonic evolution of the area

Salerno A.*[1], Foti A.[1], Tortorici G.[1] & Catalano S.[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Istituto di Geologia Ambientale e Geoingeneria, CNR, Roma.

*Corresponding author e-mail:* salerno.alberto92@gmail.com

*Keywords:* Hyblean Plateau, 3D geological model, retro-deformation.

A new processing method of subsurface geological data analysis allows us to achieve a new 3D subsurface geological model of the northwestern sector of the Hyblean Plateau, in eastern Sicily. The adopted methodology takes advantage of available well-logs for oil investigation and boreholes for water extraction. The first step of the analyses consisted of the re-interpretation and homogenization of well-logs, accordingly to the current lithostratigraphic model of the region. The elaborated data implemented a geodatabase by mean of a GIS software (ArcGIS). The second step consisted of the extraction of subsurface georeferenced punctual information like the absolute elevation of the base and the top of all the geological units drilled by the boreholes. Using the "inverse distance weighting" (IDW) deterministic method for interpolation, both the basal and the top surfaces of each geological unit was recreated and three-dimensionally visualized by ArcScene software. In the model we also considered the main tectonic regional lineaments as barriers for the lateral interpolation of data. In the final step, we progressively retro-deformed the top of each stratigraphic units to obtain the isopach map to be compared with the residual deformation in the lower levels. We obtain a series of new insights about the deformation history of the Hyblean Plateau, which are strongly supported by preliminary field data collected in the area and can be summarized as follows:

The variability of the thickness of the geological units is largely due to local tectonic thickening connected to early detachment processes, rather than the existence of original depocenters;

The effects of motion along the modern NE-SW oriented western margin of the Hyblean plateau (Comiso-Chiaramonte fault system) are clear not only in the Late Miocene-Quaternary period, when also the NNE-SSW trending Scicli Line fault is active, but also during the Upper Cretaceous-Eocene period.

An WNW-ESE oriented fault system with a left-stepping en-echelon geometry, never reported in the geological literature, seems develop from the northern tip of the NW-SE striking Tellaro Line to the western margin of the plateau.

Two detachment surfaces can be located at the base of the Buccheri formation (Middle Jurassic-Upper Jurassic) and of the Amerillo formation (Upper Cretaceous-middle Eocene).

# Constraining the slip rate of a Jurassic rift fault through the drowning history of a carbonate footwall and age of clinoforms draping its marginal escarpment

Santantonio M.[1], Cipriani A.*[2], Fabbi S.[2] & Meister C.[3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] Muséum d'Histoire Naturelle, Geneva (Switzerland).

*Corresponding author e-mail:* angelo.cipriani@isprambiente.it

*Keywords:* tethyan rifting, slip rates, Jurassic.

The methods of "classic" field mapping in sedimentary successions, where lithostratigraphy, biostratigraphy, and sedimentology meet, still have a tremendous potential for producing innovation on long-standing themes nowadays. We report an example of clinoforms in a Jurassic rifted carbonate system from Mt Acuto (Umbria-Marche Apennines, Central Italy). Based on field evidence, and relying on a multidisciplinary approach integrating geological mapping, ammonite biostratigraphy, and sedimentology, we use syn-rift clinoforms, prograding into a young hangingwall basin, to compute the slip rates of Early Jurassic rift faults, and to discriminate the syn-rift from the post-rift stages in Central Italy. This novel approach is made possible through the identification of an exhumed tract of a submarine escarpment rooted in an extensional fault, where an unconformable set of clinoforms, sourced from a residual carbonate factory, seals a thick section of the pre-rift substrate unroofed in the footwall by that fault. Biostratigraphic information, provided by a rare ammonite assemblage recovered in a clinoform bed, is used to measure the amount of displacement and the resulting slip rate along the sealed fault/escarpment. Our results show that much (if not most) of the ~1.2 km of paleostructural relief that existed between the Mt Acuto high and the Burano/Bosso basin (Santantonio & Carminati, 2011) was achieved very early in the history of this sector of the future African continental margin, and occurred in one or two short clustered slip events. Slip rates of 600-1000 m/Myr are here computed for Tethyan rift faults, producing >1 km of paleostructural relief in ~2 million years (earliest Sinemurian: Bucklandi Zone p.p. – Semicostatum Zone p.p.) (Santantonio et al., 2022). Based on our dataset and interpretation, it can also be stated that the progressive levelling of the rugged submarine topography inherited from the rifting phase, which lasted >50 million years, took place essentially in a post-rift regime in the Apennines. Exceptions are represented by local episodes of minor fault-zone rejuvenation, documented in the Umbria-Marche-Sabina region (Toarcian: Cipriani et al., 2020; early Bajocian: Galluzzo & Santantonio, 2002).

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# The geological map of the Sheet 628 "Sciacca" (CARG Project)

Sulli A.*, Gasparo Morticelli M., Agate M., Todaro S., Lo Presti V., Bonfardeci A. & Avellone G.

Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* attilio.sulli@unipa.it

*Keywords:* CARG project, Sciacca, Geological map.

The Sheet 628 "Sciacca" of the Geological Map of Italy (CARG Project) locates in southwestern Sicily, in correspondence of the outer segment of the Sicilian fold and thrust belt. Within the Sheet, which includes both emerged and submerged sectors, we identified sectors with very different geological settings:

- a segment of the Sicilian-Maghrebian chain, in different areas of the Sheet;
- a segment of the Gela thrust system, in the southeastern region;
- a segment of the foredeep basin, in a small area at the southwestern sector along the western edge of the Gela thrust system.

The upper Triassic to Quaternary sedimentary succession belongs to two main sedimentary domains:

- the Hyblaean-Saccense domain, consisting of Meso-Cenozoic carbonate rocks, outcropping along the Rocca Ficuzza-Rocca Nadore ridges (northern sector) and at Mt. San Calogero around the town of Sciacca;
- the Sicanian basin, consisting of carbonate and silico-carbonate rocks of pelagic environment, outcropping in the northeastern region;

These sequences are covered by terrigenous (upper Tortonian – lower Messinian), evaporitic and clastic (Serie Gessoso Solfifera, Upper Messinian), pelagic (Trubi, Lower Pliocene), and terrigenous-hybrid (Upper Pliocene-Pleistocene) deposits. Most of the successions appear to be intensely deformed and organized in tectonic units pertaining to the Sicilian-fold and thrust belt.

The main geological issues of the study area concern:

- the stratigraphic characters of the Saccense succession, in a key region for the understanding of the Meso-Cenozoic paleogeographic evolution of the African continental margin;
- the complex structural setting, characterized by active tectonic structures, pertaining to the Sciacca – Gela and Monte Magaggiaro – Pizzo Telegrafo Composite Seismogenic Sources (DISS–INGV);
- the occurrence of a significant tectonic structure that crosses the Sicilian Channel in the N-S direction, between the Sicilian coast and the island of Pantelleria;
- the magmatic complexes occurring in the offshore sector in correspondence with volcanic banks, the most important of which is the Graham Bank.
- the heat flows anomalies and the hydrothermal fluid circulation systems within the Meso-Cenozoic carbonate sequences (hydrothermal system of San Calogero Mt.).

The geological surveys make use of multiple techniques and methodologies, according to the different objectives, including the production of a 3D subsoil geological model. The results will help to better define the Quaternary tectonic evolution of an essential sector for understanding the recent geological evolution of the Sicilian fold and thrust belt.

# The Cenozoic paleogeographic evolution and sequence stratigraphy of the Salento Peninsula (southern Apulia platform)

Tancredi S.*[1], Margiotta S.[2], Grasso S.[2], Tentori D.[3] & Milli S.[1-3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Lecce. [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* simone.tancredi@uniroma1.it

*Keywords:* depositional setting, paleogeography, sequence stratigraphy.

The Salento Peninsula constitutes the outcropping portion of the Apulia Carbonate Platform, one of the carbonate platforms developed along the southern margin of the Tethys Ocean since the Triassic. The Salento Peninsula represents the culmination of a lithospheric anticline whose genesis is linked to the subduction of the Adria microplate below two chains with opposite vergence: the SW verging Dinarides-Hellenides and the NE verging Southern Apennines orogenic belts. The whole area is characterized by a thick and undeformed carbonate succession that develops in emerging and submerged sectors. The stratigraphy of Salento Peninsula is characterized by several lithostratigraphic units separated by unconformity surfaces deposited during the Cenozoic, and that are particularly preserved along the Adriatic side of the peninsula.

We integrated outcrop and borehole data to reconstruct WSW-ENE and NNW-SSE oriented correlation panels, to depict the stratigraphic-structural relationships during the deposition of the each lithostratigraphic unit and to show the stratigraphic architecture and paleogeography of the Salento Peninsula during the Cenozoic. The resulting paleogeographic schemes allowed us to better define how the sedimentation of the Salento Peninsula was influenced by the migration of the two chains and how the carbonate systems reacted to the close interaction among climatic changes, high-frequency eustatic sea-level variations, and coeval tectonic uplift/subsidence controlled by the westward and eastward migration of the Dinarides-Hellenides and Southern Apennines, respectively. These data allowed us to produce a sequence-stratigraphic scheme of the Salento Peninsula where we recognized composite and simple high- and low-rank depositional sequences.

# From 2D geological maps to 3D models: A case-study in the Central Alps (Lombardy, Italy)

Zuffetti C.*[1], Bersezio R.[1], Lucchelli A.[1], Stevenazzi S.[2] & Masetti M.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Ingegneria Civile, Edile e Ambientale, Università di Napoli «Federico II».

*Corresponding author e-mail:* chiara.zuffetti@unimi.it

*Keywords:* Alps, 3D model, stratigraphy.

Building 3D geological models from field data is a common task in geological studies aiming at natural resources management and hazard assessment. The geological history of sedimentary basins as well as mountain chains originates multiple-scale, nested heterogeneities which must be represented by 3D models. The most relevant input data for these models derive from field geological mapping and are integrated by remote-sensed surface surveys and geophysical subsurface images. A gap between the field survey process and the set-up of geo-models exists, mostly concerning the scale and accuracy of input data vs. the expected model outcomes. Besides the accurate representation of geological geometries, bridging this gap would imply an efficient conceptualization of topological and cross-cut relationships between the geological entities. This might be obtained by translating the geological evolution into straightforward, simple, and flexible modelling rules that should advise the field survey approach to permit the collection of efficient input datasets. We were challenged to tackle these problems while developing the 3D model of hydrostratigraphy of the Alpine rock aquifers of Lombardy, based on a set of nonuniform geological maps. Our first attempt led to combine the geological knowledge based on geological maps, with a novel approach for 3D modelling. We present it fora small part of the new 3D model of the Lombardy Central Alps, within the Southalpine fold-and-thrust belt

The heterogeneous dataset was normalized, classified, and stored into an *ad-hoc* built hierarchic Geodatabase. The 3D geological model was computed based on the potential field interpolation method of 3DGeoModeller®. The new conceptual model (1:25.000 to 1:250.000 scale) represents the palimpsest arrangement of the three components of the geological heterogeneity (structural, lithostratigraphic *l.s.*, geomorphological), accounting for the hierarchy of their assemblage and the relative chronology of the geological evolution. The separate geologic entities (bounding surfaces classified by their nature and intervening lithosomes) were ordered into a hierarchic geologic pile, permitting to codify the lithological variability and the chronology of the geo-history. The relationships set between faults and lithosomes drove the modelled cross-cut relationships coherently with the geological evolution.

The resulting 3D geological model draws the geometry of the geological heterogeneities nested into one another through the decreasing rank of the geologic pile. The present model, predisposed for hydrogeological studies, allows for instance to inspect the location of water springs in relation to the 3D representation of permeability thresholds, induced by structural and morphological features like thrust surfaces, regional fold axes, steep cross-cutting faults, deep valleys and so on.

# S36.

# Open session on Stratigraphy

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# High-amplitude, precession-controlled oscillations in Mediterranean base-level triggered gypsum-marl cycles during the final Stage 3 of the Messinian Salinity Crisis

Andreetto F.*[1], Flecker R.[2], Aloisi G.[3], Mancini A.M.[4], Guibourdenche L.[3], de Villiers S.[5] & Krijgsman W.[1]

[1] Department of Earth Sciences, Utrecht University (Netherlands). [2] School of Geographical Sciences and Cabot Institute, University of Bristol (UK). [3] Institut de Physique du Globe de Paris, Université de Paris (France). [4] Dipartimento di Scienze della Terra, Università di Torino. [5] Africa Earth Observatory Network, Earth Stewardship Science Research Institute, Nelson Mandela University, Port Elizabeth (South Afrtica).

*Corresponding author e-mail:* f.andreetto@uu.nl

*Keywords:* Messinian Salinity Crisis, Sr isotopes, Onshore-Offshore correlations.

Cyclic, precession-paced deposition of gypsum-marl couplets in both intermediate (200-1000 m) and deep (>1000 m) Mediterranean basins characterizes the last 200 kyrs of the Messinian Salinity Crisis (MSC Stage 3) prior to the Zanclean marine replenishment. The marls in these basins commonly contain shallow-water (30-100 m) Paratethyan ostracods, whereas the overlying Zanclean deposits reflect deep pelagic settings (>500 m water depth). Similar shallow-water Paratethyan ostracod assemblages also occur in shallow marginal subbasins (<200 m) interbedded with continental clastics. The longest and most continuous Stage 3 succession preserved onland accumulated in the intermediate Caltanissetta Basin (Sicily). It comprises seven gypsum-marl couplets and is exposed at Eraclea Minoa. Here, we combine micropaleontology and sedimentology with $^{87}Sr/^{86}Sr$ data to constrain the paleoenvironmental conditions, water sources and water level changes during Stage 3. The selenitic gypsum layers at Eraclea Minoa contain well-preserved calcareous nannofossils assemblages dominated by *Reticulofenestra minuta*, a marine species which tolerates stressful conditions. Some ocean water input is also required to explain the gypsum $^{87}Sr/^{86}Sr$ data, which describe a small range of ratios (0.708704-0.708813) lower than coeval ocean water. Mass-balance calculations indicate that during Stage 3 gypsum precipitation, the Atlantic made up ≤20% of a Mediterranean water mass dominated by low salinity discharge from large river systems and Eastern Paratethys. The ostracod $^{87}Sr/^{86}Sr$ values of the marls at Eraclea Minoa are commonly lower than those of the gypsums and show high-amplitude, high-frequency oscillations, characteristic of lacustrine systems. This suggests that while the gypsums formed during Mediterranean base level fall driven by a reduction in North African monsoon-fed river discharge, the shallow-water, lacustrine marls were deposited once Mediterranean water level fell below the depth of the Caltanissetta Basin. Marl deposition in intermediate and deep basins therefore occurred during Mediterranean base-level lowstands at insolation minima and out of phase with ostracod-bearing marl deposition on the margins, which occurred during insolation maxima-driven highstands. Stage 3 cyclicity suggests that the Mediterranean experienced 6-7 high-amplitude base-level changes, driven by precession-paced changes in the Mediterranean's freshwater budget and, possibly in the Atlantic inflow. A revised astronomical tuning indicates that MSC Stage 3 started at 5.515 Ma, with the first occurrence of Paratethyan ostracods on Sicily at 5.46 Ma. This model for sequential deposition in deep, intermediate and shallow Mediterranean sub-basins helps reconcile the discrepancies between offshore- and onshore-based interpretations of the final phase of the Messinian Salinity Crisis.

# Paleogeography and sedimentary evolution of the Southern Adriatic province in the Permian-Triassic

Borrelli M.*, Critelli S. & Perri E.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* mario.borrelli@unical.it

*Keywords:* Evaporite, paleogeography, paleoenvironments.

Through the study of different exploration wells, the Permian-Triassic sedimentary and paleogeographic evolution of the Southern Adriatic province is here constrained.

During Permian continental settings laterally grading to coastal lagoons developed. Successively, in the Ladinian, after a generalized subaerial exposure and a marked erosional phase, the extensional tectonic inputs linked to the Tethys rifting brought to a relative sea-level rise and to the formation of carbonate shelves in NW-SE oriented tectonic depressions. During Carnian-early Norian a further extensional tectonic pulse coupled with a relative sea-level drop, led to the isolation of the basin from the open sea with a consequent enhancing of salinity and settlement of evaporative conditions. This triggered a massive evaporite deposition that culminated during Norian, with the evaporite filling of the basin. Lastly, In the late Norian-Rhaetian a marked relative sea-level rise, restored all the connections with the open-sea and shifted the evaporite deposition to the margins of the basins that previously remained under subaerial conditions.

The late Norian-Rhaetian shift of the evaporative sedimentary environments is recorded in Puglia 1 well-borehole from which two cores were recovered and studied. The first core (5.048-5.056 m) is characterized by the presence of laminated dolomudstones with remnants of thinly microbial laminae alternated to lenticular/tabular shaped anhydrite crystal levels, suggesting a sabkha-type environment of formation. The second core (6.067-6.075 m), is dominated by massive coarse-grained crystalline dolomite with remnants of oolites and undetermined shell fragments, indicating a shallow-water environment of deposition (e.g., shore-face/offshore transition setting).

Syn-sedimentary and late-stage diagenetic processes affected both facies. Primary anhydrite crystals deposited in the sabkha, were at least affected by one hydration/dehydration cycle. Dolomitization, which is widespread in both cores, occurred mainly during the burial stage as the circulation of high saline and Sr-depleted dolomitizing fluids under general reducing conditions.

# The Messinian Salinity Crisis in the Central Mediterranean: Paleogeography and sedimentary evolution of two North Calabria basins (South Italy)

Borrelli M.*, Critelli S. & Perri E.

Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* mario.borrelli@unical.it

*Keywords:* evaporites, Messinian Salinity Crisis, paleogeography.

An integrated analysis of subsurface dataset and outcropping successions permitted to define a sedimentary and paleogeographic evolutionary model during the Messinian Salinity Crisis (MSC) of the wedge-top Rossano and Crotone Basins, located along the Ionian side of North Calabria.

During the late Tortonian-early Messinian, open normal marine conditions characterized the studied basins, as suggested by the deposition of deep-water claystones followed by diatomites (Tripoli Fm). The first basin restriction occurred during the early Messinian (ca. 5.96 Ma) when a relative sea-level still stand triggered the formation of a carbonate platform system (Calcare di Base Fm - CdB). This latter was characterized by sabkha to shallow-water environments grading into a gentle slope to basin setting. A successive relative sea-level drop (ca. 5.60 Ma) induced a general exposure of the CdB platform system and the creation of a marked erosional surface linkable with the Messinian Erosional Surface (MES). Consequently, progradational early LST forced regression wedges deposited and, as the reduction of open-sea connections, more severe restricted conditions took place. Later on, during the late LST, the massive deposition of salt dominated bodies brought to sedimentary filling of the basins and to the consequent leveling of the paleobathymetric differences. Afterwards, a transgression phase (TST) inundated again the basins, causing firstly the sedimentation of clay dominated deposits, and successively, during a further sea-level still stand (HST), the reestablishment of evaporitic conditions and the deposition of widespread shallow-water sulphate deposits.

Lastly, a new severe sea-level drop (LST) exposed again all the previous deposits, as testified by the superimposition of alluvial conglomerates along incised paleovalleys above the HST sulphate deposits. This event marks the transition to the Lago-Mare event that typifies the latest stage of the MSC, which definitely terminated with the reflooding of the Mediterranean at the Pliocene base (ca. 5.33 Ma).

# Some issues on carbonate factory classification: insight from Upper Miocene *Lithothamnion* Limestone (Majella central Apennines, central Mediterranean)

Brandano M.*[1], Cornacchia I.[2], Ruscitto V.[1] & Marianelli D.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* marco.brandano@uniroma1.it

*Keywords:* carbonate ramp, Messinian, carbonate factory.

This work aims to classify the carbonate factory of the *Lithothamnion* Limestone using the most common classifications (e.g Schlager, 2003; Reijmer, 2021). This lithostratigraphic unit, late Tortonian to early Messinian in age, constitutes the uppermost, shallow-water unit of the Bolognano Formation outcropping in the Majella structure (Central Apennines, Italy). The latter represents the northern extension of the Apulia Carbonate Platform developed in the central Mediterranean domain. The profile of the *Lithothamnion* Limestone is consistent with a homoclinal carbonate ramp, with a wide middle ramp environment in which coralline algae, mainly forming the mäerl facies, dominated the carbonate production. The outer ramp, in the aphotic zone, was characterized by bioturbated hemipelagic marls with planktonic foraminifera and pectinids. The inner ramp was widely colonized by seagrass meadows interfingering with the mäerl facies of the middle ramp. The main biota producing carbonate sediments of this vegetated area were benthic foraminifers (mainly porcelanaceous) and red algae (RA-Foralgal) together with abundant serpulids. The shallowest facies of the inner ramp consist of oolitic shoals and coral buildups generally encrusted by serpulids and red algae.

One of the classical carbonate factory classifications is based on the style of carbonate precipitation: abiotic, biotically induced and biotically controlled with heterotrophic and autotrophic modes (Schlager, 2003; Reijmer, 2021). This resulted in three main types of carbonate factories: the tropical shallow-water factory (T-factory), dominated by light-dependent biota (biotically controlled); the cool water (C-factory), dominated by heterotrophic skeletal production (biotically controlled) and the mud-mound (M-factory), with predominant microbial and abiotic precipitates (biotically induced and abiotic). Following this classification, two carbonate factories coexist in the *Lithothamnion* Limestone, the T-factory in the shallow inner ramp and the C-factory in the middle and outer ramp. Classically, the co-occurrence of the T-factory (dominated by a photozoan skeletal assemblage) and the C-factory (dominated by a heterozoan skeletal assemblage) has been interpreted to represent sedimentation in the warm-temperate realm, in a wide range of trophic conditions. However, the inner ramp of the investigated example shows also ooid deposits, typically considered exclusive components of the T-Factory developed in a tropical belt. In this work, we will try to justify or unjustify the coexistence of tropical and cool water carbonate components and to understand which environmental and climate conditions characterized the paleo-Adriatic seawater between late Tortonian and early Messinian.

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# Organic matter remains in primary evaporitic minerals: new insights on paleoenvironmental conditions and mineral crystallization during the Messinian Salinity Crisis

Cipriani M.*[1], Dominici R.[1], Costanzo A.[2], Cianflone G.[1], Miriello D.[1], Perri F.[1] & Guido A.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland, Galway (Ireland).

*Corresponding author e-mail:* mara.cipriani@unical.it

*Keywords:* gypsum, organic matter, mineralization.

Biological mineralization, also known as biomineralization, is a term that indicates mineralization processes associated to biotic activity (Perry et al., 2007). Nucleation of bio-crystallites can be: 1) controlled directly by the organisms; 2) induced by microbial communities or 3) influenced by organic matter decay. Processes involving carbonate biomineralization have been extensively studied. On the contrary, those related to precipitation of non-carbonate minerals (i.e., evaporitic minerals) did not received particular attention. Recent studies have shown that fast growth of gypsum crystals allows rapid entrapment of organic material, including microalgae and prokaryotes, and represent an excellent archive of microbial life (Natalicchio et al., 2022; Aloisi et al., 2022).

The aim of this work is to investigate the primary gypsum deposit formed during the Messinian Salinity Crisis (5.97-5.33 Ma) in the Catanzaro Trough (Southern Italy) with a geomicrobiological approach. Optical microscopy, UV-epifluorescence and micro-Raman spectroscopy have been applied to investigate the relationship between the organic material and the processes involved in the gypsum precipitation. The gypsum crystals of the banded facies (swallow-tail twin selenite) show an internal zonation, characterized by the alternation of millimetre thick turbid (cloudy) and limpid (clear) laminae. The clear laminae show a small number of fluid and/or solid inclusions. In contrast, the cloudy laminae contain abundant primary fluid inclusions and amorphous material. The latter show a homogeneous bright epifluorescence under UV-light. Raman spectra reveal that in the cloudy laminae the gypsum bands are associated to the typical G and D band of organic matter. The detection of these bands allows to link the source of UV-epifluorescence to the presence of biomolecules. Although investigation in progress, (e.g., characterization of the biomarker in GC-MS), aim to elucidate the specific composition of the organic material, the present research supports the possible use of primary gypsum as a new tool to detect and to investigate biological signature in the fossil record and to explore the possible biological role in the nucleation of evaporitic minerals.

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# Speleothem $\delta^{18}O$-$\delta^{13}C$ stratigraphy precisely constraining the Holocene inception in southern Italy (Sant'Angelo Cave, Apulia)

Columbu A.*[1], Spötl C.[2], Fohlmeister J.[3], Hu H.-M.[4-5], Chiarini V.[6], Hellstrom J.[7], Cheng H.[8], Shen C.-C.[4-5] & De Waele J. [2]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Institute of Geology, University of Innsbruck (Austria). [3] German Federal Office for Radiation Protection, Berlin (Germany). [4] High-Precision Mass Spectrometry and Environment Change Laboratory, Department of Geosciences, National Taiwan University, Taipei (Taiwan). [5] Research Center for Future Earth, National Taiwan University, Taipei (Taiwan). [6] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [7] School of Earth Sciences, University of Melbourne (Australia). [8] Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an (China).

*Corresponding author e-mail:* andrea.columbu@unipr.it

*Keywords:* Holocene, speleothems, isotope stratigraphy.

Accurately constraining the Holocene inception at middle latitudes is key to evaluate the pace and timing of northern latitudes rapid warming propagation into nowadays highly populated areas. This is especially true for the Mediterranean region, a climate hotspot, where future climate changes will likely have a more dramatic impact than in many other parts of the world (Giorgi, 2006). In Italy, the Holocene lower chronological boundary in continental settings has been mostly defined through flood plain and lacustrine proxies in between 12 and 10 ka, sometimes with low resolution/accuracy timeseries. Most importantly, it has never been constrained using speleothems (i.e., calcite cave deposits such as stalagmites). The latter allow for the construction of ultraprecise chronologies by using the U-Th method. Climate sensitive proxies, such as $\delta^{18}O$-$\delta^{13}C$, can be anchored to these chronologies procuring information about palaeorainfall dynamics and temperature-related soil bioproductivity.

Here, we present a high-resolution reconstruction of rainfall/soil activity changes in the Central Mediterranean across the last glacial termination. It is based on a novel $\delta^{18}O$-$\delta^{13}C$ (0.2 mm subsampling spacing) time series from a southern Italian stalagmite, deposited in Sant'Angelo Cave (SA1, Ostuni, Apulia) between $47.8^{+0.41}/_{-0.39}$ and $6.63^{+0.62}/_{-0.57}$ ka. In the time interval 20-9 ka, multiple U-Th ages (n=22) result in a final age model with an average uncertainty of <0.3 ka and a resolution of ~25 years. The resulting $\delta^{18}O$-$\delta^{13}C$ timeseries demonstrates high similarities with Greenland ice cores archives, as well as other regional-to-local records throughout the Mediterranean area, Middle East and Asia. A prominent shift of the isotopic curve, interpreted as enhanced rainfall and temperature, allows to set the lower Holocene boundary at $11.95^{+0.15}/_{-0.19}$ ka. This agrees, within uncertainties, with Greenland records (11.65±0.1 ka). Concurrently, this work also provides low uncertainty ages for the well-known climate chronozones related to the glacial termination, as the Bølling-Allerød ($14.04^{+0.46}/_{-0.42}$ to $13.02^{+0.31}/_{-0.30}$ ka) and Younger Dryas ($13.02^{+0.31}/_{-0.30}$ to $11.95^{+0.15}/_{-0.19}$ ka). We take this opportunity to discuss the climate significance of SA1 $\delta^{18}O$-$\delta^{13}C$ stratigraphy for the evaluation of the last deglaciation impact within the broad central and western Mediterranean area.

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# Triassic successions of Sardinia, Corsica and Briançonnais domain: analogies and correlations

Costamagna L.G.*

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* lucakost@unica.it

*Keywords:* German Triassic, W Alps, Sardinia-Corsica.

Analogies exist among the Triassic Sardinian, Corsican and Briançonnais successions, belonging to the Grand Iberian Microplate. In the Western Alps the Briançonnais Triassic successions rest unconformably either over the volcano-sedimentary Permian basins, or on the Carboniferous metamorphic rocks. The trifold partition of the Germanic Triassic is respected: a siliciclastic succession of polymict to quartzose conglomerates and quartzarenites (Verrucano Brianzonese) evolving to reddish/greenish pelites (Buntsandstein: uppermost Permian to Werfenian) (100 to 150 m); this passes through a thin evaporite-rich cavernous dolostones interval to a carbonate succession (Muschelkalk: Middle Triassic) (250 m), and then to a mixed carbonate-evaporitic succession (Carniole) (50 m) (Keuper: Upper Triassic). The succession is unconformably covered by the irregular pockets of the Siderolitico and thin carbonate breccias followed by the well-bedded carbonate schists of the Dogger a Mytilus or the Middle Jurassic Calcari di Rio di Nava Fm. Similar depositional features are shown by the Corsican autochtonous Triassic successions. The Triassic rocks are very thin (tens of metres). Nonetheless, the Verrucano Brianzonese deposits, the transitional cavernous dolostones and the Middle Triassic carbonates are recognizable, allowing their reference to the Germanic Triassic. In Sardinia, the Triassic is referred to the Germanic Domain for a long time. The Buntsandstein Group (Olenekian-Lower Anisian) rests unconformably either over the Permian red beds basins, or directly over the Variscan metamorphic rocks. Here is a siliciclastic red beds succession (50 m) locally containing evaporites and carbonate intercalations. Upwards, the Muschelkalk Group (Middle Triassic) follows: it is formed by a carbonate succession (100 m). Finally, the Keuper Group (Upper Triassic) (100 m) takes place: significant differences from the N (alternations of fine siliciclastics ad evaporites passing to cavernous carbonates) to the S (carbonates rich in evaporitic remains with rare fine siliciclastics) here exist. Upwards, while in the W of the island the succession passes to the Liassic shallow carbonates, in the E a stratigraphic gap exists: here over the Middle Triassic carbonates rest unconformably quartzose conglomerates and carbonates of Middle Jurassic age.

Thus the Sardinian, Corsica and Briançonnais Triassic successions show environmental and stratigraphic gaps similarities. At the base an alluvial red bed succession takes place. This is followed by a restricted carbonate lagoon environment with evaporites, and then by a shallow to deep carbonate ramp environment showing a transgressive-regressive evolution. Upwards, the Keuper regression evidences sabkha-type to restricted carbonate platform environments with variable siliciclastic inputs. The environment became more open to the present southwards. In this reconstruction, the Briançonnais represents a distal sector of the Germanic Realm.

# Geological setting of Turin shallow subsoil connected to Holocene deviation of the Po River

Forno M.G.*, Gianotti F., Sartori G. & Storti U.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* gabriella.forno@unito.it

*Keywords:* fluvial terraces, Pleistocene-Holocene, Turin.

Urban Geology is a topic of increasing interest in the last two decades. The present survey of the Turin subsoil (NW Italy) was carried out based on both natural outcrops (essentially located in the scarps along the Sangone and the Po river beds) and anthropic sites (excavations carried out for the building of large infrastructure and drilling of 33 boreholes for the construction of a new sewer collector by SMAT-Società Metropolitana Acque Torino).

These geological investigations allow to evaluate facies, thickness and petrographic composition of fluvial sandy gravel forming the wide proglacial fan of the Rivoli-Avigliana end-moraine system (RAES), on which Turin is built (Turin Unit) (Forno et al., 2018; Forno & Gianotti, 2021). The local finding of a truncated palaeosol, buried under it, suggests that this unit lies on a significant erosional surface shaped in more ancient fluvial sediments (Bennale Unit in Balestro et al., 2009). This discontinuity was recognized both in the outcrops along the Sangone incision and in some cores, allowing a more extensive stratigraphic reconstruction. A new radiocarbon dating of woody macrorest from fine outwash sediments above the palaeosol proves a Last Glacial Maximum age of the Turin Unit. The same investigations suggest the presence in Turin, along the current Po river bed, of subsequent erosional terraces (Molinette T1 and Murazzi T2), shaped by the Po River in the RAES proglacial sediments, and depositional terraces (Vallere T3 and Parco Stura T4), essentially formed by a sandy sequence, also linked to the Po River. Therefore, the Turin Plain first was shaped by the proglacial streams (Dora Riparia basin) and subsequently was involved by erosional/sedimentary phenomena carried out by the Po River.

Some dating of woody macrorest and gyttja into the fluvial sequence of Turin confirm the wide presence of RAES Upper Pleistocene fluvial sediments and the subsequent entrenched Po fluvial terraces, due to a significant fluvial deviation phenomenon during Holocene. This picture agrees with the research regarding the Quaternary fluvial terraces spread over the Turin Hill and suggests the involving of the Turin Plain in the Turin Hill quaternary uplift (Boano et al., 2004).

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# New geophysical data from the marine sectors of the CARG Project – Sheet n. 493 Taranto

Fracchiolla T.*[1], De Giosa F.[2], Festa V.[1], Lisco S.[1], Mastronuzzi G.[1], Rizzo A.[1], Scardino G.[1], Valenzano E.[1] & Moretti M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] En.Su. - Environmental Surveys s.r.l., Bari.

*Corresponding author e-mail:* teresa.fracchiolla@uniba.it

*Keywords:* Taranto seas, multibeam survey, submarine springs.

The Taranto area is one of the most anthropically impacted sectors of the western Europe. Heavy industries, an Italian Navy port, intensive aquaculture, an abandoned ship yard, etc. are concentrated along the Taranto coastal areas. The marine sediments of the "Taranto Seas" (Mar Piccolo and Mar Grande basins) are polluted by inorganic and organic contaminants of different origin, quality and concentration. For this reason, many projects have been carried out to evaluate the thickness and the geometry of the polluted sedimentary units in the upper portion of the Holocene marine successions. In the Mar Piccolo basin (an internal sea of 200 km$^2$) sparker and sub-bottom-profiler data and well logs allowed us to recognize the main sedimentary units which represent the substrate of the Holocene deposits (Calcare di Altamura Fm, Calcarenite di Gravina Fm and argille subappenine unit). The detailed description of well logs and the results of dating procedures show that the Holocene deposits of the Mar Piccolo Basin can be interpreted as an incised valley infill sequence resting on the LGM surface. The acquisition of new data is recently started (in the frame of the CARG Project - Sheet n. 493 Taranto) in the Mar Grande Basin: seismic multichannel reflection, seismic single channel reflection, sub bottom profiler, side scan sonar and multibeam. These data will allow us to describe the relationships between tectonics and sedimentation of the Apulian foreland – Bradanic foredeep units during the Plio-Pleistocene and to establish some correlations with the Mar Piccolo internal sea basin during the Holocene.

Another peculiar feature of the Taranto seas is the presence of several submarine springs ("citri") which represent fundamental freshwater inputs for the habitats and aquaculture of the Mar Piccolo and Mar Grande basins. New multibeam survey carried out in the Mar Grande and Mar Piccolo basins shows the origin of these springs correlating their position to the main structural features in the underlying Mesozoic carbonates. Furthermore, they have not a punctual resurgence as previously indicated, but they represent elongated "citri" fields distributed along specific tectonic structures.

# A new MSC record in the Tabernas basin (SE Spain)

Gibert L.*[1], Corbí H.[2], García-Veigas J.[3], Lozar F.[4], Pineda V.[1], Pérez-Valera F.[2], Gil M.[5], Artiaga D.[3], Lería M.[6] & Soria J.[2]

[1] Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain). [2] Departamento de Ciencias de la Tierra y Medio Ambiente, University of Alicante (Spain). [3] CCiTUB, Scientific and Technological Centers, Universitat de Barcelona (Spain). [4] Dipartimento di Scienze della Terra, Università di Torino. [5] Placo Saint Gobain Ibérica, Madrid (Spain). [6] Departament d'Arts i Conrservació-Restauració, Universitat de Barcelona (Spain).

*Corresponding author e-mail:* lgibert@ub.edu

*Keywords:* Messinian, selenites, gypsum, Betic basins.

The Sorbas and Nijar basins (SE Spain) are well known for their Messinian Salinity Crisis (MSC) records in the Western Mediterranean. The gypsum successions in Sorbas and Nijar consist of selenitic platforms that alternate with white marls occasionally containing marine fauna. These evaporitic sediments overlay the Abad cyclic marls and are assigned to the MSC Lower Gypsum by most authors. Here we present a new MSC section at Rambla de Indalecio, in the nearby Tabernas basin. This section is >150 m thick and includes, in the base, turbiditic deposits of the Turre Fm which are covered by resedimented selenitic beds above an erosional unconformity. Resedimented gypsum includes clast of carbonates and sandstones from preevaporitic Messinian lithostratigraphic units. Above the lower resedimented gypsum interval (2-3 m thick), well stratified selenitic platform deposits occur forming a 30 m thick unit. Unlike in the Sorbas and Nijar basins, the interevaporitic marls in this unit are very scarce. The top of the gypsum succession is a new erosional surface overlaid by fan delta deposits assigned to the Pliocene Abrioja Fm. We apply magnetostratigraphy and biostratigraphy to constrain the age of the Rambla de Indalecio succession, we analyze the sulfur and oxygen isotopic compositions in the gypsum together with the $^{87}Sr/^{86}Sr$ ratios to characterize its origin. Paleontological information constrains the bathymetry of the preevaporitic deposits. Gypsum geochemistry characterizes the studied gypsum succession as MSC Lower Gypsum. Preliminary paleontological data also show evidence for early Pliocene deposits above the gypsum. The water depths for the turbiditic deposits (based on foraminiferal assemblages) are estimated to occur in a deep marine zone (bathyal). The gypsum selenitic platforms are considered not to form below depths of 200 m. The presence of resedimented gypsum beds containing clast of corals and carbonates from the Azagador Mb, derived from marginal areas, above the turbiditic deposits, suggests an important sea-level drawdown in the Tabernas basin. This sea-level fall will occur during the sedimentation of the Lower Gypsum and probably is not recorded in shallower basins like Sorbas. However, the active tectonic activity during the MSC in this region should be carefully considered to evaluate the relative impact of the Mediterranean restriction *vs* local tectonic uplift of this drawdown.

# New constraints on the Holocene uplift of the Crotone Peninsula (Ionian Calabria, southern Italy) as deduced by emerged sea-level markers

Liberatore M.*, Cosentino D., Gliozzi E. & Cipollari P.

Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* marco.liberatore@uniroma3.it

*Keywords:* Calabria, Holocene, uplift.

Calabria has been experiencing rapid uplift since the Early Pleistocene. The elevation of marine terraces relative to the MIS5.5 highstand reaches and exceeds 100 m in several areas (Cerrone et al., 2021). Thus, uplift rates up to 1.3 mm/yr can be calculated for the Messina Strait, 2.2 mm/yr for Capo Vaticano, and 0.8 mm/yr for the Crotone Peninsula.

Uplift persists during the Holocene, as evidenced by bio-geomorphological and archaeological sea-level markers. These have been found well above the current mean sea level. Maximum vertical velocities occur in the Strait of Messina and decrease progressively northward toward Capo Vaticano. However, the record of Holocene coastlines is almost limited to the Tyrrhenian coast. On the Ionian side, the only dated evidence of a higher relative sea level is reported by Pirazzoli et al. (1997).

A new survey campaign on the Crotone Peninsula identified traces of Holocene coastlines higher than the current mean sea level. These were dated through 17 samples by using the $^{14}C$ method. Large blocks of Pleistocene calcarenite record a notch at 1-1.25 m a.m.s.l. that is laterally continuous for tens of meters. At the same elevation, carbonate algae concretions and balanids constrain the age of this shoreline to 2610-2090 cal. yr BP and 2600-2076 cal. yr BP, respectively. Older marine deposits have also been found up to 3 m in elevation. The mean age of five samples reveals that this shoreline was active at 7050-6579 cal. yr BP (dev.st. 103 yr). However, another sample at the same elevation could indicate that the relative sea level was always around 3 m elevation even at 4146-3237 cal. yr BP.

Relative sea-level curves computed with two different Glacial Isostatic Adjustment (GIA) models allow the elevation of these marine remains to be explained by tectonic uplift. ICE-6G(VM5a) and ANU models calculated with the open-source SELEN 4.0 software were used. Average uplift rates of 0.52-0.83 mm/yr are obtained for the lower shoreline and 0.81-0.96 mm/yr for the upper shoreline. The uplift rate for this second shoreline could be as high as 0.87-1.20 mm/yr if the younger sample age is considered. These uplift rates are almost similar to late Pleistocene values of 0.78-1.02 mm/yr, calculated in the area by several authors.

Holocene shorelines of other sectors of Calabria were finally corrected on the same GIA models so that a comparison could be made. As a result, the Messina Strait has the highest uplift rates (1.01-1.15 mm/yr), which decrease as moving apart. The Holocene uplift rates of the Crotone Peninsula are thus comparable to those of Capo Vaticano (0.71-0.77 mm/yr).

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# Neogene-Quaternary Global Stratotype Section and Points: state of the art, weakness and strength and what is it missing?

Lirer F.*

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* fabrizio.lirer@uniroma1.it

*Keywords:* GSSP, Neogene, Quaternary.

The development of interdisciplinary stratigraphic studies and the construction of stratigraphic guidelines resulted in a new scenario with the introduction and definition of the Global Stratotype Section and Points (GSSP) replacing the Mediterranean Neogene historical stages and also the guiding criteria used to define their bases.

Formally, the Neogene Period/System includes the Miocene Epoch/Series, with six Stages: Aquitanian, Burdigalian, Langhian, Serravallian, Tortonian and Messinian, and the Pliocene Epoch/Series, contains the Zanclean and Piacenzian Stages. At present, all the Mediterranean Neogene Stages (except Burdigalian and Langhian Stages) are defined by GSSPs, in land-based deep marine sections astronomically tuned (excluding the Aquitanian Stage). The following Quaternary Period/System comprises the Pleistocene Epoch/Series with three astronomically tuned Stages: Gelasian, Calabrian, Chibanian and the term Upper Pleistocene, at rank of subseries, with a base currently undefined.

On 30th January 2020, the Executive Committee of the International Union of Geological Sciences ratified the formal subdivision of subseries for the Pleistocene Series of the Quaternary System (Head et al., 2021): the Lower Pleistocene Subseries, embraces the Gelasian and the Calabrian Stages. The Gelasian GSSP identifies the base of the Pleistocene Series and of the Quaternary System; the Middle Pleistocene Subseries is defined by the GSSP of the Chibanian Stage; and the term Upper Pleistocene, at rank of subseries, with a base currently undefined but provisionally dated at ~129 ka. These ratifications complete the formal division of the Pleistocene into three subseries/subepochs, according to the similar subdivision of Holocene Series/Epoch (Walker et al., 2018).

Recently, 1st May 2021, the IUGS Executive Committee ratified the proposal for formal adoption of the chronostratigraphical/geochronological unit divisions subseries/subepoch within the International Stratigraphic Guide (Aubry et al., 2021). Consequently, 13 October 2021, the Executive Committee of the IUGS approved the proposal for formalization of the Neogene Subseries/Subepochs. The subseries/subepochs are now incorporated in a six-tiered chronostratigraphic hierarchy of units that are formally defined by a designated GSSP (Global Stage Stratotype and Point) at the base of designated type stages. The Lower/Early Miocene is comprised of the Aquitanian and Burdigalian Stages/Ages, the Middle Miocene of the Langhian and Serravallian Stages/Ages, the Upper/Late Miocene of the Tortonian and Messinian Stages/Ages, the Lower/Early Pliocene of the Zanclean Stage/Age and the Upper/Late Pliocene of the Piacenzian Stage/Age.

At present, it has been submitted to the Subcommision on Neogene Stratigraphy (SNS) the proposal for the definition of the base of the Langhian Stage in a Mediterranean land section and this proposal is currently under evaluation. Concerning the Burdigalian Stage, due to the lack of good candidate land sections, possibly in the Mediterranean, the discussion is still open regarding the possible criteria to use to identify the base of the Burdigalian Stage.

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# Astrochronology of the C20n-C20r from the Contessa Quarry Billabong section (Gubbio, central Italy) and its implications for the geological time scale

Mannucci A.*[1], Gréteau L.[2], Lanci L.[1], Reghellin D.[1] & Galeotti S.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] UMR CNRS 6112 LPG-BIAF, University of Angers (France).

*Corresponding author e-mail:* a.mannucci@campus.uniurb.it

*Keywords:* geological time scale, cyclostratigraphy, C20n-C20r.

The geological time scale for the Paleogene has been largely improved over the last decades by combining high-resolution astrochronology, biostratigraphy and magnetostratigraphy with high-precision radioisotopic dates (Speijer et al., 2020). Yet, a high-resolution astrochronological calibration of the middle Eocene has proven to be difficult to realize due to the scarcity of sedimentary archives with sufficiently clear astronomically-forced variations in the carbonate content. While an astronomical age control is now available for almost all the Paleogene geomagnetic polarity reversals, differences between published age models still persist through the "Eocene astronomical time scale gap" (Vandenberghe et al., 2012) spanning Chrons C20r through C22n (Westerhold et al., 2017; Dinarès-Turell et al., 2018). Here we present an integrated stratigraphic analysis, including magnetostratigraphy and cyclostratigraphy of the magnetochrons C20n and C20r from a newly discovered outcrop within the Contessa Quarry area, which serves as a test for existing astrochronologies across this interval.

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# Variations in mineral assemblages across the Carnian Pluvial Episode (Late Triassic): a composite section from the Dolomites

Pecorari M.*[1], Gianolla P.[1], Cruciani G.[1], Tateo F.[2] & Caggiati M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Istituto di Geoscienze e Georisorse, CNR, Padova.

*Corresponding author e-mail:* matteo.pecorari@unife.it

*Keywords:* Carnian, clays, Dolomites.

The Carnian Pluvial Episode (CPE) triggered many important consequences on the sedimentary, environment and global ecosystem evolution. Several sedimentological, geochemical and paleontological features have been studied to detect changes related to the climatic episode, and the Dolomites have been representing a helpful source of data on this topic (Dal Corso et al., 2018). Nevertheless, through more than 20 years of studies in the Dolomites, clay minerals were not considered yet, despite their formation can be linked to the climate (e.g., Rostási et al., 2011).

Here we provide the first paleoclimatic study based on qualitative, quantitative and geochemical analysis of clay minerals in the Dolomites, which encompass not only the syn-CPE succession, but also the pre- and post- event intervals. We sampled clayey beds and interbeds from the San Cassiano Fm., Heiligkreuz Fm. and Travenanzes Fm., obtaining a composite section which covers the earliest (Julian) to late (Tuvalian) Carnian time span. Collected samples were XRD-analysed both as "bulk" powders and oriented mounts. Diffraction patterns of the "bulks" were Rietveld-fitted to achieve phase quantitative analyses while oriented mounts allowed complete identification of clay minerals. XRF analyses were conducted for major, minor and trace elements.

Interestingly, the samples from the uppermost San Cassiano Fm. and the first two members of the Heiligkreuz Fm. (Alpe di Specie and Borca mbs.) displayed the same clay assemblage, dominated by Illite-Smectite mixed-layer (I/S), followed by Illite, Kaolinite and also Chlorite in several samples. Within this interval, we observed a maximum in the ratio of siliciclastic phases (clays in particular) vs. carbonates located few meters above the first Negative Carbon Isotope Excursion detected by Dal Corso et al. (2018), suggesting that clay minerals might record the environmental change connected to the first pulse of the CPE later than other proxies (e.g., palynomorphs).

Samples from the overlying Dibona Mb. show a higher dominance of siliciclastics/carbonates (confirmed also by geochemistry) and contain two different species of mixed-layer phase: the disordered I/S and the regular mixed-layer (Rectorite). In suborder, we found Illite and Kaolinite while Chlorite is absent. The mineralogy of the clay fraction leads to consider this association as representing a humid paleoclimate, if provenance changes are excluded.

The climatic configuration was reversed within the Travenazes Fm., whose samples were dominated by Illite and I/S (Illite prevailed in this case), followed by Chlorite. Kaolinite is absent, while the presence of Hematite is to be pointed out. These features allowed us to interpret the sharp change in mineralogy as a further witness of the return to arid condition in the late Tuvalian, after the CPE.

The observed variations in mineralogy through time mirrored the fluctuations detected by major chemical elements (e.g., $SiO_2$ vs. CaO content).

Dal Corso J., Gianolla P., Rigo M., Franceschi M., Roghi G., Mietto P., Manfrin S., Raucsik B., Budai T., Jenkyns H. C., Reymond C.E., Caggiati M., Gattolin G., Breda A., Merico A. & Preto N. (2018) - Multiple negative carbon-isotope excursions during the Carnian Pluvial Episode (Late Triassic). Earth-Sci. Rev., 185, 732-750.

Rostási Á., Raucsik B. & Varga A. (2011) - Palaeoenvironmental controls on the clay mineralogy of Carnian sections from the Transdanubian Range (Hungary). Palaeogeogr., Palaeoclimatol., Palaeoecol., 300, 101-112.

# The Latest Tortonian saline deposits of the Granada Basin: A marine to continental evaporite record of an ancient hypersaline lagoon

Pineda V.* & Gibert L.

Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain).

*Corresponding author e-mail:* vpinedagon@ub.edu

*Keywords:* Granada Basin, Betic Seaway, Tortonian.

The Granada Basin, in southern Spain, contains 400 m thick saline deposits including halite and anhydrite that are related to the closure of the Betic Seaway and the continentalization of the basin during the Late Tortonian. These saline deposits, known as Chimeneas Halite, are not outcropping but they were cut by 3 exploratory drilling cores up to 800 m deep. Geochemical studies have been carried out in one of these cores, but the other 2 cores remain unpublished. Here we present new petrographic, geochemical and biostratigraphic data of the 3 cores to interpret the restriction process of the Granada Basin. Stable sulphate isotopes ($\delta^{34}S$ and $\delta^{18}O$), Br concentration $^{87}Sr/^{86}Sr$ ratios indicate a gradual increase of the continental water inputs, related to the progressive restriction of the basin from the sea. Planktonic and benthic foraminifera present in the basal marls below the salt deposits allows a correlation with the outcropping gypsum of the basin margin and place the onset of the Chimeneas Halite in the Latest Tortonian. The benthic assemblage gives information about the basin paleobathimetry during that time. Characteristic coarse-fine halite alternations are similar to those described in the Dead Sea and could indicate seasonal evaporite cycles. These cycles are more common in the depocenter of the basin than towards the margins, as occurs today in the Dead Sea. We propose a model of a restricted high evaporated lagoon with progressive disconnection to the open sea, and with halite deposition in the depocenter of the basin and selenitic gypsum deposits in the margins.

# New constraints on the PETM record in shallow-marine carbonates from the Adriatic Carbonate Platform, NE Italy

Sabbatino M.*[1], Franceschi M.[1], Dell'Anno J.[1], Frijia G.[2], Consorti L.[3], Petranich E.[1], Barago N.[1], Corradetti A.[1], Covelli S.[1], Gonzo S.[1], Landucci C.[1], Melis R.[1], Papazzoni C.A.[4], Pavoni E.[1] & Lorenzo B.[1-5]

[1] Dipartimento di Matematica e Geoscienze, Università di Trieste. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [3] Istituto di Scienze Marine, CNR, Venezia. [4] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [5] INGV, Roma.

*Corresponding author e-mail:* monia.sabbatino@units.it

*Keywords:* PETM, shallow-water carbonates, N-CIE.

The Paleocene-Eocene Thermal Maximum (PETM; ~ 56 Ma) was an interval of extreme transient climate change, associated with global warming and a massive perturbation of the global carbon cycle (e.g., Zachos et al., 2003). This latter is testified by a sharp Negative Carbon Isotope Excursion (N-CIE) in the global marine and terrestrial d$^{13}$C records, linked to the injection of large volumes of isotopically light carbon into the ocean-atmosphere system. The source of such $^{13}$C-depleted carbon is still a matter of debate. The emplacement of the North Atlantic Igneous Province (NAIP) with the release of huge amounts of $CO_2$ is suspected to be one of the factors that may have caused such a relevant change in the composition of the atmosphere/ ocean carbon reservoirs and the associated abrupt climate perturbation. Research is increasingly exploring mercury (Hg) anomalies as tracers of volcanism during the Paleocene-Eocene interval mostly in deep-water and subordinately in shallow-water settings (e.g., Tremblin et al., 2022 and references therein), arguing about their possible relationship to the NAIP emplacement and its impact on the PETM onset and duration.

The aim of this contribution is to present an integrated study of sedimentology, stratigraphy (bio and chemo), and geochemistry of the deposits belonging to the Adriatic Carbonate Platform cropping out in the Classical Karst area of Friuli Region (NE Italy), encompassing the PETM event. In particular, here we show paired new carbon and oxygen isotope data combined with Hg concentrations and TOC analyses from two shallow-water marine carbonate sections across the Paleocene-Eocene boundary. This study is taking place in conjunction with a geological survey of the area in the framework of the realization of a new geological map of the area at the scale 1:50000 (CARG Project - Sheet 110 Trieste).

The two investigated sections were deposited during the migration of the foreland basin related to the Dinaric orogeny and are today exposed in the Classical Karst area near Trieste (Italy) for about 50 and 300 meters, respectively, of Paleocene-Eocene platform carbonates evolving upward to hemipelagic marls and then to siliciclastic deposits. Vertical facies evolution of the carbonate platform indicates that an initial inner to midramp setting underwent a relative deepening and then was followed by multiple emersion episodes intercalated by proximal marine deposition (i.e., innermost to inner ramp environments). This latter was followed by a return to open marine facies which then persisted until the final drowning of the Adriatic platform that in our study area occurred in the late early Eocene.

Our results show in both sections a negative excursion in the carbonisotope record that, associated with biostratigraphic data, can be correlated with the PETM N-CIE and is comparable to other coeval d$^{13}$C records, both in shape and amplitude. These negative shifts are associated with anomalies in Hg concentration, strengthening the hypothesis that magmatism effectively occurred during this time interval, and its effects are also recorded in shallow-water deposits. These findings corroborate the hypothesis that vulcanism (the NAIP?) might have played a key role in climate change at the PETM.

Tremblin M., Khozyem H., Adatte T., Spangenberg J. E., Fillon C., Grauls A., Hunger T., Nowak A., Läuchli C., Lasseur E., Roig J.Y., Serrano O., Calassou S. Guillocheau F. & Castelltort S. (2022) - Mercury enrichments of the Pyrenean foreland basins sediments support enhanced volcanism during the Paleocene-Eocene thermal maximum (PETM). Global and Planetary Change, 103794.

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# Perturbation of the carbon cycle in the late Miocene Mediterranean Sea at the advent of the Messinian salinity crisis revealed by lipids of marine Thaumarchaeota

Sabino M.*[1], Birgel D.[2], Natalicchio M.[3], Dela Pierre F.[3] & Peckmann J.[2]

[1] Istituto di Scienze Polari, CNR, Bologna. [2] Institute for Geology, Universität Hamburg (Germany). [3] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* mathia.sabino@isp.cnr.it

*Keywords:* crenarchaeol, dissolved inorganic carbon, water column stratification.

Throughout Earth history, enormous salt deposits dominated by halite and calcium sulfates were deposited in tectonically restricted basins. The deposition of salts was favored by a negative net hydrological balance, resulting in so-called salt giants. Such conditions occurred in the late Miocene, when the Mediterranean basin was almost entirely cut off from global ocean circulation during the paleoceanographic event known as Messinian salinity crisis (5.97 – 5.33 Ma). Growing evidence indicates that during the deposition of the Mediterranean Salt Giant the water body was typified by thermohaline stratification. Particularly in semi-enclosed basins, thermohaline stratification can lead to the perturbation of the carbon cycle. This work is aiming to assess the impact of the advent of the Messinian salinity crisis on the late Miocene Mediterranean carbon cycle by investigating the d$^{13}$C signatures of lipid biomarkers of mesophilic planktonic marine archaea (Group I Thaumarchaeota) enclosed in the sediments of the Piedmont Basin (NW Italy). Group I Thaumarchaeota are autotrophs, fixing dissolved inorganic carbon (DIC) with a fractionation factor of approximately 20‰. The d$^{13}$C signatures of the diagnostic biomarker crenarchaeol can consequently be used as d$^{13}C_{DIC}$ proxy in marine basins. Our results indicate that the advent of the crisis coincided with an overall $^{13}$C enrichment of the DIC pool of the Piedmont Basin, with positive d$^{13}C_{DIC}$ excursions up to +5‰ in the upper water column. We suggest that the preferential export of $^{12}$C to the seafloor after phytoplankton blooms coupled to limited replenishment of remineralized carbon due to a stable thermohaline stratification caused such $^{13}$C enrichment of the DIC pool in the upper water column.

# Understanding mechanisms of palaeoecological and palaeoclimatic trends across the Silurian-Devonian transition by palynofacies data from southern Tunisia

Sorci A.*[1], Cirilli S.[1], Götz A.E.[2], Servais T.[3] & Spina A.[1]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] State Authority for Mining, Energy and Geology, Hannover (Germany). [3] CNRS, Université de Lille (France).

*Corresponding author e-mail:* amalia.spina@unipg.it

*Keywords:* Gondwana, Palaeozoic, palynofacies.

The terrestrialization of land plants represents a fundamental process which strongly affected the climatic and environmental conditions of our planet. It reasonably started during Ordovician, continuing throughout the Silurian with most of the continents covered by primitive land plants. However, it is only during the Devonian that land plants considerably diversified their morphologies and reproductive strategies. Palaeozoic sedimentary successions in the subsurface of North Africa are well suited for the study of the early phases of plant terrestrialization and its environmental impact, due to the abundance of well-preserved palynological material (Spina & Vecoli, 2009). In this study, we analysed the sedimentary organic matter content of the Silurian to lowest Devonian section of the MG1 borehole, located in the Ghadamis Basin (southern Tunisia). The well penetrated, in ascending stratigraphic order, the Tanezzuft, Akakus and Tadrart formations. The oldest Tanezzuft Formation is characterized by shales with sandstone intercalations, deposited during the early Silurian postglacial transgression. The overlying sandstones interbedded to minor shales of the Akakus Formation represent successive regressive deposits, spanning from shallow marine to continental settings. A major regional unconformity, related to the Caledonian orogenesis, marks the contact between the Akakus and the Tadrart formations. The latter includes sandstones and mudstones deposited in continental to paralic environments during the earliest Devonian (Lochkovian). A detailed palynofacies analysis was performed in these units with the aims to 1) identify the distribution pattern of both continental (i.e., cryptospores, trilete spores and phytoclasts) and marine elements (i.e., acritarchs, chitinozoans, prasinophytes and scolecodonts) within a sequence stratigraphic framework; 2) test whether the biodiversity of cryptospores and trilete spores is related to specific depositional system tracts and climatic changes. Continental and marine organic matter variations have been compared with the transgressive-regressive trends interpreted from the sedimentary record (Carr, 2002), outlining a correlation between eustatic sea level, miospores biodiversity and abundance /variety of organic particles. Our data contribute to interpret the relation between sedimentary organic matter content and sea-level changes, revealing a good potential for high-resolution sequence stratigraphic interpretations of the Lower Palaeozoic in the northern border of Gondwana. Moreover, variations in biodiversity of sporomorphs revealed palaeoecological and palaeoclimatic changes which can be correlated with other successions from both Gondwana and Laurussia palaeocontinents.

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# High-frequency climate oscillations determined with OSL in Lanzarote (Canary Island)

Stelletti M.*[1], Sechi D.[1], Andreucci S.[2], Cossu G.[1], De Luca M.[1], Faedda G.[1], Perazzotti F.[1], Ruperti N.[1], Santonastaso A.[1] & Pascucci V.[1]

[1] Dipartimento di Architettura, Design e Urbanistica, Università di Sassari. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* myrimy@hotmail.com

*Keywords:* Mars, OSL, climate oscillation.

During the last 60 years, the robotic exploration on Mars has made many tantalizing geological discoveries, and retrieving rock samples will be the next major goal for the scientific community. An accurate estimation of absolute ages is a fundamental step to understand the evolutionary processes that led to the formation of the Red planet. In this respect, occurrence and time frequency of surficial geological processes on Mars are needed. The chronology of recent geological events on Mars is a challenging task, due to uncertainties associated with the current dating methodology (crater counting).

OSL (Optically Stimulated Luminescence) dating could be a reliable method to date recent deposits of Mars and better understand climatic and tectonic changes occurred in the recent time. The technique dates the last moment sediments were exposed to sunlight and, therefore, the time of formation of a sedimentary deposit (Aitken, 1998).

The choice of a Martian analogue is essential to understand the processes occurred on the planet and to validate the dating protocol. Lanzarote (Canary Island, SP) was chosen as the best Martian analogue since its geological features and climatic conditions are similar to those of Mars: basaltic products, low quartz and k-feldspar concentrations, dry weather, very low vegetation.

The aim of the work is to reconstruct the late Pleistocene geological evolution of the Famara cliff area pointing out which have been the different depositional environments. The Famara cliff is the remnant of a Miocene basaltic caldera. Ephemeral streams deeply incised the cliff rim and a suite of colluvial fans eventually evolving in alluvial fans developed. These alternate with aeolian deposits that become dominant toward the caldera centre. Sediments are all basalt derived except for some dust blowed from the Sahara during major storms. The described features could be considered similar to those developing on rim and floor of a Martian impact craters.

Ages of the colluvia and dunes were determinate using OSL and $^{14}C$. Results indicate that deposit formation occurred between MIS 2 and MIS 5. In particular, the obtained ages of the colluvial-alluvial sediments are associated with the wet and more humid Dansgaard Oeschger (D-O) events, while the aeolian features to the cold and dry Heinrich events.

The obtained data are encouraging and prove that OSL could be the more suitable method to date the Martian basalt derived recent deposits. Furthermore, the technique is capable of define with accuracy and precision the Terrestrial high-frequency climate oscillations occurred during Pleistocene.

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# Looking for the best thermal history of Illizi-Ghadames basin (North Africa) through diagenetic modelling

Tamburelli S.*[1], Di Giulio A.[1], Consonni A.[2] & Ortenzi A.[2]

[1] Dipartimento di scienze della Terra e dell'Ambiente, Università di Pavia. [2] Geolab, ENI S.p.A., San Donato Milanese (MI).

*Corresponding author e-mail:* silvia.tamburelli01@universitadipavia.it

*Keywords:* diagenesis, thermal history, oil and gas.

Thermal history of sedimentary basins, together with fluid flow, rocks texture and composition, stratigraphic architecture, depositional facies and burial history are what mainly drive diagenetic evolution of reservoir rock and, at the end, their reservoir quality. While rock features and partly fluid features can be investigated by studying reservoir samples, thermal history if often more difficult to ascertain as it requires to know the heat flow in the area during geologic time. This is the case for instance of North African region where the possible effect of Tertiary magmatic activity is a matter of debate and where several prolific hydrocarbon basins occur, with one of the most prolific being the Illizi-Ghadames basin (IGB) where the possible thermal effect on the petroleum system caused by the Tertiary magmatic activity of the Hoggar Dome is still discussed (Di Giulio et al., 2021) and where the understanding of when the thermal peak occurred is necessary for a correct reservoir quality prediction study.

We present here a diagenetic modelling of Devonian reservoir rocks in a sector of the IGB which is used to check which thermal scenario best reproduces the experimental data and therefore can be considered the most likely; related to this, also the evolution during time of petrophysical features have been investigated in order to study the impact of the thermal history on the diagenetic history. Thanks to this, a detailed reconstruction of reservoir petrophysics evolution due to the combined effects of compaction, cement precipitation and grain dissolution since Devonian time to present day have been obtained.

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# Traces of life in evaporites: the case of the Dead Sea deep biosphere and its relation to paleoclimate fluctuations

Thomas C.*[1], Ariztegui D.[1], Antler G.[2], Ebert Y.[3], Grossi V.[4], Ionescu D.[5] & Levy E.[6]

[1] Department of Earth Sciences, University of Geneva (Switzerland). [2] Department of Earth and Environmental Sciences, Ben-Gurion University of the Negev, Beer Sheva (Israel). [3] Institute of Earth Sciences, Hebrew University of Jerusalem (Israel). [4] Laboratoire de Géologie de Lyon, Univ. Lyon 1, CNRS, ENSL, Villeurbanne (France). [5] Department of Experimental Limnology, Leibniz Institute for Freshwater Ecology and Inland Fisheries, Stechlin (Germany). [6] Department of Climate Geochemistry, Max Planck Institute for Chemistry, Mainz (Germany).

*Corresponding author e-mail:* camille.thomas@unige.ch

*Keywords:* microbes, biosignature, diagenesis.

The Dead Sea is a landlocked hypersaline water body which responds strongly to climatic variations in the Levantine area. Current arid and hypersaline conditions in the Dead Sea prevent the establishment of sustained primary production and eukaryotic life. However, more humid conditions have permitted in the Quaternary history of the Dead Sea Basin to sustain a more diverse ecological framework. In this context, the sediments of the Dead Sea host a suit of biosignatures worth investigating to unravel the biological response to fluctuating paleoclimatic variations in evaporative settings and provide a potential analogue to salt giants formation and evolution.

A 450 m-long sedimentary archive has been retrieved by scientific drilling (ICDP-Dead Sea Deep Drilling Project) and allowed the search of varied biosignatures over the Quaternary history of the Dead Sea Basin to untangle primary and secondary processes associated to paleoclimatic and paleoenvironmental changes. We explored the lake water column ecology evolution and its impact on the deep sedimentary communities by using sedimentary DNA. Sedimentary microbial activity was shown to be tightly linked to changes in salinity and fresh organic matter inputs into the lake. In the most arid conditions leading to halite precipitation, microbial life developed unusual way of coping with salinity and the lack of nutrient and food (Thomas et al., 2019). When conditions become a bit more favorable for life, microbial activity was unleashed and led to the preservation of bio-related isotopic signals and diagenetic precipitation in the sediment. It is notably the case during the Sapropel 1 deposition period (Levy et al., 2022). Microbial sedimentary response therefore fluctuates with paleoclimatic changes, and differentially affects diagenetic processes, as observed from lipid biomarkers and changes in diagenetic mineral occurrence, morphologies and nature (Thomas et al., 2016; Ebert et al., 2018). Such biosignature record, although tightly linked to the Dead Sea limnology and chemistry, provides a framework to better understand changes in evaporation-precipitation ratio in evaporative basins, and the complex response of biogeochemical processes in evaporitic context.

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Levy E.J., Thomas C., Antler G., Gavrieli I., Turchyn A.V., Grossi V., Ariztegui D. & Sivan O. (2022) - Intensified microbial sulfate reduction in the deep Dead Sea during the early Holocene Mediterranean sapropel 1 deposition. Geobiology, 1-15.

Thomas C., Ebert Y., Kiro Y., Stein M. & Ariztegui D. (2016) - Microbial sedimentary imprint on the deep Dead Sea sediment. The Depositional Record, 1-21.

Thomas C., Grossi V., Antheaume I. & Ariztegui D. (2019) - Recycling of Archaeal Biomass as a New Strategy for Extreme Life in the Dead Sea Deep Sediment. Geology, 47, 479-482.

# Onset of the Messinian Salinity Crisis: Sedimentological, petrographical and geochemical characterization of the pre-salt sediments from a new core (Caltanissetta Basin, Sicily)

Tzevahirtzian A.*[1], Caruso A.[1], Scopelliti G.[1], Baudin F.[2] & Blanc-Valleron M.M.[3]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] Institut des Sciences de la Terre de Paris, Sorbonne Université, CNRS, Paris (France). [3] Muséum National d'Histoire Naturelle, CNRS - UMR 7207 CR2P, Paris (France).

*Corresponding author e-mail:* athina.tzevahirtzian@unipa.it

*Keywords:* Messinian Salinity Crisis, Calcare di Base, evaporites.

The Messinian Salinity Crisis (MSC) is still highly debated with the main controversies regarding the magnitude of the sea-level drawdown and the timing of its onset and evaporites deposition. The present study aims to reconstruct the environmental changes leading to the MSC during the transition from the Tortonian-Messinian marine conditions to the Messinian evaporitic environments. The core 3AGN2S04, recently drilled in the Caltanissetta Basin (Sicily), was analyzed to reveal the petrographic, mineralogical and geochemical characteristics of the late Tortonian – early Messinian pre-salt sediments. In particular, the facies characterization of the carbonates and organic-rich shales of the Calcare di Base (CdB) member allowed to understand its significance in the paleoenvironmental evolution towards salt deposition and to the reconstruct the brecciation processes inside the CdB. The sedimentological and mineralogical analyzes revealed that core 3AGN2S04 consists of the inner shelf facies of the Tripoli Formation passing to the typical carbonate platform facies of the CdB. The local transition between the upper part of the Tripoli Formation and the CdB member indicates that stressful environmental conditions were constant in the central Mediterranean shelf zones during the late Messinian. The CdB carbonates indicate the occurrence of a carbonate platform characterized by peritidal environments rich in different microbial communities and evaporitic deposits, whereas the embedded organic-rich shales suggest a confined, low energy, anoxic and stratified saline system with high productivity and good preservation of organic matter. A complex set of syndiagenetic brecciation processes, interpreted as in situ brecciation, have profoundly marked the CdB deposits.

# A high-resolution record of $\delta^{18}O$ and $\delta^{13}C$ across the Piacenzian/Gelasian boundary at Monte San Nicola (Southern Sicily)

Zanola E.*[1], Di Stefano A.[2], Fornaciari E.[1], Ferretti P.[3], Macrì P.[4] & Capraro L.[1]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Universita di Catania. [3] Dipartimento di Scienze Ambientali, Informatica e Statistica, Universita «Ca' Foscari», Venezia. [4] INGV, Roma.

*Corresponding author e-mail:* elena.zanola@phd.unipd.it

*Keywords:* paleoclimate, stable isotopes, Southern Sicily.

The Central Mediterranean region is traditionally acknowledged as a key reference area for investigating the environmental and climatic evolution of the Earth during the Pleistocene. In particular, the expanded open marine successions that are very well-exposed along the coastline of Southern Italy and Sicily preserve a manifold array of paleoclimatic proxies, which can be tightly constrained in time by means of a chronostratigraphic framework based on calcareous plankton biostratigraphy and paleomagnetism (Cita et al., 2008). In this context, the Monte San Nicola area (MSN, Southern Sicily) offers a spectacular stratigraphic succession that was employed for defining the GSSP of the Gelasian Stage (ca. 2.58 Ma; Rio et al., 1998), which has recently been revisited as corresponding to the Pliocene/Pleistocene boundary (Head et al., 2008). Accordingly, the Gelasian has increased its visibility within the scientific community, and the cluster of prominent cold episodes found immediately above the boundary (i.e., the MIS 100-MIS 96 glacials) have become of critical importance. More specifically, the glacial triplet is interpreted as the first global response to the onset of the Northern Hemisphere Glaciation (NHG; Zachos et al., 2001), a stepwise succession of events that, beginning ca. 3.3 Ma, intensified during the Early Pleistocene and eventually led to the vast glacial-interglacial contrast that characterizes the recent climate variability. Previous studies on both the classical MSN section and adjacent profiles (e.g., Becker et al., 2005; Capraro et al., 2022) provided plenty of information on the long-term climatic evolution throughout the Gelasian and across the MIS 100 glaciation. Yet, documentation across the Piacenzian/Gelasian boundary is still very sparse.

Our project is aimed at reconstructing a high-resolution stable oxygen and carbon isotope record in the period straddling this crucial interval. The results achieved so far increase the precision and reliability of the marker criteria that allow for the recognition of the boundary, such as the Gauss-Matuyama geomagnetic reversal, and provide new evidences on the dynamics of the natural system in the central Mediterranean at the onset of the NHG.

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# The Late Paleozoic Ice Age in southern Gondwana: insights from glaciomarine sequences of Tasmania (Australia)

Zurli L.*[1], Cornamusini G.[1-2-3], Liberato G.P.[1] & Conti P.[1-3]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. [2] Museo Nazionale dell'Antartide, Università di Siena. [3] Centro di Geotecnologie, Università di Siena.

*Corresponding author e-mail:* luca.zurli@student.unisi.it

*Keywords:* glaciation, paleoenvironmental reconstruction, sequence stratigraphy.

The Late Paleozoic Ice Age (LPIA) is one of the coldest periods in the Earth history which led to the development of ice covers across the entire Gondwana from Carboniferous to Permian. The LPIA view is changing from a single ice sheet covering the entire Gondwana to a series of small and diachronous ice caps widespread through the supercontinent. Stratigraphic studies and facies analysis are key tools for the evaluation of the paleo-environmental depositional setting and, consequently, of the style of glaciation. Tasmania is a key region because in the late Carboniferous to early Permian it was situated between northern Victoria Land (Antarctica) and Australia, and the LPIA deposits provide useful information to unravel the stratigraphic evolution of these two sectors of Gondwana. The lowermost part of the Lower Parmeener Supergroup (late Carboniferous to Triassic), consisting of the Wynyard Tillite and its correlatives, recorded glacial sedimentation linked with ice covers that developed in the region. We carried out a detailed facies analysis of two drillcores which recovered glaciogenic sequences deposited in the Tasmania Basin. Facies associations vary from possibly sub-glacial or ice-contact to ice-distal. Diamictite is the most common facies and its deposition is driven both by gravity and sediment remobilization processes and suspension settling with ice rafted debris accumulation. Mudstone layers, with and without dropstones, are interposed between diamictite intervals, recording ice-distal to non-glacial conditions. Facies associations are indicative of subaqueous deposition, likely glacimarine. Moreover, along the succession the glacial sequence stratigraphy approach was applied and glacial system tracts and bounding surfaces, which define glacial sequences, were identified. The stacking pattern of the facies associations allow us to demonstrate that the glacial sequences in Tasmania recorded different phases of advance and retreat of the glacial front into the basin, about at the end of the main glacial phase.

# S37.

# Sustainability of groundwater resources


*Conveners & Chairpersons*

*Manuela Lasagna (University of Torino)*

*Vincenzo Piscopo (Coordinatore Sezione di Idrogeologia, Società Geologica Italiana)*

*Glenda Taddia (Politecnico of Torino)*

# A laboratory study to define tools for monitoring asbestos mobility in aquifers

Avataneo C.*[1-2], Magherini L.[3], Belluso E.[1-2-4], Capella S.[1-2], Bianco C.[3], Lasagna M.[1], Sethi R.[3] & De Luca D.A.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi «G. Scansetti», Università di Torino. [3] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [4] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* c.avataneo@unito.it

*Keywords:* column test, groundwater, asbestos.

Given the urgent necessity of groundwater resources protection resulted after years of uncontrolled human exploitation and climate change, which affected both their quality and quantity, the assessment of possible groundwater contamination by well-known contaminants and Emerging Pollutants (EP) is of paramount importance. Airborne asbestos is widely recognized as a contaminant of concern for human health and the environment. Since its carcinogenicity when inhaled is well established, previous studies have mainly monitored its presence in air, neglecting to consider water as an exposure pathway. Asbestos in water could be ingested – especially if it reaches the tap water system – or become a secondary source of airborne fibres, in case of water-to-air migration.

An accurate risk assessment of waterborne asbestos is particularly required in mine areas or in Naturally Occurring Asbestos (NOA)-rich areas. In the first case, non-monitored mine tailings deposits can be present and contain non-exploitable fibrous minerals which may be dispersed in surface and groundwater. In the second case, NOA-rich rocks and soils weathering and erosion could result in waterborne mineral fibres diffusion. In both situations, there is a risk of mineral fibre migration through groundwater from the pollution sources, which was traditionally considered negligible. Conversely, a recent column-based laboratory study (Mohanty et al., 2021) highlighted possible chrysotile mobility through porous media. Moreover, possible mineral fibre diffusion in water was recently considered in the Lanzo Valleys and Balangero Plain (NOA-rich area in the North West Alps, Italy) as a consequence of interactions between water and ophiolitic rocks or related sediments (Avataneo et al., 2021).

In this context, a laboratory study based on column transport tests was set to investigate the fibre transport in saturated aquifers. The experimental results make it possible to better understand possible groundwater contamination by mineral fibres and their movement through porous media, providing hints to clarify the relation between fibre presence and movement in the water system and reservoir peculiarities (geology, hydrogeology). This work will provide tools to monitor asbestos transport due to groundwater flowing in NOA-rich settings or in areas where non-monitored mine tailings deposits are present.

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# Groundwater mixing assessment in the Pontina Plain (Central Italy): preliminary results of the CARG survey performed for the Terracina geological map

Barberio M.D.*[1], Gori F.[1], Barbieri M.[2], Cardello G.L.[3], Simeoni A. P.[1], Petitta M.[1] & Chiocci F. L.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Dipartimento di Ingegneria Chimica, Materiali, Ambiente, Sapienza Università di Roma. [3] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* marinodomenico.barberio@uniroma1.it

*Keywords:* hydrogeochemistry, management, Pontina Plain.

Assessing water resource quality, and ground-and-surface water interactions related to land use and climate changes is essential to groundwater assessment. In Central Italy, springs fed by carbonate aquifers are commonly the major contributors of drinking and irrigation water supply. In the Pontina Plain, they encompass mixing processes that we aim to understand. In the frame of the new geological map survey of Terracina, the groundwater flowpaths will be retrieved from a hydrogeochemical monitoring of about 20 springs. In particular, we aim at defining the hydrogeochemical processes that control the groundwater chemistry and to determine the suitability of springs and groundwater for irrigation and drinking purposes based on the water quality indexes. Additionally, in order to investigate possible temporal variations in hydrogeochemical composition, historical data were collected too as they may be related also with ongoing tectonics. Chemical-physical parameters (pH, Electrical Conductivity, and Temperature) were measured on field, and groundwater samples to analyze major, trace and isotope content ($^{2}H$ and $^{18}O$ of $H_2O$) were sampled. The Piper diagram revealed that groundwater shows a hydrogeochemical evolution from the Calcium-Bicarbonate facies to the Sodium-Chloride water type. Geochemical modeling and saturation index computation of springs and wells confirm an interaction with carbonate rocks. Most of the springs and well water samples are saturated with respect to calcite and dolomite, however the existence of mixing process with deep fluids and/or sea water cannot be excluded in some cases as supported by saturation indices of halite and anhydrite. The analysis of time series allowed the identification of trends in groundwater ions concentrations. Near the sea, these variations can be attributable to the increase in the salinization process in the coastal aquifer, while far from that it could be related to the upwell of deep fluids across major faults. Most water samples are suitable for irrigation and drinking purposes, except for the samples influenced by seawater and prolonged water-rock interaction. This study highlights the need of a detailed hydrogeological characterization for strategic groundwater management policy and planning, to avoid the decline of groundwater quality due to a decrease in recharge rates induced by climate changes.

# Radon diffusion in Non-Aqueous Phase Liquids (NAPLs): experimental data and their impact on the modelization of Rn deficit technique

Briganti A.* & Voltaggio M.

Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* alessandra.briganti@igag.cnr.it

*Keywords:* Radon diffusion, Radon deficit technique.

From the point of view of a green economy and social sustainability, the use of investigating and monitoring techniques based on natural tracers are always more studied in order to reduce environmental and economical impact. The Radon deficit technique is proved to be a good instrument to apply in case of site contaminated by Non-Aqueous Phase Liquids (NAPLs)(De Miguel et al., 2020). This model can assess NAPL contamination of soil, in both vadose and satured section, when it is known the Rn partition coefficient between present fluid phases (air, water, NAPL) at equilibrium conditions (Semprini et al., 2000). The equilibrium condition can be considered respected only in two limit cases: stagnant water and relatively high groundwater flow. In fact, in natural systems Rn mobility in groundwater is generally controlled by a combination of diffusion and water transport. Assuming an istantaneous Rn exchange at the NAPL /groundwater interface depending on $Rn^{NAPL/groundwater}$ partition coefficient, Rn contact rate from groundwater to the interface must be valued. Moreover, the same evaluations are required for residual NAPLs, in which Rn only moves by diffusion. Generally, Rn diffusion in water is well known in literature and the groundwater flux can be measured. Instead, Rn diffusion in NAPLs can be theoretically calculated by Stockes-Einstein relationship, where the viscosity plays a major role. Thus, Rn diffusion in NAPLs is still an interesting parameter to investigate by lab tests due to lack of data in literature. The possible outcomes of this study include experimental data on diffusion coefficients in NAPLs, a theoretical improvement of Radon deficit technique and an extension to its modeling equations in case of non-equilibrium conditions (Morita,1996), that cannot be studied by this method at the moment.

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# Morpho-sedimentary constraints in the groundwater dynamics of low-lying coastal area: the southern margin of the Venice lagoon, Italy

Cavallina C.*[1], Bergamasco A.[2], Cosma M.[1], Da Lio C.[1], Donnici S.[1], Tosi L.[1] & Zaggia L.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Padova. [2] Istituto di Scienze Marine, CNR, Venezia.

*Corresponding author e-mail:* chiara.cavallina@igg.cnr.it

*Keywords:* salt-water intrusion, groundwater dynamics, coastal plain.

The low-lying coastal plain at the southern margin of the Venice lagoon is the result of river diversions, channeling, and hydraulic reclamation that took place over the centuries. Most of these territories now lay at 3 m below the mean sea level and a complex network of drainage channels and pumping stations regulates the surface water flow for irrigation and flood protection. Being at the margin of a lagoon and next to the sea, the aquifers of this area are heavily affected by salt-water intrusion that severely jeopardizes the farmlands productivity. On the first 25-meters of the subsoil, in which the shallow aquifers are included, the stratigraphic record consists of Pleistocene alluvial deposits and Holocene deposits. The latter show the typical transgressive wedge with prodelta, littoral and back barrier depositional environments. The Holocene littoral sands contain the unconfined aquifer, which is almost continuous along the whole coastal strip. Paleo-channels and remnants of littoral ridges, host unconfined aquifers all over the coastal plain. Several past studies revealed the complexity of freshwater-saltwater exchanges due to the concomitance of various forcing, i.e., the proximity to the lagoon and Adriatic Sea, the tide encroachment from the river mouths, precipitations, human activities. However, the relationships between the sedimentary architecture and the dynamics of saline contamination of groundwater are still poorly studied. The results of a research integrating sedimentary and hydrogeological investigations in a test area south of the Venice lagoon, at the confluence of Brenta and Bacchiglione rivers, are here presented. The study focuses on the phreathic aquifer, in the upper 10 meters of the subsoil, where the fresh-saltwater interface fluctuates and the salinity of the groundwater can limit the growth of plants. The aim is to highlight the morpho-sedimentary constraints on groundwater dynamics of the salt-contaminated phreatic aquifer. For morpho-sedimentary constraint, we intend a stratigraphic discontinuity, causing a change in permeability, affecting groundwater dynamics, confining at its top fresher (and less dense) water. Nine sites have been investigated by collecting sediment cores for facies analysis, and by monitoring electroconductivity (as proxy of salinity) in piezometric wells. Sedimentary facies analysis identified 7 hydrostratigraphic units, while a comparison between the high-resolution hydrostratigraphic architecture and electrical conductivity profiles allowed to defines the role of the stratigraphic constraints on the phreatic groundwater dynamics. The results show that local channelized aquifers can enhance the mitigation of the aquifer if sufficient freshwater from precipitation or rivers is available. Areas where larger seasonal changes in the fresh-saltwater dynamics (i.e., more influenced by freshwater availability and thus more sensitive to any mitigation intervention), were also individuated.

# Recharge area determination of important deep groundwater aquifer (Val Maggiore, NW Italy): a hydrochemical and isotopic approach

Cocca D.*, Moriondo M., Lasagna M. & De Luca D.A.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* daniele.cocca@unito.it

*Keywords:* hydrochemistry, stable isotopes, deep aquifer.

The Maggiore Valley well field plays a fundamental role in supplying drinking water to a large territory of the Piedmont Region (north-western Italy) and has been intensively exploited since the early XX century.

This water resource is host in a deep multi-layered aquifer system. The recharge area of the deep exploited aquifer is located towards the Po Plain, west (Turin Plain) and south (Cuneo Plain) of the study area. Most likely, the deep aquifer is recharged from west by Po river, that in this area is a losing river, due to the highly permeable Quaternary gravelly sand deposits in correspondence with the river

The main purpose of this study was to determine the recharge area of deep aquifers through a hydrochemical and isotopic assessment, and to characterize the different water resource quality in this areas (Po Plain, Poirino plateau, Maggiore Valley area).

Two sampling campaigns were carried out both in the shallow and deep aquifers (March and June 2021) for a total of 128 samples. Physical-chemical analyzes of the main ions on all samples and isotopic analyzes ($\delta^{18}O$, $\delta^{2}H$) on 50 samples were conducted.

The processing of chemical data has confirmed the bicarbonate-calcium facies for the majority of the shallow and deep aquifers samples. Moreover, clear hydrochemical differences were observed between the investigated sectors; e.g., the shallow aquifer of the Poirino Plateau shows nitrate concentrations superior than the limits, unlike the deep aquifer of Maggiore Valley is characterized by low concentration of nitrate and other ions.

The processing of isotopic data, combined with previous data, made it possible to identify a gradual increase in values of the isotopic composition along the flow direction into the Cuneo deep aquifer due to the progressive interaction with the shallow aquifer; moreover, isotopic data confirmed the interaction between the Po River (more negative values) and the shallow aquifer (more positive values) along the watercourse in the Turin Po Plain, resulting with a more negative isotopic composition in the shallow aquifer compared to nearby areas.

In the Maggiore Valley, the isotopic signals of the deep aquifer, flowing from the Turin plain and interpreted as potentially influenced by the Po River showed an isotopic composition highly similar to the watercourse, with to the least enriched waters of the area.

The isotopic signals of the deep aquifers in the Maggiore Valley flowing from the Cuneo plain (more positive) and Turin plain (more negative) were distinguished and the mixing between these converging aquifers in the well field area was verified.

In conclusion, the study has been redefined the recharge areas and provides an additional tool for a better groundwater management and protection of a regional importance drinking water reserve.

# Protecting karst groundwater resources in Apulia, southern Italy

D'Ettorre U.S.* & Parise M.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* umberto.dettorre@uniba.it

*Keywords:* karst groundwater, groundwater pollution, groundwater protection.

Apulia has a considerable importance from the hydrogeological point of view, due to presence of conspicuous underground water bodies. The Apulian hydrogeological system is based on the presence of Mesozoic successions, characterized by fissured and karst limestones. In this context, the Murge plateau represents the largest hydrogeological unit in the region (Cotecchia, 2014). These karst environments are highly vulnerable to a variety of degradation and pollution problems. Pollutants in liquid and solid waste could easily move through the systems of conduits and joints in the rock mass, contaminating subsurface water (Parise & Pascali, 2003). Protecting these water resources is necessary for a variety of reasons, but first of all because they represent an important reference for the socio-economic development of communities. In Apulia they would provide about a quarter of the total amount of urban water supply (Maggiore & Pagliarulo, 1999). Pollution related to human activities is a major risk for these water resources, which have generally a high value and are considered of high quality (Polemio & Dragone, 2004). Based on current knowledge, the main measures necessary to reduce pollution and qualitative degradation of groundwater resources could concern: the identification and limitation of potentially harmful activities, the prevention of illegal waste disposal in karst areas, and the establishment of aquifer protection zones. These measures cannot be separated from educational campaigns addressed to inform the local communities about the importance of groundwater resources and the vulnerability of karst environments (Kačaroğlu, 1999).

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# Hydrogeological characterization and assessment of groundwater resource potentialities for drinking purposes of minor high-altitude springs in Central Apennines (Southern Abruzzo region)

Di Giovanni A.*, Di Curzio D. & Rusi S.

Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti.

*Corresponding author e-mail:* alessia.digiovanni@unich.it

*Keywords:* water budget, tapped springs, terrigenous aquifer.

Drinking-water supply in high altitude villages in central Apennines is ensured by springs with a limited and seasonal discharge. These allow villages self-sufficiency with some summer deficit in water availability.

In the southern portion of the Abruzzo region's mountain area, many tapped springs for drinking purpose can be found, which are located at altitude higher than 1000 m, but their exploitation is still limited because of the managing companies' exploitation and distribution strategies. In fact, investing in springs or well fields with major potentials is preferred, even if they are located at lower altitudes and therefore more energetically demanding for water distribution.

In this work, peculiarities, potential and residual capabilities of these aquifers have been pointed out and described. The structural framework is singular: tectonic relationships between formations occur mainly through faults and low angle thrusts, which put in contact terrigenous lithologies with different permeability, within the so-called "*coltre molisana*", and with the mainly carbonatic succession of the central Apennines and the *Sicilidi* calcareous-clayey one (Vezzani & Ghisetti, 1998; Festa et al., 2014).

The complex stratigraphic and tectonic relations between these formations allow groundwater to emerge as springs, which are mainly classified as "for *permeability limit*" (Civita, 1973). The aquifer is usually represented by the calcareous hydrogeological complex of the *coltre molisana* or by the Apennines limestone formations, while the clayey complex of the *Sicilidi* or the *coltre molisana* serves as aquiclude. Sometimes, the coarse slope deposits serve as aquifers, too: they come from carbonate deposits located at higher altitude, and lie over impervious complex.

The first results about groundwater potentialities of these high-altitude springs, obtained through infiltration coefficient, show recharge volumes of about 100 $Mm^3$, over a 615 $Km^2$-wide area.

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# Geochemical and isotopic characterization of groundwater in the NW Friuli Plain, Friuli-Venezia Giulia (Italy)

Di Renzo D.*[1], Nieto Yabar D.[2], Marrocchino E.[3] & Vaccaro C.[3]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS). [3] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara.

*Corresponding author e-mail:* dino.direnzo@unife.it

*Keywords:* Geochemical and isotopic characterization, Friuli Plain, Water resource management.

Groundwater constitutes about two-thirds of the world's freshwater reserves and plays an important role in the social and economic life of humans. Since the first half of the 20$^{th}$ century, rapid industrialization, urbanization and the exponential increase in population accelerated the consumption of groundwater resources. This significant use up results from the excessive and incorrect use of water resources, in particular due to the massive over-exploitation and deterioration of water (related to anthropogenic pollution), and it reduced the availability and quality of groundwaters.

Furthermore, in recent decades also climate change has impacted groundwater resources. Indeed, the IPCC Report "Climate Change 2022: Impacts, Adaptation and Vulnerability" identifies the risk of water scarcity as one of the major risk categories for Europe. In detail, the report highlights how in southern Europe the risk of scarcity of water resources is already high due to the global warming level of 1.5°C and will become very high with a rise of 3°C. It represents a big problem because in these regions, the demand for water resources already exceeds the current availability.

Due to the great vulnerability of water resources, a geochemical and isotopic study approach of groundwater at a basin scale becomes essential for an efficient domestic, industrial and agricultural water supply management of it will be helpful to understand the spatial and temporal distribution of groundwater chemistry and the hydrogeochemical processes related to hydrogeological settings for sustainable use of groundwater resources.

The aim of this work is to evaluate, at a basin scale, the hydrogeochemical processes and the geochemical evolution in the complex multi-aquifer system of the north-western portion of the Friulian alluvial plain.

The Friulian alluvial plain is one of the most important in Italy as regards the availability of water even if, it presents a high waste of water resources. Groundwater plays a significant role in the development of the regional and social economy, as private, municipal, agricultural and industrial water supplies are highly dependent on groundwater resources.

The geochemical-isotopic characterization was carried out, in the period June-July 2021, on 48 survey points (including wells, springs, and surface waters), to determine factors and processes controlling quality, origin and groundwater chemistry.

The results highlighted as the groundwater chemistry, and their evolution, is mainly controlled by geological and hydrogeological environment, but anthropogenic influence is not negligible.

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# The tritium used to define anthropogenic influence on water resource management: the study case of Fiume Veneto (PN), Italy

Di Renzo D.[1], Rizzo A.[2], Vaccaro C.[3], Salvi S.[2], Marrocchino E.[3], Nieto Yabar D.[4] & Telloli C.*[2]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Dipartimento Sostenibilità dei Sistemi Produttivi e Territoriali, ENEA, Bologna. [3] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara. [4] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS).

*Corresponding author e-mail:* chiara.telloli@enea.it

*Keywords:* Tritium, $^3$H enrichment, water resource management.

Tritium ($^3$H) is the radioactive isotope more commonly used to estimate the residence times of groundwater in aquifers. Since the 1950s it has assumed significant importance as a hydrological tracer used to discriminate young waters, characterized by fast recharging, from old waters that were infiltrated into the subsoil in the last 50 - 80 years.

Tritium is an unstable isotope of hydrogen which by the emission of $\beta^-$ particles decays into a $^3$He helium atom with a half-life of 12.32 yr ($T^{1/2}$). It is an element mainly of cosmogenic origin, as it is naturally generated in the atmosphere by the interaction between nitrogen and the flux of neutrons in cosmic radiation.

However, as a result of atmospheric nuclear tests carried out between 1951 and 1963, an important amount of anthropogenic tritium was introduced into the atmosphere by changing the geochemical footprint of rainfall, and subsequently of the sea waters. So, the concentration of tritium in surface and groundwater is strictly related to the amount of $^3$H in the atmosphere and the time of transfer of rainwater from the surface to groundwater.

At present, due to the natural decay of tritium and the prohibition of nuclear activities, environment tritium concentrations are close to natural levels of cosmic production.

This work aims to assess the recharge balance of groundwater in the different aquifers of Fiume Veneto (Pordenone, IT) and to define possible anthropogenic pollution affecting the local management of the water resource using tritium measurements.

Isotopic characterization was carried out through measurements of $^3$H, $\delta^{18}$O and $\delta$D of different water bodies (groundwaters and superficial waters) in relation to the isotopic composition of the precipitation, determining the origin and the mean residence time of groundwater in aquifers, the dynamics of processes in surface waters and their possible interconnections.

Considering that the concentrations of tritium in the atmosphere are close to the natural threshold level, to better define the older waters than 20-30 years (max 60-70 years), characterized by slow recharging, it was necessary to perform an electrolytic enrichment procedure on the water samples. The tritium enrichment and analysis procedure were carried out at the ENEA's Traceability Laboratory (FSN-SICNUC-TNMT, Bologna - Italy).

# How Italian groundwater are experiencing climate change: two examples of groundwater temperature variation from North to South

Egidio E.*[1], Stevenazzi S.[2], Ducci D.[2], De Luca D.A.[1], Mancini S.[1], Corniello A.[2] & Lasagna M.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Ingegneria Civile, Edile e Ambientale, Università di Napoli «Federico II».

*Corresponding author e-mail:* elena.egidio@unito.it

*Keywords:* climate change, groundwater temperature, Italy.

Climate change (CC) can impact groundwater (GW) resources, both from a qualitative and quantitative point of view. CC can affect the amount of soil infiltration, deeper percolation, and hence GW recharge (Wu et al., 2020), with effects on water availability. Extreme events (i.e., heavy rainfalls) can flush chemicals or faecal microbial pathogens to the water table (Lasagna et al., 2020), inducing a deterioration of GW resources. Among the physico-chemical parameters, GW temperature can respond rapidly to climatic variations: as an increase in air temperature is registered on a global scale in the recent decades, a GW temperature rise is induced for shallow aquifers and groundwater-dependent ecosystems (Menberg et al., 2014).

The aim of this study is to analyse the GW thermal sensitivity to CC (KarisAllen et al., 2022) reporting some examples in two Italian regions differing for geological, hydrogeological and climate features: Piedmont and Campania. A regional-scale investigation of the relationships between air temperature (AT) and GW temperature (GWT) was conducted for the period 2010–2019.

In Piedmont region the investigation was conducted in the alluvial plain aquifers. An analysis of 41 wells and 20 weather stations allowed to observe a general increase of both AT and GWT, up to 2.1°C/10 years for water resources. In particular, AT rise is generally more pronounced respect to GWT.

In Campania region the investigation was conducted in the northern sector of the region, in alluvial and pyroclastic aquifers. An analysis of 16 weather stations revealed an increase of AT, up to 1°-2°C/10 years, especially from 2016. Similarly, an analysis of about 40 wells revealed a general, but less pronounced, increase of GWT.

This finding for Piedmont and Campania regions suggests that AT rise is generally more evident respect to GWT, showing a greater resilience of GW to CC. Moreover, the outcomes suggest that the increase in AT, as a possible effect of CC, coupled to the decrease in rainfall, can induce an increase of the evapotranspiration and consequently a reduction of water available for GW recharge.

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# Characterization of aquifers and water balance calibration in the Laga Geological Formation (Marche Region, central Italy)

Fronzi D.*[1], Mammoliti E.[1-2], Palpacelli S.[4], Marcellini M.[1], Ianni C.[3], Tonelli M.[3], Nanni T.[4] & Tazioli A.[1]

[1] Dipartimento di Scienze e Ingegneria della Materia, dell'Ambiente ed Urbanistica, Università Politecnica delle Marche, Ancona. [2] Scuola di Scienze e Tecnologie, Università di Camerino. [3] Cicli Integrati Impianti Primari S.p.A., Ascoli Piceno. [4] External consultant.

*Corresponding author e-mail:* d.fronzi@staff.univpm.it

*Keywords:* hydrogeological balance, discharge measurements, Laga Geological Formation.

The hydrological balance represents a key point in the evaluation of groundwater availability for a certain area. Moreover, the balance between incoming precipitation and streams or springs discharge remains a challenging aspect for many scientific disciplines related to water management (Mammoliti et al., 2021). Although several physically-based approaches and complex numerical models have been developed during the last decades, the Thornthwaite-Mather approach remains one of the most used, thanks to its simple (empirical data-driven) procedure, in which the associated error to its use is smaller than the one associated with the measure of input data (Di Matteo et al., 2017). However, in areas characterized by marked lithological variability, where sparse aquifers alternated with low permeability horizons occur, the indirect hydrogeological balance (i.e., the one based on rainfall and temperature data as input, such as Thornthwaite-Mather approach) often suffers from unreliable results (Jiang et al., 2011), therefore the comparison with the springs and rivers discharge determined in the field is strongly recommended. The aim of this work is to calibrate the hydrological balance for the Laga Geological Formation of the southernmost portion of the Marche Region (central Italy), in which the peculiar geological setting makes the evaluation of water resources amount a challenging issue. The calibration of the indirect hydrogeological balance (starting from mean monthly precipitation and temperature) has been obtained by over 30 direct discharge measurements appropriately located based on a deepen hydrogeo-structural investigations, to determine the groundwater contribution to the rivers and streams supply. Besides, the comparison of these methods raised a warning about the calibration of the parameters used in the applications of indirect methods (e.g., soil moisture storage capacity). It is known that the infiltration processes occurring in the saturated portion of the aquifers should be carefully assessed by continuous in-situ monitoring systems (Gaj et al., 2015). To do this, a lysimeters and tensiometers system, together with soil temperature, soil moisture, electric conductivity probes and piezometer level monitoring is about to be installed in a small equipped basin, with the aim to continuously monitor the infiltration processes even by coupling isotope hydrology technique. These newly acquired datasets will open a window to the improvement of the calibration procedure, enhancing detailed hydrogeological balance calculations in such lithological heterogeneous geological formations. The approach presented in this study will provide the regional and other authorities with a useful tool for water management.

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# A Preliminary Analysis for Understanding Variations in Mountain Springs' Water Availability under Climate Change in Aosta Valley

Gizzi M.*, Mondani M. & Taddia G.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* martina.gizzi@polito.it

*Keywords:* hydrogeology, groundwater monitoring, mountain spring.

The availability of freshwater resources in alpine mountain areas has been affected by the impacts of climate change on groundwater storage mechanisms. A web of complex interactions characterizes climate systems, and several potential effects of climate change in such areas remain largely unknown. Therefore, examining how groundwater storage mechanisms are changing in response to climate-driven agents is becoming increasingly crucial.

To comprehend the existing relationship between changes in weather conditions and water availability in the Aosta Valley region (Northwestern Italy) and how their trends have changed over the last decade, a 7-year discharge series of different Aosta Valley springs (Promise, Alpe Perrot, Promiod, Cheserod) and precipitation data of the related meteorological stations (Aymaville-Viayes, La Thuile-Villaret, Champdepraz, Sant Vincent) were analyzed. The extent of the correlations between springs discharge measurements and hydro-meteorological data was investigated. Besides, precipitation and flow rate trend analyses using the Mann–Kendall and Sen's slope trend detection tests were performed. The Aymaville-Viayes, La Thuile-Villaret, Champdepraz, and Sant Vincent meteorological stations revealed an overall decreasing trend in annual rainfall (mm), with a slight increase in intensity (mm/day) as a result of the reduction in rainfall events (number of rainy days). Nonetheless, based on the analysis of flow rate data relating to the associated springs, Alpe Perrot, Cheserod, and Promise show an overall increasing trend of discharge over time. Although the Cheserod and Promise springs were not found to be highly correlated with rainfall, their aquifers appear to positively respond to the modified climate conditions, increasing the amount of groundwater stored. The moderate correlation values of these two springs can be a consequence of several factors such as aquifer features, distance from the weather station, and solid precipitation amounts that supply water in the following hydrogeological year.

Being able to continuously monitor the effects induced by changed climatic conditions on water reserves through simplified analysis approaches such as those presented in this paper is increasingly necessary. Moreover, implementing future studies through in-depth analyses of soil infiltration, groundwater recharge and storage mechanisms are required to predict the mountain aquifers' behavior in changing climatic conditions.

# Sustainability indicators for groundwater withdrawals from the Acque Albule Basin (Rome)

Lana L.[1], Lotti F.[1], Petitta M.[2], Piscopo V.[3] & Sbarbati C.*[3]

[1] SYMPLE s.r.l., Vetralla (VT). [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Dipartimento di Scienze Ecologiche e Biologiche, Università della Tuscia, Viterbo.

*Corresponding author e-mail:* chiara.sbarbati@unitus.it

*Keywords:* sustainable yield, thermal waters, dewatering.

Acque Albule springs, known since ancient times, are located in the Tivoli plain, about 20 km East of Rome. The thermal waters (Ca-$HCO_3$-$SO_4$ waters with temperature of 23°C) supply the thermal plant "Terme di Roma". The extraction of travertine was already practiced in the Roman era and is highly beneficial for local economic activities. Until the 1970s, the Acque Albule springs naturally emerged on the surface from two of karst origin with a flow rate higher than 2 $m^3/s$. After the 1970s, the travertine extraction activities quickly developed with a consequent increasing depths of extraction floor basins, until reaching the aquifer hosting the thermal waters. The following intervention dealt with the dewatering in the quarry area. This gave rise to a progressive decline of both groundwater level in the plain and Acque Albule springs discharge to the surface, the latter ceased completely in 2002. Consequently, water pumped from the lakes is in use for the supply of the thermal plant during the spa season. Several studies have been carried out on the hydrogeology of the Acque Albule Basin and on dewatering impacts on groundwater resources. However, the problem of groundwater management in the plain remains open.

New investigations were conducted in 2020, including measurement of groundwater outflow from the plain. A new numerical model was also implemented in order to understand the relationship between the drainage of water from the quarry area and groundwater flow in the plain. Different simulations including pre-development conditions (i.e., without the massive dewatering from the quarries) and under development conditions were processed.

Although more in-depth knowledge about flow rates, hydraulic heads and depths of the quarries extraction floors would be needed, a comparison between groundwater inflows and outflows of the system under pre-development and development conditions was carried out. An increase in inflow from surrounding carbonate aquifers, a decrease in storage and in natural discharge of the travertine aquifer result under development conditions. The aquifer quickly reaches new equilibrium conditions after the activation of the massive withdrawals from quarries due to the high hydraulic diffusivity of the aquifer. Residual discharges towards the springs and Aniene River is very sensitive to pumping flow rate from the quarries according to an inverse linear relationship, so this hydrogeological feature may be adopted as an indicator of sustainability of groundwater withdrawals from the plain. In particular, the residual discharge is most affected by the position of the pumping center in the groundwater flow net and its distance from boundaries to be captured, as well as on the depth and area of the quarries. This lays the basis for developing sustainable management models of groundwater considering the economic and environmental aspects of the issue.

# Effect of textural and hydrological properties of the soil on the residence time of infiltration water and in promoting denitrification processes in the unsaturated zone

Lobina F.*[1], Da Pelo S.[1], Biddau R.[1], Cidu R.[1], Coppola A.[2] & Vacca A.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento delle Culture Europee e del Mediterraneo: architettura, ambiente, patrimoni culturali, Università della Basilicata, Matera.

*Corresponding author e-mail:* francesca.lobina@unica.it

*Keywords:* Nitrate unsatured zone, soil texture.

The development of agricultural activities has led to an excessive use of fertilizers causing extensive nitrate contamination of groundwater in many areas worldwide. In Sardinia the plain of Arborea has been designated as Nitrate Vulnerable Zone (NVZ) since 2005, but other areas, such as southern Campidano, are affected by exceedings of the threshold value of 50 mg/L. Despite the reduction of nitrogen input imposed by the Nitrate Directive, no significant improvement in water quality has been observed (Pittalis et al., 2018; Biddau et al., 2019).

The main objective of this research is to assess the possible processes of mitigation of nitrate contamination during the filtration process from soil to aquifer in relation to the texture and hydraulic features of unsaturated zone in two areas with different geological, hydrogeological and pedological properties.

The methodology involves a multidisciplinary approach that will provide pedological, hydrological, chemical and physical characterization of the unsaturated zone, combined with the study of the aquifer. Two experimental fields sites will be equipped with soil moisture probes, tensiometers, suction cups, TDR at different depths along the thickness of the vadose zone. Sampling of soil horizons and soil water solution along the soil profile will be used for the determination of physico-chemical and hydraulic properties, as well as for the analysis of nitrogen species and environmental traces in order to define transit times in unsaturated zone. Sampling of undisturbed soil profiles will be used for subsequent column nitrate leaching experiments with the application of different nitrogen treatment cycles and controlled irrigation to determine the amount of nitrate leached after simulated events. The underlying aquifer will be properly monitored and sampled for chemical and isotopic analysis. The use of physically based unidirectional models of simulation of flow and transport of solutes in the unsaturated zone will allow to develop the future short- and long-term scenarios.

The innovative aspect of this study concerns the assessment of the impact of different textures and hydraulics characteristics on nitrate leaching processes, often disregarded. Here, indeed, isotope ratios in pore water could be helpful to understand water fluxes and transit times in the unsaturated zone and define the vulnerability of the groundwater. The study will provide a tool to the Authorities to define best management strategies to protect groundwater to nitrate contamination.

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# Distributed groundwater recharge of the Gran Sasso aquifer (Central Italy) for a sustainable management: analysis and changes during 2000-2021 period

Lorenzi V., Banzato F., Barberio M.D., Manetta M., Sbarbati C. & Petitta M.*

Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* marco.petitta@uniroma1.it

*Keywords:* groundwater resources, fractured aquifer, Central Italy.

Karst aquifers are fundamental in the water supply of European countries, providing abundant groundwater resources, available for human use and environment preservation. The need to update the groundwater budget, at local up to at the Mediterranean scale, is due to the increase of human withdrawals but also to the effect of climate change, which can affect the recharge and consequently the spring discharge in amount and regimen.

In this framework, the KARMA project granted under the PRIMA call (Horizon 2020 programme) of the European Union, is dealing with the hydrogeological understanding and sustainable management of karst water resources to obtain for the entire Mediterranean area valuable information on recharge, groundwater vulnerability and groundwater-dependent ecosystems.

The Gran Sasso karst aquifer, selected as representative study area for Italy, is characterised both by high percentage of withdrawals for drinking purposes and significant interaction between groundwater and underground works. The peculiarity of the Gran Sasso aquifer is also due to the existence of a National Park, which testifies the double need to satisfy the human requirements without compromising the environment and the related ecosystem services.

For this reason, the water balance of the Gran Sasso aquifer has been evaluated to improve the knowledge about its recharge rate with respect to the previously collected data. The recharge evaluation has been carried out considering the 2001-2020 monitoring period and comparing three different methods: the Turc and Aplis methods, on annual scale, and the Thornthwaite method, on monthly scale, territorially distributed by 100x100 m cells on GIS basis.

The results show similar mean recharge values in 2001-2021 for all methods, corresponding to 19.9, 18.5 and 19.4 $m^3/s$ respectively from Turc, Thornthwaite and Aplis methods. These values can be considered reliable with respect to real discharge of the regional aquifer. A significant contribution to recharge from snowmelt has been assessed (3.2 $m^3/s$ included in the above-mentioned values), highlighting the role of snow on infiltration for high-altitude ridges and the related risk of recharge lowering in mutated climate scenarios.

To validate the recharge calculated values, the discharge data of the main springs have been also collected and analysed. The calculated recharge by different methods shows a general underestimation of the total spring discharge, highlighting that aquifer discharge is higher than annual stored recharge. This is probably due to a "memory – effect" which modulates the response of the aquifer to meteoric recharge.

The obtained results can be used to provide updated information to the drinking water companies for a sustainable management of the available resource. The evaluations of the recharge-discharge contributions are useful also to estimate the potential impacts of climate change effect on groundwater resources, to be possibly extended at the Mediterranean scale.

# Post-seismic update of the hydrogeological setting of Sibillini Mts. system: a detail on the marchean fractured carbonate aquifers (Central Italy)

Mastrorillo L.*[1], Viaroli S.[1], Bolzonella E.[1], Mazza R.[1], Ruisi M.[2] & Taviani S.[2]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Autorità di Bacino Distrettuale dell'Appennino Centrale, Roma.

*Corresponding author e-mail:* lucia.mastrorillo@uniroma3.it

*Keywords:* groundwater balance, fractured carbonate aquifer, Sibillini Mts.

The fractured carbonate Sibillini Mts. hydrogeological system, located between the Marche, Umbria, and Lazio Regions, corresponding to the core of the 2016 – 2017 seismic crater, was affected by intense and prolonged hydrodynamic post-seismic effects (Mastrorillo et al., 2020). These effects, combined to a shortage in meteoric recharge, triggered a serious groundwater crisis in the Sibillini aquifers, that are the main sources of drinking water supply of the Adriatic coast.

The carbonate aquifers of Mts. Sibillini system belonging to the territory of Marche Region (800 km$^2$ wide area), were investigated, with the objective of comparing the post- seismic hydrogeological condition with the pre-seismic hydrogeological setting, taken from the main literature (Viaroli et al., 2021). The updated regional hydrostructural model allowed to identify 4 hydrostructures, containing several aquifers generally not connected each other. Groundwater balance of each aquifer was calculated for the post-seismic period (2016 – 2021) considering the local effective infiltration as recharge. It was calculated using the daily data recorded by 108 pluviometric and thermometric stations of Regional metereological services. The punctual data were spatialized in GIS using geostatistical tools. The outflows (spring discharge) were measured by monthly monitoring campaigns in 83 measurement sections. The quantification of groundwater used for drinking and hydropower purposes was estimated according to the data provided by the water supply companies.

The results provide a complete overview of the current availability of groundwater and its geographic distribution. It is now possible the identification of the sectors affected by persistent hydrogeological changes induced by the 2016 seismic activity and where the groundwater resources are mainly stressed by human impact.

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# Numerical modelling of the Milano metropolitan area (Italy) to assess the relevance of irrigation recharge in prediction of future groundwater levels

Mazzon P.*, Piccioli S., Colombo P. & Alberti L.

Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano.

*Corresponding author e-mail:* pietro.mazzon@polimi.it

*Keywords:* MODFLOW-NWT, Soil Water Balance 2.0, groundwater modelling.

The management of groundwater resources is crucial to secure quality and availability in the next years, considering the effects of climate changes. Groundwater models are key tools able to condense multiple information of a conceptual model into a mathematical code that can be used to make predictions of future groundwater levels. The area surrounding Milano city strongly relies on groundwater abstractions for drinking, industrial and private uses (about $480 \times 10^6$ $m^3$/year), therefore is necessary to design management plans for the area. Among other influencing factors of groundwater levels as rainfall, boundary flow rates, streams and rivers, irrigation plays an important role for this area, since an historical irrigation canal network brings water to crop fields where the water is distributed mainly through surface methods, resulting in a relevant increment of the vertical recharge rates. Therefore, a basin-scale 2014-2018 unsteady-state flow model previously implemented in MODFLOW-NWT (Capelli, 2021) was updated and further calibrated within this study. One of the main improvements was to calculate recharge combining daily gridded precipitation and temperature data (E-OBS) with Soil Water Balance 2 (Westenbroek et al., 2018). Furthermore, the irrigation recharge was thoroughly computed considering the different granted volumes of water in the different irrigation districts. A sensitivity analysis was conducted in order to evidence the most influencing parameters for groundwater levels. Finally, the model was calibrated using PEST (Doherty, 2004) and then used to make groundwater level predictions extending the simulation period to 2100, in response of possible future changes in irrigation practices due to the adoption of management guidelines for water save. Different scenarios were performed and compared to the business-as-usual irrigation practices. The results show the importance of irrigation recharge for the groundwater balance and how such variations can influence future groundwater levels. Therefore, the study underlines that changes in precipitation and temperature are not sufficient to make groundwater level predictions under climate change scenarios, but irrigation also plays an important role and has to be considered in forecast models. Furthermore, the irrigation system can be considered as a possible adaptation method for the study area.

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# Groundwater, the invisible resource: findings from the UN World Water Development Report 2022

Miletto M.*

World Water Assessment Programme, UNESCO.

*Corresponding author e-mail:* m.miletto@unesco.org

*Keywords:* groundwater, United Nations World Water Development Report.

Groundwater is central to the fight against poverty, to food and water security, to creation of decent jobs, to socio-economic development, and to the resilience of societies and economies to climate change. Reliance on groundwater will only increase, mainly due to growing water demand by all sectors combined with increasing variation in rainfall patterns. Given the growing water scarcity across many parts of the world, the enormous potential of groundwater, and the need to manage it sustainably, cannot be overlooked.

The 2022 edition of the United Nations World Water Development Report, titled "Groundwater: Making the invisible visible", describes the challenges and opportunities associated with the development, management and governance of groundwater across the world. It aims to establish a clear understanding of the role that groundwater plays in daily life, of its interactions with people, and of the opportunities for optimizing its use in order to ensure the long-term sustainability of this largely available yet fragile resource.

The United Nations World Water Development Report (UN WWDR) is a UN-Water publication on water and sanitation issues, focuses on a different theme every year. Published by UNESCO on behalf of UN-Water, its production is coordinated by the UNESCO World Water Assessment Programme.

# Lead anomalies in the Lake Accesa (Tuscany, Italy): evidence of human pollution from the Early Copper Age

Pasquetti F.*[1], Zanchetta G.[1], Bini M.[1], Vannière B.[2], Desmet M.[3], Magny M.[2], Vaselli O.[4], Petrini R.[1], Baneschi I.[5] & Fulignati P.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Laboratoire Chrono-Environment, Université Bourgogne Franche-Comté, Besançon (France). [3] Laboratoire Géohydrosystèmes Continentaux, Université de Tours (France). [4] Dipartimento di Scienze della Terra, Università di Firenze. [5] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* francesca.pasquetti@phd.unipi.it

*Keywords:* Pb, isotopes, lake sediments.

The Lake Accesa is a small karstic lake (~0.15 km$^2$) located in southern Tuscany (Italy) on the southern border of the Colline Metallifere mining district, which is characterized by widespread hydrothermal mineralization. The catchment area of the lake (about 5 km$^2$) is surrounded by sulfide polymetallic deposits exploited at least since the Etruscan times for the extraction of silver and lead (Lobell, 2002).

Here, we present a high-resolution and continuous geochemical record for lead, from a sediment core of the Lake Accesa collected in 2005. The core is about 8 meters long and covers a time spanning from today to 11000 cal. BP (Vannière et al., 2008). Lead was analyzed along the core by X-ray fluorescence (XRF). Some samples were analyzed for Pb isotopic composition by Multi Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) and observed under a Field Emission Scanning Electron Microscope (FE-SEM).

The results obtained from XRF analyses indicate that Pb concentrations varied from below the detection limit to ~362 ppm, with a mean of 33 ppm and a median of 4.4 ppm. The distribution of Pb with depth shows that the highest values were mainly localized around 5500 cal. BP (3550 yr BC) and in the uppermost part of the core, starting from 1200 cal. BP (from 750 yr AC). Pb isotopic compositions fit with the composition of polymetallic ores of southern Tuscany (e.g., Lattanzi et al., 1997) indicating that Pb is of local origin and related with the mineralization of this area. However, the observation under the electron microscope does not highlight the presence of Pb sulfide minerals (e.g., galena) but rather seems that Pb is scattered in the sample bulk.

The highlighted peaks of Pb could thus be related to human activities, and in particular to mining and smelting, which seem to be particularly intense during the Copper Age and since the Middle Age. Surprisingly, there is no evidence of Pb anomalies during Etruscan and Roman times. Moreover, the high values of Pb may have been enhanced by land management operations, such as deforestation, that favored soil erosion in the exploited areas. Further analyses on other trace elements could be helpful to discriminate the process of formation of these anomalies and their origin.

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# Innovative methodological approach for the modeling of seawater intrusion in the coastal plain of Muravera (Sardinia, Italy)

Porru M.C.*[1], Da Pelo S.[1], Davids T.[2], Oude Essink G.[2], Arras C.[1] & Piscedda F.A.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Groundwater Management Department, Deltares, Utrecht (Netherlands).

*Corresponding author e-mail:* chiaraporru3@gmail.com

*Keywords:* seawater intrusion, IMOD, Hydrogeological models.

Many coastal areas, especially low-lying deltaic areas, have high density populations and are often important economic areas. At the same time, their aquifers are often overexploited and subject to seawater intrusion phenomena. Climate change, including sea-level rise, will exacerbate the vulnerability of these sensitive areas, so it is critical to provide the complex water resource management with tools capable to consider all the variables involved to predict appropriate scenarios for action, balancing water demand of the population and the natural water equilibrium. Hydrogeological models are as such powerful instruments though they need to be calibrated with enough reliable hydrogeological data.

This study is applying an innovative hydrogeological modelling approach to simulate seawater intrusion in the coastal plain of Muravera (south-east, Sardinia). This area has been studied since the 1950s due to seawater intrusion phenomena that have led to various socio-economic and environmental problems. Thanks to the geological, hydrogeological, and geochemical data collected in the recent years, it has been possible to develop a 3D numerical groundwater model of the plain.

To simulate density dependent groundwater flow and coupled solute transport, by Deltares developed, iMOD-WQ software is used. iMOD-WQ consists of the widely used software SEAWAT, which enables density dependent fresh-salt groundwater modelling (Langevin & Guo, 2006), and the software RT3D, for reactive transport modelling, which in not applied in this study. iMOD is a source code adapted for parallellization and thus speeding up the computation up to two order of magnitudes depending on the available computer codes (Verkaik et al., 2021) and it allows fast, flexible, and consistent sub-domain modelling techniques. Unlike other groundwater modelling software, data with different cover extension can be implemented within the iMOD without a pre-processing phase for fitting model-grid resolution but it regrids the datasets automatically to the selected resolutions. The software is freely available and open source, can be implemented either using the Graphical User Interface or with Python. In this study, the latter was preferred due to its ability to facilitate working with groundwater models and for large datasets.

Based on the conceptual geological model described in Arras et al. (2019), the plain was divided into six geological layers with different hydraulic conductivity values, which was then voxelized to a model with 45 model layers. The recharge values were derived from the application of Soil Water Balance code (Porru et al., 2021). The identification of the fresh water and saltwater interface was derived from direct measurements carried out with a multiparameter probe in deep wells (20/30 m deep) in 2021. The model was then validated using piezometric heads, electrical conductivity values and chemical and multi-isotopes data collected between 2020 and 2021.

The implemented 3D model is a preliminary valuable tool to support groundwater management. It can also be used to simulate the effects of future sea water intrusion under different climate change driven sea-level and natural recharge scenarios.

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# 3D geological modelling in urban contexts for hydrogeological analysis: a case study of the city of Cassino (Central Italy)

Rompato M.*[1], Saroli M.[1-2], Albano M.[2], Moro M.[2], Bozzano F.[3] & Scarascia Mugnozza G.[3]

[1] Dipartimento di Ingegneria Civile e Meccanica, Università di Cassino e del Lazio Meridionale. [2] INGV, Roma.
[3] Dipartimento di Scienze della Terra e Centro di ricerca previsione, prevenzione e controllo dei rischi geologici, Sapienza Università di Roma.

*Corresponding author e-mail:* matteo.rompato@unicas.it

*Keywords:* 3D geological models, urban geology.

This work aims to investigate the shape and geotechnical features of the subsoil of the city of Cassino (Central Italy) through the interpretation of an extensive database of geophysical, geognostic and bibliographic data. 3D geological models of urban areas provide critical information for geological and hydrogeological analysis and studies. Particularly, the city of Cassino hosts important springs coming from the Caira-Ernici-M. Cassino hydrostructure. Currently, few data are available for the characterization of lateral and vertical contacts between the carbonate hydrostructure and quaternary alluvial deposits. To overcome such a limitation, we aim at developing a 3D subsoil model by exploiting available and new data.

The available dataset comprises 229 geognostic boreholes and 73 HVSR microtremor measurements. The collected data were processed through the 3D geological modelling software Leapfrog (Seequent Limited). In particular, the HVSR analysis proposed in Saroli et al. (2020) has been reworked in a new statistical raster surface representing the substrate's depth.

The 3D model is made by stacking on top of each of the interpolated surfaces representing stratigraphic and tectonic boundaries. Such model highlights the main structural and lithological elements of the subsoil, such as the surface of the bedrock, the quaternary fluvio-lacustrine filling, and secondary tectonic structures (i.e., faults) buried below the city.

The carbonate and flyshoid bedrock are disarticulated in a horst and graben structure by a normal fault system (pre-Miocene) oriented along the appenninic and anti-appenninic direction.

The model highlights a horst located to the south-southeast, which represents the continuation of a large-scale structure that connects the bedrock outcrops of *Terme Varroniane* and *Borgo Mastronardi* localities. The bedrock subsurface is approximately 100 m deep under the area of the town. Still, in the northern portions of the city, this surface deepens to a depth of about 300 m, as testified by deep boreholes and microtremor measurements.

The quaternary filling is composed of impermeable silty and clayey lithologies, interspersed by several lenses of sandy and gravelly layers up to about 10 m thick in the center of the city, resulting from past alluvial events of the Rapido River. These lithologies are often saturated by water filtrating upward from the buried carbonate bedrock or by lateral feeding where the sandy-gravelly lithologies are in contact with the carbonate relief of M. Cassino.

Furthermore, the 3D geological models of the Cassino area highlight vertical and horizontal filtration phenomena inside the hydrostratigraphic basin of the Cassino plain from the carbonate structure

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# Base studies on seawater intrusion in coastal aquifers in the Volturno Plain (Campania region, Southern Italy)

Stevenazzi S.*, Corniello A., Del Gaudio E. & Ducci D.

Dipartimento di Ingegneria Civile, Edile e Ambientale, Università di Napoli "Federico II".

*Corresponding author e-mail:* stefania.stevenazzi@unina.it

*Keywords:* seawater intrusion, water scarcity, southern Italy.

Scarcity of rainfall and droughts have a direct impact on groundwater resources, increasing the issue of seawater intrusion in coastal areas, where, once the phenomenon of saline contamination has been activated, it is very difficult to reverse the trend. Moreover, the saline contamination in coastal aquifers is often high over very large sectors of the coast and it is gradually increasing due to the increase in groundwater withdrawals for drinking purposes, agriculture, industry and tourism. This is aggravated by the decrease in aquifer recharge and increased evapotranspiration due to global warming and the ongoing climate changes (MedECC, 2020). Thus, a comprehensive knowledge of the seawater intrusion phenomenon and its evolution in the future should be achieved for a proper and sustainable management of groundwater resources in coastal areas.

In this study, we focus on the analysis and implementation of the methodologies to study and prevent the saline contamination in coastal areas. We intend to reconstruct the dynamics of the seawater intrusion phenomenon with the aid of 3D litho-stratigraphic models and flow models and attempt to evaluate the evolution of the freshwater / saltwater interface over a medium-to-long time span. The areas of interest are the most affected sectors of the coastal plains in the northern part of Campania (Southern Italy): the Volturno Plain, a coastal plain of about 1340 km² constituted of fluvial, pyroclastic and marine sediments (Allocca et al., 2005; Corniello & Ducci, 2014).

An interactive 3D / 4D hydrogeological geo-database for the optimization of the handling and storage of spatio-temporal data is implemented. The database includes the available geographical, geological and hydrogeological information. Geographical data include elevation, hydrography, land cover and land use. Geological data include stratigraphies from more than 700 boreholes. Hydrogeological data include piezometric levels and more than 600 hydrochemical analyses (i.e., physico-chemical parameters, major and minor cations and anions, metals, organic compounds, $H_2O$ stable isotopes) from about 300 wells and piezometers, spanning from 2002 to 2020. After a quality check, data are organised in a geographic information system (GIS) environment. Hydrogeological field surveys and monitoring activities are planned to integrate new data into the database: a selected number of wells will be instrumented with probes for a continuous monitoring of groundwater characteristics (i.e., piezometric level, electric conductivity, salinity).

The 3D / 4D hydrogeological geo-database allows the development of reliable conceptual and numerical models describing the seawater intrusion phenomenon, as well as for the implementation of medium-to-long term future scenarios. The outcomes of this study would be a useful support to groundwater managers and decision-makers for a sustainable management of the resource.

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# Water availability evaluation for a sustainable management of groundwater resources in mountainous areas

Stevenazzi S.*[1], Lucchelli A.[2], Del Gaudio E.[1], Ducci D.[1] & Masetti M.[2]

[1] Dipartimento di Ingegneria Civile, Edile e Ambientale, Università di Napoli «Federico II». [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* stefania.stevenazzi@unina.it

*Keywords:* groundwater body, groundwater budget, Italy.

Groundwater resources in mountain areas is strategically important to maintain adequate water supply both for drinking supply and for other anthropogenic activities in many parts of the world (Somers & McKenzie, 2020). This resource is getting more and more important considering that water demand in mountain areas is growing, 1.4 billion people will depend critically on mountain runoff by 2050 (Viviroli et al., 2020) and it should help to better cope with future climate scenarios to satisfy the increasing demand for clean and safe water. Within this framework, a reliable quantitative estimation of the resources in the different groundwater bodies is necessary to support their management.

Two groundwater bodies (GWBs) of about 200 km² width each, respectively located in the central Alps and in the southern Apennines, have been studied to determine the availability of local water resources. Both the GWBs are mainly composed by carbonate rock masses, extensively karstified, hosting many springs constituting important sources of safe and clean water for the local districts. The areas differ for climatic, geomorphological, and land use - land cover conditions that affect water distributions within each area. Groundwater budgets of the selected GWBs were determined through hydrogeological approaches that make extensive use of data collected and managed by the local public authorities (Regional Environmental Offices and Agencies) and by the local water managers. Groundwater budgets were evaluated resolving the classical analytical solution where the inflows are equal to the outflows within each GWB, including the budget terms: precipitation, evapotranspiration, surface runoff and groundwater recharge/discharge. Groundwater budgets were carried out on a yearly basis for the period 2014 – 2018, including an extremely wet year (2014) and a severe dry year (2017), representing two opposite climate scenarios strongly influencing groundwater recharge and storage.

The application of different approaches for the evaluation of the single components of the groundwater budget allowed to: i) identify the parameters that mostly affect the evaluation of each single component; ii) determine the general uncertainty in the estimation of groundwater resources availability (i.e., groundwater recharge and storage); iii) evaluate the consistency of public datasets to estimate groundwater budget and iv) highlight the necessity and usefulness of implementing the public datasets to increase the reliability of the estimation of groundwater resources availability.

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# Exploitation of drinking waters in Central Italy: considerations about withdrawn techniques of groundwater in the framework of the ongoing climate changes

Valigi D.*, Cambi C. & Di Matteo L.

Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* daniela.valigi@unipg.it

*Keywords:* groundwater exploitation, springs, pumping wells.

Groundwater is one of the main sources of drinking water in Italy: about 58% of drinking water in Central Italy comes from springs. This area, such as the whole Mediterranean Region, is characterized by marked variations in seasonal spring discharge, with values generally much lower during summer periods. This fact implies that the highest water demand occurs when water availability is very low, so the needs cannot be met. Furthermore, it is widely known that the ongoing climatic changes determined an increase in duration and frequency of severe droughts in Central Italy, with a strong influence on groundwater resources (e.g., Di Matteo et al., 2013; Dragoni et al., 2013). These conditions worsen water shortages and determine the urgent need for studying new techniques to improve the sustainability of groundwater exploitation. One of the more diffused approaches to solving problems related to springs water shortage is the drilling of pumping wells near the springs (i.e., close to no-flow boundaries), but the efficiency of this technique is generally low. In addition, when wells are close to springs, the natural spring discharge is affected by pumping and decreases further, with obvious consequences on both the environment and water distribution costs. An increase in the efficiency of the withdrawal management can be obtained by placing pumping wells at a far distance from the spring, with inevitable logistical difficulties and high costs in mountain regions. In the last decades, the exploitation of groundwater hosted in limestone aquifers has been carried out by pumping wells close to gaining rivers, where the potentiometric surface is at shallow depths (Valigi et al., 2021). In these conditions, the overall costs for drilling and pumping are lower than those of wells located at higher altitudes. As for mountain springs, also in this case some environmental problems can derive from the pumping, such as the interaction with surface waters that may reduce the quality of the water withdrawn (Di Matteo & Dragoni, 2005). The present work illustrates some examples of the exploitation of some linear and punctual springs in Central Italy, also considering the effects of the prolonged drought periods.

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Valigi D., Cambi C., Checcucci R. & Di Matteo L. (2021) - Transmissivity Estimates by Specific Capacity Data of Some Fractured Italian Carbonate Aquifers. Water, 13(10), 1374.

# Hydrogeological study of the perrot spring (Aosta valley, Italy)

Vescovo G.[1], Bolognini D.[2], Lasagna M.[1], Santillan L.*[1] & De Luca D.A.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Studio Geologico SiO2, Pont Saint Martin (AO).

*Corresponding author e-mail:* luis.santillanquiroga@espoch.edu.ec

*Keywords:* climate, water.

The Perrot spring is located in the municipality of Champdepraz (Aosta Valley Region) at an altitude of about 1300 m a.s.l. and contributes to the supply of the Champdepraz aqueduct network. The collected data are aimed at understanding the spring feeding mechanism and the delimitation of the potential recharge area.

From a geological point of view, the spring is located within the Piemonte oceanic unit, characterised by the presence of ophiolitic rocks, locally very fractured, with a cover of quaternary deposits represented by, lacustrine-palustrine, fluvial, fluvioglacial and, above all, glacial deposits. The substrate and the cover represent the potential water reservoir that feeds the Perrot spring.

A geophysical survey carried out immediately upstream of the spring revealed a clear contrast in P-wave velocity at a depth of approximately 5 m, represented by an erosional contact between the crystalline substrate and the overlying glacial and eluvial deposits. Consequently, the spring was classified as a contact spring.

Various chemical and physico-chemical parameters of the spring water were analysed between January 2018 and July 2020 and in detail the flow rate, temperature, electrolytic conductivity, pH, main anions and cations. These data were processed and compared with air temperature and precipitation for the study area. It was thus possible to observe the regime of the Perrot Spring, characterised by two discharge maxima, in spring and in autumn: groundwater recharge is represented by the snowmelt in spring and by rainfall in autumn. Chemical analyses carried out on the Perrot spring waters permitted to define the groundwater facies as Mg-$HCO_3$ type.

The remarkable constancy of the chemical and physical-chemical parameters of the spring waters suggests the presence of a water reservoir of considerable size and a relatively deep underground circulation, not substantially influenced by the air temperature.

Isotopic analyses of spring water and precipitation collected at different altitudes revealed an average isotopic recharge height of 2000 m a.s.l. The potential recharge area of the spring is located in correspondence with a large plateau characterised by the presence of numerous faults and glacial lakes.

# Preliminary hydrogeological and geochemical characterization of the Gioia Tauro coastal Plain (Calabria - South Italy)

Vespasiano G.*[1-2], Cianflone G.[1-2], Marini L.[3], De Rosa R.[1], Andiloro G.[4], Walraevens K.[5], Vaselli O.[6-7], Tolomei C.[8], Pizzino L.[8], Cinti D.[8], Polemio M.[9], Capecchiacci F.[6-7], Dominici R.[1-2] & Apollaro C.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] E3 (Environment, Earth, Engineering), s.c. - spin-off Università della Calabria, Rende (CS). [3] Steam s.r.l., Pisa.[4] Freelance Geologist, Gioia Tauro (RC). [5] Laboratory for Applied Geology and Hydrogeology, Department of Geology, Ghent University (Belgium). [6] Dipartimento di Scienze della Terra, Università di Firenze. [7] Istituto di Geoscienze e Georisorse, CNR, Firenze. [8] INGV, Roma. [9] Istituto di Ricerca per la Protezione Idrogeologica, CNR, Bari.

*Corresponding author e-mail:* giovanni.vespasiano@unical.it

*Keywords:* Gioia Tauro Plain, aquifers, hydrogeochemical model.

The Gioia Tauro Plain (GTP) is one of the most important industrialized and agricultural coastal areas of southern Italy extended over 500 km$^2$. The Gioia Tauro harbor is one of the most important container traffic hubs in the Mediterranean Sea and the largest transshipment terminal in Italy. Despite the presence of important infrastructures, the GTP still presents sectors completely devoid of basic services, such as sewers or connections to aqueducts for domestic use. The lack of such services increases the groundwater overexploitation. Furthermore, GTP is characterized by a complex geological and structural framework that favors the development of water chemistry not fully explainable by simple water-rock interaction processes occurring in the sedimentary aquifers and seawater intrusion (Cianflone et al., 2022).

We carried out the hydro-stratigraphic reconstruction and the geochemical characterization of the GTP. Two main aquifers were recognized: a shallow aquifer (HU3) including late Pleistocene and Holocene marine and alluvial sediments and a deep aquifer consisting of the late Miocene succession (HU1), divided by an aquitard (HU2) made by Pliocene marly clay (Cianflone et al., 2021). Deep and shallow aquifers are fed mainly by $Ca^{2+}$-$HCO_3^-$ waters from the main recharging areas except in localized borders sectors where the interaction with the crystalline-metamorphic basements favors $Na^+$-$HCO_3^-$ waters. $Ca^{2+}$-$HCO_3^-$ and $Na^+$-$HCO_3^-$ waters suffer from secondary processes, occurring during the east-to-west circulation: (i) in HU3 inputs of N-rich agriculture-related contaminants and SOx emissions represent the main processes favoring nitrate increases and evolutions towards $CaSO_4$ composition. ii) In HU1 direct cationic exchanges represents the primary factor controlling the waters geochemistry. The process produces $Na^+$-$HCO_3^-$ geochemical facies showing high Na/Cl ratios and negative CAI indexes if compared with the $Na^+$-$HCO_3^-$ group recognized in the shallow aquifer characterized by CAI values close to zero and low Na/Cl ratio. Moreover, the mixing of these waters with both connate brine and/or deep thermal waters contribute to the formation of isolated high salinity NaCl waters.

The study revealed that a direct marine intrusion seems to be very localized despite the high demand for water linked to the anthropic activities. In fact, an incipient groundwater-seawater mixing, quantified about 7% of seawater fraction, is only recognized in a restricted southwestern area. The qualitative and quantitative conditions of the aquifer are kept at acceptable levels due to the high recharge inflow (mean precipitation of 1274 mm/yr).

The obtained results confirm the importance of the multidisciplinary approach to identify and characterize sources and driving mechanisms and produce a reliable hydrogeochemical conceptual model. These results will provide an important support to the decision-making and management phases of the GTP water resource.

Cianflone G., Vespasiano G., De Rosa R., Dominici R., Apollaro C., Vaselli O., Pizzino L., Tolomei C., Capecchiacci F. & Polemio M. (2021) - Hydrostratigraphic Framework and Physicochemical Status of Groundwater in the Gioia Tauro Coastal Plain (Calabria—Southern Italy). Water, 13, 3279. https://doi.org/10.3390/w1322327.

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# Impact of the extremal climatic event Alex (2-3/10/2020) on the geochemically vulnerable peri-Alpine Roja's aquifer

Vetuschi Zuccolini M.*[1], Canepa M.[2], Parodi U.[3] & Schenone D.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Regione Liguria - Ecologia, Genova. [3] Regione Liguria - Ecosistema Costiero ed Acque, Genova.

*Corresponding author e-mail:* marino.zuccolini@unige.it

*Keywords:* hydrogeochemistry, common-ion-effect, climatic change.

Nowadays, the real-time global view of our planet through satellite systems, monitoring the status of many environmental parameters (ref) indicates that we are experiencing a period of global transition.

Intensification of weather phenomena by an increase of event number and effect exacerbation are perceived by communities as the main effect of this non-stationarity. Although silently and sometimes in a very efficient way there are other processes acting locally with even more worrying short-term impacts.

Studies on consequences of climate transition on surface waters are large due to their close linking with weather modeling providing a numerical description of the water cycle (ref). Similarly, as far as aquifers are concerned, although fewer in number, a limited number of studies assess the impact on its expected water storage.

An even smaller number of studies are aimed at defining a descriptive framework for the geochemical status of an aquifer under climatic change.

This condition can be attributed primarily to the undervaluation of the problem, to sparsity and inadequate compilation of surface water and groundwater dataset and on reluctance to consider an aquifer as result of water-rock interactions as more responsive than previously assumed.

But what can happen in a water reservoir if a geochemically pseudo-stationary hydrographic network system is hit by an extreme meteorological event altering its productivity up to obtain an aquifer almost sterile if exploited?

Here are presented the results of the hydrogeochemical investigation carried out on the trans-border coastal aquifer of the T.Roja (Roya in French) as a result of the exceptional event called Storm Alex (2-3 October 2020) that hits the Côte d'Azur (France) and the Ponente Ligure (Italy), causing considerable damages to infrastructures, deaths and missing persons.

The particular geomorphological and geological setting of the catchment embedded between southern Alps and Mediterranean Sea and the predominance of the effects that can be traced back to spotted carbonate Triassic embedded evaporites dissolution provide a perfect scenario leading toward an (ir)reversible depletion of water ressources in Roya's reservoir.

Probing deeply the water equilibria in river and groundwater dataset trying to focus the water-rock interactions, a "common-ion effect" is found as the master key to suggest the reasons why an abrupt change is recorded as a water table drop for at least 1 year after the storm and strictly related to aquifer management.

The picture that comes from research recall as in that particular trans-boundary strategic aquifer the combination of the joint management by two countries, the presence of a geologically fragile system stressed by an exceptional environmental pressure because of climate change allow to emphasize the role of the aquifer geochemistry as a key to plan management policies of aquifer resources.

# S38.

# Geosciences and shallow geothermics for the energy transition and sustainability


*Conveners & Chairpersons*

*Marco Taussi (University of Urbino)*

*Alessandro Casasso (Politecnico of Torino)*

*Alberto Renzulli (University of Urbino)*

*Chiara Boschi (CNR-IGG Pisa)*

*Valentina Volpi (OGS-Trieste)*

# Simulation of groundwater flow energy contribution in BHE systems by means of an adapted TRNSYS-type for HVAC systems design

Antelmi M.*[1-3], Turrin F.[2], Zille A.[1] & Fedrizzi R.[2]

[1] Inewa s.r.l., NOI Techpark, Bolzano. [2] Eurac Research, NOI Techpark, Bolzano. [3] Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano.

*Corresponding author e-mail:* matteo.antelmi@polimi.it

*Keywords:* numerical modeling, groundwater flow, GSHP system.

Numerical models of ground source heat pump (GSHP) systems are increasingly used as a support tool to correctly design borefield and heat pump size. Heating Ventilating Air-Conditioning (HVAC) systems provide heating/cooling of buildings and the mostly used code for their design is the TRNSYS. The implementation of the main element, i.e., Borehole Heat Exchanger (BHE), and its heat transfer in aquifer is complex and the reproduction of this element in TRNSYS is quite simplified and approximate. The numerical reproduction of the dynamic thermal behavior of the BHE both in a short-term or long-term basis is essential. Many hydrogeological codes, i.e., MODFLOW, FEFLOW or COMSOL, are able to correctly reproduce the heat transfer assuming different hydrogeological conditions but they are not able to reproduce the heat pump and its interaction between the building. The TRNSYS code overcome this issue, but on the opposite, is not adequate for the reproduction of heat exchange when a groundwaer flow is present. As Angelotti discuss (Angelotti et al., 2014), the effect of the groundwater flow presence on heat transfer is fundamental because as the flow velocity increases, higher the BHE energy performance is (maximum increase estimated approximately 90%). Therefore, a non-standard BHE type (named as type n. 285) was specifically developed for TRNSYS 18 starting from the original BHE type (named type n. 280) developed by Pahud & Hellstrom (1996) and based on the Duct Storage Model studied by Hellstrom (1989). The type was developed and tested for different groundwater flow velocities (the most frequent in nature), comparing with the energy performance increases shown by Angelotti et al. (2014). The comparison between the TRNSYS and synthethic MT3DMS simulations gave good results, hence, a set of experimental data (a real GSHP system consisting of 5 BHE installed in Lodi's heterogeneous aquifer and discussed in Alberti et al., 2018) was used to validate the approach. The TRNSYS model was modified and adapted to the hydrogeology and GSHP operation (heating period) of the field case and the results showed a divergence in exchanged energy parameter lower than 8.5%. Therefore, the new BHE non-standard type is validated and allows to simulate one or more than one vertical BHE buried in aquifer considering the variation of the advection term due to different specific hydrogeological conditions.

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# Numerical modeling and validation of a thermal response test through the MODFLOW-USG code for ground source heat pump design support

Barbieri S.*, Antelmi M. & Alberti L.

Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano.

*Corresponding author e-mail:* sara.barbieri@polimi.it

*Keywords:* MODFLOW-USG, TRT, Heat-Transport.

In the last decade, because of the growing spread in Europe of low enthalpy geothermal systems coupled to heat pumps (GSHP, Ground-Source Heat Pump), the need to numerically forecast the environmental impact of these renewable energy systems has become crucial. Specifically for closed loop systems, in the last decade efforts have been made to simulate Borehole Heat Exchangers (BHEs) through MODFLOW (Angelotti et al., 2014), the most recent showed the adaptation of Connected Linear Network (CLN) Process for this purpose (Antelmi et al., 2021). The Thermal Response Test (TRT) is recognized as a fundamental tool for the efficient design of the GSHP systems and the numerical simulation of this in situ test represents an essential further development for the BHEs design and the numerical modeling reliability improvement. In this study a numerical TRT was reproduced by means of a control volume finite difference model in the MODFLOW-USG code where the BHE modeling was performed adapting the Antelmi et al. approach, using the CLN and the Drain Return Transport (DRT) Packages. A sensitivity analysis both on the horizontal grid discretization and the groundwater flow velocity was performed; hence, several models were implemented in the MODFLOW-USG code combining 4 minimum cell size values and 4 Darcy velocities. The results of this new numerical approach were compared with a previous validated literature procedure based on MODFLOW-2000 and MT3DMS and on the analytical solutions of the Infinite Line Source Model (ILS) and the Moving Line Source Model (MLS). According to the achieved results, the new methodology was validated against experimental data by means of an automatic calibration process; in specific, the subsoil hydrogeological and thermal parameters are varied using the PEST code. This study allowed to identify the strengths of the new approach in terms of lower computational effort, more precise results accuracy and an improved application approach for real case studies.

Angelotti A., Alberti L., La Licata I. & Antelmi M. (2014) - Energy performance and thermal impact of a Borehole Heat Exchanger in a sandy aquifer: Influence of the groundwater velocity. Energy Conversion and Management, 77, 700-708.

Antelmi M., Alberti L., Barbieri S. & Panday S. (2021) - Simulation of thermal perturbation in groundwater caused by Borehole Heat Exchangers using an adapted CLN package of MODFLOW-USG. Journal of Hydrology, 596.

# Recommendations for the planning and management of ground source heat pump systems in an urban environment, considering the effects of reciprocal thermal interference

Belliardi M.*, Soma L., Perego R., Pera S., Di Sipio E., Zarrella A., Carnieletto L., Galgaro A., Badenes B., Pasquali R., Bertermann D. & Sanner B.

Istituto Sostenibilità Applicata all'Ambiente Costruito, Scuola Universitaria Professionale della Svizzera Italiana, Mendrisio (Switzerland).

*Corresponding author e-mail:* marco.belliardi@supsi.ch

*Keywords:* shallow geothermal energy, thermal interference, planning.

The "Most Easy, Efficient and Low Cost Geothermal Systems for Retrofitting Civil and Historical Buildings" (GEO4CIVHIC) project aims to accelerate the deployment of shallow geothermal systems for heating and cooling purposes when retrofitting existing and historical buildings. Analyzing the implementation process of borehole heat exchangers (BHEs), allows the understanding of how to promote the long-term sustainability of shallow geothermal energy systems. The thermal interference between BHE systems represents a problem, especially due to the increasing deployment of this technology and its spread in densely built-up areas.

The main goals of the work to be presented are: a) to analyze the design phase of a BHE system in order to prevent mutual thermal interference, b) to propose a model that encloses phases to adopt an integrated approach for preventing long term thermal interferences, c) to give technical and management suggestions to minimize thermal interference between closed-loop geothermal systems.

The method developed in this research follows the following steps: 1) literature review to determine what are the main drivers for thermal interference between shallow geothermal systems, in the context of the GEO4CIVHIC project case study sites; 2) to create a conceptual model to limit thermal interference at both design and operational phases; 3) to apply the developed method to real and virtual case studies in countries with different regulatory frameworks and to test its main strengths and weaknesses. The application of this conceptual model to specific case studies provides evidence of critical planning and operational characteristics of GSHP systems and allows the identification of measures to mitigate impacts of thermal interference to be identified.

# Borehole Heat Exchangers: A potential trigger for aquifer cross-contamination?

Casasso A.*, Ferrantello N., Pescarmona S. & Sethi R.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* alessandro.casasso@polito.it

*Keywords:* borehole heat exchanger, cross-contamination, grout.

The number of Ground Source Heat Pumps (GSHPs) has been growing steadily in the last 20 years, and so has the number of Borehole Heat Exchangers (BHEs), which perform the heat exchange between the ground and the heat pump. BHEs are generally about 100 m deep and, hence, they can cross different aquifers. Concerns have therefore been raised about the possible preferential flow of contaminants that can occur through boreholes, also known as cross-contamination (Casasso et al., 2020). The strength of such phenomenon depends on the vertical hydraulic gradient between the aquifers and the hydraulic conductivity of the grout filling. Therefore, we developed a numerical flow and solute transport model in severe conditions to assess to which extent a BHE can induce cross-contamination between a shallow contaminated aquifer and a deep uncontaminated one, separated by an aquiclude. The results show that the leakage flow and the contaminant spatial distribution in the deep aquifer are well reproduced with analytical formulae, which can therefore be used to assess the potential impact of cross-contamination. Results also confirm that the geothermal grouts available in the market, with hydraulic conductivities well below $10^{-6}$ m/s, guarantee a sufficient protection from preferential flow through borehole heat exchangers (Casasso & Sethi, 2019).

Casasso A., Ferrantello N., Pescarmona S., Bianco C. & Sethi R. (2020) - Can borehole heat exchangers trigger cross-contamination between aquifers?. Water, 12(4), 1174.

Casasso A. & Sethi R. (2019) - Assessment and minimization of potential environmental impacts of ground source heat pump (GSHP) systems. Water, 11(8), 1573.

# Underground Thermal Energy Storage (UTES): an improvement for District Heating and Cooling networks using a geothermal technology

Chicco J.M.*, Mandrone G. & Vacha D.

Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio, Università di Torino.

*Corresponding author e-mail:* jessica.chicco@unito.it

*Keywords:* heat storage, district heating and cooling, geothermal technology.

Latest policies of the EU commission, such as the "Clean Energy for all European" and the "European Green Deal" (European Commission), are aiming towards the decarbonization of the energy sector. Energy production by renewable energy sources (RES) and improved energy efficiency of buildings are considered key drivers in the pathway from a fossil fuel-based to a carbon neutral society and economy.

Air conditioning systems have increased worldwide from about 4 TW in 1990 to 11 TW (and more) in 2016, and the energy consumption for space heating and cooling is expected to more than triple by 2050 (IEA 2019). Since global energy demand for heating and cooling is growing rapidly, good economic and environmental performance are extremely important.

The pressure is high for finding solutions to reduce energy imports, enabling low carbon sources and fight against the climate change. In this framework, geothermal energy can be a feasible and sustainable solution. It has been used for decades in Europe, and its range of technological solutions can provide electricity, heating and cooling.

Underground thermal energy storage (UTES) can be a key element in improving the efficiency of the heating and cooling grids. This is due to the possibility in seasonally storing heat or cold, covering the large mismatch between energy supply and demand. Given the range of available UTES technologies, they are feasible to install almost everywhere. Compared to other storage systems, UTES have the advantage of being able to manage large quantities and fluxes of heat without occupying much surface area, although the storage characteristics are always site specific and depend on the geological and geothermal characteristics of the subsoil. It can be used as an instrument to exploit heat available from various sources, e.g., solar, waste heat from industry, geothermal, within the same district heating system. The optimization of energy production, the reduction in consumption of primary energy and the reduction in emission of greenhouse gases are guaranteed with UTES, especially when coupled with district heating and cooling networks.

A selection of the main successfully operative case studies across Europe, is here presented to testify the great efficiency of UTES technologies. As well, a short summary of the legal frameworks in specific Countries where UTES are developed, is shown. It aimed at understanding how legal framework can strongly affect the realization of these systems, making the authorisation procedures easier and promoting their dissemination also in other Countries.

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IEA, Global Energy Review 2019, Report Extract Electricity. https://www.iea.org/reports/global-energy-review-2019/electricity, last accessed 2021/12/16 (2019).

# Shallow geothermal heating for plant phenotyping greenhouses: a case study in NW Italy

Chicco J.M.*[1], Mandrone G.[1], Vacha D.[1] Tartaglino A.[2] & Fonte L.[2]

[1] Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio, Università di Torino. [2] Direzione Edilizia e Sostenibilità, Università di Torino.

*Corresponding author e-mail:* jessica.chicco@unito.it

*Keywords:* greenhouses, numerical simulations, geothermal heating.

The most important aim of a greenhouse is to create optimal microclimate to improve the growth of plants, reaching a better quality and protect them against natural environmental effects such as wind or rain. Generally, greenhouses are high energy-consuming sometimes accounting for 50% of the cost of greenhouse production. Therefore, when considering the continuous increase in energy cost, the external energy demand must be reduced to decreasing the total annual operating cost (Savytskyi et al., 2020). In this framework, renewable energies are of extremely importance for energy savings and consumption. In particular, geothermal energy plays a very important role in maintaining comfortable inside climate and reducing energy consumption for the greenhouse, which could effectively adjust the equipment such as the heating/cooling, ventilation, shading system, and coordinate them with low energy operation (Zhang et al., 2020). As part of the "Excellence Project" of the Department of Agricultural, Forest and Food Sciences of the University of Turin, led by the Prof. Reynery, the Authors were involved in the project design of a shallow geothermal plant for the heating of a an innovative plant phenotyping greenhouse which is under construction from May 2022, at the University campus in Grugliasco (few km from the city of Turin). Aimed a testifying the great thermal efficiency of this kind of plants, results of numerical simulations integrated with field analysis and ground response test (GRT), are presented. Numerical simulations were used to calibrate the system and verify that the software reasonably models the real case. Particularly useful was the back analysis based on the GRT: it allowed obtaining thermo-physical parameters such as the thermal conductivity of the soil as well as the contribution of the aquifer in terms of advection and convection, more than reasonable and very close to real ones. Numerical simulations play an important role in correctly sizing the geothermal plant, also providing data about the thermal energy production, as well as the thermal behaviour of the ground during on and off plant cycles. Results confirmed a great thermal efficiency of this plant in terms of productivity and a negligeable thermal impact on the ground: after five years of plant operation, the maximum distance of the perturbation is exhausted between 5 and 10 m from the plant.

Savytskyi M., Danishevskyy, V. & Bordun, M. (2020) - IOP Conference Series: Materials Science and Engineering, Volume 985, 15th International Scientific and Technical Conference "Problems of the railway transport mechanics" (PRTM 2020) 27-29 May 2020, Dnipro, Ukraine.

Zhang S., Guo Y., Zhao H., Wang Y., Chow D. & Fang Y. (2020) - Methodologies of control strategies for improving energy efficiency in agricultural greenhouses, Journal of Cleaner Production, 99, 39-58. https://doi.org/10.1016/j.jclepro.2020.122695.

# Evaluation of ground source heat exchangers system feasibility to contribute at the ecological transition of the Marche Region in the 2016 earthquakes reconstruction areas: numerical models and maps of the shallow geothermal energy potential

Di Pierdomenico M.*[1], Taussi M.[1], Galgaro A.[2], Dalla Santa G.[2] & Renzulli A.[1]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* mario.dipierdomenico@uniurb.it

*Keywords:* shallow geothermal energy, ground source heat exchangers, numerical modelling.

In 2016 central Italy was hit by a seismic sequence ($M_{max}$ 6.5) that caused human victims, damages, and collapses of buildings, changing hopelessly the urban landscape of many towns. After these events, the Marche Region started an economic program which involved measures for the restoration and reconstruction of damaged or destroyed buildings. In this context, the exploitation of shallow geothermal energy (SGE), through the installation of ground source heat exchangers (GSHEs) coupled with heat pumps, could be a useful tool for heating and cooling these new, or renovated, buildings, being SGE a renewable, clean and without surface impact technology solution for high efficiency space heating and cooling needs covering. This would strongly contribute to preserve the Central Apennine environment.

To identify the most suitable areas for ground source heat exchangers, a map of the geothermal potential of the southern sectors of the Marche Region (upper-middle portion of the Potenza River) was developed. By consulting the third level seismic microzonation data made available by the National Civil Protection database, it was possible to reconstruct the stratigraphy of the area. In order to estimate the geothermal potential of the study area, the main parameters (thermal conductivity, volumetric heat capacity) were averaged over the first 100 meters of the subsoil, which is the most common depth of GSHEs. After this, all the investigated points were interpolated by means of dedicated algorithms to give a visualization of the spatial distribution of the geothermal potential throughout the study area.

Further study has also involved numerical modelling approach in order to verify the thermal impact induced in the subsoil, during the time, by the system operation and detect the best solution to improve the sustainability of the geothermal solution. Indeed it was possible to reproduce, in detail, the undisturbed thermal assessment of the ground and the induced effects over time by the geothermal system operation. Starting from the 3D numerical modelling of closed loop heat exchangers field, by using the local geological and hydrogeological available features and, possibly, data produced by Ground Response Tests performed in the surrounding area, a calibration session of the modelling process was made. Several scenarios have been performed by means of the modelling analyses in order to simulate the thermal effects of GSHP running into the subsoil and detect the best countermeasures finalized to balance the heat seasonal exchange processes with the ground. A map representing the feasibility and potential of the GSHP solutions adoption is also achieved. Various graphs and images, describing the efficiency of the system and the thermal plume development in the subsoil, have been obtained.

# Innovative Smart App to support GSHP preliminary feasibility and design

Galgaro A.*[1], Dalla Santa G.[1-2], Di Sipio E.[1], Contini S.[3], Mezzasalma G.[4], De Carli M.[5], Carnieletto L.[5], Zarrella A.[5], Castelruiz A.[6], Pockelè L.[4] & Bernardi A.[7]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Dipartimento di Ingegneria Civile, Edile e Ambientale, Università di Padova. [3] MyClevergy, Chioggia (VE). [4] RED - Research and Environmental Devices, Padova. [5] Dipartimento di Ingegneria Industriale, Università di Padova. [6] Building Technologies Division, Fundación Tecnalia Research & Innovation, San Sebastian (Spain). [7] Istituto di Scienze dell'Atmosfera e del Clima, CNR, Padova.

*Corresponding author e-mail:* antonio.galgaro@unipd.it

*Keywords:* GSHP systems design, App, GEO4CIVHIC.

The spreading of closed loop shallow geothermal system is delayed by several technical, economic and social barriers as high initial costs, mainly related to drilling and installing operations and difficulties due to incorrect design. The major goal of the EU funded GEO4CIVHIC Project is to overcome some of these barriers by sustaining the deployment of shallow geothermal systems for heating and cooling also in retrofitting existing buildings, including historical buildings.

In the framework of the Project, we developed an innovative user-friendly smart phone/tablet Application (App) to support geothermal stakeholders such as drillers, designers or administrations to complete a preliminary evaluation of Ground Source Heat Pump Systems and borehole heat exchangers field also providing a first costs estimation analysis.

The App is developed to be used on site: the data elaboration starts from the site geolocation. This part is devoted to non-expert users and based on a simplified thermal characterization obtained by information related to the geomorphological context (plain-coast, valley, mountain or hilly area) and an approximate idea of the local geological and hydrogeological assessment. The user is required to choose the site environment option, a sub-environment and a lithology, provided from predefined lists. The App, considering a simplified homogenous litho-stratigraphy of about 100 m assumed in saturated conditions, provides indications in terms of (I) the best suggested drilling technology, (II) the evaluation of time consuming and costs, related to the suggested drilling method, (III) the main ground thermal properties estimation (undisturbed temperature and equivalent mean thermal conductivity). The reference data concerning the fundamental ground parameters have been previously defined on the research results obtained by the GEO4CIVHIC EU-H2020 project inserted as supporting library in the application itself.

In a second time, the user is asked to indicate the type and size of the building, to estimate its cooling and heating loads, based on specific database of climatic classes typical of the European territory and the energy profile of a pre-selection of buildings, representative of the European buildings' main typology, developed on purpose among the GEO4CIVHIC project.

As final output, the App provides a first estimation of the feasibility of the proposed system, considering a preliminary calculation of the BHEs field, in terms of number, spacing and length of probes, suggesting the best drilling method as well as a rough estimation of the time and costs drilling operations. The App functioning is now under validation by comparison with on site data, acquired in the demonstration sites developed within the project.

The App outputs are a preliminary, not refined estimation of the feasibility of a new shallow geothermal plant, but can be very useful for a first techno-economical evaluation.

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# Carbonation of Ca-rich materials: thermal activation at ambient pressure

Massa M.*[1], Cruciani G.[1], Vola G.[2], Sarandrea L.[2], Bresciani P.[2] & Ardit M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.
[2] Cimprogetti s.r.l., Lime Technologies, Dalmine (BG).

*Corresponding author e-mail:* mattia96.massa@gmail.com

*Keywords:* carbonation, amorphous, vaterite.

The purpose of this contribution is to evaluate the potential Carbon Capture Utilisation and Storage (CCUS) of different materials at the end of their lifecycle. The tested materials include construction and demolition wastes (CDWs), bottom ashes (BA), slags from electric arc furnaces (EAFs slags), and by-products of non-exhausted air filters wich are all based on phases with a high-calcium content. Carbon capture was carried out using a TG-DTA analyzer where pure $CO_2$ was fluxed at 20 mL/min in the 293–943 K T-range (heating rate 10 K/min; 1 atm) looking for the $CO_2$ uptake optimum temperature. All samples were characterized by quantitative phase analysis by X-ray powder diffraction (QPA-XRPD), before and after thermal treatment within the thermoanalyzer. Our results showed that at the ambient pressure conditions of our experiments only lime, CaO, and portlandite, $Ca(OH)_2$, are enough reactive towards the $CO_2$ capture. Although the best uptake was not fully achieved, due to the low $CO_2$ pressure, the BA samples, the air filter by-products, and EAFs slags showed a relatively high $CO_2$ uptake.

In our experimental conditions, EAFs slags showed an increase of $CO_2$ content (+ 20%) mainly due to carbonation of CaO and $Ca(OH)_2$ promoting calcite ($CaCO_3$) formation. In addition, 6 wt% of vaterite ($CaCO_3$), metastable calcite polymorphs which crystallized from a Ca-bearing amorphous phase was also detected. The $CO_2$ increase in bottom ashes and by-products is about 7 to 25% and 10%, respectively. In the latter samples rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$ – exclusively in by-products) also occurred as minor phases. Samples reactivity towards $CO_2$ is strictly related to both content and crystallite size of suitable reacting phases. Indeed, beyond their content, the crystallite size of CaO (the main $CO_2$ binder) can strongly influence the carbon uptake process. It was found that CaO with crystallite size larger than 170 nm hindered the sample uptake ability. Conversely, the transformation from $Ca(OH)_2$ to CaO at low T (portlandite dehydroxylation starts at 723 K; Menéndez et al., 2012) ensured the formation of lime with a crystallite size smaller than 90 nm which allowed the best uptake. The optimum temperature in our experimental setup (to promote the conversion of CaO and $Ca(OH)_2$ to $CaCO_3$) lie in the 730 – 770 K T-range.

Menéndez E., Andrade C. & Vega L. 2012. Study of dehydration and rehydration processes of portlandite in mature and young cement pastes. Journal of thermal analysis and calorimetry, 110(1), 443-450.

# Intensive thermal exploitation from closed and open shallow geothermal systems at urban scale: unmanaged conflicts and potential synergies

Perego R.*[1-2], Dalla Santa G.[2], Galgaro A.[2] & Pera S.[1]

[1] Istituto di Scienze della Terra, Scuola Universitaria Professionale della Svizzera Italiana, Mendrisio (Switzerland).
[2] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* rodolfo.perego@supsi.ch

*Keywords:* underground thermal management, open and closed loop shallow geothermal systems, thermal interference.

The use of shallow geothermal systems (SGS) as a proficient technology to provide clean thermal energy has become increasingly widespread throughout the world, especially in urban environments, with a significant increase in systems density. At European level, the current authorization schemes for new SGS rarely consider the current thermal state of the subsurface and the potential presence of neighbouring systems (Tsagarakis et al., 2020). The paper presents a pilot urban case study in Switzerland, showing high SGS deployment, analysed through a holistic city-scale 3D numerical model simulating mutual interactions between open and closed-loop systems (Perego et al., 2022). Results show that the high amount of installed SGS in limited space is progressively creating mutual hydraulic and thermal interferences: negative, with a reduction of SGS efficiency and sustainability or (rarely) positive, when an accidental and unmanaged synergic effect is established due to favourable exploitation patterns and SGS locations. Numerical modeling further highlighted that the restitution through the vadose zone could be a valid method to hydraulically reinstate the aquifer without significantly altering groundwater undisturbed temperature even at shallow groundwater depth. Results show that neglecting an underground holistic vision of the hydro/thermogeological processes in urban areas could result in long-term severe efficiency losses and environmental issues for SGS solutions, also given the increasing use of shallow geothermal energy in the building air conditioning sector

Perego R., Dalla Santa G., Galgaro A. & Pera S. (2022) - Intensive thermal exploitation from closed and open shallow geothermal systems at urban scale: unmanaged conflicts and potential synergies. Geothermics, 103, 102417. https://doi.org/10.1016/j.geothermics.2022.102417.

Tsagarakis K.P., Efthymiou L., Michopoulos A., Mavragani A., Anđelković A.S., Antolini F., Bacic M., Bajare D., Baralis M., Bogusz W., Burlon S., Figueira J., Genç M.S., Javed S., Jurelionis A., Koca K., Ryżyński G., Urchueguia J.F. & Žlender B., (2020) - A review of the legal framework in shallow geothermal energy in selected European countries: Need for guidelines. Renew. Energy, 147, 2556-2571. https://doi.org/10.1016/j.renene.2018.10.007.

# Influence of fault interpretation methodologies on fault geometry and the accuracy of their statistics

Robledo F.*, Butler Butler R.W.H. & Bond C.E.

Department of Geology and Geophysics, University of Aberdeen (UK).

*Corresponding author e-mail:* francisca.robledo.carvajal@gmail.com

*Keywords:* fault interpretation methodologies, fault statistics, fault uncertainty.

The ability to map faults is a fundamental requirement of almost all interpretations of the subsurface geological structure, as imaged in 3D seismic volumes. Almost all fault interpretation strategies have been widely developed for industries that extract natural resources (e.g., chiefly Oil and Gas). And many of the validation methods that track displacement patterns are derived from studies of large faults. Existing workflows commonly build fault maps by undersampling 3D seismic volumes (e.g. by defining "fault sticks" on spaced profiles). The resultant outputs are commonly smoothed to create individually rather simple fault planes. The question is: how appropriate are these approaches for mapping faults in seismic data, and for evaluating uncertainties in these interpretations, where the aim is to support engineering of geo-storage sites (e.g. for $CO_2$ or radioactive waste). Our aim is to document distinct interpretational workflows to create 3D fault maps and we examine the variation in these interpretations by comparing their individual fault statistics.

There are two distinct steps to producing images of faulting patterns - mapping and smoothing. We applied four different workflows using a high-resolution regional 3D seismic data set. Mapping was performed using vertical profiles and contrasted with fault-mapping in serial time-slices. Some of our mapping workflows used conventional under-sampling, and others worked at full resolution. Faults were drawn using poly-lines and points, joined by line segments ("fault sticks"). Following this initial mapping, we analysed each fault output and compared them. To these outputs, we applied different fault surface construction methods, which are sensitive to the smoothing level of the technique applied. Two strategies were employed, one using all elements of the initial fault mapping (poly-line traces and pick-points), the other only using (pseudo) tip points. These different workflows create distinctly different fault maps in 3D. These in turn have their own statistics. We emphasise the importance of fault mapping techniques in fault analysis and suggest this kind of analysis should be accompanied by careful descriptions of the workflows behind them. Multiple workflows should be used at least to initiate appreciation of the uncertainties in these interpretations.

# Implementing a geochemical, hydrogeological and microbiological monitoring strategy for an open-loop low-temperature geothermal system in a shallow coastal aquifer

Taussi M.*[1], Vespasiano G.[2], Gliaschera M.[3], Brunori R.[4], Cangiotti S.[5] & Renzulli A.[1-6]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [3] Studio geologico associato GEOCON, Fano (PU). [4] Comune di Fano, U.O. Ambiente, Fano (PU). [5] Sea Gruppo s.r.l., Fano (PU). [6] Geo.In.Tech. s.r.l. - spin-off Università di Urbino «Carlo Bo».

*Corresponding author e-mail:* marco.taussi@uniurb.it

*Keywords:* geothermal energy, geochemistry, groundwater.

Open-loop Ground Water Heat Exchangers (GWHEs) coupled with heat pumps are a common type of domestic and industrial air conditioning system. These systems consist of extracting groundwater which is used to exchange heat with the geothermal heat pump, before being usually re-injected into the aquifer. This operation can affect, albeit usually mildly, the thermal and chemical features of the groundwater and the local ecology. The impacts vary depending on the physico-chemical characteristics of the water, local geology, hydraulic conductivity, and the water volumes extracted and discharged by the GWHE.

The purpose of this study is to implement a monitoring plan for an open-loop low-temperature geothermal system located in the Fano Municipality (Central Italy). The urban area lies on the Metauro river alluvial plain, which mostly consists of gravel, sand and silty-clay, with intercalated lenses of sand and clay. These deposits host a phreatic aquifer that can reach a maximum thickness of about 40 m, and whose temperature is generally comprised between 15 and 17°C.

Water sampling will be carried out for at least one hydrological year on the injection and extraction wells of the geothermal system and on two wells located up- and down-hydrogeological flow of the selected GWHE. Changes in pressure and groundwater temperature may cause variations of solubility of minerals, redox processes, and sorption-desorption of dissolved components, besides the formation of carbonate and silica mineral scaling. These possible alterations of the natural state of the aquifer will likely be constrained through a monthly-based monitoring that will be aim at the evaluations of the: i) main physico-chemical parameters (i.e., temperature, pH, electrical conductivity, redox potential, and dissolved oxygen content), ii) piezometric levels, and iii) main dissolved ions concentrations (i.e., $HCO_3$, $SO_4$, Cl, $NO_3$, Br, Ca, Mg, Na, K). These measurements will be coupled by bimonthly analysis of selected trace elements concentrations (e.g., Al, Cd, Fe, Mn, Si). In addition, as the modifications of the thermal state of the groundwater might enhance the proliferation of microbial community such as the mesophilic bacteria which start to appear at about 20°C, the dynamics within the aquifer in terms of microbiology will be also evaluated.

This study will help to understand possible criticisms for the installation of GWHEs and will provide a support for the definition of a regulatory framework, often lacking at local level to enhance a sustainable use and management of this type of renewable in a fragile environment like that of the groundwaters.

# Investigations and modelling for a practical application of borehole thermal energy storage

Tinti F.*[1], Rapti D.[2], Caputo R.[2], Perez Garcia C.A.[3], Ceccarelli M.[3], Santolini E.[3] & Benni S.[3]

[1] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna. [2] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [3] Dipartimento di Scienze e Tecnologie Agro-alimentari, Università di Bologna.

*Corresponding author e-mail:* francesco.tinti@unibo.it

*Keywords:* borehole thermal energy storage, geothermal energy, renewable energy systems.

This study has been carried out within the H2020 Project RES4LIVE "Energy Smart Livestock Farming towards Zero Fossil Fuel Consumption" (2020-2024, grant agreement 101000785). The project's objective is to bring into the market integrated cost effective and case sensitive Renewable Energy Sources (RES) solutions towards achieving fossil free livestock farming. In this framework, the replacement of heating systems based on fossil fuels in pig barns represents a fundamental target. Therefore, an integrated system was conceived and designed to provide the thermal energy required for heating the alley connecting ten rooms of a nursery barn, hosting up to 2500 weaners. The integrated system is composed by photovoltaic thermal collectors (PVT), a dual source heat pump (DSHP) and a borehole thermal energy storage (BTES). The system is currently under realization at a pilot study case represented by a swine farm located in Mirandola (MO), partner in the project. The project realization has been subjected to a strict regulatory framework. Moreover, the needed antifreeze quantities are higher than those for standard borehole heat exchangers (BHE) project, in order to allow the solar energy to be stored directly in the ground, without intermediate heat exchangers. Specific constraints have been: maximum storage temperature of 35°C, authorization to intercept the aquifer at very shallow depths, obligation of BHE grouting, definition of a strategy for continuous monitoring of groundwater quality. This contribution aims to present the preliminary investigations conducted for the definition of suitability and potential of the BTES, and the actions taken for assuring environmental protection and long-term sustainability. Specifically, two piezometers 2"wide, 25 m deep and distant each other 40 m, were installed, in a line over direction North-South. They have been located around 50 m far from two existing wells, of the same depth, currently used for the farm's purposes. Between the two piezometers, two double U, PE100 PN16 DN32, BHE were installed, the first one 10 m deep (crossing the first layer of clay with sandy lens), while the second one 30 m deep (crossing the second layer of fine sand, hosting the shallow aquifer). Two thermal response tests were performed, one per each BHE, while temperature and hydraulic head values were taken in the observation boreholes, by using both fixed recording sensors and movable measurements tools. The data gathered and the results of the tests conducted have been used to select the most suitable working depth for the future BTES field, to quantify the potential for underground thermal storage, to understand the heat dispersion due to groundwater movement and to model the BTES behaviour under various operation scenarios. The conclusions obtained will be applied in the design phase to optimize the integration of PVT, BTES and DSHP. The full BTES system is planned to be installed during summer season 2022.

# Burrowed carbonates generating a dual porosity system: A case study of Cenomanian - Turonian platform carbonates from the southern Apennines (Italy)

Tommasone M.A.*[1], Di Domenico G.[1], Bortolotti V.[2], Cruciani G.[1], Chiarella D.[3], Nagmutdinova A.[2] & Frijia G.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna. [3] Department of Earth Sciences, Royal Holloway, University of London (UK).

*Corresponding author e-mail:* tmmmnt@unife.it

*Keywords:* bioturbation, *Thalassinoides*, carbonates.

Bioturbated carbonate sequences represent a challenge for reservoir characterization both for Hydrocarbons extraction and for injection and underground storage of $CO_2$ or H (Eltom et al., 2021). Previous studies on these carbonate deposits of different age show that bioturbation can have a strong impact on petrophysical properties of the rocks, creating sedimentary heterogeneities and often enhancing poro/perm properties. In this work a detailed study of a thick, intensely bioturbated carbonate succession of Late Cenomanian-Early Turonian in age belonging to the Apennine Carbonate Platform (Southern Italy) has been performed. A multidisciplinary approach has been used integrating classical petrophysical analyses, Computed Tomography scanning (CT and MicroCT), and Nuclear Magnetic Resonance (NMR) techniques in order to investigate and characterize the abundance/volume of the burrows, their connections and describe the pore size distribution. Furthermore geochemical, mineralogical and petrographic analyses were integrated to understand the correlation between bioturbation, poro/perm characteristics and diagenetic processes. The bioturbation in the studied strata reveals a boxwork pattern organized as a, preferential, horizontal network with vertical shafts having Y- or T- shaped branching morphology. This pattern suggests the domination of *Thalassinoides* ichnotaxa. The burrow conduits, as revealed by CT images, show low tortuosity with preferential vertical and oblique straight directions with circular to elliptical cross-sections. In the most burrowed intervals the volume occupied is around 39% of the total rock. The burrows are generally filled with dolomite and have a porosity substantially higher than the muddy matrix and an isotopic signature of C and O different from that of the matrix. Pore Size Distribution estimated via Hg-injection techniques coupled with NMR, evidence that pore sizes and pore throat sizes are larger in the more dolomitized samples whereas the smallest pores are found in the non-dolomitized, calcitic matrix. Micro CT images allowed us to visualize in detail the pore sizes and the pore network and to model fluid flow through it. Furthermore, the multidisciplinary dataset we present helps the detailed description of chemical/mineralogical parameters of such heterogeneous carbonates which could be used to predict fluid-rocks interaction. These preliminary studies are a mandatory step for any injection and underground storage project.

Eltom H.A., Alquabalee A.M. & Yassin M.A. (2021) - Potential overlooked bioturbated reservoir zones in the shallow marine strata of the Hanifa Formation in central Saudi Arabia. Marine and Petroleum Geology, 124, 104798.

# S39.

# Innovative strategies for sustainable agriculture and restoration of degraded soils: novel approaches, technologies, and case studies

*Conveners & Chairpersons*

*Giacomo Ferretti (University of Ferrara)*

*Paloma Campos Díaz de Mayorga (University of Seville, Spain)*

*Rizki Maftukhah (Universitas Gadjah Mada, Yogyakarta, Indonesia)*

*Giulio Galamini (University of Ferrara)*

# Recycled concrete aggregates as a component of technosols for acid mine drainage remediation. Laboratory leaching test

Barba-Brioso C.*, Jiménez J., Delgado J., Martín D., Romero-Baena A.J. & González I.

Department of Crystallography, Mineralogy and Agricultural Chemistry, Seville University (Spain).

*Corresponding author e-mail:* cbarba@us.es

*Keywords:* metal retention, iron precipitation, AMD remediation.

The environmental effects of mining activities extend far beyond the mines and the wastes scattered in their surroundings. Exposure of these wastes to surface conditions creates acid mine drainage (AMD), acidic leachates with high concentration of Fe, Al, S and potentially toxic elements (As, Cd, Cu, Zn, etc.) To reduce AMD effects on ecosystems, low-cost and long-term effective retention systems have been investigated (Delgado et al., 2019). A recent alternative is the design of technosols, "artificial soils" based on the application of certain materials on the surface soils, promoting the regeneration of their environmental functions (Jordán et al., 2017; Santos et al., 2019).

This investigation studies the improvement of AMD chemistry after leaching two recycled concrete aggregates (SF and EF), to probe their function in technosols at mine degraded soils.

150 g of SF and EF were disposed in filtering vessels and leached 7 times with 100-150 ml of AMD over 33 days. The leachates (ASF and AEF) were filtered at 0.2 µm and analysed for pH, Eh and electrical conductivity with Crison equipment. Major and trace elements (S, Al, Ca, Mg, Fe, Cu, Zn, As, Cd and Pb) were analised by ICP-OES in a Spectroblue (CITIUS, Seville University).

AMD conditions improved after the first leaching and remained almost constant until the end of the test. pH varied from 2.4 to 7.6, Eh decreased from 653 mV to 280 mV, and EC from 11.6 mS $cm^{-1}$ to 5.7 mS $cm^{-1}$.

The main elements responsible of water acidification, Fe and Al, were efficiently removed from solution, while S persisted, halving its initial concentration during the test. In contrast, soluble Ca and Mg were enriched as a result of concrete dissolution. Regarding the trace elements, Cd, As and Pb were within the detection limit of the technique. Cu was retained by the aggregates, while Zn was depleted in the first leachates but increased in solution after the fifth irrigation.

Results demonstrated that the use of recycled concrete aggregates can be considered in technosols, as they behave well in AMD remediation, due to the alkalinizing effect of their minerals and the adsorption - coprecipitation processes occurring under the promoted conditions.

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Jordán M.M., García-Sánchez E., Almendro-Candel M.B., Pardo F., Vicente A.B., Sanfeliu T. & Bech J. (2017) - Technosols designed for rehabilitation of mining activities using mine spoils and biosolids. Ion mobility and correlations using percolation columns. Catena, 148, 74-80.

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# Biochar and compost application for improving soil properties and plant physiology: the case of an intensive-olive orchard under deficit irrigation

Campos P.*[1], Miller A.Z.[2], Díaz-Espejo, A.[2] & De la Rosa J.M.[2]

[1] Department of Crystallography, Mineralogy and Agricultural Chemistry, University of Seville (Spain). [2] Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Sevilla (Spain).

*Corresponding author e-mail:* pcampos1@us.es

*Keywords:* soil organic amendments, water relations, soil properties.

Biochar is the solid by-product of the pyrolysis of residual biomass. Numerous authors have previously demonstrated that biochar addition to soils improves soil physical properties and plant growth (De la Rosa et al., 2014; Campos et al., 2020, 2021). Additionally, the production of biochar has taken attention during the last decade as a way to valorise abundant residual biomasses, such as waste from the olive oil agro-industry. Another important issue is the need for irrigation in super-intensive olive plantations, which are mainly located in the Mediterranean region, with a semi-arid climate.

In this work, the application of biochar to the soil is proposed to increase water retention, improve soil permeability, and at the same time valorise a waste product such as the residual olive pomace. Green compost was also used to compare biochar with the traditional amendment. Soils at a super-intensive plantation of arbequina olive trees under deficit irrigation ("La Hampa" field station, Coria del Río, Seville, Spain) were amended with 40 t ha$^{-1}$ of biochar, green-compost or a 50% w/w biochar-compost mixture. Un-amended plots were used as control. The field experiment lasted 380 days. Soil properties (pH, electrical conductivity, water holding capacity), soil humidity and resistance to penetrability at field, physiological status of olive trees [midday stomatal conductance ($g_s$), net photosynthesis rate ($A_N$) and maximum rate of electron transport (ETRmax)] were determined on a monthly basis. At harvest (October 2021) the productivity in olives and oil per tree was determined. All the organic amendments showed high porosity and water retention capacity. Biochar application resulted the most effective in reducing soil compaction and improving the water status of olive trees in this super-intensive olive trees plantation. Moreover, the use of biochar increased about 15% olive yields, although net olive production was maintained.

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# Is biochar an effective tool for the remediation of trace element polluted soils?

Campos P.*[1], Miller A.Z.[2], Knicker H.[2] & De la Rosa J.M.[2]

[1] Department of Crystallography, Mineralogy and Agricultural Chemistry, University of Seville (Spain). [2] Institute of Natural Resources and Agrobiology of Seville, CSIC, Seville (Spain).

*Corresponding author e-mail:* pcampos1@us.es

*Keywords:* trace element immobilization, soil remediation, microbial diversity.

Soil pollution by trace element is a worldwide concern. One possibility for the remediation of these polluted soils is the application of organic amendments. Nevertheless, organic amendments are very diverse and their properties need to be studied prior to their use. Biochar, the solid residue produced by thermal treatment of biomass under absence of oxygen (pyrolysis), has diverse properties depending on feedstock and pyrolysis conditions (Campos et al., 2020).

In this work, biochars were produced under different pyrolysis conditions, pyrolysis reactor and feedstock. The continuous pyrolysis reactor required only 12 minutes of residence time of the feedstock in the reactor to produce biochars with similar properties than those pyrolysed during at least 1 h in the fixed bed reactor. Produced biochars were tested for metal adsorption in batch experiment and greenhouse experiment. Among the biochars used, rice husk biochar may be considered the better tool to reduce metal pollution, as it showed a maximum adsorption capacity of 30.7 and 19.3 mg $g^{-1}$ for $Cu^{2+}$ and $Pb^{2+}$, respectively. The most promising biochars for degraded soils remediation (rice husk biochar and olive pit biochar) were used as amendment (8 t $ha^{-1}$) at a field experiment. The plots were located in Aznalcóllar (Spain). These soils were polluted in April 1998 by the massive dumping of mine sludge contaminated with heavy metals, called the Aznalcóllar disaster. Additionally, biochar was buried in nylon bags to determine changes in biochar composition and physical properties due to the ageing process. The experiment lasted 22 months and soil properties, enzymatic activities and plant development were periodically analysed. The biochar potential for carbon sequestration was also analysed. Soils were sampled after 6, 12 and 20 months for determining microbial diversity using the Illumina Miseq technology of the 16S rRNA gene.

The application of 8 t $ha^{-1}$ of RHB and OPB (produced at the continuous pyrolysis reactor) at field recovered soil ecological functionality in the studied polluted soils. The studied biochars significantly adsorbed the trace elements present in the studied soils after 2 years. Nevertheless, in these highly multicontaminated soils, the application of 8 t $ha^{-1}$ of biochar was not enough for an effective reduction in trace element bioavailability, which is explained by the existence of an equilibrium in such polluted soils.

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# Use of biomass ashes for the treatment of expansive clayey soils for sustainable pavement construction

Comodi P.*[1], Cambi C.[1], Fastelli M.[1], Sassi P.[1], Pandolfi E.B.[1], Pioppi L.[2] & Zucchini A.[1]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia.

*Corresponding author e-mail:* paola.comodi@unipg.it

*Keywords:* fly ashes, soil stabilization, C-S-H.

Poor physical and mechanical characteristics of clayey soils are a critical issue in geotechnical engineering. Besides the problems for foundation structures, high plasticity/compressibility, and swelling behavior make these soils unsuitable, in their natural state, as construction materials. These soils are often treated by adding lime/cement agents able to improve their physical and mechanical characteristics. Binders' production is an energy-intensive process and emits significant amounts of greenhouse gases. At the same time, fly ashes generated from biomass combustion are intended to increase due to the push for renewable energy and different employs were suggested for their re-use in a circular economy perspective: in the cement industry, in agriculture, in soil stabilization. In this work, intending to improve the geotechnical properties of clayey soils and repurpose waste material, we used 3 kinds of biomass ashes, generated by pellet, olive and grapevine pruning combustion, as possible stabilizing agents of a swelling, highly plastic and compressible clay. The mechanical effects of the treatment were evaluated using confined compressive tests at 1, 7, 14 and 28 curing days. The compressibility was determined utilizing edometric tests on raw and treated samples. The evolution of the clay ashes mixtures from the chemo-mineralogical point of view was evaluated through X-ray powder diffraction (XRPD), with Rietveld analysis for a quantitative assessment of the mineralogical and amorphous phases, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). XRPD results show mainly variations of amorphous and illite content with curing days. The FT-IR spectroscopy shows an evolution of the stretching and bending modes of Si/Al-O groups with changes in the position and shape of the bands. The deconvolution of the FT-IR spectra indicates a different amount of the Q species and so different polymerization of the tetrahedral units with treatments. The EDS-SEM analysis shows an evolution of the Ca/Si distribution and the growth of pozzolanic reaction products such as amorphous gels in the previous stage and then C-S-H/C-A-S-H nanocrystals. The preliminary results indicate that the pozzolanic reaction occurs in clayey and biomass fly ashes mixture from the dissolution of the clay minerals and/or ashes amorphous phase, in an alkaline environment, with the growth of tobermorite-like phases, in different amounts depending on biomass type (which affect the $CaO/SiO_2+Al_2O_3$ ratio) and curing time. The C-S-H/C-A-S-H formation did not vary linearly with the curing period, but the reactions affect the macroscopic behavior of clayey soils in terms of stiffening and strengthening as evidenced by edometric tests. Then selecting the type and amount of biomass fly ashes and promoting an employment protocol for the re-use of two waste products could be effectively implemented as an environmentally and economically sustainable procedure

# Metal retention in a controlled storage mine wastes system in Zaruma-Portovelo province (S Ecuador)

Delgado J.[1], Barba-Brioso C.*[1], Ayala D.[2] & Romero-Baena A.J.[1]

[1] Department of Crystallography, Mineralogy and Agricultural Chemistry, Seville University (Spain). [2] Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA (USA).

*Corresponding author e-mail:* jdelgado15@us.es

*Keywords:* sulphur oxidation, AMD generation, Fe-Harpand formation.

Zaruma-Portovelo is one of the most important mining districts in Ecuador and is one of the major producers of mine tailings. It is in El Oro province in the south of the country. Historically, mining in the area causes negative environmental impacts since the tailings were disposed in dams close to rivers or significant amounts of sulfur-rich waste are released directly into rivers or surrounding areas (Delgado et al., 2019). We constructed an experimental scale dam to demonstrate adequate disposal of 3 (acid, heterogeneous, and neutral-alkaline, respectively) tailings from the Portovelo mineral extraction plant. The tailings were covered with a reactive limestone layer promoting the formation of Fe-Al oxyhydroxisulfates rich hardpans, which should develop a limiting layer against waste oxidation (Quispe et al., 2013). Preliminary chemical and mineralogical studies suggest the appropriate function of the experiment, showing a consistent increase of Fe and S concentrations around 20 cm in the deep section of the profile. Furthermore, controlled storage generally causes inertization of waste through sulphide encapsulation processes (Delgado et al., 2018). However, a detailed geochemical study is necessary to understand the potential mobility of the metal associated with the new mineral phases. For this reason, samples collected along the 1 m depth sample cores were subjected to a four-step sequential extraction (Exchangeable, Reducible, Oxidizable and residual fraction). The metal content in each fraction was quantified by ICP-OES. The results show that the most abundant metals in the samples were Ca, Fe, Al, and Mg. During the wet station, Ca was mainly associated with F1, explaining its dissolution and its reactivity with acid tailing. Fe was mainly associated with crystalline forms (F4) derived from its global mineralogy (Delgado et al., 2018). The data reveal an increase in Fe and S concentrations at 20 cm depth ("ochre" horizon, possible precursor of the hardpan), while a decrease in As, Cu, Pb, and Zn is appreciated in this zone. Furthermore, a significant increase in the concentration of Fe and Al in F2 (reducible fraction) is consistent with the formation of poorly crystalline oxyhydroxysulfates that adsorb or coprecipitate trace elements.

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# Soil organic carbon and soil microbial diversity in vineyard agroecosystems under cover crop management practices

Deltedesco E.* & Haas F.

Centro di Sperimentazione Laimburg, Ora (BZ).

*Corresponding author e-mail:* evi.deltedesco@laimburg.it

*Keywords:* grape, C sequestration, soil microbial community structure.

Viticulture represents an economic and historico-cultural important sector of agricultural production in South Tyrol (Northern Italy). However, intensive viticulture under conventional tillage led to soil degradation, with loss of soil fertility and biodiversity, acceleration of organic matter mineralization, and an increase in $CO_2$ emissions. To cope with these challenges, it is of uppermost importance to determine techniques to improve soil (microbial)-biodiversity conservation and ecosystem services (C storage). Cover crop studies were carried out in South Tyrolean vineyards, mainly focusing on SOC content and soil fungal and bacterial diversity (high-throughput sequencing on the Illumina MiSeq platform). Results showed that long-term (7 years) management of cover crop practices increases SOC. Furthermore, cover crop management resulted in a significant increase of bacterial diversity, but no effect could be observed on the fungal diversity. Approximately one half of the fungi was assigned to saprotrophics (avg. 48.2%) and the other half were classified as potentially plant pathogenic (avg. 46.7%). Symbiotic fungi were only rarely detected (avg. 4.35%). We conclude that vineyards, if properly managed, can be considered as C sinks. Additionally, vineyards may represent a crucial cropping system, with the ability to provide pivotal ecological services such as carbon dioxide sequestration and harbors of soil microbial diversity.

# N leached from a sandy soil amended with urea, liquid digestate, struvite and $NH_4$-enriched chabazite zeolite-tuff

Ferretti G.*[1], Galamini G.[2], Medoro V.[2], Faccini B.[2] & Coltorti M.[2]

[1] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* frrgcm@unife.it

*Keywords:* natural zeolites, struvite, slow release fertilizers.

The development of new and sustainable methodologies to improve the nitrogen (N) use efficiency in modern agroecosystems is urgently needed. Nowadays, more than 50% of the N applied to soil through chemical or organic N-based fertilizers is not converted into plant biomass but it is lost as N gasses in the atmosphere or leached into the water system (Drechsel et al., 2015). These N losses are dramatically impairing the soil, water, and atmosphere quality. Efficient alternatives for granting adequate N availability to crops while reducing the nutrient losses in the environment must be therefore urgently developed and adopted.

We present a column leaching experiment in which the amount and speciation of the N lost by different slow-release fertilizers were accounted for in comparison to a synthetic fertilizer (urea) and an organic fertilizer (liquid digestate). The slow-release alternatives were represented by $NH_4$-enriched zeolite-rich tuff (Ferretti et al., 2021) and struvite, both obtained by recycling N from liquid digestate.

Treatments consisted of sandy soil fertilized with i) urea (U) ii) liquid digestate (LD), iii) $NH_4$-enriched zeolite tuff (N-CHA) and iv) struvite (STRV). 8 different flushing events were performed over 38 days, leachates were collected and analyzed for Total Kjeldahl N, Organic-N, $NH_4^+$-N, $NO_3^-$-N, $NO_2^-$-N, and pH.

Results showed that U and LD lost most of the N within the first 2 flushing events as organic N and $NH_4^+$-N, respectively. On the other hand, STRV and N-CHA lost fewer N and over the whole course of the experiment and with more balanced speciation. The mass balance outlined that native soil N was mined in U and LD treatments while in N-CHA and STRV a fraction of N from the fertilizers was still present.

STRV and N-CHA thus represent a valid method to recycle N from liquid digestate and to use it more efficiently, minimizing N losses.

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# N dynamics in a sandy soil amended with natural chabazite zeolite tuff and fertilized with different N sources

Ferretti G.[1], Medoro V.[2], Alberghini M.*[2], Galamini G.[2], Faccini B.[2] & Coltorti M.[2]

[1] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [2] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* frrgcm@unife.it

*Keywords:* natural zeolite, sustainable agriculture, fertilizers.

Unsustainable farming practices are jeopardizing soil, water, and air quality as a consequence of nutrient leaching and emissions of harmful greenhouse gases (GHGs). The fertility of soils is therefore constantly decreasing and thus it is mandatory to improve the sustainability of agricultural practices in areas that are already being cultivated by improving the soil quality and fertilizer efficiency (Gholamhoseini et al., 2013; Keiblinger & Kral, 2018).

One valid solution consists in the use of soil amendments able to improve various soil characteristics such as cation exchange capacity and water retention, of which sandy soils are poor. Within the proposed amendments, natural zeolites have been proved to be a suitable solution to this challenge since they are characterized by high and selective cation exchange capacity and reversible dehydration (Ferretti et al., 2021). Another possibility is represented by the implementation of these minerals directly into the fertilizers, to allow a more gradual release over time and an improved uptake by the plants reducing therefore the N losses in the surrounding environment.

In this work, we present the result of a 50-days incubation experiment performed on a sandy soil amended with 4 different fertilizers and with/without the addition of natural zeolites as soil amendment. The experiment was performed at 20°C and fixed bulk density and water-filled pore space (65%). N speciation and dynamics, as well as soil organic matter, pH, and electrical conductivity were accounted 5 times over the incubation. The tested fertilizers included i) synthetic-N, ii) organic natural-N, iii) organic natural-N + chabazite zeolite, iv) N-charged chabazite zeolite.

Results show a significant difference in N speciation within the different fertilizers and also a significant effect on net nitrification and ammonification. The presence of natural zeolite in the soil impacted significantly the amount of soil organic matter that was significantly higher in zeolite amended soil. Natural zeolites also probably favored soil aeration which resulted in increased nitrification through the end of the incubation.

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# Dynamics of the chiral monoterpene pulegone in soil: addition of organoclay as a tool to increase its performance as an eco-friendly herbicide

Galán-Pérez J.A.*, Gámiz B. & Celis R.

CSIC - Instituto de Recursos Naturales y Agrobiología de Sevilla (Spain).

*Corresponding author e-mail:* jagalan@irnas.csic.es

*Keywords:* allelochemicals, bioherbicides, Organo-clays.

Monoterpenes are biogenic volatile organic compounds with activity as allelochemicals. Because of their role as plant growth and germination inhibitors, they have been suggested as eco-friendly alternatives to synthetic herbicides The bioactivity of monoterpenes, however, is extremely dependent of the transformation and transport processes they can suffer in soils (Gámiz et al., 2018). Sorption, for example, has been shown to be a key process controlling the degradation of allelochemicals in soils as well as their capacity to express their phytotoxic activity (Galán-Pérez et al., 2021). For monoterpenes, very little is known about their dynamics in soils and even less about if chiral monoterpenes can display enantiomer-selective behaviors. In general, the potential of monoterpenes as eco-friendly herbicides is constrained by their volatilization and short half-lives in soils (Gámiz et al., 2018) and strategies to increase their residence time in soils would be needed. In this study, we characterized the sorption and dissipation processes of the two enantiomers of the chiral monoterpene pulegone, R-pulegone and S-pulegone, in a Mediterranean soil. We also evaluated their phytotoxic effect in Petri dishes and soil pots. Sorption of R- and S-pulegone on the tested soil resulted to be a non-enantioselective process yielding a low $K_d$ value of 0.32 ± 0.02 l/kg for both enantiomers. Dissipation studies revealed that volatilization and microbial degradation were key processes governing R- and S-pulegone losses in the soil. Under Petri-dish conditions, the phytotoxicity of pulegone to *Lactuca sativa* was enantioselective; the $IC_{50}$ value obtained for the S-enantiomer was significantly lower than that obtained for the R-enantiomer. However, the bioactivity of S-pulegone was almost completely suppressed in soil pots. The addition of a highly sorptive organoclay increased the retention capacity of the soil, reduced volatilization and biodegradation losses, and enhanced the phytotoxic effect of S-pulegone in the soil. We concluded that sorption on highly sorptive materials, such as organoclays, may represent a novel and promising way to enhance the phytotoxicity of monoterpenes in soils and might be useful to improve their performance as eco-friendly herbicides.

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# Natural zeolitic tuff in combination with struvite precipitation technology improved nutrient recovery in anaerobically digested wastewater

Galamini G.*[1], Ferretti G.[2], Medoro V.[1], Eftekhari N.[1], Favero M.[3], Faccini B.[1] & Coltorti M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [3] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* glmgli@unife.it

*Keywords:* struvite, zeolite, sustainability.

Nitrogen (N) and phosphorous (P) supply in agriculture sustain the global population growth. Thus, instead of relying on energy consuming practices, the recycling of nutrient-rich wastewaters may be a valuable way for sustainability, but the thoughtless use of these materials strongly impacts the environment, causing the degradation of water bodies, ecosystems, and greenhouse gas emissions. Thus, the development of efficient technologies for the recovery and recycling of nutrients is a priority.

Struvite chemical precipitation ($MgNH_4PO_4 \cdot 6H_2O$) is a promising strategy, but the high amounts of reagents required to overcome the low $Mg^{2+}$ and $PO_4^{3-}$ levels, compared with the more abundant $NH_4^+$, may affect the actual possibility of its real application at industrial scale.

This work investigates an innovative wastewater treatment process that foresees the use of a natural and relatively low expensive chabazite-rich zeolitic tuff (rock containing more than 50% of zeolite minerals) in combination with struvite chemical precipitation for the treatment of anaerobically digested wastewater.

The adsorption batch (phase 1) is intended to remove the excess $NH_4^+$, better balancing the $Mg^{2+}$ and $PO_4^{3-}$ molar concentrations, thus enhancing struvite precipitation (phase 2) with the use of fewer amounts of reagents.

Both the natural zeolitic tuff ($N_{ZT}$) and the K+-enriched ($K_{ZT}$) zeolitic tuff have been tested in phase 1, and $K_{ZT}$ was intended to counteract the possible interference which could occur due to the input of $Ca^{2+}$ ions in solution.

In phase 2 (struvite precipitation), 2 different $Mg:NH_4:PO_4$ molar ratios were tested: an $NH_4^+$ excess condition (MR1, 1:1.5:1) and a condition with $Mg^{2+}$ in excess (MR2, 2:1:1).

Treatments in which $N_{ZT}$ (NZT-S) and $K_{ZT}$ (KZT-S) were added prior to struvite precipitation were compared to a conventional struvite precipitation method without the use of zeolitic tuff (CNTR).

NZT-S MR1 was found to be the most feasible strategy because of the highest $NH_4^+$-N removal efficiency, highest struvite precipitation efficiency, and minor alterations of the treated wastewater. The precipitate obtained was 89.9% composed of struvite, by which 30.35% K-struvite and 59.55% "$NH_4$-struvite". with 3.5% N, and it respected the parameters, requested by the EU for fertilizing products, of organic carbon ($C_{org}$), P content and heavy metals.

The $NH_4^+$ removal efficiency was in order: NZT-S > KZT-S > CNTR, with the highest reduction of 84.8% recorded by NZT-S MR1 and the lowest by the CNTR (67.2 and 75.0% for MR1 and MR2 respectively).

The addition of a "zeolitic tuff adsorption phase" in struvite precipitation treatment represented a valuable method for improving the process efficiency, that permitted to save significant amounts of chemicals, thus significantly lowering the potential costs and unwanted alteration of the treated wastewater. Thus, it may be an interesting technology for the recovery and recycling of nutrients, and agricultural sustainability.

# Soil amendments with slow-release fertilizer properties show distinct responses in short-term incubations in a sandy arable soil

Galamini G.*[1], Ferretti G.[2], Rosinger C.[3], Huber S.[3], Medoro V.[1], Mentler A.[3], Diaz-Pines E.[3], Faccini B.[1], Coltorti M.[1] & Keiblinger K.M.[3]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [3] Institute of Soil Research, BOKU University Vienna (Austria).

*Corresponding author e-mail:* glmgli@unife.it

*Keywords:* struvite, zeolite, soil.

Both nitrogen (N) and phosphorous (P) are essential for life. These nutrients enter the agri-food system through cultivated soils, but over-exploitation interferes with the capacity of soils to recover the nutrient losses. Fertilizers supply the overwhelmed soils, but often these practices introduced environmental problems, due to low fertilizers use efficiencies.

It is thus necessary to introduce better practices that incentivize the recycling of nutrients in efficient ways.

An interesting strategy for wastewater treatment consists in the recovery of nutrients as struvite crystals ($MgNH_4PO_4 * 6H_2O$), thus lowering the nutrient loads of wastewaters, facilitating its disposal and contemporary producing a material useful for crop nutrition, with limited N and P availability in a "slow-release" form.

On the other hand, the soil's capacity to retain nutrients is highly dependent on its cation exchange capacity (CEC). Amending low CEC agricultural soils with natural zeolitic tuffs may be a valuable and relatively low expensive way to permanently increase their quality, reducing nutrient outflows and environmental impacts.

In this experiment, we investigated in a short-term incubation experiment, the effects of the innovative struvite fertilizer in an acidic, sandy-loam agricultural soil both at its natural state or amended with 2 different zeolitic tuffs (chabazite-rich and clinoptilolite-rich). We also investigated the effects of the N-charged zeolitic tuffs, used as fertilizers. These practices were compared with the use of liquid digestate (traditionally applied in organic farming) and with the unfertilized soil as negative control. The Incubation lasts for 3 days at 20°C and water filling pore space (WFPS) at 65%, without any plant growing, aiming at the definition of the abiotic and biotic (microbial) transformations of N and, in a minor way P.

In this acidic condition (pH 5.3), the struvite nutrient "slow release" was not effective, as the struvite plausibly was almost completely solubilized in a few days. The struvite, the digestate and the zeolitic tuffs affected both pH and soil electrical conductivity (EC), with effects observed on the microbial biomass, enzyme activities, and on the microbial C/N ratio.

All the fertilization practices led to an overall decreasing trend in the soil nitrate $NO_3^-$ concentration. The digestate led to significant consumption of the $NH_4^+$ pool and different effects have been observed between the two zeolitic tuffs.

# N-fertilizer reduction in olive-growing through the use of natural chabazite-zeolitite

Medoro V.*[1], Rotondi A.[2], Morrone L.[2], Faccini B.[1] & Coltorti M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Istituto per la Bioeconomia, CNR, Bologna.

*Corresponding author e-mail:* valeria.medoro@unife.it

*Keywords:* sustainable agriculture, natural zeolite, soil amendment.

The aim of N-based fertilizers is to provide the adequate amount of N to the plants to grant a good yield. However, after the fertilizers are applied to the soil, N is often not efficiently exploited byplants, but it is lost in the environment through several pathways, causing the degradation of the soil, water and atmospheric compartments. Consequently, the implementation of new agricultural practices are required to minimize the use of fertilizers and/or to improve their efficiency. ZeOliva is a project which aims at reducing the fertilizer N inputs in olive growing through the use of a zeolite-rich tuff (NZ) as soil amendment. This geologic material is characterized by an high zeolite (chabazite) content (>50%) and therefore by a very high cation exchange capacity, reversible dehydration and affinity to $NH_4^+$ ions. The aim of NZ is to preserve the N in the soil and minimize N losses in the surrounding environment, improving therefore the Nitrogen Use Efficiency and a concomitant reduction in the fertilizer use. In this work we present the results of a 3-years experimentation carried out in three experimental fields in the Emilia-Romagna region (Italy), in which young olive trees grown on zeolite amended soil and reduced amount of N input (-50%) and trees grown on unamended soil and 100% N input were compared. Soil and leaf samples were collected three times every year in each area. pH, Soil Organic Matter (SOM) and soluble anions were analyzed in soil samples, whereas total C and N, C discrimination factor ($\Delta^{13}C$) and N isotopic signature ($\delta^{15}N$) were studied for both soil and leaves.

Results showed that some parameters, such as pH and SOM, as well $SO_4^{2-}$, $PO_4^{3-}$ and deltas values, were generally linked to fertilization and irrigation regime. Results of N-species dynamics showed no differences between the control and zeolite amended soils, although the control treatment received twice the N-input from fertilization. The only variation of N-species was due to the sampling time (Pre-Fert, Post-Fert and Harvest). the total N of leaves did not show any difference between treatments and/or time, which means that plants were characterized by similar uptake regardless the N input. Principal Component Analysis (PCA) was performed in order to distinguish the sample groups depending on the treatment variable. The PCA explained 48.59% of the total variance and confirmed that no statistical difference occurred between treatments. On the other hand, also the vegetative results confirmed that trees amended with NZ and with a 50% reduction of N-fertilizers were not different from the plants grown on the control and 100% fertilizer N input. Thanks to these results, it can be concluded that the use of zeolitite in olive growing allows a reduction in the amount of fertilizers applied to the soil up to 50%, with all the consequent economical, environmental and health benefits.

# Zeolite applications in olive growing: field experience in Emilia Romagna

Morrone L.*[1], Rotondi A.[1], Faccini B.[2], Medoro V. [2] & Coltorti M.[2]

[1] Istituto per la Bioeconomia, CNR, Bologna. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara.

*Corresponding author e-mail:* lucia.morrone@ibe.cnr.it

*Keywords:* zeolite, olive tree, sustainable agriculture.

Modern agriculture contributes heavily to environment degradation so the adoption of eco-friendly solutions that lighten the impact of agriculture on pollution is more and more advisable. The use of zeolite fit this goal thanks to its eco-friendly features. In Emilia Romagna, where in recent years there has been an expansion of olive growing, trials were conducted related to the use of zeolites in olive growing. Its effects were studied as a soil amendment, in rooting substrates to improve radical development of cuttings and as a foliar treatment against *Bactrocera oleae* attacks (olive fruit fly).

In the plant nursery sector, the use of zeolite has been tested to increase rooting performance: in the early stages of rooting the presence of zeolite determined an increase in the percentage of rooting and greater development of the root system. Furthermore in the subsequent stages zeolite presence allowed to reduce the quantities of irrigation water.

The use of zeolite as soil amendment has been studied in three different olive groves in Emilia Romagna for three consecutive years. Results showed that zeolite had allowed a 50% reduction in the quantities of traditional fertilizers without affecting trees growth and the soils belonging to these sites have maintained the same characteristics.

Zeolite is a valid alternative to the use of pesticides for the control of the olive fruit fly (*Bactrocera oleae*); in fact the effectiveness of micronized zeolite foliar application was compared both with Spyntor Fly and kaolin for olive fly control. Zeolite showed the same effectiveness as Spyntor Fly in controlling infestation, without affecting the ecophysiological parameters of the trees such as photosynthesis, transpiration and stomatal conductance.

# Geochemical characteristics of mine wastes reclaimed for agricultural purposes at the east of Seville Province (Southern Spain). Preliminary results

Romero-Baena A.*, Delgado J., Barba-Brioso C., Miras A., Martín D., Campos P. & González I.

Department of Crystallography, Mineralogy and Agricultural Chemistry, University of Seville (Spain).

*Corresponding author e-mail:* aromero@us.es

*Keywords:* mine waste dumps, reclamation, potentially toxic elements.

La Preciosa II is an abandoned mine site located close to Peñaflor village, at the high meadow of the Guadalquivir Basin, in the eastern part of Seville Province (Southern Spain). The ore deposit, consisting on a copper-pyrite and chalcopyrite averaging 3% in Cu, is included in mica-schist and gneiss of the late Proterozoic (Lora Unit, Ossa-Morena Zone), which are covered by Neogene materials of the Guadalquivir Basin (calcarenite and marl). The exploitation of the mine during the 19$^{th}$ and the 20$^{th}$ centuries until the 1950s produced an important volume of mine wastes covering around 10 ha, whose acidic leachates discharge into a main stream.

Recently, a part of the waste dumps has been covered with building materials and carbonated rocks from the surroundings, as a reclamation purpose for agricultural activities such as growing citric trees. However, acid mine water is still leaching from the subsoil, so a mineralogical and geochemical study of the reclaimed area has been carried out, as a base for future remediation actions.

Several samples from the mine wastes, the recovered waste dumps and the cultivated soils were collected. The leachates from the mine wastes and the stream water were also studied, including one upstream sample, before the contaminated area. Water samples were filtered and preserved in cold until analysis. Eh, pH, temperature and conductivity were measured *in situ.* Chemical analyses of major and potentially toxic elements (PTE) were carried out in water (by inductively coupled plasma optical emission spectrometry) and solid samples (by X-ray fluorescence). The mineralogy was analysed by X-ray diffraction.

The cultivated soil was composed of quartz, calcite, feldspar, illite and traces of gypsum. The mine waste was composed of pyrite, quartz, magnetite, mica, amphibole and secondary minerals such as jarosite and gypsum. Calcite was also detected at very low content in the recovered waste dumps, suggesting that it has been completely dissolved consuming its neutralizing potential.

PTE showed very high concentrations in the mine waste (up to 0.7% of Cu, 0.8% of Pb, 0.2% of Zn, and 50 mg/kg of Ag). The high content in Pb occurred in samples with jarosite, highlighting the role of this mineral in the retention of Pb. On the contrary, most of the cultivated soil can be considered unpolluted.

The leachates of the mine wastes reached pH values down to 1.1 and very high concentrations of Fe (up to 81 g/L), $SO_4^{2-}$ (up to 98 g/L), Cu (up to 1,5 g/L) and Zn (up to 3,5 g/L). In the main stream, the pH was kept between 2.4-3.0, with concentrations of Fe, Cu and Zn up to 2283, 36 and 91 mg/L, respectively.

Although the reclaimed soils can be considered unpolluted, the underneath waste dumps continue leaching acid water and releasing PTE, which can affect the roots of the citric trees. Therefore, more efforts are necessary to mitigate the contamination and remediate the mine waste dumps.

# BeeDiversity: innovation and technology in apiculture for habitat management and conservation

Stravisi A.*[1], Pasut D.[2] & Santaliana D.[1]

[1] Polo Tecnologico Alto Adriatico «A. Galvani», Pordenone. [2] Libero professionista.

*Corresponding author e-mail:* antonella.stravisi@poloaa.it

*Keywords:* Apiculture 4.0, Intelligent hive, biodiversity.

Interreg Ita-Slo BeeDiversity project "Improvement of biodiversity through innovative management of ecosystems and monitoring of bees" creates an innovative cross-border system for the improvement and monitoring of biodiversity in conservation interest habitats, which allows the improvement, sustainable and integrated management of ecosystems. The system was implemented by partners (Veneto Agricoltura, Polo Tecnologico Alto Adriatico, University of Udine Di4A, BSC, Poslovno podporni center, d.o.o., Kranj, Univerza v Ljubljani (Biotehniška Fakulteta) in 10 case studies for a total of 8000 hectares spread between Italy and Slovenia, structured protocols and a joint model. Bee-diversity integrates the monitoring of the health status of areas with pollinators (domestic bees) through an innovative ICT system and an APP for the collection, management and aggregation of data. The work is carried out in Natura 2000 areas with the direct collaboration of the owners and management companies and stakeholders.

Experimental hives were equipped with sensors (weight, internal-external temperature, internal-external relative humidity, fly counter). Analysis of hive parameters helps optimizing apiary management, giving real time information on production, presence of brood and acceptance of a new queen, eventual bee losses and preventive potential alarm regarding important events such as swarming. Data were remotely collected, being the sensor system connected through GSM, and archived on a common database.

Pollen collected by bees has been sampled with pollen traps installed on the hives and analysed in order to describe pollen availability in the foraging areas of the bees.

Apiary and bee data were integrated with field data collection which concerned in vegetational surveys, in order to characterize environmental availability of nectar and pollen for the bees and evaluate habitat biodiversity in the foraging areas of bees.

An innovative application for smartphone was realized, which integrated remote collected data from hives with observational data inserted by beekepers: beginning of spring spawning, brood quality, presence and quality of food supplies, type and quantity of eventual supplementary emergency feeding, looting, swarming, orphanages, blooms of main essences (*Taraxacum officinale, Robinia pseudacacia, Tilia cordata, Castanea sativa*, honeydew), varroa presence; varroa control treatments; varroa fall count after treatment, peculiarities of stationary interferences (agricultural phytosanitary treatments, agricultural processing, other events), other health problems (calcified brood, European foulbrood, American foulbrood, nosema). The app also communicates technical information to professionals and general information to raise awareness among the population.

# S40.

# Environmental geology supporting the European Green Deal

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# Risk evaluation and management in lacustrine environment: bathymetric and morphologic survey of Martignano and Bracciano lakes (metropolitan area of Rome, Italy)

Argentieri A.*[1], Cristofalo G.C.[3], Fabiani M.[1], Marchetti M.[3], Piacenza M.[2], Rotella G.[1] & Taliana D.M.R.[3]

[1] Città metropolitana di Roma Capitale - Dip. IV Servizio 2 "Geologico, difesa del suolo - rischio idraulico e territoriale", Roma. [2] Città metropolitana di Roma Capitale - Dipartimento IV "Pianificazione, sviluppo e governo del territorio", Roma. [3] Fugro Italy S.p.A., Roma.

*Corresponding author e-mail:* a.argentieri@cittametropolitanaroma.it

*Keywords:* risk evaluation, Rome metropolitan area, volcanic lakes.

The metropolitan area of Rome is characterized by the presence of four main lacustrine basins, located within the volcanic districts of the Roman magmatic Province. Namely, the Lakes of Bracciano (56.5 km$^2$) and Martignano (2.44 Km$^2$) fill the calderas of the Sabatini Mounts, whereas the Lakes Albano of Castel Gandolfo (6 km$^2$) and of Nemi (1.67 Km$^2$) basins are situated in the central zone of the Alban Hills.

Lakes represent an important natural, environmental and economic value, and are thus all included in regional natural parks. Conversely, the interaction of natural hazard (endogenous gas emissions, local seismicity, landslides, water table lowering) and human activities in lacustrine environments (navigation, swimming, presence of relic weapons of war) can determine serious risk factors.

Therefore, the Metropolitan City of Rome Capital (CMRC), carrying out its duties of land planning and management, implemented in recent years a special project of survey of the lakebeds. The interest lies in combining CMRC responsibilities about control of navigation in inland waters with territorial risks assessment studies. The final goal is the constitution of a geographic information system of lakes, in order to support strategic planning and emergency management in the metropolitan area. This tool will support a positive synergy between different institutions (municipalities, local authorities, police forces, fire brigade, civil protection, management authorities of natural parks, etc.), sharing information and knowledge.

Lack of updated bathymetry represents a critical issue for rescue operations in lakes. In recent years, several tragic incidents occurred; the recovering of victims and wrecks can be hindered also by an inadequate state of knowledge. The case of Bracciano and Martignano basins is emblematic, because the available bathymetric map dates back to half a century ago (Barbanti & Carollo, 1969). Conversely, the Lake Albano got more attention in recent times, and modern disciplinary studies are available (Anzidei & Esposito, 2010).

Hence, CMRC selected the Martignano site for a multiparametric exploration of the lake; a complete bathymetric and seismic prospection, including a detailed topographic survey of the circumlacual coastal area, was performed in 2020. A second project was carried out in 2021 in the Lake of Bracciano, applying the same methodology to four test areas, selected as the most frequented sectors for swimming and sailing.

Here we present preliminary results, which will help and guide next exploration programs, starting from the upcoming survey of the new 1:50.000 scale geological map, in the framework of the CARG project. The convergence of interest between basic and applied research will foster progress of hazard assessment and risk prevention in lacustrine environments, by means of detailed knowledge of what lies beneath water surface.

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# Petrology of gold rich soil and impact of gold mining on soils in Meiganga area (Adamaoua Plateau, Cameroun)

Danala D.S.*[1], Ekengele N.L.[1], Vorster C.[2], Bitom D.L.[3] & Kramer J.D.[2]

[1] Department of Earth Sciences, University of Ngaoundere (Cameroon). [2] Department of Geology, University of Johannesburg (South Africa). [3] Faculty of Agronomy and Agricultural Sciences, University of Dschang (Cameroon).

*Corresponding author e-mail:* sdanaladanga@gmail.com

*Keywords:* lateritic soils, metallic trace elements, metallic pollution.

The soils of Meiganga, belonging to the lateritic domain of the intertropical regions, have significant mining resources that are exploited by artisanal and slightly mechanized methods, providing income to the government and local populations. However, this activity's nature remains a source of insecurity and very serious environmental transformations. This study aims to contribute to the knowledge of the macromorphological, mineralogical, geochemical and physicochemical characteristics of these soils and to assess the level of physical degradation and metallic pollution of the soils of this locality following gold mining. For this purpose, field work during which observations were made in situ; pits were dug and described macroscopically; soil samples were taken for laboratory analysis.The in situ observations show that, depending on the gold mining techniques used, the sites are exposed to deforestation risks, erosion, collapses, soil and water pollution, etc.

Two aspects have been considered in this study: 1) petrological characteristics of weathering profile shows that it can be divided into three parts, from the bottom to the top which are: weathered and decayed rock; a nodular ferruginous relict of lateritic crust and surface clay-sand. We notice a homogenization and a wathering of the primary chemical signature more and more marked as we get towards the surface. Macromorphologically, they are generally of clay texture, lumpy, polyhedral, more or less compact, and porous. The major present mineral phases are quartz, kaolinite and muscovite. One notes the presence sometimes of hematite, gibbsite and orthoclase, and also albite and calcite but with low contents. 2) Trace elements contents (Cr, Ni, Cu, Zn, As, Pb, and Cu) are high, exceeding the maximum tolerated values in the soil, and the highest values are found in the clay mineral rich horizons. Microchemical analyses (SEM) and extraction tests are in process with a view to better understanding of the retention mechanisms and the risks of release of trace elements into the environment, and their transfer to the food chain. In order to ensure a sustainable management of mineral resources and protect humans from any risk.

# Geothermal reservoir characterization and exploitation scenarios for the Acquasanta Terme area (Laga foredeep basin, Marche region)

Invernizzi C.*[1], Gambini R.[2], Mazzoli S.[1], Memmo V.[2], Pasquini G.[3], Pierantoni P.P.[1], Sansone F.[2], Teloni R.[3], Tondi E.[1] & Zambrano M.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Geological Engineering Network s.r.l., Roma. [3] GeoMORE s.r.l. - spin-off Università di Camerino.

*Corresponding author e-mail:* chiara.invernizzi@unicam.it

*Keywords:* geothermics, low enthalpy.

We analyze a geothermal system within a foredeep basin characterized by a low heat flow (HF). The system is in the Acquasanta Terme area, within the Laga foredeep Basin, in the deformational front of the Sibillini thrust belt (Northern-Central Apennine, Marche region). It shows the presence of thermal spring waters (~ 30ºC) at surface, thick travertine deposits, trace of important past thermal activity, and an endogenous karst with a role on the development of the reservoir. The purpose of this work consists in the assessment of the geological structures and petrophysical properties of the reservoir, and in the analysis of the possible geothermal applications for the Acquasanta town area and surroundings.

The proposed methodology consists in the integration of available seismic reflection data, well logs, and fracture data from analogue outcrops to characterize the reservoir from the geometric and petrophysics point of view. Seismic interpretation was aimed to map the geological structures and the boundaries of the geothermal reservoir, while, both well logs interpretation and fracture modelling have been used for estimating and constraining the porosity and permeability of the reservoir rocks into a model.

These results allow to envisage different possible scenarios of exploitation based on the estimated water flow and deep temperatures, such as a direct heat exchange between geothermal water and fresh water, the use of heat pumps, or hybrid district heating with heat pumps. Items relative to feasibility study and possible plant design, advantages and disadvantages of the different scenarios are also proposed.

The possibility of having other "blind" situations such as Acquasanta but without surface evidences hidden by the intact flysch cover is also evaluated.

# Blue energy converter & coastal protection: some solutions for the Central Adriatic sea

Invernizzi C.*[1], Maponi P.[1], Zitti G.[2], Bello M.[1-3], Bisci C.[1], Gedela S.[1] & Brocchini M.[2]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Ingegneria, Civile, Edile e di Architettura, Università Politecnica delle Marche, Ancona. [3] Agenzia Regionale per la Protezione Ambientale, Macerata.

*Corresponding author e-mail:* chiara.invernizzi@unicam.it

*Keywords:* blue energy, coastal protection, Adriatic sea.

The exploitation of renewable energy sources is one of the main points in the European strategy to speed-up the energy transition towards a low $CO_2$ emissions future. The European Green Deal includes a sustainable blue economy within its goals.

If solar and wind sources are the sectors that have the greatest cost decrease, other sources are becoming more competitive, and marine energy represents an important opportunity for EU. The Commission's Blue Growth Strategy includes the ocean energy sector as one of the five developing areas in the 'blue economy' that could help to drive job creation in coastal areas.

One of the main challenges with this respect is to scale down the possible devices to convert the energy potential offered by different seas in the best possible way.

Our aim is identifying the optimal potential sources of the wave energy and the selection of the suitable WEC (Wave Energy Converter) for Central Adriatic Sea to combine the coast protection against erosion with renewable energy production, turning an environmental challenge into an opportunity.

The Adriatic Sea is a semi-enclosed body of water about 750 km long and 200 km wide and an average depth of 270 m. Two winds dominate the surface wave situation in the Adriatic Sea: Bora and Sirocco. Based on the wave data collected, the central Adriatic has an estimated wave energy potential of 2.6 kW/m. The maximum significant height is between 0.5 and 1 m with respect to the time periods of 3 to 4 sec.

Some solutions, both in port areas (Ancona port) and along the coast, are highlighted. A pre-fesability study using commercial devices is proposed for Ancona port, while the role of breakwater barriers made active with respect to the production of blue energy is under study using small devices with optimized design.

# Geochemistry and radiogenic isotopes of total suspended solids (TSS) from the Nievole River Valley (Tuscany, Central Italy)

Maccelli C.*[1-2], Natali C.[1], Nisi B.[3], Casalini M.[1], Vaselli O.[1-3], Venturi S.[1-3] & Avanzinelli R.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* chiara.maccelli@unifi.it

*Keywords:* environmental geochemistry, Total Suspended Solids, Nievole River Valley.

The Nievole River Valley (NRV) is a sub-basin of the Arno River Basin located in Tuscany (Central Italy). Nievole, Pescia di Collodi and Pescia di Pescia rivers, and many other artificial channels, crosscut the northern part of NRV and collect effluents from many small cities and industrial districts, before inflowing into the Padule di Fucecchio, a swampy zone whose waters are regulated by the Usciana River. The NRV is characterized by a complex ecosystem including many relevant anthropic activities and small-medium enterprises, such as paper mill industries, flora-nursery farms, thermal spas, and one of the most productive tanning districts in Italy. For these reasons, the NRV was selected for this study, being aimed at identifying natural and anthropogenic inputs that affect the geochemical composition of liquid and suspended matrices and stream sediment. In this work we determined the chemical and isotopic composition of the total suspended solids (TSS) collected from the NRV river system during high and low river discharge periods in 2021 along the main courses and tributaries, distributed in an area of about 320 $km^2$. Major, minor, and trace element concentrations were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after total acidic digestion while Sr, Pb, and Nd isotopic compositions were performed by Thermal Ionization Mass Spectrometry (TIMS). According to the Italian Legislative Decree 152/2006, heavy metal concentrations in TSS approach, or even exceed, those for the Italian soils intended for green public areas for almost all the regulated elements, suggesting that a strong anthropogenic pressure is acting on the NRV. Vanadium, Cr, Co, Cu, Zn, As, Sn, and Pb showed values up to 149, 428, 31, 182, 476, 37, 22, and 109 mg/kg, respectively. Cesium concentrations were up to 46 mg/kg and decreased along the river course, highlighting a dilution trend along a tributary of the Padule di Fucecchio. Lead isotopes in TSS displayed a signature typically associated with the presence of anthropogenic contributions, especially for those samples collected from the most urbanized and industrialized areas. Enrichment Factors for Nickel, Mo, and Pb showed a positive correlation with Pb isotopic ratio with the higher values reflecting a clear anthropogenic contribution.

# Natural *vs* anthropogenic sources and distribution of grain size, nutrients and heavy metals in the sea environment (Naples Bay, Eastern Tyrrhenian Sea)

Mali M.[1], Milia A.*[2], Buonocunto F.P.[2], Di Leo A.[3], Ferraro L.[2], Giandomenico S.[1] & Giordano L.[2]

[1] Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica, Politecnico di Bari. [2] Istituto di Scienze Marine, CNR, Napoli. [3] Istituto di Ricerca Sulle Acque, CNR, Taranto.

*Corresponding author e-mail:* alfonsa.milia@cnr.it

*Keywords:* natural vs antropogenic, metals, Naples Bay.

Various aspects of human-environment interaction are mainly studied in land areas, while little is known about the sea areas facing the densely inhabited coasts. The area offshore Sarno River plain (Naples Bay) is affected by metals contamination as a result of the geogenic nature, the outflow of industrial vaste and the high demographic pressure. A geochemical and physical parameters of the sea floor sediments were analysed along a transect moving from the coast until the 120 m of water depth with the aim to explore how the onshore documented contamination affect the offshore counterpart. Sediments samples along a transect approximately oriented NE-SW were collected to analyse the distribution of grain size, nutrients (TOC, TN, TP) and heavy metals (Hg, Cd, As, Cr, Ni, Cu, Zn, Pb, Fe and Mn). The study area is generally dominated by clayey silt and sands, whereas the organic and nutrients permit to individuate the source of the sediments deposited offshore. On the other hand, the grain size distribution together the TOC percentage and metal content of natural origin in the sediments can reflect indirectly the sediment source and the direction of sediment transportation. The study highlights the distribution of all the elements and a statistical analysis was performed to individuate a correlation between them. In order to evaluate the distribution of contaminants in the seafloor sediments, a statistical study has been conducted in the area using multivariate techniques. The statistic approach was performed to gain insights on the occurrence of contaminants within the area, aiming to identify the relevant hot spots. To assess the natural vs anthropogenic origin and the source to sink pathway of the contaminant was made a comparison with the published data analysis conducted onshore in the Sarno Plain and in the shore-proximal environment. Results showed that the submarine area could be divided in different zones the one in the proximity of the coast of Torre Annunziata, with physical and geochemical association that can be related mainly to the natural origin, characterized by the influence of clastic sediments from Vesuvio volcano; others which contaminant association that are anthropogenic in origin, originated from the Sarno Plain, whereas a more distal area, characterized by low rate of contamination, mainly influenced by sediment from Sorrento Peninsula. Finally based on the contaminant and nutrient distribution it is possible to individuate the distribution of terrigenous sediments and organic matter of the Sarno delta deposits. The results show that the river should account as one of the main contribution sources of anthropogenic contaminants. Some metals contamination, anthropogenic in origin, and TOC in general decreased gradually with distance from the coast and in particular is limited to the area of deposition of the river discharge.

# Geoscience disclosure as the key to face climate change impacts: toward achieving a sustainable world

Mancini A.M.*[1], Negri A.[2] & Lozar F.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona.

*Corresponding author e-mail:* alanmaria.mancini@unito.it

*Keywords:* ecosystem services, paleoenvironmental reconstruction, climate change impact.

Human-induced climate alteration is severely impacting the ecosystem functioning and services. Ocean acidification and deoxygenation, mass extinction, sea level rising and increase of extreme meteorological events are related to atmospheric $CO_2$ rising and the consequent increase in temperature. The rate of environmental change is extremely fast, hampering biota adaptation to the ongoing new conditions, thus increasing the potential impact on ecosystem. Climate change is among the most complex scientific topic, because it is characterised by a wide range of interacting variables; therefore, to predict climate evolution and its impact on ecosystem during the near future is challenging. However, the geological record offers the opportunity to investigate trends similar to the current climate change occurred in the geological past; this represents a unique and useful tool to decipher the current climate change. The geosciences are powerful in their capability of constraining all the "evolutionary history" of past extreme events, from their onset, passing in their acme and lastly with their conclusion and the consequent recovery of the ecosystem. Environmental reconstruction of the main events related to abrupt (natural) emissions of $CO_2$ during Earth history underlines that the current climate change is outstanding in terms of rate of environmental change and impact on ecosystems. To understand and to disclose these findings is crucial in order to increase the population awareness of the current ecosystems threat and therefore, to mitigate the impact. This because anthropogenic pressure derives from individual behavior in everyday life, but mostly because governance actions are primarily boosted by the need of population. In this perspective, the geoscience, with its potential to explore and constrain past environmental changes, necessitate to be more considered in the educational career both at the school and in the mass media worldwide. Clear examples of how, and how much, the awareness of the population regarding the current climate change plays a fundamental role in stimulating sustainable governance actions derive from the "Youth for climate" movement. Here we present a geoscientific approach to constrain the current climate change in terms of magnitude and spatial occurrence, with the aim to assess future potential impacts on human life and activities. We also propose easily performable, inclusive and proactive mitigation strategies to face possible future impacts deriving from the climatic evolution, as indicated in the United Nations 2030 Agenda (Sustainable Development Goals 13: Climate Action).

# Integrated spatial mapping of natural and anthropogenic pollutants in the atmosphere for a save and health territory

Mandrone G.*[1], Chicco J.M.[1], Ferraris S.[1], Giammanco S.[2], Pollo R.[3], Sortino F.[4] & Trane M.[3]

[1] Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio, Università di Torino. [2] INGV, Catania. [3] Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio, Politecnico di Torino. [4] INGV, Palermo.

*Corresponding author e-mail:* giuseppe.mandrone@unito.it

*Keywords:* air quality, microclimate, low cost instruments.

The signs of climate change require urgent action. The variety and the extent of these impacts change in the different regions are yet uncertain. The study of this interaction and the related risks is fundamental for improve the health and quality of life of citizens. The study address at microclimate variations inside the cities, where urban heat island and physical and chemical pollution interact with urban form, citizen behavior and energy production/consumption pattern (Jauvion et al., 2000).

Despite the general framework of air quality, due to local climate, orography, and man-made emissions, site-specific countermeasures are already well known and their implementation have positive effects in terms of urban health. Unfortunately, quantification of effects of these actions is seldom and usually based on scarce and not-systematic measurements.

The recognized problems in verifying environmental parameters are linked to the significance of the measuring point, the type of sensor used and the representativeness of the data collected. The study defines these variables in a rigorous manner in order to make them consistent each other, making use of multiscale and integrated spatial logics, tested and verified in different natural and anthropic contexts. (Giovanardi et al., 2021)

The study will focus on detecting the elements with the greatest impact on society, namely the main GHGs ($CO_2$ and $CH_4$), $NO_2$ and solid particulate matter (PM10 and smaller). It integrates suitable methodologies and logics through sensors of different nature, from wearable ones to transportable instruments up to sensors placed on drones able to detect even the three-dimensionality of the various physical-chemical plumes analyzed. The result is a product/service capable of spatially reproducing the diffusion of the main atmospheric pollutants.

The potential of such a system is manifold: air quality measurement services in urban environments, emergencies linked to industrial accidents, emissions from landfills and in volcanic (Chicco et al., 2020) or seismic environments, with potential uses also for civil protection in hostile environments and for oil & gas and geothermal exploration.

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Jauvion G., Cassard T., Quennehen B. & Lissmyr D. (2020) - DeepPlume: Very High Resolution Real-Time Air Quality Mapping. arXiv, 2002, 10394. https://doi.org/10.48550/arXiv.2002.1039.

# Limits and applications of the radon deficit technique for the study of two sites contaminated by NAPLs (Non-Aqueous Phase Liquids)

Mattia M.[1], Tuccimei P.*[1], Soligo M.[1], Briganti A.[2], Voltaggio M.[2], Carusi C.[3] & Rainaldi E.[3]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] Mares s.r.l., Settore Protezione Ambiente, Roma.

*Corresponding author e-mail:* paola.tuccimei@uniroma3.it

*Keywords:* radon deficit, NAPL pollution, groundwater.

Previous works (Schubert, 2015; De Miguel et al., 2020) show that the higher solubility of $^{222}Rn$ in NAPLs (Non-Aqueous Phase Liquids) than in water or air is often used to localize the spatial distribution of a NAPL plume. However, the limitations and advantages of this technique in different real contexts have scarcely been addressed. The aim of this work is to present an evaluation of this method applied to different real situations. Two polluted areas in Rome have been studied for two years. They are both gas stations with different geological and spill characteristics. The first site is in a volcanic geological setting, with high natural radon concentrations. It is characterized by a deep aquifer with low variations in the water table level during the year and it is affected by an ancient spill. The other area is characterized by the presence of alluvial deposits, a shallow aquifer with significant oscillations of the groundwater level and a variable flow direction during the year. Furthermore, the spill on this site is much more recent than that of the other site. In both areas Rn-deficit was periodically measured in groundwater to monitor the distribution of the contamination. Several parameters have been evaluated for the interpretation of the data, such as radon and NAPL concentrations in sampled waters, precipitation rates and fluctuations in groundwater levels, as well the role of rainfalls and groundwater oscillations in the remobilisation of pollutants and consequently conditioning radon concentrations in both contexts. Multivariate statistical analysis is then applied to explain the variations and correlations between the parameters analysed, to observe the sensitivity and the validity of the technique, also in the light of the different remediation systems applied to the two sites. Multivariate statistical analysis (PCA) shows a strong negative correlation between water radon and residual NAPLs (total hydrocarbons, MTBE and ETBE) concentration and no dependence of NAPLs levels from rainfall rates in the first site affected by an old contamination, with limited fluctuations of groundwater levels. A negative covariance between radon and NAPLs is demonstrated also for the second site, even if seasonal reversal of the groundwater flow complicate NAPLs concentration and rainfall rates relationships. The role of water pumping on contaminants and radon distribution is more evident in this area affected by a much more recent NAPL spill.

De Miguel E., Barrio-Parra F., Izquierdo-Díaz M., Fernández J., García-González J.E. & Álvarez R. (2020) - Applicability and limitations of the radon-deficit technique for the preliminary assessment of sites contaminated with complex mixtures of organic chemicals: A blind field-test. Environment International, 138. 105591.

Schubert M. (2015) - Using radon as environmental tracer for the assessment of subsurface NonAqueous Phase Liquid (NAPL) contamination. A review. Eur. Phys. J. Spec. Top., 224, 717-730.

# Mercury in Quaternary sediments of the Paglia-Pagliola River system (Monte Amiata)

Montefinese S.*[1], Benvenuti M.[1], Buccianti A.[1], Costagliola P.[1], Fornasaro S.[2], Lattanzi P.[3], Morelli G.[1] & Rimondi V.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* montefinese.simone@gmail.com

*Keywords:* mercury, geochemical background, multivariate analysis.

The Monte Amiata area (southern Tuscany, Italy) hosts one of the most important Hg districts in the world. Cinnabar ores have been exploited to produce metallic Hg until the last century, causing an extensive Hg contamination of stream sediments both of the Pagliola Creek, which drains the Abbadia San Salvatore mine, and of the Paglia River, which is the main water collector of the areas affected by mining activities. Therefore, this area is characterized by a geogenic geochemical anomaly, resulting from the natural leaching process of the mineralization associated with an anthropogenic one.

The main purpose of this study is to characterize the composition of major elements and Hg within stream sediments of the Paglia-Pagliola River system that predate the onset of mining activity, trying to define a geochemical background value that allows to discriminate between the two coexisting anomalies. Sediments from Quaternary fluvial terraces along the Paglia River were sampled at three sites (total 20 samples) as part of this study; pre-, syn- and post-mining sediments (total 74 samples) from the Pagliola Creek were also analyzed as part of this work by integrating a database obtained from a previous sampling campaign.

Compositional analysis of the data indicates a common source for sediments from the Pagliola-Paglia basin. However, differences are identified in the geochemistry of major elements and their relationship with Hg. For the pre-, syn-, and post-mining Pagliola sediments, CaO, resulting from mining processing waste enriched in that oxide, can be considered a proxy for Hg. CaO enrichments thus correlate to high Hg concentrations, especially in sediments coeval with mining activity, which report up to thousands of μg/g for Hg. Along the Paglia River, instead, the alteration of carbonate lithotypes outcropping in the basin causes an enrichment in CaO of Quaternary sediments, and also a dilution of Hg value. Nonetheless, the concentrations obtained from the pre-mining sediments (0.08-2.98 μg/g) are 1-2 orders of magnitude higher than the crustal Clarke value (0.056 μg/g).

The Hg background value found is 2.3 μg/g for the Pagliola Creek and 0.3 μg/g for the Paglia River, 1.3 μg/g considering the whole investigated area (Pagliola + Paglia). As a result of this study, a new reliable regulation for Hg should be defined for this area, taking into account the high natural occurring Hg levels in the environment.

# Territorial analysis for energy supply of western Turin area from hydroelectric energy: impact and potential

Paschetto A.*[1], Leso C.[2], Manfroni F.[2] & Bonetto S.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Gruppo CIDIU, Collegno (TO).

*Corresponding author e-mail:* arianna.paschetto@unito.it

*Keywords:* mini hydroelectric, environmental impact, sustainable energy.

It is now generally assumed that a radical reversal in economy is needed in order to cope with the effects of climate change and to improve the resilience of populations in relation to these effects.

European policies for climate change and economic recovery due to Covid-19 (*Guidance to Member States, Recovery and Resilience Plans, 8th Environmental Action Program*) are supposed to work in synergy to promote green and efficient energies, shifting the cost/benefit ratio in favor of renewable natural resources. As part of these policies, Italy is increasing the number of mini hydroelectric plants, which are considered advantageous both in economic and environmental terms, avoiding many contrasts with the surrounding environment.

The aim of this study is the evaluation of potential production of hydroelectric energy by means of mini hydroelectric in the western area of Turin, considering and comparing lowland areas and high valley areas.

The study will be congruent with European and national guidelines regarding the Environmental Impact Assessment: a feasibility study will be conducted, based on geological, hydrogeological, morphological, ecological and climatic components, to evaluate environmental impact of hydrolectric plans.

# Testing Waterproofing products used in the construction industry to retain radon released from building materials and soil

Portaro M.*[1], Tuccimei P.[1], Galli G.[2], Soligo M.[1], Longoni C.[3] & Vasquez D.[3]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] INGV, Roma. [3] Mapei S.p.A., Waterproofing Line, Milano.

*Corresponding author e-mail:* manuela.portaro@uniroma3.it

*Keywords:* radon, waterproofing products.

Radon is a radioactive gas present in the environment and released from geological bedrocks and building materials, especially in case of high concentrations of its precursor elements. Moreover, radon can accumulate indoors where it can reach very high levels, using openings and/or micro-cracks in the foundations. Prolonged exposure to high concentrations of ionizing radiation, generated by radon decay, can cause a series of damages to the human body, like lung cancer. To reduce indoor radon concentrations below the risk limits for health, different actions can be applied, such as the use of waterproof membranes, forced ventilation action, or a combination of the two techniques, like in the experiments described in this presentation. This work aims to characterize some waterproofing materials, commercially available (such as bituminous emulsion, membranes, and resins), able to retain radon released from soil and building materials of volcanic origin. An accumulation chamber (scale model room), made of blocks of "Tufo di Gallese" ignimbrite of 62 cm × 50 cm × 35 cm (inner length × width × height, respectively) (Lucchetti et al., 2020) with high radon exhalation rate, was used to study the radon sealing-properties of waterproofing materials. These products were applied on the internal wall of the accumulation chamber, on removable plasterboard support panels. Two radon monitors (RAD7 and AER PLUS) were used for measuring the indoor radon concentration and two flowmeters, suitably coupled to a T-joint, to modify the air flow. The effect of ambient temperature on radon exhalation and diffusion was assessed.

First results demonstrate that the plasterboard support does not influence indoor radon levels and highlight the different ability of specific materials to reduce radon concentration. Moreover, outdoor air introduction in the model room enhances the barrier effect of waterproof materials, showing that higher rates of air exchange produce stronger radon decreases. This joint influence is more efficient for materials with lower radon diffusion coefficient. Finally, the application of outer covers (plastic films) limits the air exchange outwards through the porous walls of the accumulation chamber, with a resulting increase in radon concentration.

Lucchetti C., Castelluccio M., Altamore M., Galli G., Soligo M., Tuccimei P. & Voltaggio M. (2020) - Using a scale model room to assess the contribution of building material of volcanic origin to indoor radon. Nukleonica, 65(2), 71-76.

# Protect and heat

Tavecchio W.*

Ordine dei Geologi della Lombardia, Milano.

*Corresponding author e-mail:* emme.vu.ci@gmail.com

*Keywords:* seismic, wave, earthquakes, damping, vibration, geothermal, micropiles, heat, protect.

This project named "To Protect and Heat" aims to safeguard the environment, to reduce the carbon dioxide emissions and reduce the risk of collapse of buildings affected by earthquakes.This is a new way to heat and cool buildings and at the same time mitigate the seismic vibrations produced by earthquakes in seismically sensitive areas.To mitigate this effects and to produce geothermal energy a series of works that intercept and dampen vibrations must be created outside the buildings. They will consist of a double row of juxtaposed vertical poles made of ferrous and plastic materials that allow the emptying and replacement of a part of the surface soil. It will be possible to lay in the ground some closed-circuit geothermal probes, with the technique of "energy poles", taking advantage of the perforations of the works carried out for the attenuation of vibrations.

Encouraging results, in the damping of vibrations produced by mechanical presses, have been successfully obtained with the use of vertical poles in HDPE, located outside production sheds.The project aims to mitigate the effects produced by superficial and deep earthquakes on the ground and existing structures and at the same time produce low-cost geothermal energy with low-enthalpy system, combining the consolidation technique of the excavations with closed-circuit geothermal energy piles.

# Rapid landslide risk mitigation: design for sustainability criteria in mountain areas

Vagnon F.*[1], Umili G.[2], Bianco I.[1], Blengini G.A.[1], Costanzo D.[3], Dino G.A.[2], Ferrero A.M.[2], Migliazza M.[3], Taboni B.[2] & Vinciguerra S.C.[2]

[1] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Dipartimento di Ingegneria Strutturale, Edile e Geotecnica, Politecnico di Torino.

*Corresponding author e-mail:* federico.vagnon@polito.it

*Keywords:* sustainability, rapid landslides, LCA.

The Intergovernmental Panel on Climate Change (IPCC) report recognizes the interdependence of climate, ecosystems and human societies. Landslides triggered by climate change are a clue of this interaction: they cause enormous damages, aggravated by the degradation of infrastructures and the abandonment of inland areas. Italy is one of the countries most affected by landslides, and about a third of these are rapid phenomena, such as rockfall (RF) and debris flow (DF).

Structural adaptation responses are fundamental for reducing the associated risk. Moreover, the current economic context and the new policies related to the environment, which have set very ambitious targets of carbon neutrality by 2050, confront us with new challenges, including the design approach for protecting and safeguarding inland from landslides. The concept of "oversizing of countermeasures", which also brings an undesired additional carbon footprint associated with extra materials and works, should be rethought in the framework of sustainability while keeping the highest safety standards intact.

In this paper, a three-steps approach for the definition of RF and DF protection works, integrated with Life Cycle Assessment (LCA), is presented. In particular, the research wants to define and develop best practices for DF and RF risk mitigation, combining technical and cost-effective solutions, which allow the best safety standard and the sustainability of the overall protection system (from design to installation and maintenance). Moreover, these solutions will be evaluated in the framework of LCA approach, which is clearly underdeveloped and underexploited for these engineering works and related technologies.

# S41.

# Evolution of the Variscan crust


*CONVENERS & CHAIRPERSONS*

*Fabrizio Cocco (University of Cagliari)*

*Giovanni Luca Cardello (University of Sassari)*

*Camille Rossignol (University of Cagliari)*

*Matteo Maino (University of Pavia)*

*Leonardo Casini (University of Sassari)*

# Late Cambrian-Early Ordovician transcurrent displacement of the Ossa-Morena Zone along the northern Gondwanan margin revealed by U/Pb detrital zircon systematics

Accotto C.*[1], Martínez Poyatos D. J.[1], Azor A.[1], Simancas F.[1], González Lodeiro F.[1] & Pedrera A.[2]

[1] Departamento de Geodinámica, Universidad de Granada (Spain). [2] Instituto Geológico y Minero de España, Sevilla (Spain).

*Corresponding author e-mail:* accotto@ugr.es

*Keywords:* Variscan belt, detrital zircon geochronology, Southwest Iberia.

The Ossa-Morena Zone (OMZ) is one of the continental terranes exposed in SW Iberia. At Ediacaran-early Paleozoic times, this terrane was located along the northern Gondwanan margin, but its exact location and paleogeographic evolution is still a matter of debate (e.g., Cambeses et al., 2017; Rojo-Pérez et al., 2021).

A provenance study based on U-Pb detrital zircon geochronological data from 22 Ediacaran-Lower Devonian samples from the OMZ is reported here. Three ubiquitous detrital zircon populations characterize all of the samples: a predominant late Tonian-Ediacaran population (c. 850-540 Ma, 45-90% of the data), a secondary Paleoproterozoic (c. 2.2-1.7 Ga) peak, and a very scarce Archean (c. 2.8-2.5 Ga) population. These spectra, together with the systematic lack of Mesoproterozoic (c. 1.7-1.1 Ga) ages, are typical of West African Craton (WAC) provenance and coincide with previous data (e.g., Cambeses et al., 2017 and references therein; Solís-Alulima et al., 2022). However, a Stenian-early Tonian (c. 1.1-0.85 Ga) detrital zircon population is also sporadically present (4-8%) in a few Ediacaran-lower Cambrian samples, and becomes much more significant and systematic in Middle Ordovician-Lower Devonian rocks (c. 20% of the data). Sources of these ages are unknown in the WAC, but they have been described in NE African regions (e.g., Sahara Metacraton and/or Arabian-Nubian Shield).

Our interpretation based on these new data is that the OMZ was attached to the WAC until middle Cambrian time. Later on at late Cambrian-Early Ordovician time, a highly oblique rift favoured the right-lateral displacement of the OMZ along the northern Gondwanan margin. Therefore, since Middle Ordovician time, the OMZ would have been located close to the Saharan Metacraton, thus favouring sedimentary inputs with Stenian-early Tonian detrital zircon grains

Cambeses A., Scarrow J.H., Montero P., Lázaro C. & Bea F. (2017) - Palaeogeography and crustal evolution of the Ossa–Morena Zone, southwest Iberia, and the North Gondwana margin during the Cambro-Ordovician: a review of isotopic evidence. Int. Geol. Rev., 59, 94-130.

Rojo-Pérez E., Fuenlabrada J.M., Linnemann U., Arenas R., Sánchez Martínez S., Díez Fernández R., Martín Parra L.M., Matas J., Andonaegui P. & Fernández-Suárez J. (2021) - Geochemistry and Sm–Nd isotopic sources of Late Ediacaran siliciclastic series in the Ossa–Morena Complex: Iberian–Bohemian correlations. Int. J. Earth Sci., 110, 467-485.

Solís-Alulima B., Abati J., López-Carmona A., Gutiérrez-Alonso G., Fernández-Suárez J. & Stockli D.F. (2022) - Detrital zircon ages and provenance of a Cambrian succession in the Sierra Albarrana Domain (SW Iberian Massif). Lithos, 408-409.

# Petrology and geochemistry of marbles and calc-silicate rocks across a continental crustal section (Valle Strona di Omegna; Ivrea-Verbano Zone, Western Alps, Italy)

Bonazzi M.*[1-2] & Langone A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.
[2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* mattia.bonazzi@unipv.it

*Keywords:* Titanite, trace elements, Ivrea-Verbano Zone.

The Ivrea-Verbano Zone (IVZ, Western Alps) is a well-exposed middle-lower continental crustal section of the Pre-Alpine that escaped Alpine subduction. This crustal section records different metamorphic events related to the Variscan and post-Variscan cycles. P-T conditions increase from amphibolite to granulite facies, with increasing crustal depth. In particular, the metasedimentary sequence (the Kinzigite Formation) is best exposed along the Valle Strona di Omegna and is characterised by metapelites and metabasites with numerous marble intercalations. P-T conditions have been well constrained for both metapelites and metabasites (e.g., Kunz & White, 2019 and references therein). In this study we focused on metacarbonates that appear as layers and lenses of variable thicknesses, from a few centimetres to several tens of metres. These lithologies display a range in composition from impure marble to calc-silicates. We investigated calcite-bearing metamorphic rocks by combining petrographic analyses with geochemical data (major and trace elements) of minerals. Petrographic observation revealed that the mineral assemblages are clearly related to metamorphic grade: feldspar, amphibole and epidote are common in amphibolite facies rocks whereas scapolite, garnet and olivine appear in granulitic samples, finally clinopyroxene is present in all samples. The composition of garnets consists mainly of grossular (45-90 wt%), scapolites are present as meionite (Me> 75%) and clinopyroxene increases the MgO content as function of temperature (from hedenbergite to diopside). Trace elements concentration of major mineral phases (e.g., clinopyroxene and calcite) show a relation between chemistry and silicate modal abundances. Indeed, the thinnest layer of metacarbonate embedded within metapelites is characterized by the highest concentration of REE whereas silicate-poor or mylonitic samples shows the lowest REE concentrations.

In addition, the trace element composition of titanite shows interesting correlations with lithologies, mineral assemblages and titanite modal abundance. In order to constrain temperature, we adopted the Zr-in titanite thermometer by considering Pressure estimates from adjacent coexisting metapelitic and/or metabasic rocks. Zr-in titanite thermometer provided temperature estimates ranging from 700 up to 900°C, coherently with the metamorphic grade and comparable with temperature determined for surrounding metapelites/metabasites (Kunz & White, 2019).

Kunz B.E. & White R.W. (2019) - Phase equilibrium modelling of the amphibolite to granulite facies transition in metabasic rocks (Ivrea Zone, NW Italy). J. Metamorph. Geol., 37, 935-950.

# Exploring the Variscan syn- to post-orogenic tectonics at the Einstein Telescope site of Sardinia (Italy)

Cardello G.L.* & Longo V.

Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* glcardello@uniss.it

*Keywords:* Sardinia, crystalline rocks, faults.

The Variscan tectonics of north-eastern Sardinia is defined by syn-orogenic collision-related middle to high-T metamorphic terrains and by post-orogenic intrusions. The aim of this study lies in the understanding of the relationships between faults and intrusions in an area that has been candidate for hosting the Einstein Telescope (ET), a European third-generation underground interferometric detector of gravitational waves. Free of regional faults, the ET layout is currently projected as a triangular infrastructure (10 km long sides), whose location has been proposed because of its present-day geodynamic quietness, very low seismicity and anthropogenic seismic noise. Despite previous maps underestimated the presence of faults in the area, new fieldwork has mapped them in higher detail.

The syn-orogenic deformation of the Palaeozoic metamorphic rocks consists of distinguished fold and cleavage generations with at least two ductile phases ($D_{2+3}$) almost completely transposing the original bedding and the oldest schistosity ($S_{0+1}$), that is still visible in the south were the thermometamorphic grade is lower. The later brittle fault network affects the metamorphic-plutonic ensemble with faults that mostly run parallel to the orientation of both dykes and plutonic contacts. Fault zones are generally NNW-, and WSW-striking and are associated with either more altered bedrock and/or cataclastic bands that are locally affected by late hydrothermal circulation with thick quartz veins, thin chlorite fibers or pseudotachilites and gouge that can be as thick as a meter each. In the surroundings of the boreholes drilled at two ET vertices, multiscale morphostructural analysis and 2D Electrical resistivity tomographies was carried out. The distribution of fault zone-related morphostructures shows maximum length up to 2.5 kilometres. At depth (ca. 250 m), the tomographies show also a complex internal resistivity stratification, that consists of up to three electrolayers with variable distribution and thickness. This is related to the occurrence of faults in the bedrock corresponding to the larger morphostructural lineaments.

In conclusion, these results highlight the interaction between the syn- and the post-orogenic features that seem related to the inherited Variscan crust structure, which has a present-day implication in the groundwater flow. Evidence shows that the post-orogenic Variscan structures guided the post-orogenic dyke and vein injection. Further, the main fault zones were site of later hydrothermal circulation, possibly reactivated during the Oligocene-Aquitanian tectonics. Further studies should constrain the contribute of the eventually current differential uplift into reactivating the inherited Variscan structures to exclude the presence of neotectonics in the area.

# Ordovician tectonics in the South European Variscan Belt: correlation between Sardinia and surrounding areas

Cocco F.*[1], Loi A.[1], Funedda A.[1], Casini L.[2], Ghienne J-F.[3], Pillola G.L., Vidal M.[4], Meloni M.A.[1] & Oggiano G.[2]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [3] Institut Terre et Environnment, Strasbourg (France). [4] CNRS-IUEM, Université de Brest (France).

*Corresponding author e-mail:* fabrcocco@unica.it

*Keywords:* Gondwana, paleogeography, pre-Variscan geodynamics.

Evidence of Ordovician tectonics are well preserved in the Variscan outcrops now scattered in the Mediterranean area. The so-called Sardic Phase, a folding event deforming only the Cambrian-Lower Ordovician successions, and the related angular unconformity (Sardic unconformity), were firstly recognized in the External Zone of the Variscan basement of SW Sardinia. In SE Sardinia, another apparently time-equivalent folding event and angular unconformity (Sarrabese Phase and Sarrabese unconformity, respectively) is recorded in the shallowest tectonic unit (Sarrabus Unit) of the Variscan Nappe Zone in SE Sardinia. The Sardic and Sarrabese phases are generally considered the same event.

However, comparing the Cambro-Ordovician successions, the tectonic structures and the bio-stratigraphic data, relevant discrepancies arise between the External and Nappe Zones, suggesting that these domains did not share the same geodynamic setting and paleogeography in pre-Variscan times. The main differences include: i) a different duration of the unconformity-related gaps (17 and 6 Ma in the External and Nappe zones, respectively), ii) the presence of a thick lower Cambrian carbonate platform only in the External Zone, and iii) the occurrence of a Middle-Upper Ordovician subduction-related magmatic arc only in the Nappe Zone. Note that the activity of the volcanic arc in the Nappe Zone is coeval with uplift and erosion in the External Zone. Furthermore, the Upper Ordovician successions in the External Zone defines a rift that evolve to a passive margin, whereas in the Nappe Zone the onset of a passive margin is marked by a nonconformity above the volcanic arc. This evidence support the idea that the Sardinian block consisted of two distinct pre-Variscan terranes, entailing alternative correlations and an adjustment of the arrangement of the now scattered Variscan terranes.

The Ordovician sequences of the Eastern Pyrenees and Occitan domains share many similarities with that of Sardinia, thus these massifs have been tentatively correlated as contiguous paleogeographic domains. However, the stratigraphic and tectonic features preserved in Sardinia suggest that the Paleozoic basement of the Pyrenees and that of Occitan domains belong to two distinct pre-Variscan terrains. This suggests a correlation either with the External or the Nappe Zone and an involvement in two different geodynamic settings, according to the Sardic or Sarrabese tectonic evolution styles.

To conclude, the data from the Ordovician of Sardinia could provide key information to improve the reconstruction of the early Paleozoic paleogeography of Gondwana, as well as the complex dynamics that led to the Variscan Orogeny.

# Trace-element zoning in garnet from mylonitic micaschist of NE Sardinia

Cruciani G.*, Franceschelli M. & Fancello D.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* gcrucian@unica.it

*Keywords:* garnet, trace element, compositional zoning.

Mylonitic micaschists in the south-eastern sector of the Posada-Asinara Shear Zone in the Axial Zone of the Sardinia Variscan chain are silver-coloured foliated rocks characterized by the occurrence of reddish to brownish garnet porphyroblasts up to 1.0 cm in size. The micaschists, consist of quartz, white mica, biotite, garnet, staurolite, chlorite, plagioclase, chloritoid, and accessory ilmenite, rutile, zircon, monazite, apatite and tourmaline. The garnet porphyroblasts are enveloped by the S2 schistosity which is mainly identified by the orientation of micas. The core of the garnet contains several small inclusions of quartz, rutile, apatite and sporadic monazite and zircon grains. Iso-orientation of the inclusions results sometimes into a sigmoidal pattern resembling "snowball garnet" microstructure. Inclusions, that were observed only in the rim domain, are ilmenite, chloritoid, and staurolite. The few quartz inclusions observed in the garnet rim domain are bigger than those observed in the core. Some large garnet crystals were investigated in detail for their major and trace elements compositional zoning from core to rim. A wide core (ca. 4 mm) homogeneous in composition is $Alm_{45–50}$; $Prp_{<2}$; $Grs_{21–27}$; $Sps_{25–30}$. The grossular and spessartine garnet components show a strong and progressive decrease, counterbalanced by an either significant almandine and pyrope increase, towards a rim which is approximately up to 2 mm in thickness. The rim composition is $Alm_{85–87}$; $Prp_{10-12}$; $Grs_{2–3}$; $Sps_{1-2}$. The REE total content (∑REE) of the garnet core is significantly higher (190-370 ppm) than that observed in the garnet rim (7-13 ppm). The light-REE (i.e., La to Sm), which are detectable but lower than 1 ppm in all the analyzed cores, are below detection limit in most of the analyzed garnet rims. The higher concentrations in the core of the garnet, respect to the garnet rim, is also observed for the heavy-REE (from Dy to Lu). Yb and Lu, for example, are between 80-150 and 10-24 ppm in the garnet core, respectively, and they decrease down to >1 ppm in all the analyzed rims. The garnet cores REE patterns are strongly fractionated with chondrite-normalised abundances up to 1000 for HREE, whereas the garnet rims show less fractionated REE patterns with chondrite-normalised abundances up to 10 for the same group of elements. No noticeable Eu anomaly was observed in the REE patterns of garnet cores and rims. Among the other trace elements, the Sc, Ti, V, and Y contents are significantly enriched in the core of the garnet (Sc: 100-220 ppm; Ti: 130-235; V: 77-99; Y: 298-780), as compared to the garnet rim (Sc: 18-47 ppm; Ti: 14-45; V: 28-53; Y: 4-13). X-Ray mapping of Y shows a jump of this element content at the core/rim interface of the garnet. The above described chemical features of the studied garnets suggest that a significant role in trace element behaviour during the garnet formation was played by the growth of accessory phase, such as, for example monazite.

# Preliminary field and structural features of the Zicavo metamorphic septum, central Corsica (France)

Dulcetta L.*, Cruciani G. & Franceschelli M.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* lorenzo.dulcetta@unica.it

*Keywords:* Variscan, structures, shear zone.

The Zicavo septum in central-southern Corsica represents one of the few Variscan metamorphic units of the Corsica Island, largely intruded by late Variscan granitoids. The septum is NE-SW oriented while the main structures have a NW-SE general strike. From bottom to top, it consists of i) an orthogneiss unit; ii) a leptynite-amphibolite unit and iii) a micaschist unit. These were tectonically superposed during the D1 phase of the Variscan orogeny with the formation of wide NE-dipping shear zones with a top-to-the-SW sense of shear at the boundary between the orthogneiss and amphibolite units, and between this latter and the micaschists series (Faure et al., 2014).

The orthogneiss unit crops out with limited extension in the southern sector of the area; it is represented by two main lithological facies: a leucocratic and a melanocratic facies, both showing mm-thick quartz and feldspar porphyroblasts wrapped by biotite crystals, with the biotite amount apparently increasing in the melanocratic facies. The two orthogneiss facies show a moderate to strong mylonitic imprint with ductile rotation of porphyroblasts. The main structure is a NE-dipping, folded, mylonitic schistosity with associated a NE-plunging lineation. The leptynite-amphibolite unit crops out extensively in the central sector of the septum. It consists of banded amphibolites showing whitish to grey/black layering and intercalated a m-thick serpentinite lens, metapelitic layers, quarzites and metaconglomerates. The serpentinite crops out as a NE-dipping, seven-meters thick lens in contact with surrounding amphibolites; the metaconglomerates consist of a fine-grained matrix with cm-thick quartz porphyroblasts. In the leptynite-amphobolite unit it is sometimes possible to observe a top-to-the-SW shear component as sigma-type quartz porphyroblasts, while the main structure is a NE-dipping axial plane foliation associated with NW-SE trending, SE-plunging isoclinal folds which deform an older layering. The micaschist unit, in the northern sector of the studied area, consists of green phyllites and black metapelites in the NE and coarse-grained, biotite-garnet- and garnet-staurolite-bearing micaschists with post-kinematic andalusite in the SW, near to the contact with the amphibolite unit; an apparent increase in the metamorphic grade towards the SW has been observed. The main structure in the micaschist unit is a NE-dipping foliation, further deformed by folds with NE-dipping axes and without axial plane foliation; in few localities it is possible to recognize m-thick, sub-vertical to NE-dipping shear zones. As a whole, the Zicavo septum is largely intruded by randomly oriented plurimetric granitoids ranging from microgranites to coarse-grained sienites.

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# Incremental growth of a shallow S-type megacrystic pluton (Asinara Isl., NW Sardinia, Italy)

Langone A.*[1], Corvò S.[2], Maino M.[2] & Casini L.[3]

[1] Istituto di Geoscienze e Georisorse, CNR, Pavia. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* langone@crystal.unipv.it

*Keywords:* shallow pluton, contact metamorphism, U-Th-Pb dating.

The redistribution of magma through the lithosphere, from partially molten source zones usually localized in the lower crust or sub-lithospheric mantle to emplacement sites, is essential for the 4D chemo-thermo-mechanical evolution of the continental crust. In this contribution, we investigate the mechanism of formation of a megacrystic S-type tabular intrusion emplaced in the supra-crustal layer of a deep Variscan crustal section of the Asinara Island, N Sardinia (Italy). High-resolution LA-ICP-MS U-Pb zircon and monazite dating on granodiorite and metapelitic rocks of the contact metamorphic aureole indicate that the pluton solidified at the end of Carboniferous, between about 310 – 320 Ma. Contact metamorphic assemblages and pseudosection modelling constrain the emplacement depth in the cordierite stability field (P = 0.20 – 0.25 GPa). These petro-chronological constraints are complemented by combining field structural analysis and geochemical mapping; then, the whole geological dataset is evaluated by 2D thermal modelling to simulate various thermal histories and crystal-size distribution emerging from either multiple injection or single diapir emplacement models. The preferred emplacement mechanism is finally discussed in relation to the evolution of transient upper crustal geotherm and rheology.

# Constraints from U/Pb detrital zircon and Sm–Nd isotope data from Brittany from Cadomian and Variscan evolution

Loi A.[1], Pavanetto P.[1-2], Meloni M.A.[1] & Funedda A.*[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Instituto de Geografia, Federal University of Uberlândia (Brazil).

*Corresponding author e-mail:* afunedda@unica.it

*Keywords:* North Gondwana, Grès Armorican Formation, Brioverian.

The temporal evolution of the sedimentary source areas of the Armorican Massif, involving Ediacaran to Upper Ordovician strata, is investigated to gain insight into the palaeogeographic affinities and changes that occurred as a result of Cadomian and subsequent Variscan Orogenesis. Until now, palaeogeographic reconstructions based on geodynamic, stratigraphic and paleontological data have shown geological continuity between the Armorican Massif and the Iberian and Bohemian massifs and have allowed researchers to locate the Armorican Massif near the West African Craton and the Trans-Saharan Belt. This study goes beyond the interpretations based on lithostratigraphic correlation, which may be influenced by allocyclic factors (e.g., sea-level change) or fauna assemblages that have a wide provincial distribution, to provide a correct assessment of sediment flux. To determine the palaeogeographic location more accurately, the provenance of the siliciclastic sediments was examined in this study using U–Pb LA-MC-ICP–MS geochronology on detrital zircons coupled with whole-rock Sm–Nd and zircon Lu–Hf isotope analysis. This work was carried out on the sedimentary succession of the Medio Armorican Domain. The oldest studied sedimentary rocks were shown to belong to the Brioverian succession, which contains mainly 519–781 Ma old zircons, likely derived from sources that are still present in the Armorican basement. Successively, the lower Paleozoic succession was deposited in the rift stages of the Rheic Ocean, with contributions from a new source of 827–1,120 Ma old zircons.

A comparison of the zircon populations showed an increase in negative $\varepsilon_{Nd(t)}$ and $\varepsilon_{Hf(t)}$ values of the sedimentary supply in the post-Cadomian samples. Moreover, it revealed that the Medio and North Armorican domains had different locations during the Lower Ordovician, and that some areas of the Iberian Massif and the Medio Armorican Domain close to the Sahara Metacraton and Arabian-Nubian Shield were contiguous.

Detrital zircon age analysis of sedimentary rocks from the Medio Armorican Domain reveals a variation in source areas for the terrigenous flux between the Ediacaran and Upper Ordovician times, highlighted by the addition of new populations of zircon ages to the populations of the comparatively older strata. The first Paleozoic sedimentary strata (Initial Red Beds) have the same zircon populations provided by the erosion of the Brioverian rocks. In the Grès Armoricain Fm, zircon grains with Stenian and Tonian >800 Ma ages appear. The MAD had to be positioned toward the Saharan Metacraton and the Arabian–Nubian Shield. The lack of Stenian and late Tonian ages in the zircon populations of Ordovician sediments of the NAD implies distinct source areas that were probably located further to the west.

The result is a complex reworking of these domains during the Variscan Orogeny that amalgamates distant palaeogeographical provinces.

# Mapping heavy mineral placers bearing Ti-Zr-REE using in situ U-Th-K spectrometry: two case studies from the Variscan basement of Sardinia

Meloni M.A.[1], Loi A.[1], Cocco F.[1], Pistis M.[1], Funedda A.*[1], Naitza S.[1] & Oggiano G.[2]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* afunedda@unica.it

*Keywords:* gamma-ray logging, Rare Earth Elements, structural geology.

Heavy mineral placers deposits in marine environments are controlled by precise stratigraphic and sedimentological conditions and may host economically relevant concentrations of Rare Earth Elements (REE). A detailed field mapping aimed at defining the spatial distribution and geometry of the placer deposits is essential to properly estimate the ore relevance. In poly-deformed basements, the mineral prospection can be demanding due to structural complexity, thus additional tools to support classical mapping methods should be used to improve the accuracy of the map. In this contribution, the benefits resulting from the use of portable gamma-ray spectrometry in the mapping of heavy mineral placers are shown.

In the Nappe Zone of the Variscan basement of Sardinia, some of the Upper Ordovician siliciclastic successions are characterized by heavy minerals placer deposits mainly consisting of rutile, zircon and monazite grains. These placers have a distinctive radioactive signature related to the abundance of U and Th in zircon and monazite minerals, mainly derived from the erosion of the Middle-Upper Ordovician volcanic arc.

Performing an outcrop gamma-ray logging during the geological field survey, using a portable spectrometer connected to the GPS, allows to draw up thematic maps that identify gamma-ray facies depending on the U, Th, and K concentration in the study area. These maps make it easier to localize the geological contact and distinguish the formations characterized by different heavy mineral content, as well as define the extent of the most relevant placer deposits.

We applied this method in two areas belonging respectively to the Sarrabus unit, characterized by a polyphasic deformation and very low-grade metamorphism, and the Meana Sardo and Barbagia units, where the deformation is more penetrative and the metamorphism is higher.

In the Sarrabus unit, the gamma-ray survey allowed to accurately map the formation members with higher heavy mineral concentrations, leading to a better reconstruction of the fold geometries and the localization of the faults that affect the stratigraphic successions.

In the Meana Sardo and Barbagia units, the gamma-ray survey allowed to accurately map the thrust between the two tectonic units. In fact, the siliciclastic successions look very similar and thus difficult to be distinguished at outcrop scale; they only differ in the gamma-ray signature, characterized by higher values of U and Th in the Upper Ordovician succession of the Meana Sardo unit.

# U-Pb age constraints on Carboniferous-Permian French continental basins - implications for their depositional history and correlations with European basins

Mercuzot M.[1], Rossignol C.*[2], Bourquin S.[3], Ramezani J.[4], Ducassou C.[3], Poujol M.[3], Pellenard P.[1] & Beccaletto L.[5]

[1] Biogéosciences, CNRS-Université Bourgogne Franche-Comté, Dijon (France). [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [3] Géosciences Rennes, CNRS-Université Rennes (France). [4] Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA (USA). [5] Bureau de Recherches Géologiques et Minières, Orléans (France).

*Corresponding author e-mail:* camille.rossignol@unica.it

*Keywords:* late Paleozoic, continental Pangea basins, Variscan orogeny.

Late Carboniferous to Permian basins of western Europe (~Gzhelian to Artinskian), developed during the late stages of the Variscan orogeny in equatorial paleolatitudes. The stratigraphic context of most of these basins remains poorly constrained, because mainly based on "continental stages" (e.g., Stephanian, Autunian, Saxonian and Thuringian) that are diachronous. Therefore, correlating these basins together and with internationally recognized stratigraphic marine stages requires precise radiochronologic ages.

To the south of the Paris Basin (France), volcanic ash-fall layers (i.e., tonsteins) are interbedded in the Carboniferous-Permian sedimentary successions of the Aumance and Decize-La Machine (DLM) basins. U-Pb dating of zircon grains from these layers by laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) confirmed a late Carboniferous to Permian age (~301-290 Ma; Ducassou et al., 2019). Given the short time-intervals recorded in these basins, correlating them with other late Carboniferous to Permian basins of western Europe requires the use of high-precision chemical abrasion – isotope dilution thermal ionization mass spectrometry (CA-ID-TIMS), as successfully initiated in the neighboring Autun Basin by Pellenard et al. (2017). We therefore, we selected grains previously dated by LA-ICP-MS for analysis by CA-ID-TIMS to obtain more precise ages. The tonstein dated in the Aumance Basin (*Lien Vert* sample) together with the two tonsteins dated in the DLM Basin (LY-F well) provided ages with 2σ internal uncertainties of ± 0.35 Myr that straddle the Carboniferous-Permian boundary. In the DLM Basin, the new ages, delimiting a 151 m-thick interval (including coal, sandstones and conglomerates), suggest an outstanding sedimentation rate estimated at ~453 ± 159 m/Myr. Beyond the improvement of the French basin stratigraphy and worldwide correlations, these new ages ultimately contribute to bring new insights on both the geodynamic and climatic setting at that time. *In fine*, our new age model would also permit to refine the chronology and timing of the substantial $CO_2$ storage in sedimentary organic matter at these paleolatitudes, which is usually underestimated in climate models.

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# Post-collisional tectono-magmatic evolution, crustal fertilization, and ore genesis: the late Variscan metallogenic stages in Sardinia

Naitza S.*[1], Casini L.[2], Cocco F.[1], Funedda A.[1], Loi A.[1], Oggiano G.[2], Rossignol C.[1] & Secchi F.[2]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* snaitza@unica.it

*Keywords:* Variscan ore deposits, shear zone-driven crustal fertilization, Sardinia.

The Variscan post-collisional tectonic and magmatic events were critical for ore deposits in the Paleozoic massifs of Europe. In Sardinia, two main types of Variscan ore deposits can be recognized: (1) "orogenic", structurally-controlled deposits associated with shear zones and extensional structures; (2) granite intrusion hosted/related deposits. Both types are unevenly distributed in the Paleozoic basement and in the Sardinian batholith, being much more abundant in Southern Sardinia. "Orogenic" deposits include As-Au±Sb ± W and Zn-Cu-Pb-Ag vein systems hosted in greenschist facies metamorphics. They result from multiple mineralization stages from fluids of mixed (but dominantly metamorphic) origin at different structural levels in the nappe stack of the Variscan front, during the post-collisional extension. Large-scale antiformal structures were traps for fluids; base metal and As-Au-rich deposits prevail in deeper structural zones, whereas Sb-W (Au) deposits are related with shallower extensional structures.

Granite-hosted/related deposits consist of Mo ± Cu greisens, Pb-Zn-Cu-Fe±Sn± W±Bi±F and Pb-Zn-Cu-Fe±REE skarns, and W-Sn-Mo-Bi (±Te±Au) and Pb-Zn-F-Ba veins, also associated in magmatic-hydrothermal systems. Most intrusion-hosted/related ores may be bracketed into the latest and narrow (290-285) Ma growth stages of Sardinian Batholith. They are more abundant in southern Sardinia, associated to multiple suites of F-rich granites, including a suite of Sn-W-Mo (Bi, In)-bearing, "rare metals" granites belonging to an ilmenite rock-series (Naitza et al., 2017).

As evidenced in recent literature (Cocco et al., 2018; Secchi et al., 2022), the Paleozoic basement of Sardinia is made of micro-terranes assembled by large-scale shear zones in the post-collisional Variscan stages, when both "orogenic" and granite-related ores resulted from a wide metallogenic fertilization of the Sardinian crustal segment. These events may be tentatively framed in a context of lithospheric delamination, which triggered production and crustal-scale migration of magmas and fluids along lithospheric shear zones, widely redistributing ore-forming elements, including (a) new contributions linked to partial melting of different crustal levels and to crust/mantle interactions, and (b) widespread recycling of elements present in the pre-Variscan successions (e.g., Pb, Zn, Ba from Cambrian MVT ores of SW Sardinia; REE from Upper Ordovician paleoplacers in Eastern Sardinia). Variscan crustal fertilization was essential for the post-Variscan metallogenic stages (Middle Permian-Triassic?), during which new and widespread fluid circulation in the basement produced, in the context of the breakup of Pangea and the opening of the Tethys (Burisch et al., 2022), different kinds of low-temperature polymetallic hydrothermal ores (Pb-Zn ± Cu±Ag; Ni-Co-As-Bi-Ag; Ba-F ± Pb ± Ag), often directly remobilizing previous magmatic-hosted/related ones.

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# Sardinia a key area for the Variscan geology: main achievements in half-century of research

Oggiano G.*

Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari.

*Corresponding author e-mail:* giacoggi@uniss.it

*Keywords:* Sardinia, Variscan, geodynamics.

The Sardinian crust retains a long geological record encompassing the entire Variscan cycle. The first geological studies in Sardinia dates back to between 1820 and 1850 that is, in conjunction with the raise of modern geology - thanks to C. A. della Marmora who set the foundations of Sardinian geology toghether with the first geological map of the island. By the late $19^{th}$ century until the 1960s, mining was the driving force of in-depth studies involving specialists from all over Europe. However, researches were mostly limited to SW Sardinia where Dutch geologists significantly improved the stratigrapy and structural frame of the Paleozoic successions exposed in Sulcis-Iglesiente, where Variscan structures were firstly evidenced. On the contrary, the Variscan crystalline basement of the rest of the island was almost totally neglected until the end of the 1970s, when researches from Pisa University marked a milestone, highlighting the occurrence of regional thrusts and polyphase folding. During the 1980s, the Nappe structure of the Variscan collisional wedge was sketched and the first metamorphic zoneography outlined thanks to researches by Pisa and Siena universities. On the same time, sedimentologists from Cagliari University implemented the Paleozoic stratigraphy.

During the 1990s, a good amount of structural, petrological and geochemical data, along with the the discovery of new relict eclogites allowed to build the first self-consistent geodynamic model based on modern concepts of plate tectonics. At the start of the new millennium, the collisional frame of the Variscan segment in Sardinia was thoroughly defined thanks to new geological and structural mappings by the CARG Project and by several universities in the form of master and PhD thesis. Mean time the new methodologies in geochronology, metamorphic petrology and geochemistry applied by researchers from Cagliari, Sassari and Genoa allowed to better define the signature and the P-T-t-d paths experienced by the high-grade metamorphic rocks.

The post-collisional evolution conversely was still drawing poor attention. To bridge this gap in the 2000s, new researches focused the extensional tectonics that resulted in thermal domes, HT/LP overprinting on previous Barrovian assemblages, emplacement of the C-S batolith and Permo-Carboniferous basins. In the last years Paleomag studies were applied to reconstruct the wondering of the Sardinia crust during the dextral megashears that defined the Pangaea A configuration, whereas AMS was employed in defining the kinematic of pluton emplacement. The relationships between different series of granite, late to post-collisional tectonics and the Variscan metallogeny was finally faced with using an interdisciplinary approach by Cagliari and Sassari researchers. In spite of more than a century and half of studies, several questions stand still:

- What is the pre-Variscan palaeogeography and geodynamics, with special regard to the Sardic Phase? A detrital zircon-based study on the different structural zones has been started by Cagliari and Sassari university and it is worthy to be continue.
- What are the relationships among magmatism, HT/LP metamorphism and lithospheric shear zones? More Geochronology joined to numeric modelling is expected to get rid the uncertainty.
- What mechanism can better account for the mantle contribution to the growth of the C.S. batholith?

# Intramontane basins, magmatism and strike-slip tectonics in the late-Variscan geodynamics: evidence from North Sardinia (Italy)

Oggiano G.*[1], Gaggero L.[2], Casini L.[1] & Maino M.[3]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* matteo.maino@unipv.it

*Keywords:* late Variscan magmatism, cooling path, geochrnology.

The Corsica-Sardinia massif experienced polyphasic Variscan deformation, metamorphism and magmatism since the Devonian to Permian times. The metamorphosed Variscan crust is intruded discordantly by the Corsica-Sardinia Batholith (CSB), a huge N-S granitic ribbon composed of several plutons emplaced episodically during the Carboniferous-Permian transition (340–270 Ma; Paquette et al., 2003; Casini et al., 2012, 2015).

The evolution of the batholith reflects two main growth stages. Carboniferous plutons have a dominant crustal component and are mostly associated to conjugate E-W to NW-SE shear zones that collectively form a huge N-S granitic ribbon. The Early Permian bimodal mafic-acid complexes emplaced instead within NE-SW to NNE-SSW dilatational jogs and step-over developed along NE-SW brittle-ductile shear zones consistent with N20-40° extension. Here, the intramontane "Lu Falzu" basin consists of a thick volcano-sedimentary succession, which experienced contact metamorphism during the emplacement of the close "Bortigiadas" gabbroic intrusion. In this contribution, we show new field mapping over this unknown area integrated with U-Pb dating of both the gabbro and sediment infill. Moreover, $^{40}Ar/^{39}Ar$ data on both biotite and muscovite from the contact metamorphic aureole provide valuable information on the cooling path experienced by both gabbro and basin, with the aim to describe the tectono-metamorphic and magmatic evolution of the late-to-post collisional phases of the Sardinian Variscan crust.

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# A reappraisal of the tectono-metamorphic setting of the Variscan belt in the Baronie Region (Sardinia)

Pagano V.*, Iaccarino S., Montomoli C. & Carosi R.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* valentina.pagano@edu.unito.it

*Keywords:* Variscan belt, Barrovian metamorphism.

The metamorphic basement of the Variscan belt in Sardinia, widely crops out in a continue structural section along the Baronie Region, starting from the Low- to Medium-Grade up to the High-Grade Metamorphic Complex (L-MGMC and HGMC; Carmignani et al., 1994). The boundary between these two complexes is marked by a regional scale transpressional shear zone, the Posada Asinara Shear Zone - PASZ (Carosi et al., 2020 and references therein), whose activity was related to the exhumation of deep-seated crustal rocks. A microstructural and petrographic study was carried out along two transects orthogonal to the PASZ, showing a northward increase in the metamorphic field gradient. Three specimens of staurolite-garnet-bearing and staurolite-garnet-kyanite-bearing mylonitic micaschist have been investigated in detail for P-T estimates. The relationships between mineral growth and deformation of the main minerals, related to the Barrovian metamorphism, pointed out their growth from the late collisional stage to the beginning of transpressional shearing along the PASZ. Particularly, a post-kinematic growth of some minerals pointed out a low pressure heating stage, suggesting a polyphasic metamorphic evolution in this part of the belt. The metamorphic evolution was reconstructed with the aid of conventional (and trace element-based) thermobarometry and with the calculation of P-T pseudosections. In addition to previous petrological investigations of the area (Franceschelli et al., 1989; Carosi & Palmeri, 2002) and according to the geological literature (see Cruciani et al., 2015 and Carosi et al., 2020 for a review), these new data allow to update and refine the shape of P-T-D paths, shedding new light on the tectono-metamorphic evolution of this portion of the Sardinian belt.

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# Constraining P-T conditions in low-grade metapelites: a case study from the hinterland-foreland transition zone of the Variscan belt, Sardinia

Petroccia A.*[1], Lanari P.[2], Forshaw J.[2], Carosi R.[1], Montomoli C.[1], Iaccarino S.[1] & Vitale Brovarone A.[3-4]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Institute of Geological Sciences, University of Bern (Switzerland). [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [4] Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris (France).

*Corresponding author e-mail:* alessandrogiovannimichele.petroccia@unito.it

*Keywords:* Nappe Zone, metamorphic evolution, Low-grade metamorphism.

Although low-grade metamorphic rocks are widespread in the continental crust, they have received relatively less study than their higher-grade equivalents. Elucidating processes in low-grade rocks, and in turn their peak P-T condition, is complicated by their fine-grained nature and high variance (low number of the phases). Despite this, deciphering their P-T evolution is critical if we try to understand burial and exhumation processes during orogeny. This study examines a stack of well-exposed, low-grade tectonic units from the Nappe Zone of the Variscan belt in Sardinia. The Nappe Zone is divided into Internal and External Nappe Zones, that are separated by a major ductile shear zone (i.e., the Barbagia Thrust; Montomoli et al., 2018). In this work, we quantify the peak conditions of metamorphism, and we suggest a preliminary P–T evolution for the External and Internal Nappe Zone. This work combines detailed meso-to microstructural investigations with Raman Spectroscopy on Carbonaceous Material (RSCM; Beyssac et al., 2002) and K-white mica thermodynamic inverse modelling (Dubacq et al., 2010; detailed procedure in Lanari et al., 2012). Peak condition is ~7 kbar - 450°C and ~5 kbar - 380°C for the Internal and External Nappe Zone, respectively. We also attempted to produce a P-T path using the different compositions of the white mica. The P-T conditions suggest that both nappes experienced moderate P-T conditions during the building up of the Variscan belt in Sardinia and should therefore no longer be considered affected by only LP-LT metamorphism. The metamorphic peak conditions were probably achieved during the $D_1$ deformation stage. The exhumation started during the late $D_1$ and continued during the $D_2$ phase and the Barbagia Thrust activity.

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# Late Precambrian U-Pb zircon (LA-ICP-QMS) ages from W-Alps External Crystalline Massifs and Mendic granite (Montagne Noire)

Pin C.[1], Recourt P.[2], Guillot F.*[2] & Gerdes A.[3]

[1] CNRS, Clermont-Ferrand (France). [2] UMR8187 LOG, Univesité Lille - ULCO - IRD - CNRS, Lille (France). [3] Goethe University, Frankfurt (Germany).

*Corresponding author e-mail:* francois.guillot@univ-lille.fr

*Keywords:* Pre-Variscan basement, Alps.

The interpretation of *in situ* U-Pb radiometric data by reading a Concordia intercept on the Tera-Wasserburg diagram is debatable : the age obtained is largely constrained by data points with high ratio of non-radiogenic lead. Therefore the quoted precisions are probably deceptive (Pin & Rodriguez, 2009). An alternative approach has been tried, selecting –among the numerous measurements allowed by the GUF automated procedure– those data points showing the best concordance of the two $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ clocks. This rationale has been tested on zircon LA-ICP-QMS data obtained for the Mendic granite resulting in an age estimate of 565 ± 7 Ma (2 sd.) within error of previous results (Lévêque, 1980 and refs. therein).

The same method, for five felsic metavolcanics from the S-Belledonne, Taillefer, and W-part of the Ecrins-Pelvoux Massifs, yielded : Allemont : 531 ± 7 Ma ; Tail08-1 : bimodal distribution at 565 and 525 Ma ; Tail08-2 : 563 ± 5 Ma ; Molines : 515 ± 5 Ma ; La Motte : 510 ± 20 Ma. Rather than documenting a protracted igneous event during a 60 Ma timespan, this range of results is interpreted to reflect variable radiogenic lead loss not resolved by the *in situ* analytical approach. A Late Precambrian igneous emplacement age is believed to be most likely for all these rocks. In any case, these data clearly invalidate the classical correlations with Devono-Dinantian rocks of NE Massif Central and Vosges (Le Fort, 1973 and refs. therein).

Besides these ancient ages, about 35% of the data obtained for the La Motte sample point to a ca. 6 Ma date, suggesting a distinctive hydrothermal overprinting of Messinian age. Although this young episode waits for a confirmation, it is noteworthy that similar ages have been measured on monazites from N-Belledonne Massif (Gasquet et al., 2010).

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# Remnants of the Variscan chain across the Alps: metamorphic vs. tectonic evolution

Roda M.*[1], Spalla M.I.[1], Filippi M.[1], Rebay G.[2], Regorda A.[1], Zanoni D.[1], Zucali M.[1], Lardeaux J.M.[3] & Gosso G.[1]

[1] Dipartimento di 3Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] UMR 7329, Géoazur, Université Nice Sophia-Antipolis (France).

*Corresponding author e-mail:* manuel.roda@unimi.it

*Keywords:* Alps, tectonophysics-metamorphic evolution,Variscan crust.

Crustal slices preserving pre-Alpine metamorphic imprints are widely described in the Alps. In particular, the Variscan parageneses recorded in continental, oceanic, and mantle rocks suggest a heterogeneous metamorphic evolution across the Helvetic, Penninic, Austroalpine, and Southalpine domains. A review of tectono-metamorphic histories in all domains of the Alps, with relative age ranges, highlights that during Silurian-Devonian times (430-370 Ma) the dominant metamorphic imprint is recorded under eclogite-HP granulite facies conditions, corresponding to a mean metamorphic field gradient of 13°C/km$^{-1}$ (Franciscan). During Carboniferous (370-330 Ma) the dominant metamorphic imprints developed under amphibolite to granulite facies conditions, corresponding to a mean metamorphic field gradient of 17°C/km$^{-1}$ (Barrovian). Finally, at the Carboniferous-Permian transition (330-290 Ma) the metamorphic imprints are mainly recorded under amphibolite-LP granulite facies conditions, corresponding to a mean metamorphic field gradient of 25°C/km$^{-1}$ (Barrovian/Abukuma). This metamorphic distribution suggests a pre-Alpine burial of the oceanic and continental crust at convergent plate margins, in a context of single or double oceanic subduction, underneath a continental upper plate, followed by a continental collision (Regorda et al., 2020 and refs therein). The Variscan evolution of the Alps is discussed through the comparison with 2D numerical models of convergent systems (Regorda et al., 2020; 2021) to unravel the possible geodynamic scenario.

Regorda A., Lardeaux J.-M., Roda M., Marotta A.M. & Spalla M.I. (2020) - How many subductions in the Variscan orogeny? Insights from numerical models. Geoscience Frontiers, 11, 3, 1025-1052. https://doi.org/10.1016/j.gsf.2019.10.005.

Regorda A., Spalla M.I., Roda M., Lardeaux J. & Marotta A.M. (2021) - Metamorphic Facies and Deformation Fabrics Diagnostic of Subduction: Insights From 2D Numerical Models. Geochemistry, Geophysics, Geosystems, 22, 1-26. https://doi.org/10.1029/2021GC009899.

# A combined field, microscopic and magnetic approach to infer structural evolution mechanisms of the upper crust: an example from Serre Massif (southern Italy)

Russo D.*[1], Fiannacca P.[1], Mamtani M.A.[2], Fazio E.[1] & Cirrincione R.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Indian Institute of Technology, Kharagpur (India).

*Corresponding author e-mail:* damiano.russo@phd.unict.it

*Keywords:* microstructures, magnetic susceptibility, southern Italy.

The interplay between regional tectonics and emplacement of granitoid magmas during post-collisional evolution of the crust is often difficult to identify via traditional survey technique, since even syn-tectonic granites may not exhibit any meso- or micro-structural preferred orientation. An integrated field, microstructural and Anisotropy of Magnetic Susceptibility (AMS) study was carried out to detect any possible petrofabric, deformation microstructures and mineral preferred orientations in the granitoids that make up the upper levels of the Serre Batholith, an intermediate portion of an almost continuous and complete late Variscan crustal section. The studied units are two-mica granodiorites and granites (MBG; c. 295 Ma) passing upwards to weakly peraluminous biotite ± amphibole granodiorites (BAG; c. 292 Ma). Field investigations reveal a large transitional zone between MBG and BAG, with both rock types showing only very local anisotropic structures. Microstructures indicate deformation already at submagmatic conditions (T > 650°C), as showed by chessboard patterns in quartz crystals and limited evidence of submagmatic fractures. Grain boundary migration recrystallisation in feldspar and quartz as well as rotated larger feldspar grains surrounded by mica folia suggest high-T solid state deformation (T about 550°C), while bulging quartz grain boundaries, quartz core-and-mantle structures, deformation twins in feldspar and kinked micas are representative of subsolidus low temperature deformation (T about 450°C). Shear-related deformation is documented by sigmoidal porphyroclasts, grain boundaries orientation of polymineral aggregates and mica fish. No specific relationships between emplacement depth, age or composition and the type of deformation microstructures developed in the rocks have been found from the comparison between MBG and BAG. Exploratory AMS data reveal an internal magnetic fabric for the studied granitoids, unperceivable to field and thin-section analyses, and represented by a prevailing slightly oblate magnetic ellipsoid. Lower hemisphere equal area projections suggest a similar influence of the local stress field on the magnetic fabric orientations while magnetic foliation and lineation arrays provide hints about post emplacement tectonics or, alternatively, reflect the geometry of the batholith roof levels. This research provides new information on the Serre upper crustal granitoids and underline the importance of AMS in obtaining constraints on relationship between tectonics and magma emplacement from apparently isotropic rocks.

# High-temperature albitites from late-Variscan Sàrrabus pluton (SE Sardinia, Italy)

Secchi F.[1-2], Naitza S.*[2-3], Oggiano G.[1], Casalini M.[4], Conte A.M.[2], Ferrero S.[3] & Giovanardi T.[5]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [4] Dipartimento di Scienze della Terra, Università di Firenze. [5] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* snaitza@unica.it

*Keywords:* HT albitites, shear zone-related metasomatism, Sàrrabus pluton.

Uncommon high-temperature Na-metasomatized rocks close to sodic fenites are hosted in coeval granodiorites from the late-Variscan (286 ± 2 Ma) Sàrrabus pluton (SE Sardinia). They show sharp contacts with the host rocks and consist of small, irregular lenses of "spotted" rocks and hectometric layered, albititic bodies, scattered along a 15 km-long WNW trending extensional shear zone.

Alkali metasomatized rocks locally preserve the original textural and mineralogical features of granodiorites and display pervasive coarse recrystallization textures, with a wide range of mineral assemblages.

Spotted rocks display variably albitized plagioclase and anhedral K-feldspar, with interstitial aggregates of low-Ti diopside, partially or totally replaced by hastingsitic amphibole, producing the "spotted" macroscopic aspect. As the metasomatism becomes more pervasive, xenomorphic or granoblastic textures with low Ti-andraditic garnet coexisting with a clinopyroxene close to aegirine-augite occur in the rock. Several stages of metasomatism are revealed by dark mica + albite occurring as micro granoblastic aggregates along intergranular boundaries, and as chessboard albite replacing K-feldspar. Magnetite, titanite and apatite are ubiquitous accessory phases. Rare quartz with mortar textures occur in veinlets and pegmatitic pockets.

Albitites show $\varepsilon Nd_{286}$ in the range of -6.29 ÷ -6.78, overlapping the values observed for host granodiorites (-5.53 ÷ -6.40). $^{87}Sr/^{86}Sr_{286}$ is in the range of 0.70922 ÷ 0.71140, slightly higher than 0.70865 ÷ 0.70969 of granodiorites. This confirm alkali metasomatism of a granodioritic protholith, caused by rock-interaction with Na-enriched, silica undersaturated fluids. Phase relationships for metasomatic systems and several calibrations constrain the P-T-$fO_2$ conditions in the range of 2.0 ÷ 2.2 kbars, 450 ÷ 710°C, and -18.5 ÷ -16.2, respectively.

Several stages of metasomatism occurred inthe granodioritic intrusion while the latter was still cooling. These stages were controlled by fault development and by continuous variations in physico-chemical parameters of the fluids, with T decreasing from near-solidus to sub-solidus and hydrothermal conditions. Schematically, metasomatic stages may be summarized into: (1) HT quartz removal (desilication) + albitization + primary biotite destabilization + Ca-silicate (Cpx, Grt) formation (2) fluid-controlled metasomatic reactions leading to partial consumption of Cpx and Grt and to Amph, Tit and Mt production, and (3) final widespread albitization with hydrothermal hastingsite, Bt and local quartz precipitation. Overall, high-temperature processes resulted in a singular "sodic fenite" stage, with coarse recrystallization textures under near-solidus temperatures that overlaps those of magmatic stage. High temperature textures are then overlapped by lower temperature stages with a general increase in Na, $fO_2$ and $aH_2O$ in the fluids, with a final and widespread albitization which may be interpreted as a true episyenitization stage.

# "S" type syncollisional granite of Kasimovian age (Upper Carboniferous) from the Cap Bougaroun basement (Collo, Northeastern Algeria): Evidences from petrogeochemistry and U-Pb geochronology

Seffari A.*[1-2], Abdallah N.[1], Bruguier O.[3], Bosch D.[3], Afalfiz A.[1], Yelles-Chaouchea A.[2], Lekouia A. [4] & Ouabadi A.[1]

[1] Laboratoire de Géodynamique Géologie de l'Ingénieur et Planétologie, University Of Science And Technology Houari Boumediene, Bab Ezzouar (Algeria). [2] Center of Research in Astronomy, Astrophysics, and Geophysics, Algiers (Algeria). [3] Géosciences Montpellier, CNRS-Université de Montpellier (France). [4] Département des Sciences de la Terre et de l'Univers, Université Mohamed Seddik Ben Yahia, Jijel (Algeria).

*Corresponding author e-mail:* abderraouf.seffari@craag.edu.dz

*Keywords:* S type granite, zircon U-Pb geochronology, kabylian basement.

In the North Eastern of Algeria, metamorphic basements outcrop as a relic assigning the end of Paleozoic history, they are distributed along coastal area from Jijel to the west, Collo until Skikda to the east. The associated granite represents an important part of their lower unit. The granites of the Cap Bougaroun basement (Collo) are studied in order to shed the light on their petrographical, geochemical and geochronological characteristics. These granites are cordierite and sillimanite – rich rocks and vary in their composition from monzogranites to syenogranites. The geochemistry of these granites indicates that they are of S-type exhibiting a peraluminous character with high normative Corundum values (4.1 -9.5%) and are shoshonitic with higher K content than Na. They are enriched in LREE and LILE relative to HREE and HFSE respectively with high (La/Yb) N ratios (15.65-24.86) which is often explained by the presence of garnets in source rock during partial melting, and thus confirm that these rocks are anatectic granites. Moreover, in the geotectonic discrimination diagrams, these peraluminous anatectic rocks plot within the field of the syn-collisional granites.

New U-Pb data on zircon (LA-ICP-MS) obtained from the syn-collisional granites of Cap Bougaroun, in addition to those obtained on the post-collisional granites of the Karkera (Peucat et al., 1996) (5 km from the Cap Bougaroun basement). Allowed the distinction of two granite ages: (1) Late Carboniferous (Kasimovian) syn-collisional age of 304 ± 3 Ma, and. (2) Post-collisional Lower Permian age of 280 ± 5 Ma. According to these results, the emplacement of the S-type granites corresponds to the collision process between Gondwana and Laurussia at 304 Ma while the Kerkera granite has been probably emplaced along a detachment fault of a metamorphic core complex, during the stress release phase following the collision at 280 Ma.

Peucat J.J., Mahdjoub Y. & Drareni A. (1996) - U-Pb and Rb-Sr geochronological evidence for late Hercynian tectonic and Alpine overthrusting in Kabylian metamorphic basement massifs (northeastern Algeria). Tectonophysics 258, 195-213. https://doi.org/10.1016/0040-1951(95)00197-2.

# Ladinian biostratigraphic data from Sardinia (Italy) as a tool to reconstruct the Tethys transgression in Western Paleoeurope

Stori L.*[1], Ros Franch S.[2], Márquez-Aliaga A.[2], Goy A.[3], Marquez-Sanz L.[2], López-Gómez J.[4], Martín-Chivelet J.[3-4] & Ronchi A.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Department of Botany and Geology, Universitat de València (Spain) [3] Departamento de Geodinámica, Estratigrafía y Paleontología, Universidad Complutense de Madrid (Spain). [4] Instituto de Geociencias, CSIC-Universidad Complutense de Madrid (Spain).

*Corresponding author e-mail:* lorenzo.stori01@universitadipavia.it

*Keywords:* biostratigraphy, Tethys, Muschelkalk.

The Sardinian Middle Triassic successions (SMTs) have been studied from the end of the 19th century as they were long recognized as a key-stratigraphic element in understanding the palaeogeographical evolution of the Tethys western sector. Indeed, the debate on the precise position of the Island in this context is still open. The SMTs were ascribed for long time to the Germanic facies (Buntsandstein, Muschelkalk and Keuper). Moreover, due to the alpine tectonics, they are deeply dislocated and outcropping in different sectors of the Island, mainly in the South-West, the Central-East, and North-West. Despite these challenging features and their reduced thickness, they do contain biostratigraphic key-elements that allow fundamental insights about the timing and modalities of the Western Tethys transgression. This large-scale event happened though a complex network of marine corridors and created connections between different palaeogeographic areas which, until then, were prevented by the presence of tectonically elevated blocks. In this context Sardinia, together with Minorca and the eastern area of Castellón (E Spain), constituted an elevated area and acted as a barrier between the Paleotethys (NE) and Neotethys domains (SE).

The present work focuses on a detailed stratigraphical and paleontological analysis of the Middle Triassic p.p. (Ladinian) in Muschelkalk facies and aims to better unravel the paleogeographic evolution of the island during this time-frame. These shallow marine successions contain a significant palaeontological record comprising facies and marker fossils (ammonoids, bivalves, conodonts, foraminifera etc.) which are linked to a regional transgressive episode recorded throughout the W Mediterranean. The palaeontological content was particularly rich in the Nurra and Sarcidano-Gerrei sections, and show the progressive westward settling of carbonate platforms, and consequently the development of new migration and irradiation routes for (i) the Sephardi faunas from the SE (Paleotethys) and (ii) Alpine faunas (Neotethys) from the NW. The accurate study and revision of these paleontological associations, both from previous collection of an Italian-Spanish team and new findings, allowed us also to compare them with those of the adjacent domains (Balearic Islands, Levantine area) refining their palaeoecological distribution and to better framing Sardinia as a key-sector in the palaeogeographic evolution of the Western Tethys during the Ladinian.

# S42.

# Faults and shear zones: the pathways for fluids

*Conveners & Chairpersons*

*Laura Federico (University of Genova)*

*Matteo Maino (University of Pavia)*

*Nadia Malaspina (University of Milano-Bicocca)*

# Fluid-assisted deformation processes at the roots of oceanic transform faults: a case study

Bickert M.*[1], Kaczmarek M.A.[2], Maia M.[3] & Brunelli D.[1-4]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Géosciences Environnement Toulouse, CNRS-CNES-IRD-Université Toulouse III, Observatoire Midi Pyrénées, Toulouse (France). [3] Laboratoire Geosciences Ocean, CNRS and University of Brest, LGO-IUEM, Plouzané (France). [4] Istituto di Scienze Marine, CNR. Bologna.

*Corresponding author e-mail:* manon.bickert@unimore.it

*Keywords:* ultramafic mylonites, dissolution-precipitation creep, oceanic transform fault.

Oceanic Transform Faults (OTFs) are major plate boundaries that regularly offset the axis of Mid-Oceanic Ridges. Yet, very little is known on the evolution of fault slip mechanics at depths, mainly due to the extreme rarity of deep section' exposures. The Atobá Ridge is one of the rare structures exposing mantle rocks in correspondence of an active transform fault. This transpressive ridge is part of the northern transform fault of the St. Paul transform system in the Equatorial Atlantic (Maia et al., 2016). There, ultramafic mylonites are tectonically exhumed along the inner thrust faults of a positive flower structure.

Here we study the deformation mechanisms in ultramafic mylonites sampled at the Atobá ridge. We show that all samples experienced ductile deformation at 900-750°C in the spinel stability field, resulting in a pervasive grain size reduction. We propose fluid-assisted dissolution-precipitation creep as main deformation mechanism, forming selvages of olivine and minor phases' neoblasts (pyroxenes, spinel, and amphibole). Orthopyroxene neoblasts formed by this mechanism mimic the Crystallographic Preferred Orientation of the olivine neoblasts. This mechanism, previously reported in ophiolites and orogenic contexts (Hidas et al., 2016; Prigent et al., 2018), is described for the first time in the oceanic transform environment. Fluid-assisted dissolution-precipitation creep allows deformation of stiff minerals at significant lower stresses and temperatures than dislocation creep, possibly leading to an intense strain localization. Similar microstructures have been observed in mylonites from other OTFs, suggesting that this mechanism could be more widespread and could even represent one of the main deformation law in the lower oceanic lithosphere, with important implications on the structures of (oceanic) transform faults and long-lived detachments.

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# The structure of segmented normal fault surfaces and its impact on fluid flow

Camanni G.*[1-2], Roche V.[1-3], Childs C.[1-3], Manzocchi T.[1-3], Walsh J.[1-3], Conneally J.[1-3], Saqab M.M.[4] & Delogkos E.[1]

[1] Fault Analysis Group, School of Earth Sciences, University College Dublin (Ireland). [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Irish Centre for Research in Applied Geosciences, School of Earth Sciences, University College Dublin (Ireland). [4] Norwegian Geotechnical Institute, Perth (Australia).

*Corresponding author e-mail:* giovanni.camanni@unina.it

*Keywords:* 3D fault geometry, 3D relay zone, fluid flow.

Normal faults are often complex three-dimensional structures comprising multiple sub-parallel segments separated by intact or breached relay zones. Current models for the geometry and formation of relay zones between adjacent fault segments have been informed mainly by 2D analysis from either maps or cross-sections observed in outcrop and, to a lesser extent, by the analysis of relay zones from 3D seismic reflection data. Using high quality 3D seismic reflection datasets from a selection of sedimentary basins, we here investigate fundamental characteristics of segmentation from the analysis of 67 normal faults with modest displacements (< ca. 190 m) which preserve the 3D geometry of 532 relay zones. We initially look at individual relay zones and successively at how relay zones arrange together into forming complex fault surfaces. Our analysis shows that individual relay zones most often develop by bifurcation from a single fault surface but can also arise from the formation of segments which are disconnected in 3D. Relay zones generally occur between fault segments that step in either the dip or strike direction, and oblique relay zones with an intermediate orientation are less frequent. Cross-sectional stepping of relay zones typically forms contractional rather than extensional relay zones. Where a significant number of relay zones are mapped on a single fault surface, a wide variety of fault surface geometries occurs. The complex geometry of fault surfaces can be described in terms of the relative numbers of different types of relay zones. Comparing datasets from different geological settings suggests that the mechanical heterogeneity of the faulted sequence and the influence of pre-existing structure are the underlying controls on the geometry of segmented fault surfaces, and different combinations of these two controls can account for the variation in 3D fault zone structure observed between datasets. It is intended that the generalised description of the structure of fault surfaces can be of value for many practical applications including, among others, the evaluation of fault controls on the flow of mineralising fluids in ore systems as well as of $CO_2$, energy ($H_2$), and hydrocarbons within faulted reservoirs.

# Seismically-induced fluid-fluxed melting of continental crust (N Sardinia, Italy)

Casini L.*[1], Langone A.[2-3], Oggiano G.[1], Estrada J.R.[4] & Liesa M.[5]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] Departament de Geologia Petrologia i Geoquimica, Universitat Autònoma de Barcelona (Spain). [5] Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (Spain).

*Corresponding author e-mail:* casini@uniss.it

*Keywords:* pseudotachylites, HT-LP metamorphism, anatexis.

The Variscan high-grade metamorphic basement of northern Sardinia and southern Corsica record lower Carboniferous anatexis related to post-collisional decompression of the orogen. Migmatites exposed in the Punta Bianca locality (Italy), consist of quartz + biotite + plagioclase + K-feldspar orthogneisses, garnet and cordierite-bearing diatexite and metatexites, that is sillimanite/cordierite-bearing migmatites derived from metasediments. Field evidence, petrographic observations, ELA-ICP-MS zircon and monazite dating and pseudosection modelling suggest that anatexis involved two main stages of partial melting. Pseudosection modelling indicates that the first stage of partial melting is in the upper amphibolite facies (P>0.45 GPa, T~740°C). The age of the first anatectic event is not precisely constrained because of extensive resetting of the isotopic systems during the second melting stage; yet few lower Carboniferous zircons match the age of regional anatexis in other migmatitic massifs of the Corsica-Sardinia block. This lower Carboniferous migmatitic fabric is offset by a network of pseudotachylite-bearing faults suggestive of cooling to greenschist-facies conditions. Garnet/cordierite-bearing diatexites incorporate fragments of pseudotachylite-bearing orthogneiss and metatexites. Pseudosection modelling indicates nearly isobaric re-heating up to ~750°C, followed by further cooling below the solidus. The inferred P–T path is consistent with decompression and cooling of the Variscan crust through post-collisional extension and collapse of the thickened orogenic crust, followed by nearly isobaric re-heating at low pressures (~0.3 GPa) yielding to fluid-fluxed melting under LP-HT conditions. U/Th-Pb monazite ages of diatexite cluster around 316-310 Ma, mostly matching the age of pseudotachylites. These observations indicate that seismic deformation established a dynamic porosity triggering fluid-fluxed melting of otherwise relatively dry and refractory rocks.

# Fault-related fractures of the Rennick-Aviator shear zone (north Victoria Land, Antarctica): insight to infer the paleo fluid circulation

Cianfarra P.*[1], Locatelli M.[1], Federico L.[1], Morelli D.[1], Salvini F.[2], Läufer A.[3] & Crispini L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Scienze, Università di Roma Tre. [3] Federal Institute for Geosciences and Natural Resources, Hannover (Germany).

*Corresponding author e-mail:* paola.cianfarra@gmail.com

*Keywords:* structural inheritance, fault-related fracture, secondary permeability.

North Victoria Land (NVL), located at the Pacific-Southern Ocean termination of the Transantarctic Mountains (TAM), presents a complex architecture deriving from a long-lasting tectonic evolution. After the Paleozoic juxtaposition to the East Antarctic craton, NVL was affected by i) the Gondwana breakup which led to the Meso-Cenozoic rifting-drifting between Antarctica and Australia, ii) the rifting in the Ross Sea, iii) the uplift of the TAM and iv) the SE prosecution of the kinematics that characterize the spreading of the Southern Ocean (e.g., Tasman and Balleny Fracture Zone).

Regionally sized, crustal scale faults crosscut VL from the Southern Ocean to the Ross Sea and represent Paleozoic inherited weakness zones that have been reactivated several times until Recent. These are both first-order faults, which separate different crustal blocks (from W to E, the Wilson, Bowers, and Robertson Bay terranes), and second-order faults that cut through homogeneous lithotectonic units. This long-lived tectonic history produced zones of intense deformations, often accompanied with fluid circulations (e.g., Malatesta et al., 2021) and exhumation of deep shear zones.

In this work we present preliminary results of the analysis of fractures associated to the Rennick-Aviator km-scale fault corridor. Specifically we explore the intensity of brittle deformation, its spatial distribution and relation with the regional faults aimed to quantify the spatial variation of the hydraulic properties (e.g., secondary permeability) of the damage zones. Moreover, fault and fracture inversion for paleostress computation is applied to infer the most permeable fracture population (e.g., fracture kept open from the acting paleostress that increases the secondary permeability in a specific direction and thus enhance fluid circulation along preferential pathways).

In NVL various fault zones are characterized by hydrothermal mineral alteration (e.g., Crispini et al., 2011; Malatesta et al., 2021) this study represents the basis to identify the main fluid pathways and to estimate the rock volume affected by hydrothermal fluid circulation.

Crispini L., Federico L., Capponi G. & Talarico F. (2011) - The Dorn gold deposit in northern Victoria Land, Antarctica: Structure, hydrothermal alteration, and implications for the Gondwana Pacific margin. Gondwana Research, 19, 128-140. https://doi.org/10.1016/j.gr.2010.03.010.

Malatesta C., Crispini L., Ildefonse B., Federico L., Lisker F. & Läufer A. (2021) - Microstructures of epidote-prehnite bearing damaged granitoids (northern Victoria Land, Antarctica): clues for the interaction between faulting and hydrothermal fluids. Journal of Structural Geology, 147, 104350-104370. https://doi.org/10.1016/j.jsg.2021.104350.

# Syn-tectonic gypsum veins in the Eocene-Miocene eastern Pisco forearc basin, Peru margin

Ciattoni S.*[1], Di Celma C.[2], Mazzoli S.[2], Megna A.[3], Pierantoni P.P.[2], Santini S.[1] & Volatili T.[2]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Scuola di Scienze e Tecnologie, Università di Camerino. [3] INGV, Sismologia e Tettonofisica, Roma.

*Corresponding author e-mail:* saraciattoni@gmail.com

*Keywords:* Peru margin, gypsum veins, structural geological survey.

The Peruvian forearc basin system (4-20°S) is an example of double forearc basins parallel to the trench (Thornburg & Kulm, 1981). The area of the present study is the eastern Pisco Basin, an elongated NW-SE depression belonging to the Peruvian forearc system. The eastern Pisco Basin has experienced substantial subsidence during Cenozoic (Viveen & Schlunegger, 2018) and its exhumation is interpreted as being related to the passage of the subducting Nazca Ridge during the Quaternary. The basin is characterised by a wide occurrence of gypsum veins in different arrays. The field study showed that gypsum veins pervade the whole sedimentary succession, despite the absence of evaporitic layers in the area (Rustichelli et al., 2016). Gypsum veins are present with different patterns and sizes from the non-conformity at the base of the sedimentary sequences (Eocene) up to the most recent formations (Miocene). Moreover, paleontological studies carried out in the area pointed out that calcareous fossils are generally replaced by gypsum (Gioncada et al., 2018). The structural geological survey was integrated with digital-based data from 3D virtual models of key outcrops generated by means of photogrammetry techniques. The relationships between vein arrays and faults were also analysed. Furthermore, we performed a detailed analysis of veins for each geological formation and investigated the orientation, size, and minerals of the veins. Mineralogical and geochemical studies (Sr isotopes) were performed to obtain information on the origin of the gypsum. Understanding the timing and the mechanism that generated the veins may provide an important and innovative contribution to the study of the geological evolution of the area.

Gioncada A., Petrini R., Bosio G., Gariboldi K., Collareta A., Malinverno E., Bonaccorsi E., Di Celma C., Pasero M., Urbina M. & Bianucci G. (2018) - Insights into the diagenetic environment of fossil marine vertebrates of the Pisco Formation (late Miocene, Peru) from mineralogical and Sr-isotope data. Journal of South American Earth Sciences, 81, 141-152.

Rustichelli A., Di Celma C., Tondi E., Baud P. & Vinciguerra S. (2016) - Fibrous gypsum veins as diffuse features and within fault zones: the case study of the Pisco Basin (Ica desert, southern Peru). Journal of the Geological Society, 173(3), 405-418.

Thornburg T.M. & Kulm L.D. (1981) - Sedimentary basins of the Peru continental margin: structure, stratigraphy, and Cenozoic tectonics from 6ºS to 16ºS latitude. In: L.D. Kulm, J. Dymond, E.J. Dasch, & D.M. Hussong Eds., Nazca plate: crustal formation and Andean convergence. Geological Society of America, Memoir, 154, 393-422.

Viveen W. & Schlunegger F. (2018) - Prolonged extension and subsidence of the Peruvian forearc during the Cenozoic. Tectonophysics, 730, 48-62.

# Role of fluids and inherited compositional and structural heterogeneities in shear zone development at mid-low crustal levels: from meso- to micro-scale structural and petrological investigations

Corvò S.*[1-2], Piazolo S.[3], Seno S.[1] & Langone A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] School of Earth and Environment, University of Leeds (UK).

*Corresponding author e-mail:* stefania.corvo@unipv.it

*Keywords:* shear zone, mid-low continental crust, strain localization.

Unravelling the evolution of shear zones is crucial to understand the deformation of the crust and the evolution of rifted margins. However, despite their intrinsic importance, how strain is distributed within the lithosphere at different scale and where it localizes to initiate the development of shear zones, are key questions in geodynamic studies (Whitney et al., 2013; Pennacchioni & Mancktelow, 2018). In this contribution, we investigate a major extensional shear zone (the Anzola shear zone) developed in the middle to lower continental crust of a fossil passive margin (the Ivrea-Verbano Zone, Southern Alps, Italy) with the aim to assess the conditions promoting the strain localisation. New field data revealed that the Anzola shear zone overprinted basement rocks characterized by lithological heterogeneities and structural (folds) features. Gabbroic rocks and migmatites define the hanging wall and footwall respectively. According to the petrography and geochemistry (ultra-)mylonitic rocks developed at the expense of a multi-lithological sequence showing amphibolite to granulite facies metamorphic conditions and deformation features related to pre-shearing event. We argue that the shear zone development was promoted by the rheological contrasts between the hard isotropic gabbro and granulites at the hanging wall and migmatites at the footwall. In particular, the lithological contrast between the isotropic strong gabbro and the weaker multi-lithological assemblages provides the ideal place to drive the strain localization into a narrow rock volume. In addition, syn-deformational partial melting and small amounts of free fluids enhanced the viscosity contrasts of the multi-lithological complex, acting as further weakening mechanism controlling the strain localization. This last aspect was further investigated through a detailed microstructural and petro-chronological study performed on titanite collected from the mylonitic amphibolites of the Anzola shear zone. We observed that titanite recorded contrasting correlations between microstructural and petrochronological features at the micro-scale in dependence of the composition and rheology of the host rock. We suggest that the different titanite behaviour and dating results were strongly influenced by the fluid-rock interaction occurring along the grain boundaries. Therefore, our findings highlight those pre-existing heterogeneities relate to rock composition, deformation and metamorphism represent the preferential loci for strain localization and the infiltration of fluids controlling the initiation and development of rift-related structures at the middle/lower crust of passive margins.

Pennacchioni G. & Mancktelow N.S. (2018) - Small-scale ductile shear zones: neither extending, nor thickening, nor narrowing. Earth-Science Reviews, 184, 1-12.

Whitney D.L., Teyssier C., Rey P. & Buck W.R. 2013. Continental and oceanic core complexes. Bulletin, 125(3-4), 273-298.

# Structural evolution of fault zones developed in dolostones in the SW Matese Mts

Diamanti R.*, Camanni G. & Vitale S.

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli "Federico II".

*Corresponding author e-mail:* renato.diamanti@unina.it

*Keywords:* fault zone analysis, dolomite rheology, pulverization.

This work presents a multi-scalar and multi-methodological approach to reconstructing the structural evolution of fault zones hosted in the Triassic dolomite succession of the SW sector of the Matese Mts in the southern Apennines. These fault zones are characterized by wide damage volumes, including pulverized dolomite rocks arranged in complex geometric patterns. The analyzed fault systems show complex arrays of slip surfaces, including a major N-S normal fault crosscut by NE-SW and NW-SE strike-slip faults. Extensive powder bodies are heterogeneously distributed within the damage zone occurring in patches of variable size (10s 100s of meters) and adjacent to the fault cores of both systems of faults. We identified different brittle structural facies, including i) cataclastic to ultra-cataclastic facies; ii) wide volumes of pulverized "dolomite flour"; iii) foliated cataclasite; iv) cataclastic shear bends; v) hydrothermalized dolomite; vi) unstrained rock lithons. We analyzed several samples of deformed dolomites collected within the different tectonic facies by means of optical and electron microscopes. We gathered information on morphometric and fractal attributes of the cataclastic fabric through the image analysis on microphotographs.

# Controls of fault zone architecture on fault-related fracture density: a case study from shallow-water carbonates of southern Italy

Ferrandino V.*[1-2], Camanni G.[1], Vinci F.[3], Tavani S.[1-4], Mazzoli S.[5], Corradetti A.[6], Parente M.[1] & Iannace A.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Fisica e Geologia, Università di Perugia. [3] PanTerra Geoconsultants, Leiderdorp (Netherlands). [4] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [5] Scuola di Scienze e Tecnologie, Università di Camerino. [6] Dipartimento di Matematica e Geoscienze, Università di Trieste.

*Corresponding author e-mail:* vf.ferrandino@gmail.com

*Keywords:* fault structure, fault-related fractures, fluid flow.

Fault zones can often display a complex internal structure associated with antithetic faults, branch and tip points, bed rotations, bed-parallel slip surfaces, and subordinate synthetic faults. We explore how these structural complexities may affect the development of fault-related fractures as displacement accumulates. We analysed in detail an incipient fault zone within well-bedded, shallow-water carbonates of the southern Apennines thrust belt (Italy). The fault zone crops out with quasi-complete exposure at a reservoir scale on an inaccessible sub-vertical cliff face, and fault and fracture mapping were carried out on a 3D virtual outcrop model of the exposure built for this study using photogrammetry. Comparing the structure of the fault zone and the density of 9444 mapped fractures allowed us to unravel their spatial relationships. Our results show that the areas of denser fractures coincide with: (i) rock volumes bounded by antithetic faults developed within the fault zone, (ii) branch points between these antithetic faults and fault zone-bounding fault segments, (iii) fault zone-bounding fault segments associated with significant displacement gradients, and (iv) relay zones between subordinate synthetic faults. These findings may aid locating sub-seismic resolution volumes of dense fracturing and associated enhanced permeability and can be therefore significant for evaluating the flow of energy ($H_2$, geothermal heat), $CO_2$, and hydrocarbons within faulted reservoirs.

# Fluid circulation during the early stage of the Pangea break-up: preliminary minero-petrographic and fluid inclusion evidence from the Calizzano Massif (Pre-Piedemont Domain, Ligurian Alps).

Filipponi L.*[1], Ferrando S.[1] & Decarlis A.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Earth Science Department, Research and Innovation Center on CO2 and Hydrogen, Khalifa University, Abu Dhabi (United Arab Emirates)

*Corresponding author e-mail:* loris.filipponi@edu.unito.it

*Keywords:* metasomatism, fault, Case Tuberto-Calizzano Unit.

In the research of processes associated with divergent margins, many studies are carried out based on observation in fossil contexts and focus on the processes related to the opening of the Alpine Tethys, through evidence of metamorphic and pre-, syn- and post-rift sedimentary stages and associated fluid circulation, still present in the Alpine chain. An example is the Ligurian Alps, located in the southern sector of the Western Alps and in particular the Case Tuberto-Calizzano Unit, belonging to the Pre-Piedemont domain (Decarlis et al., 2017). In this area, the Variscan continental basement locally show transitional contact to Triassic polymictic breccias, formed by extensional tectonic-sedimentary processes involving the basement and the pre-rift carbonatic platform. Both in the basement and in the breccias, evidence of metasomatism has been reported (Decarlis et al., 2017), which suggests a possible relevant role of fluids, during the tectonics associated with rifting.

The main goal of this work is to characterize the metasomatic mineral assemblage recorded by the basement and the polymictic breccias of the Case Tuberto-Calizzano Unit, with the aim of relating its genesis within the geodynamic context of the opening of the Alpine Tethys. To achieve this goal, a detailed study was carried out in Mereta-Calizzano, in which the gradual passage from the basement to the breccias is observed.

The detailed analysis in cathodoluminescence and SEM-EDS carried out in the polymictic breccias, i.e., the lithology most affected by the metasomatic processes, allowed to identify several generations of white mica, feldspar and calcite, among the main minerals. Moreover several accessory minerals, with chemical composition closely related to circulating fluids, are also recognized. Finally, a preliminary petrography of primary fluid inclusions within quartz veins has been also carried out.

The data obtained in this work suggest that the possible genesis of the metasomatic fluids would be related to circulation of hot fluids (at least 250°C) in an epithermal system.

Decarlis A., Fellin M. G., Maino M., Ferrando S., Manatschal G., Gaggero L., Seno S., Stuart F.M. & Beltrando M. (2017) - Tectono-thermal Evolution of a Distal Rifted Margin: Constraints from the Calizzano Massif (Prepiedmont-Briançonnais Domain, Ligurian Alps). Tectonics, 36. https://doi.org/10.1002/2017TC004634.

# Hydrocarbon-bearing fluid migration produces brecciation at high pressure condition in subduction

Giuntoli F.*[1], Vitale Brovarone A.[1-2], Menegon L.[3], Siron G.[1] & Cognigni F.[4]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris (France). [3] Department of Geosciences, University of Oslo (Norway). [4] Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Sapienza Università di Roma.

*Corresponding author e-mail:* francesco.giuntoli@unibo.it

*Keywords:* hydrocarbon-bearing fluid, brecciation, EBSD.

It has been recently proposed that high-pressure genesis of abiotic hydrocarbon can lead to strain localization in subducted carbonate rocks (Giuntoli et al., 2020). However, the mechanical effects of the migration of these hydrocarbon-bearing fluids on the infiltrated rocks still need to be constrained.

In this study, we investigate omphacitite (i.e., omphacite-rich rock) adjacent to an high-pressure methane-rich fluid source from the Western Italian Alps (Italy) using a multiscale and analytical approach including petrographic, microstructural, X-ray compositional mapping and electron backscatter diffraction analyses (EBSD). In the field, omphacitite bands are 1-5 metres thick and tens of metres long and are adjacent to carbonate rocks affected by high-pressure reduction and methane-rich fluid production.

Hand specimens and thin sections display a brecciated structure, with omphacitite fragments ranging in size from a few microns to several centimetres, surrounded by a matrix of jadeite, omphacite, grossular, titanite, and graphite. X-ray compositional maps and cathodoluminescence images highlight oscillatory zoning and skeletal (jackstraw) textures in jadeite, omphacite and garnet in the matrix, suggesting a fast matrix precipitation under plausible disequilibrium conditions. $CH_4$ and $H_2$ are found in fluid inclusions in the jadeite grains. This feature suggests a potential link between the genesis of $CH_4$ in the adjacent carbonate rocks and the brecciation event.

EBSD analysis was performed on omphacitite clasts close to their borders, where omphacite grain size varies between a few microns and a maximum of 100 microns. Those omphacite grains display no crystallographic preferred orientation, abundant low angle boundaries and low (< 5°) internal lattice distortion. We interpret these textures as formed by pervasive and diffuse micro-fracturing related to the brecciation occurring at high pore fluid pressure, reaching sub-lithostatic values. This study suggests that at high-pressure conditions in subduction zones, the genesis and migration of hydrocarbon-bearing fluids can trigger fracturing in adjacent lithotypes.

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Giuntoli F., Vitale Brovarone A. & Menegon L. (2020) - Feedback between high-pressure genesis of abiotic methane and strain localization in subducted carbonate rocks. Sci. Rep., 10, 9848. https://doi.org/10.1038/s41598-020-66640-3.

# Exhumation-related mylonite, cataclasite and pseudotachylyte in the Brossasco-Isasca Unit (Dora Maira Massif, Western Alps): from field mapping to microstructures

Iaccarino S.* & Dana D.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* salvatore.iaccarino@unito.it

*Keywords:* pseudotachylyte and mylonite, frictional-viscous cycle, Brossasco-Isasca Unit.

In this contribution the relationships between mylonite, cataclasite and pseudotachylyte, hosted in the in the Brossasco-Isasca Unit (Zechmeister et al., 2007 and reference therein), in the south-western portion of the Dora Maira Massif (Western Alps) have been analyzed. A multi-scale structural geology approach, starting with the compilation of a detailed geological-structural map of the area, highlighted the occurrence of a deformation gradient into metagranitoids. Emphasis was given on the observations of overprinting relationships, of the different types of "fault" rocks, in the field, followed by their microstructural characterization on thin sections. The structural evolution of the area (Henry et al., 1993), from the greenschist facies metamorphic re-equilibration associated to non-coaxial ductile shearing, up to the latest brittle tectonics was reconstructed. Different types of mylonite, developed under general flow conditions determined through the study of kinematic vorticity, with a top-to-the SW/W sense of shear during greenschist facies metamorphism have been recognized and mapped. Pseudotachylyte and cataclasite, hosted in the mylonitic gneiss (Zechmeister et al., 2007), nucleated often on structural discontinuities (Sibson, 1980) such as the mylonitic foliation or compositional banding. In several circumstances, fluids-related (greenschist facies) overprinting of both cataclasite and pseudotachylyte is present, making difficult their recognition. Interesting overprinting relationships between the different fault rocks, e.g., cataclasite, foliated cataclasite, pseudotachylyte veins and foliated/mylonitic pseudotachylyte are described. These relationships were tentatively linked to different frictional-viscous cycles in which at least two generations of pseudotachylyte have been distinguished. The microstructural study allowed to infer useful information on the kinematics of the different fault rocks, on their overprinting features and on their possible stress-P-T formation (Bestmann et al., 2011) conditions.

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Henry C., Michard A. & Chopin C. (1993) - Geometry and structural evolution of ultra-high-pressure and high pressure rocks from the Dora-Maira massif, Western Alps, Italy. J. Struct. Geol., 15, 965-981.

Sibson R. (1980) - Transient discontinuities in ductile shear zones. J. Struct. Geol., 2, 165-171.

Zechmeister M., Ferré E., Cosca M. & Geissman J. (2007) - Slow and fast deformation in the Dora Maira Massif, Italian Alps: pseudotachylytes and inferences on exhumation history. J. Struct. Geol., 29, 1114-1130.

# Tectonic mélanges in orogenic setting (Western Alps): insights into fluid-assisted deformation and metamorphism

Locatelli M.*, Federico L., Cianfarra P., Morelli D. & Crispini L.

Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

*Corresponding author e-mail:* michele.locatelli@edu.unige.it

*Keywords:* tectonic mélange, plate interface, Voltri Massif.

Mélanges are particularly abundant in orogenic settings. Their chaotic, block-in-matrix structure can have different origins: in convergent settings, for instance, sedimentary mélanges can be overprinted by later metamorphic events or, conversely, tectonic mélanges can form directly at the plate interface, at different (shallow to deep) tectonic levels and either in prograde or retrograde (i.e., during exhumation) conditions.

The HP-metaophiolitic Voltri Massif (W Alps, Italy) contains well preserved examples of tectonic mélanges at various scales (from m- to km-scale).

Here we investigate one 100 m thick tectonic mélange at the northern edge of the massif, which is characterized by an intensely foliated matrix composed of serpentinite-schist and actinolite-bearing talc-chlorite-carbonate schist, enclosing rounded blocks of metamorphic rocks of various lithologies (e.g., metagabbro, metabasite, serpentinite and metasedimentary rocks) and sizes (m- to 10-m scale).

Structural investigations reveal a pronounced strain partitioning between the weak matrix and the strong blocks. The blocks show metamorphic layering/textures and extensional veins discordant and unrelated to the pervasive s-c-fabric and folding of the matrix.

Preliminary petrographic/microanalytical investigations on well preserved (Fe-Ti-bearing) metagabbro and metabasalt blocks indicate prograde peak metamorphism either in eclogite (grt + omp + rt ± Na-amp ± ph assemblage) or blueschist-facies (Na-amp + ttn + chl ± ep ± ph assemblage); some eclogites show either a retrograde syn-tectonic stage in blueschist facies or a static greenschist overprint.

PT estimates on eclogitic blocks indicate a peak stage at P = 18,6 ± 1,0 Kbar (gnt-ph-cpx geobarometer) and T = 530 ± 10°C and $Ar^{39}$-$Ar^{40}$ dating on high-pressure phengites an age of 52,1±0,5 Ma. Blueschist blocks show a minimum peak stage at P = 13 Kbar based on the $Si^{4+}$ amount in phengites.

Syntectonic extensional veins with fibrous amphibole crosscut the blocks departing from the contact with the external rind.

The block-matrix transition is characterized by cm-thick rinds of hybrid rocks rich in hydrous minerals, such as amphiboles and chlorite.

The study of this mélange and the comparison with the other occurrences within the Voltri Massif will allow to define their origin and role in the evolution of this sector of the Western Alps. In particular, we aim at understanding if they are related to seismic or aseismic processes occurring at the plate interface.

# Discrete Fracture Network (DFN) modelling of Triassic–Eocene Carbonates in the Ionian zone of the Hellenides, Western Greece

Massaro L.*[1], De Matteis M.[2], Tavani S.[3-4], Corradetti A.[5], Parente M.[3], Iannace A.[3], Zambrano M.[6] & Mazzoli S.[6]

[1] Department of Earth Sciences, Royal Holloway, University of London (UK). [2] ENI S.p.A., San Donato Milanese (MI). [3] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [4] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [5] Dipartimento di Matematica e Geoscienze, Università di Trieste. [6] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* Luigi.Massaro.2018@live.rhul.ac.uk

*Keywords:* discrete fracture network, fractured carbonate reservoir, fracture modelling.

In this study, we provide 3D Discrete Fracture Network (DFN) models for the potential reservoir rocks of the Ionian zone of the Hellenides, Western Greece. In this area, the main potential reservoir units are: (i) the Upper Cretaceous-Eocene reworked limestones, (ii) the Lower Jurassic Pantokrator Limestone Formation and (iii) the Upper Triassic-Lower Cretaceous dolostones.

The fluid flow migration processes in fractured carbonate reservoirs are critically influenced by the spatial distribution of their three-dimensional fracture networks. The understanding of the individual fracture sets properties has always represented a challenge, with the involvement of several techniques of investigation. These may include well logging, seismic analysis, outcrop analogues and numerical modelling. Each of these methods presents advantages and limitations. Therefore, a combined approach, applied at different observation scales, can ensure a more accurate characterisation of the fracture network.

We performed numerical modelling of the examined units by using the software Move 2019 (Petex) and its 'Fracture Modelling' tool. Field measurements from outcrop analogues were used to constrain the models with direct input data. We collected a total of 812 mesoscale outcrop data with the scanline method, including bedding, fractures and pressure solutions seams. The fractures dataset includes opening mode fractures and shear fractures. The opening mode fractures were divided into 'joints', if a visible cement infill was absent, and 'veins', when a mineral infill occurred. The orientation of the bedding surfaces was measured to enable the estimation of the unfolded orientation of the meso-structures. This procedure allowed the reconstruction of the chronological sequence of the deformation events that affected the study area, as described in Tavani et al. (2019).

The DFN modelling produced different models in order to accommodate the uncertainties related to the fracture sets distribution and the limitations of the method. To take into account the difference in aperture values between an outcropping analogue and the corresponding buried reservoir, different aperture ranges were considered, comparing the potential scenarios. Additional models were developed by subdividing the fracture sets into classes of fracture length, in order to avoid an underestimation of such a critical property. Overall, the Upper Cretaceous-Eocene limestones can rely on higher primary porosity values, whereas the Pantokrator fm. and the dolostones provide higher fracture permeability, showing, at the surface conditions, a more interconnected fracture network.

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# Fluid flow in deep seismogenic faults

Menegon L.*[1], Michalchuk S.[1], Renard F.[1], Chogani A.[2] & Plumper O.[2]

[1] The Njord Centre, Department of Geosciences, University of Oslo (Norway). [2] Department of Earth Sciences, Utrecht University (Netherlands).

*Corresponding author e-mail:* luca.menegon@geo.uio.no

*Keywords:* lower crust, fluid flow, seismogenic faults.

Rock rheology and density have first-order effects on the lithosphere's response to plate tectonic forces at plate boundaries. Changes in these properties are controlled by metamorphic transformation processes that are critically dependent on the presence of fluids. At the onset of continental collision, the lower crust is in most cases dry and strong (Jamtveit et al., 2019). However, if exposed to fluids, the lower crust will react and be converted into mechanically weaker rocks. Lower-crustal earthquakes associated with the formation of pseudotachylytes (solidified frictional melt produced by seismic slip) are the key agents for fluid introduction in the dry crust. Rupture propagation and seismic slip may trigger fluid infiltration, weakening, and a transition to interseismic viscous creep to form mylonitised pseudotachylytes along faults initially characterized by frictional melting and wall-rock damage (Menegon et al., 2017).

Despite their importance for lower-crustal seismicity and strength evolution, little is known about the mechanisms that govern fluid migration in the lower crust during the earthquake cycle. Microstructural evidence suggests that wall-rock damage caused by dynamic ruptures plays a key role in allowing fluids to enter into contact with dry and highly reactive lower crustal rocks (Petley-Ragan et al., 2021). But is this porosity transient, and how will fluid flow evolve during the seismic-aseismic deformation cycles?

To answer these questions, we have analysed samples of pristine (non-mylonitised) and mylonitised pseudotachylytes from Nusfjord, Lofoten (Norway) with electron microscopy and synchrotron X-ray microtomography. The samples record seismic-aseismic deformation that occurred at lower-crustal conditions (Menegon et al., 2017). Our results indicate that co-seismic fracturing is the primary mechanism for porosity generation in the lower crust. During the subsequent interseismic creep, porosity is reduced by up to 90% (from 0.16 to 0.03 vol%) under deformation conditions promoting grain-size sensitive creep in the mylonitised pseudotachylytes. We suggest that such porosity reduction eventually results in shear zone hardening, which might culminate in the development of new pseudotachylytes overprinting the mylonites, as frequently observed in Nusfjord. Thus, earthquake-induced rheological weakening of the lower crust is transient and occurs only as long as the infiltrated fluid can circulate in the shear zone, thereby facilitating diffusive mass transfer.

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# From outcrop-mapped structural and diagenetic heterogeneities to a 3D numerical flow model: a workflow for a sandstone aquifer

Napoleoni S.*[1], Del Sole L.[2] & Antonellini M.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* sabrina.napoleoni2@unibo.it

*Keywords:* structural heterogeneities modeling, flow upscaling, outcrop analogues.

Porous sandstones represent excellent geofluids reservoirs owing to their petrophysical properties, i.e., porosity and permeability. However, diagenetic processes (e.g., dissolution, cementation, compaction) can lead to a strong porosity reduction, which influences fluids circulation and storage in the rock volume, and these are often affected by pre-existing structural heterogeneities such as fractures and faults. This is the case of the *Loiano* Sandstones (Northern Apennines, Italy), representing middle Eocene deep-water submarine fans deposited on top of a moving thrust sheet. Previous outcrop observations have revealed bed- and fracture-parallel calcite concretions. The proposed explanation for this association has been an interplay between deformation structures, here mainly represented by low-permeability compactive and cataclastic deformation bands, and diagenetic processes. Faults and deformation bands are supposed to predate calcite cementation in the form of nodules and to selectively control their spatial distribution. The fluids interacting with the structures are of meteoric origin. The purpose of the present work is to transfer field data into a MODFLOW 2005 (Harbaugh, 2005) 3D numerical model. The modeling consists in the simulation of calcium-bearing meteoric waters infiltration and flow within the aquifer. The objective is to infer the fluid flow conditions that led to the present-day spatial distribution of calcite nodules and the impact of this distribution on groundwater movement. To build the model, a field map of the study area was created in QGIS based on a geo-referenced orthophoto acquired by UAV imagery. The map was populated with the geological structures (calcite nodules, deformation bands, zones of deformation bands, bedding) in the form of shapefiles composed of polygons and polylines. Each object in the shapefile was characterized by a permeability tensor measured in the field, which was then converted into a hydraulic conductivity tensor. The shapefiles and a topography map were then imported into ModelMuse (Winston, 2019), a graphical user interface for MODFLOW 2005, and up-scaled to the cell size of the model grid by harmonic and arithmetic averaging. Boundary conditions for the model in Modelmuse were set to be a recharge area above the exposed aquifer, a specified head, and a river system present in the downstream part of the area. Several single-phase transient and steady-state numerical experiments were run to evaluate the effect of deformation bands on flow pattern, cement precipitation, nodule distribution, and, eventually, the impact on aquifer performance considering both structural and diagenetic heterogeneities. This approach would enable better predictions of the uncertainties in aquifer petrophysical properties distribution and behavior in similar geologic settings.

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Winston R.B. (2019) - ModelMuse Version 4: a graphical user interface for MODFLOW 6. Scientific Investigations Report-US Geological Survey, 2019-5036.

# Mechanical behavior of the shallow part of megathrusts: hints from the Sestola Vidiciatico tectonic Unit (Northern Apennines, Italy)

Remitti F.*[1], Mittempergher S.[1], Festa A.[2], Cipriani A.[1] & Lugli F.[3]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Dipartimento di Scienze della Terra, Università di Torino. [3] Dipartimento di Beni Culturali, Università di Bologna.

*Corresponding author e-mail:* francesca.remitti@unimore.it

*Keywords:* megathrust, subduction zone, fluid pressure.

Notwithstanding the large wealth of geophysical and geodetic information emerging in recent years, the anatomy and processes within the shallow part of active megathrust zones are still elusive and poorly resolved. The complex and peculiar seismic behavior of the subduction plate interface is mirrored by a complex and peculiar geology. Megathrusts are not simple slip surfaces, but extremely complex shear zones of deformed rocks formed by the interaction of competing deformation processes that vary both in space and time. Megathrusts typically contain highly sheared, fluid-saturated trench-fill sediments intermingled with fragments of oceanic or continental crust that evolves downdip, in an ever-increasing pressure-temperature-strain regime, forming a fault zone marked by an heterogeneous mix of contrasting lithologies characterized by a time-dependent evolution.

Megathrusts have been recognized for a long time as weak faults localizing deformation under low shear stresses (<20 MPa) that has been related to high fluid pressure. However, fluid pressure, and therefore the modulation of the strength of a fault and the surrounding rocks, is strictly related with the permeability of the area and fluid circulation that is likely variable in space and time and poorly constrained. Starting from the studies of the Sestola Vidiciatico Tectonic Unit (Northern Apennines, Italy), which is considered an ancient analogue of the frontal part of a megathrust (Vannucchi et al., 2008; 2010; Mittempergher et al., 2018; Cerchiari et al., 2020), we investigate the relationships between structurally controlled fluid pathways and tectonic loading from seafloor to up to 100-150°C using structural and geochemical data. Results suggest that the mechanical behavior of the fault changes along both strike and depth, in tandem with the progressive decrease in competence contrast between different lithologies and a contemporaneous onset of cycle of fluid pressure related with pulse of exotic fluids.

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# Eclogitization of the oceanic lithosphere by hydration of brittle structures

Scambelluri M.*[1], Pennacchioni G.[2] & Cannaò E.[3]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [2] Dipartimento di Geoscienze, Università di Padova. [3] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* marco.scambelluri@unige.it

*Keywords:* oceanic lithosphere, subduction, faulting, hydration, eclogitization.

Metamorphism is the driving force to major changes in the mineralogy and rheology of the Earth's lithosphere, provided that mineral reaction and growth are triggered by fluid access. In absence of coupled deformation and fluid flow, the unaltered lithosphere forms long-lived stiff metastable blocks able to sustain significant differential stresses. This is relevant for subduction of the oceanic lithosphere, where presence *vs* absence of fluids affects seismicity and rock eclogitization. Hydration of the oceanic lithosphere mostly occurs in oceanic settings with formation of top-slab reactive rock volumes prone to deformation and accretion to the subduction interface. In such domains, flux of pressurized fluids causes events of seismic failure by dehydration embrittlement. Much less known is the evolution of the unaltered lithosphere from inner slab domains, too deep to be tectonically exhumed to the Earth's surface. These domains also host earthquakes.

Here we describe peridotite and gabbro from the ophiolitic Lanzo Massif (W. Alps) that largely escaped Alpine subduction metamorphism due to poor pre-subduction oceanic hydration. This made these dry rocks stiff asperities in the subduction complex, which locally developed pseudotachylyte-bearing faults at intermediate-depth depths. Overall, subduction to eclogite-facies conditions led to widespread development of meso- (meter-scale) to micro-faults. Aim of this contribution is showing the role of such seismic brittle structures in driving fluid influx and eclogitization of peridotite and gabbro in unaltered domains of this fossil oceanic plate. In the field, thin, flat-lying metric faults cause centimetre-scale offset of gabbro dykes. From micro to nano-scale, faults contain a (sub)micrometric-sized "annealed" fault gauge of fresh olivine (only locally overgrown by secondary chlorite) and orthopyroxene. Cataclastic plagioclase is progressively altered into high-pressure zoisite + paragonite ± garnet.

This indicates formation of the fault planes in the olivine stability filed and concomitant, localised access of externally derived fluids that promoted hydration of the gouge assemblages. This implies that subduction zone eclogitization is driven by faulting followed by fluid access. We discuss the deformation features of the Lanzo rocks in the frame of the rheology and seismicity of a subducting oceanic plate. They could be associated to minor slip events in domains of the Lanzo lithosphere close to areas of faulting and pseudotachylite formation during major regular earthquakes.

# Meteoritic fluid infiltration along a detachment fault triggering exhumation: A case study from the Buckskin-Rawhide metamorphic core complex

Siron G.*[1-2], Bonamici C.[2] & Roig C.I.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] WiscSIMS Laboratory, University of Wisconsin, Madison, WI (USA).

*Corresponding author e-mail:* guillaume.siron@unibo.it

*Keywords:* Oxygen isotopes, metamorphic core complex, shear zone.

In situ multi-tracer geochemical studies in mylonite can provide detailed information on the timing, composition, and thus possible rheological consequences of aqueous fluid infiltration during deformation. Here we present a microstructural and oxygen isotope study of a muscovite-free granitic mylonite from the footwall of the Buckskin-Rawhide metamorphic core complex.

Fluid-mediated myrmekitic intergrowths of oligoclase and quartz occur along foliation-parallel K-feldspar porphyroclast faces at inferred high normal stress sites. Neoblastic K-feldspar occurs in pressure shadows and along filling fractures in plagioclase porphyroclasts. Regardless of microstructural position, plagioclase ($An_{20-25}$) and K-feldspar ($Ab_8$) compositions are similar, suggesting that mineral major-element compositions were rock- rather than fluid-buffered and that recrystallizing fluids were NaCl-poor. Oxygen isotopes, in contrast, record open-system infiltration by a low-$d^{18}O$ fluid: K-feldspar and plagioclase porphyroclast cores preserve $d^{18}O$ ~6-6.5‰, whereas myrmekitic plagioclase intergrowths and neoblastic K-feldspar have $d^{18}O$ ~3-4‰. Both plagioclase and K-feldspar porphyroclasts show core-to-rim decreasing $d^{18}O$, probably due to diffusive relaxation superimposed on recrystallized boundaries. CL images reveal crack-seal features within K-feldspar porphyroclasts that are not associated with low $d^{18}O$ and are interpreted to largely pre-date low-$d^{18}O$ fluid infiltration and fluid-mediated myrmekite formation. Oxygen isotope equilibrium fractionation between biotite (~ -1‰) and the later-formed feldspars reveal that this fluid infiltration occurred at 400-450°C. The infiltrating fluid exhibit an oxygen signature of 1-2‰. Such a low $d^{18}O$ signature strongly suggests it was a meteoric fluid.

We suggest that these microstructural and geochemical patterns are consistent with an essentially isothermal (~450°C) switch in K-feldspar deformation mechanism within the shearing middle crust from crack-seal deformation to myrmekite formation and recrystallization triggered by low-$d^{18}O$ fluid infiltration. We propose that grain-size reduction through the replacement of K-feldspars by myrmekites enhanced localization of deformation, altered midcrustal rheology, and ultimately triggered the exhumation of the midcrust into the Buckskin-Rawhide core complex footwall. The finding that meteoric fluid infiltration into the middle crust could trigger its exhumation has implications for the long-term stability of the crust and needs to be evaluated in other regions.

# Unraveling the origin and impact of fluid intrusion on soft sediment deformation in a mixed carbonate-siliciclastic coastal wedge: a multi-proxy study of the Pietra di Finale

Tamburelli S.*, Mueller P., Perozzo M. & Menegoni N.

Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* silvia.tamburelli01@universitadipavia.it

*Keywords:* soft-sediment deformation structures, fluid intrusions, seismites.

Soft-sediment deformation structures (SSDS) are sedimentary structures generated by both chemical and physical disturbances. They can provide valuable information about the conditions of parent flows, the characteristics of disturbed unconsolidated sediments, and the surrounding environment. The principal formation mechanisms comprise liquefaction or fluidization, reverse density gradation, slumping or slope failure, and shear stress. Constraining the definitive triggers for the development of SSDS however remains challenging, since a complex combination of triggers can result in similar disturbance of the sediment. This study puts emphasis on pore fluid expulsion from overpressurized zones that might occur during various stages of burial and lithification of sedimentary deposits. Uncommon mineralization and intrastratal sediment mobilization is explored by a multi-proxy approach, with emphasis upon discriminating the role of earthquake-triggered liquefaction from gravitationally and diagenetically-induced sediment disturbances. The explored dataset comprises an outcrop-scale photogrammetric study of the geometry of SSDS and their stratigraphic distribution, a detailed analysis of the sedimentological characteristics at the outcrop-scale, as well as petrographic investigations of both granulometric and intergranular features (i.e., types of clasts and cement).

A wide range of styles and intensities of SSDS are documented in the Pietra di Finale, a mixed siliciclastic-carbonatic coastal wedge. The studied successions of the Miocene Finale basin are characterized by a complex lateral and vertical organization of strongly heterogeneous units, displaying rapid lithological changes within short lateral distances. SSDS show highly localized distributions at the interface between the terrigenous and carbonatic members. Based on morphological characteristics, six main types of SSDS can be distinguished. These include (1) small-scale load structures, (2) large-scale load structures, (3) flame structures, (4) pseudonodules, (5) tree-shaped deformations and (6) contorted chaotic stratification. Formation of the observed SSDS types is interpreted to result from fluid expulsion trough liquefaction/fluidization of cohesionless sediment. Seismic shocks, density inversion, and gravitational loading are thought to represent the main mechanisms triggering fluidization in the Finale Basin. The common presence of deformation bands within deformed interfaces, along with a cyclic distribution of SSDS recorded in the carbonatic members, suggest that seismic shocks played a pivotal role on liquefication. SSDS in the Langhian-Serravalian Pietra di Finale thus provide evidence of seismic activity in the studied stratigraphic interval and can serve as a regional indicator for the timing of tectonic pulses associated with the final opening stages of the Liguro-Provencal Basin.

# Numerical analysis of the post-seismic effects on groundwater flow after the Amatrice-Visso-Norcia 2016 seismic sequence

Zullo E.*[1], Albano M.[2], Saroli M.[1-2], Moro M.[2], Testa G.[1], Bonora N.[1], Petitta M.[3] & Doglioni C.[2-3]

[1] Dipartimento di Ingegneria Civile e Meccanica, Università di Cassino e del Lazio meridionale. [2] INGV, Roma.
[3] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* enrica.zullo@unicas.it

*Keywords:* groundwater flow, Norcia earthquake, numerical modelling.

The hydrogeological setting of the Sibillini Mts. is mainly characterized by the coexistence of a shallow and a basal regional aquifer (Viaroli et al., 2021) whose spatial distribution, recharge area and groundwater dynamics are strongly controlled by a complex regional tectonic framework.

The 2016 seismic sequence that struck Central Italy altered the hydrodynamic response of the carbonate fractured aquifer, causing sustained variations in the groundwater flow. In particular, after the Mw 6.5, 30 October main shock (called Norcia earthquake), caused by the dislocation of the Vettore Mt. normal fault, a surplus of groundwater discharge was observed at the springs bordering the western side of the Sibillini Mts. and in the Nera River basin. Furthermore, the Torbidone spring in the Norcia plain, exhausted since 1979, reappeared after the seismic event. The observed post-seismic groundwater surplus was attributed to a variation of the hydraulic gradient and an increase in bulk permeability probably caused by the fracture cleaning effect, which caused a shift of the groundwater divide after the fault rupture (Mastrorillo et al., 2020). Such phenomenon induced an eastward shift of the piezometric divide so that the springs located on the eastern side of the Sibillini Mts. strongly reduced their flow, thus causing several problems in the groundwater supply system.

In this work, we aim at assessing the effect of the coseismic dislocation of the Vettore fault on the crustal stress and strain field, the consequent modification of the hydraulic properties of the shallow and basal regional aquifers of the Sibillini Mts. and the related groundwater flow variations. For this purpose, we collected geological and hydrogeological data from the available literature and used them to analyse the area affected by the 30 October earthquake with 2D and 3D numerical models. We first created a simplified 2D geometric model at surface scale (up to 2 km deep), including the spatial relationship between the main tectonic elements and the boundaries of the main hydrogeological complexes, to model the groundwater flow before and after the seismic event. Then a regional-scale 3D model is developed, whose hydraulic parameters are calibrated as a function of the stress and strain changes caused by Vettore fault rupture to obtain two different hydrological scenarios: pre- and post-faulting.

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# S43.

# Transversal Tectonic Lines in the Apennines: an updated review on their role for seismicity, magmatism and fluid flow


*Conveners & Chairpersons*

*Andrea Brogi (University of Bari)*

*Domenico Liotta (University of Bari)*

*Francesco Mirabella (University of Perugia)*

*PietroPaolo Pierantoni (University of Camerino)*

# Releasing step-over along transfer zone controlling magma emplacement: the Gavorrano monzogranite

Brogi A.*[1-2], Caggianelli A.[1], Liotta D.[1-2], Zucchi M.[1], Perrini M.[1] & Ibe C.U.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* andrea.brogi@uniba.it

*Keywords:* transfer zones, extensional tectonics, magma emplacement.

The Gavorrano monzogranite, located nearby the Tyrrhenian seacoast, in the inner zone of the Northern Apennines (southern Tuscany), is a Neogene magmatic body (estimated in about 3 km long, 1.5 km wide, and 0.7 km thick) emplaced during early Pliocene. This intrusion is partially exposed in a ridge bounded by regional faults delimiting broad structural depressions. A widespread circulation of geothermal fluids accompanied the cooling of the magmatic body and gave rise to an extensive Fe-ore deposit (mainly pyrite) exploited during the past century. Data from a new fieldwork dataset, integrated with information from the mining activity, have been integrated to refine the geological setting of the whole crustal sector where the Gavorrano monzogranite was emplaced and exhumed. Our data pointed out that the tectonic evolution which determined the emplacement and exhumation of the monzogranite is constrained in a transfer zone and its interplay with low-angle normal faults developed in the frame of the extensional tectonics affecting the inner Northern Apennines since the middle Miocene.

# Geology of Montecastelli Pisano (Inner Northern Apennines, Italy): normal and transfer fault zones affecting a dismantled orogenic wedge

Brogi A.[1-2], Liotta D.*[1-2], Dini A.[2] & Rielli A.[2]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* domenico.liotta@uniba.it

*Keywords:* transfer faults, Neogene, inner Appennines.

We present a detailed geological map (1:10000) of the Montecastelli Pisano area is a key-example where the relationships between transfer and normal faults can be carefully mapped and the oceanic basement of the Ligurian Ocean analysed. The stratigraphic succession is made up of: Jurassic magmatic oceanic rocks and their related Jurassic-Cretaceous sedimentary cover and by two sedimentary successions, belonging to the Miocene Radicondoli Basin and to the Pliocene-Pleistocene Pomarance Basin. Kinematics and geometry of the faults permitted to define the NE-trending fault systems as belonging to a transfer shear zone, associated to the NW-trending normal faults. Their evolution is framed in the extensional tectonics affecting the inner Northern Apennines since early-middle Miocene, continuously.

# What is the origin and the seismogenic potential of the major transverse lineaments that cross the Italian fold-and-thrust belt?

Fracassi U.*, Vannoli P., Burrato P. & Valensise G.

INGV, Roma.

*Corresponding author e-mail:* umberto.fracassi@ingv.it

*Keywords:* seismogenesis, reactivation, foreland.

The very shape of the Italian landmass results from the peculiar evolution of the central Mediterranean basin. Its generally arcuate shape includes the Apennines, the Calabrian Arc and the Maghrebides, from north to south, thus reflecting the accruing thrust-belt in its overall eastward radial pattern.

Various mechanisms have been invoked to justify kinematically the pronounced advancement of the arcuate portions of the leading edge of the Apennines-Calabrian Arc-Maghrebides. One such view maintains that transverse systems of various orientation had to coexist with tectonic transport, also to allow the emplacement of segments of the thrust-belt.

Most of peninsular Italy and Sicily exhibit widespread seismicity, including destructive events. Earthquakes occur over a broad stretch running along the axis of the Apennines, in part mimicking their poly-arcuate shape. Kinematics encompasses virtually all tectonic mechanisms, from reverse faulting on the outer margin of the wedge to normal faulting along its extensional backbone, and from strike-slip tectonics in the foreland to subduction (either presumably relict, beneath the northern and central Apennines, or active, beneath the Calabrian Arc).

While most large earthquakes that affected the Italian landmass have been associated with the evolution of an essentially cylindrical tectonic style, a number of historical and instrumental earthquakes are seen to violate this general rule. Based on their location with respect to geodynamic province, focal mechanisms, and structural position, we highlight three categories of such events:

those occurring along major inherited Mesozoic, poly-phased structures, that dissect remnants of the Adriatic and Maghrebian foreland. These faults, likely resulting from the Tethyan break-up, are presently reactivated under the current stress regime, causing some of the most destructive events of the Italian record;

those resulting from differential motions between adjacent panels of retreating subduction. Such mechanism, tearing upward through the subduction interface, may be responsible for the creation of some of the long-discussed lineaments identified across the northern Apennines;

those occurring along the tear edge of inherited arc sectors against contrasting paleogeographic domains, inverted under the current extensional regime. Such events may include the seemingly unfavourably oriented segments activated during the 1979 and 2016-17 sequences in central Italy.

We argue that these events reveal the seismogenic role of some remnants of these transverse features, orthogonal to the cumulatively arcuate Apennines-Calabrian Arc-Maghrebides axis. We maintain that such role should not be underestimated, so as to improve our understanding of Italian seismotectonics, and to allow the location of currently unknown, potential earthquake sources.

# Fluid flow and faulting history in the Iano area (Southern Tuscany, Italy)

Fulignati P. & Molli G.*

Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* giancarlo.molli@unipi.it

*Keywords:* fluid flow, faults, Iano tectonic window, southern Tuscany.

The Iano area includes the northernmost tectonic window of Tuscan metamorphic units in the southern Tuscany. During Pliocene it formed a submarine high, easternmost shoulder, of the Volterra Pliocene basin. The area gives the opportunity to investigate the complete cycle of negative inversion from crustal thickening to crustal thinning, which characterizes the southern Tuscany. Our new data focus on the western and southern margins of the Iano ridge, and on a system of high angle normal faults that represents the youngest structures of the investigated area. These structures overprint low angle regional detachments locally juxtaposing the uppermost units of contractional nappe stack (the ophiolite-bearing Ligurian units), with a Tuscan metamorphic unit, with an almost complete excision of at least 3.5 Km thick Mesozoic to Tertiary Tuscan nappe succession. The high angle normal faults with both transversal- and Apenninic-trends show variable Plio-Quaternary vertical displacements from few meters to about 500 meters and acted as pathways for the upwelling of hydrothermal fluids, as revealed by Pleistocene travertine deposits, hydrothermal alteration, and occurrence of different generations of fluid inclusions in hydrothermal veins associated with these fault systems. Fluid inclusions were studied in quartz veins hosted in the Verrucano metasediments forming the top of the Tuscan metamorphic unit, as well as in some carbonate lithotypes (Cretaceous to Tertiary in age) of the overlying Tuscan Nappe. Two different kinds of fluid inclusions were documented. The Type 1 are multiphase (liquid + vapor + 1 daughter mineral) liquid-rich fluid inclusions whereas the Type 2 are two-phase (liquid + vapor) liquid-rich fluid inclusions. Type 1 fluid inclusions are primary in origin and were found only in quartz veins present in Verrucano metarudites, whereas Type 2 fluid inclusions occur in quartz veins in both Verrucano phyllites and quartzites and in the carbonate units of the Tuscan Nappe. These are secondary and can be furthermore distinguished in two sub-populations (Type 2a and Type 2b) based on petrographic observation and microthermometric data. Fluid inclusion investigation evidenced an evolution of the hydrothermal fluids from relatively high-T (~265°C) and hypersaline (35 wt.% $NaCl_{equiv.}$) fluids trapped at about 100 MPa, to lower temperature (~195°C) and salinity (~9.5 wt.% $NaCl_{equiv.}$) fluids, having circulated in the high-angle fault system. Based on the new data and a revision of the local tectonic setting a fluid-rock interaction history has been reconstructed with new hints and constraints for the Plio-Quaternary extensional history of the Volterra basin and of local transversal tectonic lines.

# The 'transverse faults' of the eastern Tyrrhenian margin: places, times and their meanings

Milia A.*[1] & Torrente M.M.[2]

[1] Istituto di Scienze Marine, CNR, Napoli. [2] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento.

*Corresponding author e-mail:* alfonsa.milia@cnr.it

*Keywords:* backarc extension, Eastern Tyrrhenian Margin, tectono-stratigraphy.

Apennine geologists understand "transverse faults" to mean faults built up more or less orthogonally to the Apennine chain. "Transverse faults" develop in the intermediate zone between the Apennine thrust belt and the Tyrrhenian basin, many of which in volcanic areas, and they play an important role in the evolution of the margin. However, in order to evaluate their meaning it is of fundamental importance to determine their spatial distribution and timing. In the last decades, sedimentary basins on the Tyrrhenian margin have been studied, using tectonics ad seismic-stratigraphic methodologies calibrated by well and outcrop stratigraphic data (Milia & Torrente, 2011; Milia et al., 2017a; 2017b; 2017c). These studies highlighted a non-cylindrical evolution of the margin whose " transverse" faults have had a different age and role. On the Latium margin Pliocene NE-SW faults gave rise during the Pliocene to the Ardea Basin (corresponding to the apex of the triangular Vavilov Basin). Along the Campania margin transverse lineaments may have acted as transfer faults during the rifting of the easternmost part of the Tyrrhenian Basin in the Lower Pleistocene. Middle Pleistocene normal faults have instead played an important role in the opening of the Campanian Margin forming more than 3 km deep sedimentary basins. From the geodynamic point of view, Pliocene faults on the Latial margin, lower Pleistocene transfer faults of the Campanian margin, and middle Pleistocene transverse normal faults of the Campanian margin can be associated, respectively, to the opening of the Vavilov, Marsili and Eolie backarc basins. Many volcanoes are physically linked to the transverse faults of the eastern Tyrrhenian margin, but it should be taken into account the possible role of extensional faults in localizing magmatic activity, controlling magma rise from deep to shallow reservoirs and to the surface during eruptions.

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# Pliocene-Quaternary transversal seismogenic faults in the Valdelsa Basin (Southern Tuscany, Italy)

Mirabella F.*[1], Brogi A.[2], Capezzuoli E.[3] & Braun T.[4]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro". [3] Dipartimento di Scienze della Terra, Università di Firenze. [4] INGV, Roma.

*Corresponding author e-mail:* francesco.mirabella@unipg.it

*Keywords:* transversal faults, inner Northern Apennines, earthquakes.

The seismogenic role of transversal SW-NE striking faults in the inner Northern Apennines has recently gathered a renewed attention due to the occurrence of several 3 Many of these faults, however, do not show clear surface evidence even when releasing earthquakes and their recent and/or Quaternary evidence often a matter of discussion.

For these reasons they can be extremely dangerous as they receive relatively little attention and are difficult to identify.

We focus our attention on the integration of different datasets: seismic reflection profiles, surface kinematic data and the relocation of seismological data, to identify and characterize active faults whose dimension and earthquake potential would otherwise not be large enough to make them identifiable. We take as an example the Montespertoli NE-trending fault in southern Tuscany (central Italy) with which we associate the 2016 M=3.9 Castelfiorentino earthquake. This structure is part of a wider (in the order of 15–20 km) crustal-scale shear zone, which may be responsible for strong historical earthquakes in the area.

# "Stretching Faults" in the inner northern Apennines: a new way to look the problem of LTT's

Molli G.*

Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* giancarlo.molli@unipi.it

*Keywords:* faults, LTT's, STEP, northern Apennines, southern Tuscany.

The contribution aims to discuss the present view of the Transversal Tectonic Lines (LTT's) of the Northern Apennines and to propose a new interpretation considering their role from the early paleotectonic heritage up to their Neogene-Quaternary history as "Stretching Faults". Introduced at the end of the 80s (Means, 1989) the "Stretching Faults" are a type of faults s.l. related with a tectonic setting in which the crustal volume that includes the structure is deformed as the structure itself. The fault then lengthens ("positive Stretching Faults") or shortens ("negative Stretching Faults") in the direction of slip while the slip itself accumulates. This distinctive deformation and faulting style can be associated with peculiarities in the fault propagation, space-time record (e.g., inversion of the kinematics or of the faulting type along the fault direction) and in the local characteristics of the associated structures. The Apennines, in their internal part, may represents a type-region for the "Stretching Faults" since they are characterized by geological and morpho-structural non-cylindricity and by a significant transversal compartmentalization related to a heterogeneous differential extension in adjacent crustal domains.

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# Genesis of the longitudinal extension of the chain and Miocene intra-Apennine basins formation

Penza G.*, Pierantoni P.P. & Turco E.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* giulia.penza@unicam.it

*Keywords:* transversal structure, extensional basins, kinematic model.

The kinematic models proposed in recent years imply a longitudinal extension of the Apennine chain and the resulting activation of transversal structures that from wedge-top basins (Turco et al., 2012).

This type of mechanism of formation is observed in the Apennine chain at different stages of its evolution, for instance in the proto-Apennine chain (Turco et al., 2013; Pierantoni et al., 2020; Turco et al., 2021). The most representative examples are the basins of the Monte Cervarola Sandstones and the Marnoso Arenacea. These, cover the Northern Apennine Arc in the central area and break the continuity of the chain between the Umbria-Marche and the Liguride Apennines.

Historically, this type of deposits have been considered as foredeep successions. Actually, the Apennine chain is not built by a collision process but is generated by the flexural retreat of the Adriatic slab that does not form a foredeep, in the classical meaning of the term, but only deforms the foreland.

The aim of this work is to explain the genesis of the longitudinal extension during the evolution of the Tyrrhenian-Apennine system and describe the formation of the associated intra-Apennine basins, focusing on the role of transversal faults.

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Turco E., Macchiavelli C., Penza G., Schettino A. & Pierantoni P.P. (2021) - Kinematics of Deformable Blocks: Application to the Opening of the Tyrrhenian Basin and the Formation of the Apennine Chain. Geosciences, 11, 177.

# How ancient lithospheric-scale faulting drives the segmentation of the Apennines fault system: a receiver function analysis in the area of the 2016-2017 Central Italy seismic sequence

Piana Agostinetti N.[1-2], Buttinelli M.*[3] & Chiarabba C.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] INGV, Osservatorio Nazionale Terremoti, Roma. [3] INGV, Sezione di Sismologia e Tettonofisica, Roma.

*Corresponding author e-mail:* mauro.buttinelli@ingv.it

*Keywords:* Moho depth, Central Italy, receiver function.

We compute a high-resolution topographic model of the Moho beneath the fault system activated during the 2016-2017 Central Italy seismic sequence, using Receiver Function (RF) analyses. We document that Ps conversions recorded in RF data-set vary abruptly at a very short distance across the crustal lineament called Ancona-Anzio Line (AAL). Moho depth varies from about 2530 km in the Tyrrhenian domain in the West to 35-40 km in the Adriatic domain in the East. Where the two domains are juxtaposed along the AAL, Moho depth values cluster around 50 km depth, in a stripelike area 20 km wide. Such unique features mark the deformation zone in the lithosphere and testify to the abrupt change in delamination style in the two sectors of the Apennines. Intermittent large normal faulting earthquakes are driven by across-belt extension breakthroughs such as inherited strong structural changes, conditioned by localized barriers to fluids migration and overpressuring.

# Transversal structures on the Outer Marche Apennines: structural characteristics and seismic evidence

Pierantoni P.P.*, Costa M., Teloni S. & Invernizzi C.

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* pietropaolo.pierantoni@unicam.it

*Keywords:* transversal faults, active tectonic, outer Apennine.

A multidisciplinary work integrating geomorphological, structural and seismological data was performed in the Outer Marche Apennines (central Italy) to define the seismotectonic setting of this region. The investigated area is the locus of some of the strongest historical earthquakes of central Italy and the geometry and kinematic of the seismogenic sources are still not well defined.

In the present work several Plio-Quaternary NW-SE structures have been identified in the external Apennine sector of the Marche Region. Both extensional and compressional structures are segmented by transversal faults NE-SW oriented, which were active simultaneously to the main structures they are related to.

The origin, role and relevance of these transversal structures is still debated (Pierantoni et al., 2017; Costa et al., 2021). In this regard this work aims to characterize the geometry, kinematics, and activity of the main transversal faults of the external sector of the Marche Apennines to better define their seismogenic potential.

Four main WSW–ENE to WNW–ESE transversal fault system have been investigated and mapped. They are high angle and deeply rooted fault systems that separate the external Apennine sector in two blocks (A and B) and sub-blocks (A1, A2 and A3) characterized by different structural and evolutionary features.

The combination of different geological datasets such as morphotectonic and structural data, with seismological features plus seismic reflection profiles reveals that some fault segments have recently been reactivated since they have displaced Quaternary deposits.

The spatial distribution analysis of baseline seismicity, derived from different available catalogues and authors, indicates that some clusters of hypocenters are located within the crystalline basement. Furthermore, the stress field analysis performed by WinTensor software using available focal mechanism solutions confirms the prevalence of left-lateral kinematics on roughly SW–NE oriented structures.

In this context, the transversal structures contribute to the longitudinal segmentation of the Apennine structures. In addition, the high number of seismic events evidenced by the instrumental seismicity, and the macroseismic intensity distribution of the historical earthquakes support the hypothesis that this seismogenic faults are still potentially active. This in turn plays a key role for the seismic hazard assessment and risks mitigation in most populated area close to the Adriatic coast.

Costa M., Chicco J., Invernizzi C., Teloni S. & Pierantoni P. P. (2021) - Plio–Quaternary Structural Evolution of the Outer Sector of the Marche Apennines South of the Conero Promontory, Italy. Geosciences, 11(5), 184.

Pierantoni P.P., Centamore E. & Costa M. (2017) - Geological and seismologic data review of the 2009 L'Aquila seismic sequence (Central Apennines, Italy): deep-seated seismogenic structures and seismic hazard. Italian Journal of Engineering Geology and Environment, 17(2), 5-40.

# The issue of the Olevano-Antrodoco-Sibillini thrust and the Mt. Vettore active normal fault system: barrier or cross-cutting fault? Insights after the 2016 seismic sequence

Pizzi A.*[1], Puliti I.[1], Schettino D.[1], Bonini M.[2] & Calamita F.[1]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* alberto.pizzi@unich.it

*Keywords:* active normal faulting, transversal tectonic lines, Central-Northern Apennines.

One of the main debates in earthquake geology studies concerns the role that the pre-existing structures play in the evolution of active fault systems. Inherited structures may act as "persistent structural barriers" halting fault ruptures and propagation, or they can be reactivated as transfer zones. The central Apennines constitute a perfect natural laboratory to investigate such phenomena since they have been affected by multiphase contractional and extensional deformation. Quaternary extensional fault systems striking NW-SE, indeed, often interact with pre-Quaternary oblique cross-structures, commonly NNE-striking (e.g., Neogene thrust faults). Before 2016, the issue of the relationship between the Mt. Vettore fault system (MVFS), and the Olevano-Antrodoco-Sibillini thrust (OAS) was limited to the structural geology investigation (Pizzi & Galadini, 2009). In 2016, the MVFS broke during three earthquakes (Mw 6.0, Mw 5.9, Mw 6.5), producing coseismic ruptures. This event stimulated the exploration of these aspects through different approaches. Based on the seismological, GPS and InSAR data, several 3D geological models have been developed (e.g., Scognamiglio et al., 2018), some also suggesting the partial or total reactivation of the OAS thrust (e.g., RETRACE-3D project). By finite-extent fault inversion of the main events using near-source strong motion records, we observed that earthquake nucleation and rupture propagation were controlled by segmentation of the NW-SE trending MVFS. We showed that the southern tip of the system corresponds to the deeper, high-angle fault zone of the OAS cross-structure, which might have acted as a barrier to rupture propagation of the first two events defining an area of large stress concentration until it played as the initiator of the rupture originating the largest (Pizzi et al., 2017). Data supporting the presence of a deep barrier can also be found on the fault system surface expression. Based on high-resolution topography, geological data, and measurements of field ruptures, the distributions of the coseismic and the morphological displacements exhibit similar asymmetric shape, suggesting self-similar slip profiles over the last 18 kyr (Puliti et al., 2020). This evidence along with the observed segment interactions and the more widespread deformed area to the south might suggest that the maximum throw could be related to the presence of a main structural barrier at depth. The barrier that is likely the high-angle OAS thrust (below 5 km of depth) prevents the natural free southward propagation and evolution of the fault system, enhancing a southern-tip deformation through increment high vertical displacements. Our data brought a contribution to the understanding of the significance and the role of the pre-existing cross-structures during a seismic event. In the scenario of the Central Apennines investigations, deepening the issue remains fundamental for anticipating modalities of fault ruptures and propagation.

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# Evidence of tectonic inversion in the Northern Apennines hinterland basins: examples from the Valdelsa and Valdera (Central Tuscany)

Poneti G.*[1], Scarselli N.[2], Benvenuti M.[3], Craig J.[4] & Marsh B.[5]

[1] Dipartimento di Scienze della Terra, Università di Pisa.[2] Department of Earth Sciences, Royal Holloway, University of London (UK). [3] Dipartimento di Scienze della Terra, Università di Firenze.[4] ENI S.p.A., San Donato MIlanese (MI) [5] Alcatel Submarine Networks.

*Corresponding author e-mail:* giovanni.poneti@phd.unipi.it

*Keywords:* positive inversion, hinterland basins, Northern Apennines.

Hinterland basins at the back of orogenic belts, such as those of the Northern Apennines, Andes and Himalayas, form densely populated low-lying areas with great socio-economic importance. Understanding their tectono-stratigraphic setting and regional geological evolution is critical to assessing their potential subsurface resources and geohazards. This study focuses on the Neogene-Quaternary tectonic-sedimentary evolution of the Northern Apennines hinterland basins which have been the object of scientific debate around their origin and development as:

– graben, half-graben or bowl-shaped basins evolving into graben as an effect of large-scale back-arc processes or gravitational instability of thickened crust following the Apennine orogeny since the Early Miocene;
– basins mainly controlled by out-of-sequence thrusts and backthrusts accommodating in the inner portion of the chain the compressive stress accumulated in the frontal zones until the Late Pliocene-Pleistocene.

~700 km of 2D seismic reflection data and wireline logs from 4 wells are analysed with the aim to unravel the relationship between tectonics and sedimentation in the evolution of the NW–SE oriented Valdelsa and Valdera Basins (Central Italy). These hinterland basins form depressions ~30 km wide ~60 km long filled with a succession up to 2 km thick made of upper Miocene to Pleistocene fluvio-lacustrine to marine deposits.

Early results indicate that the Valdelsa Basin underwent a late Miocene extensional stage as evidenced by normal faults bordering the basin in a half-graben configuration. A later Late Miocene-Late Pliocene(?) compressional phase ensued as shown by positive inversion of normal faults generating harpoon geometries within the syn-extension wedges as well as thinning of syn-inversion strata. The existence of a sub-basin with a NE-dipping border normal fault with no evidence of inversion suggests that the direction of compression relative to the basin geometry was an important control on the development of the inversion.

The tectonic history of the Valdera basin involves polyphase activity of NW-trending border faults. A Messinian-Zanclean compressional phase deforming the basin-infill is suggested by the presence of onlaps onto folded strata located within the hanging wall of the basin's border faults. During the Piacenzian, the border faults underwent a major extensional phase as indicated by the presence in their hanging wall of sedimentary wedges thickening towards the NE. A positive inversion took place at the end of the Piacenzian as shown by the broad folding of the shallow sedimentary succession.

Potential geodynamic mechanisms within the wider evolution of the Northern Apennines are explored to develop a framework for the timing and style of structuration of the two hinterland basins unravelled so far in this research.

# $CO_2$ and steam emissions controlled by enhanced fracture permeability in the Monterotondo Marittimo-Sasso Pisano crustal transfer fault system (Larderello Geothermal Field, Italy)

Taussi M.*[1], Brogi A.[2-3], Liotta D.[2-3], Nisi B.[4], Perrini M.[2], Vaselli O.[4-5], Zambrano M.[6] & Zucchi M.[2]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [3] Istituto di Geoscienze e Georisorse, CNR, Pisa. [4] Istituto di Geoscienze e Georisorse, CNR, Firenze. [5] Dipartimento di Scienze della Terra, Università di Firenze. [6] Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* marco.taussi@uniurb.it

*Keywords:* fault zone permeability, $CO_2$ and steam emission, geothermal exploration.

Carbon dioxide is one of the most important gases naturally released from geothermal systems. Establishing the processes and pathways that regulate the $CO_2$ diffuse degassing can provide valuable information for exploration and exploitation purposes of geothermal reservoirs. Areas with high $CO_2$ emissions are indeed able to reveal major upflow zones from deep reservoirs through deep-reaching permeable fault zones. In this work, a high-resolution $CO_2$ flux (with records up to 2927 g $m^{-2}$ $d^{-1}$) and soil temperature (with records up to 98.8°C) survey was carried out along with detailed fracture parameters measurements in a selected area of the Monterotondo Marittimo-Sasso Pisano transfer fault (Larderello geothermal system, Tuscany, Italy). The main aim is to define the behavior of diffuse $CO_2$ through the fault system and investigate how the soil $CO_2$ flux and steam change with respect to the architecture of the fault damage zone (i.e., volumetric fracture intensity, permeability, and persistence of the fractures). The presence of multiple populations of $CO_2$ flux suggested that soil degassing is controlled by three different transport mechanisms which can be defined as: i) purely diffusive, ii) mixed diffusive-advective, and iii) purely advective. These three mechanisms are characterized by efflux values of <20, between 20 and 300 and >300 g $m^{-2}$ $d^{-1}$, respectively. The spatial distribution of these fluxes well agrees with the fracture distribution and characters of the Jurassic radiolarite (Diaspri Fm) dissected by NNE-striking faults. The interaction between pre-existing fractures and fracture-related fault-zone locally enhances the secondary rock permeability as highlighted by the correlation between Discrete Fracture Network (DFN) modeling and advective flux. The pivotal role of transfer fault zones in controlling fluid emissions is also confirmed by the normalized $CO_2$ output to the fault strip (1350 $m^2$) that resulted in ~155 t $d^{-1}$ $km^{-2}$, although when the area characterized by advective flux (460 $m^2$) was considered the efflux rose to 326 t $d^{-1}$ $km^{-2}$.

# Morphostructural and seismotectonics analysis of the Umbria-Marche Apennines (central Italy): new insight of active tectonics setting using GIS-based morphotectonic investigation

Teloni S.*[1], Valente E.[2], Ascione A.[2], Mazzoli S.[1], Pierantoni P.P.[1], Invernizzi C.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II».

*Corresponding author e-mail:* simone.teloni@unicam.it

*Keywords:* active fault, tectonic geomorphology.

The Umbria Marche Apennines and foothills is the locus of moderate to intense tectonic activity, as shown by the occurrence of historical strong earthquakes and recent seismic sequences making this sector one of the most seismically active areas of central Italy. In addition, the lack of reliable instrumental data for strong seismic events and the poor exposures of fault planes affecting Quaternary sediments make the characterization of active seismogenic faults problematic. To tackle this issue a GIS-aided morphotectonic study has been carried out through a large-scale analysis of the topography and the river network, combined with available instrumental seismicity, and structural geology data. Topography analysis includes swath profiles roughly perpendicular to the main geological structures of the study area. Analysis of the river network includes river long profile and transformed (χ) long profile coupled with the slope/area analysis. The former allowed the location of knickpoints/knickzones whereas the latter allowed the spatial distribution of the Ksn index to be deciphered.

Combined data from topography and river network suggest a difference between the northern and the southern sector of the Umbria-Marche Apennines. In fact, high values of the mean and minimum elevations, the diffuse presence of large knickzones and high to very high Ksn values, which are all clustered to the south of the Umbria-Marche Apennines, suggest the presence of a locus of enhanced vertical motions (i.e., surface uplift) towards the south. Here, the Umbria-Marche-Sabina thrust zone, which develops from the Foglia River to the north to Olevano Romano to the south, is locally segmented by WSW-ENE transversal fault systems (Pierantoni et al., 2017). These are generally high-angle regional structures, deeply rooted into the crust (Costa et al., 2021). Transversal structures play a key role on the Apennine fold and thrust belt growth, separating the study area in blocks with different evolutionary characteristics and influencing the seismic sequence (e.g., 1997 Colfiorito and 2016-2017 Amatrice-Visso-Norcia seismic sequences) confining the seismicity in cluster. In this regard, the identification and parametrization of active faults have major implications on the correct seismic hazard assessment and risk mitigation for large and densely populated areas of the Marche Region.

Costa M., Chicco J., Invernizzi C., Teloni S. & Pierantoni P.P. (2021) - Plio–Quaternary Structural Evolution of the Outer Sector of the Marche Apennines South of the Conero Promontory, Italy. Geosciences, 11(5), 184.

Pierantoni P.P., Centamore E. & Costa M. (2017) - Geological and seismologic data review of the 2009 L'Aquila seismic sequence (Central Apennines, Italy): deep-seated seismogenic structures and seismic hazard. Italian Journal of Engineering Geology and Environment, 17(2), 5-40.

# S44.

# Faults and shear zones from near the surface to the deep crust: clues from micro-structural analyses, geochronology and geochemistry


*Conveners & Chairpersons*

*Chiara Montemagni (University of Milano - Bicocca)*

*Manuel Curzi (University of Bologna)*

*Stefania Corvò (University of Pavia)*

*Alessio Lucca (University of Parma)*

# The long-term evolution of the Monte Pettino seismogenic fault

Arriga G.*[1], Brilli M.[2], Cosentino D.[1], Rossetti F.[1], Hu H.-M.[3-4], Shen C.-C.[3-4] & Soligo M.[1]

[1] Dipartimento di Scienze, Università di Roma Tre. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [3] High-Precision Mass Spectrometry and Environment Change Laboratory HISPEC, Department of Geosciences, National Taiwan University, Taipei (Taiwan). [4] Research Center for Future Earth, National Taiwan University, Taipei (Taiwan).

*Corresponding author e-mail:* giorgioarriga@gmail.com

*Keywords:* normal faulting, stable isotopes, U-Th carbonate dating.

The seismogenic fault pattern of the central Apennines of Italy provides a natural laboratory to study interactions and feedbacks between long- and short-term deformation in extensional settings. The Monte Pettino seismogenic fault (MPF) forms the NE basin boundary fault of the Pliocene-Quaternary L'Aquila intermontane basin. The total offset along the MPF is ~1.4 km, as reconstructed by the stratigraphic separation (hanging wall: Lower Cretaceous Maiolica Fm; footwall: Lower Jurassic *Palaeodasycladus* limestones). Despite the short-term behaviour of the MPF is well constrained by paleoseismological evidence and historical seismicity, its long-term activity is still poorly defined. In this study, we integrated fieldwork, geochemical (C and O stable isotopes), and geochronological (U-Th method) investigations to constrain the long-term activity of the MPF. Our results show two main deformation stages characterized by different structural styles. The early stage corresponds to the development of a m-thick panel of SW-dipping (65-70°) cataclastic rocks, exposed at the piedmont of Monte Pettino. The cataclastic rocks are sealed by the Middle Pleistocene (ca. 250-350 ka) L'Aquila Breccias Fm. The $\delta^{13}C$ and $\delta^{18}O$ systematics of the cataclastic matrix and calcite slickenfibers range from +0.71 to +2.67 ‰ and +0.02 and -2.68 ‰ (V-PDB), respectively, in the range of the carbonate bedrock. This indicates a "closed" system behaviour and suggests a deformation environment dominated by dissolution creep, which is typical of exhumed fault zones. The second stage is mainly recorded within the L'Aquila Breccias Fm. and in discontinuous volcaniclastic deposits, interpreted as Pozzolane Rosse Fm. of the Albani Hills volcanic district, which both unconformably cover the bedrock. It consists of anastomosed WNW-ESE striking fault strands, spaced m to hm apart and with cm to m displacements, associated with carbonate veins and layered carbonate concretions (calcareous tufa). Stable isotopes measured from the fault slickenfibers show a progressive re-equilibration with the meteoric fluids, as attested by a lowering trend of the and $\delta^{18}O$ values down to -10.35 and -6.86 ‰, respectively. The carbonate veins and concretions systematically show negative $\delta^{13}C$ and $\delta^{18}O$ values, clustering at -8.21/-10.47 ‰ and -5.83/-7.06 ‰, respectively, and indicating a dominant meteoric fluid supply ("open" system) and an important contribution of organic carbon. The U-Th ages of the veins and concretions overlap in the range 182 ± 17 and 331 ± 26 ka, supporting the temporal constraints from stratigraphic data. Remarkably, the field and the isotopic data have provided no evidence of tectonic reactivation of the cataclastic core of the MPF during the Middle-Upper Pleistocene, suggesting that the core of the MPF was already exhumed at that time. Further geochronological studies are in progress to further constrain the temporal evolution of the MPF in space and time.

# Open-closed-open paleofluid system conditions recorded in the tectonic vein networks of the Parmelan anticline (Bornes Massif, France)

Berio L.R.*[1], Mittempergher S.[2], Storti F.[1], Bernasconi S.M.[3], Cipriani A.[2], Lugli F.[4] & Balsamo F.[1]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [3] Geological Institute, ETH Zürich (Switzerland). [4] Dipartimento di Beni Culturali, Università di Bologna.

*Corresponding author e-mail:* luigi.berio@gmail.com

*Keywords:* folding, paleofluids, Alps.

We performed a multidisciplinary study of syntectonic calcite cements to decipher the plaeofluid evolution during the polyphasic tectonic history of an external sector of the Dauphinois domain (external Bornes) that underwent syn-orogenic extension before its incorporation in the orogenic wedge. We focused on Lower Cretaceous carbonates which underwent sub-aerial exposure during flexural bulging, layer-parallel shortening, folding, and post-folding oblique contraction. Through detailed petrographic observations, we distinguished five generations of syntectonic cements on which we performed geochemical analyses (stable and radiogenic isotopes, major and trace elements, fluid inclusion and clumped isotopes thermometry). The older calcite cements associated with the pre-folding and early syn-folding deformation structures have $\delta^{18}O$ - $\delta^{13}C$ values in the field of the host rock, $^{87}Sr/^{86}Sr$ ratios incompatible with marine Cretaceous seawater, high Fe and Mg contents and lack Ce anomaly. These cements precipitated from an $^{18}O$-enriched fluid ($\delta^{18}O$ = +8.6 - +11.6 ‰ SMOW) having temperature between 90 and 115°C, low Ca/Fe molar ratios and Mg/Ca molar ratios significantly lower than Cretaceous and Tertiary seawater (lower than 0.35). This first fluid type has been interpreted as a mixed marine-meteoric fluid that extensively interacted with the host rock in a closed system and that was thermally equilibrated under maximum burial conditions (3.5 - 4 km), concurrently with the development of tectonic deformation structures produced by pre-folding layer-parallel shortening, incipient thrusting and early folding. The younger calcite cements associated with the late syn-folding and post-folding deformation structures have lower $\delta^{18}O$ values, low Fe and Mg contents and precipitated from an $^{18}O$-depleted ($\delta^{18}O$ = -7.5 - -4.3 ‰ SMOW) meteoric fluids possibly heated in the more internal sector of the belt (fluid temperature between 40 and 80°C) and then migrated towards the foreland inside the fractured Cretaceous units with calcite precipitation in thermal disequilibrium with the host rock. $^{87}Sr/^{86}Sr$ ratios exclude any contribution from basement-derived ascending fluids and rule out a possible downward circulation of meteoric fluids at basement depths.

# The Late Pleistocene and Anthropocene neotectonic evidence of the La Sassa cave (Volsci Range, Italy)

Cardello G.L.*[1], Alessandri L.[2], Attema P.A.J.[2], Baiocchi V.[3], De Angelis F.[4], Del Pizzo S.[5], Di Ciaccio F.[5], Fiorillo A.[6], Gatta M.[6-7], Monti F.[3], Onori M.[3], Rolfo M.F.[6], Romboni M.[4], Sottili G.[8] & Troisi S. [5]

[1] Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari. [2] Institute of Archaeology, University of Groningen (Netherlands). [3] Dipartimento di Ingegneria Civile, Edile e Ambientale, Sapienza Università di Roma. [4] Centro di Antropologia Molecolare per lo studio del DNA antico, Dipartimento di Biologia, Università di Roma «Tor Vergata». [5] Dipartimento di Scienze e Tecnologie, Università di Napoli «Parthenope». [6] Dipartimento di Storia, Petrimonio Culturale, Formazione e Società, Università di Roma «Tor Vergata». [7] Department of Archaeology, University of York (UK). [8] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* glcardello@uniss.it

*Keywords:* Apennines, speleology, geoarcheology.

We present the outcomes of a novel investigation method comprehensive of geomatic, structural geology, palaeontological, archaeological and radiometric data applied to solve the morphostructural evolution of a cave of the Apennines (La Sassa cave) and its surroundings (Volsci Range). Both structural and 3D survey highlighted the step-like shape of the cave due to normal fault steps that allowed the localized formation of concretions also enveloping archaeological layers. Sixteen $^{14}C$ ages on fauna and human bones and thousands of archaeological finds provided chronological constraints of faulting in the Late Pleistocene and possibly also after the Middle Bronze Age. This method enabled us to recognize that the shape of the cave is associated with normal faults with similar orientation also occurring in the surroundings. In the cave, Late Pleistocene (32,930-30,6744 calBC) hyena and bear bones, were found partially to fully embedded in concretions near the wall of a major fault marking the onset of syn-sedimentary faulting in the cave. There, syn-sedimentary pockets generated within small step-like metric-scaled basins preserving rich archaeological finds belonging to the Copper Age (CA, 3300-2000 calBC) and the Early and Middle Bronze Age (EBA-MBA, 1900-1200 calBC). Finally, Middle Bronze Age to Medieval collapse of blocks and concretions are found near fault zones. In our interpretation, the CA deposits progressively infill room floors, while the concretioned collapse covering the MBA hearth is evidence of crack-and-seal processes along a secondary fault zone of a segmented major normal fault of the Volsci Range with cumulative subsurface rupture length reaching up to 10-12 km and displacement in the order of 0.8-1 km, which could possibly be capable of generating an earthquake of magnitude $M_w$ comprised between 5.1 and 5.8 depending on the fault segmentation. The structural evidence is relevant for understanding the speleogenesis from the Late Pleistocene and the human occupation of the cave. Overall, these results set the timing of faulting and thus represent the first neotectonic evolution ever documented in the Volsci Range. The outcome is of regional relevance as Late Pleistocene to Holocene/Anthropocene neotectonics were poorly constrained by the structural studies of the Apennine Tyrrhenian passive margin in southern Latium. As a result, the La Sassa findings provide temporal constraints to the recent regional tectonic evolution with implications for the local seismic hazard assessment.

# Constraining the timing of evolution of shear zones in collisional orogens: an interplay between structural geology and geochronology

Carosi R.[1], Montomoli C.*[1], Iaccarino S.[1], Benetti B.[1], Petroccia A.[1] & Simonetti M.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* chiara.montomoli@unito.it

*Keywords:* shear zone, structural geology, geochronology.

Constraining the timing and the shear activity is one of the main topics in the last decades of researches about the tectono-metamorphic evolution of orogenic belts. We present a combined structural and geochronological approach from two major ductile regional shear zones: the first one affecting the Variscan basement in Northern Sardinia (Italy) (Carosi et al., 2020) and in the External Crystalline Massifs Structural (East Variscan Shear Zone; EVSZ) (Simonetti et al., 2018 e 2020) and the second one deforming the medium to high-grade rocks of the metamorphic core of the Himalaya (High Himalayan Discontinuity) (Carosi et al., 2018). High-resolution, texturally and chemically controlled monazite geochronology applied in separated shear zones of the Variscan Belt allowed to recognize a similar timing of activity ranging between c. 340-330 and 300 Ma. This approach led to a better understanding of the evolution of the EVSZ, supporting a model where several branches were active by growth by linkage model. Following a similar approach, in situ U-Th-Pb analysis of monazite constrained the timing of top-to-the S/SW shearing between c. 28 Ma and 17 Ma of the High Himalayan Discontinuity. Earlier exhumation of the hanging wall was triggered by shear zone activity, whereas at the same time, the footwall was still experiencing burial with increasing P-T conditions. The timing of shearing of this shear zone fits with an in-sequence shearing tectonic model for the exhumation of the Himalayan mid crust. Those examples demonstrate that a multidisciplinary approach is essential for obtaining useful results from the study of regional scale shear zones and to understand their role in the tectonic evolution of orogens.

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# Field and remote sensing investigations of deformation structures within the Rotondo granite around the Bedretto Underground Laboratory (Gotthard massif, Central Alps)

Ceccato A.*, Zappone A.S. & Behr W.M.

Department of Earth Sciences, ETH Zürich (Switzerland).

*Corresponding author e-mail:* aceccato@erdw.ethz.ch

*Keywords:* shear zone, fault zone, Gotthard.

The Rotondo granite (Gotthard massif, Central Alps) hosts the Bedretto Underground Laboratory, a multidisciplinary research infrastructure developed to shed some new light on the development of engineered geothermal systems, induced seismicity and earthquake physics. Many of the projects implemented in the Bedretto Underground Laboratory focus on the analysis of the hydro-mechanical response to fluid injection of the Rotondo granite, which is characterized by a complex network of natural deformation structures developed during Alpine tectonics. These deformation structures include NE-SW striking ductile shear zones, showing top-to-SE kinematics, which seem to have controlled the development at lower temperatures of coplanar dextral, strike-slip brittle fault zones. Despite the general characterization and understanding of the relative chronology of deformation structures within the Rotondo granite, a detailed analysis of the geology, and spatial and temporal relationships of such deformation zones is still missing. In this contribution, we present the preliminary results of field and microstructural investigations on the Rotondo granite focusing on: (i) the definition of the detailed sequence of ductile and brittle deformation structures; (ii) the pressure-temperature conditions of deformation during the exhumation of the Rotondo granite, (iii) the role of high-temperature ductile microstructural characteristics in controlling the localization of brittle fault zones. In addition, through multiscale remote sensing techniques, photogrammetry and structural analyses on virtual outcrop models we have constrained the multiscale geometry and roughness of ductile and brittle shear zone network in the Rotondo granite. Such integrated, multiscale characterization provides fundamental constraints on the quantification of permeability properties of the network of ductile and brittle fault zones in the Rotondo granite controlling fluid flow during injection and fault stimulation experiments.

# Tectonics of the Eastern Southern Alps: a perspective from new structural and radiometric constraints

Curzi M.*[1], Viola G.[1], Aldega L.[2], Billi A.[3], Carminati E.[2], Zuccari C.[1], van der Lelij R.[4], Kylander-Clark A.R.C.[5] & Vignaroli G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [4] Geological Survey of Norway, Trondheim (Norway). [5] Department of Earth Science, University of California, Santa Barbara, CA (USA).

*Corresponding author e-mail:* manuel.curzi@unibo.it

*Keywords:* radiometric datings, tectonics.

The Eastern Southern Alps (ESA) are the south-verging fold-and-thrust belt of the Alpine orogen. It formed during Paleogene-Neogene times. The ESA represent an excellent natural laboratory to study the long-lasting evolution of complex fold-and-thrust belts and are highly attractive to geologists and geoscientists. Along the ESA, spectacular exposures at the seismic scale offer unique possibilities to study the details of past tectonic processes. However, despite a few published papers regarding the deformation processes and mechanisms of a major thrust in the ESA (The Belluno Thrust), modern, multiscale and multidisciplinary studies dealing with fault zones in the ESA are still missing, such that detailed reconstructions of the tectonic events through space and in time still require further studies. We present the preliminary results from still ongoing structural, microstructural, and radiometric investigations on selected, key outcrops along two main thrusts of the ESA. In detail, we focus on the (i) Valsugana Fault, which is a first order thrust that separates the Dolomites to the north from the Venetian Pre-Alps to the south, and (ii) the more external Belluno Thrust. We couple structural analysis and microstructural observations with U-Pb dating on syn-tectonic carbonates and K-Ar dating of fault gouges. Our results thus far document that the Valsugana Fault represents an inherited pre-Alpine paleotectonic structure that (i) strongly influenced the geometry and kinematics associated with deformation structures formed during the Alpine deformation phases and (ii) records multiple reactivations during Alpine deformation, including remarkable out-of-sequence compressional movements that occurred after the propagation of the frontal Belluno Thrust.

# Insights into deep episodic tremors and slip events from High-Pressure continental metasedimentary successions of the Northern Apennines

Giuntoli F.*[1], Viola G.[1] & Eske Sørensen B.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Department of Geoscience and Petroleum, Norwegian University of Science and Technology, Trondheim (Norway).

*Corresponding author e-mail:* francesco.giuntoli@unibo.it

*Keywords:* deep episodic tremors and slip events, dilational shear veins, carpholite.

The geological record of deep seismic activity in subduction zones is generally scanty due to its common overprinting during exhumation and only a few regions allow studying well-preserved exhumed deep structures. The Northern Apennines are one such area, granting access to continental units (Tuscan Metamorphic Units) that were subducted to high-pressure conditions, were affected by brittle-ductile deformation while accommodating deep tremors and slips and then exhumed back to surface, with only minor retrogression.

Our approach is based on detailed fieldwork, microstructural and petrological investigations. Field observations at the Island of Giglio reveal a metamorphosed broken formation composed of boudinaged metaconglomerate enveloped by metapelite displaying a pervasive mylonitic foliation. Dilational shear veins occur in both lithotypes but are more common and laterally continuous in the metapelite. Veins are generally parallel to the metamorphic foliation and are composed of iso-oriented stretched quartz and Mg-carpholite ($X_{Mg}$>0.5) fibres, which form single-grains up to several centimetres long. These fibres define a stretching direction consistent with that of the hosting metaconglomerate and metapelite, which is marked by K-white mica and quartz. Thermodynamic modeling constrains the formation of the high-pressure veins and the mylonitic foliation to ~ 1 GPa and 350°C, corresponding to c. 30-40 km depth in the subduction channel (Giuntoli & Viola, 2022). Microstructural analysis suggests that dilational hydroshear veins formed by incremental crack-sealing at supralithostatic pore pressure values. Successively, the veins deformed by dislocation creep. Blueschist facies mylonites formed mainly by a combination of dissolution-precipitation creep and slip along phyllosilicate bands.

Dilational shear veins in subducted metasedimentary successions have been suggested to be potential records of episodic tremors and slip events (e.g., Fagereng et al., 2011). We propose that these structures reflect the cyclic and repeated alternation of localised brittle failure, with Mode I fracturing making it possible for dilational shear veins to form, and more diffuse viscous deformation. These cycles probably related to the fluctuation of pore pressure that repeatedly reached supralithostatic values (Giuntoli & Viola, 2021). Concluding, these structures can be considered part of the geological record of episodic tremors and slip events occurring at >30 km of depth in the Apenninic subduction channel.

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# Dating the shear zone activity at mid to lower continental crustal levels (Ivrea-Verbano Zone, Italy): the power of monazite and titanite

Langone A.*[1], Simonetti M.[2], Piazolo S.[3], Bonazzi M.[4], Corvò S.[4] & Maino M.[4]

[1] Istituto di Geoscienze e Georisorse, CNR, Pavia. [2] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [3] School of Earth and Environment, University of Leeds (UK). [4] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* langone@crystal.unipv.it

*Keywords:* shear zone, monazite and titanite U-(Th)-Pb dating, Ivrea-Verbano Zone.

Dating the time of shear zone activity remains challenging. Here we present a study from shear zones which transect mid to lower crustal section exposed in the Ivrea-Verbano Zone (e.g., Rutter et al., 1993). Some of those structures are interpreted to be related to different stages of Mesozoic rifting (e.g., Petri et al., 2019). Up to now only a few geochronological constraints (e.g., Ar-Ar data) are available, mainly restricted to the upper crustal, lower grade shear zones. We here report an attempt to date amphibolite-facies deformation at mid-crustal levels, i.e., the Forno-Rosarolo Shear Zone (FRSZ, Siegesmund et al., 2008) by integrating monazite and titanite U-(Th-)Pb data.

The FRSZ is a sub-vertical structure with a thickness of about 500 m. It is located at the transition from amphibolite- to granulite-facies metamorphic supracrustal rocks and is characterized by anastomosing planes of high strain surrounding low strain domains. Mylonites developed mainly at the expense of paragneisses, mafic rocks and minor calc-silicates. The low strain domains are mainly composed of mafic rocks and felsic granulites. Metapelites and calcsilicates were selected for *in-situ* U-(Th-)Pb monazite and titanite geochronology, respectively. Mylonitic paragneisses consist of garnet, sillimanite, feldspar and biotite with accessory zircon, monazite and rutile. Monazite occurs in different microstructural positions (included in porphyroclasts or along the mylonitic foliation) and commonly presents complex chemical zoning of Th and Y allowing to identify three different generations of monazite. Preliminary data suggest a late Triassic-Jurassic deformation induced recrystallization event.

Mylonitic calc-silicates are made of fine-grained calcite surrounding clinopyroxene, feldspar, amphibole, epidote and garnet porphyroclasts. Large titanite grains (up to 1 mm) occur both along the foliation and as inclusions within porphyroclasts. Titanites are strongly zoned and shows evidences for intracrystalline deformation (e.g., deformation twins and systematic crystal lattice bending). SEM-BSE imaging revealed that titanite consists of large and brighter cores (BSE image) surrounded by small and irregular rims. The boundary is sharp and often lobate.

The application of two independent geochronometers may allow to shed light on the age and potential provide some insight in the duration of high strain deformation. Our approach is particularly appropriate when dealing with large-scale shear zones involving different types of rocks.

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# Early Permian extensional structures of the central Southern Alps (N Italy), characterized by Boron-rich hydrothermalism

Locchi S.*[1], Trumbull R.B.[2], Moroni M.[3], Zanchi A.[1] & Zanchetta S.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Department of Inorganic and Isotope Geochemistry, German Research Centre for Geosciences, Potsdam (Germany). [3] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* s.locchi@campus.unimib.it

*Keywords:* extensional tectonics, hydrothermalism, Early Permian geodynamics.

The Alpine region after the Variscan orogeny was characterized by an extensional regime associated to crustal thinning and an intense magmatic activity developed at different crustal levels during the Early Permian (e.g., Schaltegger & Brack, 2007).

At that time, in the central Southern Alps (cSA, N Italy), the opening of intracontinental fault-controlled extensional basins (e.g., the Orobic Basin) filled with volcanics and volcanoclastic sediments was controlled by a combination of Low- and High-Angle Normal Faults. Some parts of these Early Permian Low-Angle Normal Faults (LANFs) partially escaped the Alpine deformation, preserving their original features. Fault rocks formed along the contact between basement and cover, consisting of cataclastic rocks, are still discernible and are often sealed with cm to dm thick layers of dark, cryptocrystalline to microcrystalline tourmalinites (e.g., Zanchetta et al., 2022; Locchi et al., 2022) resulting from a metasomatism promoted by the circulation of Boron-rich fluids. Tourmalinites, composed of up to 70% in volume of tourmaline, are recurrent in various sites of the cSA (e.g., De Capitani et al., 1999) and are invariably located along Permian faults. Their age is indirectly constrained by their occurrence along Early Permian faults, especially LANFs, and in Upper Permian conglomerate where they occur as clasts. However, their genesis has never been deeply investigated, even if they are likely linked to the Uranium mineralization of the Novazza-Val Vedello district (De Capitani et al., 1999 and references therein).

To further characterize and assess the source of the hydrothermal activity responsible for Boron-rich fluid circulation during the Early Permian intracontinental extension, we studied several tourmalinite-bearing LANFs in the cSA. We applied a multidisciplinary approach: field-based structural analysis are combined with microstructural studies, mineral and whole-rock geochemistry, geochronology and determination of Boron isotopic composition of tourmaline. The isotopic and geochemical data provide important clues on this hydrothermal event and highlight its regional relevance, pointing to a magmatic source for the Boron-rich fluids. Preliminary results demonstrate a temporal relationship between tourmalinites and Early Permian magmatism in the cSA and exalt the role played by the extensional fault system as a preferred pathway for circulation of fluids of magmatic origin at shallow crustal levels. For this reason, the occurrence of tourmalinites can be considered as a proxy of Early Permian extensional structures in the cSA.

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# Relative and absolute ages of deformative processes at the base of the seismogenic crust from geochronological, microstructural and geochemical studies of the Gole Larghe Fault (Adamello, Italy)

Mittempergher S.*[1], Di Toro G.[2], Bistacchi A.[3], Zanchetta S.[3], Aretusini S.[4], Villa I.M.[3] & Giovanardi T.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Dipartimento di Geoscienze, Università di Padova. [3] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [4] INGV, Roma.

*Corresponding author e-mail:* silvia.mittempergher@unimore.it

*Keywords:* pseudotachylyte, geochronology, microstructures.

During their activity, faults experience multiple seismic cycles, which progressively modify their inner structure, mineral composition and mechanical properties. We integrated microstructural, geochemical and geochronological investigations on fault rocks from the Gole Larghe Fault Zone (northern Adamello) to constrain the relative and, where possible, absolute age of the deformative processes.

The Gole Larghe Fault Zone is a dextral transpressive fault zone of about 800 m, composed of hundreds of cataclasite-pseudotachylyte-bearing fault strands. Crosscutting relationships in the field and at the microscale indicate that single fault strands bear multiple generations of cataclasites and pseudotachylytes, with pseudotachylytes mostly postdating cataclasites. Quantification of the grain size distribution of rock fragments in cataclasites indicates that, with increasing finite strain, the average grain size decreases, the fractal dimension increases (from 1.6 to 2.8 in two dimensions) and the faults develop multiple domains of foliated cataclasites and ultracataclasites. Where ultracataclasite is present, faults accommodate high finite strain, suggesting strain localization. In contrast, faults accommodating low finite strain have a less evolved grain size distribution and show a foliation associated with mineral segregation, indicative of stress driven mass transport processes associated with mineral reactions. Both low and high strain cataclasites display a widespread hydrothermal cementation predating frictional melting. Cataclastic comminution and hydrothermal induration appear a precursor for earthquake nucleation and coseismic slip. $^{40}Ar/^{39}Ar$ ages of four pseudotachylytes and one cataclasite span between 31 and 26 Ma, with the sample of cataclasite displaying one of the youngest ages, in contradiction with crosscutting relationships. We suggest that post-cementation fluid-rock interactions in the cataclasite matrix caused Ar loss which obliterated its absolute age. The timespan between the formation of high strain cataclasite and frictional melt remains therefore unconstrained. The protracted (about 5 My) seismic activity and the low cumulative strain (on the order of 1 km over an 800 m thick fault zone) suggests that the Gole Larghe Fault Zone hosted a seismicity sharing several characteristics with intraplate seismic sources (scattered hypocentres and low strain rate).

# Slip rates of the Mt. Morrone active normal fault system (Central Apennines) constrained by cosmogenic dating of morphotectonic markers

Puliti I.*[1], Benedetti L.[2], Pizzi A.[1], Fleury J.[1], Guillou V.[1] & Aster Team[1]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] CNRS, IRD, INRA, Coll France, CEREGE, Aix Marseille University, Aix-en-Provence (France).

*Corresponding author e-mail:* irene.puliti@unich.it

*Keywords:* active faults, slip rates, Central Apennines.

The slip rate evaluation of active faults is a critical requirement to understand the fault behavior and its implication for a seismic hazard assessment. Located at the easternmost portion of the Central Apennines range, the Mt. Morrone fault system is associated with a high seismic risk (Pace et al., 2006) because it is assumed to be one of the most relevant seismic gaps of the central Apennines considering the elapsed time since the last event (inferred 2$^{nd}$ century AD). Besides, there are a few data on its last activation in the historical age, and its Holocene paleo-earthquake history is still very inaccurate. Moreover, geological and morphological evidence reveals a ~23 km-long NW-SE trending structure composed of two parallel fault branches (SAF and PRPF), that could potentially trigger earthquakes of magnitude 6-7. Assessing the slip rates is thus crucial to constraining the pace at which strain is accumulated on this system at a temporal scale encompassing its seismic cycle. Here, we estimated the slip rate of its northern segments bounding the Quaternary Sulmona Basin between Popoli and Roccacasale (PRPF). We accurately mapped the segments and associated offset Quaternary markers based on high-resolution topography (e.g., 1 m/px LiDAR dataset) combined with field investigations at higher resolution with drone photogrammetry. Cumulative displacements of a few to tens of meters apparently displaced slope/alluvial/fluvial deposits. We measured these offsets through topographic profiles and dated the displaced morphological markers (i.e., alluvial terraces) using $^{36}$Cl exposure dating. The yielded slip rate is of 0.2-0.4 mm/yr over the last ~40 kyr. Similar slip rates have been retrieved both for a shorter period (i.e., ~0.45 mm/yr over ~9 ka from Galli et al., 2015), and for a longer time period (i.e., ~0.4 mm/yr over ~92 kyr from Galli et al. (2015) and 0.4 ± 0.07 mm/yr over $10^{5-6}$ yr from Gori et al., 2011), suggesting that the PRPF slip-rate has been constant over the Holocene, at least. Lastly, we observed that among the fault systems also located in the eastern portion of the Apennines, the yielded slip rates are higher (e.g., 1.1 mm/yr for the Mt. Vettore fault system). Further investigations are needed to fully assess the slip rates of the Mt Morrone fault system, especially the SAF segment, and have more constrained data on the evolution of the entire system.

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# The Jurassic rift-related fault system and its Alpine re-activation history (central Southern Alps, N Italy): clues from structural analysis and paleo-fluid characterization

Rocca M.*[1], Gasparrini M.[2], Zanchetta S.[1], Berra F.[2] & Zanchi A.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* m.rocca@campus.unimib.it

*Keywords:* Southern Alps, Jurassic fault system, paleo-fluid characterization.

The central Southern Alps (Seriana Valley, Bergamo) is characterized by a complex polyphasic evolution (Zanchetta et al., 2015) resulting from the re-activation of extensional faults related to the Jurassic rifting during the Alpine deformation, as well as the development of new structures. At least three different events were identified on the base of cross-cutting relationships between structures and magmatic bodies (Zanchi et al., 1990): 1) Early Jurassic N-S oriented normal faults, several kilometers in length, bordering a graben; 2) the intrusion of E-W trending andesitic dikes dated at 40 Ma (U-Pb zircon ages; D'Adda et al., 2011); 3) the reactivation of Jurassic normal faults as sinistral or dextral strike-slip faults during the N-S oriented Alpine compression, which caused southward translation of the Dolomia Principale dominated thrust sheet, probably during the late Cenozoic (Zanchi et al., 1990).

To understand this complex tectonic evolution, field work has been performed North of Bergamo (Amora, Selvino area) where the transition from pre-rift (Rhaetian) to syn-rift (Hettangian) succession is preserved and where the Alpine tectonics, postdating this Jurassic extensional event, is well expressed by transcurrent and reverse faults. Furthermore, clear cross-cutting relationship between the main tectonic features are well exposed in this area; field work focused on the reconstruction of the geometrical features of reverse, normal and strike-slip faults, joints, and veins, allowing for the identification of at least three tectonic phases, as described by Zanchi et al. (1990).

Field work led to the identification of a graben filled by Jurassic basin sediments whose bordering faults (N-S trending) were activated as transcurrent faults during the Alpine compression. Despite the Alpine reactivation, the syndepositional Lower Jurassic activity of these faults is documented by stratigraphic evidence, such as slump overfolds and mass flow deposits in the Lower Jurassic cherty limestone filling the basin (Moltrasio Limestone). Statistical methods for palaeoflow definition (Rodrigues et al. (2021) have been applied to the mass-transport deposits exposed within the Moltrasio Limestone in the hanging wall of the reactivated Jurassic extensional faults.

The preliminary field data highlighted the importance of this area for the understanding of the evolution of the central Southern Alps: microstructural analyses on syn-tectonic calcite veins from the Norian to the Lower Jurassic successions, fluid inclusions analysis, O-C stable-isotopes, and clumped isotopes ($\Delta_{47}$) analyses, together with U-Pb dating of calcite, will help in the reconstruction of the tectonic, burial, thermal and paleo-fluid flow history of this sector of the central Southern Alps.

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# Is the fault scarp analysis a reliable method for fault activity quantification in anthropized areas? A case study from the active Mt. Marine normal fault system (Central Apennines)

Salvatore N.*[1], Puliti I.[1], Francescone M.[1], Boncio P.[1], Iezzi F.[1-2], Morelli F.[1], Piacentini T.[1], & Pizzi A.[1]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] Università Di Napoli "Federico II".

*Corresponding author e-mail:* nadia.salvatore@unich.it

*Keywords:* fault scarps analysis, seismic hazard, Central Apennines.

Over the last decades, seismic hazard assessment has focused on tectonic slip rates determination, retrieved by analysis of the fault scarps. This is a widely used methodology quantifying slip rates and identifying fault distribution and localization at the surface (e.g., Roberts & Michetti, 2004). This work attempts to perform a morphotectonic study of fault scarps for the active Mt. Marine normal fault system (Central Apennines), which is characterized by anthropized areas where human activities might have strongly modified quantifiable geomorphic markers over centuries. Fieldwork attests to an ~8-km-long NW-trending fault system, with a complex structural setting characterized by two different sectors. The Barete sector to the NW is a narrow deformation zone localized on a fault branch affecting Jurassic-Cretaceous substratum, identified by well-developed triangular facets and locally by outcropping bedrock fault planes. To the SE, the Pizzoli-Arischia sector shows a widespread distribution of fault scarps (up to 600 m-large), mostly affecting the alluvial fans filling the Quaternary basin in the hanging wall block, with an E-trend in the central part and a NW-trend in the southern part. In such a wide deformation zone, anthropized areas (both urbanized and cultivated) partially masked and re-elaborated the cumulative morphological evidence of the faults' activity, preventing fault scarps preservation. The morphotectonic study took advantage of a high-resolution (1-m/pixel resolution) LiDAR dataset. Through ~120 topographic profiles across cumulative fault scarps of the southern portion of the system (2.8 km long), we investigated the continuity of each splay and try to quantify the related throw. The fault scarps were estimated either by manually identifying displaced geomorphic markers (i.e., erosional/depositional surfaces) or by semi-automated fault scarp measurements (SPARTA, Hodge et al., 2019). Preliminary results show total variable cumulative surface throws ranging from 1 to 19 m, with higher displacements focused on the inner portion where faults affected older alluvial fans, at higher elevations (above an altitude of 880 m asl).

The combination of the two approaches (manual and automated) showed to be a reliable methodology for depicting fault scarp in anthropized areas. Identifying a pure-tectonic fault scarp is better described by the presence of a displaced marker and the consistency of the fault scarp parameters (height, width, and slope from SPARTA) along the geomorphic scarp with a progressive decrease toward the fault tips. Conversely, cases where those conditions are not encountered, are more likely to be not pure tectonics or anthropic. Overall, we observed how combining different methodologies could help the scarp detection and quantification with ranges of uncertainty that remain within the measurements error bars, even in anthropized areas where conditions do not allow good preservation of the cumulative fault scarps.

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# Reconstruction of paleo-fluid flow along the Val d'Agri extensional faults systems (Southern Apennines, Italy)

Schirripa Spagnolo G.*[1], Aldega L.[1], Bernasconi S.M.[2], Billi A.[3], Carminati E.[1] & Smeraglia L.[3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Geological Institute, ETH Zürich (Switzerland).
[3] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma.

*Corresponding author e-mail:* giulia.schirripaspagnolo@uniroma1.it

*Keywords:* paleo-fluid flow, fault-related calcites precipitates, fluid-fault relationships.

Reconstruction of paleo-fluid flow (i.e., origin, migration, and rock interaction) in seismically active zones is useful to understand the fluid-fault relationship. Fault zones modulate fluid circulation acting as conduits or barriers and play a fundamental role in many stages of the seismic cycle. In extensional environments, the relationship between fluids flow and earthquakes can be active, when fluids trigger fault ruptures, or passive, when fluids migrate along coseismic fractures.

Understanding the relationship between paleo-fluids and faults allows to recognize the possible passive and/or active fluids behavior. This is even more important in productive oil fields where induced seismicity is a potential threat, like along the Val d'Agri (VA) extensional fault systems, that hosts the largest exploited oil field onshore of western Europe. In this area, the present-day fluid circulation is not well constrained, and several societal issues are still unsolved due to these hydrocarbon extraction (Improta et al., 2017).

Multidisciplinary approach that combines meso/micro-structural analyses and geochemical data show how faults-related calcite precipitates can be used to decode paleo-fluid paths. The study area is characterized by the juxtaposition of different tectonic units (D'Adda et al., 2017): two carbonate platforms (Apulian at bottom and Apenninic at top) separated by the Lagonegro deep-water units and covered by synorogenic sediments. We sampled faults-related calcites precipitates (i.e., veins and slikenfibres) either at the east site of the VA along the East Agri Fault System (EAFS) or at the west site of the VA along the Monti della Maddalena Fault System (MMFS). We combined field, petrographical, cathodoluminescence, and clumped stable isotopes analysis both on calcite precipitates and on host rocks to trace the paleo-fluid flow, that can be summarized as follows: a) fluids from the Lagonegro unit, are geochemically buffered by the host rock due to their long residence time; b) fluids within the veins of the Apenninic Platform are of meteoric origin with minor interaction with the host-rock; c) some mineralizations from the Apenninic Platform show mixing of meteoric and diagenetic fluids in an open system; d) fluids of deeper origin in some mineralizations of the MMFS-Apenninic Platform and of synorogenic sediments.

Our multidisciplinary results highlight the importance of considering influence of lithology, stratigraphy, and tectonics in the reconstruction of paleo-fluid flow in complex fault systems, such as the VA. Paleo-fluid flow reconstructions, and in particular the identification of deep fluids upwelling along faults, are necessary information for the evaluation of seismic and pollution hazard.

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Improta L., Bagh S., De Gori P., Valoroso L., Pastori M., Piccinini D. Chiarabba C. Anselmi M. & Buttinelli M. (2017) - Reservoir structure and wastewater-induced seismicity at the Val d'Agri Oilfield (Italy) shown by three-dimensional Vp and Vp/Vs local earthquake tomography. Journal of Geophysical Research: Solid Earth, 122(11), 9050-9082.

# Multidisciplinary study of the wedge-top Epiligurian Basins as source of inputs to the reconstruction of the deformation history of the Northern Apennines (Italy)

Stendardi F.*[1], Vignaroli G.[1], HsunMing H.[2-3], Chuan-Chou S.[2-3] & Viola G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Department of Geosciences, National Taiwan University, Taipei (Taiwan). [3] Research Center for Future Earth, National Taiwan University, Taipei (Taiwan).

*Corresponding author e-mail:* francesca.stendardi2@unibo.it

*Keywords:* Northern Apennines, Epiligurian Units, wedge-top basins.

Wedge-top basins are dynamic elements of foreland systems that are strictly linked to the evolution, through time and space, of the underlying accretionary prism. Wedge-top basins can thus be affected by tectonic structures formed during the shortening, extension and exhumation of the prism accretion and its propagation towards the undeformed foreland. We focussed on the structural setting of the wedge-top Epiligurian Basins (Northern Apennines, Italy), which consist of middle Eocene – upper Miocene bathyal to shallow-water siliciclastic deposits. The Epiligurian Basins show a complex structural architecture that is reflected in their stratigraphic-sedimentological record characterised by poor lateral continuity of the sedimentary infill, by the common heterogeneity of the lithological composition and thickness and by the local occurrence of erosional unconformities. Our field analyses addressed the spatial distribution, geometry, and kinematics of the main faults cross-cutting the Epiligurian succession, with particular attention devoted to unveiling their crosscutting and overprinting relationships to understand the relative timing of slip events. We also integrated field investigations with remote sensing analysis of lineaments mapped at regional scale. Our multiscale structural analysis indicates that the Epiligurian Basins have recorded multiphase tectonic evolution characterised by: i) an early compression documented by NNE-SSW and WNW-ESE-striking reverse faults with overall tectonic vergence towards the eastern quadrants; ii) a subsequent extension forming NW-SE and NE-SW-striking normal faults, having a planar geometry and lengths and offsets reaching several kilometres, which intersect, cut and downthrow the reverse faults; iii) a further later extension producing normal faults characterised by short length, limited offset and variable orientation to form a polygonal pattern in map view. Geochronological investigations by U-Th methods have been carried out to constrain the age of syn-kinematic mineralisations (calcite veins, slickenlines and slickenfibers) decorating normal faults and, therefore, to provide age constraints upon the activity of the structures themselves. Preliminary U-Th dates constrain to the Middle-Late Pleistocene (between 280 and 65 ka) the activity of the NW-SE and NE-SW-striking normal faults down throwing the reverse faults. Our new results (i) indicate that the polyphasic tectonic evolution of the Epiligurian Units accommodated significant changes in stress field orientation and faulting regime during the NE-verging accretion of the Northern Apennines wedge and (ii) contribute to the refining of the tectonic model of regional-scale faults that localised syn- to -post-orogenic deformation in the Northern Apennines.

# Tectonic pattern, age, and fluid circulation of the extensional faulting along the active Mount Morrone Fault System (central Apennines, Italy)

Vignaroli G.*[1-2], Rossetti F.[3], Petracchini L.[2], Argante V.[3-4], Bernasconi S.M.[5], Brilli M.[2], Giustini F.[2], Yu T.L.[6], Shen C.C.[7-8] & Soligo M.[3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma. [3] Dipartimento di Scienze, Università di Roma Tre. [4] Leibniz Institute for Applied Geophysics, Hannover (Germany). [5] Geological Institute, ETH Zürich (Switzerland). [6] Marine Industry and Engineering Research Center, National Academy of Marine Research, Kaohsiung (Taiwan). [7] High-Precision Mass Spectrometry and Environment Change Laboratory, Department of Geosciences, National Taiwan University, Taipei (Taiwan). [8] Research Center for Future Earth, National Taiwan University, Taipei (Taiwan).

*Corresponding author e-mail:* gianluca.vignaroli@unibo.it

*Keywords:* active faulting, mineralising fluids, central Apennines.

Reconstructing the fault/host rock fluid interactions contributes to refine the recurrence model of seismic failure during the geological history of major fault systems. This work integrates data from field geology with geochemical and geochronological constraints to understand the spatio-temporal evolution of the paleofluid circulation in the Mount Morrone Fault System (MMFS) of the central Apennines (Italy). The MMFS is a Quaternary extensional structure with a 25 km-cumulative length and is currently classified as a silent seismic fault. The MMFS cuts through a Mesozoic-Cenozoic multilayer carbonate succession with ca. 2 km stratigraphic separation cumulated during its Pleistocene-Holocene activity. The development of the secondary permeability in the MMFS evolved from a diffuse deformation at the damage zone towards progressive localisation of a narrower core along medium-to-low angle (dip in the order of 30°-50°) normal faults, later displaced by NW-SE-striking and SW-dipping high angle (dip > 55°) discrete slip surfaces formed at very shallow crustal conditions. Multiple generations of carbonate mineralisations, including veins and slickenfibers, occur along the main fault surfaces attesting for pulses of fluid discharge during the tectonic activity of the MMFS. Microstructural investigations document that carbonate mineralisations are fractured and variably incorporated within the surrounding cataclasites. The geochemical ($\delta^{13}C$ and $\delta^{18}O$ stable isotope) analyses on selected samples indicate a progressive chemical shift of the fluids from marine (in host rock and in cataclasites) to meteoric waters (in carbonate mineralisations). Clumped-isotope data from carbonate mineralisations yield formation temperatures in the range between 23 and 40°C. The U-Th dating of veins and slickenfibers constrains the fault-controlled fluid circulation to the Middle Pleistocene, with ages spanning from 270 to 180 ka. Significantly, the dating of mineralisations documents a 10-15-kyr cyclicity of the fluid infiltration in the fault zone. The polyphase deformation system of the MMFS constitutes a record of fault activation and reactivation of discrete slip surfaces at shallow crustal conditions controlled by the seismic cycle.

# Dating deformation: the role of atomic-scale processes

Villa I.M.*

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano Bicocca.

*Corresponding author e-mail:* igor.villa@unimib.it

*Keywords:* hygrochronology, thermochronology, petrochronology.

Dating deformation is difficult, as textures and petrogenesis of deformed rocks are complex. Moreover, geochronometer categories are pursued by communities that often do not communicate.

Hygrochronology dates the retrograde metasomatic/metamorphic reactions caused by aqueous fluid circulation events.

Thermochronology models time-temperature histories by assuming that mineral ages can be uniquely assigned to a "closure temperature $T_c$", the only process occurring in rocks being Fick's Law diffusion. Diffusion by definition produces a bell-shaped concentration profile. In contrast, patchy intra-grain isotope concentration profiles denounce aqueous retrogression, whose rate is orders of magnitude faster than diffusion.

Petrochronology is based on opposite assumptions, as the mobility of structure-forming major cations is higher than that of radiogenic Pb, Ar, and Sr. Whenever the formation of a mineral occurs at $T<T_c$, its apparent age dates its formation.

Nanochronology analyzes samples at the nm-scale. These analyses illuminate atomic-scale processes, e.g., open-system transport of soluble ions along self-sealing networks of nanopores.

The key to dating deformation and producing correct, regional-sized (up to 100s of km) tectonic models is the realization that minerals consist of atoms, whose behavior is only firmly constrained by nm-scale analyses.

# Fault Architecture in Space and Time – "FAST"

Viola G.*[1], Balsamo F.[2] & the FAST Team

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma.

*Corresponding author e-mail:* giulio.viola3@unibo.it

*Keywords:* brittle deformation, fault characterization, fault dating.

Faults shape the plumbing system of the Earth's crust, promoting mass and heat transfer and steering fluid migration, storage and mineralizations. Although they occupy only a small volume of the crust, they govern its modes of deformation by localizing earthquake slip and aseismic creep, thus being sources of seismic hazard that deserve great attention by the scientific community.

To improve our understanding of faulting and produce time-constrained models firmly based on physical and chemical constraints, a deep knowledge of the structural, mechanical, hydrogeological and petrophysical properties of faults is required. We present here the recently funded PRIN 2020 FAST project "Fault Architecture in Space and Time (FAST)". FAST aims to make a forward quantum leap in the understanding of faulting in absolute space and time coordinates.

FAST will employ an innovative, multidisciplinary and multitechnique approach on five regional-scale faults representative of a broad spectrum of geological conditions such as different tectonic regimes, fault geometry and kinematics, depth of deformation, displacement amounts, presence and abundance of fluids. For each fault, the overall architecture and its variably deformed domains (Brittle Structural Facies; BFS) will be characterized by (i) field and laboratory structural analysis, (ii) K-Ar and $^{40}Ar$-$^{39}Ar$ dating and X-ray diffraction analysis of syn-deformational clay minerals and phyllosilicates, (iii) P-T and composition determination of fluids assisting fault nucleation and growth, (iv) in situ and laboratory determination of fault mechanical and petrophysical properties, and (v) laboratory friction experiments on the main fault rock assemblages. The expected results will provide unprecedented quantitative constraints on the incremental evolution of faulting by linking the age of deformation within each BSF with the corresponding petrophysical and mechanical properties. This approach will generate sound inputs to deterministic and stochastic models of the localization and rupturing history as a function of faulting regime and depth of deformation, thus constraining the key processes of seismogenesis, multiscalar fluid compartmentalization and metallogenesis.

FAST will promote a step forward by the geological community in the understanding of the timing and mechanics of active and fossil faults to better deal with seismic hazard assessment, aquifer management, nuclear waste disposal and $CO_2$ and H underground storage. FAST will engage with outreach activities specifically meant to narrow the gap between science of faulting and society in terms of the project application potentialities and scientific and technological impact. After the end of the project, FAST participants will keep on committing to pedagogic initiatives devoted to the creation of a new generation of skilled and laterally thinking graduate and post-graduate students and early-career researchers.

# Structural characterization and K-Ar illite dating of reactivated, complex and heterogeneous fault zones: Lessons from the Zuccale Fault, Northern Apennines

Viola G.*[1], Musumeci G.[2], Mazzarini F.[3], Tavazzani L.[4], Torgersen E.[5], van der Lelij R.[5] & Aldega L.[6]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] INGV, Pisa. [4] Istituto di Geochimica e Petrologia, ETH Zürich (Switzerland). [5] Geological Survey of Norway, Trondheim (Norway). [6] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* giulio.viola3@unibo.it

*Keywords:* brittle deformation, fault architecture, fault dating.

We studied the Zuccale Fault (ZF) on Elba Island, Northern Apennines, to unravel the complex deformation history that is responsible for the remarkable architectural complexity of the fault. The ZF is characterized by a patchwork of at least six distinct, now tightly juxtaposed Brittle Structural Facies (BSF), that is, volumes of deformed rock characterized by a given fault rock type, texture, color, composition, and age of formation. Fault rocks vary from massive cataclasite to foliated ultracataclasite, from clay-rich gouge to highly sheared talc phyllonite. Understanding the current spatial juxtaposition of these BSF's requires tight constraints on their age of formation during the fault life span to integrate current fault geometries and characteristics over the time dimension of faulting. We present new K-Ar gouge dates obtained from three samples from two different BSF's. Two top-to-the E foliated gouge and talc phyllonite samples constrain a faulting phase to the Aquitanian (ca. 22 Ma), constraining E-vergent shearing along the ZF already in the earliest Miocene. A third sample documents later faulting along the exclusively brittle, flat-lying ZF principal slip surface to < ca. 5 Ma. The new structural and geochronological results reveal an unexpectedly long faulting history spanning a ca. 20 Ma long time interval in the framework of the evolution of the Northern Apennines. The current fault architecture is highly heterogeneous as it formed at very different times under different environmental conditions during this prolonged history. We propose that the ZF may have started as an Aquitanian thrust, which then became selectively reactivated by early Pliocene out-of-sequence thrusting during the progressive structuring of the Northern Apennines wedge. These results require the critical analysis of existing geodynamic models and call for alternative scenarios of continuous convergence between the late Oligocene and the early Pliocene with a major intervening phase of extension in the middle Miocene allowing for the isostatic re-equilibration of the Northern Apennines wedge. Extension started again in the Pliocene and is still active in the innermost portion of the Northern Apennines. In general terms, long-lived, mature faults can be architecturally very complex. Their unraveling, including understanding the dynamic evolution of their mechanical properties, requires a multidisciplinary approach combining detailed structural analyses with dating the deformation events recorded by the complex internal architecture, which is a phenomenal archive of faulting history and faulting conditions through time and in space.

# Kinematics and geochronological evolution of the Vinschgau Shear Zone (N Italy): large-scale thrusting within the Austroalpine domain of the central-eastern Alps

Zanchetta S.*[1], Montemagni C.[1], Rocca M.[1], Villa I.M.[1], Morelli C.[2], Mair V. [2] & Zanchi A.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] Ufficio Geologia e Prove Materiali, Provincia Autonoma di Bolzano

*Corresponding author e-mail:* stefano.zanchetta@unimib.it

*Keywords:* shear zones, geochronology, kinematic evolution.

The Vinschgau Shear Zone (VSZ) is an E-W striking ductile shear zone developed within the central-eastern Austroalpine domain. Along the VSZ the Ötztal-Stubai nappe with an amphibolite facies Alpine metamorphism overthrusted the Campo nappe (and respectively the Engadine Dolomites) characterized by low-to-medium metamorphic conditions (Schmid & Haas, 1989). In the eastern part the shear zone involves also the Texel Unit below the Ötztal nappe. Foliation gently dips northward and lineation constantly strikes E-W, with kinematic indicators that point to a top-to-NW sense of shear. The VSZ developed mostly under amphibolite to greenschist-facies conditions. A remarkable variation in finite strain distribution can be observed: lenses of protomylonites are bounded by deeply sheared ultramylonites, mylonites and phyllonites, these occurring in the western part of the VSZ.

In order to fully assess the evolution of the VSZ a multidisciplinary approach based on structural and petrochronological analyses has been carried out on three representative transects of the shear zone from W to E: Eyrs, Schlanders and Juval. The dip of the mylonitic foliation increases from W to E and the lineation dips towards the W in Schlanders and Juval, whereas towards the E in Eyrs, probably due to a folding event related to Cenozoic shortening. Chemical and microstructural analyses suggest that deformation temperatures of 350-400°C have been reached during shearing, as testified by Ti content in biotite and by bulging and subgrain rotation as dominant recrystallization mechanisms in quartz. Timing of deformation along the VSZ has been constrained through $^{40}Ar/^{39}Ar$ dating of syn-shearing micas confirming previous geochronological data of Thöni, 1981, which reveal a Late Cretaceous age of the VSZ mylonites. A systematic younging trend of deformation towards the central part of the shear zone has been observed in the studied area. Vorticity analyses show a clear decrease in simple shear component correlated to the younging direction of mica ages (i.e., towards the core of the shear zone). This evolution is clearly consistent with Type 2 evolution of Fossen & Cavalcante (2017), where strain localizes into the core of the shear zone during deformation. Our data confirm the age of the VSZ only supposed on the base of indirect observations and demonstrate that the Austroalpine domain was severely affected by W-NW verging thrust stacking much time before the Adria-Europe continental collision.

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# Key features for the reconnaissance of synsedimentary extensional faults in the Early Permian Orobic Basin, central Southern Alps (N Italy)

Zanchi A.*, Locchi S. & Zanchetta S.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* andrea.zanchi@unimib.it

*Keywords:* normal faults, Permian, synsedimentary tectonics.

The opening and evolution of the Early Permian Orobic Basin of the central Southern Alps (N Italy) has been strictly conditioned by the activation of low-angle normal faults active along the cover basement interface (Zanchi et al., 2019, Zanchetta et al., 2022). In the past, the presence of synsedimentary faults in the Pizzo del Diavolo Formation has been established considering strong facies variations associated to coarse-grained conglomerates along the faulted margins of the basins and fine-grained lacustrine facies, occurring within their depocenters. In addition, marked thickness variations also suggest active faulting during sedimentation, which were possibly responsible for seismic shaking (Berra & Felletti, 2011).

In addition to these stratigraphic and sedimentological aspects, we have also observed the occurrence of a rich mesoscopic record of synsedimentary activity given by hundreds of small-scale normal faults with meter-scale displacements. Fault systems consist of high-angle conjugate Andersonian as well as domino-style faults. Their synsedimentary activity is testified by the occurrence of sedimentary dikes, disrupted bedding, ball and pillows, pillars, and small slumps pointing to their formation in hydroplastic conditions.

According to our structural observations, these high-angle normal faults affecting the Lower Permian successions are concentrated along growth faults, which have been described in recent work ("Aga Growth Fault" in Zanchi et al., 2019; "Trona Line" in Locchi et al., 2022). These faults are closely associated with the low-angle normal faults developed along the interface between the Permian cover and the Variscan basement (Zanchi et al., 2019; Locchi et al., 2022; Zanchetta et al., 2022), both pointing to a geodynamic setting characterized by pure extension. Statistical analyses of the geometrical features of the measured normal faults suggest a dominant ENE-WSW strike, which fits the orientation of several other Permian normal faults which have been inverted during the Alpine shortening as high-angle reverse faults (Zanchetta et al., 2015; Zanchi et al., 2019).

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# The Meran-Mauls segment of the Periadriatic Fault System, Italy: pure thrusting across the brittle-plastic transition

Zanchi A.[1], Zanchetta S.*[1], Montemagni C.[1] & Mascandola C.[2]

[1] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [2] INGV, Milano.

*Corresponding author e-mail:* stefano.zanchetta@unimib.it

*Keywords:* Periadriatic Fault System, paleostress, Late Cenozoic.

The Meran-Mauls Fault (MMF) connects the North Giudicarie Fault with the Pustertal segment of the Periadriatic Fault System (PFS), which separates the Southern Alps from the Europe-vergent Alpine collisional belt. Our study is based on detailed multiscale analyses carried out within the CARG project for the survey of the Meran (Bargossi et al., 2010), San Leonhard and Sterzing geological sheets of the 1:50,000 geological map of Italy. In the frame of this project, we performed detailed geological mapping along key-sections, mesoscopic and microscopic structural analyses of fault rocks, vorticity analyses of mylonites, paleostress estimates and radiometric dating of pseudotachylytes. Although several models suggest that the PFS developed in a dextral transpressional regime during the Cenozoic, following the Adria-Europe collision, our analyses suggest that the MMF and related structures were active with a marked reverse kinematics, displaying several switch in the late stages between ductile and brittle deformation. The repeated switch between the two deformation regime is testified by the occurrence of several generation of pseudotachylytes, the former being sheared during successive stages of ductile deformation.

Reverse motion is chiefly suggested by down-dip mineral lineations in early mylonites developed in greenschist-facies conditions within the Austroalpine units in the hanging wall of the fault zone, as well as in the footwall within the Brixes Phyllites and in the Ifinger Permian intrusive, part of the the crystalline basement of the Southern Alps. SE-vergent thrusting was followed in time by a dextral reactivation in brittle conditions, which is evident especially in the eastern portion of the MMF starting from the Pennes Pass area.

Our reconstruction is corroborated by the analyses of other important fault zones mainly developed in the Austroalpine thrust stack in the hanging wall of the MMF, showing a similar kinematic evolution. Strike-slip to normal faults with different trends ranging from NW-SE to NE-SW followed in time the dextral motion along the MMF, displacing previous structures. Paleostress reconstructions indicate a progressive switch of the main direction of compression from NW-SE to N-S, as previously suggested by us in the Central Alps (Agliardi et al., 2009).

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# First documentation of aragonite-bearing HP-LT assemblages within the Precambrian Hajir Fm., Jabal Akhdar Dome, Oman Mountains

Zuccari C.*[1], Vignaroli G.[1], Giuntoli F.[1], Novella D.[2], Nestola F.[2], Callegari I.[3], Guillong M.[4] & Viola G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Dipartimento di Geoscienze, Università di Padova. [3] Department of Applied Geosciences, German University of Technology in Oman, Muscat (Oman). [4] Institute of Geochemistry and Petrology, ETH Zürich (Switzerland).

*Corresponding author e-mail:* costantino.zuccari2@unibo.it

*Keywords:* Oman Mountains, aragonite-calcite transition, subduction.

Aragonite is a polymorph of calcite and, due to the general absence of other index minerals (e.g., phyllosilicates), it is commonly used as an indicator of high pressure - low temperature (HP-LT) blueschist facies conditions in subducted carbonates. Unfortunately, preservation of metamorphic aragonite is uncommon, primarily due to the fast kinetics of the aragonite-calcite transformation during retrogression associated with exhumation. Aragonite preservation, however, may locally be possible in the case of rapid exhumation and/or within localised structural (micro)domains acting as archives of the HP conditions. A multi-technique approach (including microtectonics, petrography, cathodoluminescence, Raman spectroscopy and X-ray powder diffraction) is crucial to constrain the possible occurrence of aragonite in metamorphosed and sheared carbonate successions.

The northeastern Oman Mountains offer the possibility of an in-depth investigation of the structural-metamorphic signature of carbonates that experienced a complete cycle of subduction-exhumation concurrently with the Semail Ophiolite obduction. Here we report the first evidence of aragonite preserved in the Hajir Formation, a ≈ 100 m thick succession of Precambrian carbonates located in the core of the Jabal Akhdar Dome (JAD) of the Arabian plate.

The Hajir Formation is deformed by up to 50 cm thick reverse top-to-the NE shear zones characterised by proto- to ultramylonites and containing evidence of brittle-ductile cyclicity. Structural observations document multiple generations of mode I carbonate fibre veins both transposed into the mylonitic fabric and cutting it. Low Sr (<1%) aragonite and graphite define the penetrative mylonitic foliation. Raman spectroscopy (RSCM) on tabular layers and plagues of syn-kinematic graphite constrains a peak T of ≈ 350°C for the formation of the mylonitic foliation. U-Pb dating of syn-kinematic aragonite and calcite fibres, the latter interpreted as pseudomorphs over aragonite, yielded an Upper Cretaceous age for mylonitic fabric formation. We suggest that the JAD experienced P-T conditions of ≈ 0.9 GPa (based on the aragonite-calcite stability field) and ≈ 350°C during subduction and the subsequent obduction of the Semail Ophiolite in the Upper Cretaceous. These new results i) pave the way for new possible interpretations of the evolution of the Oman subduction system, extending the current distribution of blueschist facies conditions towards much more internal areas of the Arabian continental crust, and ii) shed new light on the mechanical and rheological properties of carbonates in subduction contexts.

# New perspectives on the folding to faulting transition in carbonate multilayer successions. Insights from the fold-and-thrust belt of the Italian Eastern Southern Alps

Zuccari C.*[1], Viola G.[1], Curzi M.[1], Simpson G.[2], Aldega L.[3] & Vignaroli G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Section of Earth Sciences, University of Geneva (Switzerland). [3] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* costantino.zuccari2@unibo.it

*Keywords:* folding-faulting transition, carbonate multilayers, seismic vs. aseismic.

Understanding the deformation processes and boundary conditions controlling how folds and faults nucleate and grow is key to unravelling the tectonic and seismic evolution of both active and fossil fold-and-thrust belts. To better understand these complexities, we studied mesoscopic parasitic folds associated with regional-scale S-verging thrusts affecting the Mesozoic carbonate multilayer succession of the seismically active Italian Eastern Southern Alps. We aimed to constrain: i) the geometrical and lithological parameters steering the spatial and temporal transition from folding to faulting, and ii) the seismic vs. aseismic behaviour during the folding-faulting transition in carbonates. Our approach relied on i) the structural analysis of symmetric and asymmetric folds, which are locally cut by mesoscopic thrusts, to assess the overall structural style and derive geometrical constraints upon the documented deformation features, ii) XRD analysis of the deformed carbonate multilayer to define its mineralogical composition and to establish the influence thereof upon deformation, and iii) numerical modelling based on the Finite Element Method (FEM) to study the factors governing fold symmetry versus asymmetry.

Parasitic folds evolve from symmetric and open to south-verging asymmetric and close to tight before eventually being decapitated by discrete thrusts. The folding to faulting transition occurs once fold forelimbs exceed ~80° and the ratio between fore- and back limbs dip angle exceeds ~3.3. The mesoscopic thrusts that dissect asymmetric folds firstly localise along the gently dipping back limbs, exploiting clay-rich beds therein, and then propagate toward the foreland by cutting across the steep forelimbs, producing cataclastic domains. Layer-parallel shearing and cataclasis are the dominant deformation modes during thrusting along the back limb and forelimb, respectively. FEM modelling shows that the transition from symmetric to asymmetric parasitic folds is mainly controlled by i) the thickness and vertical distribution of different lithotypes and ii) the growth of first-order folds at larger scales.

Based on field evidence and numerical modelling, we propose that the fold evolution and the transition from folding to faulting, steer the localisation of aseismic and seismic deformation through space and time in fold-and-thrust belts.

# S45.

# Mapping crystalline basements: traditional and innovative approaches

*Conveners & Chairpersons*

*Matteo Simonetti (Servizio Geologico d'Italia - ISPRA)*

*Martina Zucchi (University of Bari)*

*Diego Pieruccioni (Servizio Geologico d'Italia - ISPRA)*

# The Carboniferous-Permian metamorphic units of Risanguigno Stream (southern Tuscany, Italy)

Brogi A.*[1-2], Bagnoli G.[3], Capezzuoli E.[4], Liotta D.[1-2], Lucci F.[1], Molli G.[3], Regoli R.[5], Spina A.[6] & Zucchi M.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Istituto di Geoscienze e Georisorse, CNR, Pisa. [3] Dipartimento di Scienze della Terra, Università di Pisa. [4] Dipartimento di Scienze della Terra, Università di Firenze. [5] Associazione Mineralogica Paleontologica Senese, Siena. [6] Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* andrea.brogi@uniba.it

*Keywords:* structural analysis, metamorphism, palinology.

We present an integrated study based on field mapping, stratigraphic, petrographic, fluid inclusion and palynological analyses on the metamorphic succession exposed in the Risanguigno Stream, crossing the Middle Tuscan Ridge in southern Tuscany (Italy). The deeper part of this succession has been always considered as the Variscan Basement of the inner Northern Apennines, referred to Devonian and unconformably overlain by a Permian succession. Stratigraphic and structural studies, coupled with analyses of the organic matter content, have refined the age and structural setting of the so called "basement" exposed in the Risanguigno Stream, and has defined its geometrical relation with the overlying Permian succession. Based on the low diversification of palynoflora, the content of sporomorphs, this succession is referred to late Tournaisian - Visean (Middle Mississippian). The petrographic and structural setting indicate that it was not affected by pre-Alpine deformation. Structures are only referred to the Apennine evolution and consist of two superposed fold systems cut by shear zones active during the exhumation. Structural and petrographic investigations were developed on the high-P quartz-carpholite-pyrophyllite-white mica metamorphic assemblage occurring as boudins within a main retrogressive foliation made up of a second generation of white mica – chloritoid and chlorite. Micro-textural observations highlight also a post-tectonic chloritoid growth in "rosetta" shape and static recrystallization of quartz. Fluid inclusion analyses were performed in quartz veins developed within the shear zone. Most of fluid inclusions are two-phase (liquid+vapour), and occur along trails suggesting secondary or pseudo-secondary origin. Results highlight fluids of metamorphic origin with relatively low salinity values (up to 6.0 wt.% NaCl equiv.) and T of about 350°C. This conclusion leads us to underline that no exposures of rocks involved in the Variscan orogenesis occur in the Risanguigno Stream. The whole succession was only involved in the overthickening of the Northern Apennines occurred during the involvement of Adria in the Oligocene-early Miocene collisional event.

# An updated map for the Modi Khola and Mardi Himal areas (Annapurna Range, central-western Nepal): new cartographic and structural constraints

Carano G.*, Montomoli C., Iaccarino S. & Carosi R.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* giorgia.carano@edu.unito.it

*Keywords:* Himalayan Chain, structural geological mapping, meso and microstructural analysis.

Along the Modi Khola and Mardi Himal transects, in the Annapurna Region the main units of the Himalayan range crop out. From the lower to the upper structural levels, it is possible to recognize the medium-low grade metamorphic rocks of the Lesser Himalayan Sequence (LHS), the medium- high-grade metamorphic rocks of the Greater Himalayan Sequence (GHS), and the weakly or non-metamorphic rocks of the Tethyan Himalayan Sequence (THS). The main foliation in the three metamorphic units has a trend NW-SE and is generally dipping 40-45° towards N-NE.

Two of the main tectonic discontinuities of the Himalaya, separate these units: the structurally lower Main Central Thrust Zone (MCTZ) with reverse kinematics and the structurally upper South Tibetan Detachment System (STDS) with normal kinematics. The MCTZ is comprised between the Lower MCT and the Upper MCT.

The position of the MCTZ supported by this work agrees with the one proposed by Parsons et al. (2016) and is formed at the expense of the LHS (as reported in Martin et al., 2010) and in minimal part (~500 m) of rocks from the Lower GHS.

The STDS is represented in the area by a complex system of normal faults at different structural levels; from the top to the bottom: Upper Hiunchuli–Machapuchare Detachment (uHMD), Lower Hiunchuli–Machapuchare Detachment (lHMD) and Mardi–Himal Detachment (MHD). Hodges et al. (1996) distinguished a further lower structure, the Deorali Detachment, which is overprinted by a reverse kinematic linked to the activity along the Modi Khola Shear Zone (MKSZ). From several observations it is evident that the current kinematic is top-to-the-S and it largely transposes any normal kinematics, which remains still very uncertain. For this reason, only the MKSZ was mapped.

In addition to the MKSZ in the study area other discontinuities within the GHS are present, from top to bottom: the Sinuwa Thrust (ST) and the Bhanuwa Fault (BT) both identified only on the base of petrochronological arguments and still with debated kinematic.

Regarding the ST, for the first time clear and univocal kinematic indicators were recognised both at the meso and microscale pointing out a reverse kinematic top-to-the-S. No clear mesoscopic kinematic indicators were found for the BT, however, thanks to the quartz c-axis fabric analysis carried out on sample collected close to the BT, it was possible to recognize a reverse kinematic top-to-the-S.

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# Geological and structural mapping 2.0 in metamorphic and basement rocks

Carosi R.*, Montomoli C. & Iaccarino S.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* rodolfo.carosi@unito.it

*Keywords:* Himalaya, geological maps, tectonic and metamorphic discontinuities.

The mapping of tectonic-metamorphic discontinuities (TMD) in metamorphic rocks is challenging because they involve strain localization in metamorphic conditions for several Ma at the point that deformations affect the P-T-t paths of the footwall and hanging-wall rocks (Montomoli et al., 2013; TecTask terminology: http://www.tectask.org/). To better unravel the TMD an integrated approach among meso-and micro-structural, petrology and petrochronology is suggested in order to gain the most information to build up a reliable tectonic model and to map often "cryptic" tectonic-metamorphic discontinuities (Carosi et al., 2018).

In the Himalayan belt the largest crystalline unit representing the mid-crust is the Greater Himalayan Sequence (GHS) which stretches all over the 2400 km of length of the belt. The GHS has been considered for a long time as a single coherent tectonic unit, exhumed by the contemporaneous shearing along the Main Central Thrust and the South Tibetan Detachment System in the time span ~25–17 Ma. A multidisciplinary approach, focusing structural geology (from regional to microscale), petrology, geochemistry and geochronology, allowed to better constrain on its internal architecture characterized by several levels of tectonic-metamorphic discontinuities on the regional scale with a top-to-the-S/SW sense of shear and active since ~40 Ma. The GHS is consequently divided in three main tectonic units exhumed progressively from the upper part to the lower one by ductile shear zones, later involving the Lesser Himalayan Sequence.

Above the Main Central Thrust a sometimes-cryptic tectono-metamorphic discontinuity (High Himalayan Discontinuity; HHD) has been recognized and mapped from Western to Central-Eastern Himalaya (Carosi et al., 2022). A new map of Western Nepal is here presented including the new HHD.

In this framework the popular models of exhumation of the GHS mainly based on the contemporaneous activity of the two bounding shear zones (Main Central Thrust and the South Tibetan Detachment) and considering the GHS as a coherent tectonic unit, should be reconsidered. An in-sequence shearing tectonic model, from the deeper to the upper structural levels, further affected by out-of-sequence-deformation, is more appropriate to explain the deformation, metamorphism, and exhumation of the mid-crust in the Himalayan belt.

Geological mapping of basement and metamorphic rocks in orogenic belts will benefit of this integrated approach to properly map discontinuities and possible structural break often underestimated in geological mapping not using an integrated approach. The 2.0 geological maps are the useful base also to infer processes leading to strain localization and shear zone growth/development in the lithosphere and its short- and long-range rheological evolution.

Carosi R., Montomoli C. & Iaccarino S. (2018) - 20 years of geological mapping of the metamorphic core across Central and Eastern Himalayas. Earth-Science Reviews, 177, 124-138.

Carosi R., Montomoli C., Iaccarino S., Montemagni C. & Benetti. (2022) - A review of localization of the deformation in Garhwal Himalaya: younging activation of shear zones from the metamorphic core of the belt towards the foreland. Himalayan Geology, 43, 221-230.

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# Geological-structural map of the Briançonnais units along the Aiguilles de Chambeyron – Denti di Maniglia Massifs (France, Italy)

Dana D.*[1], Iaccarino S.[1] & Michard A.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Départment Sciences de la Terre, Université Paris-Sud, Orsay (France).

*Corresponding author e-mail:* davide.dana@edu.unito.it

*Keywords:* Briançonnais, Western Alps, polyphase deformation.

The structural transect along the Ubaye – Maira Valley represents a complex geological section of Western Alps, where different units ranging from the anchizone facies Helminthoid Flysch to the high pressure, blueschist facies, Schistes Lustrés Units are present (Michard et al., 2004). Between these Alpine Tethys-derived units, a stack of continental Briançonnais-derived units is present. Each unit of this stack shows different stratigraphy and metamorphic imprints, the latter increasing from sub-greenschist to blueschist facies going towards E (Gidon et al., 1994; Michard et al., 2004 and references therein). These units are, i) represented by different metasedimentary sequences from Carboniferous to Eocene, and ii) variably detached and deformed by a polyphase structural evolution. Particularly, this transect is characterized by the importance of backfolding and backthrusting towards ENE. In this contribution we present a geological - structural map of the area around the Aiguilles de Chambeyron – Denti di Maniglia Massifs at the scale 1:15.000. The main aim of this map is to illustrate the polyphase tectonic evolution of this transect. The geological data presented in the map have been integrated with lithostratigraphic reconstruction, meso and microstructural investigations and with RSCM thermometry (Lahfid et al., 2010). The map highlights the different units, their tectonic contact, metamorphic grade and stratigraphic sequence. Four deformation phases are identified in the study area: (1) a rarely preserved earlier phases D1; (2) a successive phase which fold the previous surfaces, associated to a S2 foliation, well recognizable mainly in the hinge of F3 folds; (3) the main deformation phase, D3, connected to the NE backfolding (F3) and backthrusting; (4) a later, shallower phase (D4) associated to minor upright kink folds with nearly E-W oriented axis, that we tentatively linked to the late strike-slip tectonics. This new detail mapping and associated analyses help restoring the original paleogeography of the Briançonnais margin in the frame of our regional structural studies (Michard et al., 2022). We particularly emphasize the affinities of the Marinet and Aiguilles de Mary units with the Acceglio-type units derived from the shoulder of the rifted margin.

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# The metamorphic basement of the new Borgo Valsugana sheet (n. 61, CARG project)

Gosio F.* & Modesti A.

Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* francesco.gosio@studenti.unipd.it

*Keywords:* CARG, Borgo Valsugana, Sudalpine basement.

As part of the CARG project, the new Borgo Valsugana geological sheet (n. 61) is being built with an extension of over 600 $km^2$ including approximately 190 $km^2$ consisting of a varisican metamorphic basement and the permian intrusive bodies of Cima d'Asta. Following detailed bibliographic research, it emerged that the studies developed in this area are few and dated, indeed most of the contributions date back to the 1950s/60s with the exception of the most recent slope hazard map of Trento Province which however shows several criticalities.

The main problems found during the geological survey on the ground and during the data processing phase include the metamorphic basement units characterization and their comparison on a regional scale with the Sudalpine units outcropping in the areas of Bressanone, Comelico, Recoaro-Schio and in particular with the nearby basement of the Agordo-Cereda area. During the realization of the Borgo Valsugana sheet a detailed study of the basement units will be developed in order to enrich and re-evaluate the lithostratigraphic and metamorphic comparison proposed by previous authors (e.g., D'Amico, 1964; Sassi & Zirpoli, 1968; Ring & Richter, 1994) and provide an innovative regional tectonic-metamorphic interpretation.

In addition to the characterization of the crystalline basement, the definition of its structural set-up is crucial, in particular the age and exhumation process, to be associated with the Valsugana fault that is known as a very complex lineament extending over 100 km. The Valsugana thrust evolved in middle-upper Miocene, however its evolution was conditioned by Permian extensional framework during which the paleoline was a morphostructural barrier to the expansion of the Atesine volcanites (Selli, 1998).

Inside the basement, the contact metamorphism produced by the emplacement of Cima d'Asta intrusive bodies, to date, has never been studied in detail and in a systematic way. Despite the limited extent of the contact aureoles, its study is necessary to obtain more data about the nature of the intrusion and the thermo-barometric conditions.

The Borgo Valsugana basement, after all, is quite complex from a tectono-metamorphic and petrographic point of view and needs a revision using an approach based on both more innovative techniques for field mapping and more modern analytical methods.

D'Amico C. (1964) - Le metamorfiti della Valsugana occidentale. Acta Miner. Petr., 10, 1-42.

Ring U. & Richter C. (1994) - The Varisican structural and metamorphic evolution of the eastern Southalpine basement. J. Geol. Soc., 151, 755-766.

Sassi F.P. & Zirpoli G. (1968) - Il basamento cristallino di Recoaro. Mem. Soc. Geol. It., 7, 227-245.

Selli L. (1998) - Il lineamento della Valsugana fra Trento e Cima d'Asta: cinematica neogenica ed eredità strutturali Permo-Mesozoiche nel quadro evolutivo del Sudalpino orientale (NE-Italia). Mem. Soc. Geol. It., 53, 503-541.

# 3D structural characterisation of onshore Caledonian basement rocks: a key to unravel unconventional hydrocarbon plays hosted by basement highs of the offshore domain off Central Norway

Hodge M.*[1], Venvik G.[2], Knies J.[2] & Viola G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] Geological Survey of Norway, Trondheim (Norway).

*Corresponding author e-mail:* matthew.hodge@unibo.it

*Keywords:* 3D, basement, modelling.

Fractured basement rocks represent an opportunity to characterise rock volumes in terms of fracture networks, rock-fluid interaction, and fluid flow and storage potential. Basement rocks on Smøla Island, within the Mid-Norwegian margin (offshore Central Norway), are an excellent training ground for this, having experienced a prolonged tectonic evolution from the Palaeozoic to the Early Cenozoic. Basement rocks are generally under-explored as unconventional georesource reservoirs and potential storage repositories for greenhouse gases. Smøla Island is considered an onshore analogue of offshore basement highs, such as the Frøya High, a potential unconventional hydrocarbon play. In this ongoing study, we use diamond drill holes from Smøla, allowing for a new 3D perspective to augment multiscale surface and geophysical data for this portion of the Mid-Norwegian margin. Combining these datasets, we aim to produce 3D structural and stochastic discrete fracture network models and provide preliminary insights into the complex, multiply deformed architecture of studied basement rock volumes. Thus far, detailed and multiscalar structural data has been collected from four oriented diamond drill holes and representative surface outcrops. Downhole hydrologic test data has also been collected during drilling. In drill core, a variety of deformation features are present from major brittle faults with spectacular core and damage zones (locally exploiting ductile precursors) to pervasive fracture and vein arrays. These features have distinct cross-cutting relationships and possess characteristic mineral infill/alteration features, with slickensides present in places. Discernible systematic structural 'sets' have been recognised from drill hole and field observations. This dataset has undergone paleostress inversion to produce a relative tectonic history. The obtained stress patterns broadly correlate with known deformation episodes of the Caledonian orogeny and subsequent rifting and opening of the North Sea. Multiscale drill core and surface deformation features, 2D resistivity profiles, downhole hydrologic test data, and DTM lineament mapping have been integrated using 3D software. From these 3D models, stochastic discrete fracture network models are being produced in order to generate scaling laws accounting for the spatial distribution of the deformation features as well as of their properties, such as permeability and connectivity anisotropy. Initial results offer key insights into the internal structure of basement rock volumes in this sector of the margin, and the applicability to offshore basement highs.

# A comprehensive 1:250000 scale geological map of the Convoy Range and Franklin Island quadrangles (Victoria Land, Antarctica)

Montomoli C.*[2], Capponi G.[1], Simonetti M.[3], Salvatore M.C.[4], Casale S.[4], Musumeci G.[4], Cox S.[5], Smith Lyttle B.[5] & Pertusati P.C.[4]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. [3] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [4] Dipartimento di Scienze della Terra, Università di Pisa. [5] GNS Science, Dunedin (New Zealand).

*Corresponding author e-mail:* chiara.montomoli@unito.it

*Keywords:* Convoy Range, Antarctica, Victoria Land.

In this paper we provide a comprehensive geological map of the Convoy Range - Franklin Island USGS quadrangles (Victoria Land, Antarctica), obtained by the integration of the previous geological map by Cox et al. (2012) and new field data (Capponi et al., 2020), collected during the 2017/18 and 2018/19 austral summers, in the context of the XXXIII and XXXIV ItaliAntartide expeditions. This new geological map allows a complete coverage of Victoria Land, by filling the gap between the GIGAMAP program (to the north) and the maps by the New Zealand Antarctic program (to the south).

New field activity was helicopter-supported and was organized in daily missions from the Italian Mario Zucchelli Station (2017/2018) and in a period of stay in a tent camp (2018/2019), at Starr Nunatak (75°54′S 162°35′ E), in order to be able to reach the most distant sectors of the study area. Mapping was coupled with the collection of rock samples that we later studied at the microscale, in order to better characterize the different lithologies.

We mapped an Early Paleozoic granitic basement, and a flat-lying cover of sedimentary and igneous rocks, spanning in age from Devonian to Early Jurassic. The mapping highlighted some key features of this region, such as the scarce occurrence of rocks of the Wilson Metamorphic Complex, the occurrence of mafic rocks belonging to the Granite Harbour Igneous Complex and the possible activity of fault with vertical offset, linked with the post-Ross tectonics. The activity of such faults is highlighted by an evident difference in the elevation of the Kukri erosion surface in several sectors of the map. Direct evidences are provided by the presence of cataclasites and brittle planes with possible pseudotachylites formed at the expense of granitic rocks. Changes in the height of the erosion surface can be due to differential erosion or to the activity of subsequent faults with some vertical offset. This new map can be used as the starting point for any future geological investigation of this region.

Capponi G., Montomoli C., Casale S. & Simonetti M. (2020) - Geology of the northern Convoy Range, Victoria Land, Antarctica, Journal of Maps, 16(2),702-709.

Cox S.C., Turnbull I.M., Isaac M.J. Townsend D.B. & Smith Lyttle B. (2012) - Geology of Southern Victoria Land Antarctica. GNS 1:250000 Geological map 22. 1 sheet, 135 pp, Lower Hutt, New Zealand.

# Structural-controlled glacial erosion in high erosion-resistance crystalline bedrock

Musso Piantelli F.*, Truttmann S. & Herwegh M.

Institute of Geological Sciences University of Bern (Switzerland).

*Corresponding author e-mail:* ferdinando.musso@geo.unibe.ch

*Keywords:* glacial erosion, crystalline bedrock, structural preconditioning.

The susceptibility of catchment rocks to glacial erosion may control the evolution of valley morphology in high-relief mountain ranges such as the Alps. Non-uniform proneness to bedrock erosion may indeed localize abrupt changes in the glacier flow direction and overdeepenings characteristic of glacial valleys. Yet, little is known about the explicit influence of bedrock properties (i.e., lithology, hardness, and geological structures) on glacial erosion processes. In this study, we select the Great Aletsch Glacier (Swiss Alps) as a natural laboratory to document and investigate the relationship between bedrock properties and subglacial erosion mechanisms. The Great Aletsch Glacier with a length of more than 20 km and an ice thickness of up to 800 m is the largest glacier in Central Europe. The underlying bedrock consists of the crystalline basement units of the Aar massif (gneiss, granite, and granodiorite) and is dissected by a large number of steep faults and former ductile shear zones. Geological and remote sensing lineament mapping combined with 3D geological modelling allowed us to make a large-scale characterization of the lithologies and structures' spatial frequency over the entire length of the glacier. Additionally, we performed field structural mapping and field-based rock hardness analyses (Schmidt hammer) along the glacier's bedrocks (intact rock and faulted/sheared domains) to testify for structure-controlled erosion behaviour. Obtained results demonstrate that: (i) the typology and distribution of faults and shear zones are not uniform over the entire length of the glacier; (ii) high-frequency structure domains correlate with overdeepenings and/or abrupt glacier flow deflection in the direction of the strike of the structures; (iii) low-frequency structure domains correlate to the absence of overdeepenings and a straight glacier trajectory. In terms of erosive resistance domains of intact rock masses show high hardness values for each of the investigated lithologies without substantial variability between the different basement rocks. On the contrary, faulted or sheared domains show a significant drop in hardness value. Based on these results we propose that differences in the mapped crystalline basement lithologies do not exert an important role in glacial erosion. We postulate instead that the non-uniform spatial distribution of geological structures imposes a major control on the development of the glacial valley. The substantially reduced bulk hardness within high-frequency structure domains renders indeed the bedrock to be more prone to efficient glacial erosion process at these sites (i.e., glacial quarrying) and therefore to the development of large-scale overdeepenings, local scouring, or changes in the glacier flow direction. By contrast, the more massive undeformed and therefore less erosive low-frequency structure domains coincide with sections with no knickpoints or overdeepenings.

# Mapping polyphase deformation linked to the nappe stacking in a collisional framework: a case study from the Nappe Zone of the Variscan Belt

Petroccia A.*, Carosi R., Montomoli C. & Iaccarino S.

Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* alessandrogiovannimichele.petroccia@unito.it

*Keywords:* Variscan basement, polyphase deformation, RSCM.

Orogenic wedges consist of stacked tectonic nappes accreted from the lower plate. The growth of orogenic wedges is controlled by shear zones, which are responsible for the exhumation of units from different structural levels. The transition from the hinterland to the foreland of belts is usually characterized by large-scale nappe stacks with different generations of superimposed folds and cleavages that complicate the understanding of the structural architecture. Several difficulties arise from the overprinting of the latest deformation phases that modify the original attitude of pre- and syn-nappe stacking elements (e.g., secondary foliations, tectonic contacts, folds vergence). Thus, untangling the geological complexity derived from the geological survey and outcrop observation requires a multidisciplinary approach. The Sardinian orogenic wedge (Carmignani et al., 1994) has been subdivided into External and Internal Nappe Zone. The boundary between both nappes is marked by the Barbagia Thrust (BT; Carosi & Pertusati, 1990; Carosi & Malfatti, 1995; Montomoli et al., 2018), a thrust-sense movement, regional ductile to brittle shear zone. In this contribution, we present a 1:10.000 scale geological map that aims to illustrate the polyphase tectonic evolution of a sector of the contact zone between the Internal and External Nappe Zone. The geological data presented in the map have been derived from the integration of meso- and microstructural investigations and lithostratigraphic reconstruction, combined with Raman Spectroscopy on Carbonaceous Material thermometry (RSCM). In particular, we recognized: (i) an early deformation phase, generally observed far from the BT and mainly in the External Nappe Zone ($D_1$), (ii) a syn-nappe ductile deformation and a top-to-the S-SW sense of shear, linked to the Barbagia Thrust activity ($D_2$); (iii) a large-scale nappe refolding ($D_3$) and (iv) a late extensional stage ($D_4$), with the development of collapse folds that marks the end of the orogenic cycle. We point out that the BT represents a full-fledged tectonic boundary that divides the internal sector of the Sardinian orogenic wedge from the external one.

Carmignani L., Carosi R., Di Pisa A., Gattiglio M., Musumeci G., Oggiano G. & Pertusati P.C. (1994) - The hercynian chain in Sardinia (Italy). Geodinamica Acta, 7(1), 31-47. https://doi.org/10.1080/09853111.1994.11105257.

Carosi R. & Malfatti G. (1995) - Analisi Strutturale dell’Unità di Meana Sardo e caratteri della deformazione duttile nel Sarcidano-Barbagia di Seulo (Sardegna centrale, Italia). Atti della Società Toscana di Scienze Naturali, Serie A, 102, 121-136.

Carosi R. & Pertusati P.C. (1990) - Evoluzione strutturale delle unità tettoniche erciniche nella Sardegna centro-meridionale. Bollettino della Società Geologica Italiana, 109, 325-335.

Montomoli C., Iaccarino S., Simonetti M., Lezzerini M. & Carosi R. (2018) - Structural setting, kinematics and metamorphism in a km-scale shear zone in the inner nappes of Sardinia (Italy). Italian Journal of Geoscience, 137, 294-310. https://doi.org/10.3301/IJG.2018.16.

# Remote sensing technologies and GIS 3D: a new method for crystalline basement mapping

Pieruccioni D.*[1] & Tufarolo E.[2]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] AYA Engineering Ltd., Accra (Ghana).

*Corresponding author e-mail:* diego.pieruccioni@isprambiente.it

*Keywords:* remote sensing, GIS 3D, geological map.

Mapping crystalline basements is difficult due to their polyphase deformation and because they generally crop out in a morphologically complex area and/or are difficult to access through the traditional geological survey.

Recent advancements in technology, over the past decade, in aerial data acquisition from aircrafts and Unmanned Aerial Vehicles (UAVs), have changed the way geoscientists both acquire and plot their data, leading to a revolution in the performance of field mapping. Now, it is possible to capture high-resolution rock surface images, in areas characterized by sparse low-lying vegetation, and analyse geological structures within those datasets in a 3D digital enviroments.

In the present study, we propose an innovative working method capable of reducing to a minimum the entities of both costs and fieldwork, going to represent substantial support, sometimes an alternative, to the in situ geological surveys. It is the application of digital photogrammetry based on Structure from Motion algorithms (SFM), an expeditious, economic, and effective technic for three-dimensional surveying and mapping of large and morphologically complex areas of geological interest. With constant technique improvements for data acquisition and processing, the photogrammetric processing products, such as three-dimensional georeferenced point clouds, Digital Elevation Models (DEM), and orthophotos with detail and accuracy always better, represent a new frontier in the geological analysis of the crystalline basements.

The acquired data are elaborated within the ESRI ArcGIS Pro environment that affords to analyse in a practical way of the three-dimensional models and directly digitizing in a 3D environment, creating consequently an innovative geothematic database. Using this platform, the digital models coupled and integrated with the data of the geological survey can be used to improve three-dimensional geologic photointerpretation. In this way, it is possible to characterize the main ductile and brittle geologic elements with high precision benefitting of 3D visualization of the area from more points of view and are inserted into a database by acquiring directly the complete spatial information. The software makes it possible to combine 2D and 3D data and allows users to work by loading multiple views of the same data or the same view for different data. From the direct comparison between bidimensional and three-dimensional images, it is possible to directly edit points, lines, or polygons improving in some cases the precision and the reliability of the photo-interpreted geologic data.

# Dataset integration for the reconstruction of the pre-Alpine history of Fornovolasco area (Alpi Apuane, Italy)

Pieruccioni D.*[1], Spina A.[2], Brogi A.[3-4], Capezzuoli E.[5], Liotta D.[3-4], Zucchi M.[3], Sorci A.[2] & Molli G.[6]

[1] Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma. [2] Dipartimento di Fisica e Geologia, Università di Perugia. [3] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [4] Istituto di Geoscienze e Georisorse, CNR, Pisa. [5] Dipartimento di Scienze della Terra, Università di Firenze. [6] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* diego.pieruccioni@isprambiente.it

*Keywords:* geological mapping, palynology, Alpi Apuane.

A new stratigraphic and structural study, coupled with analyses of the organic matter content, has been carried out on the Paleozoic successions exposed in the Fornovolasco tectonic window (Alpi Apuane, Tuscany, Italy) in order to refine its uncertain age and the local geological setting. The studied succession consists of muscovitic-quartzitic phyllite, alternating with discontinuous centimeter-thick levels of quartzite, known as the Scisti di Fornovolasco Formation (Pandeli et al., 2004). Such a succession was affected by greenschist metamorphism during Alpine orogenesis. Due to the lack of fossils, the Scisti di Fornovolasco Formation, was attributed to the ?lower Cambrian-Middle Ordovician by lithostratigraphic correlation with metasedimentary formation cropping out in SE Sardinia (Italy) dated by acritarchs and detrital zircons (Pieruccioni et al., 2018). Other authors (Ciarapica & Zaninetti, 1983) referred the Scisti di Fornovolasco Formation to Ladianian-Carnian, based on benthic foraminifers found within the main carbonate succession ("Tinello Metacarbonates") which overlie the formation.

In this study, new palynological data add new age constrain and give additional inputs for better define the stratigraphical/structural settings of this debated geological formation, allowing us to distinguish two main different units: i) the lower-middle portion is characterized by quartz-metasandstone with levels of graphitic metapelite, cut by tourmaline veins. This unit is characterized by acritarch microflora of late Cambrian age; ii) the upper portion consists of graphitic metapelite and fine-grained metasandstone, characterized by well preserved and diversified sporomorphs microflora of late Permian age. This is the first evidence of post-Variscan unit forming the Paleozoic succession of the Eastern Alpi Apuane. In this frame, the new palynological data allowed us to better characterize the age and stratigraphic setting of the debated Scisti di Fornovolasco Formation, contributing to a refinement of the existing geological maps.

Ciarapica G. & Zaninetti L. (1983) - Faune a foraminiferes ladino-carniens dans les Schistes de Fornovolasco "Unità delle Panie". Rev. de Paleobiologie, 2(1), 47-59.

Pandeli E., Bagnoli P. & Negri M. (2004) - The Fornovolasco schists of the Apuan Alps (Northern Tuscany, Italy): a new hypothesis for their stratigraphic setting. Boll. Soc. Geol. Ital., 123, 53-66.

Pieruccioni D., Vezzoni S. & Petrelli M. (2018) - A petrographic and U-Pb geochronological approach to the reconstruction of the pre-alpine history of Alpi Apuane (Tuscany). Atti Soc. Tosc. Sci. Nat. Mem. Ser. A, 125, 69-80.

# Mapping metamorphic basements in the CARG project: the example of the Sheet n. 425 "Isola Asinara" (northern Sardinia)

Simonetti M.* & Pieruccioni D.

Dipartimento per il Servizio Geologico d'Italia, ISPRA, Roma.

*Corresponding author e-mail:* matteo.simonetti@isprambiente.it

*Keywords:* geological mapping, crystalline basements, CARG project.

In the CARG project several geological maps including portions of crystalline basement are under production. Mapping crystalline basements is difficult due to their polyphased deformation and metamorphism. Furthermore, the emplacement of intrusive bodies can determine metamorphic processes in the hosting rocks overprinting previous ones.

The CARG project started with a traditional approach to geological mapping and subsequently was implemented with a digital database. However, up to now it was never regulated and coded how to deal with the issues linked to the mapping of crystalline rocks.

Thanks to the experince derived from previous CARG sheet realized in such contexts, it is now clear that a useful approach is the integration of field mapping, also performed with new digital mapping tools (Gencarelli et al., 2022), and many other disciplines. Such an integrative approach contributes to solve issues that cannot be directly resolved from the fieldwork.

The Sheet n. 425 - "Isola Asinara" is the first attempt to use this new approach integrated with the CARG project normatives. Mapping was performed combining classical methods and digital instruments such as FieldMove Clino and Qfield apps. Furthermore photointerpretation of remote sensing data was a powerfull tool to improve the geological and structural data.

In this area variscan medium- to high-grade metamorphic rocks crops out and they are intruded by late variscan granitoids. Four ductile deformation phases are recognized (Carosi et al., 2004): D1 is locally preserved and the S1 is visible in D2 hinges; D2 is the most pervasive deformation phase and S2 is the main foliation that progressively become a mylonitic foliation approaching to the Posada-Asinara shear zone; D3 is weak and produced upright folds; D4 is associated to a sub-horizontal crenulation cleavage.

For each deformation phase the pre-, syn- and post-tectonic minerals as well as to micostructures (observed in field-oriented thin sections) were recognized in order to have a preliminary and qualitative information about the P-T conditions associated to deformation. The termo-metamorphic aureoles associated to the intrusions were recognized thanks to the static growth of index minerals.

These preliminary data will be further refined thanks to detailed P-T estimations, geocronology and characterization of deformation regime and finite strain.

The integration of several disciplines allow to enhance the quality and the accuracy of the geological maps of the CARG project. This approach is therefore reccomended for the realization of the future CARG maps.

Carosi R., Di Pisa A., Iacopini D., Montomoli C. & Oggiano G. (2004) - The structural evolution of the Asinara Island (NW Sardinia, Italy). Geodin. Acta, 17(5), 309-329.

Gencarelli C.N., Voltolina D., Hammouti M., Zazzeri M. & Sterlacchini S. (2022) - Geospatial Information Technologies for Mobile Collaborative Geological Mapping: The Italian CARG Project Case Study. ISPRS Int. J. Geo-Inf., 11, 192.

# Integrated structural mapping of crystalline basements: a fundamental tool to unravel mountain building processes

Spalla M.I.*[1], Zucali M.[1], Filippi M.[1], Rebay G.[2], Roda M.[1], Zanoni D.[1] & Gosso G.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* iole.spalla@unimi.it

*Keywords:* fabric gradients, rock memory, tectono-metamorphic units.

Tectonic units in metamorphic belts form and modify along active margins, where coupling and decoupling of crustal slices work in competition, determining their size and shape. Consequently, the structural and metamorphic histories of crustal fragments constituting crystalline basements are the Ariadne's thread to define their trajectories through different structural levels during the formation of orogenic belts. Therefore, the individuation of volumes recording analogous structural and metamorphic evolution becomes crucial. For this purpose, the concept of tectono-metamorphic units was introduced, about twenty years ago, with the aim of identifying volumes, even transient over time, which recorded a coherent metamorphic and structural history. The proposed procedure requires an analytical approach that integrates structural, petrological, lithostratigraphic and, where possible, geochronological techniques. It produced very interesting results, though its application to crystalline basement has been limited by the time-consuming factor. This multidisciplinary approach has been refined through the evaluation of degree of fabric evolution (deformation gradients) and of mineral reaction progress (metamorphic transformation gradients). The effectiveness of this integrated method has been tested on Alpine terrains, multiply-deformed under different thermal regimes, aiming at: i) exploring the influence of thermal regimes on fabric evolution and reaction progress; ii) investigating the influence of inherited textures, degree of fabric evolution, bulk rock, and mineral compositions on degree of reaction progress; iii) obtaining quantitative 3D architecture of deformation and metamorphic transformation gradients; iv) the individuation of critical thresholds making strain rate the dominant factor influencing the accomplishment of metamorphic reactions. The assemblage of all these data allows producing integrated structural maps that constitute keystones to shed light on the deep-seated tectonic mechanisms effective along active margins and on the size of tectono-metamorphic units they generate.

# Ground-based geological mapping integrated by UASs in the Chiavenna area (Central Alps): examples of application in the frame of the CARG project

Tartarotti P.*[1], Apuani T.[1], Arrigoni F.[1], Conforto A.[1], Pigazzi E.[1], Tantardini D.[1] & Toffolon G.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Contractor CARG-Valchiavenna Project.

*Corresponding author e-mail:* paola.tartarotti@unimi.it

*Keywords:* crystalline basements, geological mapping, UAS.

Traditional ground-based mapping of crystalline basements is essential to unravel their tectono-metamorphic evolution. However, the structural setting of metamorphic terranes is most of the time complicated by the polyphase history, not least by neotectonics. Many scientific difficulties can be overcome by implementing the field work with analytical investigations, such as chemical or geochronological analyses, that may solve several geological issues as long as the structural and microstructural features are well constrained. Recently, an interest has been growing in advanced technologies dedicated to data acquisition and applications in geological mapping. Nowadays, unmanned aerial systems (UASs) such as drones are more and more utilised, especially in mineral exploration and mine exploitation (e.g., Honarmand & Shahriari, 2021). Drone photogrammetry is particularly useful in inaccessible areas, opening a new perspective for all kinds of ground operators.We used DJI Mavic 2 Pro and DJI Mavic Mini drones to implement the traditional field work on crystalline basements in the Chiavenna area (Central Alps), within the frame of the project "Carta Geologica d'Italia at scale 1:50.000 – CARG", covering ca. 700 kmq. This area is characterized by altitudes ranging between 200 and 3300 m a.s.l., and by a hostile topography with steep slopes and few road access that make many outcrops scarcely or not reachable. Most of the territory sees the exposure of polymetamorphic basements of the Penninic Suretta, Tambò, and Adula Nappes, separated by sheets of Mesozoic metasedimentary rocks, the Chiavenna unit, interpreted as a remnant of the Valais Ocean, and the Gruf Complex, whose attribution is still uncertain, intruded in the southeastern portion by the Bergell pluton (Schmid et al., 1996). UAS tools turn to be fundamental in such kind of terrains, whose applications regard the recognition of different lithologies on exposed surfaces, structures, morphologies, and landslides. Reiteration of field and intermediate laboratory work, with UAS-assisted surveys is necessary to finalise the geological mapping and its interpretation.

Honarmand M. & Shahriari H. (2021) - Geological Mapping Using Drone-Based Photogrammetry: An Application for Exploration of Vein-Type Cu Mineralization. Minerals, 11(6), 585.

Schmid S. M., Pfiffner O. A., Froitzheim N., Schönborn G. & Kissling E. (1996) - Geophysical-geological transect and tectonic evolution of the Swiss-Italian Alps. Tectonics, 15(5), 1036-1064.

# A petrographic and geochemical approach to map hydrothermal alteration in polymetamorphic basement (Alpi Apuane)

Vezzoni S.*[1], Pieruccioni D.[2], Galanti Y.[3], Biagioni C.[4] & Dini A.[1]

[1] Istituto di Geoscienze e Georisorse, CNR, Pisa. [2] Servizio Geologico d'Italia, ISPRA, Roma. [3] Agenzia Regionale per la Protezione Ambientale, Pistoia. [4] Dipartimento di Scienze della Terra, Università di Pisa.

*Corresponding author e-mail:* simone.vezzoni@igg.cnr.it

*Keywords:* crystalline basements, hydrothermal alteration, Alpi Apuane.

Crystalline basements can record a long geological history characterized by multiple metamorphic events related to the geodynamic evolution of one or more orogenic cycles. Generally, the petrographic features of crystalline basement rocks are interpreted as the result of metamorphic recrystallization on primary sedimentary and/or magmatic rocks while pre-metamorphic hydrothermal alterations are rarely recognized (e.g., Franz et al., 2013).

The Paleozoic basement of the Northern Apennines is discontinuously exposed in the Mid-Tuscan Ridge, and the Alpi Apuane hosts the largest outcrop of these rocks (Molli et al., 2020). In the southern area (Sant'Anna tectonic window - SAtw), the Paleozoic rocks are mainly represented by grey-greenish phyllites and quartzites interpreted as a metamorphic product of sandstones and pelites of ?lower Cambrian-Middle Ordovician depositional age (*Filladi Inferiori Fm.*). These rocks are spatially associated with Permian sub-intrusive bodies and hydrothermal mainly pyrite±barite ore bodies (Vezzoni et al., 2018), making SAtw an ideal case study for investigating hydrothermal alteration effects in the Northern Apennines basement.

We illustrate the results of a petrographic and geochemical study based on sample collection performed using a grid of around 150 m x 150 m covering the whole outcrop of the Paleozoic rocks of SAtw. We show that the *Filladi Inferiori Fm.* records a Permian tourmalinization and sericitization event giving rise to whitish schists. The hydrothermalized rocks were recrystallized and reworked during the Alpine tectono-metamorphic event, but partially preserved the original hydrothermal features. We apply a litho-geochemical approach (the alteration box plot; Large et al., 2001) initially developed for magmatic rocks and we prove that it is a useful tool for identifying hydrothermal alteration, also in polymetamorphic basement rocks with sedimentary protoliths.

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# Tectono-metamorphic map of the Zermatt-Saas Zone ophiolite, Valtournanche, Western Alps

Zanoni D.*[1], Luoni P.[1], Rebay G.[2] & Spalla M.I.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* davide.zanoni@unimi.it

*Keywords:* Alpine ophiolite, Alpine subduction, oceanic lithosphere.

In upper Valtournanche, structural and geological mapping carried out at 1:5000 scale, along with high-resolution mapping in key areas and optical and electronic microscope analyses, reveals up to four ductile deformation stages (D1, D2, D3, and D4) that affect ophiolite rocks of the Zermatt-Saas Zone tectonic unit. The mapped area is dominated by serpentinites associated with metamorphic Fe- and Mg-gabbros, carbonatic metasediments, and metabasites. Serpentinites host also variably deformed rodingite dykes (Zanoni et al., 2016). As a whole this rock assemblage may represent a metamorphic equivalent of a complete oceanic lithosphere. D1 comprises a foliation and rare vestigial of centimetre-sized rootless folds. D2 and D3 stages produced isoclinal and thigh folding with sub-parallel axes and shallower and steeper axial plane and foliation, respectively. D4 produced upright folding with weak local foliation. Locally in serpentinite metre-sized hinges of recumbent D2 folds are preserved. D2 produced also the development of the dominant regional foliation in all rock types and for the almost complete transposition of the lithostratigraphy. In metabasites and carbonatic schists, microstructural analysis revealed that minerals marking the dominant foliation indicate high-pressure conditions. Thermobarometric estimates on these assemblages suggest that D2 structures developed under a thermal state compatible with a cold subduction, which in serpentines was dated at Cretaceous - Palaeocene transition (Rebay et al., 2018). Thus, during subduction the lithostratigraphy was re-structured and in particular hundred metre-sized gabbro bodies were disrupted into tectonic lenses that in place are extremely reduced in size and dispersed within serpentinites. Afterwards, exhumation took place under a thermal state compatible with the Alpine collision. PT estimates for mineral assemblages marking pre-D2 relict fabrics indicate a P-prograde evolution developed during subduction-related burial. This evidence is in contrast with pre-D2 relicts in serpentinite (Luoni et al., 2018) whose PT estimates indicate a retrograde evolution. These differences indicate that the Zermatt-Saas Zone preserves heterogeneous tectono-metamorphic evolutions opening the question whether different tectono-metamorphic units were amalgamated into the Alpine subduction system, during the development of the regional S2 foliation.

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# S46.

# From Micro to Macro – How to unravel the nature of the Large Magmatic Events


*Conveners & Chairpersons*

*Massimo Coltorti (University of Ferrara)*

*Anna Cipriani (University of Modena and Reggio Emilia)*

*Vincenza Guarino (University of Napoli)*

*Lorella Francalanci, (University of Firenze)*

*Alberto Zanetti (CNR - IGG)*

*Manfredo Capriolo (University of Oslo)*

# Crystallization kinetics in hydrous trachytic and latitic melts due to variable degrees of undercooling

Appiah E.*[1], Krasheninnikov S.P.[2], Holtz F.[2], Stabile P.[1], Arzilli F.[1] & Carroll M.R.[1]

[1] Scuola di Scienze e Tecnologie, Università di Camerino.
[2] Institut für Mineralogie, Leibniz Universität Hannover (Germany).

*Corresponding author e-mail:* ernestina.appiah@unicam.it

*Keywords:* hydrous trachytic and latitic magma, Campi Flegrei, crystallization kinetics.

Magma undergoes variable degrees of undercooling due to decompression and cooling within the volcanic conduit during magma ascent in eruption. Hydrous magmas, when subjected to decompression can be expected to lose water and crystallize due to the effects of $H_2O$ loss on magma liquidus temperature. Decompression-induced crystallization may thus produce large changes in magma viscosity during magma ascent towards the surface and potentially influence magma eruptive styles (e.g., effusive vs. explosive). Hydrous basaltic magmas are able to crystallize rapidly even during fast ascent and decompression rates within conduits, promoting highly explosive eruptions (Arzilli et al., 2019). Trachytic and latitic magmas of Campi Flegrei (Naples, Italy) produced highly explosive eruptions in the phlegrean volcanic area, but the effect of crystallization on magma viscosity during magma ascent and on the eruptive style is poorly investigated. In this study, we investigate the effect of continuous cooling and decompression on crystallization kinetics of trachytic and latitic melts through cooling and decompression experiments conducted in an internally heated pressure vessel (compositions more mafic than the trachy-phonolite studied by Arzilli et al. (2016). We conducted $H_2O$-saturated isobaric cooling experiments (continuous cooling at 0.125, 0.5, 3, and 12.5°C/min) at P of 200 and 50 MPa, and isothermal decompression experiments (1.15, 6.92, and 23.03 MPa/min) at 975°C and 200 to 50 or 25 MPa. Preliminary observations suggest that the presence of $H_2O$ in these experiments aids the nucleation and growth of feldspar crystals compared with the dry case (Iezzi et al., 2008). The results indicate that the effects of $H_2O$ on crystallization kinetics in the more mafic trachytic and latitic melts discussed here could be slightly less than the effects observed for trachy-phonolitic melts (Arzilli et al., 2016). However, this depends on the effect of water on the crystallization temperature of the individual phases and on crystallization kinetics which are controlled by melt water content and diffusivity.

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# Petrogenesis of a Cenozoic magmatic province in the Mandak-Mandal-Gobi zone, Central Mongolia

Beltrame M.*[1], Spizzamiglio M.[2], Yondon M.[3], Venier M.[1], Velicogna M.[4], Milani S.[5], Chiaradia M.[6], Ziberna L.[1] & De Min A.[1]

[1] Dipartimento di Matematica e Geoscienze, Università di Trieste. [2] Dipartimento di Geoscienze, Università di Padova. [3] Geoscience Center, School of Geology and Mining, Mongolian University of Science and Technology, Ulaanbaatar (Mongolia). [4] Dipartimento di Territorio e Sistemi Agro-Forestali, Università di Padova. [5] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [6] Earth and Environmental Sciences, University of Geneva (Switzerland).

*Corresponding author e-mail:* marco.beltrame@phd.units.it

*Keywords:* petrogenesis alkaline magmatism.

The Cenozoic intraplate alkaline volcanism in Mongolia is diffuse and widespread, extending from NE China to Lake Baikal in Siberia. Different hypothesis has been suggested for the origin of such magmatism, but the main ones contemplate the involvement of a plume (Yarmoluk et al., 2015) or an asthenospheric upwelling caused by sinking slabs of the Mongol-Okhotsk Ocean (Sheldrick et al., 2020). Here we report the result of a field campaign and petrographic and geochemical study of the alkaline magmatic products from the Mandak-Mandal-Gobi area. The available geochronological datum (K/Ar) has been obtained for one single sample from this area (Yarmoluk et al., 2019), which suggest an age of 51 Ma. The aim of this work is to obtain more insights about the features of the involved mantle source(s) and the plumbing system. The sampling, performed in 2019, include lava flows (also sampled in recognizable stratigraphic sequences), dikes and necks. Chemical (major and trace elements) as well as Sr, Nd and Pb isotopic analyses were performed on about 50 and 10 whole rocks, respectively. Electron microprobe analyses have been performed on the phenocryst and xenocryst assemblages, which are constituted by olivine and clinopyroxene and minor oxides and plagioclase. The rocks span from basanite to phonotephrite and from trachybasalt to basaltic trachyandesite, showing Na and K affinities. Possibly stronger K affinity might have been partially overprinted by hydrothermal alteration related to the final stages of the magmatic event. Rare earth elements (REE) and other incompatible trace elements suggest an OIB-like signature as well as low degrees of partial melting of a garnet-bearing mantle sources, heterogeneous on a small scale. The occasional potassium affinity and some chemical characteristics shown by few samples suggest that in the source a memory of the past subduction is still present and therefore, the partial involvement of the Sub-Continental Lithospheric Mantle (SCLM) it is here assumed to explain the formation of these rocks. Finally, the chemistry of clinopyroxenes, many of which sampled according to the stratigraphic sequence of the two main volcanoes, suggests different inputs inside several magma chambers located mainly in underplating and secondarily at lower pressure conditions.

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# Lifetime of the Early Permian giant caldera-system of Bolzano/Bozen (North-eastern Italy)

Boscaini A.*[1], Davies J.H.F.L.[2], Sassi R.[1], Mazzoli C.[1], Callegaro S.[3], De Min A.[4] & Marzoli A.[5]

[1] Dipartimento di Geoscienze, Università di Padova, [2] Département des Sciences de la Terre et de l'Atmosphère, Université du Québec, Montréal (Canada). [3] Centre for Earth Evolution and Dynamics, University of Oslo (Norway). [4] Dipartimento di Matematica e Geoscienze, Università di Trieste. [5] Dipartimento Territorio e Sistemi Agro-Forestali, Università di Padova.

*Corresponding author e-mail:* andrea.boscaini@phd.unipd.it

*Keywords:* caldera-system, Early Permian, Southern Alps.

The post-Variscan evolution of the Southern Alps witnessed a significant magmatic activity between ca. 290 and 275 Ma associated to the tectonic riequilibration of the Variscan orogeny. In North-eastern Italy, the Early Permian magmatism is represented by several mafic to felsic plutonic bodies and the mainly silicic volcanics of the Athesian Volcanic Group (AVG). New high-precision zircon U-Pb geochronology (CA-ID-TIMS) yields emplacement ages between ca. 282 and 279 Ma for the intrusions of Cima d'Asta-Caoria, Pergine Valsugana, Monte Sabion, Monte Croce/Kreuzberg, and Bressanone/Brixen, as well as for the AVG. Our results show that the overall lifetime of this magmatic activity is significantly shorter than previously reported and highlight the overlap in age between the intrusives and the volcanics. These data suggest that intrusives and extrusives are remnants of a giant caldera-system and its shallow crustal plumbing system extending over more than 4200 $km^2$ in the Athesian magmatic district. The Bolzano/Bozen supervolcano is coeval with other mega-calderas in the Southern Alps, which deeply affected both the tectonomagmatic evolution and the ecosystems of the South Variscan realm during the Early Permian.

# Magma-host rock interaction in basaltic sills from the Siberian Traps (Tunguska basin, Russia): mineral scale and whole-rock perspectives

Callegaro S.*[1], Svensen H.H.[1], Deegan F.M.[2], Jerram D.A.[3], Planke S.[4] & Polozov A.G.[5]

[1] Centre for Earth Evolution and Dynamics, University of Oslo (Norway). [2] Department of Earth Sciences, Natural Resources and Sustainable Development, Uppsala University (Sweden). [3] DougalEARTH Ltd., Solihull (UK). [4] Volcanic Basin Petroleum Research, Oslo (Norway). [5] Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow (Russia).

*Corresponding author e-mail:* sara.callegaro@geo.uio.no

*Keywords:* Siberian Traps, halogens, volcanic basin.

The Tunguska volcanic basin in Siberia (Russia) hosts an extensive network of sills, part of the Siberian Traps Large Igneous Province. High-precision geochronology links the initial phase of sill emplacement to the end-Permian cascade of environmental catastrophes that almost expunged life on Earth (Dal Corso et al., 2022). The end-Permian atmosphere was impacted by a voluminous cocktail of thermogenic gases, likely produced by sills emplaced within the evaporitic and coal-rich series of the Tunguska basin. Basin-scale observations and thermal modelling provide evidence of thermogenic gas production and release (Svensen et al., 2018). For the Tunguska sills, whole-rock geochemistry (Callegaro et al., 2021) and micro-analyses reveal multiple processes of magma host-rock interaction occurring at different levels across the plumbing system and the volcanic basin. Whole-rock trace elements and radiogenic isotope signatures reflect assimilation of variable crustal lithologies, from the crystalline basement to local carbonate covers. Assimilation of sulfur-rich anhydrite-dominated evaporites is revealed by sulfur isotopic signatures measured on whole-rocks. Late-stage halogen mobilization is tracked by detailed mineral analyses. We found widespread evolved late-stage pockets in the doleritic Tunguska sills, occupying the interstitial spaces among the larger plagioclase and clinopyroxene crystals. The late-stage interstitial pockets have an evolved, volatile-rich mineralogy, dominated by biotite and quartz, with minor K-feldspar, chloro-apatite, Cl-rich amphibole, sulfides and occasional baddeleyite and zircon. Biotite in the pockets is extremely enriched in Cl, especially at the rims. Plagioclase surrounding the pockets shows highly albitic rims. These compositions are widespread across the Tunguska basin, where sills intruded halite- and anhydrite-rich evaporites. This suggests extensive mobilization of crustal halogens and sulfur associated with the emplacement of the Tunguska sills, along with previously demonstrated thermogenic carbon production. Notably, most investigated sills are geochemically correlated with Siberian Traps intrusions dated coeval with the main extinction horizon (Callegaro et al., 2021).

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# Synchrotron Light X-ray microtomography data constrain the magma plumbing system of mass extinction-related Large Igneous Provinces

Capriolo M.*[1], Callegaro S.[1], Dal Corso J.[2], Newton R.J.[3], Baker D.R.[4], Renne P.R.[5], Storm M.[6-7] & Marzoli A.[8]

[1] Centre for Earth Evolution and Dynamics, University of Oslo (Norway). [2] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan (China). [3] School of Earth and Environment, University of Leeds (UK). [4] Department of Earth and Planetary Sciences, McGill University, Montreal (Canada). [5] Berkeley Geochronology Center and University of California, Berkeley, CA (USA). [6] Diamond Light Source, Manchester (UK). [7] Helmholtz-Zentrum Hereon, Institute of Materials Physics, Geesthacht (Germany). [8] Dipartimento di Territorio e sistemi agro-forestali, Università di Padova.

*Corresponding author e-mail:* manfredo.capriolo@geo.uio.no

*Keywords:* magma plumbing system, LIPs, melt inclusions.

Synchrotron Light X-ray microtomography is a powerful tool to reconstruct and study the microstructures within magmatic rocks, unveiling the evolution of crystals, melts and volatiles in magma plumbing systems. The fossil example of magma plumbing systems from Large Igneous Provinces (LIPs) may shed light on the cause-effect relationship between magmatic volatiles, especially $CO_2$, and the most catastrophic mass extinction events in Earth's history. $CO_2$-rich melt inclusions within clinopyroxene-dominated crystal clots in basaltic rocks from the Central Atlantic Magmatic Province and the Deccan Traps indicate not only $CO_2$ abundance in the magma plumbing system, but also its early exsolution during magma ascent (Capriolo et al., 2020). Bubble-bearing melt inclusions and glomerocrystic aggregates in basaltic samples from both these LIPs were imaged by Synchrotron Light X-ray microtomography at Diamond Light Source (UK). The main constituting mineral phases, as well as the glass and the bubbles, occupied by the volatile phase, were distinguished and characterized based on their different density. The 3D reconstruction of analysed crystal clots and melt inclusions allowed investigating the distribution of melt inclusions within crystal clots and estimating the glass/bubble ratio within the melt inclusions. The latter operation is fundamental to constrain the original concentration of volatile species in the melt prior to gas exsolution and post-entrapment processes, such as crystallization and glass shrinkage. The X-ray microtomography data of these LIPs revealed the microstructural features of bubble-bearing melt inclusions and their host glomerocrystic aggregates. A multi-phase mush constituted the transcrustal magma plumbing system of LIPs, where interstitial melt and exsolved $CO_2$ may have migrated through a porous crystalline framework, interacted with crustal material and driven magma ascent and eruption. Hence, the magma plumbing system of LIPs played a key role in the transfer from the mantle to the surface of carbon, being responsible for the most devastating mass extinctions in Earth's past.

Capriolo M., Marzoli A., Aradi L.E., Callegaro S., Dal Corso J., Newton R.J., Mills B.J.W., Wignall P.B., Bartoli O., Baker D.R., Youbi N., Remusat L., Spiess R. & Szabó Cs. (2020) - Deep $CO_2$ in the end-Triassic Central Atlantic Magmatic Province. Nat. Commun., 11, 1670.

# Adakitic dacites near Siliqua (Southwestern Sardinia): slab melting or arc rock re-melting?

Cariddi B.*[1], Costamagna L.G.[2], D'Antonio M.[1], Guarino V.[1], Morra V.[1] & Melluso L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II».
[2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* bruna.cariddi@unina.it

*Keywords:* adakites, calcalkaline domes, Sardinia.

Two calcalkaline andesitic-dacitic lava domes (Monte Truxionis and Acquafredda) outcrop near Siliqua, in the Cixerri graben, in SW Sardinia. The ages, the Pb peak and Nb-Ta-Ti troughs in primitive mantle normalized diagrams make these rocks akin to the "subduction-related" magmatic activity developed in Sardinia during the Upper Eocene-Middle Miocene period (38-12 My; Lustrino et al., 2009 and references therein). The domes are porphyritic, with zoned plagioclase and amphibole phenocrysts included in a groundmass composed by the same phases plus quartz, alkali feldspar and oxides. The Monte Truxionis dome has also mica and clinopyroxene. Amphibole geobarometers indicate higher crystallization pressure for Acquafredda magmas (~8 kbar) than for Monte Truxionis (~3 kbar). The Acquafredda dacites have marked adakitic affinity, as highlighted by the HREE and Y depletion (Sr/Y > 70, $La_N/Yb_N > 20$). In the chondrite normalized REE diagram, Acquafredda dacites have the same pattern as Monte Truxionis andesites, but two times less enriched in REE. This is a newly observed feature in the Cenozoic magmatism of Sardinia.

The similar isotopic composition between the Acquafredda *adakite* ($^{87}Sr/^{86}Sr_i = 0.70625$; $^{143}Nd/^{144}Nd_i = 0.51248$) and less evolved samples ($^{87}Sr/^{86}Sr_i = 0.70599$-$0.70638$; $^{143}Nd/^{144}Nd_i = 0.51241$-$0.51248$) point to a common source; *adakites* could be the product of re-melting, at high pressures, of an amphibole-bearing arc rock with isotopic composition like the basaltic andesite of Siliqua. The high crystallization pressure calculated for amphibole in the adakites corroborates this hypothesis. Petrogenetic modeling of Acquafredda *adakites* indicates that they could be the result of low degree re-melting of the removed assemblage in the transition from basaltic andesite to andesite, with a significant input of amphibole. The hypothesis that Acquafredda *adakites* are the products of AFC is not compatible with trace elements and Sr-Nd-isotopes variation.

The occurrence of adakites in arc magmas is generally explained with slab melting of hot and young subducted lithosphere (Moyen, 2009). Slab melting under Sardinia can be excluded because the Cenozoic igneous activity is related to the NW-ward directed subduction of the ancient Tethys Ocean.

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# Evolution of current unrest at Campi Flegrei, southern Italy

Carlino S.*[1], Kilburn C.R.J.[1-3], Danesi S.[2] & Pino N.A.[1]

[1] INGV, Osservatorio Vesuviano, Napoli. [2] INGV, Bologna.
[3] Department of Earth Sciences, University College London (UK).

*Corresponding author e-mail:* stefano.carlino@ingv.it

*Keywords:* Campi Flegrei, caldera, unrest.

Campi Flegrei is a large caldera extending west from the suburbs of Naples to the Tyrrhenian Sea, and it is home to more than 360,000 people. The caldera has been restless since 1950 and erupted for the last time in 1538 after an interval of about 3,000 years. Caldera-wide ground movement has raised the coastal town of Pozzuoli, near the centre of greatest uplift, by more than 4 m and twice triggered evacuations of about 40,000 people. The ongoing uplift began in 2005 with a previously unseen style of behaviour. The unrests have been attributed to the ascent of magma or of magmatic gas (D'Auria et al., 2015; Chiodini et al., 2021) to depths of about 3 km. Both interpretations assume a change in the external conditions feeding the volcano's magmatic system. We propose that the current uplift is instead being driven by internal changes in Campi Flegrei's crust as sections of faults are partially reopened. The re-opening favours new pathways to the surface for magmatic fluids, ranging from escaping gases to magma itself.

Campi Flegrei's current unrest began in 1950 and has developed in four major episodes (Kilburn et al., 2017), with maximum uplift at Pozzuoli: c. 74 cm in 1950-52, 159 cm in 1970-72, and 175 cm in 1982-84. The fourth episode was followed by twenty years of subsidence that lowered Pozzuoli by 93 cm, and then by seventeen years of uplift that by the end of February 2022 had returned the surface to its 1984 position. The amounts and timescales of the first three episodes are consistent with the intrusion of magmatic sills; those of the fourth, and ongoing, episode is consistent with the permeable flow of a combination of magmatic gas and meteoric water (Kilburn et al., 2017).

We propose that the complete sequence describes the progressive stretching of the crust by repeated intrusions until its permeability had increased sufficiently for a major change in the flow of pore fluids. Our interpretation is supported by new data, which show that, by 2021, the regime of crustal deformation had changed from quasi-elastic (elastic with subordinate fracturing and faulting) to inelastic (dominated by fracturing and faulting). The change marks an evolution towards crustal rupture and has been observed at several volcanoes, including large calderas (Kilburn, 2018). Rupture does not guarantee a magmatic eruption. However, it does favour an increase in the rate of escape of pressurized fluids that may trigger phreatic explosions. The presence of a new rupture also increases the possibility that any new magma reaching shallow depth will erupt, rather than intrude as had occurred between 1950 and 1984. As a result, it is unlikely that the volcano will replicate its behaviour during the past 70 years of unrest, so that new scenarios for emergency response must take account of its dynamical and structural evolution.

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# Estimating the viscosity of silicate melts from the vibrational properties of their parental glasses

Cassetta M.*[1], Di Genova D.[2], Zanatta M.[3], Boffa Ballaran T.[2], Kurnosov A.[2], Giarola M.[4], Biesuz M.[5], Sorarù G.D.[5], Giannetta B.[6], Zaccone C.[6], Daldosso N.[1] & Mariotto G.[1]

[1] Dipartimento di Informatica, Università di Verona. [2] Bayerisches Geoinstitut, University of Bayreuth (Germany). [3] Dipartimento di Fisica, Università di Trento. [4] Centro Piattaforme Tecnologiche, Università di Verona. [5] Dipartimento di Ingegneria Industriale, Università di Trento. [6] Dipartimento di Biotecnologie, Università di Verona.

*Corresponding author e-mail:* michele.cassetta@univr.it

*Keywords:* viscosity, glass, spectroscopy.

The temperature and chemical dependence of the viscosity of melts is obiquitous in the numerical modeling of the volcanic dynamics, as well as the glass production and design. The fast incursion of modifications at the nano-scale (i.e., crystallization), affect drastically the measurements and our knowledge of viscosity results quite elusive. This stimulates the need to quantify pure melt phase contribution to the measured viscosity of a probable crystallizing system. Here we show a new method that allows a careful estimation of the viscosity of melts at eruptive temperatures starting from the vibrational dynamics (by Brillouin and Raman scattering) of their parental glasses. Our results show that the melt fragility is intimately related to the ratio between bulk and shear moduli and the boson peak frequency position of glasses. However, a universal law addressing the why some of these quantities are related in the glassy state, is still missing. At this effort, we explored the extension of the observed trend by testing the conventional binary system $Na_2O$-$SiO_2$ and other industrial borosilicate standard glasses. Concluding, our strategy offers the possibility of estimating the melt viscosity at a given temperature, avoiding its measurements and unwished artifacts produced by crystallization.

# Dating Triassic-Jurassic rift-related deformation through microstructural and petrochronological analyses: insights on the evolution of a middle continental crustal shear zone (Ivrea-Verbano Zone, Italian Southern Alps)

Corvò S.*[1-2], Maino M.[1-2], Piazolo S.[3], Kylander-Clark A.R.C.[4], Seno S.[1] & Langone A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] School of Earth and Environment, University of Leeds (UK). [4] Department of Earth Science, University of California, Santa Barbara, CA (USA).

*Corresponding author e-mail:* stefania.corvo@unipv.it

*Keywords:* U-Pb titanite dating, petrochronology, shear zone.

The Ivrea-Verbano Zone (IVZ, Western Alps) is an exhumed section of the pre-Alpine middle to lower continental crust made of (ultra-)mafic rocks intruded into high grade metapelites and metabasites that escaped Alpine subduction. Following the Variscan orogeny, indeed, the IVZ was affected by post-orogenic extension and subsequently, in the Triassic-Jurassic time interval, by a complex and polyphasic episode of rifting stage which resulted in mid/lower crustal shear zones (Beltrando et al., 2015; Petri et al., 2019). While magmatism and amphibolite to granulite metamorphism are well constrained between the Carboniferous and Permian times (e.g., Karakas et al., 2019), the timing of extensional shear zones activities is still poorly constrained. In this contribution, we combine microstructural and petrochronological data of zircon and titanite from mylonitic amphibolites with the attempt to constrain the activity of the Anzola shear zone (Val d'Ossola, IVZ). In particular, we performed quantitative orientation analysis by SEM-EBSD to characterise the deformation features of the potential geochronometers and investigate their relationship with isotopic signatures and consequently, with the age dating. Preliminary zircon data revealed a weak or absent intracrystalline deformation and a wide range of U-Pb dates (310-230 Ma), mainly overlapping with the Carboniferous-Permian magmatic and metamorphic events. However, the studied mylonitic amphibolites contain abundant titanite along the foliation, which shows sigmoidal shapes, intracrystalline deformation and incipient recrystallization with a maximum orientation change within an individual grain up to 20°. Petrochronological results suggest that titanite recorded a main deformation induced recrystallization event under amphibolite facies at about 185 Ma, which is coeval to deformation occurred at different crustal levels in the IVZ (Simonetti et al., 2021). The present study highlights that titanite can be used as a reliable petrochronometer that allow interesting constrains on the role of major rift-related structures during lower crustal deformation.

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# Sound velocities and single-crystal elasticity of hydrous Fo90 olivine to 12 GPa

Faccincani L.*[1], Criniti G.[2], Kurnosov A.[2], Boffa Ballaran T.[2], Withers A.C.[2], Mazzucchelli M.[3] & Nestola F.[4]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Bayerisches Geoinstitut, University of Bayreuth (Germany). [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [4] Departimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* luca.faccincani@unife.it

*Keywords:* hydrous olivine, high-pressure Brillouin scattering, NAMs.

Although commonly referred to as nominally anhydrous minerals (NAMs), the dominant phases of Earth's upper mantle may contain significant amounts of water and constitute a significant reservoir for mantle hydrogen. The occurrence of water in NAMs is closely related to the presence of defects in their crystal structures, where hydrogen is structurally bound to oxygen atoms to form hydroxyl groups ($OH^-$) and its incorporation is typically charge-balanced by the formation of cation vacancies. Although this hydrous component is known to substantially alter several physical properties, its effect on the elastic properties of many NAMs is still poorly constrained.

Olivine is considered to be the most abundant mineral of Earth's upper mantle and to constitute about 60 vol.% of a pyrolitic mantle. Although natural olivine samples from mantle xenoliths commonly contain $10^1 – 10^2$ ppm wt. of water (e.g., Peslier et al., 2010), numerous experimental studies indicated that the water storage capacity of olivine significantly increases to 0.2 – 0.5 wt.% $H_2O$ at deep upper mantle conditions (e.g., Hirschmann et al., 2005). Therefore, determining the elastic properties of olivine samples with a more realistic water content expected for deep upper mantle conditions could help us interpreting both seismic velocity anomalies in potentially hydrous regions of Earth's mantle as well as the observed seismic velocity and density contrasts across the 410-km discontinuity.

In this study, we conducted simultaneous single-crystal X-ray diffraction (SCXRD) and Brillouin spectroscopy experiments at room temperature up to 11.96(2) GPa on hydrous (~ 0.2 wt.% $H_2O$) Fo90 olivine to constrain its full elastic tensor. Our new elasticity measurements, compared to literature data for anhydrous Fo90 olivine, demonstrate that the incorporation of 0.2 wt.% $H_2O$ into the olivine crystal structure causes no substantial effects on its elastic properties and sound wave velocities which, at pressures corresponding to the base of the upper mantle, are indistinguishable within uncertainties. Contrary to previous claims (Mao et al., 2010), our data suggest that water in olivine is not seismically detectable, at least for contents consistent with deep upper mantle conditions. In addition, our data rule out that the hydration of olivine may be being a key factor in reconciling seismic velocity and density contrasts across the 410-km discontinuity with a pyrolitic mantle.

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# The inner structure of the Marsili seamount revealed by coupling petrological and geophysical data

Gennaro E.*[1], Iezzi G.[1], Cocchi L.[2] & Ventura G.[2]

[1] Dipartimento di Ingegneria e Geologia, Università "G. d'Annunzio", Chieti. [2] INGV, Roma.

*Corresponding author e-mail:* emanuelagennaro@live.it

*Keywords:* Marsili seamount, plumbing system.

The Marsili seamount (800 ka - 2.7 ka), located in the Tyrrhenian Sea back-arc basin, is still active being characterized by hydrothermal activity, shallow seismicity (D'Alessandro et al., 2009; Lupton et al., 2011) and historical eruptions. Rocks (lava and tephra) range from basalts to trachytes depicting an evolution trend consistent with the fractionation of olivine, pyroxene, plagioclase and alkali-feldspar (e.g., Iezzi et al., 2014; Trua et al., 2002).

New phase-melt *equilibrium* thermo-, baro-, hygro- and oxy-metric evaluations are presented. The results (T: 1000-1200°C, P: < 500 MPa, $H_2O$: 0-4 wt.% and $fO_2$: 0-3 log units above the FMQ buffer) are independently corroborated with thermodynamic simulations of solidifications at variable P, $H_2O$ and $fO_2$. Data and petrological models indicate that $SiO_2$-rich and cold magmas (andesite/trachytes/latite) reside at Moho depth of the Marsili volcanic complex, whereas $SiO_2$-poor (< 55 wt.%) magmas ascend and stop only within the seamount. This petrological model is validated by gravimetric and magnetic data, whose modelling details the location and geometry of the magma reservoirs. The merging of petrological and geophysical data can be applied to other volcanic complexes with the aim to check how the unusual features of the Marsili plumbing system are common in other back-arc ridges.

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# Fossil recycled subducted volatiles ignite the Cenozoic magmatism of Northern Victoria Land (Antarctica): insights from olivine-hosted melt inclusions

Giacomoni P.P.*[1], Bonadiman C.[2], Casetta F.[3], Faccini B.[2], Ferlito C.[4], Ottolini L.[5] & Zanetti A.[5]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [3] Department of Lithospheric Research, University of Wien (Austria). [4] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [5] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* pierpaolo.giacomoni@unipi.it

*Keywords:* melt inclusions, primary magmatism, volatile elements.

Olivine-hosted melt inclusions (MI) in basic alkaline volcanics provide a direct estimation of the volatile concentration in undifferentiated melts of the Cenozoic magmatism of Northern Victoria Land (NVL, Antarctica). The occurrence of spinel-lherzolitic mantle xenoliths in these lavas allow us to link the volatile concentration in MI with their mantle source through melting modelling and ultimately to speculate about the origin of volatiles.

$H_2O$, $CO_2$, F, Cl and S concentrations in olivine-hosted melt inclusions were determined by Secondary Ion Mass Spectrometry (SIMS). The most undegassed $H_2O$ and $CO_2$ values varies from 1.14 to 2.64 wt.% $H_2O$ and from 2320 to 3900 ppm $CO_2$ for the least differentiated alkaline basalts and basanites, respectively. The same MI have F and Cl contents varying from 471 to 888 and from 474 to 1135 respectively, although some other MI can get up to 1377 of F and 1336 of Cl. A $H_2O/(H_2O + CO_2)$ molar ratios from 0.88 to 0.92 were determined, and taking into account the MI with the highest water content, a $CO_2$ content in the melts up to 4400 and 8800 ppm for basaltic and basanitic compositions respectively were inferred. Assuming that these magmas were produced by about 3 to 7% of partial melting, the volatile content in the mantle sources were estimated and compared with the estimates obtained from amphibole-bearing mantle xenoliths abundantly entrained in the McMurdo basic lavas. The two approaches converge in obtaining the following values: $H_2O$ = 1160±436 ppm; $CO_2$ = 304±64 ppm. Some discrepancies are observed for F and Cl, mainly due to the uncertainties in the F and Cl contents of amphibole and its modal content, both parameters spanning a rather large range.

The resulting $CO_2$/Nb and $CO_2$/Ba ratios are lower and $H_2O$/Ce higher than those estimated for Depleted MORB Mantle (DMM), suggesting that the NVL Cenozoic alkaline magmatism could be originated by an enriched mantle source composed by 60 to 70% Enriched Mantle (EM) and from 40 to 30% DMM. A global comparison of fluid-related, highly incompatible and immobile/low incompatible elements such as Li, K, Cl, Ba, Nb, Dy and Yb allow to put forward that the prolonged (~500 to 100 Ma) Ross subduction event played a fundamental role in providing the volatile budget to the lithospheric mantle before the onset of the Cenozoic continental rifting.

# The NW Paraná Magmatic Province: Age, geochemistry and mantle source of the Alto Diamantino basalts

Giovanardi T.[1], da Costa P.C.C.[2], Girardi V.A.V.[3], Weska R.K.[2], Vasconcelos P.M.[4], Thiede D.S.[4], Mazzucchelli M.*[1] & Cipriani A.[1-5]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Faculdade de Geociências Universidade Federal de Mato Grosso, Cuiabá (Brazil). [3] Instituto de Geociências, Universidade de São Paulo (Brazil). [4] School of Earth and Environmental Sciences, University of Queensland, Brisbane (Australia). [5] Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY (USA).

*Corresponding author e-mail:* maurizio.mazzucchelli@unimore.it

*Keywords:* Paraná basalts, Ar-Ar dating, mantle source.

The Paraná-Etendeka is one of the major and most thoroughly investigated large igneous provinces in the world. It formed in a very narrow time-range (i.e., 1.6-3.0 Ma) between 135-132 Ma. The South American portion of this province, i.e., the Paraná Magmatic Province, is characterized by a mainly mafic, coeval bimodal magmatism of low- and high-Ti magmas. Despite the large body of literature, the mantle source origin and contribution to this magmatism is still debated. Some studies call upon different degrees of melting of a homogenous mantle source, while others implicate plume activity and metasomatism of the sub-continental mantle.

In this work, we present new geochronological, geochemical and isotopic data of basalts from the under investigated Alto Diamantino region (southern Mato Grosso, Brazil) in the framework of PRIN 20178LPCPW. These basalts have tholeiitic affinity and can also be classified in two different suites based on $TiO_2$ content (L-Ti < 3 wt.%; H-Ti > 3 wt.%) which are compatible with Ribeira and Pitanga basalts of Paraná Magmatic Province. $^{40}Ar/^{39}Ar$ geochronology of the two suites provides statistically equivalent ages for the two series between 134.4±1.6 and 132.9±2.0 Ma. The ages and geochemical characteristics suggest that the Alto Diamantino basalts constitute the northwestern extension of the Paraná-Etendeka Magmatic Province never reported before.

Sr and Nd isotope ratios are close to the EM-I field pointing to a metasomatized mantle source, in agreement with the positive Ba anomalies of the two suites and their Rb/Sr and Ba/Rb ratios, which indicate the occurrence of amphibole in the mantle source. Compositional differences and the different evolution of the L-Ti and H-Ti basalts could be explained by different degree of melting at different depths of the same metasomatized mantle source, where H-Ti magmas are compatible with low degree melting in depth while L-Ti units record large degree melting. $T_{DM}$ ages suggest that the metasomatic event occurred after Proterozoic, possibly during the formation of Gondwana supercontinent during Neoproterozoic.

# Mantle xenoliths from Los Gemelos volcano (Canquel plateau, Patagonia Argentina): new insights into ultra-depleted lithologies in the SCLM

Grammatica M.*[1], Bertotto G.W.[2], Zanetti A.[3], Mazzucchelli M.[1], Jalowitzki T.[4], Santos A.[4], Orihashi Y.[5], Gervasoni F.[6] & Cipriani A.[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia [2] INICITAP CONICET, Universidad Nacional de La Pampa, Santa Rosa (Argentina). [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] Programa de Pós-graduação em Geologia, Universidade de Brasília (Brazil). [5] Department of Earth and Environmental Sciences, University of Hirosaki (Japan).
[6] Faculdade de Ciências e Tecnologia, Universidade Federal de Goiás, Goiânia (Brazil).

*Corresponding author e-mail:* michela.grammatica@unimore.it

*Keywords:* Patagonia, xenoliths, mantle.

From the Oligocene, Patagonia recorded an intense magmatic intraplate activity developed in the back-arc setting of the Pacific subduction below the South America continent. Often these magmatic products contain mantle xenoliths useful to reconstruct the evolution of the Patagonian sub-lithospheric mantle from their chemical records of depletion, metasomatism and refertilization processes related to the subduction factory.

In this contribution, in the framework of PRIN 20178LPCPW, we present the first chemical data, major and trace element mineral composition, of the mantle xenoliths recovered from Los Gemelos volcano (Canquel plateau, Chubut Argentina).

The xenoliths contain olivine, orthopyroxene, clinopyroxene and spinel and are mainly harzburgites with subordinated lherzolites, all equilibrated in the spinel-facies. All xenoliths are characterized by the occurrence of basaltic veins. Phlogopite was detected in two mantle peridotites at the contact with orthopyroxene and basaltic veins but too small to be analyzed. Major elements were analyzed at the Universidade de Brasilia by electron microprobe. We performed LA-ICP-MS trace elements analysis on clinopyroxene in 30 μm-thick thin sections using a 193 nm ArF Excimer Laser GeoLas coupled with QQQ-ICP-MS Agilent Series 8900 at the laboratories of the CNR of Pavia.

The major element composition of olivine (Mg# 0.91), orthopyroxene (Mg# 0.92), clinopyroxene (Mg# 0.94) and phlogopite (Mg# 0.92) is very homogeneous. On the contrary, spinel Mg# and Cr# vary from 0.69 to 0.74 and from 0.42 to 0.53, respectively.

Based on the clinopyroxene REE patterns, we recognize three significant groups: I) clinopyroxenes with enriched patterns highly fractionated in LREE compared to the HREE (two harzburgites) II) clinopyroxenes characterized by flat LREE and weakly enriched HREE (four xenoliths) and, III) clinopyroxenes with depleted patterns and slight enrichment in LREE (four peridotites). The patterns of groups II and III, from Eu to Lu, approach the model curves for clinopyroxene in equilibrium with 15-20% of partial melting of a primitive mantle source, pointing to a sub-chondritic, ultra-depleted composition of the SCLM (ΣREE of 2.57 ppm for group II and 1.91 ppm for group III). The degree of melting F based on the spinel composition varies from 15% to 20%, in agreement with the REE data. Conversely, clinopyroxenes from group I show an enriched nature compatible with melt/rock reaction processes related to the infiltration of the host, possibly alkaline, basalt. Geothermometric calculations based on two pyroxene equilibria suggest that Los Gemelos xenoliths have re-equilibrated at the average T of 881±47°C. The equilibrium pressures based on the clinopyroxene geotermobarometer provide an average P of 24±1.09 kbar.

Xenoliths from Los Gemelos are unique in Patagonia: similar depletion degrees were only found in Paso de Indios xenoliths, which, however, show a higher degree of refertilization.

# Large Igneous Provinces and alkaline magmatism: a review of Early Cretaceous ultramafic-alkaline-carbonatite magmatism intruded in the Shillong Plateau-Mikir Hills massif, NE India

Guarino V.*[1], Srivastava R.K.[2] & Melluso L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Department of Geology, Centre of Advanced Study, Banaras Hindu University, Varanasi (India).

*Corresponding author e-mail:* vincenza.guarino@unina.it

*Keywords:* carbonatites, alkaline rocks, Shillong Plateau-Mikir Hills.

Large Igneous Provinces (LIPs) related to Gondwana dispersal are commonly associated with alkaline (and alkaline-carbonatite) magmatism. The isotopic composition of alkaline (and alkaline/carbonatite) intrusions are very useful to constrain mantle composition in the area as alkaline magmas less prone to crustal contamination during the ascent through the crust than generally evolved, hotter, and incompatible element-poor tholeiitic flood basalts. In many cases, for significant periods of time, alkaline magmas can be ponded in crustal reservoirs and therefore they could be susceptible to interaction with continental crust, as often seen in the isotopic composition of slowly cooled intrusive/cumulate rocks. The Indian Shield comprises a number of ultramafic/mafic and alkaline igneous intrusions often associated with carbonatite intrusions; a best example is the Shillong Plateau-Mikir Hills uplifted region, where six Early Cretaceous intrusions (Sung Valley, Jasra, Swangkre-Rongjeng, Mawpyut, Samchampi-Samteran and Barpung) are found. These intrusions emplaced ca. 115-102 Ma ago are significantly younger than the tholeiitic flood basalts erupted in Rajmahal-Sylhet province (ca. 118-115 Ma). They are characterized by intrusive lithologies (dunites, clinopyroxenites, melilitolites) to mafic (ijolites, gabbros *s.l.*, shonkinites) to felsic (syenites, nepheline syenites) and carbonatites (mostly calcite-rich varieties), while volcanic-subvolcanic facies (lamprophyres, phonolites) are less abundant.

By combining mineral chemistry, bulk-rock geochemical and Sr-Nd isotopic composition several different processes acted in the petrogenesis of these intrusions have been recognized: (i) a carbonate-bearing lithospheric mantle have produced different melts, (ii) the high variability in the initial Sr-Nd isotopes of silicate rocks (*s.l.*) and their geochemical features suggest the presence of different parental magmas (alkali basalts, basanites, nephelinites, melilitites) associated with crustal contamination, (iii) the initial Sr-Nd isotopes of Sung Valley and Samchampi-Samteran carbonatites are similar to those of the Rajmahal Group I basalts, suggesting a similar mantle source placed at the base of lithospheric mantle in areas far from the influence of perturbed (hotter than normal) geothermal gradients, and (iv) the presence of economic minerals and soils (REE, P, Ti, Ba, Th, U, Nb, Ta) in most of these six intrusions will be useful for their expanding applications in various strategic and high green technological fields.

# Boron isotope analysis in silicate and carbonate matrix

Lugli F.[1-2], Giovanardi T.*[2], Di Giuseppe D.[2], Gualtieri A.F.[2] & Cipriani A.[2]

[1] Dipartimento di Beni Culturali, Università di Bologna. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

*Corresponding author e-mail:* tommaso.giovanardi@gmail.com

*Keywords:* boron isotopes, Neptune, LA-MC-ICP-MS.

Boron is highly soluble in aqueous fluids and highly incompatible during magmatism and due to the large mass difference between its two isotopes, the B isotope composition is useful to trace the fate of deep fluids and subducted materials in convergent margins. In the low temperature world, it is a powerful tracer for $CO_2$ change over geological time because the distribution of its isotopes in seawater is a function of pH.

Here, we present the method and the first in-situ boron isotope analyses performed at the laboratories of the Centro Interdipartimentale Grandi Strumenti (CIGS) of the Università di Modena e Reggio Emilia within the framework of the PRIN 20178LPCPW project.

Analyses were performed using a double focusing MC-ICPMS with a forward Nier-Johnson geometry (Thermo Fisher Scientific, Neptune™), coupled to a 213 nm Nd:YAG laser ablation system (New Wave Research™). We investigated both silicate and carbonate matrix samples.

For silicate materials, the instrument was tuned using NIST-612 reference material which was also analysed during the analytical sessions to check accuracy and precision and used later for the $\delta^{11}B$ calculation. For carbonate materials, reference sample JCt-1 was used for tuning and control.

Data reduction was performed with an *in-house* Excel spreadsheet. $^{11}B/^{10}B$ ratios were converted in delta notation, reported to NIST-951 by using NIST-612 ($\delta^{11}B$ = -051‰) or JCt-1 ($\delta^{11}B$ = 16.30‰) after bracketing.

To validate the method, three international reference materials (NIST-610, NIST-614 and JCp-1) were analysed as unknown to test the presence of instrumental bias on different matrices and the effect of the B mass fraction on the final ratio. In addition, an obsidian from Lipari (similar to sample B6 in Tonarini et al., 2007) was analysed. Finally, the B isotope ratio was determined on two unknown samples, namely a tourmaline from the Elba island (elbaite) and an obsidian from Lago di Venere (Pantelleria).

Reference materials measured as unknown provided values consistent with the literature. Reference material NIST-614 showed instead inconsistent values possibly due to its low B mass fraction (~3 µg/g), yielding low signals (0.003-0.004 V for $^{11}B$). Unknown tourmaline provided isotope values akin to the Elba tourmaline reported by Tonarini et al. (2007), while the obsidian from Lago di Venere is slightly lower compared to the Lipari sample. Noticeably, we checked the B content of the sample-embedding epoxydic resins to check possible exogenous contaminations. One resin sample produced high B signals (0.02-0.05 V for $^{11}B$) with a $\delta^{11}B$ = -8/-13 ‰, pointing out the need of carefully checking the laboratory material for B isotope analysis.

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# Origin of Giant Plagioclase Basaltic flows from the Deccan Traps, India

Marzoli A.*[1], Renne P.R.[2-3], Andreasen R.[4], Spiess R.[5], Chiaradia M.[6], Ruth D.C.[7], Pande K.[8], Tholt A.J. [2-3] & Costa F.[9]

[1] Dipartimento Territorio e Sistemi Agro-Forestali, Università di Padova. [2] Berkeley Geochronology Center, Berkeley, CA (USA). [3] Department of Earth and Planetary Science, University of California, Berkeley, CA (USA). [4] Geosciences Department, Aarhus University (Denmark). [5] Dipartimento di Geoscienze, Università di Padova. [6] Departement des Sciences de la Terre, Université de Gèneve (Switzerland). [7] U.S. Geological Survey Volcano Science Center, Menlo Park, CA (USA). [8] Department of Earth Science, Indian Institute of Technology, Mumbai (India). [9] Institut de Physique du Globe de Paris, Universite de Paris (France).

*Corresponding author e-mail:* andrea.marzoli@unipd.it

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Giant Plagioclase Basalt (GPB) flows from the Deccan large igneous province contain cm-sized plagioclase crystals and crystals clots. These are either not zoned (Anorthite, $An_{65-60}$) or show relatively high-An cores (ca. $An_{75}$) and low-An rims ($An_{60}$). EBSD analysis indicates that some plagioclase clots were deformed at high-temperature, possibly during arrival of magma from the deeper magma plumbing system. Minor and trace element compositions of plagioclase crystals are generally correlative to those of their host-rocks, but Fe contents strongly increase at the outermost rims. On the contrary, some plagioclase cores yield Sr isotopic compositions different from those of the crystal rims and of the surrounding matrix in several samples. Trace element and isotopic compositions suggest maximum residence times of decades to centuries. Fe-Mg minerals are rare and include olivine (forsterite 75-60), augite (Mg# 80-50) and occasionally pigeonite. Augite-whole rock data generally yield shallow crust crystallization pressures.These mineralogical, geochemical, and textural characteristics of the analyzed GPBs suggest that they were derived from a crystalline mush, which was crystallized and stored for variably long periods in the shallow magmatic plumbing system and was repeatedly flushed and partially deformed by magma rising from deeper levels. Finally, shortly before eruption the buoyant plagioclase-rich shallow crystalline mush was entrained in Fe-rich, dense magmas possibly mobilized by increased $CO_2$ concentrations heralding the arrival of new mantle-derived magmas. Field evidence clearly shows that the GPBs form irregular bodies of variable dimension (often > 10's of m) within less phyric lavas.

# Unveiling plumbing system dynamics and magmatic processes at the Kolumbo submarine volcano prior to the 1650 C.E. explosive eruption

Mastroianni F.*[1-2], Fantozzi I.[1], Petrone C.M.[3], Vougioukalakis G.E.[4], Braschi E.[5], Bragagni A.[1] & Francalanci L.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Natural History Museum, London (UK). [4] Hellenic Survey of Geology and Mineral Exploration, Athens (Greece). [5] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* filippo.mastroianni@unifi.it

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The Kolumbo submarine volcano, located about 7 km NE of Santorini, is the largest and most active volcanic cone present within the transtensional Anydros basin. Kolumbo explosively erupted in 1650 C.E. causing the death of 70 people on the nearby island of Santorini. Based on historical accounts and recent studies (Cantner et al., 2014), the eruption started with submarine activity, eventually became subaerial with the generation of plumes, and the most violent Plinian activity dispersed volcanic ash as far as Turkey (distant > 160 km).

Volcanic products have been collected by ROVs and divers during explorative cruises, showing a high heterogeneity of both juvenile products from the 1650 C.E. eruption and fresh lithic clasts. We subdivided the samples in groups that are well reflected by their chemical composition. The lithics can be distinguished in: i) Crystal-rich Andesites; ii) Andesites; iii) Rhyodacites; whereas the juvenile samples are represented by mafic enclaves and host variably vesiculated, rhyolitic pumices. Based on their structure, the latter were subdivided in: White pumices; Light Grey pumices; Banded pumices; Convoluted pumices; Dense juveniles. Besides whole-rock geochemical and Sr-Nd-Pb isotope analyses, we conducted detailed petrographic, mineral chemistry and micro-analytical isotopic investigations on selected samples. In particular, detailed micro-Sr-Nd isotope analyses were performed on matrix glasses and on single crystals, micro-drilled from thin sections. Among the juvenile samples, rhyolites are characterized by the presence of plagioclase, biotite and orthopyroxene, whereas enclaves have plagioclase, amphibole and clinopyroxene. Plagioclase chemistry shows distinct crystal populations in juvenile samples: a Low-An group ($An_{15-25}$) for rhyolitic samples and a High-An group for the enclaves ($An_{80-95}$). Some rhyolitic samples show also an intermediate $An_{25-40}$ population, together with more orthopyroxene and higher-Mg# biotite than samples with only $An_{15-25}$ plagioclases. The latter are instead richer in enclaves. These characteristics suggest the presence of two main rhyolitic reservoirs undergoing different interaction processes with mafic magmas. One of these reservoirs was interested by an earlier mixing mechanism with a rhyodacitic melt, whereas processes of mingling, micro-mingling and enclave disaggregation successively occurred in the other reservoir. Furthermore, micro-Sr-Nd isotope data on mineral phases suggest the presence of a complex and dynamic mafic feeding system, differentiating and producing consecutive mafic inputs reaching the rhyolitic reservoirs prior to the 1650 C.E. eruption.

Cantner K., Carey S., Nomikou P. (2014) - Integrated volcanologic and petrologic analysis of the 1650AD eruption of Kolumbo submarine volcano, Greece. J. Volcanol. Geotherm. Res., 269, 28-43.

# A Poorly Depleted Mantle Source under Southern Payenia as revealed by the Mantle Xenoliths from Huanul Volcano (Central-West Argentina)

Mazzucchelli M.*[1], Bertotto G.W.[2], Conceiçao R.V.[3], Zanetti A.[4], Schilling M.E.[5], Bernardi M.I.[2], Ponce A.D.[2], Jalowitzki T.[6], Gervasoni F.[7] & Cipriani A.[1-8]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] INCITAP, CONICET, Universidad Nacional de La Pampa, Santa Rosa (Argentina). [3] Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre (Brazil). [4] Istituto di Geoscienze e Georisorse, CNR, Pavia. [5] Instituto de Ciencias de la Tierra, Universidad Austral de Chile, Valdivia (Chile). [6] Instituto de Geociências, Universidade de Brasília (Brazil). [7] Faculdade de Ciências e Tecnologia, Universidade Federal de Goiás, Goiânia (Brazil). [8] Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY (USA).

*Corresponding author e-mail:* maurizio.mazzucchelli@unimore.it

*Keywords:* Huanul, Patagonia, mantle xenoliths.

Mantle xenoliths were collected from lava flows erupted during the Pleistocene of the Huanul shield volcano. Huanul is located in the southern part of the Payenia Volcanic Province, which is among the largest Neogene-Quaternary volcanic provinces of South America. Its southern part is occupied by the Río Colorado Volcanic Field constituted by pahoehoe lava flows in a northwest–southeast direction. Here, the most important eruptive center is Huanul, a shield volcano built from basaltic lava flows and pyroclastic aggregates. Its crater is 4 km in diameter and rises ca. 20 m from the surrounding. The basaltic flows overlay the sedimentary rocks of the Neuquén Basin (Jurassic to Paleogene) and the Quaternary sediments of the Colorado river. Eight lava units are currently recognized in the field, and the oldest one, named El Corcovo lava flow, covers a distance of ca. 70 km for an area of ca. 415 $km^2$. El Corcovo consists of alkaline basalts with a K-Ar age of 0.84±0.05 Ma.

The volcanism of the Payenia Volcanic Province has been ascribed as the northernmost expression of the back-arc volcanism of the Andean Southern Volcanic Zone. We present the first petrographic and mineral chemistry study of these mantle xenoliths (funded by PRIN 20178LPCPW) with the aim of reconstructing directly the mantle source of this region. Xenoliths are commonly small (< 5 cm in radius) but scarcely crossed by basaltic veins. All xenoliths have a fertile lherzolitic modal composition and are equilibrated in the spinel-facies. Most of them exhibit an almost primitive-mantle geochemical affinity, characterized by slightly depleted clinopyroxene REE patterns reproducible by partial melting degrees between 0 and 4% of a PM source. Geothermobarometric P-T estimates of clinopyroxene-orthopyroxene couples form a linear trend between 10 and 24 kbar with constant increase of T from 814 to 1170°C along a 50-60 $mW/m^2$ geotherm. Evidences of interaction with the host basalts occur as spongy textures in clinopyroxene and reacted spinel, which tend to became more restitic in composition and show chromatographic or complete overprinting of the trace element compositions. Detailed investigation of these microstructures was made using a JEOL JXA-8200 electron microprobe housed at the Università di Milano which permitted the identification and the analyses of micrometric inclusions.The occurrence of plagioclase and calculated P-T values constrain this melt/rock reaction process between 6 and 14 kbar, during magma ascent, and fit the mantle adiabat model. Calculated melts in equilibrium with the primary clinopyroxenes do not fit the composition of the host basalt and, together with the geothermobarometric estimations, point to an asthenospheric mantle source for the magmatism in southern Payenia. The PM geochemical affinity of the xenoliths of Huanul is an extremely rare finding in the South America lithospheric mantle, which is commonly extensively refertilized by subduction-derived melts.

# The geochemistry of recent Nyamulagira and Nyiragongo potassic lavas, Virunga Volcanic Province, and implications on the enrichment processes in the mantle lithosphere of the Tanzania-Congo craton

Minissale S.*[1], Casalini M.[2], Cucciniello C.[1], Balagizi C.[3], Tedesco D.[4-5], Boudoire G.[6-7], Morra V.[1] & Melluso L.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Goma Volcano Observatory, Goma (Democratic Republic of the Congo). [4] Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Università della Campania «Luigi Vanvitelli», Caserta. [5] INGV, Osservatorio Vesuviano, Napoli. [6] Laboratoire Magmas et Volcans, UCA-CNRS-IRD-OPGC, Aubière (France). [7] INGV, Palermo.

*Corresponding author e-mail:* silvia.minissale@unina.it

*Keywords:* basanites, olivine melilitites, potassic rocks.

We here investigate the geochemical and isotopic variability of primitive and evolved magmas of the Nyamulagira and Nyiragongo volcanic complexes (Virunga Volcanic Province, Western branch of the East African Rift), including the very last products of the Nyiragongo's May 22, 2021 eruptive event and the Nyamulagira lava lake in February, 2020 (Burgi et al., 2018; Minissale et al., 2019). The different degree of silica undersaturation (i.e., potassic basanites/tephrites at Nyamulagira vs. potassic olivine melilitites/melilite nephelinites at Nyiragongo) and distinct incompatible element enrichment between the two volcanoes (e.g., Zr/Nb = 3.3-4 at Nyamulagira vs. Zr/Nb = 1.2-2.1 at Nyiragongo) are remarkable. Concentration of volatile elements (especially F and S) is also markedly different at the same level of magma evolution for the products of the two volcanic complexes, suggesting distinct volatile concentration of the primary magmas. The Sr-Nd-Pb isotopic range (e.g., $^{87}Sr/^{86}Sr$ = 0.7052-0.7059 at Nyamulagira vs. $^{87}Sr/^{86}Sr$ = 0.7045-0.7047 at Nyiragongo; $^{206}Pb/^{204}Pb$ = 19.19-19.31 at Nyamulagira vs. $^{206}Pb/^{204}Pb$ = 19.41-19.75 at Nyiragongo) overlaps with previous analyses obtained in the VVP, and is discussed with respect to other potassic/ultrapotassic rocks from different tectonic settings. The Ba/Nb and La/Nb ratios and Cs concentration of Nyamulagira and Nyiragongo indicate a negligible role for subducted sediments as a mantle-added geochemical component, as instead took place in the source of other primitive potassic/ ultrapotassic rocks. The genesis of the primitive lavas of Nyamulagira and Nyiragongo is related to partial melting of a heterogeneous lithospheric peridotite hosting phlogopite and variable amounts of carbonates (Foley et al., 2009; Rosenthal et al., 2009), which was moderately to highly enriched in incompatible elements, particularly Nb, Ta, LREE, (K), Ba and Sr.

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Foley S.F., Yaxley G.M., Rosenthal A., Buhre S., Kiseeva E.S., Rapp R.P. & Jacob D.E. (2009) - The composition of near-solidus melts of peridotite in the presence of CO2 and H2O between 40 and 60 kbar. Lithos, 112S, 274-283.

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# Evidence of mafic magma replenishment in the feeding systems of the Middle Triassic volcanoes in the Southern Alps

Nardini N.*[1], Casetta F.[2], Ntaflos T.[2], Zanetti A.[3] & Coltorti M.[1-4]

[1] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [2] Department of Lithospheric Research, University of Vienna (Austria). [3] Istituto di Geoscienze e Georisorse, CNR, Pavia. [4] INGV, Palermo.

*Corresponding author e-mail:* nrdncl@unife.it

*Keywords:* crystal zoning, mixing, dolomites.

Crystal zoning provides an efficient tool for studying the geometry and dynamics of the feeding systems of active and ancient volcanoes. Detailed textural and compositional investigations among Middle Triassic volcanics in different localities of the Dolomites (Southern Alps) such as Predazzo, Mt. Monzoni, Cima Pape, and Sciliar, led to the identification of compositional zoning in the clinopyroxene population. The recurrent zoning pattern consists of one or more high-Mg# and $Cr_2O_3$-rich diopsidic bands (Mg# 79-91; $Cr_2O_3$ up to 1.2 wt.%) growing in between augitic cores and rims with lower Mg# and Cr contents (Mg# 67-77; $Cr_2O_3$ < 0.1 wt.%). The diopsidic composition is also documented in some cores that appear resorbed and coated with augitic rims. Chondrite-normalized incompatible trace element patterns of the low-Mg# portions show Nb, Ta, Sr, Zr, and Ti negative and Th-U positive anomalies. The high-Mg# domains have similar patterns but lower trace element abundances. REE patterns in both high-Mg# and low-Mg# domains have a convex-upward shape and $La/Yb_N$ from 1.3 to 2.1. At Cima Pape, thermobarometric and hygrometric models showed that the diopsidic bands formed in equilibrium with a primitive, hot, and $H_2O$-poor basaltic melt (Mg# 65-70; T = 1130-1150°C; $H_2O$ = 2.1-2.6 wt.%), while the augitic cores and rims formed in a cold, $H_2O$-rich trachyandesitic melt (Mg# 43-45; T = 1035-1075°C; $H_2O$ = 2.6-3.8 wt.%). These results are consistent with the occurrence of one or multiple mafic replenishment by primitive, $H_2O$-poor basaltic magmas into the shallower portions (7-14 km) of the Cima Pape plumbing system where a mush-like system of trachyandesitic composition was ponding (Nardini et al., 2022). The textural and geochemical equivalence with the clinopyroxenes hosted in volcanic products belonging to different magmatic provinces through the Dolomites suggests that periodic replenishment of the feeding system before the eruption was a common process among the main eruptive centers of the Mid-Triassic magmatism. The results at Cima Pape allowed us to treat these ancient volcanoes with the same approach used in the active ones representing a new frontier for investigating the dynamics of the Mid-Triassic magmatism in the Southern Alps. On the other hand, the Mid-Triassic intrusive counterpart can help in highlighting what is currently occurring underneath the active volcanoes. Hence, understanding the magmatic processes beneath these systems is a great opportunity for discovering the nature of the Middle Triassic magmatic event in the Southern Alps and for testing the methods currently adopted for investigating the plumbing system dynamics beneath active volcanoes.

Nardini N., Casetta F., Ickert R.B., Mark D.F., Ntaflos T., Zanetti A. & Coltorti M. (2022) - From the Middle Triassic Cima Pape complex (Dolomites; Southern Alps) to the feeding systems beneath active volcanoes: Clues from clinopyroxene textural and compositional zoning. J. Volcanol. Geoth. Res., 422, 107459.

# Changes in geochemical signatures of magmatism from the end of amalgamation to the onset of breakup of Pangea recorded by Permian-Triassic felsic dykes from central Ivrea-Verbano Zone, Southern Alps

Ogunyele A.C.*[1-2], Dellarole E.[3], Bonazzi M.[1-2], Langone A.[2] & De Carlis A.[4]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] Geoparco Sesia-Val Grande, Varallo (VC). [4] Earth Sciences Department, Khalifa University of Science and Technology, Abu Dhabi (United Arab Emirates)

*Corresponding author e-mail:* abimbola.ogunyele01@universitadipavia.it

*Keywords:* felsic dyke swarms, Gondwana-Laurasia boundary, Permian-Triassic magmatism.

Felsic dyke swarms intruding granulite-facies metasedimentary rocks of the lower crustal section of the Ivrea-Verbano Zone (Southern Alps) were characterized to elucidate the tectono-magmatic evolution of the Gondwana-Laurasia boundary from the end of amalgamation to the onset of breakup of Pangea. These felsic dykes are spatially associated and two varieties, outcropping parallel to sub-parallel to each other, can be recognized. The first variety shows irregular contact with apophysis entering the host. It is constituted mainly by andesine, K-feldspar, apatite, biotite and quartz. The second variety is characterized by sharp and straight contact with the host, containing essentially albite, K-feldspar, corundum and biotite. Biotites from the corundum-bearing dykes show high contents of $Al_2O_3$ (17.2-20.5 wt.%), $FeO_T$ (~28 wt.%) and low Mg# (0.16-0.26), straddling the biotite to siderophyllite fields. Biotites from the corundum-free dykes show relatively low contents of $Al_2O_3$ (~15 wt.%), $FeO_T$ (~15 wt.%) and high Mg# (0.57-0.61). The compositions of the biotites from the corundum-bearing and corundum-free felsic dykes resemble those segregated from peraluminous to alkaline and calc-alkaline melts, respectively. In terms of trace elements, the biotites from the corundum-bearing dykes show significant enrichment in Nb (~2462 ppm) and Ta (~197 ppm), while biotites from the corundum-free dykes is relatively depleted in Nb (~35 ppm) and Ta (~0.9 ppm). The occurrence of columbite-euxinite in the corundum-bearing dykes is further evidence of the enrichment of Nb and other HFSEs in this dyke variety. U-Pb analysis of zircons with oscillatory zoning from the corundum-free dykes points to Lower Permian emplacement age (288.7±3.9 Ma), which corresponds to that of the well-documented, main magmatic pulse of the IVZ, being younger than the granulite-facies metamorphism peak occurred at about 314 Ma. Field relationships and large U/Th of apatite, in addition to zircon data, further suggest that these dykes are segregated from melts containing significant crustal components, as consequence of crustal anatexis or vast assimilation of crustal components in Permian mantle melts. Conversely, the corundum-bearing dykes are Late Triassic in age (223±7 Ma) with large positive εHf(t) values in zircon (av. +13) which points to a derivation from depleted to mildly enriched mantle source (Bonazzi et al., 2020). Their mineralogical assemblages and geochemical signatures of the mineral phases suggest their formation from HFSE-rich peraluminous melts exsolved from volatile-rich mantle-derived alkaline magma in anorogenic extensional-related geodynamic setting.

Bonazzi M., Langone A., Tumiati S., Dellarole E., Mazzucchelli M., Giovanardi T. & Zanetti A. (2020) - Mantle-derived corundum-bearing felsic dykes may survive only within the lower (refractory/inert) crust: Evidence from zircon geochemistry and geochronology (Ivrea-Verbano Zone, Southern Alps, Italy). Geosciences, 10(8), 281.

# Geochemical changes in parental melt sources and metasomatic overprinting of alkali-rich dykes from Ivrea-Verbano Zone, Southern Alps: further evidence from petrography, mineral chemistry and U-Pb zircon geochronology

Ogunyele A.C.*[1-2], Giovanardi T.[3], Bonazzi M.[1-2], Mazzucchelli M.[2-3], De Carlis A.[4], Cipriani A.[3] & Zanetti A.[2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [4] Earth Sciences Department, Khalifa University of Science and Technology, Abu Dhabi (United Arab Emirates).

*Corresponding author e-mail:* zanetti@crystal.unipv.it

*Keywords:* mantle sources, Mesozoic magmatism, Southern Alps.

At the boundary between Europe and Africa, Paleozoic mantle-continental crust sequences are well-exposed in the Ivrea-Verbano Zone (IVZ, Southern Alps). They have been intruded by dyke swarms of varying lithological compositions and age in a post-collisional setting before the breakup of the Pangea supercontinent. Here, we report new data for dyke swarms emplaced into the mantle Finero Phlogopite Peridotite (northern IVZ) and composed of cumulus hydrous peridotite, hornblendite, gabbro, diorite and anorthosite. They range in thickness from a few cm to >1 m, often cutting the mantle foliation at a high angle. Field observations show that these dykes' conduits underwent multistage evolution and melt recharge.

The cumulus hydrous peridotite, composed of olivine and sulphides with minor interstitial amphibole and phlogopite, occurs as layers and pods associated with hornblendite. The gabbroic and dioritic dykes are composite, showing variable proportions of melanocratic and leucocratic layers. Anorthositic dykes are composed mainly of albite-oligoclase. Amphibole, phlogopite and apatite occur in all the dykes.

The dyke swarms can be grouped into two series. The first series consists of gabbro and hornblendite containing Al-rich pargasite ($Al_2O_3$ up to 16.3 wt.%) and phlogopite, associated with apatite, calcite, sulphides and sometimes sapphirine, spinel, plagioclase (An 69.6-86.5) and pyroxenes. The amphiboles from these dykes show (i) large LILE and LREE contents, and (ii) negative Nb, Ta, Zr and Hf (HFSEs) anomaly as in orogenic magmatism, supporting the occurrence of recycled continental crust components in the parent melts.

The second series comprises diorite, anorthosite and hornblendite dykes, and veinlets in the cumulus peridotite. They mainly consist of Al-poor pargasite ($Al_2O_3$ < 13 wt.%) + phlogopite + apatite + calcite + sulphides ± albite-oligoclase (An 6.4-13.3) ± zircon ± monazite ± Nb-rich oxides ± titanite ± ilmenite ± allanite. Amphiboles are still LILE-and-LREE-enriched, but show extreme Nb, Ta, Zr and Hf enrichments.

Calculated parent liquids using the amphibole-melt partition coefficient show an affinity with EM-II alkaline melts for the HFSE-depleted series. In contrast, those of the HFSE-enriched series have a strongly "anorogenic" alkaline affinity.

A particular dioritic dyke, however, shows amphiboles with both "orogenic" and "anorogenic" affinities with geochemical gradients in the HFSEs contents from the centre to the rim of the dyke. This dyke provides significant evidence for multiple pulses of melt injection, metasomatic overprinting of HFSE-depleted amphiboles by HFSE-enriched melt(s), and transition from orogenic-like to intraplate magmatism within a single conduit. Few zircon grains analyzed from this dyke yielded $^{206}Pb/^{238}U$ mean age of 200.7±6.5 Ma which is closely related to the concordant ages from the anorthositic (198.5±9 Ma) and Nb-rich dioritic (221±9 Ma to 192±8 Ma) dykes.

# Geochemistry and origin of albite-dominated anorthositic dykes from Ivrea–Verbano Zone, Southern Alps: evidence for ultra-alkaline magmatism at the Gondwana-Laurasia boundary during Late Triassic-Early Jurassic times

Ogunyele A.C.*[1-2] & Bonazzi M.[1-2]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia.

*Corresponding author e-mail:* abimbola.ogunyele01@universitadipavia.it

*Keywords:* ultra-alkaline magmatism, anorthositic dykes

The geochemical and geodynamic evolution of the Gondwana-Laurasia boundary in the area now corresponding to the Southern Alps during the Late Paleozoic to Early Mesozoic is still intensely debated. This issue is complicated by the widespread alteration of outcrops and the complex paleogeography of the area. To provide further constraints to better understand the tectono-magmatic framework of this area prior to the breakup of the Pangea supercontinent, we report the petrology, mineral chemistry and geochronology of some anorthositic dykes intruding the mantle peridotite of the northern Ivrea-Verbano Zone, Southern Alps.

The studied anorthositic dykes are composed almost entirely of albite-oligoclase (An: 8-13%; > 95 vol.%) with minor amounts of pargasite, phlogopite and apatite. Accessories in the dykes include zircon, allanite, titanite and magnetite. In literature, albite-dominated anorthosites are also referred to as albitite and are usually associated to ultra-alkaline (-carbonatite) magmatism and to strategic Ta-Nb deposits. The pargasite from the studied dykes are K-rich with Mg# values between 68 and 74%, and show strong enrichments in Nb, Ta, Zr and Hf, with large LILE and LREE contents. Phlogopite also shows strong enrichments in the HFSEs. Plagioclase is enriched in LREE with a positive Eu anomaly but extremely depleted in M-HREE. Apatite is enriched in Th, U and REE, with Th/U (1.4-2) and Ce/Pb (230-340) ratios typical of apatites derived from mantle melts.

Zircons from these dykes are anhedral, show homogeneous to relic oscillatory and sector internal structures and reflect intense deformation owing to volatile overpressure in the dyke's conduits. U-Pb dating provided concordant ages of 198.5±9 Ma pointing to Early Jurassic-Late Triassic emplacement ages. The geochemical signatures of the major mineral phases in the dykes point to "anorogenic" ultra-alkaline affinity of the melt(s) from which these dykes segregated. Our data suggest that these dykes were probably segregated from evolved, volatile-rich silicic melts exsolved from mantle-derived alkaline magma(s) and "violently" emplaced in conduits in a trans-extensional setting at the boundary between Gondwana and Laurasia shortly before the breakup of the Pangea supercontinent. The emplacement of these alkali-rich anorthositic dykes probably represents a late stage of alkaline magmatism at the Gondwana-Laurasia boundary which can be correlated with the 221±9 Ma alkaline magmatism which produced some composite HFSE-rich dioritic dykes also intruding the mantle peridotite in the northern Ivrea-Verbano Zone. The genetic relationships of the studied anorthositic dyke swarm with concomitant Na-carbonatites and corundum-rich felsic dykes documented in the central IVZ will also be discussed.

# Sanidine megacrysts from *Monte Amiata*: elemental, Sr-isotope and melt inclusions studies

Paternostro S.*[1], Valeriani L.[1-2], Casalini M.[1], Orlando A.[3], Braschi E.[3], Esposito R.[4], Petrelli M.[5-6], Avanzinelli R.[1-3] & Conticelli S.[1-7]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Istituto di Geoscienze e Georisorse, CNR, Firenze. [4] Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca. [5] Dipartimento di Fisica e Geologia, Università di Perugia. [6] Istituto Nazionale di Fisica Nucleare, Perugia. [7] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM).

*Corresponding author e-mail:* simone.paternostro@unifi.it

*Keywords:* megacryst, isotope chemistry, Central Italy magmatism.

The Pleistocene *Monte Amiata* volcano is part of the Radicofani-Monte Amiata volcanic system, an igneous complex responsible of a wide domed area in which the two volcanic centres cluster the central portions of its main axis.

The *Monte Amiata* and *Radicofani* volcanoes are characterised by different eruption styles and rocks. The *Radicofani* centre outpoured few mantle-derived shoshonitic lava flows at about 1 Ma, whilst the *Monte Amiata* outpoured differentiated trachy-dacitic to trachytic lavas and domes at about 300 ka. The differentiated magmas of *Monte Amiata* derived by the fractional crystallisation and crustal assimilation from a Tuscany-type mantle-derived silica-saturated magma, similar in composition to the Radicofani shoshonite. Subsequent complex interaction between silica-saturated melts and newly arrived leucite-bearing magmas provided a further element of complexity. The occurrence in the *Monte Amiata* rocks of rounded magmatic enclaves testifies this complexity. The arrival of Roman-type mafic magma within the differentiated magmatic reservoir lead to mingling and mixing with the viscous and extremely differentiated trachytic resident magma to form magma batches with intermediate compositions and give the thermal-energy to induce convective motions within the magma chamber. Large K-feldspar megacrysts do occur in both host rocks and rounded enclaves of *Monte Amiata* volcano, suggesting that they are solid witnesses of this interaction processes. Alternatively, they can are also hypothesised as xenocrysts derived by ancient crustal derived granitoids, introducing a fourth element of igneous complexity. To tackle this issue we report a detailed mineralogical, petrographic, micro-thermometric, chemical and isotopic study on K-feldspar megacrysts and their melt inclusion with the aim to investigate their nature.

Major and trace element compositions of K-feldspar megacrysts show evidence for interaction between magmas found in correspondence with the oscillatory zoning and resorbed bands of the crystal. Isotope chemistry investigation shows the presence of a higher Sr-radiogenic megacryst core (0.71338) compared to the most-differentiated rock outcropped (0.71300). Microthermometric approach show a glass entrapment temperature of about 1050°C and a $CO_2$-rich vapour phase entrapped at ≈ 1-2 kbars.

Our results support the presence of a high Sr-radiogenic magma not erupted to the surface, located at the top of the magmatic chamber and in a melt-impregnated regime condition (< 20% melt), which simulates the presence of a plutonic partially-molten intrusive body. The extent of the mixing process to the outcropped trachytic differentiated body is justified by the presence of melt inclusions with $CO_2$-rich vapour phase in sanidine pheno- and mega-crysts.

# Heterogeneous nucleation of crystals in synthetic trachybasalts

Peres S.*[1], Griffiths A.T.[1], Colle F.[2], Iannini Lelarge S.[2], Masotta M.[2], Pontesilli A.[3] & Mancini L.[4]

[1] Department of Lithospheric Research, University of Vienna (Austria). [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] INGV, Roma. [4] Elettra-Sincrotrone Trieste.

*Corresponding author e-mail:* stefano.peres@univie.ac.at

*Keywords:* heterogeneous nucleation, SR-μCT, CORs.

In systems that are weakly to moderately supersaturated with respect to a mineral, heterogeneous crystal nucleation on a pre-existing surface is energetically more favourable than homogeneous nucleation from a melt (Lofgren, 1983). For this reason, heterogeneous nucleation is considered one of the most important clustering mechanisms occurring in both natural magmas and experimental analogues (Hammer et al., 2010). However, in volcanic samples with a complex pressure-temperature crystallization history, robust criteria for proving heterogeneous nucleation are lacking.

In this study, we present microstructural observations supporting heterogeneous nucleation of clinopyroxene (cpx) and oxides (ox) in time-series dynamic crystallization experiments performed at 4 kbar using a piston cylinder apparatus on dry (nominally 0 wt.% $H_2O$) and wet (2 wt.% $H_2O$ added) trachybasaltic melts. After 30 minutes of superheating at 1300°C, the samples were cooled at a rate of 80°C/min to the final resting temperatures of 1050, 1100 and 1150°C, corresponding to degrees of undercooling (ΔT expressed as $T_{liquidus} - T_{experiment}$) ranging from 30° to 160°. The duration of the experiments at the resting temperature varied from 5 minutes to 22 hours in the different experiments.

High resolution synchrotron X-ray microtomography (SR-μCT), electron backscatter diffraction (EBSD) maps, and microprobe (EMPA) chemical analysis have been used to extract the 3D distribution and the crystallographic orientation relationships (CORs) between touching crystals, and the compositional zoning of crystals and melt. All the experimental samples contain cpx (5 to 55 vol.%), and ox (1 to 5 vol.%). Cpx and ox morphology varies respectively from skeletal to dendritic, and from skeletal to anhedral with increasing ΔT.

Microstructural observations supporting the hypothesis of heterogeneous nucleation of ox on top of cpx crystals and vice versa are the following: a) a high fraction of ox touching cpx crystals (> 0.95); b) radial arrangements of cpx crystals around single ox crystals (rosette structures); c) ox crystals decorate the tips or the edges of cpx crystals, with flat to curved cpx-ox interfaces; d) adjacent oxides on the same dendritic branch are regularly spaced, and e) the fraction of total cpx-ox boundary length following a COR exceeds 70%. Combining multiple methods, including 3D and crystallographic information, is essential to identify heterogeneous nucleation with confidence.

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# The Pleiades volcanic complex, Antarctica: a plumbing system modulated by ice cover fluctuations

Rocchi I.*[1], Tomassini A.[1], Masotta M.[1], Petrelli M.[2] & Rocchi S.[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* irene.rocchi@dst.unipi.it

*Keywords:* The Pleiades, complete differentiation trend, ice cover fluctuations.

The timing of volcanic eruptions in glaciated terrains is potentially modulated by climate-controlled variations in the glacio-lithostatic load, that modify the pressure conditions acting on underlying volcanic plumbing systems and, in turn, the residence times in the crust during glacial periods. In northern Victoria Land (Antarctica), volcanism occurred in both attenuated and thick cratonic lithosphere. Among the inland group built on thick crust, the Quaternary Pleiades volcanic complex (PVC) is made up of some 20 monogenetic, partly overlapping scoria and spatter cones, that erupted over the last 900 ka. The erupted products, cropping out from the ice close to the head of Mariner Glacier, vary in composition from hawaiite to trachyte, defining a complete mildly Na-alkaline differentiation trend. Mafic samples have OIB within-plate affinity and variable radiogenic isotopic ratios, supporting the hypothesis of open-system evolution with significant crustal assimilation coupled with fractional crystallization. The occurrence of a complete differentiation trend with large assimilation rate is unusual among the alkaline monogenetic volcanic fields.

Samples from PVC, representative of the whole differentiation trend, have been investigated by means of electron microscopy, electron microprobe and laser ablation ICP-MS. The paragenesis of mafic-intermediate rocks includes dominant clinopyroxene and plagioclase and minor olivine, whilst sanidine is the only feldspar in trachytes. Olivine and clinopyroxene commonly show resorption textures with deep embayments and abundant glass inclusions with significantly more evolved composition (phonolitic-trachytic composition) than the bulk rock. Both clinopyroxene and plagioclase phenocrysts show complex textures characterized by coarse to fine sieve texture cores/mantle and compositionally zoned mantle and rims. These observations suggest that the magma firstly experienced a rapid decompression, followed by a prolonged residence time that caused the resorption of early formed mineral phases and consequent crystallization at isobaric conditions. This prolonged residence time led to the formation of the products representing the observed complete differentiation trend and to the development of the complex micro textures of clinopyroxene and plagioclase. Finally, a late supply of magma led to the formation of reverse zoning and of recrystallisation features. Machine-learning-based thermobarometric estimates consistently suggest crystallization of clinopyroxene and plagioclase at a pressure ranging from the crust-mantle interface (early crystallization) to shallow crust (late crystallization in a shallow plumbing system under glacial load). This petrological evidence leads to hypothesize a pre-eruptive mixing process between a freshly injected mafic magma and a magma which resided for a significant time in the crust, probably due to the eruption lag associated to increased ice load.

# Precambrian large igneous province records of the Indian Shield - an overview: constraints from precise dating and geochemistry of distinct mafic magmatic units

Srivastava R.K.*[1], Samal A.K.[1] & Ernst R.E.[2-3]

[1] Department of Geology, Institute of Science, Banaras Hindu University, Varanasi (India). [2] Department of Earth Sciences, Carleton University, Ottawa (Canada). [3] Faculty of Geology and Geography, Tomsk State University (Russia).

*Corresponding author e-mail:* rajeshgeolbhu@bhu.ac.in

*Keywords:* large igneous provinces, Indian Shield, DHABASI.

The Indian Shield is a collage of five major Archean cratons: three of them (i.e., Dharwar, Bastar and Singhbhum) are placed south of a major tectonic feature, viz., the Central Indian Tectonic Zone (CITZ), and the other two (Aravalli and Bundelkhand cratons) are north of the CITZ. All these Archean cratons of the Indian Shield have a spectacular record of large igneous provinces (LIPs) throughout Precambrian (cf. Samal et al., 2019; 2021; Söderlund et al., 2019; Srivastava et al., 2022). Based on field cross-cutting relationship, emplacement trends, precise geochronology and geochemistry of distinct mafic dyke swarms and associated other magmatic bodies, 15 different LIPs (3 Archean and 12 Proterozoic) are identified in the Indian Shield (Samal et al., 2019; 2021). Based on identified LIPs which span an age range of c. 3.35-1.77 Ga, we identify a Precambrian megacraton 'DHABASI', consisting of the Dharwar, Bastar and Singhbhum cratons (Srivastava et al., 2022), which should be considered as a distinct building block for palaeocontinental reconstructions rather than using the individual Dharwar, Bastar and Singhbhum cratons. Geochemical characteristics of the plumbing system of the identified LIPs are used to explore likely mineral systems. Many of these LIPs are identified as key targets for mineralization of Cu-Ni-Co-platinum group elements (PGEs), Fe-Ti-V and Cr; both as oxides and sulfides. REE, U-Th, Nb-Ta, P, and Cu mineralization are also reported to be associated with the ca. 0.80-0.75 Ga alkaline-carbonatite complexes from the southern Indian Shield.

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# Permian post-Variscan mafic dykes of Gallura Region (North Sardinia), a first look

Velicogna M.*[1], Boscaini A.[2], Ogunyele A.C.[3-4], De Min A.[5], Zanetti A.[4], Chiaradia M.[6] & Marzoli A.[1]

[1] Dipartimento di Territorio e sistemi agro-forestali, Università di Padova. [2] Dipartimento di Geoscienze, Università di Padova. [3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [4] Istituto di Geoscienze e Georisorse, CNR, Pavia. [5] Dipartimento di Matematica e Geoscienze, Università di Trieste. [6] Section des Sciences de la Terre, Université de Genève (Switzerland).

*Corresponding author e-mail:* matteoveli87@gmail.com

*Keywords:* Permian, mafic dykes, Variscan belt.

During the Late Carboniferous-Early Permian the collapse of the Variscan orogeny triggered an extensive dyke magmatism that affected the entire Corsica-Sardinia Batholith (C-SB). Dyke swarms crosscut the crystalline basement, Variscan plutons and post-orogenic Permian volcanics. In both Sardinia and Corsica, late to post-Variscan dyke activity developed in two main phases, partially overlapping in time: 1) Late Carboniferous to Early Permian, which shows an orogenic signature and consists of medium- and high-K calc-alkaline basic and intermediate rocks associated with metaluminous and peraluminous dykes, rhyolitic in composition; 2) Late Permian to Early Triassic represented by dominant transitional basalt issued from the subduction-modified shallow mantle and minor tholeiitic basalts derived from a DMM-dominated hot mantle source (Traversa et al., 2003; Boscaini et al., 2020). In this study, we present U-Pb ages, new major-trace element and Sr-Nd-Pb isotopic data for a series of NE-SW trending Permian mafic dykes outcropping in the Gallura Region (north-eastern Sardinia). The Gallura dykes are predominantly moderately alkaline with few tholeiitic basalts and yield isotopic ratios similar to those of the coeval Ajaccio dykes.

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# S47.

# New insights on the study of gem-quality minerals and their synthetic analogous

*Conveners & Chairpersons*

*Giovanna Agrosì (University of Bari)*

*Gioacchino Tempesta (University of Bari)*

*Maria Cristina Caggiani (University of Catania)*

*Alessia Coccato (University of Oxford - UK)*

# Raman and photoluminescence of gem-quality corundum of different colours

Barone G.[1], Caggiani M.C.[1], Coccato A.[2] & Salini S.[3]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK). [3] Gioielliere e gemmologo, Catania.

*Corresponding author e-mail:* germana.barone@unict.it

*Keywords:* corundum, Raman spectroscopy, photoluminescence.

Corundum ($Al_2O_3$) is widely appreciated in jewellery, especially in the red and deep blue varieties that are the gems ruby and sapphire. Recently, other colours of corundum, asides the bright orange Padparadscha, have appeared on the market. Natural and synthetic corundum can display structural defects, and host transition metals (chromium, titanium, iron and vanadium, replacing $Al^{3+}$) in different oxidation states and coordination, which can occur simultaneously yielding various shades (Jasinevicius, 2009).

In the framework of an ongoing collaboration between the department of Biological Geological and Environmental sciences of University of Catania with local jewellers, a modern piece of jewellery was selected as representing the available variety of coloured corundum on the market. The object is a ring with 26 stones, displaying a variety of colours from pale yellow, to red and pink hues, to blue and greenish ones.

A combination of laser-based techniques was tested. Raman spectroscopy was applied on each gemstone to confirm the mineralogical species (Barone et al., 2014, 2016). Additionally, laser-induced photoluminescence bands linked to the present chromophores were investigated. Specifically, trivalent chromium in octahedral coordination have been identified in literature with 532 nm laser, as a doublet at 4366-4396 $cm^{-1}$ (693-694 nm, corresponding to R2 and R1 lines) (Gaft et al., 2005). These bands, even though related to a chromophore, have been also detected in colourless samples (R060020 as reported in Jasinevicius, 2009). Heat treatment and beryllium diffusion appear to affect the position and intensity of the $Cr^{3+}$ luminescence lines. Other ions' luminescence bands (e.g., $Mn^{2+}$, $Mn^{4+}$, $Fe^{2+}$) have been identified with 532 nm excitation in silicates and Al-containing minerals, however blue and UV laser wavelengths could support a more systematic study (Gaft et al., 2015).

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# Garnets compositional data from Raman spectroscopic analyses

Bersani D.[1], Mazzoleni P.*[2] & Barone G.[2]

[1] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* pmazzol@unict.it

*Keywords:* garnets, Raman spectroscopy, solid solution.

Garnets are commonly studied in different research fields, ranging from strictly mineralogical and petrological studies to archaeometrical investigations on ancient sourcing and trading of gemstones, including the detection of fakes and forgeries, to gemmological applications for jewellery. As garnets can accommodate for a variety of divalent and trivalent ions in their crystalline structure, their actual chemical composition can be indicative of the conditions of crystallization and of specific localities. This is normally achieved with electronic microprobes, offering high spatial resolution and accurate quantification of all the elements of interest.

However, in the case of museum objects, or of jewels for sale, sampling for chemical analyses is not an option. As garnets form solid solutions within the pyralspite and ugrandite series, and across the two via grossular, the gradual substitution of one cation for another inside the lattice gradually modifies its structure. Variations in bond angles and lengths can be easily probed with vibrational spectroscopies and used to estimate the chemical substitutions taking place, when moving from one end member to another, and even in more complex mixtures.

The Ramanita method (Smith, 2005) is based on a linear combination of weighted band positions, the weight being the proportion of a specific end member, and the band position being that of the pure end member. It has been used for pyroxenes and for garnets.

More recently, a set of MatLab routines has been developed and optimized to obtain the chemical composition of a garnet from its Raman spectrum, based on electron microprobe data (Bersani et al., 2009; Moltifiori, 2006). The input phase has been adjusted to be more user friendly, and different computational functions have been tested. The current version of the program can yield the composition of a pyralspite garnet with a relative error lower than 10% on the main component, and even lower for the series grossular-andradite, based on fast and completely non-destructive Raman analyses.

The results of this Raman-based semi-quantitative study of garnet specimens from mineralogical collections and jewels will be here presented.

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# Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) investigation of colored gemstones

Caggiani M.C.*[1], Fugazzotto M.[1], Coccato A.[2] & Barone G.[1]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Faculty of Classics, Ioannou Centre for Classical & Byzantine Studies, University of Oxford (UK).

*Corresponding author e-mail:* mariacristina.caggiani@unict.it

*Keywords:* diffuse reflectance infrared spectroscopy, colored gemstones, surface.

Infrared spectroscopy working in External Reflection (ER) has been recently used to analyze gemstones; its usefulness in this field has been demonstrated especially in tourmaline study, for example to distinguish natural ones from composites and imitations (Li et al., 2011) or to detect thermal treatments (Thongnopkun & Naowabut, 2018).

This technique has the clear advantage of being non-destructive, non-invasive and portable *in situ*; on the other hand, the spectral modifications, such as inversion, distortion, enhancement, or abatement of infrared bands generated when working in Diffuse Reflection (DR) mode can make the correct interpretation of data particularly challenging (Invernizzi et al., 2022). Therefore, a proper exploitation of its benefits requires the support of spectral databases concerning the materials to be studied. To the authors' knowledge, one work only in literature reports a database of ER infrared spectra of gemstones, among other materials constituting cultural heritage (Izzo et al., 2020). It must be considered that the quality of ERFTIR spectra of minerals and rocks can be strongly affected by their surface treatment, favoring in turn the diffuse reflection or the specular one. For these reasons, the aim of this work is to compare reflectance FTIR spectra obtained on the same mineralogical phases of gemological interest with rough or shiny surface appearance, using different sides of the specimen or, respectively, raw and cut gemstones of the same species. Furthermore, analyses along different crystallographic directions are considered. With this purpose, a selection of materials from the Museum of Mineralogy, Petrography and Volcanology of the University of Catania was chosen, and the analyses performed *in situ* thanks to a portable infrared spectrometer equipped with a non-contact head, where the contribution of the diffuse reflectance prevails on the specular one.

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# An unusual italian gem: the Datolite of Campotrera (Reggio Emilia, Northern Apennines)

Caucia F.[1], Scacchetti M.*[2], Salvioli E.[3], Marinoni L.[1] & Gilio M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] AMI - Associazione Micromineralogica Italiana. [3] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma.

*Corresponding author e-mail:* mauscacchetti@alice.it

*Keywords:* ophiolite, fluid inclusions, trace elements.

This work presents the potential as a gem use of the datolite from the famous field of Campotrera (Reggio Emilia, Italy). This mineral is found in widespread multi-centimeter veins, together with calcite and prehnite, within polygenic breccias in basaltic ophiolites, as in other ophiolites of the northern Apennines, such as Cinghi, Valmozzola, Serra dei Zanchetti, and Sasso di Castro (Bertolani, 1948; Zaccarini et al., 2008). This datolite can sometimes be cut as a gem, with satisfactory results (Bartoli et al., 2008; Cook, 2010).

On some samples of this mineral we have conducted gemological analyzes, mineralogical analyzes by X-Ray Powder Diffractometry, main chemical elements analysis by SEM-EDS, trace elements by LA-ICP-MS, Raman spectroscopic analyzes on fluid inclusions, and petrographic analysis of the thin sections of the host rock. The most evident characteristic of the Campotrera datolite is the pink or reddish color, due to microinclusions of hematite, which can be observed in the petrographic sections and are also confirmed by the analyzes on the trace elements. The small amounts of other chromophoric elements, such as Mn, do not appear to have influenced the staining. The studied datolite contains numerous fluid inclusions (5-70 mm in size), both primary and secondary, mainly two-phase. Raman spectroscopy performed on the liquid and vapor phases revealed the presence of aqueous saline solution, $CO_2$, $CH_4$, traces of $N_2$ and $H_2$. The salinity of the aqueous solution is quite homogeneous, with values of 3.48% NaCl equivalent, with the exception of one sample with values up to approximately 7% NaCl equivalent. The gems obtained, with mixed or carrè cut, are colorless or salmon pink, transparent, with a vitreous luster and weight between 1 and 5 carats.

Although in some cases, fractures and polyphasic microinclusions are observed within the crystals, we believe that the Campotrera datolite has good aesthetic characteristics for a gemological use.

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# Orientational dependence of Raman spectra in gemstones: the case of tanzanite

Coccato A.*[1], Bersani D.[2] & Caggiani M.C.[3]

[1] Faculty of Classics, University of Oxford (UK). [2] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* alessia.coccato@classics.ox.ac.uk

*Keywords:* Raman spectroscopy, orientational effects, zoisite.

The observation of different Raman spectra according to the reciprocal orientation between the crystallographic axes and the incident beam was already done by C. V. Raman himself, as quartz was one of the first materials tested by the Nobel laureate (Saksena, 1940). Gem-quality anisotropic minerals showing this behaviour are, amongst others (Bersani & Lottici, 2010, and references therein; Snider Pommier, 2003): aragonite in pearls, beryl (emerald, aquamarine, morganite), danburite, spodumene (kunzite), topaz.

Often, the observed effect is that of intensity ratios variation, which can sometimes lead to the complete disappearance of one or more bands in certain configurations. This could hamper identification of the materials, as the expected bands might be missing. Raman spectra obtained with a portable device on a necklace composed of 46 rounded tanzanite beads clearly showed to which extent spectra can be affected (Coccato et al., 2021).

In order to assess this variability, a reference colourless zoisite was oriented according to the crystallographic axes, and the Raman spectra fully described. Moreover, different laser wavelengths were tested, both on zoisite and on tanzanite, for evaluating the presence of photoluminescence bands due to transition ions and REEs. Finally, the performance of portable Raman instruments was compared with that of laboratory instruments, to confirm the feasibility and effectiveness of the technique in the gemmological field.

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# Cobalt-diffused beryl

Costa E.*[1] & Navone R.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Laboratorio Analisi Gemmologiche R.A.G., Torino.

*Corresponding author e-mail:* emanuele.costa@unito.it

*Keywords:* cobalt, beryl, diffusion.

In early 2015, the RAG Laboratory (Turin, Italy) received a 2.18 ct pale blue faceted aquamarine. The stone was described as "coated," but examination showed no trace of coating. Gemological characteristics matched those of aquamarine, with a refractive index of 1.568-1.571 and a specific gravity of 2.73. The stone showed no fluorescence or luminescence under long wave or short wave UV light; radiation was not detected. No pleochroism was observed, probably because of the stone's very pale color, which may also explain why no features were visible in the handheld spectroscope.

The stone was examined by means of microRaman spectroscopy (using a 532 nm green laser beam) and IR spectroscopy, and both identified the stone as beryl. The stone's apex was recut to obtain a secondary "reference" table without any kind of coating or diffusion for EDS analysis. Chemical composition values are in good agreement with natural beryl, with low Fe content (up to 0.3-0.5% in mass). Only Al, O, Si, and the chromophore elements Fe, Cr, and Co were detected. This point to an absence of coating, as coating is usually obtained using fluoride or metal oxides easily detected by EDS (Gabasch et al., 2008). The presence of cobalt is very strange in a natural aquamarine, but in synthetic beryl the use of Co as dopant is well known, although it led to the formation of red beryl (Shigley et al., 2001).

We tried to evaluate the thickness of the cobalt containing layer, but with no success nowadays. The few results we obtained indicated that the diffused or implanted layer is lesser than a micrometer thick. We are a little bit amazed by the presence of cobalt, because cobalt could induce a red tinge in the stone, and because a diffusion process in beryl could induce damaging due to high temperature. On the other side, ionic implantation seems to be a very expensive way to induce deeper tone in aquamarine, a not-so-expensive stone in the market. We are still investigating about this specimen.

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# Preliminary results on e-beam treatment of gem quality Topaz from two different localities

Elettivo G.S.*[1], Agrosì G.[1], Bloise A.[2], Vadrucci M.[3] & Tempesta G.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [3] Laboratorio Sviluppo di Acceleratori di Particelle e Applicazioni Medicali, ENEA, Frascati (RM).

*Corresponding author e-mail:* giuseppe.elettivo@uniba.it

*Keywords:* topaz, e-beam treatment, gems.

One of the most important and discussed aspects in the gemological field is the treatment to improve the color in gemstone (Nassau, 1985). The e-beam irradiation makes color enhancement possible in many mineral species. Topaz is one of the most famous gemstones commonly undergoing to treatment, even if the causes of color variation need to be fully known. To deeply investigate the processes of color variation during the treatment, we study, before and after e-beam irradiation, samples coming from Tanzania and Mozambique. Three anhedral topazes from Tanzania named Tanz-1, Tanz-2 and Tanz-5 and one from Mozambique named Moz-2 with crystal faces, all transparent and colorless except Tanz-5 which was very light blue in color, were sliced and irradiated by electron beam. Mineralogical and chemical characterization was performed by EPMA, XRPD and UV-VIS. EPMA analysis performed before irradiation show that samples are similar respect to major, minor elements and trace elements content. The optical properties were investigated with UV-VIS spectroscopy to determine the absorption variations in the visible spectrum range (200-900 nm) before and after treatments. The e-beam irradiation treatment was performed using the REX machine (Vadrucci et al., 2019) based on a 5 MeV linear accelerator, at ENEA Frascati research center, employing fluences accordingly with Maneewong et al. (2019). All irradiated topazes at a low dose, accordingly with Krambrock et al. (2007), changed color. Tanz-1 and Moz-2 became light brown, Tanz-2 showed two zones slight brown and dark brown, while Tanz-5 turned brown.

The annealing to eliminate the brown color has been performed with a muffle furnace under ambient pressure conditions. At the end of the heat treatment all the samples are bleached. Only Tanz-2 and Tanz-5 revealed a slight absorption in the visible spectrum around 600 nm, showing a very slight blue color. Further studies will be necessary to understand the different behaviour under the same treatment process of samples with very similar chemical composition.

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# Gemology applied to archeology: a case study

Elettivo G.S.*[1], Smeriglio A.[2], Caputo S.[2], Crocco M.C.[2], Beltrano J.J.[2], Nucera A.[2], Castriota M.[2], Formoso V.[2], Barberi R.C.[2], Taliano Grasso A.[3], Chiodo G.[3] & Agostino R.G.[2]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Fisica, Università della Calabria, Rende (CS). [3] Dipartimento di Culture, Educazione e Società, Università della Calabria, Rende (CS).

*Corresponding author e-mail:* giuseppe.elettivo@uniba.it

*Keywords:* gemology, archeology, archaeometric.

Gemology is a science that can be applied to many case studies. The focus of scientific gemology today is to describe completely natural gems, to characterize the effect of the treatments performed on natural gems and synthetic gems. These topics are really important for different scientific contexts, but also be used in the gem market. An interesting aspect is the application of gemologist method to archaeometry. As a matter of facts, it happens very often that precious stones are set in jewelry objects found in archaeological campaigns. In a recent survey an archeological group found a gold artifact of Hellenistic age in Serre Boscose in Cariati (CS) Italy. This gold artifact probably was a part of an earring with a red gem set in its center. The purpose of the preliminary research on this Hellenistic jewelry object is to identify the nature of the materials with which it was produced as well as the production methodology. This study was performed by means of non-destructive techniques such as X-ray microtomography, XRF and micro-Raman to identify the nature of gemstone set in the Hellenistic jewel (Kolesov & Geiger, 1998; Culka & Jehlička, 2019).

The identification of materials can be used to trace the network of commercial and social relations that existed in the Hellenistic period at the center of Mediterranean area (Spier, 1989; Pappalardo et al., 2005).

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Spier J. (1989) - A Group of Ptolemaic Engraved Garnets. J. Walters Art Gall., 47, 21-38.

# Bright pink-orange and yellow fluorescence of tsavorite garnet from Merelani Hills, Tanzania

Idini A.*[1], Angeli C.[2], Frau F.[1], Ennas G.[1] & Argazzi R.[3]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. [2] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [3] Istituto per la Sintesi Organica e la Fotoreattività, CNR, Ferrara.

*Corresponding author e-mail:* alfredo.idini@gmail.com

*Keywords:* tsavorite, garnet, fluorescence.

Tsavorite is the trade name for the green vanadium-chromium variety of grossular. The occurrence of tsavorite plays a key role in the geological research inherent to the formation of Gondwana continent because it is hosted exclusively in the metamorphic unit from the Neoproterozoic Metamorphic Mozambique Belt (NMMB). The studies on the tsavorite deposit of the NMMB contributed to determining the metamorphic evolution of these Precambrian terrains (Feneyrol et al., 2013). The areas of Merelani Hills (Tanzania) and Tsavo Park (Kenya) are by far the most important source of gem grade specimens of tsavorite that are used for high jewellery (Cairncross, 2020). Because of the popularity of tsavorite, the price is raised up to ~8000 € per carat for top-grade faceted gems. Furthermore, the tsavorite crystals from Merelani Hills exhibit a peculiar feature: the fluorescence is easily recognizable lighting up centimetric crystals with a common portable led lamp. Using the long UV we observe a bright pink-orange colour while exciting with the short UV the effect is a pale yellow. To the best of our knowledge, this phenomenon is unusual among the members of the garnet group and only a few research papers have investigated this phenomenon in natural garnets (Gaft et al., 2013). With the aim of characterizing the fluorescence, up to 25 grams of tsavorite crystals were meticulously sampled from the rocky matrix under the UV lamp and then pulverized in an agate mortar to perform an accurate XRPD acquisition. The results show that no other phases than garnet are present and, thanks to the high quality of the XRPD acquisition, the Electron Density Map was calculated and plotted against a CIF grossular standard, showing that an excess of negative charge is clearly pinpointed in the Y(6) crystallographic site, occupied by $Al^{3+}$ in the grossular standard structure. The bulk elemental analysis, performed on the same powder used for XRPD acquisition, shows that the contents of Fe, Mg and Mn are < 0.5 wt.%, while $V_2O_3$ and $Cr_2O_3$ are respectively 0.32 and 0.015 wt.%, showing a good consistency with bibliographic data (Feneyrol et al., 2012) The fluorometry with an excitation beam at 408 nm shows a complex emission pattern with the most intense emission at 701 and 716 nm and subordinately at 592 nm. The colour perception of the emitted light is dominated by the emission band at 592 nm which is close to the peak sensitivity of the human eye at 555 nm, while the contribution of the red band, though more intense, is perceived as much weaker due to the lower eye sensitivity and modulates the colour ranging from bright orange to pink-red. Because of the characteristic colour perceived under UV light, the use of a common led lamp can serve as a diagnostic tool to identify tsavorite whenever a rapid test is required, e.g., in the case of field survey or in the gem market. By the way, the investigation to understand exactly the nature of the emission centre is still ongoing.

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# A non-invasive procedure in the identification of emerald provenance

Medeghini L.[1], Mignardi S.[1], De Vito C.[1], Aurisicchio C.[2], Lottici P.P.[3] & Bersani D.[3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Geoscienze e Georisorse, CNR, Roma.
[3] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma.

*Corresponding author e-mail:* laura.medeghini@uniroma1.it

*Keywords:* emerald, provenance, spectroscopies.

The provenance studies of emerald continue intriguing the scientific community, indeed the widespread diffusion of this gem, also far from its mines, reflects its economical and religious importance.

Mineralogically, it is a cyclosilicate of Al and Be with general formula $Be_3Al_2Si_6O_{18}$. The structure is composed by tetrahedra ($Si_6O_{18}$) forming six-member rings horizontally and vertically linked together. The Si–O rings are aligned along *c* axis forming continue channels where ions (alkali) and molecules (water) can be present (Aurisicchio et al., 1988).

Studies highlighted the potentiality of the spectroscopies in the provenance study of emeralds (Moroz et al., 2000). On the basis of shape and position of vibrational modes associated to the Si-O vibration (1067-1072 $cm^{-1}$) and those of water (3300-3800 $cm^{-1}$) in Raman spectra as well as the bands in the range 3500-3800 $cm^{-1}$ (associated to OH stretching mode of water) and the shape and position of vibrational modes associated to the Si-O stretching (main peak ~1200 $cm^{-1}$ and shoulder at ~1140 $cm^{-1}$) of FTIR spectra, it could be possible define the genetic model for each deposit and consequently their provenance.

The present work is aimed to define a non-invasive procedure that could be applied in provenance studies of emeralds. Indeed, in the field of cultural heritage a non-destructive approach is necessary to conserve and preserve the precious artefacts.

In particular, the results of a Raman and FTIR study on samples from the main deposits exploited in antiquity such as Malyshevsk (Russia), Jos (Nigeria), Pajshir Valley (Afghanistan), Habactal (Austria), Sikait, Zabara (Egypt) and Swat Valley (Pakistan) are here reported to link spectroscopic markers to the different mines and the genetic models that drove their formation.

The spectroscopic "markers" connected to the different deposits are compared to the genetic models proposed for each deposit by Giuliani et al. (2019). Therefore, a comparison among spectroscopic and chemical data can give an overview about the potentiality of this procedure (Aurisicchio et al., 2018).

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Giuliani G., Groat L.A., Marshall D., Fallick A.E. & Branquet Y. (2019) - Emerald deposits: A review and enhanced classification. Minerals, 9, 105.

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# Baltic vs. Sicilian amber characterization by means of a multi-technique spectroscopic approach

Occhipinti R.*[1], Mazzoleni P.[1], Barone G.[1] & Longobardo U.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Gioielliere, Catania.

*Corresponding author e-mail:* roberta.occhipinti@unict.it

*Keywords:* amber, simetite, spectroscopy.

Fossil resin is a solid organic material deriving from chemical transformation processes of different types of conifers and angiosperms resins; its deposition for long periods can result in different degrees of maturation. Some authors (Bogdasarov, 2007) maintain that the definition of "amber" must be restricted to succinite variety, mainly found on the South-West coasts of the Baltic Sea and in the Dnepr basin; nevertheless, this term is also used to define solidified resins of different origin, principally constituted by alcohols, esters, and complex mixtures of terpenoids.

Baltic amber has surely been the most used throughout the centuries and for this reason it is one of the most studied varieties: in this work, comparison between succinite and amber of sicilian provenance (simetite) will be reported. "Simetite" term comes from the river Simeto, its principal source being the ionic coasts of Sicily near the town of Catania; it is considered one of the most precious ambers for its chemical and physical properties and for its rarity (Barone et al., 2016; van der Werf et al., 2016).

In the analysis of complex materials like amber, the combination of different analytical techniques is often necessary for a complete characterization, definition of the provenance of geological and archaeological samples and evaluation of alteration degree. One of the most used techniques with the aim of discriminating Baltic provenance from other European origins is infrared spectroscopy (Angelini & Bellintani, 2005). In this work, it will be shown how Raman spectroscopy too is efficient in the recognition of simetite, also coupled with Nuclear Magnetic Resonance (NMR) and statistical treatments (Barone et al., 2016), based on spectral features that are connected to different maturation degrees.

Furthermore, samples of amber kept in the Museum of Mineralogy, Petrography and Volcanology of the Department of Biological, geological and Environmental Sciences of Catania University will be considered: the provenance and the possible surface alteration will be evaluated by means of a non-invasive spectroscopic approach, including Fourier Transform Infrared spectroscopy both in Attenuated Total Reflectance (FTIR-ATR) and in Diffuse Reflectance (DRIFT) modes.

Angelini I. & Bellintani P. (2005) - Archaeological ambers from Northern Italy: an FTIR-DRIFT study of provenance by comparison with the geological amber database. Archaeometry, 47, 441-454.

Barone G., Capitani D., Mazzoleni P., Proietti N., Raneri S., Longobardo U. & Di Tullio V. (2016) - 13C Solid State Nuclear Magnetic Resonance and μ-Raman Spectroscopic Characterization of Sicilian Amber. Appl. Spectrosc., 70, 1346-1355.

Bogdasarov M.A. (2007) - Mineralogy of Fossil Resins in Northern Eurasia. Geol. Ore Dep., 49, 630-637.

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# Relationship between chemical and structural features of Baoshan topaz to unravel its formation conditions: a multidisciplinary approach

Precisvalle N.*[1], Bonadiman C.[1], Langone A.[2], Gigli L.[3], Plaisier J.R.[3], Hansen T.C.[4], Gianoncelli A.[3], Bonanni V.[3], Gariani G.[3] & Martucci A.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Istituto di Geoscienze e Georisorse, CNR, Pavia. [3] Elettra-Sincrotrone Trieste. [4] Institut Laue-Langevin, Grenoble (France).

*Corresponding author e-mail:* prcncl@unife.it

*Keywords:* topaz, gemstones, Baoshan.

Topaz [$Al_2SiO_4(OH,F)_2$, *Pbnm* space group] is one the principal fluorine bearing silicates that occurs as accessory minerals in fluorine rich silicates rocks associated with magmatic or hydrothermal events. In this work, we propose a geochemical model to link the crystal structure to a possible geological environment, thus possibly determine the gem identity and provenance for colourless topaz from the Tengchong-Baoshan Sn-polymetallic metallogenic belt (China) and propose a geochemical model to link the crystal structure to a possible geological environment through a multi-technical approach. The successful strategy to combine chemical microanalyses (SEM-EDS for major elements and LA-ICP-MS for trace elements) with synchrotron X-Ray and neutron powder diffraction in situ measurements (in the 298-1300 K temperature range) allowed to accurately determine the mineral structure. On the basis of neutron diffraction data, topaz F content is estimated to be ~1.59 with OH/F = 0.240 in agreement with the EDS (F ~1.52 a.f.u). The topaz – mullite transformation (that for the first time here has been reconstructed through heating ramp diffraction analyses) has been interpreted as the potential initial crystallization temperature of topaz in a fluid-dominated system. In such a view, it is possible to infer that Baoshan topaz started to form at ~1203-1225 K from a water poor / fluorine rich fluid ($(fH_2O/fHF)^{fluid}$ ~ 1.2 log units). It resulted that the Baoshan topaz is related to a greisen type reaction, thus reducing the number of possible topaz source deposits present in the area. These results were then compared with those of Precisvalle et al. (2021), concerning the Padre Paraiso blue topaz. Altogether these data allowed a fair identification of both topaz deposits. Furthermore, using the micro-X-ray mapping it has been studied spatial distribution of Al, Si, Ga, Ge, As, as well as those of F and OH on topazes' surface confirming a random distribution of O and F in octahedra, Al-Ga and Si-Ge substitution and showing an ambivalent behaviour of As that can be both included as a substitute for Si (Padre Paraiso topaz) or absorbed in the cavities between octahedrons (Baoshan topaz).

Precisvalle N., Martucci A., Gigli L., Plaisier J.R., Hansen T.C., Nobre A.G. & Bonadiman C. (2021) - F/OH ratio in a rare fluorine-poor blue topaz from Padre Paraíso (Minas Gerais, Brazil) to unravel topaz's ambient of formation. Scient. Rep., 11, 2666.

# Relationships between OH/F content and elastic properties in natural topaz

Precisvalle N.*[1], Martucci A.[1], Gigli L.[3], Plaisier J.R.[3], Bonadiman C.[1] & Speziale S.[2]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Chemistry and Physics of Earth Materials, German Research Centre for Geosciences, Potsdam (Germany). [3] Elettra-Sincrotrone Trieste.

*Corresponding author e-mail:* prcncl@unife.it

*Keywords:* topaz, Brillouin scattering, elastic properties.

Topaz $Al_2SiO_4(OH_X,F_{1-X})_2$, where X = OH/(OH+F), is a major fluorine-bearing silicate occuring as an accessory mineral in rocks from different geological settings. Its composition ranges from a nearly OH-free $Al_2SiO_4F_2$ (X=0) in acid igneous rocks, to $Al_2SiO_4F_{1.4}(OH)_{0.6}$, (X = 0.3) in hydrothermal deposits. Since the elastic properties of natural topaz have so far only been investigated in few studies (Sema & Watanabe, 2017; Tennakoon et al., 2018) , the aim of this work is therefore to characterize the dependence of the elastic properties of topaz as a function of their OH/F ratio. We have experimentally determined the full elastic tensors combined of a suite of natural topaz crystals from different geological settings whose structures and OH/F ratios were accurately characterized. The selected topaz samples are from Padre Paraiso (pegmatite, Minas Gerais state, Brazil), Veronica mine (rhyolites, Zacatecas municipality, Mexico), Baoshan (greisen deposits, Yunnan province, China), Brown Derby Mine (pegmatite, Colorado, USA), Ouro Preto (hydrothermal veins, Minas Gerais state, Brazil). We determined the chemical composition of the samples by means of electron microprobe analyses (EMPA) JEOL JAX8600 and JEOL-Hyperprobe JXA 8500F. We also refined the structural parameters of all the studied samples by X-ray powder diffraction (XRPD) at MCX line (Elettra Sincrotrone Trieste) and STOE Stadi P diffractometer at GFZ-Potsdam. Brillouin scattering measurements were performed at the GFZ-Potsdam for all the samples and the full tensor were determined. Among the 9 non-zero independent tensor coefficients $C_{11}$ and $C_{12}$ and $C_{55}$ are the most sensitive to the OH/F ratio with $dC_{ij}/dX$ = -6.1, 0.6 and -8.2 GPa, respectively.

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Tennakoon S., Perg Y., Mookherjee M., Speziale S., Manthilake G., Besara T., Andreu L. & Rivera F. (2018) - Single crystal elasticity of natural topaz at high-temperatures. Scient. Rep., 8, 1372.

# Raman signature of pearls: insights on characterization criteria by using different excitation sources and Raman spectrometers

Raneri S.*[1], Bersani D.[2], Fornasini L.[2], Bergamonti L.[3], Barone G.[4], Mazzoleni P.[4] & Lottici P.P.[2]

[1] Istituto di Chimica dei Composti Organo-Metallici, CNR, Pisa. [2] Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma. [3] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [4] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

*Corresponding author e-mail:* simona.raneri@pi.iccom.cnr.it

*Keywords:* pearls, Raman spectroscopy, dyes.

Pearls are considered important and complex organic gems, constituted by both inorganic and organic materials. Several studies have been carried out to investigate structure and composition of pearls by non-destructive methods, even with the aim to discriminate among different classes of pearls and to recognize their origin.

Pearls may be natural or cultured, influencing their commercial value. The naked-eye observation and the inspection under a microscope not always allow a differentiation between natural and cultured, freshwater and saltwater pearls. The identification of the coloring agent of a pearl is of further help for a correct evaluation. Natural pigments consist of a mixture of polyene molecules but color may be also artificially produced, by dyeing or irradiating pearls, giving back several brilliant nuances. Literature on the Raman investigation of pearls is wide, but often difficult to retrieve. Several insights on pearls identification and classification were proposed over the time, even if the usefulness of some proposed methods need further verification.

In this work, the most relevant results reported in literature on the Raman analysis of pearls are reviewed and tested on a wide set of pearls with different nature and geographical origin, using different, fixed and mobile, spectrometers. The influence of the experimental conditions, in particular the laser line used for excitation, is discussed. Nature and provenance identification by Raman spectroscopy remains a very hard task, even if some clues are shown. Natural and artificial colors are discriminated. Finally, the possibilities offered by mobile Raman spectrometers are discussed, highlighting limits and merits of in situ pearls characterization.

# Preliminary results of electron beam irradiation effect of tourmaline coming from different localities

Rizzo F.*

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari "Aldo Moro".

*Corresponding author e-mail:* floriana.rizzo@uniba.it

*Keywords:* e-beam irradiation, enhancement color, treatment.

Tourmaline is one of the most popular and desirable gemstone in the world mainly thanks to their wide range of colour that reflect a very flexible structure and a complex chemistry (Pezzotta & Laurs, 2011).

In gemological trade tourmaline's crystals are commonly treated with different sources of radiation to enhance their original color and increase their value as gem. In this study ten samples of tourmaline ranging from colorless to pale pink, pink, pale blue, blue and zoned have been treated with electron beam irradiation and examined by using UV-VIS spectroscopy. This study was focused on representative samples of the major existing tourmaline deposits located in Brazil, Madagascar, Afghanistan, Russia, Pakistan and Italy.

UV-VIS spectra were acquired before and after e- beam treatment to better understand the behavior of the transition elements known as chromophores ($Mn^{2+}$, $Mn^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $V^{3+}$, $Cu^{2+}$, $Ti^{4+}$) responsible for tourmaline colors. All tourmaline samples were mounted on an aluminum plate equipped with a special cooling system and irradiated with $5.1 \times 10^{-4}$ Gray at temperature of 20°C. After the e-beam irradiation all samples showed a stronger color enhancement, the colorless samples became respectively yellow-brown and pinkish-red. Furthermore, electron irradiation did not affect the color of the blue tourmaline sample.

Pezzotta F. & Laurs B.M. (2011) - Tourmaline: The kaleidoscopic gemstone. Elements, 7, 333-338.

# First crystal-chemical characterization of a "watermelon" variety of tourmaline from Anjanabonoina pegmatite (Madagascar)

Rizzo F.*[1], Bosi F.[2], Tempesta G.[1] & Agrosì G.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* floriana.rizzo@uniba.it

*Keywords:* tourmaline, crystal-structure refinement, watermelon.

A polychrome tourmaline, from the Anjanabonoina pegmatite (Madagascar), was characterized using a multi-analytical approach. The sample shows a complex concentric zoning and a wide range of colour typical of a variety known as "watermelon" in the gemological trade. The entire sample (length 3.5 cm) was cut into several slices perpendicular to *c-axis*. The basal slices exhibit a rim characterized by narrow layers, alternate in a rhythmic manner with a triangular core relatively homogeneous. Four mains pronounced colour zones were identified from the rim to the core: (1) dark green rim; (2) pale green rim; (3) pale pink rim; (4) brownish-yellow core. The polished slices were investigated performing traverses of microanalysis by Scanning Electron Microscopy (SEM-EDS) and Electron Microprobe Analysis (EPMA, WDS mode). The Li content was obtained by micro-Laser Induced Breakdown Spectroscopy (μ-LIBS) (Tempesta et al., 2020). Four fragments were also extracted from the aforementioned zones and analyzed by single-crystal X-ray diffraction (XRD). The crystal structure of the four fragments were refined to statistical indices $R1 < 2\%$.

Based on chemical and structural data, zones (1), (2), (3) of the studied crystal correspond to the fluor-liddicoatitic composition, whereas the (4) zone corresponds to Mn-rich fluor-elbaite with a small amount of Ti.

Tempesta G., Bosi F. & Agrosì, G. (2020) - Crystal Chemical Characterization of Red Beryl by 'Standardless' Laser-Induced Breakdown Spectroscopy and Single-Crystal Refinement by X-Ray Diffraction: An Example of Validation of an Innovative Method for the Chemical Analysis of Minerals. Geostand. Geoanal. Res., 44, 685-693.

# S48.

# Resource availability, critical raw materials and by-products for the ecological transition and sustainability

*Conveners & Chairpersons*

*Francesco Di Benedetto (University of Ferrara)*

*Luca Pardi (CNR)*

*Sabrina Nazzareni (University of Perugia)*

*Gabriele Giuli (University of Camerino)*

# New insights on the distribution of Ce, La, Y and Sc in soils combining the compositional data analysis (CODA) and machine learning techniques: the case study of the Campania region

Ambrosino M.*[1], Albanese S.[2], Guarino A.[2], De Vivo B.[3-4], Lima A.[2] & Cicchella D.[1]

[1] Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento. [2] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [3] Department of Geosciences, Virginia Tech, Blacksburg, VA (USA). [4] Università Telematica Pegaso.

*Corresponding author e-mail:* maambrosino@unisannio.it

*Keywords:* rare earth elements, statistical learning, compositional data analysis.

In 2015 began the "Campania Trasparente" project (http://www.campaniatrasparente.it), a monitoring plan with the objective of assessing the environmental conditions of the Campania region territory.

Among the different environmental matrices (air, water, top and bottom soil, vegetables, biological samples) 7,300 samples of the topsoil (10-15 cm) were collected and analysed. Chemical analyses were performed at Bureau Veritas laboratories (Canada) and involved 52 elements. They were determined through an analytical methodology combining ICP-MS and ICP-ES. For more information on sampling procedures, chemical analysis methods and QA/QC protocols see De Vivo et al. (2021).

This study focused on the geochemical distribution of La, Ce, Sc and Y; the results of this work are extendable to the whole REEs group. Through statistical learning techniques and multivariate statistics, we tried to understand the behaviour of these elements in different geogenic and anthropogenic conditions and their interaction with other elements. Through the lasso regression and principal component analysis applied to the CLR-transformed data (centered log-ratio), it was possible to select the variables most involved in the processes that more determined the variability in the distribution of REE concentrations.

Our results show that median concentration values of the investigated elements (Ce = 80.3, La = 41.3, Y = 15.4 and Sc = 3.3 mg/kg) are significantly higher than those of European and Italian soils (Reimann et al., 2014; Cicchella et al., 2018). The type of lithologic substrate and the degree of soil alteration are the main factors responsible of the REEs concentrations. In general, Ce and La are more abundant in soils of volcanic areas and Sc in clayey soils while Y has an intermediate behavior. High degrees of alteration contribute to an enrichment of REEs, associated with high values of low-mobile elements like Th, Fe, Hf, Zr, Mn, in correspondence with the oldest volcanic products. In particular, our findings show that Fe and Th are the elements most closely related to REEs, therefore they can be used to estimate their natural concentration in soils.

Cicchella D., Zuzolo D., Albanese S., De Vivo B., Dinelli E., Lima A. & Valera P. (2018) - Geochemical atlas of agricultural and grazing land soil of Italy. The GEMAS Project in Italy. Aracne, Roma.

De Vivo B., Cicchella D., Lima A., Fortelli A., Guarino A., Zuzolo D., Esposito M., Cerino P., Pizzolante A. & Albanese S. (2021) - Monitoraggio geochimico-ambientale dei suoli della regione Campania. Progetto Campania Trasparente, Vol. 1. Aracne, Roma.

Reimann C., Birke M., Demetriades A., Filzmoser P. & O'Connor P. (2014) - Chemistry of Europe's agricultural soils. Part B: General background information and further analysis of the GEMAS data set. Geologische Jahnbuch Reihe B, Hannover.

# Recycling of ornamental stone scraps through gravity and magnetic methodologies: the case study of Buddusò Quarrying District (Northern Sardinia, Italy) - Part I

Aquilano A.*[1], Marrocchino E.[2] & Vaccaro C.[2]

[1] Dipartimento di Architettura, Università di Ferrara. [2] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara.

*Corresponding author e-mail:* qlnnnl@unife.it

*Keywords:* critcal raw material, recycling, quarry waste.

Waste generated by the ornamental stone industry has a strong environmental impact on soil and aquifers (Medina et al., 2017), representing approximately 58% of the total production of the quarry and plant (Rana et al., 2016). Nowadays, reuse and recycling solutions are the most widely promoted by institutions and the recycling of extraction waste could also be addressed for the recovery of critical raw materials (CRM). For example, the presence of minerals such as allanite opens up the possibility of using this waste for the recovery of rare earth elements (Cavallo & Dino, 2022).

This study will present preliminary results from a PhD project and is focused on the methodologies used for mineral separation from ornamental granite scraps of the Buddusò quarrying district (Northern Sardinia) and aims to develop a protocol for the processing of granite waste to obtain a CRM enriched product.

The granite waste samples object of this study were subjected to a gravity separation process, obtaining 7 subsamples from each of them, then magnetically separated obtaining a further 21 subsamples.

Initially, samples were treated using a jaw crusher and then sieved to retain the material with a grain size between 0.850 mm and 0.125 mm. This material was subjected to a gravity separation using a Gemini Masa G-150 wet shaking table (Onur Makina, Eskisehir, Turkey). This process was carried out to concentrate the high-specific gravity minerals separating the lighter ones. The 7 subsamples obtained were then dried in an oven at 105°C for 24 hours. Subsequently, the ferromagnetic minerals were removed with a magnet and the remaining fractions were magnetically separated using an L-1 magnetic isodynamic separator (S.G. Frantz Co., Tullytown, USA). This allowed separating the sub-samples into paramagnetic fractions and diamagnetic ones. This procedure was performed in two steps: i) a first separation, performed at low intensity to separate minerals with high magnetic susceptibility; ii) a second separation, at a high intensity, of the material that appeared non-magnetic in the previous step, to separate the minerals with low magnetic susceptibility from the diamagnetic part.

The next step of this study will investigate the effectiveness of this process through petrographic, geochemical, and mineralogical analyses.

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Medina G., Del Bosque I.S., Frías M., De Rojas M.S. & Medina C. (2017) - Granite quarry waste as a future eco-efficient supplementary cementitious material (SCM): Scientific and technical considerations. J. Clean. Prod., 148, 467-476.

Rana A., Kalla P., Verma H.K. & Mohnot J.K. (2016) - Recycling of dimensional stone waste in concrete: A review. J. Clean. Prod., 135, 312-331.

# Micronization of ceramic colorants. From understanding to energy efficiency of the process

Ardit M.*[1], Molinari C.[2], Conte S.[2], Zanelli C.[2], Cruciani G.[1] & Dondi M.[2]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Istituto di Scienza e Tecnologia dei Materiali Ceramici, CNR, Faenza (RA).

*Corresponding author e-mail:* rdtmtt@unife.it

*Keywords:* micronization of ceramic colorants, energy management, raw material saving.

With over 16 billion m$^2$ worldwide, in 2020 the ceramic industry marked a new record in tile production (Baraldi, 2021). Similarly, the global demand for ceramic pigments and dyes (ceramic colorants), driven by the ceramic tile industry, has also grown rapidly in the last decades leading to a growing need for raw materials and energy.

Nowadays, inkjet printing (IJP) with micronized inks has become the decoration technology par excellence for ceramic tile (Molinari et al., 2020). Through this technology, the finished product is no longer a powdered colorant, but a micronized colorant dispersed in a carrier, i.e., an ink that undergoes a high-energy stirring milling process where particles must have a median size ($d_{50}$) of ~300 nm to fulfill IJP requirements (Hutchings, 2010).

Being mainly dependent on the specific energy input (i.e., the energy supplied to the grinding chamber per mass of product), pigment micronization down to the requested particle size proves to be the most energy-consuming comminution process per unit weight of product (Wang & Forssberg, 2007). It follows that comminution of ceramic colorants is a key issue for ink production, which has strong repercussions on color strength, mechanical properties and resistance to amorphization of the colorants' crystal structure, as well as on the energy management of the entire process. On the other hand, a deep understanding of the comminution dependence on many of these aspects is still lacking.

In this contribution, the micronization effects on a set of five industrial ceramic colorants are thoughtfully investigated through a simulation of the industrial process at a pilot plant, where particle size distribution and energy consumption are monitored during the comminution process.

The combined analytical approach (i.e., X-ray diffraction, scanning electron microscopy, and diffuse reflectance spectroscopy) aided by a physical/semiempirical modelling of the colorants' elastic features versus the energy response of the particle reduction has yielded details on the nature of the micronization-induced microstructural changes in ceramic colorants.

The results obtained represent a fundamental development towards the optimization of the comminution process. A proper energy modulation allows to limit harmful emissions and save raw materials.

Baraldi L. (2021) - World production and consumption of ceramic tiles. Ceram. World Rev., 143, 26-40.

Hutchings I. (2010) - Ink-jet printing for the decoration of ceramic tiles: technology and opportunities. Proc. 12th World Congress on Ceramic Tile Quality, QUALICER, 1-16.

Molinari C., Conte S., Zanelli C., Ardit M., Cruciani G. & Dondi M. (2020) - Ceramic pigments and dyes beyond the inkjet revolution: From technological requirements to constraints in colorant design. Ceram. Int., 46, 21839-21872.

Wang Y. & Forssberg E. (2007) - Enhancement of energy efficiency for mechanical production of fine and ultra-fine particles in comminution. China Particuol., 5, 193-201.

# Heritage of mining: Hg removal by ferrates in contaminated water at Abbadia San Salvatore

Baroni T.*[1], D'Acapito F.[2], Filip J.[3], Montegrossi G.[4], Vaselli O.[1] & Di Benedetto F.[5]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto Officina dei Materiali, CNR, Grenoble (France). [3] Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc (Czech Republic). [4] Istituto di Geoscienze e Georisorse, CNR, Firenze. [5] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* francesco.dibenedetto@unife.it

*Keywords:* ferrate, mercury, environmental remediation, liquid ferrate, XAS.

High-valent iron anions, commonly called ferrates (IV-V-VI), have drawn lot of interests as sustainable chemical treatments for drinking water/wastewaters/industrial effluents remediation. In the past three decades, they have demonstrated high capability of removing a wide range of organic and inorganic compounds from all kind of water sources collected worldwide through oxidation and the in situ formation of Fe oxy-hydroxide nanoparticles, which serve as an efficient adsorbent for oxidized pollutants and suspended/colloidal materials. Abbadia San Salvatore former Hg-mining area, Mt Amiata region, was one of the largest Hg districts in the world, exploited for decades by intense mining activities. The ground-water system of Abbadia shows Hg contents well above the EU Directive (1 μg/L) with values up to 853 μg/L (Vaselli et al., 2015). An original wet chemical synthesis procedure was developed in order to overcome the lack/high price of ferrate-based products from the official chemical suppliers. Avoiding separation/purification steps, the resulting *liquid ferrate* showed a $FeO_4^{2-}$ content in line with the best results published, in addition to a relevant amount of chemicals saved (-38% on the final cost) (Sun et al., 2013). The Hg-removal tests using a laboratory Hg(II) solution revealed high efficacy, comparable to more traditional Fe(III) reagent (91 vs 96% removal respectively) while the real Abbadia water presented a similar outline while accounting for a more complex system, due mostly to the presence of deposit and fine suspended particulate matter. The XANES investigation of the precipitates from the Hg-removal efficiency test performed at the LISA – BM08 (ESRF, Grenoble, France) showed how the resulting Hg speciation is affected. The comparison between *liquid ferrate*, a solid-synthesized ferrate product (Fe(IV+V+VI) ~ 27/30% of total Fe) and a Fe(III) based reagent reveals how *liquid ferrate* is clearly capable of converting the HgS-dominated scenario in the original water filtered material to a HgO-dominated situation, while the other reagents affect only marginally the Hg speciation distribution. While further research is needed, this study investigates for the first time the Hg-removal from water by ferrates while starting to elucidate its removal mechanism.

Sun X.H., Lei W., Wen C.L. & Wan Q.T. (2013) - Preparation of Liquid Ferrate and the Optimization of Process Parameters. Adv. Mater. Res., 772, 884-887.

Vaselli O., Nisi B. Rappuoli D., Bianchi F., Cabassi J., Venturi S., Tassi F. & Raco B. (2015) - Geochemical characterization of the ground waters from the former Hg-mining area of Abbadia San Salvatore (Mt. Amiata, central Italy): criticalities and perspectives for the reclamation process. Ital. J. Geosci., 134, 304-322.

# Resource depletion: the EROI issue

Celi L.*

Istituto per i Processi Chimico-Fisici, CNR, Pisa.

*Corresponding author e-mail:* luciano.celi@cnr.it

*Keywords:* resource depletion, EROI, fossil fuels.

Among the non-renewable energy resources, that humanity should abandon as soon as possible to avoid climate catastrophe, are fossil fuels. We are facing a real trap: the world basically works thanks to fossil energy sources and is structurally dependent on them, but it should put in place as soon as possible an energy transition that would allow to decouple energy demand from the extraction and refining of gas, oil and coal.

In addition to this, there is another problem that is quite easy to understand: the “easy” fossil sources - including what was technically defined as “conventional oil” - are in fact exhausted and recovering new resources is increasingly (energetically and economically) expensive.

One of the indexes that in literature measures this difficulty is the EROI, acronym of “Energy Return On Investment”, that is the ratio between the energy recovered (ER) and the energy invested (EI) to obtain it. This index, to get an idea, of the values involved, at the beginning of the $20^{th}$ century, in the United States, was about 100:1, i.e., it took the energy equivalent of one barrel of oil to get 100. Less than a century later, in 1990, the value dropped to an average of 35:1, while in more recent years, up to the present day, despite the positive effects of energy efficiency, it has fallen progressively from 20:1 to 10:1 worldwide, as confirmed by Celi (2021).

Celi L. (2021) - Deriving EROI for Thirty Large Oil Companies Using the CO2 Proxy from 1999 to 2018. Biophys. Econ. Res. Qual., 6, 1-12.

# Residual materials of secondary aluminum plants converted into lightweight inorganic polymers: a circular economy case study for the environmental sustainability

Ercoli R.*[1], Renzulli A.[1-2], Prałat K.[3], Ciemnicka J.[3], Buczkowska K.E.[4-5], Le S.V. [4], Nguyen V.V.[4], Łoś P.[4] & Louda P.[4]

[1] Dipartimento di Scienze Pure e Applicate, Università di Urbino "Carlo Bo". [2] Geo.In.Tech. s.r.l. - spin-off Università di Urbino «Carlo Bo». [3] Institute of Civil Engineering, Warsaw University of Technology, Płock (Poland). [4] Department of Material Science, Technical University of Liberec (Czech Republic). [5] Department of Materials Technology and Production Systems, Lodz University of Technology (Poland).

*Corresponding author e-mail:* r.ercoli@campus.uniurb.it

*Keywords:* circular economy, secondary aluminum, industrial by-product, chemical neutralization, geopolymer foam.

The European Union has adopted a green policy for the achievement of environmental targets such as resource management efficiency, constant industrial processes optimization, and lowering of environmental impact (the reduction of waste output and gas emissions). The Italian Ministerial Decree of 13 October 2016, n. 264, defined the "indicative criteria to facilitate the demonstration of the existence of the requirements for the qualification of production residues as by-products and not as waste. The activation of de-manufacturing logistics of end-life and industrial waste materials is the main factor that improves the relative residual values through specific operations and treatments. Such materials need to be considered a resource, involving also considerable savings for the industries. Here we present a case of study regarding the recovery of by-products derived from the industrial processes of secondary aluminum production (screening, pyrolysis, and fusion processes). The aluminum-rich by-products were classified according to the regulation 1357/2014 (waste hazardous characteristics). These materials can potentially develop flammable gases and form explosive mixtures with air, and for this, classified as special hazardous wastes. Experimental procedures defining the inertization processes and the relative indicators, such as LOI, through which the residual material can be considered inert, are mandatory before the re-use. Thermodynamic reactions were deeply investigated in a stainless-steel batch mini-reactor mixing the reactive substances with an aqueous alkaline solution: fast oxidation occurs determining the process from which a hydrogen-rich gas (up to 96%) is generated. These basic proceedings think up the reuse of the special hazardous wastes from the entire recycling process of the secondary aluminum industry, precisely, neutralizing, and at the same time reusing them as foaming agents to synthesize innovative inorganic polymers called geopolymers, a three-dimensional natural-based material. So, even more, the chemical neutralization of hazardous industrial waste from the secondary aluminum industry for producing geopolymers represents a brand-new green horizon. Not only do geopolymers display a wide range of excellent physical properties, but they are a valid alternative to Portland cement manufacturing, a process that demands large amounts of energy and releases significant $CO_2$ amounts. In terms of carbon dioxide emission, it is estimated that geopolymer impacts around 95% less than the cement industry, which alone is responsible for around 7% of the carbon dioxide globally every year, being one of the main causes of global warming.

# Resource availability and long term sustainability of the energy supply by wind turbines: preliminary results

Millacci G.*[1], Sanginesi F.[1], Giaccherini A.[1], Buccianti A.[1], Fusi L.[2], Pardi L.[3] & Di Benedetto F.[4]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Matematica e Informatica "Ulisse Dini", Università di Firenze. [3] Istituto per i Processi Chimico-Fisici, CNR, Pisa. [4] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

*Corresponding author e-mail:* giumillacci@gmail.com

*Keywords:* neodymium, compartmental model, energy transition.

Fossil fuel, once regarded as abundant and low cost, was the main engine for global development in industrial history. However, today, we are confronted with an unprecedented energy crisis, with pollution of all kinds, with climate change caused by atmospheric greenhouse gas accumulation and much more. There is an emerging demand to invest in the renewable energy sector, which could mitigate these problems and integrate traditional energy sources or even allow an energy transition from traditional to renewable sources.

This study focuses on wind power plants as a renewable energy source. The key component in the efficiency of wind turbines is neodymium. It is present in the permanent magnets of the turbines and is considered to be one of the most critical elements in the Rare Earth (REE) family in the development of modern society. However, the growing expansion of the wind sector implies the use of a large amount of this resource and a lot of energy from traditional sources. We developed an original compartmental model, based on the Hubbert theory, to obtain an assessment of the times of exhaustion of the resource and the the energy invested to create this new energy source**.** The model was constrained to the present situation from the consideration of the historical production of REE, and Nd in particular. Being Nd involved in a technology aimed at producing energy, the energy costs of the Nd beneficiation and of the wind turbines production was evaluated from thermochemical and engineering data.

The preliminary results obtained in different scenarios reveal a non-obvious dependence of the energy input (this means fossil energy to date) by wind turbines to satisfy the global energy demand on the chosen parameters (Nd share on technology and recycling rate). However, scenarios where the global energy demand is progressively and fully satisfied by wind turbines could be envisaged. As for other critical raw materials, the future uses and production of Nd should be carefully governed.

# Unusual REE enriched zircons from Agua de Pau syenites (São Miguel, Azores Islands)

Nazzareni S.*[1], Giuli G.[2], Petrelli M.[1], Di Michele A.[1] & Pacheco J.[3]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Scuola di Scienze e Tecnologie, Università di Camerino.
[3] Instituto de Investigação em Vulcanologia e Avaliação de Riscos, Universidade dos Açores, Ponta Delgada (Portugal).

*Corresponding author e-mail:* sabrina.nazzareni@unipg.it

*Keywords:* rare earth elements, zircon, Azores.

Accessory minerals are able to incorporate trace-elements whose content is affected by factors that include lattice strain, melt polymerization and the water content of the melt. Most of High Field Strength Elements (HFSE) including rare earth elements (REE), yttrium (Y), zirconium (Zr), hafnium (Hf), niobium (Nb), and tantalum (Ta) are used in a vast array of devices such as lasers, electronic screens, permanent magnets, battery alloys, and ceramics. A worldwide increasing demand on HFSE supply produced a growing amount of studies on exploiting new deposits, improving extraction processes, REE recovery from waste for reuse. In this framework it is critical that the physical and chemical properties of REE- and REE-bearing minerals could be understood fully.

We focused on accessory minerals present in syenite xenoliths enclosed in the pyroclastic eruption of Agua de Pau volcano (São Miguel, Azores archipelago, Portugal). Água de Pau is one of the three Holocene stratovolcanoes on the island of São Miguel. Syenite xenoliths frequently occur in numerous pyroclastic sequences erupted during the Holocene activity. Such xenoliths are characterised by a peculiar mineralogy, the main minerals being feldspar, amphiboles, clinopyroxene, and Fe-Ti oxides. But minor accessory components are represented by apatite, titanite, aenigmatite, eudyalite, zircon, chevkinite, pyrochlore, and dalyite and several other REE and REE-bearing minerals.

We selected 52 zircon crystals that were analysed by FE-SEM and LA-ICPMS at the Dept. of Physics and Geology (University of Perugia).

Compositional maps showed zoning only on few crystals. We observed two groups of zircons in the ternary Zr-Th-Hf diagram: a) with only Hf-Zr substitution; b) with Hf-Th-Zr substitution. An unusual REE content was measured by FE-SEM and LA-ICPMS with a significant entering of REE up to 4000 ppm Ce, 4000 ppm La, 1000 ppm Nb, 4000 ppm Y, 3000 ppm Nd, 1500 ppm Gd, 5000 ppm Dy, 4500 Yb. This strong enrichment on REE suggests an important solubility of several REE in zircon and possibly a revision of available partition coefficients.

# Effect of the crystal chemistry on the structural and thermo-elastic properties of natural REE-arsenates and phosphates

Pagliaro F.*[1], Lotti P.[1], Comboni D.[2], Fumagalli P.[1], Battiston T.[1], Guastoni A.[3], Rotiroti N.[1] & Gatta G.D.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] ESRF, Grenoble (France). [3] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* francesco.pagliaro@unimi.it

*Keywords:* REE, XRD, synchrotron.

The wide group of $ATO_4$ minerals ($A$ = Sc, Y, Ln, U and Th, whereas $T$ stands for tetrahedrally-coordinated cations as P, As and minor Si), includes the important REE-bearing minerals xenotime-(Y) (nominally $YPO_4$) and monazite-(Ce) (nominally $CePO_4$), as well as the rare REE-arsenates chernovite-(Y) (nominally $YAsO_4$) and gasparite-(Ce) (nominally $CeAsO_4$). The Y- and HREE-rich chernovite-(Y) and xenotime-(Y) share the same zircon-type structure (space group $I4_1/amd$), while gasparite-(Ce) and monazite-(Ce) represent the LREE-rich $ATO_4$ minerals, crystallizing in the monoclinic monazite-type structure (space group $P2_1/n$). The renowned REE-bearing site of Mount Cervandone (Lepontine Alps, Italy), has been chosen as a case-study: all the above-mentioned minerals occur in hydrothermal quartz veins crosscutting previously metamorphosed pegmatitic dykes. The present study focuses on 1) the chemical composition of the selected minerals, 2) the role played by crystal chemistry on the structural and thermo-elastic features, and 3) the structural response to T and P stimuli, including the occurrence of phase transitions.

A chemical and structural characterization has been performed via EPMA-WDS, Raman spectroscopy and single-crystal X-ray diffraction analysis. Chemical data showed that the zircon-structured minerals chernovite-(Y) and xenotime-(Y) are characterized by a very similar (Y,HREE) composition and the same conclusion can be drawn for the LREE content of the two monazite-type minerals. An almost complete solid solution has been found between xenotime-(Y) and chernovite-(Y), while a wide miscibility gap has been observed within the monazite series minerals of Mt. Cervandone. Despite strong similarities in the composition of the REE-site within the zircon- and monazite-type series, respectively, isostructural phosphate and arsenate differ in some structural features. In particular, both the unit-cell and the REE-coordination polyhedron volumes are strongly controlled by the cationic population at the $T$-site: an increase in As not only expands the volume of the $TO_4$ tetrahedron, but even that of the REE-polyhedron, irrespective of the $A$-site population. A comparative analysis of the thermo-elastic behavior of selected minerals has been conducted, by in situ high-P, high-T and combined HPHT X-ray diffraction experiments using conventional and synchrotron facilities. The non-ambient data confirm the central role played by the $T$-site in controlling the structural deformation and, consequently, the bulk thermal expansion and compressibility. In conclusion, zircon-type structure has been found to be always less compressible than monazite-type counterparts, while, within each structural type, phosphates are systematically less compressible than arsenates. The occurrence of P-induced phase transitions in both chernovite-(Y) and xenotime-(Y) leads to a larger HP stability field of phosphates if compared to arsenates with a zircon-type structure.

# Hellandite group minerals from alkali syenite ejecta (Roman Region of Central Italy): mineral chemistry, crystal chemistry structure, genetic conditions, and associations with other REE-mineral phases

Perna M.G.*[1], Zaccaria D.[1], Rosatelli G.[1], Stoppani F.S.[2], Curti E.[2], Spratt J.[3], Humphreys-Williams E.[3], Najorka J.[3], Brownscombe W.[3], Nestola F.[4] & Stoppa F.[1]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti.
[2] Gruppo Mineralogico Romano, Roma. [3] Natural History Museum, London (UK).
[4] Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* mariagrazia.perna@unich.it

*Keywords:* hellandite, rare earth elements, Vico volcanic complex.

Hellandite group minerals (hellandite s.s., cipriianite, ferri-hellandite, ferri-mottanaite, mottanaite and tadzhikite) represent a complex group of rare REE-rich borosilicates. We analysed several hellandite crystals from alkali syenite ejecta from the Vico volcanic complex, Roman Region of central Italy. A vast range of REE-rich minerals in the Roman Region is mainly associated with a network of fluorcarbonatite and alkali syenites dikes and stocks, plus carbothermal deposits of fluorine-ore (e.g., Stoppa et al., 2019). Alkali syenites represent the most frequent ejecta of igneous subvolcanic rocks with some fine grained, mineralised peripheral zones with Th-, U-, Zr-, Nb-, V- and LREE-bearing phosphates, silicates, vanadates, oxides and carbonates, that occur as disseminated grains among k-feldspar phenocrysts or cavity-lining druses.

The analysed hellandite crystals offer an insight into a complex history of intergrowth-overgrowth and zoning of hellandite-(Ce), mottanaite-(Ce) and ferri-mottanaite-(Ce), accompanied by brockite and pyrochlore crystallisation. We present a new structural refinement of hellandite-(Ce) and the first Raman spectrum of ferri-mottanaite-(Ce), several representative new analyses and a new molar-fraction recalculation scheme.

We distinguished two different main crystal types, in which we observed a chemical transition from hellandite s.s. to mottanaite to ferri-mottanaite. These observations pose the basis for calculating the molar fractions between the different chemical species of the hellandite group and the possible presence of an immiscibility gap.

Following Oberti et al. (1999, 2002) for the crystal chemical structure, our data confirms the positive correlation between the cell parameters a, b, c and V with the increase of CaO wt.%, but also our hellandite *s.s.* shows a peculiar high ss (site scattering) at the T site (epfu) and the shortest bond concerning literature data.

Crystal texture, crystallisation hierarchy and the association with other HFSE-REE phases indicate a complex evolution and crystal composition variation during the late stage of syenite crystallisation and a possible contribution of REE-rich carbothermal/hydrothermal fluids.

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# Structural modelling and tensile failure study of the karstified Dammam formation

Romagnoli R.* & Al-Shakban J.

Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* raffaele.romagnoli@polito.it

*Keywords:* pore pressure, in situ stress, rock strength.

Dammam is one of the most tiresome formations that drillers challenge while drilling in the oil fields which located in south of Iraq and north of Kuwait. Therefore, the development of a geomechanical study may play a meaningful role in identifying the causes and establishing appropriate solutions to minimize the drilling cost. This research paper is to define the Geostatic stresses, Pore pressure, Rock mechanical strength, Elastic Modulus and build one-dimensional mechanical earth model utilizing the most common failure criteria; Mohr Coulomb, Mogi Coulomb and Stassi d'Alia. The best failure envelopes which anticipated the shear failure are Mogi and Stassi d'Alia in contrast with Mohr, while all criteria accord the same results with respect to the tensile failure. No laboratory test such as Tri axial, Uni axial and Brazilian tests are available to be utilized for calibration purposes, for that reason the only log derived parameters have been employed to construct the mud window (MW). MW assists determining the maximum mud weight to avoid drilling induced tensile failure while cementing and overbalanced drilling. The same thing regarding the horizontal stresses, no Leak of test or hydraulic fracture data are obtainable to match the geostatic horizontal stresses. On the other hand, measured pore pressure at two points of different intervals within the formation were exploited to accommodate the predicted pore pressure. However, many empirical equations are available to define the pore pressure from sonic and resistivity logs as well as from seismic velocity modeling. Eaton sonic technique was the most appropriate equation to anticipate the pore pressure especially at young basins, therefor it was adopted to establish a continuous profile of Pore pressure along the Dammam interval.

# Feasibility and long term sustainability of the transition to electric mobility

Sanginesi F.[1], Millacci G.[1], Giaccherini A.[1], Buccianti A.[1], Fusi L.[2], Di Benedetto F.*[3] & Pardi L.[4]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Matematica e Informatica "Ulisse Dini", Università di Firenze. [3] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. [4] Istituto per i Processi Chimico-Fisici, CNR, Pisa.

*Corresponding author e-mail:* francesco.dibenedetto@unife.it

*Keywords:* lithium sustainability, compartmental model, reserves and resources scenarios.

A sustainable global mobility where Internal Combustion Engine (ICE) vehicles, are replaced less impactant, electric vehicles (EVs) powered by lithium-ion batteries (LiBs), is still possible? The present study aims at providing an answer to this question, through the design of an innovative compartmental predator (the vehicle battery packs)-prey (the Li resource) model. Model scenarios have been considered accounting for three different estimates of the available resource, i.e., the declared reserves, the hypothesized resources, and the full beneficiation of dissolved Li in the oceans. Input data were provided from the historical data of Li primary production, EVs production, recycling rates.

According to the obtained results, the replacement of the ICE vehicles fleet is accounted only under extreme, unrealistic situations, unless the Li "stored" in the oceans is considered. The main available policies, i.e., the optimisation of the resource share (almost entirely dedicated to mobility issues) and of recycling strategies (evaluated up to more than 90%) have a modest effect on the achievement of fleet replacement. The total amount of geological lithium resources results as the main limiting factor for the full transition to EVs. The peak of production according to the developed model will occur between 2078 and 2130, unless seawater Li is accounted for.

The future of the global mobility in a resource-constrained world should be driven toward a model based on the service rather than the individual property of vehicles. Planning a total number of electric vehicles able to assure long term sustainability will be also highly relevant.

# Recycling of ornamental stone scraps through gravity and magnetic methodologies: the case study of Buddusò Quarrying District (Northern Sardinia, Italy) - Part II

Vaccaro C.[1], Aquilano A.*[2] & Marrocchino E.[1]

[1] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara. [2] Dipartimento di Architettura, Università di Ferrara.

*Corresponding author e-mail:* qlnnnl@unife.it

*Keywords:* critcal raw material, recycling, quarry waste.

In recent years, Critical Raw Materials (CRM) have become a key issue for the European Union due to the economic importance and the risk of procurement. In fact, they represent a key factor in addressing the ecological transition process. In this context, the EU is heavily dependent on non-EU countries for the supply of CRM and their supply chains are particularly fragile ecosystems. For these reasons, the EU is adopting a series of initiatives and policies to achieve a certain degree of independence in CRM procurement through reuse and recycling (European Commission, 2020).

In the context of waste recycling for the procurement of raw materials, quarrying and processing scraps from ornamental granite rocks can potentially represent a valid source of secondary CRM. This, especially considering the large amount of waste produced by these activities.

The aim of this study, which is part of a PhD project, is to verify the effectiveness of gravity and magnetic separation in obtaining fractions enriched in minerals containing CRM, starting from scraps of granite rocks from the Buddusò quarrying district (northern Sardinia).

Firstly, the ferromagnetic material (manually removed by a magnet from the 7 fractions captured by the wet shaking table) was weighted.

The semiquantitative main oxides compositions of 21 subsamples, obtained by gravity and magnetic separation, were acquired through SEM-EDS spectrometry on pressed powder tablets, using a Zeiss EVO MA15 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an INCA 300 EDS spectrometer (Oxford Instrument, Abingdon, Germany). Moreover, SEM-EDS observations of 7 paramagnetic mineral fractions, obtained by magnetic separation, allowed identifying minerals containing CRM. For representative results, the minerals of each paramagnetic fraction were randomly attached to a circular stub (area of 1.12 $cm^2$). Furthermore, the specific gravity of the paramagnetic fractions was determined through an Accupyc II gas pycnometer (Micromeritcs, Norcross, United States).

The sub-sample, in which the heavier minerals were accumulated, compared to the other sub-samples showed the following characteristics:

- higher percentage of recovery of ferromagnetic minerals;
- higher specific gravity;
- higher content of Fe, which was associated with lower content of Si, Al, K and Na;
- greater quantity of minerals identified through SEM observations (10 minerals identified) containing CRM such as La, Ce, Pr, Nd, Sm, Gd, Th. In the other sub-samples, these minerals were absent or present in a very small quantity (1-2 minerals identified).

These preliminary results, accomplished on a selection of samples, highlighted that gravity and magnetic separation represent a suitable approach for obtaining heavy minerals with high mining potential from ornamental granite scraps.

European Commission (2020) - Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability. COM/2020/474 final.

# La Queglia carbonatitic melnöite: a notable example of an ultra-alkaline rock variant in Italy

Vichi G.[1], Perna M.G.*[1-2], Ambrosio F.[1], Rosatelli G.[1-2], Cirillo D.[1-5], Broom-Fendley S.[3], Vladykin N.[4(†)], Zaccaria D.[1-2] & Stoppa F.[1-2]

[1] Dipartimento di Scienze Psicologiche, della Salute e del Territorio, Università «G. d'Annunzio», Chieti. [2] Centro Studi e Tecnologie Avanzate, Università «G. d'Annunzio», Chieti. [3] Camborne School of Mines, University of Exeter (UK). [4] Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences, Irkutsk (Russia). [5] Centro interuniversitario per l'analisi sismotettonica tridimensionale con applicazioni territoriali, Università «G. d'Annunzio», Chieti.

*Corresponding author e-mail:* mariagrazia.perna@unich.it

*Keywords:* ultramafic lamprophyres, melnöites, carbonatites.

Very primitive ultramafic igneous rocks occur at La Queglia Mt. (Abruzzo, Italy). They form a strongly deformed sill–dyke system now tilted at 90°. These rocks were initially classified as ålnöite and, subsequently, have been suggested to be a carbonatitic olivine melilitite. However, further investigation and interpretation of these rocks is needed due to the presence of hand-specimen-scale textural variation suggesting a complex petrogenesis. We study the texture, mineral chemistry, and whole-rock geochemistry to define three main rock-types. (1) A brecciated rock with an ocellar texture which consists of calcite pseudomorphs after olivine and melilite, plus fresh diopside in a groundmass of phlogopite, biotite, aegirine, kaersutite, andradite, calcite, apatite, perovskite and chlorite. Zoned ocelli in this rock show an amoeboid shape, agglutination, and menisci typical of a plastic state. (2) A quenched rock with a spinifex texture containing long feathery phenocrysts of diopside and biotite suspended in a groundmass of nepheline, aegirine, apatite, Ti-magnetite, plus abundant carbonate and some K-feldspar and zeolites. (3) A coarse-grained rock composed of calcite plus intergranular glauconite, a mixture of Si-Al-spinel and Ti-magnetite, accessory barite, pyrite, and chabazite-K. The igneous rocks at La Queglia show extreme $SiO_2$-undersaturation (33.5-37.3 wt.% $SiO_2$), high MgO content and $TiO_2/Al_2O_3$ ratios. Rock-type 1 has a lower Mg number (Mg# = 100*(Mg/(Mg+$Fe^{2+}$))), higher Ca number (Ca# = 100*(Ca/(Ca+Mg))), high Cr+Ni (up to 1100 ppm) and rare earth elements (REE) contents and La/Lu ratio, compared to rock-type 2 at La Queglia. Perovskite and chromite accumulation seems an important agent during rock differentiation. Rock-type 3 shows REE cross-over with rock-type 2 suggesting light (L)REE concentration in a carbothermal residuum. La Queglia rocks are an end-member compared to other Upper Cretaceous and Paleogene Italian lamprophyres, suggesting a low degree of melting of a HIMU garnet-bearing mantle source.

# Humankind as geological super-agent and the Anthropocene predicament

Zampieri D.*

Dipartimento di Geoscienze, Università di Padova.

*Corresponding author e-mail:* dario.zampieri@unipd.it

*Keywords:* Anthropocene, planetary boundaries.

Humans move tremendous amounts of soil and rock. Construction and mining activities account for about 30% of all the material transported, while the remaining 70% is unintentionally moved as by-product of agriculture. Natural processes have lowered continental surfaces by a few tens of meters per million years. In contrast, human activities lower continental surfaces by a few hundred meters per million years. This difference makes Homo sapiens the most important geomorphic agent, who has modified nearly 80% of the ice-free area in both the form and sediment fluxes of the landscapes.

The emergence of the new epoch Anthropocene, different from the relatively stable Holocene epoch, makes clear that global population and economic growth are challenging the safe operating space for humanity. In particular, two core boundaries – climate change and biosphere integrity – have been identified. The climate change due to Earth energy imbalance following the carbon cycle perturbation requires a rapid exit from fossil fuel use and the adoption of low-carbon technologies to produce energy. This paradigm shift in energy production and consumption, will require a wide range and high quantities of minerals and materials to meet the rapidly growing need for more wind turbines and solar PVs. The clean energy transition will be significantly mineral intensive. In turn, mining will continue to affect the ecosystems, through fossil fuel use, deforestation, fragmentation of biomes, biodiversity loss, freshwater exploitation and contamination. The Anthropocene predicament cannot be solved the way a problem is solved. The answer is not simply scientific and technological, but also social, cultural and political.

# S49.

# Application of cutting edge techniques in global geochemistry: isotopic reservoirs from deep earth, food traceability and $CO_2$ storage

*Conveners & Chairpersons*


*Elena Marrocchino (University of Ferrara)*

*Valeria Medoro (University of Ferrara)*

*Tommaso Giovanardi (University of Modena and Reggio Emilia)*

*Pierangelo Romano (INGV)*

# How can $CO_2$ diffusion impact seal efficiency: a reactive transport modelling investigation

Beduschi M.V.*[1], Geloni C.[2], Gherardi F.[3] & Toscani G.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Geolab, ENI S.p.A., San Donato Milanese (MI). [3] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* mariavittoria.beduschi01@universitadipavia.it

*Keywords:* Carbon Capture & Storage, numerical models, reactive transport.

Storage of carbon dioxide in geological formations, including depleted oil and gas reservoirs or deep saline aquifers, is one of the strategies to mitigate the environmental consequences of the rising level of anthropogenic $CO_2$ emissions to the atmosphere and thus to reducing the greenhouse impact on climate change.

It is known that injected $CO_2$ can induce chemico-physical changes in connate fluids (density and viscosity variations, pH drop and carbon increase) with possible perturbations on the hydrodynamic regime and the geochemistry of the natural state of the system. Numerical models represent one of the most efficient tools to investigate and quantify these subsurface phenomena giving information on $CO_2$ migration paths, $CO_2$ accumulations, and $CO_2$ driven mineralogical transformations in medium-long terms if any.

Non-isothermal multiphase flow and reactive transport models are among numerical techniques nowadays available for simulating $CO_2$ reactive dynamics. The predictive strength of such numerical models is greater the larger the set of experimental data and field observations that contribute to reducing the degree of uncertainty affecting multi-physical and multi-parametric numerical models. At the same time, the more site-specific the petrophysical and mineralogical characterization, the more realistic are the proposed numerical models. Over the last years a modelling protocol was developed by ENI for simulating the behavior of the storage complex in terms of $CO_2$ volumes accommodated in the reservoir in order to assess its effects on minerals, connate fluids, and caprock sealing efficiency. The workflow consists of a preliminary thermodynamic description of site-specific mineral phases conducted in synergy with experimental analysis (SEM, XRD), a series of 0D-batch geochemical models to define the mineral assembly and kinetic parameters, and a final step of 1D reactive transport models which couple mass migration to geochemical-mineralogical reactivity. This last step represents the ideal link between experimental activity and reservoir models.

A case of $CO_2$ diffusion from reservoir into the seal is presented to address the alterations of clays, micas and carbonates affecting seal porosity in the post injection period. In this first application, the reservoir conditions are maintained fixed. A sensitivity analysis on diffusion coefficient, calcite kinetic parameters and chemical composition of water boundary was conducted to assess different geochemical scenarios, from the most severe conditions (acidic conditions, fast calcite reaction rates and high diffusion coefficient) to mild conditions (pH = 6, slow calcite reaction rates and slow diffusion). Models showed that when reservoir buffers pH are around 5.0, the seal caprock efficiency is enforced. On the other hand, reservoir fluids with persistent pH below 4.9 indicate a potential risk of $CO_2$ leakage.

A proprietary software platform (e-muflot) is used for this numerical investigation.

# The experimental laboratory activity at DST-Unifi and CNR-IGG (Florence, Italy) as a strategic tool in $CO_2$ storage projects

Bicocchi G.[1], Orlando A.[2], Borrini D.[1] & Ruggieri G.*[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* giovanni.ruggieri@igg.cnr.it

*Keywords:* Carbon Capture and Storage, fluid-rock Interaction, experimental mineralogy and petrology.

Carbon Capture and Storage (CCS) practice received favourable scrutiny during the COP 26 conference. This approach is considered useful to remove $CO_2$ from the atmosphere and sequester it underground. However, CCS projects are still challenging both in their design and in their actualization. Indeed, a lot of different parameters should be well known before initiating a CCS project and starting injecting $CO_2$-rich fluids underground. The mineralogy and geo-mechanical characteristics of the rocks of underground reservoir are crucial parameters to be characterized in order to ensure a positive outcome of the project (i.e., a safe storage of $CO_2$ by reacting it with the host rocks). CCS projects feasibility is often evaluated by geochemical numerical models, which are requested to provide scenarios for the underground injection of $CO_2$. Despite the constantly increasing capability of numerical modelling software over the last decades, numerical models still depend on prior accurate characterization of rock samples, on the availability of coherent thermodynamic database for mineral phases and on the results of experimental activity, the latter helping to calibrate the geochemical models to achieve more reliable outputs of the numerical simulations. The Experimental Mineralogy and Petrology laboratory (DST-UNIFI and CNR-IGG, Florence), worked in different kinds of CCS projects investigating at variable P-T conditions (1-60 bar and 25-250°C) the $CO_2$ and $CO_2$-$H_2S$ fluids reaction paths with ultramafic and metamorphic rocks (Orlando et al., 2011, 2012; Bicocchi et al., 2020). To carry out replicable and comparable fluid-rock interaction experiments, procedures were standardized to find the best analytical procedures for the characterization of the solid materials used before and obtained after the experiments and the composition of the liquid resulting from the fluid-rock interaction experiments. The instrument used is a 25 ml stainless-steel PARR 5500 HP reactor equipped with a magnetic stirrer in which solid (powders or rock blocks) and fluids (liquid and/or gas) are inserted. The reactor is equipped with a thermocouple and an analog manometer for the monitoring of T and P during the runs. Special valves allow for the "in situ" injection of gas and sampling of fluids. After the experiments liquids are filtered and analysed for the content of major ions and trace metals via IC and ICP-MS, respectively. Before runs liquids have been degassed through a $N_2$ flux in the runs in which $O_2$ of atmospheric origin was to be removed as much as possible to better simulate the redox conditions of deep reservoirs. XRD, SEM-EDS and EPMA analyses are used routinely on the pristine and reacted solids to determine changes in the mineralogical and chemical compositions. These analyses give pivotal information about the chemical and mineralogical changes occurring in underground reservoirs in which $CO_2$ is being injected.

Bicocchi G., Orlando A., Ruggieri G., Borrini D., Rielli A. & Boschi C. (2020) - Towards zero emission geothermal plants in the framework of the H2020 GECO project: Insights on gas re-injection in geothermal reservoir and serpentinite carbonation from batch reactor experiments. EGU General Assembly 2020, EGU2020-691. https://doi.org/10.5194/egusphere-egu2020-691.

Orlando A., Borrini D. & Marini L. (2011) - Dissolution and carbonation of a serpentinite: Inferences from acid attack and high P-T experiments performed in aqueous solutions at variable salinity. Appl. Geochem., 26, 1569-1583.

Orlando A., Lelli M. & Marini L. (2012) - Production of amorphous hydrated impure magnesium carbonate through ex situ carbonation. Appl. Geochem., 27, 2500-2510.

# Towards *in-situ* Ti isotope determination in silicates

Cannaò E.*[1], Tiepolo M.[1], Forni F.[1], Sessa G.[1], Greber N.D.[2] & Storck J.-C.[2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Institute of Geological Sciences, University of Bern (Switzerland).

*Corresponding author e-mail:* enrico.cannao@unimi.it

*Keywords:* titanium isotopes, in-situ analyses, LA-MC-ICP-MS.

Among non-traditional stable isotopes, titanium (Ti) isotope systematic is one of the most suitable for investigating Earth's processes, with main applications ranging from early solar system evolution to magma differentiation and continental crust formation (Millet et al., 2016). Although Ti has been generally considered immobile in metamorphic aqueous fluids, experimental investigations on rutile and natural rock record have shown the high solubility of Ti in halogen-bearing aqueous fluids (Rapp et al., 2010). This evidence outlines the potential use of Ti isotopes to investigate low- to medium-temperature metamorphic processes in combination with other common isotopic tracers, such as $\delta^{18}O$, $\delta^{11}B$ and $\delta^{7}Li$. Titanium has 5 stable isotopes, $^{46}Ti$ (8.25%), $^{47}Ti$ (7.44%), $^{48}Ti$ (73.72%), $^{49}Ti$ (5.41%) and $^{50}Ti$ (5.18%), and show small variations in their ratios related to mass-dependent (expressed as $\delta^{49}Ti$) and mass-independent (expressed as $\varepsilon^{x}Ti$) isotope fractionation (ca. 1‰ at the δ-scale and ca. 20‱ at the ε-scale). As a consequence, precise Ti isotope signatures have been obtained on whole-rock and mineral separates in solution-mode after chemical purification applying double-spike technique. So far, *in-situ* Ti isotope determination by LA-MC-ICP-MS has been limited to Ca-Al-rich inclusions in meteorites (Williams et al., 2016) and little is known about the *in-situ* Ti isotope determinati on in major Ti-bearing silicates to disclose geological processes through isotope disequilibrium. Here, we present a pilot project aimed at filling this gap providing an analytical protocol to determine the *in-situ* $\delta^{49}Ti$ through LA-MC-ICP-MS of different minerals of magmatic and metamorphic derivation: amphibole, titanite, clinopyroxene, Ti-clinohumite, rutile, garnet and mica. Our preliminary results report that internal and external precision is commonly better than 0.3 and 0.2‰, respectively, but suffer matrix effects that can be managed by acquiring interference masses and with minor offline data treatment. The proposed LA-MC-ICP-MS procedure allows to achieve adequately precise and accurate $\delta^{49}Ti$ data thus opening new scenario for micro-analytical research activities in the fields of geo- and cosmo-chemistry.

Millet M.A., Dauphas N., Greber N.D., Burton K.W., Dale C.W., Debret B., Macpherson C.G., Nowell G.M. & Williams H.M. (2016) - Titanium stable isotope investigation of magmatic processes on the Earth and Moon. Earth Planet Sci. Let., 449, 197-205.

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Williams C. D., Janney P.E., Hines R.R. & Wadhwa M. (2016) - Precise titanium isotope compositions of refractory inclusions in the Allende CV3 chondrite by LA-MC-ICPMS. Chem. Geol., 436, 1-10.

# Microwave-assisted serpentine reactions with $CO_2$ as a transferrable technology for carbon capture and storage

Corti M.*, Maroni P., Barbarossa S., Campione M., Capitani G.C. & Malaspina N.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* nadia.malaspina@unimib.it

*Keywords:* mineral carbonation, microwave-assisted reactions, serpentine.

In the last decades many studies have been focusing on carbon capture and storage to find a possible remedy to reduce the large increase of anthropogenic carbon dioxide. Mineral Carbonation is a potential solution for almost irreversible chemical long-term carbon capture and storage. It concerns the combination of CaO and MgO with $CO_2$ forming spontaneously and exothermically dolomite and magnesite. However, kinetic barriers pose sever limitations for the practical exploitation of this reaction.

High fractions of MgO are available in silicates such as olivine, orthopyroxene, clinopyroxene and serpentine. To date, data reported that serpentine polymorphs, above all antigorite, is an excellent candidate for fixing the $CO_2$ as the reaction efficiency is approximately 92% compared to lizardite (40%), and olivine (66%).

The microwave assisted process for carbon capture and storage is an innovative technology that can be employed to catalyse the reaction through thermal and non-thermal mechanisms. Some pioneering tests of direct carbonation by microwave hydrothermal equipment have been performed on olivine, lizardite and chrysotile powders (White et al., 2004) but not on antigorite. The structure of serpentine is characterized by stacked layers of $SiO_2$ and brucite, $Mg(OH)_2$. For this reason, mineral carbonation of serpentine involves in principle dissolution of $SiO_2$ layers, dissolution/dehydration of $Mg(OH)_2$ layers, and precipitation of magnesium carbonate.

To address the carbonation reaction mechanism of serpentine, experiments have been performed on model crystalline powders with the aid of a microwave reactor operating at controlled pressure, temperature and environment. Aliquotes of pure brucite, chrysotile, and lizardite, synthesised in our laboratories, were reacted with $CO_2$ under controlled conditions and duration. The characterisation of the structure and morphology of the processed powders was performed by X-Ray Diffraction and by Scanning and Transmission Electron Microscopy.

White W.B., Silsbee M.R. & Kearns B.J. (2004) - Reaction mechanisms of magnesium silicates with carbon dioxide in microwave fields. Pennsylvania State University (US).

# Combined UAS measurements for monitoring dangerous volcanic contexts: applications at the Pisciarelli fumarolic field (Campi Flegrei) and Vesuvius crater

Fedele A.*, Somma R., Matano F., Troise C. & De Natale G.

INGV, Osservatorio Vesuviano, Napoli.

*Corresponding author e-mail:* alessandro.fedele@ingv.it

*Keywords:* Unmanned Aerial Systems, volcanology, monitoring, Pisciarelli fumarolic field.

Recent developments and availability of Unmanned Aerial Systems (UASs) in volcanology have contributed to major advances in monitoring active volcanoes and characterizing volcanic landforms and risks. In the past 5 years, hydrothermal activity in the Pisciarelli fumarolic field of the Campi Flegrei caldera (southern Italy) has increased dangerously. This has led local and civil protection authorities to restrict access to volcanological monitoring in the area. In this scenario, sUAS are useful in collecting immediate and real-time data, especially in inaccessible, instable, and/or hazardous, volcanic environments. Main products generated from UAS quadcopter photographs, such as digital terrain data, 3D models, orthophotos and thermal images allowed for the quickly identification of the geomorphologies of the craters at cm-scale resolution and thermal anomalies. Two different drones have been used for mapping, thermal imaging, slope stability studies, and as platforms for sensors to measure outgassing of $CO_2$, $H_2S$, CO and $CH_4$. Analysis derived from the digital imagery captured by the UAS allowed to identify fumaroles, thermal anomalies and volcano-tectonic structures to determine accurate landform changes and in combination with thermal image and atmospheric measurements of hydrothermal gasses to assess hazards in this dangerous volcanic contexts.

# Tracing the provenance of Tuscan Extra Virgin Olive Oil using Sr isotopes and Rare Earth Elements

Ghiotto M.*[1], Ferrari M.[1], Valeriani L.[1-2], Bragagni A.[1], Pucci C.[3], Malpaganti A.[3], Casalini M.[1], Pelacani S.[1], Conticelli S.[1-4], Riccio R.[3], Moretti S.[1] & Tommasini S.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa. [3] Biochemie Lab s.r.l., Campi Bisenzio (FI). [4] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* matthias.ghiotto@unifi.it

*Keywords:* extra virgin olive oil, Sr isotopes, REEs.

The geographical traceability of extra virgin olive oils (EVOO) represents an important issue to guarantee the quality and authenticity of this product, which is mainly produced in the Mediterranean area and exported worldwide. For this purpose, we present a geochemical and isotopic study based on the analysis of the REEs content and the $^{87}Sr/^{86}Sr$ ratio of olives and oils. The REEs content and the $^{87}Sr/^{86}Sr$ ratio are transferred from the bioavailable soil fraction to the olive pulp, and then to the oil, without any significant elemental and isotopic fractionation, making this method promising for olive oil traceability.

The study sites are located in Tuscany, in the Chianti area, High Tiberina Valley, and Maremma with different geological bedrocks and geomorphological settings. Particular attention was paid to minimize local differences in climate, topography, and cultivar. Samples of soils, olives and EVOO were analysed from each olive grove.

The main challenges are represented by the low REEs and Sr content in EVOO and by the complex fatty nature of the matrix, so efficient pre-concentration is required to obtain reliable and precise results. To overcome these difficulties, we set up a procedure to extract REEs and Sr from olive oil and olives involving mechanical stirring and ultrasound assisted extraction (Turk et al., 2019), followed by Sr purification using standard chromatographic techniques. $^{87}Sr/^{86}Sr$ measurements in soil, olives and olive oil were performed by TIMS, while the REEs content was determined by ICP-MS.

Preliminary results highlight that the adopted analytical procedure is able to concentrate Sr and REEs from EVOO, allowing precise measurements. Preliminary data on the whole (i.e., independent of the geological bedrocks) dataset show an appreciable variability of the $^{87}Sr/^{86}Sr$ values among the bioavailable soil portion (0.7079 to 0.7117), olives (0.7081 to 0.7118) and EVOO (0.7085 to 0.7097). The results on the isotope compositions of soil, olives and olive oil will be finally compared with that of the local geology and used to corroborate the traceability method.

Turk M.F., Epova E., Barre J., Berail S., Donard O.X. & Zuliani T. (2019) - Development of the analytical method for $^{87}Sr/^{86}Sr$ determination in olive oil. In: Alexandre J., Janssens S. & Van Loco J. Eds., Book of Abstracts of the 4th International Conference on Metrology in Food and Nutrition. 25, Sciensano.

# Investigating prograde metamorphism and pegmatites formation using tourmaline compositional and B isotopes variations. The case of the Adamello Massif (Southern Alps, Italy).

Magnani L.*[1], Farina F.[1], Pezzotta F.[2], Dini A.[3] & Cannaò E.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] Museo di Storia Naturale, Milano. [3] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* lorenzo.magnani@unimi.it

*Keywords:* tourmaline, metamorphism, pegmatites.

Tourmaline is the main boron (B) host in many magmatic and metamorphic rocks. It is characterized by a complex crystalline structure, with a general formula of $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ featuring three different atomic sites that can host a great variety of elements of widely different charge and ionic radius. This, coupled with the low B diffusivities in its structure and high thermal resilience, makes tourmaline an ideal indicator of its host environment. We investigated the chemical and B isotopic composition of tourmaline in the contact aureole of the Adamello pluton intrusion. These data are used to shed light into the prograde metamorphic history of pelites from low-grade to the upper amphibolite facies where they underwent partial melting generating tourmaline-bearing pegmatites, occasionally lithium enriched. The major elements composition of tourmalines has been characterized by electron microprobe analysis and their $\delta^{11}B$ was determined in-situ by LA-MC-ICP-MS. In the low grade pelites, dravitic tourmaline rims with positive $\delta^{11}B$ (+4 to +6‰) overgrow schorlitic detrital cores ($\delta^{11}B$ between -15 and -10‰). This event may be connected to clay minerals fluid-related loss of adsorbed B during diagenesis and low-grade metamorphism. In medium grade pelites, neoblastic slightly negative dravitic tourmalines (-3 to -4‰) can be linked to white mica dehydration during prograde metamorphism. At amphibolitic facies conditions, the tourmalines are homogeneous dravites, suggesting complete recrystallization. In the contact aureole two types of partially molten metapelites have been recognized. The orbicular pelites formed in a closed system and the tourmaline B isotope composition is ca. +1‰. Banded metapelites, which recorded external fluid influx, exhibit more calcic tourmalines with lower $\delta^{11}B$ (ca. -3‰), allowing us to infer that the fluids interacted with the surrounding carbonates. In the connected anatectic system, tourmaline recorded the cooling history of the pegmatitic melts, particularly in the zoned lithium enriched pegmatites. Interestingly, the average $\delta^{11}B$ values (between 0 and -3‰) of the studied Adamello pegmatites are markedly different from the usual range of $\delta^{11}B$ values of pluton-related LCT pegmatites (e.g., Elba island, $\delta^{11}B$ from -8‰ to -10‰) suggesting a possible different origin. In the Adamello pegmatites, tourmaline composition traced the early fractionation of the most mafic and compatible elements as Mg and Fe in early dravitic cores with isotopic signature similar to that in the banded metapelites. Towards the center of the dyke, tourmaline becomes increasingly schorlitic and then elbaitic (mostly fluor-elbaite). Its $\delta^{11}B$ evolution allowed us to identify fluid exsolution events, during which the $\delta^{11}B$ of pocket tourmalines sharply increased up to 3‰ compared to the magmatic tourmalines.

# Geochemical and isotopic characterization as a tool for identification of relationships between soil and tomato: the case study of Massenzatica (Ferrara)

Marrocchino E.*[1], Aquilano A.[2], Wibisono K.F.[1] & Telloli C.[3]

[1] Dipartimento di Scienze dell'Ambiente e della Prevenzione, Università di Ferrara. [2] Dipartimento di Architettura, Università di Ferrara. [3] Dipartimento Fusione e Tecnologie per la Sicurezza Nucleare, ENEA, Bologna.

*Corresponding author e-mail:* mrrlne@unife.it

*Keywords:* geochemistry, traceability, geographical origin, stable isotope.

Historically, socio-cultural factors and available local natural resources have conditioned food consumption patterns. Links between food and territory are however disappearing due to various causes, including changes in food production and transportation technologies, urbanization, and consumer exposure to non-local experiences through travel and media. In this light, studies on territoriality are becoming relevant for the determination and authentication of the geographical origin of food products. The study on territoriality is based on the hypothesis that chemical elements detected in plants and their products reflect those contained in the soil. The geographical features of the production area, such as soil type and climate, are relevant factors affecting the specific designation, therefore an accurate determination of geographical origin could also be necessary to guarantee the quality and territoriality of the products. Moreover, the increasing demand for healthy and high-quality food products is leading to the development of regulations for the certification of authenticity relating the geographical origin. For this reason, geochemical characterization, based on the determination of major and trace elements detected in some tomato plants, in their products and in the soils where they grew up (Katerinopoulou et al., 2020), is the basis of this work, which aims to present preliminary results to establish a method to identify the geographical origin. The purpose of this study is to apply an established method to identify the geographical origin of tomato variety cultivated in a well-defined area in Massenzatica (Municipality of Mesola, Ferrara, NE of Italy). Sampling was undertaken at the beginning of August 2021 and samples were collected from a randomized field. Together with the tomato plants also fruits, roots and soils have been collected to analyse each part and correlate the geochemical data obtained using ICP-MS and IRMS techniques (on fruits, plants, roots, and soils) and XRF analysis (only on soil samples). The results confirm that some major and trace elements could be used as geochemical markers according to the geological areas. These elements, therefore, could be useful to establish geochemical fingerprints for testing the origin of this product and create a protected designation of origin label.

Katerinopoulou K., Kontogeorgos A., Salmas C.E., Patakas A. & Ladavos A. (2020) - Geographical Origin Authentication of Agri-Food Products: A Review. Foods, 9, 489.

# Olives traceability by REE *and trace elements* amount: a statistical approach to determine the geochemical composition from soils and leaves

Medoro V.*[1], Ferretti G.[2], Galamini G.[1], Rotondi A.[3], Morrone L.[3], Faccini B.[1] & Coltorti M.[1]

[1] Dipartimento di Fisica e Scienze della Terra, Universita di Ferrara. [2] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara. [3] Istituto per la Bioeconomia, CNR, Bologna.

*Corresponding author e-mail:* valeria.medoro@unife.it

*Keywords:* agri-food traceability, geomaterials, sustainable agriculture.

In the last decade, the need for quality and food safety has become more pressing, still providing the requirement of agri-food products with unequivocal geographical identification. Furthermore, the environmental problem is a core issue and involves an implied demand in terms of eco-friendly and human healthy agricultural practices. In this framework, the work aims at investigating soil, leaves and olives REE and trace elements compositions under different treatment managements to check the amount uptaken by the plant and verify the feasibility of the geochemical traceability. Two sites, Montiano (MN) and San Lazzaro (SL) where three different foliar treatments were carried out for each site, allowing an inter and intra comparison between treatments and localities. Principal Component Analysis (PCA) of leaves and olives highlighted that different foliar treatments can be identified based on different geochemical contents (total variance: 95.64% and 91.08% in MN; 71.31% and 85.33% in SL of leaves and olives, respectively). Slightly lower, although still quite good, results are given by PCA applied to area discrimination (87.46% and 80.43% of total variance). Partial Least Squares-Discriminant Analysis (PLS-DA) confirmed good discrimination between different treatments in each area, as well as between the two areas. Variable Importance in the Projection (VIP) analyses provided to identify which elements could be considered as potential discriminators in the model in order to correlate leaves and olives from the same area: i) Sm and Dy in MN site and ii) Rb, Zr, La and Th in SL field; in order to discriminate different areas Rb and Sr were the best identifiers.

# An integrated multiscale approach to estimate the $CO_2$ storage and sealing capacity of carbonate rocks: case studies from the Umbria-Marche Apennines

Mitillo N.*[1], Urbani M.[1], Barchi M.R.[1], Cirilli S.[1], De Paola N.[2] & Trippetta F.[3]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Department of Earth Sciences, Durham University (UK).
[3] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* nicola.mitillo@studenti.unipg.it

*Keywords:* $CO_2$ storage, petrophysical properties, fracture density.

The study is part of a multidisciplinary project devoted to the investigation of the influence of fracturing on primary porosity and permeability of carbonate rocks. Carbonate-bearing reservoirs host most of the largest known natural gas and hydrocarbon reserves due to their high primary porosity and typical brittle rheological behavior prone to develop a, sometimes complex, system of fractures. At the same time, such characteristics, in particular primary porosity, can be influenced by different diagenetic processes, such as pore-filling and/or dissolution phenomenon, causing sometimes a drastically change of rock texture and petrophysical properties. Moreover, the presence of faults and fractures increases the complexity of porosity estimation, depending on the lithofacies type. In porous lithofacies, fracturing usually produces a porosity decrease, whilst on tight lithofacies, fracturing usually produces a porosity increase. However, the complex interactions between porosity and fractures results difficult to be predicted and consequently, a multiscale characterization is necessary. In this work we present data and results coming from the northern sector of the Apennines, the Umbria-Marche domain, where we characterized the large petrophysical variability (both vertical and horizontal) of carbonate Jurassic successions including both shallow-water platform limestones (e.g., Calcare Massiccio Fm) and the overlying basinal lithofacies (e.g., Corniola, Calcari Diasprigni, Maiolica formations). At the macro-mesoscopic scale, laser-scanner techniques were used to characterize fault and fractures at the outcrop scale obtaining 3D-images of the outcrops, to analyze in detail both the propagation of fractures in the different lithofacies and possible conjugate fracture-systems. Starting from the 3D-images we built Discrete Fracture Networks to evaluate the effects of fracturing on primary porosity and the behavior of the rocks in terms of permeability and fluid flow at the outcrop scale. At the microscopic scale, a detailed sedimentary petrography study was carried out through optical microscope, describing for each sample the rock-fabric and porosity (both primary and secondary). Moreover, core analyses were performed to measure both effective and total porosity, in order to validate the data coming from thin sections. Lastly, the macro-mesoscopic scale data were correlated and integrated with those obtained at microscopic scale to find relationships and to highlight the effects of different fracturing intensity on primary porosity. As a result, such study permits to evaluate the potential of different carbonate rocks, in terms of permeability and storage capacity, providing a multiscale reading key for the identification of reservoir/seal behavior of carbonate rocks for CCS purposing.

# Integrating mineral-scale processes into global geochemical changes: a journey into the evolution of the continental crust

Moreira H.*

CNRS, Géosciences Montpellier, Université de Montpellier (France).

*Corresponding author e-mail:* hugo.moreira@umontpellier.fr

*Keywords:* zircon inclusions, crustal evolution, plate tectonics.

The growth and the evolution of the continental crust influenced subtle and dramatic changes in the atmosphere, the lithosphere, and the mantle. Although the remnant geological record has been intensively studied, ascertaining the early history conditions of these changes in the early Palaeoproterozoic and further back in the Archaean has been proven challenging given the scarcity of the geological record. This has led to a multitude of conflicting models for the crustal evolution in the early Earth.

A unifying link between the changes and the evolution of mantle-crust-atmosphere-hydrosphere interaction is yet to be fully reconciled. For instance, secular transformations of the ocean and atmosphere are evident from several proxies but the repercussions of these transformations on magmatic and geochemical processes in the lithosphere remain unclear. Moreover, no clear consensus has been reached on the timing of modern-style plate tectonic initiation and the evolution of net growth of the continental crust.

To explain overt and cryptic global trends in the geochemistry of magmatic rocks, a better understanding of mineral reactions and how these control trace element evolution in magmas and residue at the lithosphere-scale is paramount. For example, the elemental composition of apatite inclusions hosted by zircon and titanite offers a better understanding of recharging and crystallising magmas; whereas the Sr isotope variation can be used to constrain the nature of the magma source. These proxies rely on the robust data acquisition of other isotope systems with different geochemical behaviour, such as U-Pb and Lu-Hf analyses in the host zircon crystal. A great deal of interpretation is based in the intercomparison between these isotope systems and, as such, it is important to develop analytical technics to optimise both precision and spatial resolution in tiny inclusions and small zircon grains.

In this talk, I aim to cover recent developments in in-situ analyses of accessory phases, in particular zircon and its inclusions, and how these can be used to better understand the parental rocks from which they crystallised. I will present recent developments on measuring the elemental composition via EPMA, the $^{86}Sr/^{87}Sr$ isotopic variation via LA-MC-ICP-MS, and the fugacity of apatite inclusions based on S speciation via μ-XANES. The large information from several inclusions from co-magmatic rocks is then interpreted in the light of previous U-Pb, Lu-Hf, trace elements and oxygen isotope analyses of the host zircon grains. Altogether, I hope to demonstrate that looking into small mineral scale variations can offer in-depth insights into the evolution of the atmosphere-crust-mantle system.

# Assessing the transfer factors (TFs) of contaminants from soil to plants: the case study of Campania region (Southern Italy)

Pacifico L.R.*[1], Guarino A.[1], Brambilla G.[2], Pizzolante A.[3] & Albanese S.[1]

[1] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [2] Dipartimento di Sicurezza Alimentare, Nutrizione e Sanità Pubblica Veterinaria, Istituto Superiore di Sanità, Roma. [3] Istituto Zooprofilattico Sperimentale del Mezzogiorno, Portici (NA).

*Corresponding author e-mail:* luciarita.pacifico@unina.it

*Keywords:* Transfer Factor, soil, plant.

The presence of potentially toxic elements (PTEs) derived from anthropogenic sources in soil represents a serious issue for animal and human health. These elements can easily move from the geological compartment to the biological compartment through to the food chain. (Jarup, 2003).

The geochemical knowledge of a territory allows to assess the degree of contamination of the environment, to locate the sources of environmental hazard and, possibly, to manage the anomalous concentrations of the PTEs in environmental matrices with the purpose of eliminating or minimizing their negative impact on the health of living beings. (Reimann & de Caritat, 2005).

Several studies have been already carried out to determine the distribution patters of PTEs in soil of Campania region (Southern Italy) (De Vivo et al., 2022) but little is known about the transfer processes of contaminants from soils to agricultural products.

In light of above, we present the results of a new study whose purpose was to determine the Transfer Factors (TFs) of PTEs from soil to a serie of agricultural products commonly grown in Campania.

Considering the complex geological and geomorphological settings of the region and the diffuse presence of an historical anthropization related with industry, agriculture, and urbanization, TFs were calculated for a relevant number of fruit and vegetable samples (3731 specimens). They were collected across the whole regional territory to detect differences between analysed species and to highlight the spatial changes in TFs occurring for individual species.

The TFs were calculated starting from the quasi-total (based on Aqua Regia leaching) and bioavailable (based on Ammonium Nitrate leaching) concentrations of PTEs in 7000 and 1500 soil samples, respectively.

Preliminary results show that TFs determined for the various agricultural species vary in space and in amount independently from the original elemental concentrations in soils. High values of TFs are found in areas where PTE concentrations in soil are low and vice versa, thus suggesting that multiple regression and multivariate analyses could be performed to investigate if some additional chemical and physical characteristic of soil (pH, grainsize, OM, etc.) could have a relevant weight on the transfer processes of contaminant from the soil to the plant life.

De Vivo B., Albanese S. & Cerino P. (2022) - Monitoraggio geochimico-ambientale dei suoli e dell'aria della Regione Campania. Piano Campania trasparente. Vol. 4. Aracne editrice, Genzano di Roma.

Järup L. (2003) - Hazards of heavy metal contamination. Br. Med. Bull., 68, 167-182.

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# Calcium oxalates for mineral carbon capture: a new, green and performing method

Pastero L.*[1], Curetti N.[1], Pazzi M.[2], Bernasconi D.[1], Cotellucci A.[1], Corazzari I.[2] & Pavese A.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Chimica, Università di Torino.

*Corresponding author e-mail:* linda.pastero@unito.it

*Keywords:* carbon capture, carbon mineralization, calcium oxalate.

The concentration of $CO_2$ in the atmosphere is steadily increasing due to human activities that add to natural outputs. Many synergic capture methods coupled with reducing emissions need to be considered to maintain concentration levels below the no-return threshold. Mineralization as a permanent carbon capture method and mineral trapping and accelerated weathering of silicate rocks have been suggested as the most suitable hosts for mineralized carbon. Natural weathering can remove some $CO_2$ from the atmosphere, estimated at 300 Mt/yr. Even if the natural process can be accelerated for industrial purposes, the natural weathering kinetics are slow (De Stefanis et al., 2020).

Within this framework, we demonstrated a mineral capture method that involves the reduction of carbon from C(IV) to C(III) using ascorbic acid (vitamin C) as a green $CO_2$ reductant (Pastero et al., 2019; 2021) to precipitate almost insoluble calcium oxalate, doubling the carbon capture efficiency compared to conventional carbonation. Depending on the experimental setup, the reaction's effectiveness was evaluated under variable conditions and reached very high values, with up to 80% of $CO_2$ removed from the pure carbon dioxide atmosphere.

The reaction products are limited to calcium oxalate dihydrate (weddellite), and occasionally the monohydrate phase (whewellite). The system was intentionally kept out of the stability field of the carbonates to avoid competition in the carbon capture process.

The calcium oxalate's thermal degradation was evaluated *in situ* by HT-XRPD and TGA (Curetti et al., 2022). The dissolution of calcium oxalates does not directly produce $CO_2$, avoiding its straight release into the environment. The ascorbic acid degradation products have no or just feeble interference with the production of calcium oxalate from $CO_2$ and are not harmful.

Curetti N., Pastero L., Bernasconi D., Cotellucci A., Corazzari I., Archetti M., Pavese A. (2022) - Thermal Stability of Calcium Oxalates from $CO_2$ Sequestration for Storage Purposes: An *In-Situ* HT-XRPD and TGA Combined Study. Minerals, 12, 53. https://doi.org/10.3390/min12010053.

Destefanis E., Caviglia C., Bernasconi D., Bicchi E., Boero R., Bonadiman C., Confalonieri G., Corazzari I., Mandrone G., Pastero L., Pavese A., Turci F. & Wehrung Q. (2020) - Valorization of MSWI Bottom Ash as a Function of Particle Size Distribution, Using Steam Washing. Sustainability, 12, 9461. https://doi.org/10.3390/su12229461

Pastero L., Curetti N., Ortenzi M.A., Schiavoni M., Destefanis E. & Pavese A. (2019) - CO2 capture and sequestration in stable Ca-oxalate, via Ca-ascorbate promoted green reaction. Sci. Total Environ., 666, 1232-1244.

Pastero L., Marengo A., Boero R. & Pavese A. (2021) - Non-conventional $CO_2$ sequestration *via* Vitamin C promoted green reaction: Yield evaluation. J. CO2 Util., 44, 101420.

# Application of stable isotope techniques to detect the authenticity of high value food products

Perini M.* & Pianezze S.

Centro di Trasferimento Tecnologico, Fondazione Edmund Mach, San Michele all'Adige (TN).

*Corresponding author e-mail:* matteo.perini@fmach.it

*Keywords:* stable isotope ratio analysis, food authenticity, traceability.

Consumers are increasingly interested in products having a specific Geographical Indication (GI) (e.g., PDO, PGI or TSG), healthy food, food supplements and natural compounds, which are usually expensive and therefore more subject to attempts at adulteration. Methods to test the authenticity of these products are thus needed and the analysis of stable isotope ratios (SIRA) of bioelements such as carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), sulfur ($^{34}S/^{32}S$), oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) could meet this requirement. Some recent applications of the SIRA are here presented. The isotope ratio analysis of bulk samples was performed using an isotope ratio mass spectrometer interfaced with an elemental analyzer and a pyrolizer. Furthermore, the $^{2}H/^{1}H$ and $^{13}C/^{12}C$ compound-specific analyses of the single ingredients of different products (e.g., single amino acids or fatty acids) were carried out by using an isotope mass spectrometer connected to a combustion/pyrolysis gas chromatograph. Incorrect labeling and/or adulteration (consisting in, for example, samples watering, addition of exogenous sugars or incorrect geographical origin labelling) can be easily detected in products such as GI wine and must, balsamic vinegar of Modena (Perini et al., 2014) or cheese like Parmigiano Reggiano (Pianezze et al., 2020). In various types of food and dietary supplements the fraudulent use of synthetic or biosynthetic products instead of the natural ones can be identified. Products like Monacolin K, which is naturally present in fermented red yeast rice (Perini et al., 2017), natural L-theanine (extracted from *Camellia Sinensis*) (Perini et al., 2021), vanillin (from the *Vanilla* species) (Perini et al., 2019a), curcumin (from *Curcuma Longa*) and *Serenoa repens* oil (from *Saw Palmetto*) (Perini et al., 2019b) are frequently subject to this type of adulteration.

Perini M., Carbone G. & Camin F. (2017) - Stable isotope ratio analysis for authentication of red yeast rice. Talanta, 174, 228-233.

Perini M., Paolini M., Pace R. & Camin F. (2019b) - The use of stable isotope ratio analysis to characterise saw palmetto (Serenoa Repens) extract. Food chem., 274, 26-34.

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Perini M., Pianezze S., Ziller L. & Camin F. (2021) - Characterization of L-theanine in tea extracts and synthetic products using Stable Isotope Ratio Analysis. J. Food Drug Anal., 29, 312-319.

Pianezze S., Bontempo L., Perini M., Tonon A., Ziller L., Franceschi P. & Camin F. (2020) - $\delta^{34}S$ for tracing the origin of cheese and detecting its authenticity. J. Mass Spectrom., 55, e4451.

# Element mobility during $CO_2$ storage in basaltic rocks: comparing natural systems and laboratory experiments

Romano P.* & Liotta M.

INGV, Palermo.

*Corresponding author e-mail:* pierangelo.romano@ingv.it

*Keywords:* $CO_2$ storage, basalt weathering, carbon cycle.

Our ability to mitigate climate changes is one the most ambitious challenge of the modern society. Basalt rocks are abundant on Earth surface (≈ 10%) and very abundant in the ocean floors and subaerial environments. Glassy matrix and minerals constituting these rocks contain metals ($Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$) that can react with carbonic acid to form metal carbonates ($CaCO_3$, $MgCO_3$ and $FeCO_3$). In this work we first report a data compilation of chemical composition of waters circulating in basalt aquifers worldwide, then we present the first results of laboratory experiments performed with a simple setup of water and $CO_2$ interacting with basalt rock powder, for different rock-fluid ratios. Induced or naturally occurring weathering of basalts rocks release elements in waters and elemental concentration is strictly dependent on water $CO_2$ concentration (and hence on water pH). It results in a clear correlation between cation concentrations and total alkalinity. Laboratory experiments (Galeczka et al., 2013 and reference therein) evidenced that in the first stages of water-rock interaction the high content of $CO_2$ dissolved in water accelerates the basalt weathering process releasing in water not only elements that can form carbonate minerals but also other elements which depending on their concentration can be essential or toxic for life. The final aim of this study is the to compare experimental findings and natural evidences to better understanding the processes in basaltic aquifer hosted in active and inactive volcanic systems. Results will be discussed in light of the potential environmental impact of $CO_2$ storage in mafic and ultramafic rocks.

Galeczka I., Wolff-Boenisch D. & Gislason S. (2013) - Experimental studies of basalt-H2O-CO2 interaction with a high pressure column flow reactor: the mobility of metals. Energy Procedia, 37, 5823-5833.

# Multielement fingerprinting for traceability of Sorrento and Amalfi PGI lemon juices: the role of non-essential elements at short and large territory scale

Ruggiero L.*, Amalfitano C. & Adamo P.

Dipartimento di Agraria, Università di Napoli "Federico II", Portici (NA).

*Corresponding author e-mail:* luigi.ruggiero@unina.it

*Keywords:* non-essential elements, Limone di Sorrento PGI, Limone Costa d'Amalfi PGI.

For agri-food product traceability geochemical fingerprinting is one of the most important tools which gives information about product origin. The mineral composition of agri-foods reflects mostly the available element composition of the respective cultivation soils, but it is also influenced by the cultivation environment (climate and management). The accumulation in agri-foods of plant essential elements could be more affected by seasonal variations of cultivation management and climate, both affecting the nutritional status of plants and their products. Instead, a more stable signature over time could arise from plant uptake of the non-essential elements, generally scarce for the great part and in a lower competitive absorption regime than nutrients. In this work, mineral composition (Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Rb, Sr, Ti, V, Zn) combined with chemometric analysis is used to discriminate the geographical origin on short and large territory scale of lemon juices from different cultivars cropped in two consecutive years; further the effectiveness of the non-essential elements for origin discrimination is investigated. In the short-scale approach, a total of 169 lemon juices of 2018 and 2019 productions of six different cultivars, grown in the "Limone di Sorrento PGI" area and in other two Campania region areas outside PGI area, was used for provenance discrimination (Ruggiero et al., 2021). The explorative analysis by PCA on the mineral profile of the lemon juices shows natural groupings according to provenance and not by cultivars. The applied discriminant model S-LDA, according to territorial provenance of lemon juices, shows 97.73% correct classification, 98.48% accuracy, and 93.83% external validation. The discrimination models applied for each production year show annual variation of discriminant elements regarding nutrients rather than not nutrients (Ba, Rb, and Sr), suggesting the use of the latter as stable indicators of lemon juice provenance. In the large-scale approach, the previous discriminant model was extended to juices from "Limone Costa d'Amalfi PGI" area, two groups from Calabria region (Italy), and two groups of samples from a local market in Berckeley, CA (USA). All elements were divided into three datasets, i.e., all elements, essential elements, and non-essential elements, and each set was treated with S-LDA models. The model based on the whole dataset gave the 97.0% of accuracy and 97.3% of samples were correctly validated. The model based on the essential elements gave the 82.0% and 63.1%, while the model based on non-essential elements gave the 91.04% of samples correctly classified with 89.4% of correct validation. These results indicate that the contribution of non-essential elements was higher than that of essential elements in the all-element profiles for origin discrimination both on a short and large territory scale.

Ruggiero L., Fontanella M.C., Amalfitano C., Beone G.M. & Adamo P. (2021) - Provenance discrimination of Sorrento lemon with Protected Geographical Indication (PGI) by multi-elemental fingerprinting. Food Chem., 362. https://doi.org/10.1016/j.foodchem.2021.130168.

# S50.

# Open Poster Session

*CONVENERS & CHAIRPERSONS*

*Rodolfo Carosi (University of Torino)*

*Daniele Castelli (University of Torino)*

# Multiscale analysis of physical rock properties at Stromboli Volcano: what controls the frictional properties?

Alcock T.*[1], Vinciguerra S.[1] & Benson P.[2]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Rock Mechanics Laboratory, School of Earth and Environmental Sciences, University of Portsmouth (UK).

*Corresponding author e-mail:* thomas.alcock@edu.unito.it

*Keywords:* fracture density, frictional coefficient, slip tendency.

Stromboli volcano, located in the north-easternmost island of the Aeolian archipelago (Southern Italy) and well known for its persistent volcanic activity, has experienced at least four sector collapses over the past 13 thousand years. The most recent activity resulted in the formation of the Sciara del Fuoco (SDF) horseshoe-shaped depression and a tectonic strain field believed to have promoted flank collapses and formed a NE / SW trending weakness zone across the SDF and the western sector of the island. The tectonic strain field interplayed with dyking and fracturing appears to control the episodes of instability and the onset of slip surfaces. This study presents new data identifying areas of damage that could promote fracturing via remote sensing and rock friction measurements taken on rocks around the SDF and the coupled "weak" zone. We have carried out a multiscale approach by integrating satellite observations with block and sample scale physical and mechanical properties and frictional tests carried out in triaxial configuration on cm scale slabs. Over 5000 individual fractures have been at first processed through the MatLab toolbox FracPaQ to determine fracture density, slip and dilatancy tendency around the collapse scarp with results showing that dilation and slip 0.6< is more common the northern side of the SDF as well as around areas of eruptive activity.

Key units have been sampled on the field (Paleostromboli, Vancori and Neostromboli) with reference to SDF and the weak zone. Physical and mechanical properties defined using elastic wave velocities, electrical resistivity, uniaxial compressive strength and elastic moduli have been assessed and inverted for comparison to field scale geophysical investigations. Finally, direct-shear tests in triaxial configuration were carried out to explore the frictional properties using rectangular basalt slabs at 5-15 MPa confining pressure in dry and saturated conditions. Preliminary results show a variation in the friction coefficient ($m$) between 0.5 and 0.8 with a general $m$ decrease with increasing confining pressure and saturation. The most porous Neostromboli units show the lowest friction. This suggests that the textural and pre-existing crack damage variability due to the complex and different magmatic history and cooling rates do control the evolution of the frictional properties and evolving fracturing processes. Further work will structurally quantify the slip evolution throughout post-mortem microstructural observation in order to interpret the relations to the field scale weakness zone and the SDF.

# Cretaceous dinosaur tracks of Periadriatic carbonate platforms: new evidence for a palaeogeographic review

Antonelli M.*[1], Petti F.M.[2], Romano M.[1], Sacco E.[1], Wagensommer A.[3], Petruzzelli M.[4], De Sario F.[1] & Pignatti J.[1]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Museo delle Scienze, Trento. [3] Gruppo Archeologico Valle d'Itria ONLUS, Cisternino (BR). [4] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro».

*Corresponding author e-mail:* matteo.antonelli@uniroma1.it

*Keywords:* Adria, Mesozoic, palaeobiogeography.

The occurrence of several ichnological and skeletal dinosaur remains from the Upper Jurassic to Cretaceous deposits of Central and Southern Italy raises the question about their dispersal from Laurasia or Gondwana to the Western Tethys (i.e., Adria). The diversified terrestrial ecosystem within the Periadriatic carbonate platforms (*sensu* Zappaterra, 1994) during the Cretaceous led some authors (e.g., Zarcone et al., 2010) to challenge the traditional palaeogeographic scenario, according to which Adria was characterised by isolated shallow-water carbonate platforms, separated by pelagic basins and far from continental areas. New ichnological data, obtained by combining traditional methods and new tools, such as photogrammetry and Principal Component Analysis, allowed us to refine the trackmakers identification, achieving a more detailed taxonomic level. Herein, we summarise the results obtained from the ichnological analysis of four tracksites from Latium (Sezze) and Apulia (Borgo Celano, Molfetta and Altamura), ranging from the Hauterivian-Barremian to the early Campanian. The Hauterivian-Barremian to early Albian interval, documented from Borgo Celano and Molfetta, represents the first snapshot. It reveals the likely occurrence in the Apulia carbonate platform of large-sized theropods, such as abelisauroids and carcharodontosaurs. Geological evidence support the hypothesis of a Gondwanan origin for the Apulian large theropods, with a dispersal route from Africa to Apulia through the Constantine and Panormide carbonate platforms, intermittently emerged and connected from the Late Jurassic to the late Cenomanian. The second snapshot is represented by the early-middle Cenomanian of Sezze, where the ongoing studies confirm the occurrence of oviraptorosaurs, thus raising three possible hypotheses: i) their dispersal from Laurasia to the Apenninic carbonate platform; ii) their presence in North Africa, to date not documented by skeletal remains; iii) the presence in Gondwana of an unknown clade of theropods with the structure of the foot converging with that of the oviraptorosaurs. The last snapshot focuses on the early Campanian, documented from Altamura. The ichnological analysis points to the occurrence of small- to medium-sized ankylosaurs, similar to the coeval European nodosaurids, and medium-sized hadrosaurs, similar to *Tethyshadros insularis*, a non-hadrosaurid hadrosauroid from the lower Campanian of north-eastern Italy. The dispersal of these clades finally provides a constraint for a palaeobiogeographic connection between Eurasia and the Periadriatic area.

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# Evaluation of hydrological process using SWAT in an intensively used agricultural lowland area, Lombardy, Italy

Bernini A.*[1], Becker R.[2] & Maerker M.[1]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] Department of Agroecosystem Analysis and Modelling, University of Kassel (Germany).

*Corresponding author e-mail:* alice.bernini01@universitadipavia.it

*Keywords:* SWAT, hydrology, irrigation.

Uncertainties about the quantity and quality of water are increasing in the future due to global change. Water requirements affect a wide range of human activities, in particular agriculture, which is increasingly affected by climate change, with more intense rains in short period of time and longer dry periods. For these reasons, hydrological models have been developed and refined in the last years to model proper water management and to analyze how climate change and land use change impact hydrological processes. (Devi et al., 2015).

However, modelling processes are often challenging in an intensively used agricultural area (Becker et al., 2019) due to the complexity of the hydrological process, strongly conditioned by anthropic activities (e.g., irrigation). An example of such a human altered hydrological system is the micro-scale basin analysed, located in the Ticino Valley in Lombardy region, Italy. This area is intensely cultivated, irrigated through artificial canals and without a natural channel network. In this area, artificial canals guarantee the irrigation of the fields and document that the area is strongly influenced by agricultural activities going on already since the Middle Ages.

The goal of this work is to apply the Soil Water Assessment Tool (SWAT) (Arnold et al., 1998), a physically based model operating at basin scale. In particular, we analyze the vertical soil water dynamics, and related issues such as infiltration, evapotranspiration, and groundwater recharge, in order to evaluate the amount of water requested by different landuses and different types of irrigation impacting on hydrological processes.

SWAT, however, requires a calibration, which is complex in this ungauged area. For this reason, remote sensing data has been used. The calibration was done using MODIS evapotranspiration data at monthly time steps for the period of 2007-2013. To calibrate the model, we used the method of Sequential Uncertainty Fitting (SUFI) and selected the Kling-Gupta efficiency (KGE) as objective function. Initial results show good correlation between simulated and observed data. However, the area is strongly influenced by irrigation and different landuse, showing that hydrology is strongly controlled by human activities. Thus, calibration is quite complex taking to account all the parameters that trigger hydrological processes.

Moreover, we validate the model through local soil moisture measurements (using a TEROS 12 soil moisture sensor). Finally, the calibrated and validated SWAT model allows hydrological analysis of a system altered by human activities. Particularly, we evaluate vertical soil water dynamics and assess future scenarios of land use and land management.

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# Monitoring meteo-marine extreme events in the Mediterranean area using the microseism: "Apollo" case study

Borzì A.M.*[1], Minio V.[1], Cannavò F.[2], Cavallaro A.[3], D'Amico S.[4], De Plaen R.[5], Lecocq T.[5] & Cannata A.[1-2]

[1] Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Catania. [2] INGV, Catania. [3] Ac2 s.r.l., Zafferana Etnea (CT). [4] Department of Geosciences, University of Malta, Msida (Malta). [5] Seismology-Gravimetry, Royal Observatory of Belgium, Brussels (Belgium).

*Corresponding author e-mail:* marcoborzi23@gmail.com

*Keywords:* microseism, medicane, Apollo.

During the period 25 October - 5 November 2021, the eastern part of Sicily, and in particular the areas between Catania and Siracusa, was affected by the effects of a Mediterranean tropical depression, that, on 28 October 2021, acquired the characteristics of a Medicane (MEDIterranean hurriCANE) called Apollo.

The impact of the Medicanes on the sea state and in particular the development of violent wave motions involve a significant energy transfer from the sea waves to the solid Earth. This energy transfer brings to the "formation" of the so-called microseism, the most continuous and ubiquitous seismic signal on the Earth, caused by the interaction between the hydrosphere and the solid Earth.

On the basis of both source mechanism and spectral content, it is possible to divide this signal into: primary microseism, that shows the same spectral content as the oceanic waves with a period between 13-20 s, is associated with the energy transfer of oceanic waves breaking against the shoreline and exhibits low amplitudes (Hasselmann, 1963); secondary microseism, that is generated by sea waves with the same frequency traveling in opposite direction and shows frequency about twice the frequency of the oceanic waves (corresponding with a period of 5-10 s) and amplitude higher than the primary microseism (e.g., Longuet-Higgins, 1950); short period secondary microseism, whose period is shorter than 5 second, is generated by the interaction between local wave motions near the coastline. Several studies highlight a correlation between microseism and cyclonic activity considering in particular the Secondary Microseism and Short Period Secondary Microseism bands. In detail the links between hurricanes, typhoons, tropical cyclones and microseism were analyzed by different authors, while the relationships between microseism and Medicanes have never been explored.

For this reason in this work, we approach the study of the microseism signal recorded during the Medicane "Apollo" and in particular we analyse the microseism spectral content, the space-time distribution of its amplitudes, as well as track its development and position by using a double approach, a grid search method based on seismic amplitude decay and the array f-k beamforming.

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# Method for assessing the coastal vulnerability to erosion and flooding at the physiographic unit scale

Buttò S.*[1], Corradino M.[1-2], De Leo F.[3], Besio G.[3] & Pepe F.[1]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [3] Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova.

*Corresponding author e-mail:* samanta.butto@unipa.it

*Keywords:* sea level rise, coastal vulnerability, numerical modelling.

The Intergovernmental Panel on Climate Change foresees a significant global sea-level rise (SLR) during the 21$^{st}$ century, which will cause an increase in coastal vulnerability (CV) to erosion and flooding. CV can be estimated at various scales, both in space (from national to local) and time (from tens to hundreds of years). However, flooding and erosional scenarios need to be calculated at the physiographic unit (P.U.) and on a decadal scale to plan strategies for defending communities living in the coastal areas and to protect critical infrastructures and natural habitats.

We present preliminary results of a study for assessing the coastal vulnerability to erosion and flooding at the P.U. scale and on the ten-year time scale. This study is based on the analysis of natural marine near-shore factors (e.g., waves, currents) that control the sediment transport and flooding. The method consists of assessing how these factors control the phenomena of erosion and flooding under the influence of the SLR.

We have performed two-dimensional models of wave propagation, sediment transport and morphological changes in the nearshore area and sand/gravel beaches using XBeach model. We have integrated grain-size data, bathymetry, meteorological and wave data. The latter derive from the DICCA hindcast database.

For testing the method, 18 P.U. were chosen in the coastal zone between Capo Mongerbino and Cefalù (northern Sicily). This area is ~70 km long and is characterized by rocky and low sand/gravel beaches. About 37% of the coastal perimeter suffers from important erosive phenomena resulting in coastal regression with rates that in some cases exceed the value of 1 m/year (Regione Siciliana - Assessorato Territorio E Ambiente, 2006). Moreover, the coasts are characterized by different orientations and, thus, it is possible to test the influence of different exposure to wind and waves.

The expected result is a map of CV to erosion and flooding at the physiographic unit scale and on a decadal scale. This study will help to better understand the natural near-shore processes controlling the CV.

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# Remotely-sensed shorelines variation in the last 30 years in southern Sicily (Central Mediterranean): possible link with atmospheric circulation pattern

Caldareri F.*[1], Parrino N.[1], Maltese A.[2], Sulli A.[1] & Todaro S.[1]

[1] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [2] Dipartimento di Ingegneria, Università di Palermo.

*Corresponding author e-mail:* francesco.caldareri@unipa.it

*Keywords:* shoreline variations, remote sensing, automatically coastline extraction.

Morphological variations of shorelines are caused by a wide range of processes mainly influenced by climate changes, sea level variations, meteo-marine conditions, tectonic and anthropogenic activities.

Understanding and predicting shoreline change along coasts is of paramount importance for coastal managers and policy-makers. Whereas coastline monitoring programs are scarce and limited in time and in geographical coverage, growth in the availability of data from satellites provides the opportunity to analyse 30+ years of imagery with global coverage. Observations of shoreline variability are essential to quantify long-term recession trends, regulate coastal development and design coastal protection (National Research Council, 1990).

For the purpose of contributing to the global effort aiming at monitoring sub-annual to multi-decadal shorelines variation, we applied a series of image analysis steps in order to extract the shoreline position on Rapid-Eye, Planetscope, Landsat and Sentinel satellite images in 2 beaches located on the southern coast of Sicily (Central Mediterranean).

The extraction of instantaneous shoreline was conducted automatically in QGIS software, applying three different approach, via raster to vector algorithm using the conversion in binary images that distinguish water and non-water pixels and then verified by field GNSS data acquisition.

The results obtained from the high spatial resolution images demonstrated that remote sensing techniques provides information where traditional methods present some limitations.

The comparisons of these images with the publicly available satellite imagery with a lower resolution showed comparable seasonal and multi-decadal long trends.

We noticed that, for the observation period covered by the high resolution images, the shorelines of the study sites have undergone variations towards both inland and sea, of decametric order. This factor indicates the high dynamism of this coastal area.

Moreover, our preliminary results of both high and low resolution satellite images analysis, shows a cyclicity of 3-4 years which could be linked to the teleconnections between El Niño Southern Oscillation (ENSO) and the Mediterranean circulation pattern.

In this work we presented and compared three cost-effective and practical methods for automatic shoreline extraction that can be adopted for the evaluation of sub-annual to multi-decadal shoreline variations which can be useful for the management and the monitoring of coastal areas.

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# Conventional data display and implications for the interpretation of seismic profiles: a discussion on the ViDEPI seismic database offshore Apulia (southern Italy)

Cicala M.*[1], Chiarella D.[2], De Giosa F.[3] & Festa V.[1]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari «Aldo Moro». [2] Department of Earth Sciences, Royal Holloway, University of London (UK). [3] Environmental Surveys s.r.l. - spin-off Università di Bari "Aldo Moro", Taranto.

*Corresponding author e-mail:* marianna.cicala@uniba.it

*Keywords:* wavelet shape and polarity, ViDEPI project, offshore Apulia.

The Visibility of Petroleum Exploration Data in Italy (ViDEPI) project is the most complete database of technical documents related to hydrocarbon exploration in Italy. As far as we know, it is one of the largest public database in the Mediterranean area which includes seismic profiles and exploration well logs. The data, held by the Ministry for the Economic Development of the Italian Government, have been collected since 1957 and are publicly accessible online from 2007 on www.videpi.com. The seismic profiles located offshore the Italian Peninsula have been divided into seven Marine Zones named from A to G; in particular, the offshore Apulia region, currently listed in the Marine Zones B, D and F of the ViDEPI project, has been investigated through seismic lines acquired from '60s to the mid-'70s of the last century. These seismic data underwent to a preliminary processing standard sequence procedure, and consequently some important information for a correct geological interpretation are missing, i.e., the basic shape of the seismic wavelets and the seismic polarity. Nevertheless, the reflectors are quite clearly visible in several cases giving the possibility to make considerations on the polarity of the seismic wavelets and allowing to interpret correctly, as much as possible, the position of geological boundaries. In this study, a methodological approach is proposed in order to revealing the shape and polarity of the seismic profiles from the marine zones B, D and F. A review of the basic pulse shape and polarity of seismic wavelets, as well as the shape and polarity of principal reflectors has been addressed. Then, by comparing the pattern of the reflectors visible in the seismic line with the reconstructed theoretical reflectors expected at the acoustic impedance boundary, the seismic pattern of the reflectors at the sea floor has been analysed. Finally, lithostratigraphic and sonic logs have been used to identify abrupt interval velocity variations between different lithostratigraphic successions, resulting in a geological meaning of the principal reflectors.

# The value of vintage seismic reflection data: an example from the eastern Tyrrhenian margin (Italy)

Conti A.*[1], Maffucci R.[1] & Bigi S.[2]

[1] Istituto di Geologia Ambientale e Geoingegneria, CNR, Montelibretti (RM). [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma.

*Corresponding author e-mail:* alessia.conti@igag.cnr.it

*Keywords:* Tyrrhenian Sea, vintage seismic data, seismic interpretation.

Seismic reflection surveying is one of the most common geophysical methods used for imaging the structure of the Earth subsurface. This technique has undergone great improvements in terms of technological and computational developments since the last century, when the first seismic experiment was carried out (Romberg, 1961). Nowadays, the high-quality digital data that are acquired are not usually freely available, especially in the Academia context; on the other hand, huge datasets of vintage seismic reflection data are often stored in public repositories, both in paper and scanned copies. Such vintage seismic profiles can have strong potential to be used both in research than in commercial context; in fact, they constitute a valuable resource for example in areas with no recent coverage or with current environmental limitations in obtaining exploration permits. The conversion of these old paper seismic profiles into usable format (SEG-Y), readable by modern processing and interpretation software, makes them an even valuable resource despite their poor quality (compared to modern data) due to the old acquisition equipment and limited processing techniques (Miles, 2007; Diviacco et al., 2015; Sopher, 2018).

The study we present has the aim to illustrate a case of re-use of vintage seismic profiles in the area of the eastern Tyrrhenian margin (Italian offshore), using data from the ViDEPI public database (http://www.videpi.com). Digital SEG-Y files were created from old paper sections and these were interpreted to unravel the stratigraphic and structural architecture of the offshore sedimentary basins (Conti et al., 2022). Despite the dated seismic dataset, the main evolutionary tectonic steps affecting the area are outlined, proving the still relevant value of such datasets. Considering important current topics such as environmental issues, funding difficulties, data accessibility, this kind of data represents a valuable heritage for the scientific community to rescue and exploit.

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# Arc and forearc rifting in the Tyrrhenian subduction system

Corradino M.*[1-2], Balazs A.[3], Faccenna C.[4] & Pepe F.[2]

[1] Dipartiento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo. [3] Department of Earth Sciences, ETH Zürich (Switzerland). [4] Dipartimento di Scienze, Università di Roma Tre.

*Corresponding author e-mail:* marta.corradino@unipa.it

*Keywords:* backarc basin, arc-rifting, Tyrrhenian Sea.

The evolution of backarc and forearc basins is usually treated separately, as the volcanic arc represents a clear barrier between them. We analyse their spatial and temporal relationships in the Tyrrhenian subduction system, using seismic profiles and numerical modelling. Our results highlight that the Marsili volcano, commonly interpreted as the spreading centre of the Marsili backarc basin, was instead a part of an old (Pliocene) volcanic arc associated with the development of the Vavilov backarc basin (4.3-4.1 to 2.6 Ma). The old volcanic arc was successively affected by arc rifting. This process caused the shift of the Marsili volcano eastwards and the formation of an oceanic backarc basin (~ 1.8 Ma) located between the Marsili volcano and the old remnant arc, which remained fixed. The eastern side of the Marsili basin, previously considered as the other half of the oceanic backarc basin, is instead a part of the forearc domain floored by serpentinised mantle. As slab rollback continued, volcanism migrated towards the trench and a new volcanic arc (Aeolian Island) formed at ~1 Ma in the forearc domain. The formation of the new volcanic arc represents the onset of the forearc-rifting that could lead to the opening of a new backarc basin between the old and young volcanic arc, resulting in the decrease of the initial forearc region extension.

The example of the Tyrrhenian Sea illustrates how the evolution of forearc and backarc domains is intimately interconnected. Fluids, released from the downgoing plates, control lithospheric hydration and mantle serpentinisation as well as asthenospheric mantle melting. Fluids and melts induce weakening of the volcanic arc region and drive the arc-rifting that led to the backarc basin formation. Later, the slab rollback causes the trench-ward migration of volcanism that led to the forearc- rifting under the control of fluids released from the downgoing plate.

# Microfracturing in basalts from Stromboli volcanic edifice: new insights from physical properties and microstructural observations

Cova M.*[1], Vinciguerra S.C.[1], Vagnon F.[2] & Alcock T.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* mcova97@gmail.com

*Keywords:* Stromboli, thin sections, island scale.

18 samples from different representative lithostratigraphic units of Stromboli volcanic edifice were analysed to characterise microfracturing and to assess fracture orientations with relation to the main structural features and structural weakness to test the hypothesis of a NE-SW trending weakness zone (NEZ) destabilizing and promoting flank collapse. Petrophysical properties such as effective porosity, density, P and S wave velocity and apparent resistivity, measured under both dry and water saturated conditions, were determined for all samples. Anisotropies and relations between physical properties and porosity are found. Distribution maps of physical properties with respect the unit location allow to visualize the degree of fracturing of the edifice.

On two samples of the units of Malpasso and Ginostra (L3 i and L7 i) in particular optical microstructural observations were carried out to study the fracture density and their average orientation of fractures using the FracPaq software. The two units are located respectively outside the NEZ (L3 i), and within the NEZ but in proximity of the left scarp of the Sciara del Fuoco (L7 i). The results obtained allowed to identify different degrees of fracturing and anisotropy and comparison to the structural main fracturing directions at the island scale. The highest fractures and anisotropy are found with correspondence to main structural and morphological features of the island such the Sciara del Fuoco caldera scarps. Results show that the assessment of the fracture state and its geometric attributes is key to identify areas structural weakness and sectors prone to instability and/or flank collapse.

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# The implementation of the Geological Map of Italy in Piedmont: state of the art

Drago D.*, Magosso P. & Piccini C.

Regione Piemonte, Settore Geologico, Torino.

*Corresponding author e-mail:* daniele.drago@regione.piemonte.it

*Keywords:* CARG, mapping.

The CARG project envisages the realization of geological and geotemathic sheets encompassing the entire national territory at a scale of 1:50.000, which will update the previous framework of sheets at the scale of 1:100.000, which realization started since Italy was unified. The beginning of this project dates back the 1980s and it was repeatedly funded throughout several laws of financing across the years. *Regione Piemonte*, in collaboration and through *Arpa Piemonte*, has took part to the project from the very beginning, implementing a number of geological sheets and some thematic ones, focused upon propensity to instability. By means of specifics agreements with National Council of Researches (CNR) and University of Turin (UNITO), *Arpa Piemonte* and *Regione Piemonte* have accomplished 9 geological sheets at the 1:50.000 scale, to which are added the ones made by neighboring regional administrations, that are presently 4. Moreover, Arpa Piemonte has completed two sheets upon the propensity to hydro.geological instability. After a period of standstill a new pulse comes with the 169/2019 budget law, which provided new appropriations, renewed in 2020 and 2021 too. As a consequence of this act, *Regione Piemonte* has launched a new surveys campaign and enter into agreements with various subjects for the making of them: in cooperation with Turin CNR-IGG of Turin the sheets “Tortona” and “Novi Ligure”; with the University of Turin – Department of Earth Sciences for the making of the sheet of “Pinerolo”, which realization was recently approved by ISPRA. The neighboring Regions have restart this activity as well, implementing maps that includes areas of Piedmont: *Regione Liguria* is about to complete the sheet “Albenga” and the project for the sheet “Ormea” has been approved. Correspondingly, *Regione Valle d’Aosta* has approved the proposal for the sheet “Monte Rosa”. *Regione Piemonte* considers it essential the completion of the geological mapping on its territory, as a strategical tool for the implementation of environmental and economical policies.

 

# Geology and mining activities: an essential link

Fissore M.* & Previale M.

Regione Piemonte - Direzione Opere Pubbliche, Difesa del Suolo, Protezione Civile, Trasporti e Logistica - Settore Geologico, Torino.

*Corresponding author e-mail:* marco.fissore@regione.piemonte.it

*Keywords:* quarry, erosion, prevention.

Geological knowledges are of utmost importance in quarry and mines activity. Unsurprisingly, as exposed by Simon Winchester in "*The Map That Changed the World: William Smith and the Birth of Modern Geology*" the first geological map of the history was concerning coal seams in England.

However, if the quarry mining design cannot be implemented without geological consideration, the territory too is consistently affected by mining activities, which may leads to significant transformations of the landscape and to severe alteration of the hydro-geological balance.

For such reasons geology have a key role to play not only in locating profitable mineral layers but also in assessing management plans of mines and quarries, with the aim to prevent and reduce the effects of natural hazards.

The Geological Service of the Regione Piemonte, according with regional law n. 45/89 "*Nuove norme per gli interventi da eseguire in terreni sottoposti a vincolo per scopi idrogeologici*", (after T.U. 3267/1923) is in charge, since several years, of the "hydro-geological" (i.e.: geological) permission, as competent authority. This permission is intended to mitigate the harmful interference due to poor geological management that quarry exploitation could have on the surroundings. These issues may have to do with slope stability, erosion, groundwater regime and water quality and could affect a much larger area than the extraction site only, as for instance service roads, work sites, spoil dump sites and water discharge areas.

The evaluation of these effects is remarkably complex and, depending on the geographical, geomorphological and geological context as well as public official professional training, can be approached quite differently. In this context it appeared necessary to achieve a standard procedure for the issuance of permissions at a regional level; at the same time efforts was made to making them, as much as possible, a more effective tools for prevention of hydro-geological instability. This goal has been pursued by undertaking a constant, multi-annual, update process, consisting in joint inspections (also in "back-analysis"), as well as software creation and lecture notes. The last step of this process, currently in progress, is the creation of a technical specifications set addressed both to the companies exploiting quarry/mines and their technical personnel, including advisor and consultants. Those notes are carefully harmonized according to the geological context where the mining activity take place.

# GIS-based ground motion simulations of historical earthquakes: insights from the Fabriano (1741) and Camerino (1799) earthquakes (central Italy)

Gironelli V.*[1-2], Volatili T.[1], Luzi L.[3], Brunelli G.[1-3], Zambrano M.[1] & Tondi E.[1-2]

[1] Scuola di Scienze e Tecnologie, Università di Camerino. [2] INGV, Roma. [3] INGV, Milano.

*Corresponding author e-mail:* veronica.gironelli@unicam.it

*Keywords:* earthquakes, Vs,30, ground motion simulations.

The high seismic activity of central Italy is broadly documented by seismic records since historical times. The intense seismicity of this area is also testified in recent times by the occurrence of three seismic sequences with moderate to significant mainshocks (Mw ≥ 6.0) during the last decades.

Nowadays, it is possible to rapidly assess the intensity distribution related to the ground shaking of an earthquake using software packages like ShakeMap (Wald et al., 2006). This is possible for events highly constrained by observed instrumental data. However, this approach seems to be less efficient in estimating the ground motion of historical earthquakes given the increasing number of uncertainties (i.e., absence of strong motion records, estimated magnitudes and epicenters location, unknown or debated seismogenic sources, etc.). Besides the limitations due to the lack of information related to historical seismicity, the uncertainty associated with the integration of local geological conditions is a crucial aspect of this procedure.

In this work, we propose a novel approach to producing ground motion simulations, incorporating a reliable dataset of the local near-surface properties by means of a Geographical Information System (GIS). The workflow presented in this study was used to analyze the two largest events occurred in the Marche region during the 18$^{th}$ century, the Fabriano (1741, Imax IX MCS) and Camerino (1799, Imax IX-X MCS) earthquakes (DBMI15 v4.0, Locati et al., 2022).

We created a multilayer base map of the Umbria and Marche regions. This hybrid raster map with a spatial resolution of 30 m is obtained from a combination of data including topography, lithology, and seismic velocities (Vs,30 measurements from the Italian seismic microzonation datasets). Statistical analysis was performed to evaluate the dependency of Vs,30 with lithology and slope topography.

To reproduce the ground motion of the Fabriano and Camerino historical earthquakes including site effects, we integrated in GIS the resulting base map with the Ground Motion Prediction Equation (GMPE, ITA18) proposed by Lanzano et al., (2019) and shapefiles of the seismogenic sources associated to these events. The outcomes include maps of peak ground acceleration (PGA), peak-ground velocity (PGV), and ground-motion shaking intensity.

The presented workflow can improve the analysis of historical seismicity, therefore enhancing the seismic hazard assessment.

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# Microfacies of methane-derived authigenic carbonates potentially related to gas hydrates: examples from the Piedmont Basin and the Polish Outer Carpathians

Giunti S.*[1], Dela Pierre F.[2], Martire L.[2], Natalicchio M.[2] & Bojanowski M.J.[1]

[1] Institute of Geological Sciences, Polish Academy of Sciences, Warsaw (Poland). [2] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* s.giunti@twarda.pan.pl

*Keywords:* cold seeps, authigenic carbonates, gas hydrates.

Methane-derived authigenic carbonates (MDACs) are rocks related to the anaerobic oxidation of methane (AOM), and are often found in sites where active cold fluid seepage is detected. In modern environments, they are often associated with gas hydrates. The presence of MDACs is also reported in the geological record, representing, together with chemosynthetic fossil assemblages, one of the few physical insights for the past presence of cold seeps. Gas hydrates on the other hand are not preserved in the geological record, rendering their former presence, and their role in the formation of seep carbonates, difficult to assess.

Because methane is involved in the formation, MDACs are commonly depleted in $^{13}C$, while their $\delta^{18}O$ values can vary considerably, depending, among other parameters, on the role played by gas hydrate formation or dissociation. The most frequently applied method to distinguish hydrate-related MDACs from other authigenic carbonates in the geological record is their unique C and O isotope signature, whereas petrographic reports are rather scarce in the literature, especially detailed microfacies studies. This impoverishment of petrographic data causes the absence of commonly accepted criteria on how to recognize gas hydrate-related carbonates in the geological record.

Here, microfacies of seep carbonates that are potentially related to gas hydrates are presented. The studied carbonate rocks come from two areas: the Piedmont Basin and the Polish Outer Carpathians. For both, the presence of a past seepage activity has been previously demonstrated, and gas hydrates are inferred to have been present as well. Carbonate cements, locally showing multiple generations and potentially related to gas hydrates have been recognized in the Miocene sections of Alfiano Natta (AL), Marmorito (AT) and Ripa dello Zolfo (Costa Vescovato, AL) in Piedmont, in the Oligocene sections of Świątkowa Wielka and Siary and in the recently discovered Paleocene section of Pluskawka in the Outer Carpathians. These paleoseeps experienced contrasting diagenetic histories. The Carpathian material is characterized by a much stronger diagenetic overprint related to deep burial with respect to the rocks from Piedmont, which are almost pristine. Therefore, a comparison of seep carbonates from both areas is not only useful to find common microfacies being associated with common formation processes related to fluid seepage or gas hydrate, but also to better understand the diagenetic transformations that modify them postdepositionally.

The purpose of studying these rocks is to find common features, which can be directly related to the former presence of gas hydrates, in order to eventually propose consistent and uniform criteria to identify gas hydrate-related authigenic carbonates in the geological record.

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# The IPANEMA Project: a permanent eye on the $CO_2$-dominated hydrothermal degassing occurring off the coast of Panarea (Aeolian Islands)

Italiano F., Caruso C., Castorina G., Gagliano L., Gattuso A., Lazzaro G., Longo M., Romano D.*, Scirè Scappuzzo S., Semprebello A. & Sposito F.

INGV, Palermo, ufficio di Milazzo (ME)

*Corresponding author e-mail:* davide.romano@ingv.it

*Keywords:* seafloor observatory, hydrothermalism, continuous monitoring.

The Island of Panarea is located in the eastern sector of the Aeolian archipelago, a geologically active region where subduction processes, tectonic activity and volcanism coexist. This area hosts one of the most active shallow-water hydrothermal field of the whole Mediterranean Sea, where a constant discharge of $CO_2$-dominated gases ($CO_2$ > 90%) and thermal brines take place. In November 2002 a sudden input of deep magmatic fluids into the geothermal reservoir provoked the unrest of the hydrothermal activity culminated in a low-energy submarine explosion. The $CO_2$ flow rate increased by orders of magnitude and made the marine environment anoxic killing the living matter occurring in the area.

Due to its unique environmental features, the Panarea area is considered the perfect place where investigating the migration of $CO_2$ along the Earth's crust and the impact of acidic gases on the marine ecosystem. For this reason, the Panarea site was chosen by the ECCSEL (European carbon dioxide capture and storage laboratory) infrastructure to host a laboratory (ECCSEL Nat Lab, Italy) over an area representing a proxy of a $CO_2$ leakage related to capture and storage processes. It is noteworthy to remark that the ECCSEL initiative is framed in the field of the geosciences applied to the research of $CO_2$ capture and storage techniques, which are essential to pursue the net-zero greenhouse gas emissions plan.

As a consequence of the 2002 explosion and in the view of testing the efficiency of new monitoring strategies, it emerged the need to install a submarine observatory in the Panarea area, which could be able to continuously collect geochemical data. The target is to gain insight on the short and long term behaviour of the $CO_2$ injection into the sea water. In 2007 a seafloor monitoring station for near real-time data transmission was finally deployed within the shallow-water hydrothermal field at a depth of 23 m. Various upgrades of the system were made in the 2010s and the current version of station is composed of a bottom observatory equipped with a set of sensors consisting of pH, dissolved $CO_2$ and $O_2$, pressure, electrical conductivity and temperature sensors coupled with wide-band hydrophones, connected by cable to an elastic beacon that provides power to the whole system and allows continuous data transmission. In this context, the Ipanema Project (funded by PON 2014-2020) is thought to boost and improve the ECCSEL laboratory of Panarea and make the seafloor observatory infrastructure permanent.

The geochemical database regarding the emissions occurring off the coast of Panarea covers ~35 years of periodical analyses and ~8 years of nearly-continuous data, whereas the ongoing and future challenges are focused on: i) modelling and simulating the dispersion of $CO_2$ in the seawater and in the atmosphere; ii) monitoring the underwater gamma radiation and the acoustic signals in order to identify any variation in the hydrothermal system feeding the $CO_2$ venting.

# Application of technologies and geological knowledge to improve natural hazards management. Some experiences of the geological service of Piedmont

Magosso P.*, Bianchi E., Cordola M., Drago D., Manazzale A., Negro N., Roagna P. & Tonanzi P.

Regione Piemonte. Direzione Opere Pubbliche, Difesa del Suolo, Protezione Civile, Trasporti e Logistica - Settore Geologico, Torino.

*Corresponding author e-mail:* paola.magosso@regione.piemonte.it

*Keywords:* landslides, avalanches, SAPR.

Piedmont is an italian region with an highly diversified territory. This implies a wide array of geological hazards: from avalanches and rockfalls in the mountains, to flood risk in the plains, until various phenomena of slope instability. To aim those issues and give a proper governance response, the geological regional service (*Settore Geologico* della *Regione Piemonte*) has developed several mitigation activities, including the following examples.

In Piedmont the significant number of landslides (according to the last report *APAT 2007* they amount to 34,000) requires the development of a considerable monitoring system. A monitoring network called *RERCOMF* has been created by *Regione Piemonte*. *RERCOMF* is coordinated by the *Settore Geologico* and managed by the regional environmental agency *ARPA*, it has been in operation for 20 years and today it counts 1500 measurement instruments, distributed beyond 250 active landslides.

The avalanche risk prevention is instead with specific regional legislation to land use and with application of prevention strategies. In the land use co-planning procedures, the hazard is especially defined with the avalanche analysis affecting urbanized areas. The *Settore Geologico* also provides a support function for the mayors's decisions by a technical body called *Commissione Locale Valanghe*. In ski areas, the risk of avalanches is aimed with defense works, but sometimes the risk can be mitigated with temporary suspension of activities, supported by artificial releases of avalanches managed by qualified operators.

In order to implement its technological services, the *Settore Geologico* is today equipped with a Remotely Piloted Aircraft System (in italian *SAPR*), in order to acquisition of video and photographic images for its institutional activities. In this regard, with specific training courses recognized by *ENAC* (the italian authority of national civil aviation), internal operators of the *Settore Geologico* have been trained to the *SAPR* use. The use of drones is extremely useful to aerial survey, or to verify architectural structures affected by earthquakes. It is aimed to carrying out surveys after natural disasters, also avoiding the use of personnel in contexts often characterized by a significant risk.

To mitigate the effect of landslides and rockfall, is frequently required an interdisciplinary engineering and geological approach, in order to ensure a proper design for projects of active and passive consolidation systems. Since in *Regione Piemonte* those projects are often committed to local municipalities, the *Settore Geologico* is in charge to evaluate projects of protection facilities submitted for a national funding procedure. For that purpose a work group has been established, in order to provide expert advice to local administration and professionals. In the last five years this interdisciplinary group (called *GIV*) analyzed hundreds of projects, giving a substantial contribution in technical evaluation and remarks.

# Pockmark-like seabed features in the Adventure Plateau (Sicily Channel)

Maiorana M.*, Parente F., Sulli A., Agate M., Caldareri F. & Todaro S.

Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* mariagiada.maiorana@unipa.it

*Keywords:* pockmark, fluids circulation, morphobathymetry.

The Adventure Plateau, one of the shallowest sectors of the Sicily Channel (Central Mediterranean), has formed along the convergent margin between the African and European plates. It represents the south-western segment of the Sicilian-Maghrebian chain formed mainly during the Neogene. The resulting structures, in the northwestern part of the Adventure plateau, are associated to the foredeep-foreland system of the Fold and Thrust Belt. During the Plio-Pleistocene an E-W extensional tectonic event occurred favoring the onset of different magmatic manifestations, especially in the northern and eastern sectors, as well as the uprising of fluids of different origin. The interpretation of acoustic (MBES, SSS), seismic (sparker, airgun) and visual (ROV) data allowed us to identify depressions, interpreted as pockmarks, which are features linked to fluids emissions. A classification based on their morphological (diameter, external shape) and genetic (fault-or loading-related) evidence has been performed. These seabed features have been plotted in a 3D bathymetric model and then observed in the seismic reflection profiles where they are associated to acoustic turbidity (or blanking), bright spots, enhanced reflection zones and columnar disturbances (chimneys) (Hovland & Judd, 1988), all characteristics typical of pockmarks occurrence. These, both buried and outcropping, have been classified as strings of pockmarks (Hovland et al., 2002) since they are aligned in the same direction of a fault system, NW-SE oriented. We consider the latter as the main way for vertical fluids migration towards surface and we reconstructed this pathway in the entire survey area in order to identify the source of the fluids.

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# Multiscale geological and geophysical characterization of a chaotic complex

Paletto F.[1], Caselle C.*[1], Bonetto S.[1], Vagnon F.[2] & Comina C.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Ingegneria dell'Ambiente, del Territorio e delle Infrastrutture, Politecnico di Torino.

*Corresponding author e-mail:* chiara.caselle@unito.it

*Keywords:* electrical survey, ERT, 3d visualization.

The characterization of geo-mechanical behaviour of chaotic bodies or bim (block-in-matrix) rocks represents a key challenge in geotechnical engineering, due to the lithological heterogeneity of these rock massed and, consequently, to the spatial variability of mechanical parameters.

The present study proposes a multi-scale and multi-approach characterization of the Valle Versa Chaotic Complex outcropping in an underground quarry site in the Monferrato area (NW Italy). The characterization included field geological work and geo-electrical survey. The field work allowed for a detailed reconstruction of lithological and geo-structural features of the complex. Outcomes were then integrated with a geo-electrical survey campaign from the surface. Collected results were summarized in a three-dimensional representation of lithologies distribution and fracture network pattern.

# Potassic and ultrapotassic rocks from the Roman Magmatic Province: crustal and mantle processes involved in terrains' Au (in)fertility

Palozza F.*[1], Braga R.[1], Moroni M.[3], Fiorentini M.[2], Loucks R.[2] & Nogueira Mafra C.[2]

[1] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [2] School of Earth Sciences, University of Western Australia, Crawley (Australia). [3] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.

*Corresponding author e-mail:* francesco.palozza96@gmail.com

*Keywords:* ore deposits, precious metals, magmatic sulfides.

The Central-Western Mediterranean is one of the most important and studied regions worldwide to investigate the occurrence and genesis of potassic and ultrapotassic rocks and analyze the complex interactions between crust and mantle at convergent plate margins.

The spatial association between potassic magmatic rocks and porphyry Au and Cu-Au deposits and precious-metals epithermal deposits is long recognized, raising interest in evaluating the prospectivity of the terrains where they intruded. Furthermore, K-rich alkaline rocks host significant rare earth element deposits worldwide, and some may even be intrinsically enriched in platinum-group elements.

However, it is still unclear why some major potassic-alkalic igneous provinces are barren. In this context, the Pleistocene-Quaternary, barren K-rich igneous rocks of the Roman Magmatic Province represent an excellent Au-devoid reference province to refine geochemical tools to discriminate between fertile and infertile arc magmas and identify the crucial factors that led to such sterility.

The present study analyzed 13 potassic and ultrapotassic lavas from the Vulsini Volcanic District, Sabatini Volcanic District and Alban Hills Volcanic District and one lava-hosted ultramafic xenolith in lavas from the Alban Hills Volcanic District. Petrographic microscopy, whole-rock and mineral geochemistry were used to investigate the features of these lavas and provide additional data for constraining the conditions for formation of the Roman Magmatic Province.

The resulting mineralogy of the 13 lava samples is almost identical, consisting mainly in an assemblage of clinopyroxene, olivine, leucite, nepheline and spinel (Ti-rich magnetite- hercynite), with rare fluorapatite and F-rich phlogopite.

Trace element patterns indicate subduction-related geochemical signatures (low Ta–Nb, high Rb–Cs–LREE) and suggest sourcing of these magmas from a peridotitic sub-continental lithospheric mantle intensely metasomatized by reaction with melted metapelites.

Mineral chemistry results highlight the influence of carbonatic wall-rock assimilation in shifting the composition of the magmas towards more undersaturated compositions.

The ultramafic xenolith consists of coarse-grained, cumulus-textured clinopyroxenite rich in F- bearing phlogopite and fluorapatite. Clinopyroxene hosts mono- to polyphase Fe-rich sulfide blebs and droplets absent from the lava in all districts considered. Hence, this xenolith has been further investigated to detect Au anomalies by evaluating the micron-sized sulfide blebs' composition and Au signals (pyrrhotite, pentlandite, chalcopyrite) through electron EMPA chemical maps and scanning electron microscopy (SEM).

A geological model is proposed to account for Au-bearing Fe-Cu-Ni sulfide blebs in the xenolith and contextualize the results to illustrate the processes likely involved in the Au- infertility of the Roman Magmatic Province.

# Integrated methodological approach for the investigation of slope dynamics in the Scoltenna basin, Northern Apennines (Italy)

Parenti C.*[1-3], Rossi P.[2-3], Soldati M.[1-3], Pattuzzi E.[4] & Mancini F.[2-3]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. [2] Dipartimento di Ingegneria "E. Ferrari", Università di Modena e Reggio Emilia. [3] Centro interdipartimentale di Ricerca e per i Servizi nel Settore delle Costruzioni e del Territorio, University of Modena and Reggio Emilia. [4] Agenzia regionale per la protezione ambientale, Bologna.

*Corresponding author e-mail:* carlotta.parenti@unimore.it

*Keywords:* slope dynamics, geomatic surveying, Northern Apennines.

Slope dynamics include different processes capable to influence fluvial dynamics and affect the channel network. Mass wasting processes can represent an important source of sediments supply into riverbeds. On the other hand, water courses can re-shape or erode the foot of a landslide and re-activate slope movements (Nones, 2020). The objective of this study is the application of an integrated geomatic methodological approach in the frame of a more general assessment of the interaction between slope and fluvial dynamics (Gustavsson et al., 2008). The study area is situated in the Scoltenna basin in the Northern Apennines (Italy) and displays both active and dormant landslides.

The research so far conducted foresaw the analysis of slope dynamics, including remote and proximal sensing techniques, repeated field surveys and geomorphometric analysis. The key for understanding such dynamics is the combination and the integration of different geomatics methodologies and technologies. In this study, satellite interferometry, global navigation satellite systems surveys (GNSS), uncrewed aerial vehicle (UAV) photogrammetry, and terrestrial laser scanning were used. All ancillary data related to the in-situ surveying practice were incorporated and integrated. An in-depth review of existing literature and thematic maps was performed, analysing the pre-existing digital data on online platforms and archives (e.g., historical aerial photos, high-resolution satellite images, orthophotos, hydrological datasets etc.). All datasets were organized in a multitemporal perspective, each product was referred to the same georeferenced system and implemented in a Geographic Information System (GIS) environment.

Three study sites, reflecting the interaction between slope and fluvial dynamics in the Scoltenna basin, were selected to be analysed in detail and monitored through time. The first site shows geomorphological evidence of recent activity and was investigated by means of Terrestrial Laser Scanning, UAV photogrammetry and GNSS surveys. The second site displays a complex style of activity combining multiple mechanisms; in this case UAV photogrammetry and GNSS surveys were performed. The third site is characterized by a recent reactivation at the foot of the slope; here UAV photogrammetry and GNSS surveys were carried out. In each study site, two monitoring campaigns were performed to recognize and monitor possible movements and displacements through time. The next steps of the work foresee further seasonal monitoring campaigns and the integration of the collected data on slope movements with the evidence of fluvial morphodynamics.

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# Past and present as the key to predicting future geological trends: focus on Marine Isotope Stage 3 as enigmatic period

Perazzotti F.*[1], Sechi D.[1], Andreucci S.[2], Cossu G.[1], Faedda G.[1], De Luca M.[1], Ruberti N.[1], Santonastaso A.[1], Stelletti M. [1] & Pascucci V.[1]

[1] Dipartimento di Architettura, Design e Urbanistica, Università di Sassari. [2] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

*Corresponding author e-mail:* fperazzotti@uniss.it

*Keywords:* marine isotope stage 3 (MIS 3), abrupt climate changes, future scenarios.

The marine isotope stage 3 (MIS 3) spanned between 25 and 60 ka ago. From a climatic perspective MIS 3 is a crucial stage characterised by frequent (millennial) and abrupt thermal oscillations. The sea level dropped to 60 and 90 m below present during this stage, and even if it is considered a glacial period, it was characterized by high frequency warm to cold temperature fluctuations. These have been divided into six Heinrich (H) events related to phases of rapid temperature drop (cool and dry) and fourteen Dansgaard-Oeschger events (DO) associated with an abrupt climate warming to close to interglacial conditions. The marine and coastal environments are the most sensitive system to abrupt climate changes and important archives of past climate changes and can be used to reconstruct possible future scenarios under extreme climatic events.

In this abstract, we present a preliminary database of MIS 3 based on so far known literature in order to constrain the climatic fluctuations that occurred within the MIS 3 along the Mediterranean area. For simplicity, three pilot macro-areas were chosen, Tuscany coasts, Sardinia and Mallorca islands. These are located roughly within the same latitude, and different sub-areas were identified for each macro-areas. The age of deposits, altitude(m) above current sea level, depositional system interpretation and age dating techniques were used for the dataset. All data were plotted against on $\delta O^{18}$ fluctuations related to the last 70 ky.

The preliminary results of this work highlighted that, for the western Mediterranean area, the D-O events can be associated with extreme depositional episodes characterized by stream reactivation, sheet flood and development of alluvial and apron-fan systems. In contrast, vast coastal dune systems are the depositional response to the abrupt cooling and drying of climate related to the H events.

Further research steps will be:

i) carry out new sampling in the study areas on which has been done bibliographic research.
ii) update the database by integrating the new sampled data with those reported in the literature.
iii) check whether what has emerged so far is applicable to other study areas outside of Mediterranean basin.

In conclusion MIS 3 was a climatic phase of the Quaternary era and, although it represents a relatively short period of time compared to the global chronological scale, it is extremely peculiar because it is characterised by great climatic instability. To date, it is unclear whether the baseline climate during MIS 3 should be a stadial or interstadial state, neither is it clear that there is affectively a baseline climate, as climate states can be intrinsically oscillatory. For this reason it is of crucial importance to deepen this period cause the study of MIS3 can help us understand how the climate behaves when it undergoes rapid changes.

# Definition of the framework of the dissest relating to municipalities that have not yet adapted their urban planning tool to the PAI

Pesando G., Piccini C.G.*, Roagna C., Tonanzi P., Troglia A. & Zaccagnino M.

Regione Piemonte - Direzione Opere Pubbliche, Difesa del Suolo, Protezione Civile, Trasporti e Logistica - Settore Geologico, Torino.

*Corresponding author e-mail:* carlo.piccini@regione.piemonte.it

*Keywords:* dissest, planning, risk.

In order to regulate the actions concerning the hydrogeological defence of the territory, the Piedmont Region must have an updated knowledge of the situations of instability. A useful tool to achieve this goal is represented by the municipal urban planning tools that contain geological studies related to the framework of the instability, drawn up at the local scale, and provide information about the geological hazard and the relative suitability for urban use of the territory. The *Piano stralcio per l'Assetto Idrogeologico* (PAI - Master Plan for Hydrogeological Structure), approved by Decree of the President of the Council of Ministers of 24 May 2001, mandates the municipalities to carry out, through the revision of their urban planning instruments, the verification of the actual situations of instability and hydraulic and hydrogeological risk present on the territory with respect to those identified by the PAI itself. More than 20 years after the entry into force of the PAI, however, not all municipalities have proceeded with the checks mentioned above. In order to fill the lack of information resulting from the lack of a homogeneous framework of the instability, also in order to quantify the needs of mitigation interventions of geological hazard at the regional scale, the Directorate of Public Works, Soil Protection, Civil Protection, Transport and Logistics of the Piedmont Region, through the Geological Sector, or the Seismic Sector for the territorial areas of competence, has prepared, according to the DGR n. 25-7286 of July 30, 2018, the framework of the instability of the municipalities that have not yet started any procedure of adaptation to the PAI. The definition of the framework of the instability takes place on the basis of the information present in the various regional and national databases, inspired by the principle of greater caution. In order to make binding the limitations to the use of the territory deriving from the conditions of dangerousness emerged from the studies carried out by the regional offices, for some municipalities the procedures for the application of the precautionary measures of art. 9 bis of the Regional Urban Law n. 56/1977 have been started. These procedures provide for limitations on the use of the territory, if falling within the instability as identified above, in accordance with the limitations provided for in Article 9 of the Implementation Rules of the PAI, until the adoption of the variant adaptation to the PAI of the municipal planning tool. To date, 55 Regional Council resolutions have been prepared with which the aforementioned precautionary measures have been applied to as many municipalities. After completing the studies on the municipalities that have not yet started any procedure for adaptation to the PAI, we are proceeding to define the framework of the instability of those municipalities that have an adjustment to the PAI in progress but not yet shared at the regional level in order to assess the opportunity to apply to these municipalities the precautionary measures mentioned above.

# Seismic Profile analysis of the Interval Stacking Velocities for its interpretation and time-to-depth conversion: a case study from the offshore Lampedusa Island (Sicily Channel Rifting Zone, Central Mediterranean sea)

Qadir A.*[1], Maiorana M.[2], Chizzini N.[1], Artoni A.[1], Torelli L.[1] & Sulli A.[2]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

*Corresponding author e-mail:* aasiya.qadir@unipr.it

*Keywords:* stacking velocities, Plio-Quaternary sequences, Moho.

Dotted in the Pelagian foreland with E-W orientation, Lampedusa is an island part of the Central Mediterranean that encompasses the Sicily Channel Rifting Zone (SCRZ). It is the abode of NW-SE trending troughs viz. Pantelleria, Linosa and Malta. There are a number of extensional faults found in SCRZ, in both WNW-SSE and NNW-SSE trends (Torelli et al., 1995; Distefano et al., 2019). This study focuses on the high penetration seismic reflection profile crossing the eastern portion of the Lampedusa high which is a seismically active area. This deep seismic reflection profile is useful to unriddle the stratigraphic and structural complexities as well as the active fault systems. The application of statistical operations to the stacking velocities provided along with the profile are taken into consideration to convert the P wave travel time (two way time - TWT) into depth so as to constrain the depth of the reflections and the geological model along the investigated seismic profile.

The preliminary results from the evaluated depth data show that the reflections are present as far as 28 km depth. In agreement with previous seismo-stratigraphic studies, four units are related to the three major reflections bounding these units. The result shows that Lower Cretaceous is 3.5 km thick, the thickest unit, the Upper Cretaceous is 3 km, the Upper to Middle Eocene unit is 2.1 km and the Plio- Quaternary sequence ranges between 1 and 1.5 km. The structural features were also interpreted, suggesting the horst-graben setting that develops in the extensional tectonic regime. The faults are mainly steep faults and the main faults show listric geometry that flatten at 11 km depth. There is the presence of approximately 14 km long and 0.8-2 km deep Plio-Pleistocene syn-rift basins in the hanging walls of the half grabens. This study also shows that the average depth range of Moho is 15-23 km corresponding to 7.5-11.2 s of TWT in agreement with Cassinis et al. (2003). The Moho has not a continuous extension and constant depth (Torelli et al., 1991; 1995). This study would aim to contribute to better understand the geological model of the SCRZ useful for its seismo-tectonic analysis.

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Distefano S., Gamberi F., Baldassini N. & Di Stefano A. (2019) - Neogene stratigraphic evolution of a tectonically controlled continental shelf: The example of the Lampedusa Island. Ital. J. Geosci, 138, 418-431.

Torelli L., Grasso M., Mazzoldi G., Peis D. & Gori D. (1995) - Cretaceous to Neogene structural evolution of the Lampedusa shelf (Pelagian Sea, Central Mediterranean). Terra Nova, 7, 200-212.

Torelli L., Zitellini N., Argnani A., Brancolini G., De Cillia C., Peis D. & Tricart P. (1991) - Sezione geologica crostale dall"avampaese pelagiano a1 bacino di retroarco tirrenico (Mediterraneo centrale). Mem. Soc. Geol. It., 47, 385-399.

# Permafrost and greenhouse gas leakage: results from a deep electrical resistivity tomography in Taylor Valley, Antarctica

Romano V.*[1], Fischanger F.[2], Lupi M.[3], Wilson G.[4], Sciarra A.[5], Mazzini A.[6], Mazzoli C.[7], Florindo F.[5], Tartarello M.C.[1], Ascani M.[5], Anderson J.[8], Worthington R.[8], Hardie R.[9], Dagg B.[8], Bigi S.[1] & Ruggiero L.[5]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Geostudi Astier s.r.l., Livorno. [3] Department of Earth Sciences, University of Geneva (Switzerland). [4] GNS Science, Lower Hutt (New Zealand). [5] INGV, Roma. [6] Center of Earth Evolution and Dynamics, University of Oslo (Norway). [7] Dipartimento di Geoscienze, Università di Padova. [8] Department of Marine Science, University of Otago, Dunedin (New Zealand). [9] Department of Internal Affairs, Wellington (New Zealand).

*Corresponding author e-mail:* valentina.romano@uniroma1.it

*Keywords:* permafrost, greenhouse gasses, electrical resistivity tomography.

Permafrost is globally distributed throughout 17% of our planet and freez-thaw dynamics strongly affect climate and ecosystems. In particular, the gradually increasing permafrost thawing at high latitudes is a key indicator of climate change. It is estimated that Arctic regions store almost twice the carbon currently present in the atmosphere and that the irreversible trend of permafrost thawing can release $CO_2$, $CH_4$ and other gases in the atmosphere, exacerbating the greenhouse effect. Here we present some of the results acquired in the framework of the SENECA-PNRA project.

During the 2020 Antarctic summer we conducted a deep electrical resistivity tomography survey in Taylor Valley, McMurdo Dry Valleys, Antarctica, and integrated these data with geochemical and flux measurements (e.g., $CO_2$, $CH_4$). The goal was to map the distribution and the boundaries of the permafrost, through several intersecting profiles, and the potential conduits for gas flow from beneath the permafrost to the surface. The collected resistivity values span several orders of magnitude (~ 40-5000 Ohm m) because of the strong heterogeneity of lacustrine and glacial deposits. We identified two different domains: the first one is located close to the edges of Lake Fryxell and shows the presence of low resistivity brines also at shallow depths. The second one is characterized by higher mean apparent resistivity, affected by the proximity of Coral Ridge, with deep permafrost/brine boundary. Permafrost thickness varies considerably from ~ 30 m, close to the edges of Lake Fryxell to ~ 400 m, by Coral Ridge. By comparing these values with the geochemical data, we find a correlation between regions where the permafrost is thinner and $CO_2$ flux, $CO_2$, $CH_4$ flux and He concentrations anomalies. While the origin of the gas is not constrained, the presence of abundant brine circulation underneath the areas where the permafrost is thinner, is likely the vector for the gas leakage from the subsurface. As global temperatures continue to rise, our results highlight the dramatic interplay between permafrost thawing and greenhouse gas release.

# Mapping the termophysical properties of Apennines rocks: implication for the geothermal potential

Sabatini A.*[1], Pauselli C.[1], Fastelli M.[1], Comodi P.[1], Trippetta F.[2] & Marmottini F.[3]

[1] Dipartimento di Fisica e Geologia, Università di Perugia. [2] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [3] Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia.

*Corresponding author e-mail:* alessandro.sabatini1@studenti.unipg.it

*Keywords:* heat flow, thermophysical properties of rocks, geothermal potential.

In this paper, some preliminary results on measurements of thermophysical properties of outcropping carbonate rocks of the Northern Apennines, are presented.

We collected 16 samples coming from formations of Umbria - Marche and Tuscany succession and thermal conductivity, diffusivity, porosity (micro, meso and macro), and density were measured for each sample. The mineralogical composition was defined using X-ray powder diffraction techniques coupled with quantitative phase analyses applying Rietveld method.

The measurements were done on 2/3 samples per formation, either under dry (left in an oven for 24h at 105°C) and saturated conditions (left in distilled water for at least three days). In addition, for some samples measurements were made parallel and perpendicular to mineralogical foliation or fracturing, if present, to assess how the direction of the measurements can affect the bulk measured thermal conductivity values.

From early results, the mineralogical composition seems to have the greatest control on measured thermal conductivity values, while porosity and density should play a less important role in defining conductivity values. Specifically, there is an increase in conductivity as the quartz content increases. The obtained values are comprised between 2.4 W/mK and 3.3 W/mK for sample with quartz content less than 30%. The highest values of 3.6 W/mK was measured in two samples of Scaglia Rossa and Maiolica fms. containing mainly chert nodules that gives a mineralogical composition with 93.93% and 52.4% of quartz, respectively.

The measured conductivity values are independent of the measurement carried out parallel or perpendicularly to the foliation or fracturing because these systems are not so important in the studied samples.

The obtained values have been used to map the thermal conductivity of outcropping rocks and to find theoretical relationships between the thermophysical and lithological properties, which can be valid under different geological conditions and that can be applied on samples with similar compositional chemical / mineralogical characteristics.

The definition of thermal properties of rocks is useful to evaluate the temperature gradient with depth and so the integration of these results with site geological knowledges may be important to define both the geothermal and rheological models of the studied area.

# Numerical modelling of stress-strain analysis at an underground quarry in the Apuan Alps marble district (Italy)

Salvini R.*[1], De Lucia V.[1], Beltramone L.[1], Silvestri D.[1], Rindinella A.[1], Ermini A.[1], Gullì D.[2], Marchetti D.[2], Guido S.[3], Pandolfi O.[4], Berlinghieri M.[4], Vaselli L.[5] & Sirgiovanni E.[6]

[1] Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente e Centro di Geotecnologie, Università di Siena. [2] USL Toscana Nord Ovest - Unità Operativa Ingegneria Mineraria, Carrara. [3] SIAL.TEC Engineering s.r.l., Montello (BG). [4] Studio di Ingegneria Pandolfi, Carrara. [5] Professional Geologist, Massa. [6] Professional Geologist, Massa.

*Corresponding author e-mail:* luisa.beltramone@unisi.it

*Keywords:* stress-strain analysis, numerical modelling, underground marble quarry.

The stress-strain analysis of rocky slopes is a valuable tool for checking and monitoring the stability conditions and guaranteeing safety conditions of the workplaces for the personnel involved in mining activities. The present research, which has been carried out in the framework of a project involving the University of Siena and the *USL Toscana Nord Ovest - Unità Operativa Ingegneria Mineraria* supported by Tuscany Region (Italy), represents the application of a methodological approach for studying the stress-strain distribution in some quarries of the Apuan Alps mining area. The project provides for an in-depth study of the knowledge on the in-situ stress field and on the deformability of the rock. It was carried out by means of numerical modeling according to Finite Elements Methods (FEM) and Distinct Elements Methods (DEM). The survey method involved: i) acquisition of the 3D geometric information of the quarry area by means of a georeferenced ground-based and aerial laser scanner survey; ii) acquisition of data about the rock mass through engineering-geological survey; iii) laboratory tests on samples for determining the physical and mechanical characteristics of the marbles; iv) in situ rock stress measurement campaign by four CSIRO-type tests and six Doorstopper-type tests executed at different positions and at various depths in the underground extraction chamber hanging wall (a CSIRO-type cell was installed in a predrilled borehole – at a depth of 10.1 m – as a future monitoring sensor); v) creation of numerical models of the chamber, both in 2D and 3D, and their calibration on the in situ results; vi) extrapolation of the calibrated models to the future planned excavation phases; vii) comparison of foreseen behavior with assumed strength criteria or crack initiation thresholds. The data obtained from the various steps flowed into several numerical models that were validated by a rigorous back analysis assessment using least squares procedures. Numerical modelling of stress-strain analyses will allow to increase the safety conditions for the personnel of the underground marble quarry, to improve the excavation efficiency and continuous production and, finally, to design the long-term planning of mining activities.

# Metamorphosed Mafic Igneous Rock: a nomenclature aenigma

Srivastava R.K.*

Department of Geology, Banaras Hindu University, Varanasi (India).

*Corresponding author e-mail:* rajeshgeolbhu@bhu.ac.in

*Keywords:* mafic igneous rock, metamorphism, nomenclature.

Many Precambrian mafic igneous rocks commonly experience metamorphic changes in different facies for which no agreement on the nomenclature has yet been reached. Commonly, Metamorphoic Mafic Igneous Rocks (MMIR) are grouped by researchers not expert in petrology under the single term "amphibolite" without taking into consideration the real mineral assemblage. In other cases, MMIR under greenschist facies are referred to as metabasite, greenstone, amphibolite, greenschist, low-temperature metabasite, and so on. Similarly, a MMIR under amphibolite facies is named as metabasite, amphibolite, epidiorite, metabasite, etc. Similar problems exit with naming MMIR under granulite- and eclogite-facies conditions. Probably this is due to variable chemical compositions of the protoliths grouped under the very generic term of "basaltic rock". Broadly speaking, a metamorphic rock can be classified on the basis of three essential variables, i.e., temperature, pressure and bulk composition, without direct link to specific geological tectonic settings. However, less attention has been given to the MMIR; a systematic study of the MMIR may provide useful results to understand evolution of a metamorphic terrain. This is simply because many of the MMIR are intrusive in nature and can have datable igneous minerals (e.g., zircon or baddeleyite) surviving the metamorphic event, which ultimately can provide key information to figure out the evolution of that terrain. Therefore, it is essential to characterise and classify the MMIR properly with a proper nomenclature. Therefore, a classification scheme for the MMIR for their proper naming with a proper consideration of their mineral assemblages and metamorphic grades is proposed (Srivastava, 2012). It is preferred to use term metabasite to denote a bulk composition and classify the mafic rocks into six categories as follows:

1) *Very low-grade (VLG) metabasite*: for Zeolite and Prehnite-Pumpellyite P-T condition,
2) *Low-grade (LG) metabasite* for greenschist and transitional P-T condition,
3) *Medium-grade (MG) metabasite* for amphibolite P-T condition,
4) *High-grade (HG) metabasite* for granulite P-T condition,
5) *High-pressure (HP) metabasite* for blueschist P-T condition, and
6) *High-pressure high-temperature (HPHT) metabasite* for eclogite P-T condition. In addition, some eclogites show high-pressure low-temperature condition; this can be named as the *high-pressure low-temperature (HPLT) metabasite*.

Srivastava R.K. (2012) - Appraisal of classification for metamorphosed mafic igneous rocks (MMIR): igneous petrologist's perspective. Him. Geol., 33, 97-99.

# Seismic response to tidal stress perturbations sheds new light on how fault patches become unstable

Zaccagnino D.*[1], Telesca L.[2] & Doglioni C.[1-3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ). [3] INGV, Roma.

*Corresponding author e-mail:* davide.zaccagnino@uniroma1.it

*Keywords:* earthquake triggering, fault stability, preparatory phase.

The stability state of fault systems is mainly controlled by the frictional properties of weak interfaces and by the available energy accumulated in the volumes beside them. Heterogeneities, roughness, and topological features play a key role in driving seismic dynamics and tectonic stress dissipation. However, the physics of the processes fostering mechanical instability in the stages just before failures is still poorly understood. Do peculiar processes occur before major failures? How long do such destabilizations last, if any? Do they share common features or each of them is a one of a kind? A possible approach consists in perturbing fault systems and studying how seismicity changes after additional stress is applied: if the starting energy state is stable, it will oscillate around it; otherwise, the background seismic rate will be modified. Tides provide natural stress sources featured by a wide range of frequencies and amplitudes, which make them a suitable candidate for our needs. Analyses prove that the brittle crust becomes more and more sensible to stress modulations as the critical breaking point comes close. Our results are compatible with past literature (e.g., Métivier et al., 2009; Tanaka, 2012; Varga & Grafarend, 2019). The correlation between the variation of Coulomb failure stress induced by tidal loading, ΔCFS, and seismic energy rate progressively increases as long as seismic stability is preserved; conversely, abrupt drops are observed as foreshocks and pre-slip happen. A "preparatory phase", characterized by increasing correlation, is detected before large and intermediate ($Mw \gtrsim 5$) shallow (depth $\leq 50$ km) earthquakes. The duration of the anomaly, T, is suggested to be connected to the seismic moment M of the impending mainshock by the scaling relation $T \propto M^{0.3}$ for $M < 10^{19}$ N· m while $T \propto M^{0.1}$ for $M > 10^{19}$ N·m. We apply this method to noteworthy seismic sequences in California, Greece, Iceland, Italy, Japan, and New Zealand. Even though our results cannot be of practical use for seismic hazard because of large error bars and variability of the investigated phenomenon, the procedure may help us to better understand the physics of earthquakes.

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Tanaka S. (2012) - Tidal triggering of earthquakes prior to the 2011 Tohoku-Oki earthquake ($M_w$ 9.1). Geophys. Res. Lett., 39(7), L00G26. https://doi.org/10.1029/2012GL051179.

Varga P. & Grafarend E. (2019) - Influence of tidal forces on the triggering of seismic events. In: Braitenberg C. & Rossi G. Eds., Geodynamics and Earth Tides Observations from Global to Micro Scale. Birkhäuser, Cham. https://doi.org/10.1007/978-3-319-96277-1_6.

# Gaining acuity on crystal terminology in volcanic rocks

Zellmer G.F.*

Volcanic Risk Solutions, Massey University, Palmerston North (New Zealand).

*Corresponding author e-mail:* g.f.zellmer@massey.ac.nz

*Keywords:* volcanic rocks, crystal size, crystal origin.

Given the prolific work on the petrography and mineral chemistry of volcanic rocks to understand magmatic processes for well over a century, it is surprising that there are no quantitatively rigorous size classifications or commonly accepted terminologies regarding the origin of such crystals. This causes some confusion when attempting to make meaningful statements about the origin of crystals in porphyritic volcanic rocks. Here, more rigorous size and genetic terminologies for the crystals in volcanic rocks are proposed (size: ultrananolite, nanolite, microlite, microcryst, mesocryst, macrocryst, megacryst; genesis: autocryst, antecryst, xenocryst). And some caveats are discussed. The genetic terminology may also be employed when interpreting crystal zoning patterns and can be applied to crystal fragments. Adoption of the proposed size classification scheme (Zellmer, 2021) is expected to lead to quantitatively more precise descriptions of the dimensions of the crystal cargo in volcanic rocks in the literature. Adoption of the proposed genetic terminology (Zellmer, 2021) is expected to lead to less ambiguous discussions of the genetic processes that operate in magmatic systems in the lead-up to volcanic eruptions.

Zellmer G.F. (2021) - Gaining acuity on crystal terminology in volcanic rocks. Bull. Volcanol., 83, 78. https://doi.org/10.1007/s00445-021-01505-9

# PhD Day 2022

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# The occurrence of abelisauroids in the Apulia carbonate platform: evidence in the Hauterivian-Barremian tracksite from Borgo Celano (Southern Italy)

Antonelli M.*[1], Petti F.M.[2] & Wagensommer A.[3]

[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma. [2] Museo delle Scienze, Trento. [3] Gruppo Archeologico Valle d'Itria ONLUS, Cisternino (BR).

*Corresponding author e-mail:* matteo.antonelli@uniroma1.it

*Keywords:* theropods, photogrammetry, PCA.

More than sixty dinosaur tracks are preserved on seventeen isolated blocks stored in the Palaeontological Museum and Dinosaur Park of Borgo Celano (Gargano promontory, Apulia). The original track-bearing surface, discovered in 2000 by a team of geologists, cropped out in a working quarry near the town of Borgo Celano, within a carbonate succession of inner platform environment, late Hauterivian-early Barremian in age. Ten track-bearing blocks were analysed by Petti et al. (2008): the specimens, preserved as natural casts, are represented by tridactyl footprints, described as *Kayentapus*-like morphotype and attributed to theropods, and roundish footprints, attributed to ornithischians. Recently, an ichnological review, supported by the use of close-range photogrammetry, was carried out on the original material, also including seven new blocks never described before. This study focuses on the theropod footprints. They are medium- to large-sized, weakly mesaxonic and characterised by robust morphologies. Phalangeal pads and sharp claw traces are recognisable. An additional, proximal pad is observable on digit III, likely representing the metatarsal-phalangeal joint. Numerous tracks show a semi-plantigrade posture, and the photogrammetric images also reveal, in several specimens, the occurrence of digit I behind the proximal tip of digit II. Additionally, five theropod tracks are characterised by the metatarsal impressions. The detailed morphological features deduced by the 3D contour maps allowed us to virtually restore the autopodium of the trackmakers, according to the arthral condition of the theropod feet. Following the method proposed by Romano & Citton (2017), the osteological parameters (i.e., metatarsal, digits and phalanges length) of about 60 theropod hindlimbs and those restored on the elite-tracks of the Borgo Celano ichnosite were subjected to Principal Component Analysis and Cluster Analysis. Four attempts were performed, combining different datasets. The results clearly suggest a strong affinity between the hindlimbs of abelisauroids and those obtained from the tetradactyl footprints described herein. The palaeobiogeographic history of this clade lead to hypothesise a Gondwanan origin for the Apulian abelisaurs, thus providing a constraint for a dispersal from Africa to the Periadriatic sector during the Early Cretaceous.

Petti F.M., Conti M.A., D'Orazi Porchetti S., Morsilli M., Nicosia U. & Gianolla P. (2008) - A theropod dominated ichnocoenosis from late Hauterivian-early Barremian of Borgo Celano (Gargano Promontory, Apulia, southern Italy). Rivista Italiana di Paleontologia e Stratigrafia, 114(1), 3-17.

Romano M. & Citton P. (2017) - Crouching theropod at the seaside. Matching footprints with metatarsal impressions and theropod authopods: a morphometric approach. Geological Magazine, 154(5), 946-962.

# Widespread lawsonite occurrence in the blueschist-facies ophiolitic bodies of the albergian unit (Liguria-Piemonte zone, western Alps)

Corno A.*[1], Mosca P.[2], Groppo C.[1], Borghi A.[1] & Gattiglio M.[1]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Istituto di Geoscienze e Georisorse, CNR, Torino.

*Corresponding author e-mail:* alberto.corno@unito.it

*Keywords:* Lawsonite, tectono-metamorphic evolution, Western Alps.

The Albergian unit, belonging to the Liguria-Piemonte oceanic zone of the Western Alps, comprises a thick sequence of calcschists wrapping minor meta-ophiolitic bodies, from metric to kilometric in size. Although the occurrence of fresh lawsonite in the meta-sediments of this unit is known since the end of the XIX century (Franchi, 1897), few data exist on the lawsonite occurrence in its meta-mafic bodies.

Referring to the Albergian unit exposed in the Monte Albergian – Gran Mioul area (upper Chisone valley), the aim of this contribution is twofold: (i) to report the occurrence of fresh lawsonite also in the meta-mafic rocks and, (ii) to constrain its tectono-metamorphic evolution. In the examined area, the Albergian unit consists of a kilometric body of diabase meta-breccias (with minor meta-gabbros and meta-plagiogranite clasts and blocks), covered by discontinuous layers of quartzitic meta-sandstones, black micaschists, and eventually a thick sequence of calcschists. Through a detailed petrographic and minero-chemical study of these lithologies, we recognized preserved magmatic textures in the meta-mafic clasts, and the occurrence of fresh lawsonite, only partially replaced by retrograde phases.

A block of Mg-Al meta-gabbro and a meta-breccia with plagiogranite clasts were investigated for phase equilibrium modeling. Applied for the first time in this unit, the isochemical phase diagrams approach (i.e., P-T pseudosections) allowed to constrain the metamorphic peak in the lawsonite blueschist-facies, at about 18-21 kbar and 380-430°C, followed by a partial re-equilibration in the epidote-stability field.

These results, supported also by published literature (e.g., Agard et al., 2001), allow to better constrain the tectono-metamorphic evolution of the Albergian unit in the complex tectonic framework of this sector of the Western Alps.

Agard P., Vidal O. & Goffé B. (2001) - Interlayer and Si content of phengite in HP–LT carpholite-bearing metapelites. J. Metamorph. Geol., 19(5), 479-495.

Franchi S. (1897) - Sopra alcuni nuovi giacimenti di roccie a lawsonite. Boll. Soc. Geol. Ital., 16, 73-76.

# Chemical and mineralogical characterization of Bottom Ashes (BA) from Municipal Solid Waste Incineration (MSWI)

De Matteis C.*[1], Mantovani L.[1], Toller S.[1], Funari V.[2], Dinelli E.[3] & Tribaudino M.[4]

[1] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma. [2] Istituto di Scienze Marine, CNR, Bologna. [3] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [4] Dipartimento di Scienze della Terra, Università di Torino.

*Corresponding author e-mail:* chiara.dematteis@unipr.it

*Keywords:* bottom ashes, chemical and mineralogical characterization.

The environmental issue can be considered at the same time as a resource and a duty. As a resource it should be a primary need to enjoy during human's life; as a duty it is a responsibility, taking care of other living beings and future generations. A deep and critical knowledge of everyday life employed materials, their provenance and their potential reuse can be a good starting point as respecting and protecting the environment. Despite the use of separate waste collection is constantly growing (about 65% on average in Italy in 2016, ISTAT 2017), we still have very high undifferentiated waste values (about 89 kg/ inhabitants pro years, ISPRA 2017), with the consequent rise of the related output products. Bottom ashes (BA) are, together with fly, the modification of the undifferentiated waste after an incineration process. Actually, BA are currently classified by the European Waste Catalogue (EWC) as industrial non-hazardous waste, but a focal point debated after the European Council Regulation 2017/997 talk about the heavy metals (both glass and minerals) bearing phases, their identification and characterization as well as their weathering behaviour. For these reason the main goal of this work is the knowledge of the exact composition of the raw materials, what are they made of, if there are potential risks for environment and human health and their behaviour in case of re-use. In this work Bottom Ashes from 5 northern Italy Waste to Enery (WtE) plants were sorted by different grain size. For each grain size, X-ray fluorescence (XRF), X-ray powder diffraction (XRD) and Rietveld refinement and leaching test were performed. XRD analysis showed a similar mineralogical composition between the different WtE plants and between the different grain size; the mineralogy phases identified belong mainly to silicates, carbonates, sulfates and metal oxides. On the major phases, Rietveld refinement was carried out and results showed that the amount of the amorphous fraction is variable in the different WtE plants analyzed (30-90%) but always increases with grain size. The amount of mineralogical phases analyzed varies between the different WtE plants and this is probably due to the different input of waste. Silicates are most present in large grain size while carbonates and Ca-rich hydrated phases in smaller ones. XRF analysis confirm the opposite trend between Si and grain size, LOI and Ca content. Few elements follow the Si behaviour, namely Rb, Zr, K and Na, whereas the Ca trend is followed by Zn, Cl and S. Other elements, like Fe and Al show different trend with different incinerator. Leaching test showed higher extraction in smaller grain size and the release of PTE (i.e., Pb, Zn and Cr) is different in the 5 WtE analysed. In some cases, the concentrations of PTE found in the eluate exceed the legal limits and this is an obstacle to their recycling.

# A geoportal for the sustainable management of coastal areas

Domicici R.[1], Donato P.[1], Imbrogno G.[2], Lirer S.[3], Tenuta M.*[3] & De Rosa R.[1]

[1] Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Rende (CS). [2] E3 (Environment, Earth, Engineering), s.c. - spin-off Università della Calabria, Rende (CS). [3] Dipartimento di Scienze Ingegneristiche, Università «Guglielmo Marconi», Roma.

*Corresponding author e-mail:* mariano.tenuta@gmail.com

*Keywords:* coastal systems, sustainable management, geoportal.

In order to identify the most suitable strategies and to support territorial decision-making processes, it is necessary to operate with an integrated vision of coastal systems, considering the complex phenomena of sediment production, erosion and subsequent transport from the supply systems to the coastal areas.

In this work we propose a new approach to the management of coastal areas based on a sustainable and low impact management of sediments and integrated with a WebGIS-based system.

To achieve this goal, sediment production is estimated using the EPM model and a series of implementations that have allowed us to estimate only the sediment component capable of influencing the relative physiographic unit. Finally, the development of a webgis represents the most suitable solution for promotes the sharing and synthesis of multi-source data, and enables widespread sharing of the sediment production model.

The program interface design was made using the Lizmap plug-in. Lizmap is a proxy for web services aimed at building maps. The server configuration was instead made on a clean machine ubuntu 20.04, created specifically for the installation of the geosever. In order to ensure access to data that was efficient and effective from the point of view of consultation, and to have a solid data structure based on consolidated and widespread technologies, it was decided to also design a relational database, stored and managed at the internal of an Open Source DataBase Management System.

The overall structure of the system was abstracted into five layers: user layer, presentation layer, processing layer, domain layer, and data layer.

The webgis platform was developed to allow interactive and intuitive navigation between the different layers. The platform allows to identify the municipal / provincial / regional territory of interest and to identify the areas characterized by greater or lesser sediment production. Other layers allow you to analyze information regarding: the hydrographic network of the Ofanto basin, the distribution of the various physiographic units present, the presence of coastal defense structures, the state of coastal areas (retreat, advancement, stable) and the temporal variations of the coastline for the reference physiographic unit.

The result is the creation of a webgis platform, accessible by anyone, which allows to identify, in the territorial planning process, the strategic areas for sediment production, and consequently to minimize the impact of the sediment deficit for the system coastal. This approach therefore represents a low-impact solution that will make it possible to mitigate the risk of coastal erosion and increase the resilience of coastal systems, also in consideration of the ongoing climate changes.

# Continental slope stability evaluation through morphological analyses using 3D seismic data at the Brazilian Equatorial Margin

Fonseca J.C.L.G.*[1], Vannucchi P.[2], Iacopini D.[3], Maestrelli D.[4], Vital H.[5] & Perez Y R.[5]

[1] Dipartimento di Scienze della Terra, Università di Pisa. [2] Dipartimento di Scienze della Terra, Università di Firenze. [3] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli «Federico II». [4] Istituto di Geoscienze e Georisorse, CNR, Firenze. [5] Departamento de Geociências, Universidade Federal do Rio Grande do Norte (Brazil).

*Corresponding author e-mail:* julia.carvalho@phd.unipi.it

*Keywords:* seabed morphology, equatorial margin, slope instabilities.

Deep-water infrastructures (e.g cables for telecommunication or oil and gas platforms) require the assessment of geohazards on continental shelves and slopes, particularly gravitational and tectonic instabilities. Here we focus on the Potiguar Basin a sedimentary basin located on the Brazilian Equatorial Margin (BEM) – a transform passive margin. BEM's rift started in the Cretaceous and the predominant strike-slip motion is marked by Ocean Fracture Zones (OFZs) that are impinging the margin at angles <45°.

Our analysis started with a detailed map of the seabed horizon (SBH) in a 3D high-resolution seismic cube of ~1850 km² and well-logs, both provided by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). The SBH evidenced at least 15 canyons eroding the seabed with 9 of them forming erosive well-defined valleys like channels. The shelf-slope stability was evaluated through flow pathways by calculating the sinuosity index (SI) and by extracting the slope profiles of the canyons. In the eastern portion of the dataset where faults are not present, the flow pathways vary from rectilinear (SI=1.1) with one knick-point (steepness ~7.6º) located in the outer slope coincident with an abrupt discontinuity on the seafloor (interpreted as a mass-waste deposit), to sinuous (SI=1.3) with a smooth concave upward profile (average steepness ~1.76º), to meandering (SI= 1.4) with profiles that vary from relatively smooth to broken by strong knick-points on the outer part of the slope (~34º). In this latter case, the knick-point coincides with a "meander cut-off". Two erosive valleys are also present in the central portion of the area where several faults were mapped. They both have SI=1.2 indicating low sinuosity. The first presents a concave upward profile (steepness ~2.36º) until it reaches the outer part where a knick point is identified (steepness ~ 11.29º) coinciding with several mapped faults. The other erosive valley, despite presenting a very sharp curve that deviates the flow pathway abruptly to the west, does not show any knick-point (average total steepness ~2.0º).

Our preliminary analysis shows that fault activity seems to have limited control of slope stability. Slope stability seems instead to be related to sediment dynamics with mass-waste deposits derived from canyon walls that cause migration of flow pathways, cut-off of meanders, and knick points initiation.

# Reconstructing landforms and surface processes from declassified intelligence satellite imagery

Forti L.*[1-2]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano.
[2] Istituto di Geoscienze e Georisorse, CNR, Pisa.

*Corresponding author e-mail:* luca.forti@unimi.it

*Keywords:* declassified intelligence satellite imagery, fluvial geomorphology, seasonality.

Historical declassified intelligence satellite imagery (e.g., CORONA and Hexagon) are used in archaeology to assess the distribution and preservation of archaeological site in many parts of the Old World, and especially in arid lands, where the poor plant cover does not hamper the opportunities offered by earth observation tools. The same approach can be applied to geomorphology to reconstruct the evolution of surface processes and landforms in areas where recent urbanization had obscured natural features. In this contribution, we illustrate a first application of this approach to reconstruct the riverscape of the Tigris River in northern Iraq. The Mosul Dam reservoir in the Kurdistan Region of Iraq was built along the Tigris River between 1981 and 1988, submerging the course of the Tigris River for ca 100 km. Geomorphological mapping based of historical images derived from declassified Corona satellite imagery acquired between December 1967 and August 1968 reveals the pristine pattern of the Tigris River. Different spy images are snapshots of the seasonal changes of the Tigris riverbed, shifting from meandering to anabranching across the hydrological year, and illustrate the dynamic fluvial landforms such as the floodplain and point, middle, and longitudinal bars. Our approach underlines the relevance of historical declassified intelligence satellite imagery to reconstruct the ancient fluvial landscape below the Mosul Dam Lake and correlate it with litho-structural factors. We demonstrate the importance of historical aerial/satellite imagery in interpreting past natural geomorphic processes and landforms that suffered altering by human agency.

# Laboratory assessment of rock fracturing state using infrared thermography

Franzosi F.*, Casiraghi S., Colombo R., Crippa C. & Agliardi F.

Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca.

*Corresponding author e-mail:* f.franzosi@campus.unimib.it

*Keywords:* IRT fracturing.

The fracturing state of rocks is a fundamental control on their hydro-mechanical properties at all scales and provides a descriptor of the evolution of brittle deformation around faults, underground excavations, and slopes.

Descriptors of rock fracturing are diverse depending on considered scale, fracture topology (traces, surfaces) and sampling dimension (linear, areal, volumetric). A complete representation of fracturing state can be obtained in the laboratory by non-destructive imaging techniques (e.g., X-ray CT), in terms of volumetric fracture intensity ($P_{32}$) and porosity ($P_{33}$). Nevertheless, geophysical imaging is usually unable to resolve small objects in fractured media at field scale. Window and scanline sampling strategies are easily applied in the field to measure fracture intensity descriptors (e.g., $P_{10}$, $P_{21}$) or empirical rock mass quality indices (e.g., GSI), but are affected by scale and fracture orientation biases. Some authors suggested that rock mass fracturing states can be characterized by measuring their heating and cooling response through infrared thermography (IRT), but a physically-based, generalized approach to prediction is lacking.

In this perspective, we carried out an experimental study on the thermal response of rock samples with known fracturing state. We studied cylindrical samples of gneiss (7) and schist (8), pre-fractured in uniaxial compression that produced complex fracture patterns constrained by rock composition and fabrics.

Using MicroCT (voxel: 0.625 mm) we reconstructed the 3D fracture network and computed the $P_{32}$ and $P_{33}$ of each sample. Then, we set up cooling experiments in both laboratory (controlled environment) and outdoor (daily heating-cooling) conditions. Sample surface temperature during cooling was imaged in time lapse using a FLIR$^{TM}$ T1020 IRT camera.

The acquired multi-temporal thermal images were processed to extract: a) spatial temperature patterns corresponding to the response of individual features and fracture networks; b) time-dependent cooling curves, described in terms of Cooling Rate Indices and a Curve Factor. These descriptors show statistically significant correlations with fracture abundance measures, stronger with $P_{33}$ than with $P_{32}$ and more robust for gneiss samples, characterized by more distributed fractures than schist. More fractured rocks cool at faster rates and the corresponding cooling curve shapes can be normalized to remove the effects of lithology and boundary conditions to obtain a predictive tool. Experimental results have been reproduced by 3D finite-element modeling of the cooling process in numerical samples including explicit fracture objects. Results of outdoor experiments show that differences in thermal response can be significantly detected even in natural conditions. Our results provide a starting point to develop an upscaled, quantitative methodology for the contactless *in situ* assessment of fracturing state of rock masses using thermal data.

# Hydrogeological exploration perspective for groundwater springs potential assessment: the case study of Val Sabbia

Lucchelli A.*[1], Pedretti D.[1], Gisolo M.[2] & Fiandaca G.[1]

[1] Dipartimento di Scienze della Terra "A. Desio", Università di Milano. [2] A2A Ciclo Idrico S.p.A., Brescia.

*Corresponding author e-mail:* alice.lucchelli@unimi.it

*Keywords:* 3D modelling, Airborne EM.

Climate change is undeniably one of the main elements of today's era and affects all the natural resources, including groundwater, which already provides 49% of the water withdrawn for domestic use by the global population (United Nations, 2022). Water supply from groundwater springs has the potential to provide climate change adaptation, so it becomes crucial to find strategies to support sustainable management of this resource, that entail a deep comprehension of the groundwater resources.

The study focuses on Val Sabbia, in the eastern Lombardy Southern Alps (Italy), characterized by a complete Permian-Cenozoic succession (Cassinis et al., 2008). In this area karst-fissured rocks represent the groundwater reservoirs, and the groundwater flow is controlled by lateral and vertical variation in hydrostratigraphic units. Here a large-scale multidisciplinary approach, involving geology, geophysics, and hydrogeology, is proposed. To understand and conceptualize the groundwater flow, the first step is to build a detailed 3D geological-hydrostratigraphic model based on lithological and structural data available in literature and from surface geological information acquired during field survey.

Furthermore, to enhance the characterization of a complex karst-fissured aquifer system, particularly its deepest geological levels, the 3D model is integrated with large-scale dense-coverage geophysical surveying, based on geolectrical and electromagnetic methods. In particular, more than 4.000 line-kilometers of time-domain Airborne EM data will be acquired within 2022, and a complementary ground-based field campaign comprising 20 line-kilometers of ERT data, and 150 line-kilometers of EM data is ongoing. These methods will provide unprecedented spatial coverage for the characterization of the aquifers and will help in identify variations in rocks hydraulic properties.

Once the 3D geological-hydrostratigraphic model is built, integrated and validated with geophysical data, the study proceeds with the numerical simulation of the groundwater flow and the projection on how this is susceptible of seasonal variations and thus can affect the springs discharge, also considering different climate change scenarios.

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# Heavy metals and radiogenic isotopes in river systems affected by urban and industrial activity: the Valdinievole sub-basin (Tuscany, Italy) case study

Maccelli C.*[1-2], Natali C.[1], Nisi B.[3], Casalini M.[1], Vaselli O.[1-3], Venturi S.[1-3] & Avanzinelli R.[1]

[1] Dipartimento di Scienze della Terra, Università di Firenze. [2] Dipartimento di Scienze della Terra, Università di Pisa.
[3] Istituto di Geoscienze e Georisorse, CNR, Firenze.

*Corresponding author e-mail:* chiara.maccelli@unifi.it

*Keywords:* environmental geochemistry, heavy metals, radiogenic isotopes.

The Usciana River is located in the lower part of Valdinievole, one of western sub-basins of the Arno River Basin (Tuscany, Central Italy). It represents the only emissary of the Padule di Fucecchio, a swampy zone which acts as a collector of all creeks and channels draining the highly anthropized northern part of the basin. This PhD project is aimed at characterizing the natural and anthropogenic contributions of heavy metals in the river system of the Valdinievole sub-basin by analyzing waters, suspended solid loads, and stream sediments. Many relevant human activities and small-medium enterprises, such as paper mill industries, flora-nursery farms, thermal spas, and one of the most productive Italian tanning districts are located in this area, making it an ideal laboratory to investigate how the anthropogenic pressure affects surface waters. In this work we present preliminary analytical data on waters and suspended solids obtained by Ionic Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the determination of major, minor, and trace concentrations, respectively. Radiogenic isotope composition was analyzed by Thermal Ionization Mass Spectrometry (TIMS) on suspended solid (Sr, Nd and Pb) and in water samples (Sr). A relatively large geochemical variability is shown by the water samples, whose composition is affected by seasonal variations, ranging from $Ca^{2+}(Mg^{2+})$-$HCO_3^-$ to $Na^+$-$Cl^-(SO_4^{2-})$ geochemical facies. The most relevant variations are recorded for the dissolved N-bearing species during high and low river discharge periods, as they varied from 36 to 80 ($NO_3^-$), from 1.2 to 2.4 ($NO_2^-$), and from 12 to 23 ($NH_4^+$) mg/L, respectively. A relatively high concentration of Cs was detected in a few waters and suspended solids where concentrations up to 170 µg/L and 46 mg/kg, respectively, were measured, highlighting a dilution trend along the river system. The Pb isotopic signature of the suspended solids reflects the contribution by anthropogenic sources, especially for those samples collected in the most urbanized and industrialized areas. The Enrichment Factors of Ni, Mo, and Pb are positively correlated with the Pb isotopic ratios since a clear trend between geogenic and anthropogenic sources is evidenced. On the other hand, the Sr isotopic composition of waters mainly reflects selective dissolution of carbonates with respect to silico-clastic rocks. The Nd isotopes are presently in progress.

# Mechanisms of heavy metals incorporation in hollandite and pyrochlore

Margheri S.*, Bindi L., Bonazzi P. & Lepore G.O.

Dipartimento di Scienze della Terra, Università di Firenze.

*Corresponding author e-mail:* simone.margheri@unifi.it

*Keywords:* heavy-metal removal, cation exchange, crystal structure.

Natural presence or anthropic dispersion of toxic elements in aqueous matrices represents a main environmental concern and a serious hazard for human health. Finding new solutions to such problem is necessary for the welfare and the progress of our society.

Heavy metals pollution in waters accounts for a particularly challenging matter, due to high mobility and persistence in the environment of these kind of elements.

Hollandite and pyrochlore have been often shown to be effective in incorporating large-radius cations via ionic exchange. Their structures are built by rigid frameworks that surround tubular cavities, which can accommodate a wide variety of large-radius cations.

Indeed, over the past forty years, such minerals have been the subject of numerous studies aimed at the investigation of their ability to incorporate and retain radioactive elements (e.g., Ringwood, 1978), to be exploited as ionic conductors (e.g., Feng et al., 1995) or as catalysts (e.g., Jitta et al., 2015).

The aim of this Ph.D. project is to investigate the ability of pyrochlore-like and hollandite-like structures to incorporate pollutant elements like Tl and Pb via ionic exchange in aqueous matrices. The project involves capture and release experiments, carried out through imbibition processes under controlled condition.

Natural samples of hollandite and pyrochlore will be evaluated; uptake experiments will be supported by chemical and structural analysis by means of wavelength-dispersive spectroscopy (WDS), X-ray diffraction (SC-XRD, XRPD) and spectroscopy (XAS) techniques.

The investigations will be carried out also on synthetic analogues in order to improve both incorporation capacity and selectivity: the basic structures of these tunnel oxides will be conveniently modified, adding minor amounts of selected elements in the framework.

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# Petrophysical and chemical characterization of carbonate rocks for $CO_2$ storage purpose: case studies from Umbria-Marche Apennines (Italy)

Mitillo N.*

Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* nicola.mitillo@studenti.unipg.it

*Keywords:* reservoir characterization, petrophysical properties, $CO_2$ storage.

The aim of PhD project concerns the physicochemical characterization of potential reservoir rocks in order to evaluate the influence of different lithologies on carbon geological storage activities. In particular, a petrophysical, mineralogical and geochemical studies will be conducted in order to investigate the feasibility and impact of $CO_2$ injected in reservoir rocks for evaluating their potentiality to act as repositories and natural catalyst for the $CO_2$ conversion into new green useful fuels. For this reason, several sedimentary rocks, different for lithology (carbonate and sandstone) and facies, coming from different geological contexts, will be collected and analysed through a multidisciplinary approach. As well know, the petrophysical properties can be strictly controlled by the occurrences of different sedimentary and diagenetic processes, making difficult the study of reservoir quality prediction. In particular for carbonate rocks, different processes such as: dissolution and cementation, compaction, neomorphism, dolomitization and precipitation of new minerals may occur, modifying texture and interface contacts between the different phases involved. As a consequence, evaluate the influence of new assemblage and arrangement of the petrophysical properties triggered by different diagenetic processes resulted fundamental in order to predict evolution of storage capacity of rock. The preliminary results here presented are referred to different carbonate units (both dolomitized and not) cropping out from different study areas of the Umbria-Marche Apennines. In order to reconstruct the petrophysical properties evolution, a preliminary and detailed sedimentary petrography study was performed through optical microscope analysis, describing for each sample the rock-fabric and porosity (both primary and secondary). Contemporaneously, porosity measurements (both effective and total porosity) were performed through the helium pycnometer tool on the most representative samples, in order to compare porosity values with the different lithofacies involved. Moreover, a 3D micron-scale characterization of pore structure through the X-ray micro-Computed Tomography (XR-mCT) technique, resulted necessary for studying microporosity in order to improve the knowledges about grains size, shape and sorting of sediments with the corresponding 3D pore network features (specific surface, pores size, morphology, distribution and connectivity), all characteristics which exerts a strong control on hydraulic properties of rocks. Furthermore, mineralogic and spectroscopy analyses have been performed, providing preliminary results concerning the main mineralogic phase and element distribution on carbonate minerals in order to predict potential geochemical variations due to $CO_2$-water-rock interaction and verify the availability of catalyst elements.

# Relationships between polyphasic deformation and fracture network: insights from the Ligurian Briançonnais

Perozzo M.*, Maino M., Menegoni N. & Seno S.

Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

*Corresponding author e-mail:* michele.perozzo01@universitadipavia.it

*Keywords:* field mapping, inversion tectonics, Ligurian Alps.

The Briançonnais domain (Bd) of the Ligurian Alps represents a complex sector showing intricate structures interpreted as the result of inherited pre-collisional structures influence and a polyphase deformation (Bonini et al., 2010). To reconstruct the kinematic evolution of this domain, each structure should be analysed considering the summation of the contribution of overlapping multiple deformation phases, both fragile and ductile, as well as the continuous feedback between pre-existing conditions and changing stress domains.

The simpler example is represented by the inversion of pre-Alpine normal faults that could be preferentially reactivated as thrust (Seno et al., 2005) during the collisional stacking.

The multiphase Alpine deformation produces further complexity overlapping several stages of repeated brittle and ductile deformation associated with variation in the kinematic orientation, metamorphic conditions and strain intensity. Ascribable to fold interposition of the two main ductile phases, type 3 interference pattern is commonly associated with coeval sets of fault and fractures. The first fracture pattern drives the nucleation and the development of the following deformation stages. However, how the early fault and fracture network influences the following evolution of brittle structures is poorly quantified.

We aim to study the influence of the early deformation features (folds and faults/fractures) on the development of the following stages. Field-based and digital Photogrammetry techniques are integrated to build a three-dimensional structural model where the orientation pattern of fracture may be evaluated in relation with the fold morphology. This approach is addressed to the Mesozoic sequences of the Bd Castelvecchio-Cerisola unit (Decarlis et al., 2017), outcropping in the 245-Albenga sheet. Field survey has been implemented within the Italian Geological Survey Project (CARG) finalized in producing the 1:50.000 geological map. Close to Finale Ligure, the Monte Carmo unit displays a km-sized recumbent fold characterized by a curvilinear fold axis resulting in a sheath-like fold morphology. The integration of field analysis and Digital Outcrop Modelling techniques show that, despite the polyphasic evolution, the fracture pattern keeps the orientation associated with the first (and principal) folding stage. It results in a strong control of the inherited structure in the evolution of polyphasic deformation. Fault and fracture pattern of post-ductile deformation are monitored through the analyses of the Pietra di Finale Fm., which is Miocene carbonate-siliciclastic coastal wedge (Brandano et al., 2015) unconformably laying on folded Bd rocks.

This work highlights the importance to investigate the early deformation pattern, to predict the behaviour of the rock system in the following deformation phases, generating a space-time interconnection among structures.

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# The Sardinian Variscan belt: new tectono-metamorphic constraints from the hinterland-foreland transition zone

Petroccia A.*[1], Carosi R.[1], Montomoli C.[1], Iaccarino S.[1] & Vitale Brovarone A.[2-3]

[1] Dipartimento di Scienze della Terra, Università di Torino. [2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. [3] Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris (France).

*Corresponding author e-mail:* alessandrogiovannimichele.petroccia@unito.it

*Keywords:* Nappe Zone, Variscan Belt, P-T-D-t path.

The geodynamic evolution of collisional orogens has been classically described using an orogenic wedge model, where different rock packages experience different metamorphism. The hinterland-foreland transition zone making the fold-and-thrust belt is defined by the progressive transition from tectonic units that occurred in the metamorphic core of the belt to others deformed at shallower crustal levels and steadily included in the orogenic wedge. The Variscan basement in Sardinia offers an excellent opportunity (Carmignani et al., 1994) to investigate a continuous section of metamorphic rocks where the progressive metamorphism and deformation is clearly recognizable. Although the northernmost Sardinia has been strongly investigated, i.e., the medium-high grade metamorphic complexes (see Cruciani et al., 2015 for the review), the central sector or the hinterland-foreland transition zone, has been poorly studied and understood (Montomoli et al., 2018). This is related to the difficulty of unravelling the complex pattern of the deformation and the P-T-t condition in low-grade metamorphic rocks. In our study, we investigated meso- and microstructures, the thermal architecture with Raman Spectroscopy on Carbonaceous Material, the P-T conditions and the timing of the deformation from different sectors belonging to the Sardinian hinterland-foreland transition zone. These data led us to implement the existing knowledge of the Sardinian belt and give new information to revisit its tectono-metamorphic evolution.

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# Structural modeling for geothermal potential evaluation in Southern Apennines

Pontikou C.*[1], Toscani G.[1], Ricciato A.[2] & Di Cuia R.[3]

[1] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. [2] GePlan consulting s.r.l., Ferrara. [3] Delta Energy Ltd., London (UK).

*Corresponding author e-mail:* chrysanthi.pontikou01@universitadipavia.it

*Keywords:* geothermal potential, 3D model, Southern Apennines.

In the framework of a 3-years Ph.D. project started at the beginning of 2022, the research activity focuses on the Campania-Lucania sector of the Southern Apennines where, based on previous studies, a geothermal positive anomaly has been detected (Enel, 1987; Enel/Eni/Cnr/Enea, 1994; Della Vedova et al., 2001; ViGOR, 2014; ViDEPI, 2017). The broader geological context of the identified study area is re-evaluated by integrating public available data like seismic reflection profiles, deep wells, gravimetric information (ISPRA website) while it is supplemented by extensive research of the publicly literature where different and sometimes contrasting structural styles have been proposed from various authors for the tectonic configuration of the area. The presence of this heat anomaly and in particular the mechanism for heat transfer has not been satisfactorily explained from a structural point of view. We present a comprehensive synthesis of the public available data and a preliminary seismic interpretation and structural reconstruction of the study area. Previous studies on the geothermal potential of the area and the research program needed to assess its geothermal prospectivity will be also presented and discussed.

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# Former melt inclusions in garnet from UHP gneisses of the Seve Nappe Complex (Scandinavian Caledonides)

Slupski P.*[1], Cesare B.[1], Bartoli O.[1], Majka J.[2], Klonowska I.[3] & Remusat L.[4]

[1] Dipartimento di Geoscienze, Università di Padova. [2] Department of Earth Sciences, Uppsala University (Sweden). [3] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Krakow (Poland). [4] Institut de Mineralogie, Physique des Materiaux et Cosmochimie, Museum National d'Historie Naturelle, Paris (France).

*Corresponding author e-mail:* pawelmichal.slupski@studenti.unipd.it

*Keywords:* anatexis, nanogranitoids, UHP metamorphism.

Ultrahigh pressure metamorphism has been recently reported in the Seve Nappe Complex (SNC) of the Scandinavian Caledonides (Klonowska et al., 2017). This study is focused on former melt inclusions (nanogranitoids, Bartoli et al., 2016; Cesare et al., 2015) and anatectic processes occurring during the ultradeep subduction of paragneisses from Åreskutan, SNC, where the presence of microdiamond was reported (Klonowska et al., 2017). The mineral assemblage of the paragneiss is K-feldspar, garnet, quartz, plagioclase, biotite, white mica, kyanite, sillimanite and rutile. Garnets occur as porphyroblsats or aggregates of coalesced crystals up to 3 mm in diameter and they are randomly spread in the matrix. Clusters of inclusions are present in most of the garnets, and they are composed of small multiphase inclusions (MPI), less than 5 µm in size and represent former fluid. MPI consist of various carbonates such as calcite, siderite, magnesite, biotite, pyrophyllite rarely quartz, graphite, or rutile and a residual fluid made of $CO_2$ and $CH_4$. Within the clusters, relatively larger (5 – 20 µm) and rarer inclusions are nanogranitoids, composed of quartz, biotite, K-feldspar, plagioclase and rarely carbonates. The presence of microdiamonds coexisting with nanogranitoids and MPI in the clusters was confirmed by Raman spectroscopy. Seven re-homogenization experiments at different conditions were conducted in a piston cylinder apparatus to remelt nanogranitoids and determine the composition of the anatectic melt. The best homogenization was acquired at 900˚C and 4.5 GPa. The entrapped melt is mostly rhyolitic to trachytic in composition, with a systematic high alkali content (~10 wt% $N_2O$+$K_2O$). The $H_2O$ and $CO_2$ content of the remelted nanogranitoids analyzed by NanoSIMS is respectively ~ 5 wt% and 2000–5000 ppm. The chemical composition of reconstructed anatectic melt from paragneisses of SNC is consistent with experimental studies of UHP melts derived from metapelites.

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# Influence of fracturing on primary porosity and implications for $CO_2$ Capture and Storage (CCS): case studies from the Umbria-Marche Apennines

Urbani M.*

Dipartimento di Fisica e Geologia, Università di Perugia.

*Corresponding author e-mail:* marco.urbani@studenti.unipg.it

*Keywords:* fault zone porosity, fracture network, $CO_2$ storage.

$CO_2$ geological storage represent a viable option to reduce the greenhouse-gas emissions, moreover, it's an immediately applicable technology resulting from experiences gained in oil and gas exploration.

Large sedimentary basins are best suited because they have tremendous pore volume and are widely distributed across the globe. In order to obtain a significant result, the number of CCS projects needs to increase worldwide. Naturally Fractured Reservoirs (NFRs) are ubiquitous across the world, but still, they've received little attention in $CO_2$ storage, mainly because the presence of faults and fractures can affect the porosity, so the efficiency, of the reservoir. Faults and fractures must be taken into account even when considering the properties of sill, being fundamental in the security of the storage sites.

To achieve significant results with CCS, NFRs need to be studied with different approaches. The main target of this PhD project will be focused on a structural characterization of fractured reservoirs to define the main features that allow their safely use for CCS, throughout the following approaches:

Analysis of the variations in primary porosity and permeability related to the presence of tectonic structures like faults and fractures that can affect the efficiency and the security of the reservoir for CCS;

Caprock and his sealing capacity during and after the injection of $CO_2$;

Analysis of the deformation processes in the rock before/after the injection of $CO_2$.

All the work will be conducted with a structural-geological approach, principally at the outcrop scale, considering lithologies which will be already characterized from a sedimentological point of view; in this way, the geological field work will be conducted in order to consider these lithologies where they're displaced by faults; this will allow to compare the porosity values in the undeformed rocks (protolith) with the ones measured in the fault zone (damage zone and core zone, respectively) and to quantify the influence of fracturing on the primary porosity.

All the data regarding faults/fractures at the outcrop scale will be obtained with Laser Scanner techniques to study the fracture network. The measured linear parameter will be used to build different Discrete Fracture Networks (DFN) to study the effect of fracturing on primary porosity and the behavior of the host rock in terms of permeability and fluid flow simulation.

To achieve these aims, a site characterization for CCS by studying representative areas will be realized. The first case study will be in the northern sector of the Apennines, the Umbria-Marche domain, where will be investigated large variability (both vertical and horizontal) of Jurassic successions including both shallow-water carbonate platform (e.g., Calcare Massiccio Fm) and the overlying basinal lithofacies (e.g., Corniola, Calcari Diasprigni, Maiolica formations), in order to evaluate potential case studies of a reservoir-caprock system for CCS.

# Chemical-Petrographic characterization of construction and demolition waste for valorization and recycling

Volpintesta F.*

Scuola di Scienze e Tecnologie, Università di Camerino.

*Corresponding author e-mail:* francesco.volpintesta@unicam.it

*Keywords:* CDW, recycling, characterization.

Construction and demolition waste (CDW) represents the most important waste stream in EU (as well as in the world) and its production is estimated growing in next years, due to building renovations and ageing of concrete infrastructures. Its importance is also testified by the legislative choices made by EU. In fact, the Waste Framework Directive (WFD) states that CDW recycling has been set at a minimum of 70 wt.% by 2020. Despite excellent results of most member States to comply with EU requirements, this praiseworthy goal has been reached by considering also backfilling in the recycling quote, which is a downcycling process, whereas about 35 wt.% of CDW is conferred to landfill.

Benefits of an appropriate management and valorization of this material would have a favourable impact on saving extraction of raw materials, but also on economic and social effects of a new industrial production, focusing on green economy. However, mainly due to the heterogeneous nature in both time and geographical provenience, CDW hides many difficulties for recycling. It is made up of concrete, bricks/tiles, cement, rocks fragments and soils components, as well as others (e.g., wood, glass, metals, plastic, gypsum and eventually asbestos), and being their distribution changing, properties of materials containing CDW cannot be not constant over time. Furthermore, materials like gypsum, although less important quantity, could play a fundamental role for recycling applications affecting negatively the performance of the recycled products. Therefore, even little quantity variations, can results in variable outcomes.

The aim of this PhD project is to determine the CDW potentials for industrial applications. First of all, the mineralogical and chemical composition of the CDW samples have been preliminary characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF) allowing to determine the extent of compositional variations, useful to focus on specific applications.

Mechanical separation tests at high and low intensity have been carried out on selected samples. A planetary mill without balls was used to ensure energetic interactions between grains, while for the latter a protract sieving (about 5 h) was performed. Separation processes were followed with image analysis and leaching tests in order to estimate changes in the samples. The separation tests revealed that an energetic abrasion is not convenient as it is more energy-consuming, and more prone to producing large quantities of the finest grain size (<355 μm) more difficult to recycle but also where more useful components concentrate. However, adopting a less energetic treatment the sample does not change its modal composition, but it separates the finest fraction that covers grains thus making the CDW more suitable for recycling applications making the industrial approach easier.

The recycling potential of the material obtained following mechanical separation is under investigation to make different construction materials. Tests using CDW as the aggregate component in cement and geopolymers binders as well as the fine fraction in cement binders have been tested and compared for physical and mechanical properties, showing promising results.

# Oral Session Platinum Sponsor

# Sustainable and complete cement solution by Bruker XRD and XRF

Schmidt R.*

Bruker AXS GmbH, Karlsruhe (Germany)

*Corresponding author e-mail:* Lucia.Robba@bruker.com

*Keywords:* cement, carbon dioxide, X-rays.

The cement production process is a major contributor to carbon dioxide emissions, accounting for about 8 percent of the global releases.

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# IODP-Italia and the Italian participation in ECORD-IODP and ICDP in the transition towards a new drilling partnership

Argnani A.[1-2], Boschi C.[1-3], Camerlenghi A.[1-4], Erba E.[1-5]*, Florindo F.[1-6], Frezzotti M.[1-7], Iadanza A.[1-8], Raffi I.[1-9], Ravazzi C.[1-10], Sacchi M.[1-2], Sagnotti L.[1-6] & Tribuzio R.[1-11]

[1] IODP-Italy (The national IODP-Italia Committee and Scientific Secretariat). [2] CNR-ISMAR. [3] CNR-IGG. [4] OGS. [5] Università degli Studi di Milano – La Statale. [6] INGV – Roma. [7] Università degli Studi Roma Tre. [8] CNR – DSSTTA. [9] Università di Chieti – Pescara. [10] CNR – IGAG. [11] Università di Pavia.

*Corresponding author e-mail:* acamerlenghi@inogs.it

*Key words:* IODP-Italia, ECORD, ICDP, Coordination and support.

The *International Ocean Discovery Program* (IODP, 2013-2024), which currently involves 21 countries, is the longest-running international collaboration in the field of the Earth Sciences, built on the legacy of the Deep Sea Drilling Project (DSDP), the Ocean Drilling Program (ODP) and the Integrated Ocean Drilling Program (IODP). Scientific drilling and coring, remarkably representing the only means to recover the sediments and rocks below the seafloor and retrieve information on millions of years of Earth's History, has transformed our understanding of the Earth System over the past five decades, addressing fundamental questions about Earth's dynamics, types and rates of surface and deep processes, climate changes and the evolution of the marine biosphere.

In 2003, the *European Consortium for Ocean Research Drilling* (ECORD) was created to coordinate the European contribution to IODP as a single partner. Twenty years later, ECORD unites 15 countries and acts as the third program platform provider for those expeditions that need to be implemented with Mission Specific Platforms (MSPs).

IODP is currently in the process of reshaping its international governance, to define a new and more flexible drilling partnership based on the new IODP Science Framework 2050. In this evolving scenario, ECORD plays a prominent role thanks to its consolidated and streamlined management structure that strongly reaffirms its commitments to implement a "philosophy" for the next ocean drilling program (post-2024), through the promotion of the "Mission-Specific Platform (MSP)" as a key for more sustainable and flexible drilling expeditions. From January 2022 until the end of the running program, the ESSAC Office (ECORD Science Support and Advisory Committee) is being hosted at OGS (Trieste), chaired by Angelo Camerlenghi and managed by Hanno Kinkel.

Italy joined the drilling program ODP in 1986 and then became a member country of ECORD since its foundation, in 2003. Thanks to national funding annually allocated by MIUR since 2013 and managed by the CNR Dept. of Earth System Science and Environmental Technologies (DSSTTA), IODP-Italy regularly operates through an advisory committee and a scientific coordinator (www.iodp-italia.cnr.it). The CNR Committee "ECORD-IODP and ICDP" is composed of experts in different research fields presently chaired by Elisabetta Erba (Univ. of Milan) and is committed to implementing a joint IODP-ICDP support to the Italian involvement in the international scientific drilling, including the *International Continental Scientific Drilling* Program (ICDP). IODP-Italy primarily coordinates and facilitates initiatives to foster participation of Italian scientists in IODP expeditions and in all research, institutional, education (summer schools), and outreach activities.

IODP-Italy has recently implemented its funding scheme, to provide Italian scientists with additional financial support to develop their post-cruise research. The application process guidelines and forms for shipboard and shore-based scientists, as well as for eligible post-moratorium researchers, are available on the webpage http://www.iodp-italia.cnr.it/index.php/it/opportunita/finanziamento-iodp-italia. The number of funding recipients will be subject to the annual financial resources. In 2022, IODP-Italy also launched the third edition of the "*Bando per il finanziamento di progetti di ricerca nell'ambito della perforazione oceanica ECORD - IODP*", a call for three Postdoctoral Fellowships (2 years) to conduct projects on data and samples collected over the past decades during DSDP/ODP/IODP expeditions.

All opportunities to get involved are regularly circulated through the mailing list iodp-italia@cnr.it and published on the website www.iodp-italia.cnr.it.

# Evolution of in-situ Rb/Sr by LA-MC-ICP-MS/MS: from Proteus to Neoma MS/MS

Craig G.[1], Pellegrini M.[*1], Bevan D.[2], Roberts J.[1], Bouman C.[1], Lloyd N.S.[1], Wehrs H.[1], Elliott T.[2] & Schwieters J.[1]

[1] Thermo Fisher Scientific, Hanna-Kunath Str. 11, 28199 Bremen, Germany. [2] Bristol Isotope Group, School of Earth Sciences, University of Bristol, Queens Road, Bristol, BS8 1RJ, UK

*Corresponding author e-mail:* maura.pellegrini@thermofisher.com

*Keywords:* In-situ Rb/Sr dating, MC-ICP-MS/MS, Collision/reaction cell.

The introduction of ICP-MS/MS instrumentation in the last decade, such as the Thermo Scientific™ iCAP-TQ™ and Agilent Technologies™ 8800 and 8900, has seen new analytical methods developed. One method which has seen much interest is in-situ Rb/Sr dating by laser ablation (e.g., Bolea et al., 2016; Tillberg et al., 2020). However, Rb/Sr dating is a technique which traditionally benefits from the significantly higher isotope ratio precision which can be achieved by multicollection, such as in MC-ICP-MS or TIMS. This naturally led to the conclusion that for this application what was required was an instrument combining the excellent precision of isotope ratio measurements from MC-ICP-MS with the full analytical versatility of established ICP-MS/MS designs.

In-situ Rb/Sr dating has been reported for two prototype MC-ICP-MS/MS developed by Thermo Fisher Scientific™: Proteus MC-ICP-MS/MS and Vienna MC-ICP-MS/MS. The Vienna MC-ICP-MS/MS was built upon the experiences collected from the preceding Thermo Scientific Proteus, borne from a cooperation between the University of Bristol and Thermo Fisher Scientific, introducing a groundbreaking, novel pre-cell mass filter design [Craig et al., 2021). Both Proteus and Vienna were highly successful for in-situ Rb/Sr analysis, providing a hundred-fold increase in sensitivity and 25 times improvement in $^{87}Sr/^{86}Sr$ precision over single collector ICP-MS/MS instrumentation (Bevan et al., 2021).

Here we report on the analysis of in-situ Rb/Sr using the new Neoma MS/MS MC-ICP-MS, an upgrade option for the latest Neoma MC-ICP-MS platform. The larger detector array, wider dispersion, seamless laser-instrument software integration, all combined with its unique MS/MS technology: the Neoma MS/MS dramatically improves precision and accuracy of in-situ Rb-Sr, revolutionizing in-situ geochronology.

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