X-ray microspectroscopic investigations of Ni(II) uptake by argillaceous rocks of the Boda Claystone Formation in Hungary

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One of the main aspects for evaluating the safety case of a potential radioactive waste repository in a deep geological formation is to understand and quantify the geochemical and physical processes that influence the mobility of the radionuclides in the geochemical environment imposed by the host rock. This information is needed to make reliable predictions of the long-term retardation behaviour of radionuclides. The present study focuses on the interaction of a key radionuclide with the Boda Claystone Formation (BCF) of the planned high level radioactive waste repository in Hungary. BCF is rich in illite and hematite. The aim is to identify the mineral phases responsible for the uptake of Ni by BCF, and to investigate the uptake mechanisms of radionuclides on clays and other minerals present in the host rock.

Small pieces of selected BCF core hole samples from a depth of 540 m were prepared as thins sections and equilibrated with $NiCl_2$ solutions at pH = 7.05 in a 0.1 M NaCl background electrolyte. Combined μ-XRF/XAS/XRD measurements were performed at HASYLAB Beamline L (Hamburg, Germany) and μ-XRF/XRD at the ANKA FLUO Beamline (Karlsruhe, Germany). μ-XRF maps were recorded from pre-selected areas of the samples, using a step size comparable to the beam size (20 μm at HASYLAB and 5 μm at ANKA) and 1 s counting time per pixel. The elemental maps served as a basis for selection of small areas of interest where μ-XRD images were collected by a CCD detector. The μ-EXAFS measurements were measured in fluorescence mode at HASYLAB Beamline L, at 20 μm lateral resolution for certain points of interest.

The distribution maps indicate that Ni is mainly associated to K- and Fe-rich phases. μ-XRD analyses with a 5 μm beam diameter indicate that the composition of the argillaceous rock matrix on the micro-scale agree well with the mineral composition of the clay rich areas obtained by bulk-XRD measurements. The good correlation of Fe with K is mainly caused by the high K content in illite (a K-rich 2:1 clay mineral). Micro-EXAFS investigations demonstrated that inner-sphere complexation of Ni occurred to clay minerals. At higher Ni concentrations (10^{-3} M Ni) surface precipitation processes prevailed. The formation of Ni precipitated phases such as Ni-phyllosilicates has important geochemical implications because layered silicates are stable minerals in mildly acidic to basic pH conditions and can irreversibly bind metals in waste and soil matrices. The uptake of contaminants on mineral surfaces forming inner-sphere complexes strongly reduces the mobility of metals in the geosphere. The results of the analyses demonstrated that for Ni(II) the clay mineral illite is an effective sinks in the BCF sample.

Tracing Euxinia in Ancient Oceans with molybdenum

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Elevated molybdenum (Mo) concentrations in organic-rich sediments are a characteristic feature of deposition in sulfidic waters. A comparative study of modern sediment cores from more than 200 marine sites worldwide show that all euxinic basins display >25 ppm Mo [1]. Conversely, all organic-rich sediments with >25 ppm Mo are deposited from a permanently or intermittently sulfidic water column. We show that this last observation can now be determined in <30 seconds using handheld X-Ray absorption Fluorescence spectroscopy (HH-XRF). The new tool enables euxinic classification in the field.

The Mo enrichment process in euxinic settings is expected based on the critical role that aqueous H_2S plays in breaking Mo=O double bonds when soluble MoO_4^{2-} forms reactive Mo sulfides [2]. However, we have identified Neoproterozoic euxinic settings based on Fe-speciation indicators [3] with only small sedimentary Mo enrichments [4]. The Fe speciation technique is unlikely to give false-positive identifications of euxinia, and the question remains what controlling factors could have obstructed the Mo enrichment process at that time.

First, we speculate that the Mo supply to the basins was particularly slow. However, the Mo enrichment process takes place today even in settings with low Mo supply, whether limited by basinal restriction and a slow deepwater renewal rate (e.g. Black Sea) or low Mo load in the source waters of only (e.g. 10 nM in Lake Cadagno).

We have established a one-box model for the oceanic Mo cycle, where Mo burial rates are linked 1st order with respect to ambient Mo reservoir. It shows that seawater Mo concentrations, today 105 nM, never decreased below modern riverine values (~6 nM). Hence, a low seawater inventory is insufficient to obstruct the Mo enrichment process in settings with supply comparable to Lake Cadagno, but a combination of both widespread euxinia (lowering seawater Mo inventory) and basinal restriction (lowering basinal Mo relative to open ocean) could potentially compromise Mo enrichment in the Neoproterozoic sediments.

This illustrates how expansion of oceanic euxinia derived from our models rests on a rigorous understanding of the key factors involved in the removal pathway of Mo from oxic surface waters to euxinic sediments. We discuss how laboratory and field-based studies elucidate which factors, other than H_2S, could influence the Mo burial pathway in the past. Overall, we illustrate the linkage between studies of modern euxinic systems and reconstructions of global-scale ocean conditions of the past.

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The nature of orogenic lithospheric mantle: constraints from geochemistry of postcollisional mafic-ultramafic rocks in the Dabie orogen

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Oceanic and continental arc volcanic rocks are a window into crust-mantle interaction in oceanic subduction zones, with involvement of the asthenospheric mantle. They are assumed to originate from partial melting of altered peridotite in the overlying mantle wedge, with trace element geochemical signature inherited from aqueous fluids released from subducting oceanic crust. While this process-product link has been a common percept in geochemistry, it is intriguing whether there is the similar relationship in continental subduction zones. Ultrahigh-pressure (UHP) metamorphic rocks are a typical product of continental deep subduction to mantle depths, but arc magmatism is absent above continental subduction zones. While the subducted continental crust can be reworked as postcollisional granitoids, it is unclear whether the overlying subcontinental lithospheric mantle (SCLM) was involved in postcollisional mafic magmatism.

Postcollisional mafic-ultramafic rocks from the Dabie orogen were studied for their zircon U-Pb ages and Lu-Hf isotopes, whole-rock major-trace elements and Sr-Nd-Pb isotopes as well as whole-rock and mineral O isotopes. The results provide insights into the nature of orogenic lithospheric mantle in the continental collisional orogen. The zircon U-Pb dating gave consistent ages of 125 ± 3 to 129 ± 1 Ma for magma crystallization. Few residual zircon cores have U-Pb ages of 234 ± 5 Ma and 739 ± 9 Ma, respectively, in agreement with tectonothermal events for UHP metamorphism and protolith formation in the Dabie orogen. The mafic-ultramafic rocks have high contents of MgO (up to 18.0 wt.%), Cr (up to 1546 ppm) and Ni (up to 349 ppm), but low contents of SiO_2 (41.0-51.9 wt.%), and show the arc-like patterns of trace elements distribution and the enriched signature of Sr-Nd-Pb-Hf isotopes. These geochemical features indicate their derivation from partial melting of the orogenic lithospheric mantle that is fertile in lithochemistry and enriched not only in LILE and LREE but also in radiogenic isotopes. The orogenic lithospheric mantle is suggested to be generated by metasomatic reaction of the overlying SCLM-wedge peridotite with hydrous felsic melts derived from the subducted continental crust during the Triassic continental collision, with the enriched signatures imparted by the felsic melts. In this regard, the crust-mantle interaction is implicated during the continental deep subduction, with the postcollisional mafic-ultramafic rocks as its derivatives. On the other hand, significant differences in elemental and isotopic compositions between different mafic-ultramafic intrusions suggest that the orogenic lithospheric mantle is geochemically heterogeneous, with the possible presence of hornblende-rich and pyroxene-rich lithologies in mantle sources. This difference is attributed to differences in the compositions of subducted crustal-derived melts with a tectonic affinity to the South China Block, but the same SCLM wedge of the North China Block was involved in the crustal metasomatism. Therefore, the compositional variations in the orogenic lithospheric mantle are recorded by the geochemical compositions of postcollisional mafic-ultramafic intrusions.

A spatially-structured model for Proterozoic ocean biogeochemistry

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The picture for Proterozoic ocean biogeochemistry from marine proxy data and simple box models has been of an anoxic and ferruginous ocean prior to 1.85 Ga, with a switch to either oxic or euxinic conditions then responsible for removing iron from the deep ocean and halting Banded Iron Formations ~1.85 Ga [1]. However, recently-gathered geochemical data from what remains of the Proterozoic ocean margins reveal a more complex picture with some euxinic intervals prior to 1.85 Ga, and a largely ferruginous ocean with only some sulphidic intervals and/or sulphidic waters at intermediate depths post-1.85 Ga [2],[3].

Here we use a spatially-structured biogeochemical model GENIE to propose a scenario consistent with proxy data, and also consistent with constraints from both oxygen demand and ventilation, and ocean mixing and Fe, S residence timescales. A robust feature of scenarios that avoid global euxinia is a vertical redox gradient from an oxygenic mixed layer, through euxinic mid-depths in shelf or upwelling regions, to a suboxic deep ocean. A suboxic (rather than fully anoxic and ferruginous) deep ocean is consistent with evidence from hematitic cherts [4]. This model makes two testable predictions: (i) that the "ferruginous" water column state inferred from iron-speciation proxy data arises from iron transport in a marginally suboxic or anoxic region underlying euxinic region, and (ii) that feedback processes must exist to balance the deep ocean on the edge of anoxia.

Nitrogen cycling in the mixed aerobic/anaerobic surface/mid-depth regions results in relatively high levels of denitrification and nitrification with small marine nitrogen reservoirs and short residence times.

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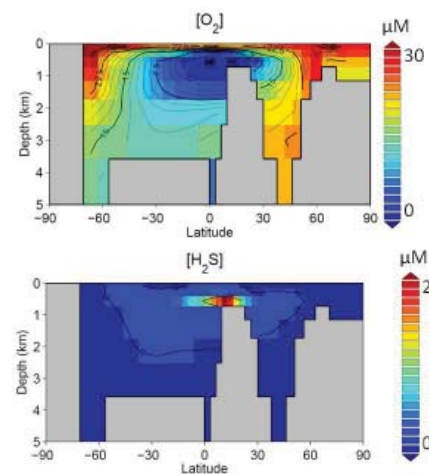

Figure 1: Meridional sections for [O_2] and [H_2S] with localized euxinia and suboxic deep ocean.

Selection for Gaia at multiple scales

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Biological regulation of the environment is present at scales from individuals, to ecosystems, to the global biosphere. However, the emergence of regulation at scales which cannot have been units of natural selection is a very different problem from the Darwinian evolution of organism-level homeostasis. Nevertheless, at local ecosystem level, regulation is beginning to be understood as a consequence of "niche construction" [1]. Recent work [2] has also demonstrated the evolutionary emergence of global regulation from local selection in spatially structured environments that tend to distribute the benefits from regulation preferentially to regulators (and not free-riders or organisms with a destabilising effect). At global scales, biosphere regulation must in addition be reconciled with geochemical feedbacks, often involving well-mixed global reservoirs such as the atmosphere, or geological time delays. This temporal and/or spatial decoupling of effects from actors make evolutionary explanations problematic.

Here we investigate mechanisms by which global regulation might emerge by a non-evolutionary process of self-organisation. We argue that the global biota is assembled over time by a process analogous to ecological community assembly [3], but operating at global scale over geological and macroevolutionary timescales and perturbed by macroevolutionary innovations [4] and geological events. By a process of "sequential selection" [5], fragile systems, or those that destabilise their environment, are then short-lived, and result in extinctions and reorganisations until a relatively stable (but possibly lifeless) state is temporarily reached. We employ simple conceptual models for community assembly, evolutionary innovation, life-environment interaction, and anthropic bias to test three hypotheses for the implications of this mechanism for the stability and regulation of an observed biosphere. The limited information input and the "satisficing" (rather than optimising) nature of the sequential selection mechanism make it probable that: (i) regulation at the global level involves only simple configurations of multiple (individually local and Darwinian) physiologically limited "biotic plunder" mechanisms [7],[8] combined with abiotic feedbacks, and (ii) regulation of the environment is strongest at limits, rather than at optimal conditions for life. Anthropic bias [6] applies a further filter to the distribution of biosphere properties such that (iii) our observed biosphere need be only sufficiently stable for the evolution of complex life.

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A bottom-up perspective on N and P cycling in low oxygen environments: the Baltic Sea versus the Peruvian shelf

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This study presents a combination of field measurements and state-of-the-art modeling to investigate N and P cycling in sediments of two contrasting oxygen stressed systems. Boknis Eck is a 28 m deep channel in the southwest Baltic Sea which experiences severe hypoxia (< 2 μM O_2) in boreal summer lasting until October [1]. A time series analysis of benthic nutrient analyses based on monthly samplings from February to December 2010 revealed that N and P fluxes were elevated in winter due to porewater pumping by bioirrigating organisms which efficiently flushed the upper 10 cm of sediment. During hypoxia, no bioirrigation was measurable, macrofauna were absent and phosphate accumulated to concentrations exceeding 400 μM, resulting in a large diffusive flux to the water column. At the same time, denitrification rates were elevated yet dissimilatory nitrate reduction to ammonium (DNRA) by sulfide oxidizing bacteria (*Beggiatoa* spp) played a much larger role in recycling N between the water column and sediments, thus conserving reactive N in the system. By January 2011, typical winter conditions were once again established.

In the Peruvian OMZ, anoxia is more permanent and ventilation events are less predictable. Benthic N and P cycling investigated at six stations along 11 °S using landers revealed very high rates of ammonium and phosphate fluxes on the shelf and upper slope (80 – 250 m water depth) where extensive areas of mats of *Beggiatoa* were present [2]. DNRA dominated total N turnover (≤ 2.9 mmol N m^{-2} d^{-1}) and accounted for ≥ 65 % of nitrate uptake by the sediments from the bottom water. Only at greater water depths within the OMZ (300 – 1000 m) were the sediments a net sink for reactive N due to denitrification. Overall, our findings in Peru and the Baltic Sea show that high measured benthic uptake rates of oxidized N within OMZs do not necessarily indicate a loss of fixed N from the marine environment, but are instead recycling sites converting nitrate into ammonium. Phosphate release is elevated in both environments, which altogether indicate that similar processes occur in sediments underlying seasonal and more permanent OMZs. Due to the high rates of benthic N and P turnover in OMZs, pelagic models ought to incorporate benthic dynamics in their calculations.

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Osmium and oxygen isotopes in Etendeka picrites and their olivines: mantle melts and crustal interaction

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The existence of basal picrites and picritic dykes in the Etendeka large igneous province (LIP) provides the opportunity to study high-degree, relatively unfractionated melt products from a hot plume head and hence gain the best insight into the source composition. Moreover, highly magnesian olivine phenocrysts (occasionally up to Fo 93.3), which reflect crystallisation from melts with up to 24 wt% MgO [1], provide particularly primitive isotopic information. Such high MgO melts require mantle potential temperatures up to 1700°C [1], amongst the highest known for the Phanerozoic. At the same time, the eruption of the picrites through continental crust allows the role of assimilation, in imparting an isotopic signature, to be investigated.

Here we present major and trace elements and Sr, Nd, Pb and Os isotopes for whole rocks, and combine these with major elements and osmium and oxygen isotopes for olivine phenocrysts. Highly siderophile element abundances are also presented.

The Pb isotopic compositions of whole rocks covary with Pb content and are clearly controlled by a local crustal sedimentary input, and give little information on the source. Strontium and Nd isotopes in the Horingbaai dykes covary negatively, indicating variable contributions from depleted and slightly enriched endmembers, the latter likely local crust.

The $^{187}Os/^{188}Os$ compositions of the primitive Horingbaai and more evolved Spitzkoppe picrites (0.128-0.131) are in the same range as some other high-T plume melts (e.g. North Atlantic Igneous Province picrites: 0.127-0.134 [2]). The least radiogenic values support a predominantly mildly-depleted peridotite source for the highest temperature volcanism in the region, which is also consistent with MORB-like REE patterns. The Os data exclude the possibility of a long-term strongly Re-depleted source input, such as old lithosphere. The more radiogenic values could reflect a contribution from an isotopically enriched mantle component. Olivines from the Horingbaai and Spitzkoppe picrites, however, have similar or slightly lower isotopic compositions than their respective whole rocks, suggesting that, at least in part, the more radiogenic Os isotope values are a result of crustal assimilation after olivine crystallisation, even in these Os-rich picritic melts.

Oxygen isotope compositions in olivines ($\delta^{18}O$ up to 6.5‰) extend higher than typical mantle, and are associated with more radiogenic $^{187}Os/^{188}Os$. Although it is difficult to rule out a mantle eclogite component as a source of coupled O-Os enrichment, a crustal input is the likely cause of this effect, and is supported by the combined isotopic and elemental data.

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Fe(III) reduction by the Gram-positive bacterium *Desulfotomaculum reducens*

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Microbial Fe(III) reduction, specifically that of solid phase Fe(III), presents a challenge to bacteria as electrons must be transported to an extracellular electron acceptor. This process has been studied extensively for Gram-negative bacteria such as *Shewanella oneidensis* and *Geobacter sulfurreducens*. Several strategies have been documented in these microbes: (a) the secretion of endogenous redox mediators that are reduced by cells following oxidation by Fe(III); (b) direct contact of outer-membrane multi-heme cytochromes with the solid-phase substrate or (c) the extension of micron-long electroconductive pili that can transport electrons away from the cell. The transfer of electrons in the latter two cases was dependent on several multi-heme cytochromes located in the cytoplasmic and outer membranes as well as in the periplasmic space.

In the case of Gram-positive bacteria, there is evidence either for the involvement of redox mediators [1] or the requirement for direct contact with the electron-receiving surface [2]. In both cases, the mechanism remains unknown. In this study, we probe the reduction of soluble Fe(III) [as Fe(III)-citrate] and of solid-phase Fe(III) [as hydrous ferric oxide, HFO] by the Gram-positive bacterium *Desulfotomaculum reducens*. The best growth was obtained with pyruvate due to fermentation but some growth was detected with lactate as an electron donor. In the presence of HFO, pyruvate was rapidly (~3 days) converted to acetate and Fe(III) slowly reduced over 25 days. Tests with spent medium from pyruvate- and HFO-grown cells indicate the presence of an endogenous redox mediator able to reduce anthraquinone disulfonate (AQDS). In contrast, HFO reduction occurred concomitantly with lactate oxidation to acetate and there was no evidence for a redox mediator. Experiments with HFO enclosed in glass beads (and thus only accessible to diffusable redox mediators) confirmed those findings as reduction of Fe(III) was observed in the pyruvate case but not detectable in the lactate case.

The *D. reducens* genome harbors a sole multi-heme *c*-type cytochrome complex (NrfHA) with homology to the nitrite reductase in *Desulfovibrio vulgaris*. Quantitative reverse transcription PCR (qRT-PCR) showed that while *nrf*HA was expressed during fermentation, there is no evidence for expression during Fe(III) reduction. Hence, we conclude that (a) HFO reduction occurs via a redox mediator with pyruvate while it is mediator-independent in the presence of lactate; (b) the sole *c*-type cytochrome complex present in the genome of *D. reducens is* not involved in Fe(III) reduction. Ongoing work focuses on the characterization of the mechanism of lactate-dependent HFO reduction and aims at providing a mechanistic understanding of electron transfer across the Gram-positive cell wall.

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Continental surface temperatures inferred from the investigation of fossil hydrothermal systems

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Plutonic and sub-volcanic igneous rocks have been shown to be a promising source of data relevant to paleo-temperature reconstruction. A first Antarctic terrestrial record of climate variations through the Cenozoic has been recently published, based on the hydrogen isotope composition of hydrothermally altered minerals of intrusive rocks from the coastal areas of the Wilson Terrane, Northern Victoria Land, Antarctica (Dallai & Burgess, 2011). Cenozoic land surface temperature data for this remote area located at 73-74°S latitude are poorly known but may be crucial to understand how and possibly why, the climate changed in continental Antarctica before and during the Eocene-Oligocene transition. In this investigation, the variations of hydrogen isotope composition of hydrothermal waters have been studied in detail. By dating the minerals formed upon hydrothermal alteration, a record of meteoric-hydrothermal water compositions has been reconstructed, enabling the atmospheric conditions during the Cenozoic era to be inferred. This continental record of polar climates in Antarctica is in reasonable agreement with the global climatic records derived from oceanic deep cores and with the model curve for atmospheric pCO_2. These observations give insights into the climatic evolution of continental areas in an important region over a critical time interval suggesting that temperature fluctuations as large as 20°C occurred repeatedly during the Eocene. The aim is to determine continental paleo-temperatures for different periods of the Cenozoic and to merge data from hydrothermal systems from high latitude regions of both hemispheres to define bi-polar climatic conditions through geological time. Preliminary data of hydrothermal systems from high latitude regions of the Northern Hemisphere fit the hydrogen based paleo-temperature curve, thereby implying that extending this study to other Cenozoic (and older) intrusive bodies may better constrain continental paleo-temperature records both in space and in deeper times.

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Evolution of silicic magmas and the origin of the Daly Gap at Santa Barbara volcano, Terceira, Azores

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The origin of compositional gaps (e.g. the Daly Gap) and high volumes of silicic rocks among volcanic deposits in ocean islands have remained controversial subjects. Although silicic magmas can be produced by fractional crystallization of parental basalts, the paucity of intermediate compositions and the relatively large volumes of silicic compositions amongst erupted materials are difficult to explain by this mechanism. Several hypotheses have been proposed for the scarcity of erupted intermediate rocks, including development of physical/chemical properties (density, viscosity and/or volatile content) that may inhibit them from erupting [1]. Alternatively, melting of altered mafic crust may produce bimodal volcanism without formation of intermediate magma compositions, and can potentially explain large volumes of silicic deposits [2].

Santa Barbara volcano (Terceira, Azores) is an ideal locality for investigating these problems. Terceira has an uncommonly high percentage (~50%) of silicic volcanic rocks relative to mafic compositions [1], and Santa Barbara exhibits a well defined Daly Gap from 54 to 64 wt.% SiO_2 amongst eruptive products, including flank basalts and trachytes erupted from the central vent [3]. However, we show that the compositional gap closes if plutonic nodules contained in air fall deposits from Santa Barbara are considered.

We have performed petrographic, major and trace element, and Sr–Nd–Pb isotopic analyses on eruptive products from the relatively recent (<2ka) Santa Barbara-G trachyte deposit [4], as well as flank basalts [5] and plutonic nodules collected from older trachytic air fall deposits from Santa Barbara. These data demonstrate an essentially continuous compositional variation from 45 to 69% SiO_2, with the plutonic nodules ranging from 45 to 65 wt% SiO_2, and thus effectively filling in the compositional gap defined by the bimodal basaltic-tracyhtic volcanic products. Trace element systematics indicate that the plutonic nodules are genetically related to the basalts and trachytes, following a common fractional crystallization path. The plutonic nodules exhibit large (~4- to 10-fold) variations in concentrations of trace elements including highly incompatible elements (Hf, Nb, and Zr) and compatible elements (Ba and Sr). Most significantly, some of the plutonic nodules have incompatible element concentrations equal to those in the Santa Barbara G trachytes. Together, these data suggest that the plutonic nodules represent liquid rather than cumulate compositions, as inferred for syenites from Fogo volcano (Sao Miguel, Azores; [6]).

These results indicate that intermediate magma compositions are produced during fractional crystallization from parental basalts to trachytes, and that these intermediate magma compositions generally fail to erupt as volcanic products. Ongoing Sr-Nd-Pb and planned U-series isotopic analyses of the plutonic nodules will further constrain their genetic relationship to the Santa Barbara basalts and trachytes, and potentially allow evaluation of their crystallization ages.

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Analysis and modelling of arsenic dynamics in coastal sediments

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Sediments of the Toulon bay (SE, France) are significantly polluted by trace metals, metalloids and organic contaminants, due to historical events (2nd World War...). Contaminants behavior in sediments and transfer to the water column should be investigated to evaluate the risks linked to such pollution. This work focused on As dynamics in the Toulon Bay by studying two major processes: effect of early diagenesis and subsequent diffusive flux.

Interface sediment cores were sampled at contrasted locations and seasons, followed by porewater analysis of physico-chemical parameters (pH, Eh, DOC), diagenesis tracers (Fe, Mn, S, Ca, DIC, …) and As species. The obtained sediment depth profiles showed a significant variation of Eh, SO_4^{2-}, DOC and arsenic in porewaters between the campaigns. Such observation could result from different diagenesis activities, linked to inputs of labile organic matter (e.g. plankton bloom). Additionally, in the deepest layer (> 15 cm), As appeared to be significantly correlated (R^2 0.89) to the DOC content, indicating a possible association between As and organic matter.

Based on the measured phyco-chemical parameters and the dissolved species concentration (majors, diagenesis tracers, arsenic,...), PHREEQC was used to calculate As chemical speciation [1]. Then, PROFILE fitting of diagenesis tracers and As depth profiles allowed the evaluation of their diffusive fluxes at the sediment/water column interface [2]. Finally, As depth profiles were successively simulated by PHREEQC, taking account of solid As concentration, dissolved organic matter, carrier solid phases (clays, calcite, iron oxy(hydroxide), iron (mono)sulfide), and the affinity of these components for each As species.

The As dynamics in Toulon coastal sediment appears to be mainly controled by its chemical speciation in porewater, immobilization on carrier phase, and interaction with dissolved organic matter (as AsV but also as AsIII). Association of analysis and modelling tools (thermodynamic calculation, reactive transport fitting and sorption simulation) is suitable to better understand trace elements behavior at the sediment/water interface.

[1] Couture et al. (2010) *Geochim. Cosmochim. Acta* **74**, 1238-1255.
[2] Berg et al. (1998) *Limnol. Oceanogr.* **43**, 1500-1510.

Colloidal stability of TiO_2 nanoparticles in the presence of phenolic carboxylic compounds

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Nanotechnology is a rapidly growing industry, which leads to an increased amount of synthetic nanoparticles released into the environment. Nanoparticles generally have higher reactivity than larger particles of the same material. As the particle size is decreased to the nanometer size range (1-100nm), the surface chemistry changes and this might influence the surface charging and aggregation behavior. Further, nanoparticles can interact with natural organic material (NOM), such as humic and fulvic acids, which is present in most natural waters. Adsorption of NOM affects the surface speciation and net charge of the nanoparticles and is therefore of great importance for their colloidal stability. This might alter the mobility of nanoparticles in surface waters and in soils, thus determing their bioavailability and toxicity.

The focus of the present study was to investigate the aggregation behavior of nanoparticles in aqueous solution as a function of pH, ionic strength, and in the presence of NOM. Well-characterized TiO_2 nanoparticles obtained from hydrolytic synthesis were used as test nanoparticles, and selected phenolic carboxylic compounds were used as model substances to mimic the interactions of nanoparticles with NOM. The selection of organic compounds was based on the possibility of determining the influence of various types, numbers, and positions of functional groups on the surface charging and colloidal stability of the TiO_2 nanoparticles. The aggregation and surface charging of the particles were studied by simultaneously monitoring the changes in particle size and zeta potential during the reactions.

Testing efficacy of zircon (^{238}U/^{230}Th) + (U-Th)/He and radiocarbon dating methods on the New Zealand late Quaternary tephras

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Combined ^{238}U/^{230}Th disequilibrium and (U-Th)/He dating of zircon [1] is a novel approach for dating young (<350 ka) volcanic eruptions. This method with great potential for the Quaternary geochronology has been successfully applied in various settings [e.g. 2,3], however its accuracy and limitations has not been rigorously tested and validated by independent methods. New Zealand's record of late Quaternary tephras provides an excellent natural laboratory for conducting such inter-calibration experiments.

In this study we apply the combined ^{238}U/^{230}Th disequilibrium and (U-Th)/He zircon dating to the deposits of the coeval Rotoiti and Earthquake Flat eruptions in the Taupo Volcanic Zone to investigate consistency of the method. In addition, wood sampled below and above the Rotoiti tephra is dated by high-precision radiocarbon method to provide independent constraints on the accuracy of the zircon eruption ages.

Results and Conclusion

The two independent methods revealed concordant ages, which are also in accord with the stratigraphic position of the samples. Based on these results we assign new ages of ~45 ka to the Rotoiti and Earthquake Flat eruptions. This is by ~16 kyr younger than the currently accepted age, which has implications for paleoclimatic reconstructions and volcanic hazards assessment in the Taupo Volcanic Zone. This study proves the combined ^{238}U/^{230}Th disequilibrium and (U-Th)/He dating of zircon reliable at late Quaternary time scale and also demonstrates demonstrates reliability of the radiocarbon dating method at higher end of its sensititvity at ~50 ka.

[1] Schmitt *et al.* (2006) *J. Volcanol. Geoth. Res.* **158** (3-4), 281-295. [2] Schmitt *et al.* (2010) *Earth Planet. Sci. Lett.* **295** (1-2), 91-103. [3] Schmitt *et al.* (2011) *Contrib. Mineral. Petrol.* **162** (6), 1215-1231.

The Pantelleria shallow plumbing system: extreme differentiation processes and dynamics in an intraplate volcanic field

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The island of Pantelleria, the type locality for pantelleritic rocks, is an active volcanic field located in the Sicily Channel Rift Zone, an intraplate setting affected by transtensional tectonics related to the complex geodynamics of the Western Mediterranean area. The island, dominated by a nested, resurgent caldera, has been affected by regional tectonism and volcano-tectonism that controlled both evolution of the magmatic system and distribution of eruption vents. The eruptions were fed through time by magmas of variable composition, typically bi-modal, both mafic and silicic. The island is divided into two sectors by a NE-SW fault system, which likely represents a crustal discontinuity along the axial ridge of the rift. The north-western sector, affected only by NW-SE crustal structures, includes most of the exposed transitional to alkaline basaltic rocks. The south-eastern sector includes silicic peralkaline rocks, variable from comenditic trachyte to rhyolite (pantellerite). Eruption of differentiated magmas and occurrence of the nested caldera, suggest that crustal magma chambers were established in this sector, probably at the intersection of the main tectonic lineaments. On the other hand, eruption of abundant mafic magmas in the north-western sector of the island suggests a deeper plumbing system linked to the mantle source region. The geochemistry of volcanics representative of the younger-than-15 ka activity has been investigated with the aim of better understand the magmatic processes governing the behaviour of the Pantelleria shallow plumbing system. The investigated volcanic rocks, products of both explosive and effusive activity, range in composition from comenditic trachyte to pantellerite, matching the typical range of evolved peralkaline composition of Pantelleria. Alkali-feldspar-rich enclaves are common in these rocks, testifying to diffuse mingling phenomena. Electron microprobe and micro-Raman analyses of interstitial glass of enclaves has revealed unusual compositions even more evolved than the host rocks. These data, integrated with recent experimental petrology results on peralkaline silicic magmas, allowed us to put forward hypotheses on the extreme differentiation processes and dynamics occurred within the Pantelleria shallow plumbing system in the past 15 ka.

Olivine record of crystal residence times and the internal dynamics of magmatic plumbing systems

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Analysis of the kinetics of post-entrapment re-equilibration of melt inclusions in high-Fo olivine phenocrysts in lavas suggests their common short residence times (< 6-12 months). This implies that if eruption does not happen within a few months after a primitive magma begins cooling and crystallisation within the plumbing system, early formed olivines are unlikely to be erupted as phenocrysts, being efficiently separated from the melt, and rapidly incorporated into the cumulate layers within the plumbing system.

These results suggest that in most cases erupted high-Fo olivine phenocrysts retain their original composition, which explains commonly observed large compositional variations between olivine phenocryst cores in a single sample. Short residence times imply that large unzoned cores of high-Fo phenocrysts cannot reflect diffusive re-equilibration of originally zoned phenocrysts. The unzoned cores are a result of fast efficient accumulation of olivines from the crystallising magma, i.e., olivines are separated from the magma faster than melt changes its composition. Thus, the main source of high-Fo crystals in the erupted magmas is the mush zone of the plumbing system. Olivine-phyric rocks represent mixtures of an evolved transporting magma (which forms the groundmass of the rock) with crystals that were formed during crystallisation of more primitive melt(s). Unlike high-Fo olivine phenocrysts, the evolved magma may reside in the magmatic system for a long time. This reconciles long magma residence times estimated from the compositions of rocks with short residence times of high-Fo olivine phenocrysts.

Olivines incorporated in the cumulate layers are sometimes erupted in gabbroic/ultramafic xenolith. Unlike phenocrysts in lavas, olivines in xenoliths commonly have uniform compositions, reflecting diffusive re-equilibration during long residence times.

Slow cooling rates and extensive re-equilibration within the plumbing systems results in complete re-equilibration of the cumulate crystals at near solidus temperatures. In parts of these systems where cumulate compaction and intercumulus melt migration were minimal, correlations between compositions of olivine and the bulk samples can be used to estimate the compositions of the parental magmas and the amount and composition of phenocrysts they carry. Having established the composition of parental magmas, comparing them to the bulk compositions of different parts of the plumbing system can indicate their open or closed behaviour.

Using the Dovyren magmatic system (Northern Baikal region, Siberia, Russia) as an example, we show that the parental magmas were phenocryst rich, the supplying conduits were thermally and compositionally zoned, and the large layered intrusive body of the complex represented an open plumbing system feeding the associated volcanic centres.

Are the "magnetite lava flows" of El Laco (Chile) magmatic? Comparison of trace elements in magnetite with other magmatic Fe-oxide deposits

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Magnetite forms under a wide variety of conditions, crystallizing at high temperature from silicate magmas or precipitating at low temperature from hydrothermal fluids or seawater. Trace element content of magnetite may reflect the differences in these conditions. Therefore as part of a larger project examining the trace element content of magnetite, by laser ablation ICP-MS, we have characterized magnetite in magmatic massive Fe-oxide deposits (magnetite-ilmenite, ± apatite) from layered intrusions (Bushveld and Sept Iles Complexes) and a massif anorthosite (Lac St. Jean) in order to study how magmatic processes affect the trace element compositions. We have also collected trace element data from the enigmatic "magnetite lava flows" from El Laco, Chile, in order to consider whether these magnetites are indeed of igneous origin.

Magnetite from the layered intrusions record the evolution of the fractionating silicate liquid (Fig. 1a), with those found lower in the sequence (more primitive) being richer in Cr, Mg, V and Ni whereas those found higher (more evolved) being richer in Ti, Nb and Ta. Magnetite layers from the uppermost parts of the intrusions contain apatite and this magnetite shows the most evolved composition (Fig. 1a). Magnetite from the anorthosite shows similar compositions to those of the layered intrusions. However, magnetite from the El Laco lava flow are much richer in Si (0.4 wt.%), Ca and P and poorer in Ti (<0.1 wt%), Al (<0.2 wt%) and Ga than magnetite from any magmatic Fe-oxide deposit (Fig. 1b) which raises doubts about the El Laco "magnetite lava flow" having formed by igneous processses.
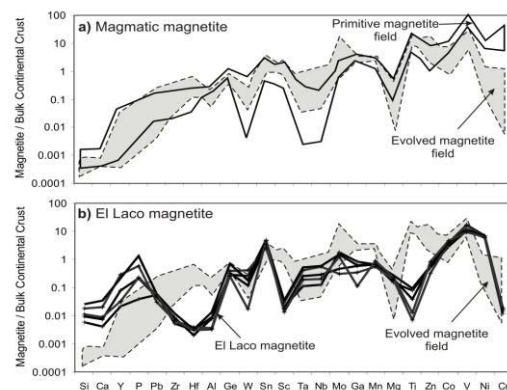

Figure 1: Trace element patterns for (a) magmatic magnetite and (b) El Laco magnetite compared to evolved magmatic magnetite. Order of elements: increasing compatibility into magnetite to the right.

Zircon U-Pb geochronology of the Nuvvuagittuq Greenstone Belt

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The Nuvvuagittuq Greenstone Belt in northern Québec is a rare ~10 km^2 fragment of the Earth's early crust. The belt contains metamorphosed supracrustal rocks that are at least 3.77 billion years old [1,2], and amphibolites (the Ujaraaluk Unit) that may have protoliths as old as 4.3 Ga [3]. Primary contacts and relative age relationships have been obscured by multiple episodes of intensive ductile deformation, however the geological history of the belt is beginning to be unraveled via geochronology and geochemistry.

In this study we have undertaken SHRIMP U-Pb analysis of zircons from key meta-igneous and meta-sedimentary units of the belt. The analysed samples fall into three categories: (a) felsic bands (0.5 to 1 m in width) and tonalitic orthogneiss interlayered with the Ujaraaluk Unit; (b) fuchsite-bearing quartz-rich bands and a newly identified metasedimentary unit; (c) garnet-biotite amphibolite from the Ujaraaluk Unit and a meta-gabbro.

The felsic lithologies place constraints on the minimum age of the supracrustal assemblage. Oscillatory zoned zircons separated from a plag-qtz-bt schist form a discordant array with an upper intercept of 3774 ± 32 Ma, consistent with previous analyses of similar lithologies [1,2]. The tonalitic orthogneiss yields concordant zircon ages between 3740 and 3800 Ma, consistent with the observation of oscillatory zoned cores and rims from CL imaging.

Zircons from the fuchsite-bearing quartz band are subrounded and have oscillatory zonation textures very similar to the orthogneiss zircons, with little textural variation, and concordant ages of between 3750 and 3800 Ma, similar to the orthogneiss. In contrast, a quartz-albite-clinozoisite dominated metasediment identified within a lower strain domain, interfolded with amphibolites, has highly variable zircon CL textures. The zircons are dominated by concordant ages of 3630 to 3680 Ma, similar to the age of nearby tonalites [2], with minor concordant populations at ca. 3800 and 3500 Ma. Accordingly, the belt must have been exhumed following intrusion of the ca. 3660 Ma tonalite [2], and prior to high-T metamorphism and deformation.

Electron microscopy of polished thin sections was used to locate zircons within 4 samples of the Ujaraaluk Unit mafic amphibolites. Large (≤ 500 μm) zircons separated from a gt-bt rich sample, together with those from the meta-gabbro sample, are sector zoned and yield metamorphic ages of ca. 2700 Ma.

Although unequivocal constraints on the primary age of the Ujaraaluk Unit amphibolites remain elusive for now, continued geochronological studies are revealing that the belt contains a detailed record of Eoarchaean to Paleoarchaean crustal processes.

[1] Cates and Mojzsis (2007) *EPSL* **255**, 9-21
[2] David et al. (2009) *GSA Bulletin* **121**, 150-163
[3] O'Neil et al. (2008) *Science* **321**, 1828-1840

Zircon-adhering, crystallized melt inclusions in peritectic garnet from the western Adirondack Mountains, New York State, USA.

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Micrometer-scale, multiple-solid inclusions occur in garnet from metapelitic gneiss extracted from the hydroelectric plant on the Black River at Port Leyden, NY (western Adirondack Highlands). The garnet host grains are small (0.5-1.0 mm diameter), euhedral neoblasts that formed peritectically during biotite dehydration melting accompanying the Ottawan phase of the Grenville Orogeny (ca. 1040 Ma; [1]). Partial melting conditions of 4 to 6.4 kbar and 735°C, and a peritectic reaction of bio + sil + vapor = gar + melt, or bio + sil + qtz = gar + melt ± K-feldspar have been proposed for these rocks [1].

The inclusions are typically 10-20 μm in diameter and occur randomly in garnet. Both negative crystal and irregular inclusion morphologies are present. Many, if not all, of the inclusions contain a large (5-8 μm), often euhedral, zircon grain surrounded by finer-grained (some less than 1 μm) phases with EDX spectra consistent with biotite, K-feldspar, quartz, and albite. The inclusions are similar in size and composition to those described in garnet from other migmatites (e.g. [2], [3], [4]) and are similarly interpreted as anatectic melt inclusions.

Low Zr solubility in silicate melts [5] indicates the large zircon grain in each inclusion is a trapped phase. Therefore, it appears that micrometer-scale droplets of anatectic melt adhered to refractory zircon grains while peritectic garnet grew around them.

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Spectrophotometric determination of alkalinity and pH in freshwaters

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The different compartments of the hydrosphere are major sinks or sources of CO_2 and the role of freshwaters in the global carbon cycle has been recently reevaluated as substantial [1]. Freshwaters show variations of the carbonate system variables at hourly time scales and in a large range. A key limitation for the carbonate system studies is the necessity of accurate, *in-situ* and high frequency measurements that would provide data with suitable spatial and temporal resolutions to enlighten the processes affecting the carbonate system.

With the aim of *in-situ* and high frequency sensor development to assess the freshwaters whole carbonate system with the simultaneous measurement of the pH-Alkalinity couple [2], spectrophotometric measurement of these parameters is developped. Spectrophotometric pH measurements already exist [3] this work focuses mainly on the alkalinity (Alk) measurement, which is an original contribution. This new method, based on [4], consists to neutralize all the basic species taken into account in the Alk by a weak acid mixed with a pH sensitive dye to measure accurately the pH end point value and thus deduce the alkalinity of the sample.

The performance of spectrophotometric methods is assessed in low pH buffer solutions for pH, commercial mineral and spring waters for Alk and natural freshwaters for both, by a comparison to conventional potentiometric measurements and theoretical calculations.

pH measurements show a precision of ±0.005 and an accuracy of 0.01 pH unit; Alk measurements show a precision of ±8μM and an accuracy ranging from 19 to 2 μM. The best accuracy is obtained by downplaying the excess acid term and thus its associed uncertainty. Additionnaly, accuracy relies upon the performance of the spectrophotometer, carefully prepared and defined indicator solution and all very controlled and reliable thermodynamic constants with their temperature and ionic strength dependence. The somewhat poorer precision reported might be ascribed in a larger part to the totally handmade procedure steps that introduce more errors than an automatic device. Tests on our pH and Alk *in-situ* sensor (still in development), shows that a precision better than ±0.001 unit on pH and better than ±2 μM on Alk are expected.

This work provide a strong theoretical basis for its future use as an *in-situ* high frequency sensor, which precision and accuracy meet the requirements of scientist working on freshwaters systems.

[1] Prairie (2008) *Can. J.Fish.Aquat. Sci.* **65**, 543-548.
[2] Park (1969) *Limnol. Oceanogr.* **14** (2), 179-186.
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Using Noble Geochemistry to Identify the Genetic Fingerprint of Natural and "Fugitive Gases" in the Marcellus Play of Northern Appalachian Basin

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Abstract

Osborn et al [1] recently reported 17-times higher concentrations of thermally mature methane (CH_4), consistent with production gases from the Marcellus shale, in drinking water wells within 1km of hydraulically fractured horizontal drilling sites producing from the Marcellus Shale in northeastern Pennsylvania. We employ a combination of hydrologic (groundwater age dating [^{3}H-^{3}He and fluid flow modeling]), noble gas geochemistry, and carbon isotopic composition to distinguish the potential sources of gases present in drinking water aquifers within the region. These techniques simultaneously distinguish Marcellus/Devonian gas from deeper Trenton Group/Ordovician gases and other potential sources (e.g. shallow biogenic methane, stray landfill gases, other organic-rich lithologies, and natural gas that has migrated naturally over geologic time) providing a powerful technique for delineating the source and potential for fugitive gas migration in areas active or targeted for drilling. We will present preliminary results of noble gas and isotope geochemistry for Pennsylvania and New York areas of the Marcellus fairway.

[1] Osborn SG, Vengosh A, Warner NR, & Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences* 108:8172-8176.

Precise Pb-Pb dating of Precambrian zircon using thermal extraction-condensation (TEC) and [202,205]Pb double spike

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Method

Demonstrating reproducibility of Pb isotopic ratios in zircon is sufficient for accurate dating of Precambrian samples without the need for isotope dilution and U analysis, which require total dissolution of sample and chemical processing to remove Zr. The Kober [1,2] and Davis [3] methods of thermal extraction of Pb are simple but both provide relatively inefficient ionization and neither is amenable to double Pb isotope spiking, which limits the accuracy of ages that they can provide. We have experimented with a modification of Kober method that overcomes these limitations. Zircon is folded into a 0.03 in x 0.0005 in Re filament and thermally pre-treated at about 1450C for 30-45 min in vacuum to evaporate disturbed Pb from chemically altered domains. A condensation surface is then exposed to the sample and the zircon is heated at 1600C over 15 min to totally evaporate Pb. The condensation surface consists of either a 0.25 in wide Re ribbon (thermally cleaned using high current in a carbon coating chamber) or the inside of a 3 ml Savillex vial. Condensation of common Pb from the posts of the filament is prevented by the use of blinders welded to the posts of the evaporation filament. Operations are carried out inside a bell jar normally used for filament outgassing. Deposited silica from the zircon is subsequently removed using HF, by swabbing the Re surface using a pipette or open fluxing in the vial. The recovered Pb in the solution is dried, converted to HCl and spiked with ET2535 [202,205]Pb-[233,235]U spike, then loaded onto a conventional Re filament with phosphoric acid and silica gel for conventional TIMS analysis. The vial condensator is more convenient than the wide filament but it produces relatively high blanks probably because of partial melting of a thin teflon surface layer by the hot silica. The Re condensator gives negligible blank but is less efficient for collecting Pb.

Results

The TEC method has been tested on two Precambrian zircon populations from northwest Ontario previously dated by conventional methods. One of them is from the Marmion tonalite which has a conventional U-Pb age of 3002.6 ± 1.5 Ma [4]. Four fractions of it gave an average TEC age with 2 standard deviation of 3001.9 ± 0.6 Ma. The other one consists of two zircon fractions from a rhyolite at Nevison Lake (conventional age of 2998.6 ± 0.8 Ma) with a TEC age of 2998.5 ± 0.4 Ma.

[1] Kober (1986) *Contrib. Min.& Petr.* **Vol. 93**, 482-490. [2] Kober (1987) *Contrib. Min.& Petr.* **Vol. 96**, 63-71.[3] Davis (2008) *Geol.* **Vol. 36**, 383-386.[4] Tomlinson et al. (2003) *Contrib. Min.& Petr.* **Vol. 144,** 684–702.

Noble gas and radionulcides study of chondrules from Dhajala and Bjurbole chondrites

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Chondrules were formed ~ 2-3 Myr after the formation of CAIs (the first solid condensates of solar system) and then accreted into large bodies with fine-grain matrix material [e.g.,1]. Chondrules might experience excess exposure to energetic solar particles and cosmic rays before their compaction. To investigate such pre-compaction exposure, cosmogenic noble gas isotopes and radionuclides were studied for individual chondrules from Dhajala and Bjurböle.

Separated individual chondrules from Bjurböle (L/LL4) and Dhajala (H3.8) meteorites were crushed to small and uniform grain size and then divided into three aliquots for composition, radionuclide and noble gas analyses. To calculate production rates of cosmogenic nuclides, major element compositions of the samples were determined by a Thermo Electron Corporation iCAP 6000 series mass spectrometer. Measurements of ^{10}Be, ^{26}Al, and ^{36}Cl were performed by AMS at Primelab, Purdue University. He, Ne and Ar measurements were carried out using noble gas mass spectrometry at Washington University in St. Louis. The cosmic ray exposure age of Bjurböle (> 8 Myr, [2]) is greater than five half-lives for all the radionuclides measured, indicating that the production rate is equal to the activity of the sample. The production rates of ^{10}Be, ^{26}Al, and ^{36}Cl were calculated based on irradiation depth using the model suggested by [3]. Estimates for the pre-atmospheric size of Bjurböle are ~ 400kg with a density of 2.28 g cm^{-3} [4]. Assuming a spherical shape, the pre-atmospheric radius of Bjurböle is ~ 35 cm. From radionuclide analysis, we find the Bjurböle samples were located from 2-5 cm inside the parent body. For Dhajala (CRE age ~ 4 Myr, [5]), ^{36}Cl and ^{26}Al activity is at the saturation point. Based on ^{26}Al, the most likely size and location of the sample is 70 cm inside a 120 cm body. At this depth, the ^{10}Be activity is saturated and the minimum CRE age is 6.8 Myr. The noble gases in chondrules are dominated by cosmogenic component however a detectable amount of trapped gases are also present. We are initially using the ^{22}Ne/^{21}Ne as a depth indicator, allowing us to calculate production rates of ^{3}He, ^{21}Ne and ^{38}Ar [6]. An alternative method is to deduce the irradiation depth based on radionuclide activity [3]. ^{3}He, ^{21}Ne and ^{38}Ar CRE ages suggest that chondrule D#10C from Dhajala and chondrule BC06C from Bjurböle were exposed to cosmic rays longer than the host matrix. The remainder of the chondrules show CRE ages similar to matrix. The excess exposure duration is within the range of earlier reports [2, 5]. Radionuclide data in this study were used to find size and depth profile of the samples; future radionuclide data will be used to quantify recent exposure history with the goal of elucidating pre-compaction exposure from the total exposure history.

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Phase transformation of two-line ferrihydrite: Effects of pH, temperature, and adsorbed arsenate and molybdate

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Introduction

A dominant control on the mobility and speciation of many toxic elements from mining and milling operations is their adsorption onto the surface of iron oxy-hydroxides, of which two-line ferrihydrite (hereafter called ferrihydrite) is one of the most common and reactive. For example, tailings generated from uranium (U) mining and metallurgical operations are a potential source of As, Mo, Se, and Ra^{226} (termed Elements of Concern; EOCs) to the geosphere and biosphere. Generally, these elements are removed from oxic, acidic leach solutions (pH ~1.5) in the U mill via neutralization with lime and co-precipitation with ferric iron. Ferrihydrite starts to precipitate at pH ~3.5-4 during this neutralization process, which ultimately increases the pH to ~9.5 in the tailings prior to discharge. The EOCs subsequently adsorb onto the ferrihydrite, which thus controls their mobility in the pore waters. Because ferrihydrite is metastable and can transform to more structurally ordered oxy-hydroxide phases such as goethite and, under certain geochemical conditions, hematite, this study was conducted to assess the ability of ferrihydrite to act as a long-term sink for As and Mo in U tailings bodies. The results will also be useful in determining the long-term stability of ferrihydrite in other mine environments.

Materials and Methods

A comprehensive study was carried out to determine the rate of transformation of pure ferrihydrite (i.e., no adsorbed As or Mo) to goethite and hematite as a function of temperature (25, 50, 75, and 100°C) and pH (2, 7, and 10) via batch experiments. Subsequently, the impact of adsorbed arsenate and molybdate on the rate of ferrihydrite transformation was determined based on As/Fe (0.500-0.010) and Mo/Fe (1.000-0.010) molar ratios (to approximate elemental concentrations measured in the tailings) at pH ~10 and 75°C. These rates were extrapolated to the environmental conditions measured in the tailings (i.e., 1°C and pH=10) at Cameco Corporation's Deilmann Tailings Management Facility, Saskatchewan, Canada. Pure and transformed phases were characterized and quantified using XRD, XANES, AFM, SEM, BET, and Raman spectroscopy.

Results and Discussion

The rate of transformation of pure ferrihydrite to hematite increased with increasing temperature at all pH values considered and followed first order reaction kinetics. In the case of As adsorbed to ferrihydrite, the rate of ferrihydrite transformation decreased by two orders of magnitude as the As/Fe ratio increased from 0.010 to 0.018. No transformation was observed at higher As/Fe ratios (0.050, 0.100, and 0.500). Calculations show that the rate of ferrihydrite transformation under *in situ* conditions (~1°C; pH ~10; As/Fe ratio >0.250) is negligible and thus the ferrihydrite should continue to act as a sink for As for at least 10,000 years. Results of the ferrihydrite-molybdate testing remain to be analyzed.

Carbon solution and partitioning between metallic and silicate melts in a shallow magma ocean: implications for the origin and distribution of terrestrial carbon

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Carbon in the Earth's mantle has critical influence on planetary geodynamics, chemical differentiation, long-term climate, and habitability. But how early did the bulk silicate Earth acquire its current inventory of carbon? Is the mantle carbon mostly recycled or primordial? Answering these questions requires knowledge of the element's fate during magma ocean processes and parameters such as carbon solubility and partitioning between metal and silicate during core formation are key.

Experiments were performed at 2-7 GPa, 2000-2100 °C on mixtures of silicates (tholeiitic basalt/ komatiite/ fertile peridotite) and Fe-Ni-Co-C-S mix contained in graphite or MgO capsules. All the runs produced immiscible Fe-rich metallic and silicate melts at fO_2 between IW-1.0 and IW-2.2. Carbon concentrations of basaltic glasses and non-glassy quenched silicate melts were determined using secondary ionization mass spectrometry (SIMS) and speciation of dissolved C-O-H volatiles in silicate glasses was constrained using Raman spectroscopy. Carbon contents of metallic melts were determined using both electron microprobe and SIMS. Our experiments indicate, that at reduced, core-forming, conditions, carbon in mafic-ultramafic magmas dissolves primarily as a hydrogenated species and its storage capacity remains low. The total C content in our reduced melts at graphite saturation increases with increasing melt depolymerization (NBO/T), consistent with a recent spectroscopic study [1]. Carbon behaves as a metal-loving element during core-mantle separation and D_C (metallic melt/ silicate melt) varies between ~3500 and ≥100 and increases with increasing pressure and decreases with increasing melt NBO/T.

Our data suggest that if only a trace amount of carbon (~730 ppm C; [2]) was available to participate in the early differentiation of Earth, most of it was partitioned to the core and no more than ~10-30% of the present-day mantle carbon budget (50-200 ppm CO_2) can be derived from a magma ocean residual to core formation. With core formation removing most of the carbon initially retained in the terrestrial magma ocean, explanation of the modern Earth carbon inventory requires a later replenishment mechanism. Addition of volatile-rich, late veneer and inefficient core formation both remain viable mechanisms. Alternatively, carbon ingassing by magma ocean-atmosphere interaction, soon after core formation, may also make the Earth's primordial carbon inventory similar to that of the present-day budget.

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Insights on the Late-Stage Evolution of Glacial Lake Ojibway

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Meltwater released at the southern margin of the Laurentide ice sheet during the last deglaciation led to the development of Lake Ojibway in NE Ontario and NW Quebec. The late-stage evolution of Lake Ojibway was marked by ice (Cochrane) readvances, while recent mapping of low-elevation lakeshores indicate abrupt drawdowns of Ojibway lake level prior to its final discharge into Hudson Bay ~8200 cal yr BP. Additional late-stage events are also suggested by the presence of thick (10-15 cm) bands of massive silt that truncate Ojibway rhythmites. This silt band is in turn overlain by ~1 m of rhythmites. Although this sequence suggests the occurrence of drainage episode(s), the late-stage history of Lake Ojibway remains inadequately documented. Here we report results from the study of 12 Ojibway sediment sequences that contain the silt band.

Grain-size analyses of bulk Ojibway rhythmites (winter and summer beds) show a textural composition consisting of 73% clay (<2 μm) and 25 % of fine silt (2–8 μm), with the remaining material being composed of medium silt (8–16 μm). This contrasts with the thick silt band that consist primarily of ~54–86% of fine to coarse silt (2–63 μm), with the clay fraction typically representing < 20%. The detrital carbonate content of rhythmites samples shows values ranging from 0.72 to 2.02%, while silt band samples commonly show a slight increase with respect to the bounding rhythmites, going from 1.85 to 3.34%. Ostracods were extracted from specific sediment intervals for oxygen isotope ($\delta^{18}O$) measurements. Preliminary results indicate that ostracods from the silt band and underlying rhythmites have $\delta^{18}O$ values ranging from –23.26 to –25.04 ‰ (vs VPDB), typical of glacial metltwater. In contrast, the rhythmites overlying the silt band show $\delta^{18}O$ ranging from 10.03 to 16.62 ‰.

Interpretation of the results is still limited at this stage of the study. Nonetheless, the textural changes reported could be associated with a drainage episode(s) that was followed by a deepwater phase(s). Alternatively, this *drainage varve* (?) could represent a drastic change in the sediment supply (or source) to the lake. This appears to be supported by the increase in detrital carbonate of the silt band. Because the Ojibway basin lies primarily on crystalline bedrock, the presence of detrital carbonate in Ojibway sediments is commonly attributed to the late-glacial dynamics (metltwater runoff or ice readvances) of the decaying ice in Hudson Bay, which is underlain by carbonate rocks. Any explanation for the origin of this silt band and associated compositional changes must also take into account the sharp change in $\delta^{18}O$ composition obtained for the sediments overlying the silt band, which shows an evolution towards post-glacial values. Upcoming ^{14}C ages from the ostracods extracted from the silt bands and bounding rhythmites should also help refining our understanding of these events.

A surface complexation model for the copper-bacteria-iron oxide system

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Laboratory experiments were performed to track the fate of dissolved Cu and Fe at a fixed pH of 5.2 during the gradual, incremental oxidation of dissolved Fe(II) and precipitation of iron oxide in the presence of *Anoxybacillus flavithermus* cells. The experimental data reveal significant and complex controls on Cu immobilization, related to progressive changes in 1) ratio of Cu to dissolved Fe(II) concentration, inferred to result from competition for bacterial sorption sites; 2) ratio of precipitated iron oxide to bacteria, inferred to result from desorption of Fe(II) initally associated with the bacterial surface; and 3) reaction time, inferred to result from Cu complexation by increasing quantities of biogenic dissolved organic matter. Surface complexation models were developed to describe the experimental data, with constraints on reaction mechanims provided by polarography and X-ray absorption spectroscopy. Differential pulse polarography demonstrated that Cu complexes form with dissolved organic ligands in filtered bacterial suspensions. The concentration and Cu complexation capacity of these bacterial exudates could be quantified and related to the conditions and history of the suspensions. The bacterial exudates significantly inhibited Cu adsorption onto the bacterial cells but slightly enhanced adsorption onto the iron oxide under the experimental conditions. X-ray absorption spectra were collected at the Cu K-edge on the bacterial exudates and wet pastes of the bacteria, the iron oxide, and the bacteria-iron oxide composites. The EXAFS data suggest that Cu complexation by the bacterial exudates involves binding by carboxyl or phosphate sites. The EXAFS data also show that under the experimental conditions Cu in the solid phase is associated predominantly with carboxyl structures on the bacterial cell walls, not with bacterial phophoryl structures or with binding sites on the iron oxide. This study demonstrates that the immobilization of metal cations in bacteria-bearing settings should not be examined independently of progressive oxidation, hydrolysis and precipitation of iron.

Iron isotope geochemistry with a synchrotron light beam

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Previous studies have suggested that iron isotopes could be good tracers of redox conditions during melting [e.g., 1]. However, we lack a reliable database of equilibrium fractionation factors between melts and igneous minerals such as olivine to interpret the rock record [2]. Iron equilibrium fractionation factors (or more specifically reduced partition function ratios, β) can be derived from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) experiments at a synchrotron facility [3,4]. We have developed a new method (i.e., the *general moment* approach), based on a Bernoulli expansion of the reduced partition function ratio, to calculate β-factors from the moments of raw NRIXS spectra [4]. The first term in this expansion corresponds to the mean force constant of the iron bonds [5], a quantity that is readily measured and often reported in NRIXS studies [6]. We have used this technique to determine the β-factors of olivine and geologically relevant silicate glasses.

At a given Fe^{3+}/Fe^{2+} ratio, the force constants of basaltic, andesitic, and dacitic glasses are almost identical. However, the force constant of rhyolitic glass is higher. For all samples, the force constant increases with the Fe^{3+} content. Thus, for mafic melts, there is little structural control on iron isotopic fractionation; redox effects seem to dominate. The relationship between force constant and Fe^{3+}/Fe_{tot} for basalt, andesite, and dacite is approximately linear. We can estimate the force constants of Fe^{2+} and Fe^{3+} in basalt by interpolating the data to $Fe^{3+}/Fe_{tot}=0$ and $Fe^{3+}/Fe_{tot}=1$. At 1,100 °C, we calculate an equilibrium $\delta^{56}Fe$ fractionation of +0.25 ‰ between the two oxidation states of iron in magmas. The olivine-melt and melt Fe^{2+}-Fe^{3+} iron isotopic fractionations derived from NRIXS data may explain the heavy iron isotopic compositions measured in MORBs.

This study provides a solid reference for interpreting Fe isotopic variations in igneous rocks. Specifically, it reveals the potential of using Fe isotopes to trace redox variations and magmatic differentiation processes in planets.

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Cyclic growth layers in calcareous biominerals

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Mollusc shells are among the best known calcareous biominerals. The calcitic prisms of *Pinna* and *Atrina* are often used because of their large size and simple geometry. As other biominerals, they are organo-mineral composites [1,2]. Thin sections observed in polarized light show they behave as monocrystals [3]. However, polished and etched sections show they are composed of growth zonations. Thickness of a growth line is about 1-3 μm. Moreover, the distribution of chemical elements is not uniform. Outer organic walls have low Mg and high S contents. Within the prisms, more or less intense zonations are visible. In both structural and chemical images, zonations are synchronous across adjacent prisms, showing the strict physiological control of the biomineralization processes. The comparison of chemical maps show that the rhythm and intensity differ according to the element.
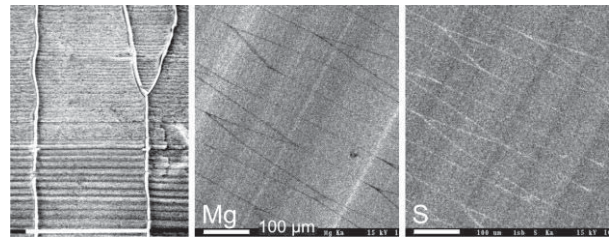

Figure: structural growth lines and chemical zonations in the calcitic prisms of *Pinna*

AFM images show that prisms are made of granules surrounded by a cortex. TEM data show that in distinct regions of a prism, granules are amorphous, while others are crystallized as subunits of a large single crystal. At the boundary of the two regions, granules display a crystallized core and an amorphous rim [4]. Such a limit probably marks out an arrested crystallization front having propagated through a previously biocontrolled architecture of the piling of amorphous micro-domains.

Such a crystallization process, developed within the organic matrix, differs from the usual model occurring within a fluid, the composition of which is assumed to be close to sea water. Such a model, used in the palaeo-climate/ geochemical areas, cannot account for any species-specific property of the calcification process. A matrix-driven crystallization within the spheroids of the growth layers provides us a reasonable way to explain the black-box of the "vital effect".

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Does diopside dissolve like glass? Insights from measurements of nano- to macroscale dissolution rates

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Whereas the dissolution rate of silicate minerals has been extensively studied at far-from-equilibrium conditions, extrapolating such rates over a broad range of solution compositions has proven challenging. In particular, a growing amount of studies have pointed out that the simplest TST-based rate-affinity dependence commonly implemented into most of geochemical codes was the source of dramatic overestimations of the actual fluid-rock interaction rates [1, 2]. Such limitations acted as a driving force for developing alternative dissolution models of solids over the past 10 years [3, 4].

Diopside was shown to belong to that category of minerals for which rate-affinity relationships do not follow a simple TST-like model, since an unexpected drop of the rate was evidenced at ΔG_r(diopside) as low as -76 kJ.mol^{-1} [5]. An examination of these data led us to envisage that two different, non-exclusive aspects were worth investigating: (i) the possible passivating ability of interfacial, nm-thick Si-rich layers developed on weathered silicate surface, and (ii) the stop of etch pits formation on crystal surface, which were found to be responsible for drops of olivine [2] and albite [3] dissolution rates, respectively. The former mechanism should be evidenced by the dependence of diopside dissolution rate on [SiO$_2$(aq)], whereas the latter should verify a strong anisotropy of diopside dissolution, with ($h\ k\ l\neq0$) faces dissolving noticeably faster than ($h\ k\ l=0$) faces. Both of these models were tested by running either classical flow-through experiments with controlled [SiO$_2$(aq)], and face specific dissolution experiments. In this latter case, single crystals were immersed in solution. The dissolution features were monitored by AFM imaging and the dissolution rates were calculated by measuring the global surface retreat between masked and unmasked regions using VSI [1].

Our results show that the dissolution rate of diopside drops as SiO$_2$(aq) is added to the solution, consistently with a dissolution mechanism controlled by the stabilization of a passivating, interfacial Si-rich layer, as already suggested for glass [6]. On the other hand, our preliminary results on the face-specific dissolution of diopside show that the dissolution rate of faces varies following: (021) >> (110) ~ (1$\bar{1}$0) >> (010) ~ (100), which does not invalidate the etch pit nucleation control of diopside dissolution kinetics. The results of the ongoing experiment on (001) face, as well as upcoming investigations of the interfacial layers by TEM, will help to make a final decision between the two proposed models.

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Differentiation and source controls along the Lesser Antilles arc

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The fluxes of elements into, and out of, subduction zones dictate both the composition of the crust and the heterogeneity of the mantle. Most flux estimates are predicated on the basis of the compositions of magmas erupted from arc volcanoes. However, volcanic rocks represet only 10-20% of the total magma flux from the mantle at arcs, and these magmas have undergone the maximum amount of filtering, having passed through the entire thickness of the upper plate lithosphere. In order, therefore, to realistically determine the contributions from the mantle wedge and slab (sediments and fluids) to arc magmas, it is critical to account for the effects of differentiation.

We have done this at the Lesser Antilles arc for two volcanoes; The Quill (Statia) in the north and Mt Pelee (Martinique) in the central part of the arc. An evaluation of the volcanic rocks, their constituent minerals and associated cumulate blocks allows us to show that 1) differentiation was controlled by an amphibole-plagioclase-dominated assemblage, as reflected in the cumulate blocks, and 2) differentiation was open system, involving assimilation of the arc crust.

Even though amphibole is not present in the phenocryst assemblage of the volcanic rocks, it is common in the cumulate xenoliths. Thus fractionation control is cryptic, with compositions determined largely by mineral assemblages not represented in the erupted fractionates. Indeed amphibole may be more common as a fractionating phase at arcs than has previously been appreciated [1]: By increasing SiO$_2$ and generating LREE enrichment, amphibole might have an important role in generating crust-like differentiates at arcs. The inferred assimilation of the arc crust modifies Pb and Sr isotope compositions in the magmas, suggesting that even at intra-oceanic arcs the isotopic compositions of erupted magmas cannot a priori be taken as indicative of their mantle source.

Once differentiation trends are established they can be back-extrapolated. When this is done, differentiation trends for The Quill and Mt Pelee do not converge on a common primitive/ parental composition, suggesting that mantle source compositions vary along the arc. The mantle sources of both volcanoes can be modlled by addition of <5% sediment or <1% sediment melt, along with LILE-bearing fluid. The differences between the sources of the two volcanoes can be explained by different sediment compositions delivered along the arc, or a slightly greater sediment contribution at Mt Pelee [2].

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A Particle-Based Approach to Modelling Water Flow and Residence Times in a Small Catchment

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Introduction

Understanding water flow processes in the near-surface environment is crucial in determining movement of nutrients and pollutants. The majority of hydrological models used employ continuum-based expressions to derive mass flow linked with advective dispersive equations (ADEs) if transport is also considered. The appliability of these approaches to real soils which contain structural heterogeneities is questionable. Continuum-based models requires sub-grid equilibrium of potentials and fluxes, leading to impractically fine grid-scales if the heterogeneities are to be represented, and the assumption of Brownian motion in ADEs is not representative of preferential flow features that allow solute movement at velocities much in excess of the wave celerities.

Multiple Interacting Pathways Model

The Multiple Interacting Pathways (MIPs) concept is an alternative approach to modelling transport and flow that directly acknowledges the presence of preferential flow pathways. Water in the slope or catchment is represented as a set of discrete particles, the movement of which is simulated through random particle tracking. Velocity distributions are applied to the particles, which attempt to characterise the range of pathways available to the water. These pathways are interacting as movement between them is simulated with exchange probabilities, which may also be used to simulate evapotranspiration or bedrock losses.

This concept provides unified simulation of transport and flow, allowing analysis of input/output/storage residence times and water origin, with the potential of adding chemistry to the particle interactions.

Application to Hydrometric and Isotopic Data

The MIPs model has previously been applied to simulating plot scale hydrometric and artificial tracer data at a site in Gårdsjön, Sweden with some success [1]. This modelling has been extended to simulate a catchment-scale step-change in isotopic input that occurred at the site on construction of a roof. Hypotheses are sought which provide consistent results across both spatial scales and temporal scales of transport. Having found a behavioural model, a fuller analysis is made of the input/output/storage residence time distributions suggested by the model.

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Geochemical and isotopic insights into the origin of the 'Scourie' Dykes

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The 'Scourie' dykes are a NNW trending dyke swarm in the Lewisian gneiss terrain of Northwest Scotland. They represent important time markers in the evolution of the Lewisian as the majority were intruded between two regional high-grade metamorphic events – the Inverian (~2.5 Ga) and the Laxfordian (~1.7 Ga). Importantly, the area around Loch Assynt was variably affected by the Laxfordian event leaving some of the dykes un-metamorphosed with primary igneous textures and minerals. The dykes therefore are perfectly placed to distinguish between the metamorphic events and provide information on the Paleoproterozoic history of the Lewisian terrain. Numerous field, geochemical and geophysical studies have been conducted on the Scourie dykes over the past 30 years, despite this the age and origin of the dykes is still poorly known.

Field relationships and geochronology indicate that there are at least four separate Paleoproterozoic dyking events intruding the Lewisian crust spanning a period of more than 400 m.y. The majority of dated dykes using high precision U-Pb zircon/baddeleyite geochronology were emplaced between 2420 and 2380 Ma, which is the time period focus of this study. Whole rock and clinopyroxene oxygen isotopic analyses have shown that some of the dykes have low δ^{18}O signatures (~2‰) whereas other dykes have normal mantle values (~5.5‰). Geochemical studies of the dykes indicate that there maybe at least two mantle sources involved in dyke genesis that are variably enriched in trace elements.

Here we combine new Sm-Nd, Rb-Sr, δ^{18}O, geochronological and trace element data on the dykes to suggest a new model for the origin of the 'Scourie' dykes. Preliminary results indicate that the initial pulse of dyke emplacement (~2420-2400 Ma) was characterized by normal mantle oxygen isotope signatures and mantle source enrichment. A second period of dyke emplacement occurred subsequently (~2400-2380 Ma) in which the dykes are less geochemically enriched and contain low δ^{18}O signatures possibly indicating the involvement of subducted oceanic crust. Using the new geochemical and geochronological classifications we define the 'Scourie dyke suite' senso stricto as those emplaced between ~2420 and 2380 Ma with a concentration of these dykes in geographic proximity to the town of Scourie.

Effective mixing and reaction front kinetics in porous media

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The effective reaction kinetics of chemical species transported in solution in the subsurface depends on the probability of reactants to mix. While chemical reactions ultimately occur by diffusive mixing at the molecular scale, the effective reaction kinetics can be greatly enhanced by the shear and stretching action of the flow field, which increases the surface available for diffusive mass transfer [1]. Understanding and quantifying the effect the flow field heterogeneity on the upscaled mixing and reaction rates is thus a key issue for the prediction reactive transport in the subsurface.

We use pore scale Smooth Particle Hydrodymanic (SPH) simulations to investigate effective mixing and reaction kinetics for reaction fronts where an initially resident reactant is displaced by an incoming reactant. The reaction kinetics is found to be faster than that of homogeneous diffusion-reaction fronts, for which the mass of product grows like the square root of time. At early time, the effective reaction rate is controlled by the formation of fingers of incoming reactant, which invade the porous media, rapidly increasing the reaction front area. At late time, the reaction kinetics is governed by the longitudinal dispersive growth of the mixing area and by the spatial distribution of concentration gradients in the mixing zone, which characterize a persistent state of incomplete mixing [2.3]. We discuss the effect of changing the relative contribution of advective and diffusive motions (quantified by the Peclet number) on the temporal evolution of effective mixing and reaction rates.
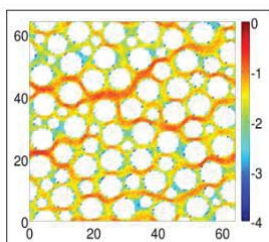
Pore scale flow field
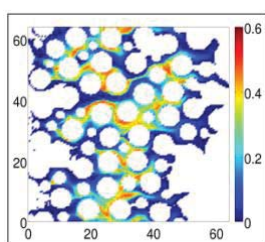
Distribution of product concentration within the reaction front

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[2] Le Borgne T., Dentz M., Davy P., Bolster D., de Dreuzy, J. R. and Bour O. (2011) Phys. Rev. E, **84**, 1
[3] de Anna, P., T. Le Borgne, M. Dentz, D. Bolster and P. Davy (2011) J. of Chem. Phys., **135**, 174104

Contrasting Biogeochemical Cycling of Iron and Aluminium along the GEOTRACES West Atlantic section

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The thus far longest (13,000 km) complete deep ocean section of iron (Fe), aluminium (Al) and a suite of other trace elements and isotopes was realized in 2010-2011 in the West Atlantic Ocean. The more than 1200 data values reveal the major sources and processes controling Fe and Al in the oceans. Overall Fe is decoupled from Al except in the uppermost surface layer of dust input. Overall the Al shows an amazing inverse relationship with Si.

The background concentrations of Fe are quite uniform around 0.5 nM but there are several major enhancements. In the 10-30 ºN region the uppermost samples (10m depth) have maximum concentrations of Fe exceeding 2nM and Al exceeding 40 nM, respectively, due to partial dissolution of dust supply from the Sahara. This extra Fe supports N_2 fixation by diazotrophs in the Sargasso Sea, that upon sinking of plankton debris and mineralization causes a high anomaly of the nitrate/phosphate ratio in the 200-800m depth zone. The Amazon River plume provides a signal of high Fe and Mn but Al is not enhanced. Underlying the equator the strong oxygen minimum zone contains higher Fe concentrations, that by upward mixing may well be the major source of Fe to surface waters supporting plankton growth. The Confluence zone (~30 ºS) of the Brazil and Malvinas Current is a well known region of high biological productivity and chlorophyll biomass. We now find this is supported by very high dissolved Fe from below at ~3 nM or more, the supply of which may also be due to influence of the Rio de la Plata or submarine groundwater discharge. The North Atlantic Deep Water shows a very strong correlation of Al and silicate (Si) in the subArctic Gyre, yet going southwards the NADW content of Al decreases and of Si increases and far south no relationship exists anymore. This is consistent with ocean simulation modeling of steady remineralization of Si versus continuous loss of Al due to adsorptive scavenging. An enhanced Fe pool at 2000-3000m depth below and south of the equator (4ºN - 15ºS) is consistent with hydrothermal input, confirmed by higher Mn but no extra Al.

Dissolved Iron in the Arctic and Antarctic Oceans

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Iron (Fe) is an essential trace element for all biota but the dissolved Fe in ocean waters is extremely low and limiting for phytoplankton growth in over 40% of world ocean surface waters. Indeed in the Southern Ocean extremely low dissolved Fe was found in surface waters along the Greenwich meridian, both in the Antarctic Circumpolar Current and in the most southerly Weddell Gyre adjacent to the ice-covered Antarctic continent [1]. The low dissolved Fe is maintained in solution by organic complexation [2]. The extending continental ice-sheet floating over the continental shelf is unique in largely preventing biological processes and cycling. As a consequence Antarctica is the only continent that does not supply Fe [1] and Mn [3] from shelf sediment sources into adjacent surface and intermediate waters. In contrast the shelves at both sides of the Antarctic Peninsula are a source for dissolved Fe, Mn and Al into the western Weddell Sea and southern Drake Passage, respectively. Otherwise dissolved Fe concentrations are extremely low in the entire water column of the Weddell Sea and Drake Passage. In West Antarctica the local Pine Island Glacier is a source of dissolved Fe [4] fueling intensive phytoplankton blooms [5] in the Amundsen Sea where organic complexation [6] of Fe plays a key role. In deep waters there is a significant hydrothermal plume of Fe and Mn over the Bouvet Triple Junction region. One water mass in Drake Passage also shows hydrothermal Fe and Mn associated with δ^3He anomalies originating from the Pacific Ocean [7]. In the Arctic Ocean a very strong hydrothermal Fe and Mn plume was found over the Gakkel Ridge [8, 9]. The large spatial extent of Fe of hydrothermal origin is ascribed to its stabilization in solution by organic complexation [10]. Surface waters in the central Arctic Ocean have fairly high dissolved Fe concentrations due to the Transpolar Drift bringing along coastal waters, mainly of Siberian riverine origin with high dissolved Fe contents [11]. As a result the Arctic Ocean has fairly adequate Fe abundance for phytoplankton growth, this in contrast to the very low and bio-limiting dissolved Fe in large areas of the Antarctic Ocean.

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Atmospheric gases: the archaeological glasses memory

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The atmospheric components of past climatic changes are often constrained from ice records of polar ice sheets. In temperate areas, this kind of study is more difficult to apply due to the low spatial and temporal resolution of the iced records.

In this study, we propose an alternative method based on analyses of atmospheric gases trapped in bubbles of archaeological glasses from the Western Europe and dated between the I[st] century BC to the present. Indeed, during the shaping of ancient glasses, bubbles are created in glass paste, from the melting of raw materials inside furnace and glass-paste degassing, or from the step of glass working in open air. In this second case, the surrounding atmosphere could be trapped, particularly during the glass-making of ancient and medieval stained windows.

While the study of Vesicule Size Distribution (VSD) [1] of archaeological flat glasses show a bimodal size bubbles distribution in flat glasses, the distribution of the other kind of glasses (blown cup or vessel, and raw glasses) are unimodal. Geochemical analyses of major gases included in bubbles in flat glasses, show a chemical dichotomy between two groups of bubbles, independent of chemical composition of glass paste. The smallest bubbles (Ø<100-500 μm) are exclusively composed of CO_2. In contrast, the largest bubbles (Ø>250-500 μm) are N_2 rich (~80%), CO_2 poor and contained Ar (~1%), and sometimes O_2. So, the origins of the two populations of bubbles are obviously different and the largest vesicles seem to have an atmospheric origin (the Ar/N_2 ratios of these large bubbles are closed to the modern atmosphere).

Despite these gases look like an atmospheric composition, the CO_2 contents are too high and the oxygen contents are too low. The carbon excess could have different origins (mixing between atmosphere and furnace/combustion gases, and/or chemical reactions between trapped gases and particular soots). SEM analyses have shown some deposits in the inner wall of the largest bubbles (graphite, carbon oxides etc.), supporting the idea of a catch of elements as alien to glass and in-situ chemical reactions.

We need to take care of these soot-reactions and the gases diffusion rates through the glass, to estimate the initial compositions of gases included in vesicles, and to extract the atmospheric contribution from the bubbles gases set using mixing models. Finally, we suggest that the archaeological glasses could appear like a new but complex source of archeo-climatic recording.

[1] Sarda & Graham (1990), EPSL 97, 268-289.

Mixing of Contrasting Silicate Melts: preliminary Raman Spectra

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Glasses melts and magmas

A widely debated question in Geosciences is how viscous magmas with extreme viscosity contrast mix under natural conditions. In order to study how chaotic dynamics may control chemical interactions, and therefore timescales of hybridization during magma mixing, we developed a modified Journal Bearing System device [1] for experiments on chaotic mixing silicate melts at high temperature [2]. In this work we focus on preliminary Raman spectra of mixed glasses obtained by mixing two end-members at 1,673K: (i) a peralkaline haplogranite melt (HPG8N5K5), and (2) a haplobasaltic melt corresponding to the 1-atm eutectic composition of the Anorthite-Diopside (An-Di) binary system. These two compositions are intended to act as analogues for natural dry granitic and basaltic magmas. Raman spectra were obtained along two transects along filaments from the resultant glasses, next to the same points analysed for major and trace elements (microprobe and Laser Ablation ICP-MS) [3]. Experimental conditions were kept 'extreme', since most of melt fraction consisted of a high-viscosity melt (95%) and small amounts of lower viscosity mafic melt (5%).

Figure 1: Raman spectra along two transects crossing filaments of mixed haplogranite and An-Di
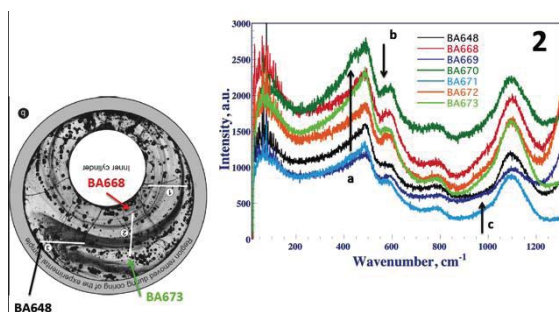
Results and Conclusion

We observe some changes, in particular the arrows a, b and c show changes in the Raman spectra, and they can link at changes in the polymerization network. Spectra 648 is probably more polymerized than spectra 666 (not shown in Figure 1). This observation is also confirmed for the spectra 670, consisting of the more polymerized melt. Although the changes are still subtle, these point towards changes in the polymerization degree, which are due to differential hybridization of the two stating compositions. For the preliminary results peak-changes vary with the geometry and interaction degree among filaments. Results are consistent with those obtained from microchemical studies along the same lines [3].

[1] Ottino etal. (1988) *Nature* **333**, 419-425; [2] De Campos et al. (2011) *Contrib. Mineral Petrol* **161**, 863-881; [3] Perugini et al. (*in prep.*).

Case study of an abandoned Zn-Pb mine: Ingurtosu (Sardinia, Italy).

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Ingurtosu mine characterization

The Ingurtosu Pb-Zn mine (S-W Sardinia) was in production for about a century until 1968. Huge amounts of tailings were abandoned, resulting in long-term heavy metal dispersion in both stream sediments and waters. Downstream from the mine wastes, the Naracauli waters discharge directly into the Mediterranean Sea. At least two biomineralization processes (Fig. 1) are known to be effective in the abatement of Zn and other heavy metals transported in solution.

In this work, many different techniques were used to study the mineralogy and geochemistry controlling the biomineralization processes. Microbial consortia within biofilm associated with seasonal precipitation of an amorphous mineral made of Si, Zn and O were examined. In addition, the load of metal dissolved in the Naracauli waters was measured using hydrologic tracers with synoptic sampling.

The results presented in this work show that a) the consortium of bacteria changes along the river, creating a cascade of processes that results in biologically mediated formation of different Zn-bearing minerals [1]; b) the changes in water chemistry along the river are moderate for the major constituents, but large changes in trace-element concentrations are observed [2]; c) the heavy metals load derives from the interaction between mine wastes and Naracauli water, and about half of the metal load comes from tributaries with high water flow but relatively low heavy metal concentrations.

Figure 1. SEM images of Naracauli biominerals: hydrozincite on the left, and Zn-Si-O phase on the right.
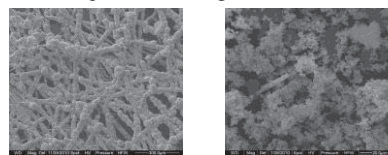
Conclusion

This work indicates that any remediation plan for the Ingurtosu abandoned mine must take into account the whole Naracauli basin, and water treatment is needed before river water is allowed to discharge to the sea. Finally, biomineralization processes could offer a way for a natural abatement of Zn and some other heavy metals.

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Modelling the nucleation of hydroxyapatite at a collagen template

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The biomineral hydroxyapatite nucleates at an organic collagen matrix, which controls the growth process and eventual morphology of the apatite crystallites. An important but largely unresolved issue is the way in which nature controls the nucleation, growth and morphology of the inorganic crystallites and the function of the templating biomolecules, here collagen, in these reactions. However, as it is not yet possible to study directly, by experiment alone, the molecular mechanisms of biomineralisation processes, we have employed a combination of *ab initio* and classical Molecular Dynamics simulations to investigate the early processes of the nucleation of hydroxyapatite at a collagen template, by immersing a triple-helical collagen molecule in a stoichiometric solution of Ca^{2+}, PO_4^{3-} and OH^- ions.

The average number of water molecules in the first hydration shells of the Ca ions and PO_4 groups from the classical MD simulations are all in excellent agreement between with the *ab initio* MD and experiment. Very quickly, a number of stable calcium phosphate (CaP) clusters form in solution, although preferential CaP formation occurs at the collagen matrix.
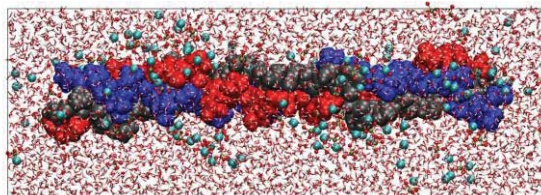

Figure 1: Graphical representation of the collagen triple helix in stoichiometric hydroxyapatite solution.

Electrostatic attractions are prevalent between calcium ions and oxygen atoms of the glycine and hydroxyproline residues, which were the starting point for the formation of the calcium phosphate clusters. At body temperature, calcium ions interact with water molecules to form stable complexes, but attracted by electrostatic forces, they coordinate to PO_4 ions and start forming clusters. Some phosphate ions form hydrogen-bonds with the hydroxy groups of hydroxyproline residues, whereas due to strong water-OH interactions most of the hydroxy ions stay in solution, although some become attached to calcium phosphate clusters. These results agree with suggestions that HA growth follows initial amorphous CaP formation.

Comparison of our results[1] with those of Kawska et al.[2] shows that fluoride ions inhibit calcium phosphate formation by competitively binding the Ca ions into calcium fluoride clusters.

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Geochemical modelling of long-term mineral alteration induced by the injection of CO_2 in a saline aquifer: the Ketzin site

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The assessment of expected long-term CO_2-induced mineral alterations of reservoir and cap rock is crucial to ensure the long-term stability of the storage project, and to evaluate the potential carbon trapping provided by mineralization. In the first european on-shore pilot site at Ketzin, nearby Potsdam, Germany, about 60,000 t of CO_2 were injected (as of February, 2012) in a saline aquifer in a Triassic sandstone at about 650 m depth. A rich set of analyses of pristine formation fluids [1] as well as mineralogical and geochemical composition of the reservoir rock [2] made possible a precise parametrization of the reference geochemical model.

Batch 0-D simulations including reaction kinetics were run using the speciation code PHREEQC under the assumption of a constant CO_2 pressure over the simulation time of 5,000 y. The pore pressure itself was found to have a negligible impact on mineral alterations, at least in the considered range of approximately 50 to 80 bar expected for the site. The reference simulation predicts the precipitation of kaolinite, K-feldspar, and plagioclase (represented by the end-member albite) which greatly compensate the partial dissolution of illite, Fe-rich chlorite, and anhydrite cement. Of all carbonate minerals included in the model (siderite, magnesite, calcite, and dolomite), siderite is the only one which precipitates in significant amounts, and thus contributes to mineral trapping. However, the precipitation of carbonates always starts after several hundreds years in the models.

To investigate the robustness of these results, different scenarios were run, each representing a different choice for primary and secondary minerals and different hypothesis for the parametrization of mineral reactive surfaces with respect to the reference model. The simulated results are quite variable, but the simulated total relative change in pore volume after 5,000 years was always below 2%. This can be considered irrelevant in terms of influence on the hydrodynamic properties of the rock. These results are confirmed by the observations from laboratory experiments on core samples exposed to CO_2.

[1] Würdemann et al. (2010) *CO₂SINK—From site characterisation and risk assessment to monitoring and verification: One year of operational experience with the field laboratory for CO₂ storage at Ketzin, Germany* **International Journal of Greenhouse Gas Control** 4(6)**, pp** 938-951
[2] Förster et al. (2010) *Reservoir characterization of a CO₂ storage aquifer: The Upper Triassic Stuttgart Formation in the Northeast German Basin*, **Marine and Petroleum Geology** 27, 2156-2172.

Sulfur Isotope Fractionation During Basaltic Degassing

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We examine S degassing and S isotope fractionation at basaltic volcanoes using S isotope compositions of scoria and magmatic gases from three active basaltic volcanoes in contrasting tectonic settings: Masaya and Cerro Negro (Central American Arc), and Erta Ale (East African Rift). We present S contents and S speciation of gases and melt inclusions to constrain degassing conditions. An equilibrium isotope fractionation degassing model is used to assess the S systematics considering oxygen fugacity, temperature, and pressure of degassing.

Erta Ale is a reduced system at Δ QFM ~0 [1]. Pristine scoria from Erta Ale have an average $\delta^{34}S$ value of $+0.9 \pm 0.3$ ‰ (n = 5) and gas samples have $\delta^{34}S$ values of $+0.7$ ‰ to -1.9 ‰, spanning the MORB range of $+0.3 \pm 0.5$ ‰ [2] and extending to lighter values. Synchrotron micro-X-ray Absorption Near Edge Spectroscopy (XANES) analysis of an olivine-hosted melt inclusion from Erta Ale indicates that S^{2-} is the dominant S species in the melt (rather than S^{6+}). High temperature (1086°C) fumarolic gas samples have SO_2 as the dominant S species. Significantly, the scoria are isotopically heavier than the gases, which is the opposite of that expected for equilibrium conditions between S^{2-} in the melt and SO_2 gas because at equilibrium the more oxidized S species retains the heavy isotope. We interpret the low $\delta^{34}S$ values of the gas to reflect a kinetic effect that occurs as S diffuses from the melt into the gas phase (on the bubble scale) that favours the transfer of the light isotope into the gas.

Gas and scoria samples from the oxidized arc volcanoes (Cerro Negro and Masaya; ~ΔQFM +2 [3]) have a range of $\delta^{34}S$ values from $+2.2$ ‰ to $+9.3$ ‰. Scoria are isotopically heavier than the gases by ~3 ‰ at Masaya and by ~5 ‰ at Cerro Negro. XANES analysis of an olivine hosted melt inclusion from Cerro Negro shows that S^{6+} is the dominant S species in the melt. The negative $\Delta^{34}S_{gas-melt}$ relationship observed at Masaya and Cerro Negro is consistent with degassing of SO_2 or H_2S from a melt containing S^{6+}. However, equilibrium modelling predicts that the gas should be isotopically lighter than the melt by only 1‰ to 1.7‰ for degassing between 1 bar and 4 kbar (higher degassing pressure favours H_2S over SO_2, resulting in larger fractionation between gas and S^{6+} in the melt). The large $\Delta^{34}S_{gas-melt}$ observed at Masaya and Cerro Negro can be explained by equilibrium fractionation in addition to a kinetic effect as observed at Erta Ale. In all three cases the compositions of the gases are isotopically lighter than predicted by equilibrium modelling by 2 ‰ to 4 ‰, suggesting a common kinetic effect that favours the transfer of the light isotope into the gas phase.

[1] Giggenbach and Le Guern (1976) *GCA* **40**, 25-30. [2] Sakai et al. (1984) *GCA* **48**, 2433-2441. [3] Mather et al. (2006) *JGR* **111**, D18.

Ex situ carbonate mineralization: a novel way to sequester CO₂ at the expense of saline wastewater

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In situ and ex situ technologies based on carbonate mineralization offer ways to insure the permanent and safe storage of this greenhouse gas. In our opinion, both anthropogenically produced CO_2, at a cement plant, for example, and saline wastewaters can be utilized as valuable resources. The brines recovered from desalination operations and produced water associated with oil and gas exploitation are promising sources of alkalis and alkaline earths needed in the carbonation process. Our ex situ approach involves the formation of hydrated carbonate minerals (e.g., nesquehonite, $MgCO_3 \cdot 3H_2O$) at room temperature through the reaction of gaseous CO_2 bubbling in Mg (7 g L^{-1}) wastewater, similar to what is commonly available industrially [1]. The reaction rate is rapid, with carbonate deposition in about ten minutes. We have demonstrated that the method can be efficiently applied to more concentrated solutions, up to 32 g L^{-1} of Mg. The efficiency of the carbonate mineralization process ranges between 65 and 80%, depending on the salinity of the solution [2]. The thermal behavior and structural stability of the nesquehonite precipitate suggest that it will remain stable at the temperature conditions that prevail at the Earth's surface, i.e., below 600 K, the threshold of periclase nucleation [3]. Moreover, our results indicate that if this mineral is left in contact with the simulated brine or heated, it can be expected to transform to other carbonates thermodynamically more stable, up to about 650 K, e.g., dypingite $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O]$ and hydromagnesite $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$. These experimental results also provide information about the fate of secondary carbonates that form in a CO_2 injection environment.
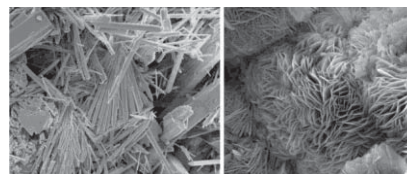

Figure 1: Nesquehonite (left), obtained by direct synthesis, and dypingite (right), obtained by transformation of early-formed carbonate.

The resulting carbonate precipitates formed in our approach can profitably be used in many applications, for example in the production of building materials. Our approach offers a complementary solution to CO_2 abatement in countries where the production of saline waste is significant.

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[2] Mignardi *et al.* (2011) *Journal of Hazardous Materials* **191**, 49-55.

[3] Ballirano *et al.* (2010) *Journal of Hazardous Materials* **178**, 522-528.

Peat bog Records of Atmospheric Dust fluxes - Holocene palaeoenvironmental and paleoclimatic implications for South America

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Abstract

Few attention has been given to pre-anthropogenic signals recorded in peat bogs, especially in the Southern Hemisphere. Yet they are important to 1/ better understand the different particle sources during the Holocene and 2/ to tackle the linkage between atmospheric dust loads and climate change and 3/ to better understand the impact of dust on Holocene palaeoclimate and palaeoenvironments in a critical area for ocean productivity.

In this poster, we will present the preliminary results and the main objectives of the PARAD project, which are: 1) to provide high-resolution continuous records of natural atmospheric dust using the elemental and isotopic signature of peat cores from Tierra del Fuego, and 2) to assess the linkage between dust inputs and climate.In this project, we will explore the use of a broad range of trace elements as dust proxies (soil particles, volcanism, cosmogenic dusts, marine aerosols). Radiogenic isotopes (Pb, Nd, Hf) will be used as tracers for fingerprinting predominant sources. Coupling these findings with biological proxies (plant macrofossils, pollen) and detailed age-depth modeling, we expect not only to identify and interpret new links between atmospheric dust chemistry and climate change but also to significantly improve our understanding of peat bogs as archives of climate change, and the role of dust in both palaeoenvironmental and palaeoclimatic changes.

Non-classical pathways of mineralization: Pre-nucleation clusters and oriented attachment

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Introduction

Recent investigations of crystallization in the calcium carbonate and phosphate systems have conclusded that classical concepts of crystal growth fail to predict observed pathways of nucleation. These pathways appear to start with pre-nucleation clusters and depend upon particle mediated growth processes that involve amorphous precursors. These conclusions follow upon a body of research documenting aggregation-based growth mechanisms in which primary crystalline particles are found to be co-aligned in the final crystal structure. However, little is known about the formation, structure and energetics of pre-nucleation clusters, and the mechanism by which co-alignment of primary particles occurs has not been established. Here we report results of novel simulations and experiments exploring these phenomena.

Results and Conclusion

Using replica-exchange molecular dynamics techniques previously applied to protein folding, we investigate initial formation and onset of order within hydrated calcium carbonate clusters. The clusters initiate as short linear chains that rapidly evolve into 2D and 3D structures with continued growth. Establishment of order is hindered by incomplete ion desolvation. However, in ~1 nm diameter particles, ordered motifs emerge that resemble the local order within crystalline carbonate phases. The free energy along the simulated growth pathways is currently being calculated to determine whether the clusters are thermodynamically stable or metastable with respect to ions in solution and to predict the free energy barrier that separates the cluster species from supercritical nuclei.

We investigated mechanism of oriented attachment (OA) of iron oxyhydroxide nanoparticles using high-resolution fluid cell TEM. The particles undergo continuous rotation and interaction until they find a perfect lattice match. A sudden "jump to contact" then occurs over < 1nm, followed by lateral atom-by-atom addition at the contact point. Interface elimination proceeds at a rate consistent with the curvature-dependence of the chemical potential. Translational and rotational accelerations show that strong, highly-

Vegetation uptake controlling groundwater solute evolution on a southeast Australian granite

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Groundwater geochemical signatures are typically considered derived from rock-water dissolution and weathering interactions. However, many major ions (Ca^{2+}, K^+, HCO_3^-, Mg^{2+}, S, and Si) are essential plant nutrients, and are removed from rainfall, soil-water and groundwater, where soils are depleted in these species. This in turn affects the solute composition of infiltrating water.

Conventional methods [1] of determining relative groundwater solute contributions from specific rock weathering reactions were carried out for a pair of sub-catchments in the Dwyer Granite, southwest Victoria, Australia. This method was adapted for semi-arid, southwest Victoria by standardising all ions to rainfall Cl^- to remove the effects of evapotranspiration. While this step is commonly omitted in high rainfall, northern hemisphere studies [2], it is important for the Australian setting, where groundwater solutes are primarily derived from the concentration of rainfall by evapotranspiration [3,4].

In a few groundwater samples in the study area, enrichment with respect to rainfall of Na^{2+} and H_4SiO_4 is ascribed to plagioclase weathering, while SO_4^{2-} enrichment is ascribed to pyrite oxidation, indicating that rock weathering reactions play a role in this setting. However, in most samples, after subtracting rainfall input (as per [1]), there is wholesale depletion of all measured ions. This prevents the use of the plagioclase, biotite and k-feldspar chemical weathering reactions in the mass-balance, as these release cations (Na^{2+}, K^+, Mg^{2+} and Ca^{2+}), all of which are depleted in the groundwater with respect to rainfall.

This ion depletion is not due to mineral precipitation as neither geochemical modelling nor X-ray diffraction analyses show evidence of this occuring. Nor is it due to ion exchange as there is no balancing import of ions or significant acidification of the groundwater. Having already ruled out evapotranspiration effects through Cl^- standardisation, the depletion is instead attributed to vegetation uptake, which has been identified as a significant process elsewhere in the region [5], causing depletion of recharge solutes.

[1] Garrels and Mackenzie (1967) *Equilibrium Concepts in Natural Water Systems* **Advances in Chemistry Series**, 222-242. [2] Velbel and Price (2007) *Appl. Geochem.* **22**, 1682-1700. [3] Herczeg *et al.* (2001) *Mar. Freshwater Res.* **52**, 41-52. [4] Bennetts *et al.* (2006) *J. Hydrol.* **323**, 178-192. [5] Edwards and Webb (2009) *Hydrogeol. J.* **17**, 1359-1374.

Equilibrium Partitioning of Li between Olivine and Clinopyroxene at Mantle Conditions

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Abstract

The lithium isotope system holds great allure as a tracer of recycled subducted materials in the Earth's interior, owing to the striking isotopic contrast between lithium at the Earth's surface and that in the mantle, combined with the presence of Li at measurable quantities in mantle minerals. Unfortunately, measurements of lithium isotope ratios in mantle xenoliths have proven difficult to interpret. Mantle xenolith data compiled from samples worldwide have revealed that lithium elemental and isotopic distribution between olivine and clinopyroxene is highly variable. At high temperatures such as those found in the mantle, the isotopic fractionation factor $\alpha_{ol/cpx}$ [$=(^7Li/^6Li)_{ol}/(^7Li/^6Li)_{cpx}$] is expected to approach 1, and experimental constraints on equilibrium partitioning show that the partition coefficient ($D^{Li}_{ol/cpx}$) is between 1.5-2. Many xenolith samples exhibit equilibrium behavior with respect to both isotopic fractionation and equilibrium partitioning, but some samples do not. Xenoliths with apparent $D^{Li}_{ol/cpx} < 1$ trend toward isotopically lighter Li in clinopyroxene relative to olivine, with Δ^7Li_{ol-cpx} [$=\delta^7Li_{ol} - \delta^7L_{cpx}$] ranging from 3 - 25‰. A physical process explaining this relatively extreme isotopic fractionation between co-existing mantle phases has yet to be satisfactorily demonstrated. One proposed hypothesis to explain the apparent Li isotopic disequilibrium in mantle xenoliths is that upon exhumation, closed system redistribution of Li between mantle minerals occurs as a function of cooling, meaning the partition coefficient is temperature dependent. Richter et al. (2003) have shown potential for considerable kinetic isotopic fractionation of Li during diffusion. Thus if Li is redistributed under dynamic conditions preceding or concurrent with eruption, kinetically driven isotopic fractionation might be "locked in" to the mantle minerals upon reaching closure conditions. We have conducted a series of piston cylinder experiments at 1.5 GPa and 700-1100 ˚C, the results of which show that $D^{Li}_{ol/cpx}$ is 2.0 ± 0.2 regardless of temperature over this range. It seems that a new explanation is needed to explain the Li signature in mantle xenoliths. Mantle olivine contains some amount of iron (~10% FeO*), and the ambient fO2 controls the relative amount of Fe^{+2}/Fe^{+3}. Variation in the amount of Fe^{+3} could potentially influence the incorporation of Li^+ into the octahedral site of olivine by providing a charge-balancing mechanism. This could allow for a redistribution and isotopic fractionation of Li in response to changing fO$_2$. Experiments at 900°C and 1.5 GPa with solid state fO$_2$ buffers of Re-ReO, Ni-NiO, and Mo-MoO are currently underway to determine whether oxygen fugacity plays a role in controlling Li partitioning.

[1] Richter et al. (2003) *Geochimica et Cosmochimica Acta* **67**, 20, 3905–3923.

Stagnant-lid tectonics in early Earth revealed by [142]Nd variations in late Archean rocks

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The progressive μ^{142}Nd decrease in early Archean rocks from +20 to 0 between 3.9 to 3.6 billions years (Gyr), with rocks younger than 3.5 Gyr showing no μ^{142}Nd anomalies, is thought to indicate the efficient remixing of the first primitive crust into the Archaean convecting mantle that ultimately produce a well-mixed present-day convecting mantle with μ^{142}Nd = 0 [1]. The implied long mixing time of ~1 Gyr from the Hadean to Archaean for the whole mantle is paradoxical on several levels. This is much longer than the rapid mixing time (<100 Myr) inferred for the Archean due to vigorous mantle convection related to Earth's hotter thermal regime [2], and similar to the mixing time inferred for the present-day Earth's mantle [3].

Here we report a resolvable positive ^{142}Nd anomaly of μ^{142}Nd = +7 ± 3 ppm relative to the modern convecting mantle in a 2.7 Gyr old tholeiitic lava flow from the Abitibi Greenstone Belt in the Canadian Craton. Our result effectively extends the early Archean convective mixing time to ~1.8 Gyr, i.e. even longer than present-day mantle mixing timescale [3], despite a more vigorous convection expected in the Archean. Different hypotheses have been examined to explain such a protracted mixing in the Archean, such as mantle overturn, two-layer convection or the existence of a dense layer at the bottom of the mantle. We postulate that the requirement of a delayed mixing in a strongly convective mantle is best explained by long periods of stasis in the global plate system, with scarce episodes of subduction throughout the Hadean and Archean [4].

Our numerical model confirms that in absence of continuous plate tectonics, the convective mantle mixing is relatively inefficient in erasing the chemical heterogeneities inherited from the primordial differentiation of the early Earth. This constrains the tectonic regime of the Hadean and Archean to a stagnant-lid regime with episodic subduction. In this case, the timing for the onset of continuous modern plate tectonics can only occur shortly before or after 2.7 Gyr.

[1] Bennett et al. (2007) *Science* **318**: 1907-1910. [2] Coltice and Schmalzl (2006) *GRL* **33**: L23304. [3] Kellogg and Turcotte (1990) *JGR* **95**: 421-432. [4] O'Neill et al. (2007) *EPSL* **262**: 552-562.

The effect of aqueous organic ligands on forsterite dissolution rates

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Forsterite is an abundant mineral which reacts exothermically with CO2 to form secondary minerals including carbonates. As such it is viewed as the most promising source material for the divalent metals required for mineral carbonation [1]. Mineral carbonation could potentially be accelerated if catalyses that accelerate forsterite dissolution can be identified. This study was initiated to determine if common aqueous organic ligands can accelerate forsterite dissolution rates. Aqueous organic species have long been considered as potential catalyses for enhancing silicate mineral dissolution rates (e.g. [2], [3]).

Forsterite dissolution rates were measured at 25 ºC in 10-2 M NaCl using mixed-flow reactors as a function of pH and concentration of 13 organic ligands (acetate, alginate, oxalate, Na-glutamate, citrate, EDTA, L-glutamic, humic, malic, malonic salicylic, tartaric and L-aspartic). Stoichiometric dissolution was observed. Selected measured dissolution rates as a function of organic ligand concentration is presented in figure 1.
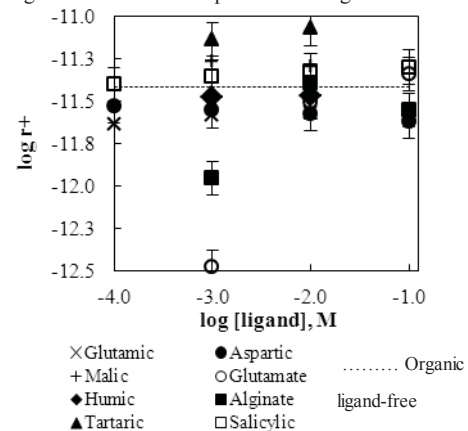

Figure 1: Summary of pH 3 olivine steady-state dissolution rates as a function of ligand concentration.

As depicted in Fig. 1, aqueous organic ligands in general have weak effects on pH 3 forsterite dissolution rates. Humic, salicylic and aspartic acid have no detectable effect on these rates, while the tartaric and malic acid decreases these rates.

Overall, results of this study demonstrate that organic ligand do not affect sufficiently forsterite dissolution rates at mildly acidic conditions. As these pH conditions likely to be characteristic of the fluids at carbon storage sites due high CO2 pressure carbon storage, it seems likely that organic additives will not accelerate substantially forsterite carbonation.

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[3] Pokrovsky et al. (2009) *Am. J. Sci.* **309**, 731-772.
[4] Wolff-Boenisch et al. (2011) *Geochim. Cosmochim. Act.* **75**, 5510-5525.

Crustal versus source processes on the Northeast volcanic rift zone of Tenerife, Canary Islands

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The Miocene-Pliocene Northeast Rift Zone (NERZ) on Tenerife is a well exposed example of a major ocean island volcanic rift. We present elemental and O-Sr-Nd-Pb isotope data for dykes of the NERZ with the aim of unravelling the petrological evolution of the rift and ultimately defining the mantle source contributions.

Fractional crystallisation is found to be the principal control on major and trace element variability in the dykes. Differing degrees of low temperature alteration and assimilation of hydrothermally altered island edifice and/or sediments elevated the primary $\delta^{18}O$ and the Sr isotope composition of many of the dykes, but had little to no discernible effect on Pb isotopes. Minor degrees of sediment contamination, however, may be reflected in the Pb isotope composition of a few samples that plot to slightly higher $^{207}Pb/^{204}Pb$ values.

Once the data are screened for alteration and shallow level contamination, the underlying isotope variations of the NERZ reflect a mixture essentially of Depleted Mid-Ocean Ridge-type Mantle (DMM) and young High-μ (HIMU, where $\mu = ^{238}U/^{204}Pb$)-type mantle components. Furthermore, the Pb isotope data of the NERZ rocks ($^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ range from 19.591-19.838 and 15.603-15.635, respectively) support a model of initiation and growth of the rift from the Central Shield volcano (Roque del Conde), consistent with latest geochronology results [1]. The similar isotope signature of the NERZ to both the Miocene Central Shield volcano and the Pliocene Las Cañadas central edifice suggests that the central part of Tenerife Island was derived from a mantle source of semi-constant composition through the Miocene to the Pliocene. This can be explained by the presence of a discrete "blob" of HIMU material, ≤ 100 km in vertical extent, occupying the melting zone beneath central Tenerife throughout this period. The most recent central magmatism on Tenerife appears to reflect greater entrainment of DMM material, perhaps due to waning of the blob with time.

[1] Carracedo *et al.* (2011) *Bull. Geol. Soc. America,* **123,** 562-584.

Uranium mineralogy and factors of stability in the mill tailings of the COMINAK mine at Akouta (Niger)

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The world's largest uranium underground mine, at Akouta (Niger), has been mined for more than 30 years. Since that time, around 14 million tons of mill tailings were accumulated on site. After the processing of the ore, with an extraction process efficiency reaching ~95%, some U is left within the mill tailings. Some U reconcentrations may be observed in the storage heap, pointing out potential migrations. This study aims at an assessment of U mobility for revaluating/rehabilitating mill tailings stored in heaps and preventing any U releases in the environment.

The ore deposit occurs in continental lower Carboniferous sandstones, containing quartz and feldspar with detrical clays and organic matter. Pitchblende is associated with minor coffinite, U-Ti and U-Mo oxides, with an average U concentration of 4‰ associated to trace metals (V, Zr, Mo...). Ore processing is based on an oxidative dissolution in sulfuric acid. As a result, a gypsum-indurated duricrust is formed at the upper surface of the tailings heap, referred to as a gypscrete crust.

Gypscrete samples were analyzed using different mineralogical methods: SEM, TEM, electron microprobe, XRD and cathodoluminescence. Micrometer-size U-bearing phases are observed: UO_2, U-Ti oxides (brannerite-type) and secondary phases such as uranyl phosphates. At the nanometer scale, supposedly neoformed U phases are associated with clay minerals, together with evidence of U sorption.

Brannerite-type minerals are most likely inherited from the ore, as they are more resistant than uraninite to the process. Such as UO_2 included in quartz grains, they appear as stable hosts for U. The main source of U^{VI} may rather come from more accessible U-rich phases which have suffered from oxidation and solubilization. The formation of secondary U minerals, in association with U sorption on clay minerals, may delay U^{VI} transport. The comparison of ore samples with their associated tailings sampled before their storage, provides complementary data on the processes governing U mobility.

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Monitoring dynamics of species and adsorption reactions at the corundum-oxalate-solution interface by *in situ* ATR-FTIR spectroscopy

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Introduction

We addressed the molecular level description of the interactions occurring at low pH between oxalate ions and the surface of corundum colloids, for oxalate in the low concentration range relevant to freshwater (1-50μM). We monitored the dynamics of species at the corundum- solution interface during the oxalate sorption process by using a highly sensitive technique, namely Attenuated Total Reflectance – FTIR spectroscopy, joint to a method of layer deposition of corundum particles on the ATR crystal [1-3].

Results and conclusion

Examining changes in IR spectra during the oxalate sorption process, for frequency regions characteristics of oxalate, surface hydroxyls and ClO_4^- electrolyte ions, has revealed the existence of two types of sorption mechanisms dependent on the oxalate concentration.
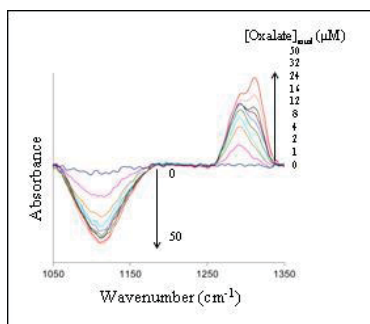

Figure 1: In situ ATR-FTIR monitoring of the corundum-solution interface during gradual increase of $[Ox]_T$ at pH 4.7, 0.01M $NaClO_4$.

In the trace level concentration range, the uptake of oxalate is accompanied by removal of ionisable surface hydroxyls and weakly adsorbed ClO_4^-. This is direct spectroscopic evidence that a reaction of surface ligand exchange controls the oxalate sorption. The other sorption reaction involves no surface hydroxyls or counter-ions and it exists in a wider range of oxalate concentration, indicating weak sorption of hydrated oxalate via H-bonds. Our study suggests that the sorption of oxalate at the trace level influences surface reactivity and charge of oxides in soils, as well as colloid aggregation and mobility.

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Laser spectrometry for tracing evaporation in a Mediterranean wetland (Rhône delta, France)

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Context

Evaporation from wetlands may contribute significantly to local atmospheric moisture, and may thus provide an additional water source to regional precipitation. In the context of global change, the distribution of wetlands is expected to vary, making necessary to better understand the influence of wetlands on climate. Isotopic tracing ($\delta^{18}O$, δD) is an efficient tool for detecting the contribution of local vapor to the atmospheric component of the water cycle, because the fractionation that occurs during evaporation induces a modification of the deuterium excess [1].

Results and conclusions

We performed continuous measurements of the isotopic composition of the atmospheric vapor during summer 2011, near a lagoon located in the Rhône delta, using wavelength-scanned cavity ring-down spectrometer (WS-CRDS). Calibrations were regularly performed with 3 different water compositions, and for mixing ratio varying between 4 to 33 g/kg. Linear calibration results were obtained, except for mixing ratio higher than 25 g/kg. Laser spectrometer measurements were compared to atmospheric vapor samples collected by cryogenic trapping (65 samples). The difference between results from the two methods was acceptable for $\delta^{18}O$ (±0.36‰ on average), while the laser spectrometer slightly overestimated δD, by 4.3‰ on average. Based on hourly-averaged time series, we evidenced a clear difference in deuterium excess between day-time and night-time data (Figure 1), resulting from the influence of local evaporation. Further work is under way to elucidate the shift in deuterium measurements. Preliminary attempts for a quantitative interpretation of deuterium excess variations in terms of evaporation fluxes [2] will be discussed at the meeting.
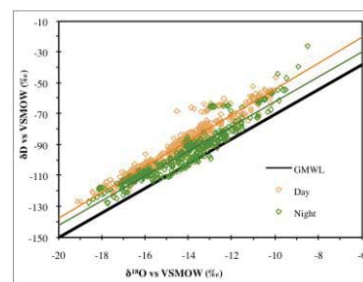

Figure 1: Isotopic composition of atmospheric water vapour between 2011/07/19 and 2011/08/13. Data are hourly averaged. Solid lines represent linear regressions (orange: $\delta^2H=8.3x\delta^{18}O+30.1$; green: $\delta^2H=8.0x\delta^{18}O+18.5$), with the Global Meteoric Water line in black.

[1] Gat & Airey (2006) *Global and planetary change* **51**, 25-33. [2] Lai & Ehleringer (2011) *Oecologia* **165,** 213–223.

Events control of karst aquifer recharge

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Fissured karst aquifers are vulnerable resources that react very sensitive to the dynamics of recharge events
The description of water and tracer flow in fissured aquifers and recharge event integration are generaly roughly depicted. In fact, there are characterized by multiple water transit velocities ranging from fast flow through fissured network to slow water infiltration in porous media.

An experimental field site located in French Burgundy under a topographic hill with well recognized boundaries has been monitored in-situ (head, temperature, conductivity, discharge flow), continously sampled for stable isotopes and major ion analyses on several sites (springs and boreholes) since two years. This long time monitoring allow us both to define baselines and discuss the impact of recharge events on groundwater dynamics.

The tracers $\delta^{13}C$, ^{14}C, $\delta^{2}H$, $\delta^{18}O$ and major chemical constituents have been used to describe the temporal response of the water flow through the unsaturated zone. The geochemical signals have been monitored at different levels of the system (precipitation, boreholes and springs) during several rainfall events. The preliminary results highlight a wide distribution of transit velocities during a recharge event.
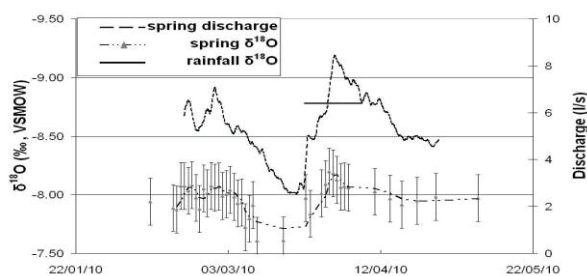

Figure 1: Times series of discharge and $\delta^{18}O$ at R14 spring.

Specific velocities or residence times of the different reservoirs as determined by recharge event characterisation, can be supported by tracers as ^{85}Kr, ^{39}Ar, ^{3}H, ^{3}He, CFCs, SF6 [1]. A recharge event will be monitoring (February 2012) on 2 springs and 1 boreholes. Tracers will allow to realize a geochemical deconvolution and to obtain the water residence times in the fractures and the matrix of this fissured aquifer.

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Biogeochemical dynamics related to seasonal changes and biomass-density patterns in rhyzosphere sediments of a *Zostera noltii* meadow

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This study was conducted in the Arcachon bay that shelters the largest *Zostera noltii* meadow in Europe [1]. A severe but non-homogeneous decline of this meadow coverage has been recently observed. In this context, we investigated seasonal changes and short-scale spatial variability of sediment biogeochemistry in a tidal mudflat of this lagoon colonized by a stable eelgrass meadow. Cores were collected at low tide on vegetated and unvegetated sediment over an annual cycle from autumn 2010 to summer 2011. Additional sediment cores were collected along a density-biomass gradient of seagrass in autumn and summer. Concentrations of major redox species were measured in sediment porewaters. In sediment solid-phase, two reactive fractions of Fe and P were extracted. Total oxygen fluxes were determined under light and dark conditions and used to calculate the benthic gross primary productivity (GPP).
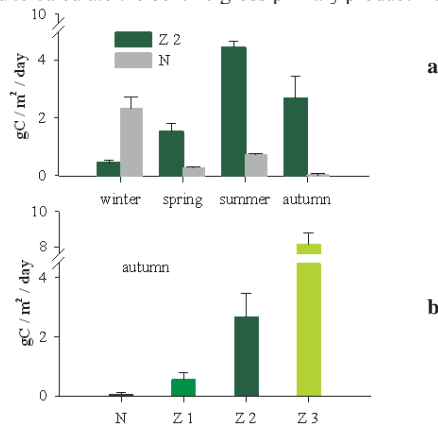

Figure 1: Daily GPP calculated for vegetated (Z) and unvegetated sediments (N) over an annual cycle (**a**), and in autumn 2010 (**b**) along a density-biomass gradient of *Z. noltii* (Z1 to Z3) (*n=4 - 6*).

Some redox species such as dissolved iron did not show significant seasonal changes and along the biomass gradient. For other parameters, e.g. DIP or GPP, the variability observed along the biomass gradient was higher than the one observed between seasons (Fig.1). Results suggest that the effect of seagrass on sediment biogeochemistry can be strongly dependent on the plant biomass, which highly vary with seasons but also on short and large space scales. Hypothesis to explain how this component influences the biogeochemistry of superficial sediments are proposed.

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The record of human impact in the sedimentary record at *Portus,* the harbor of ancient Rome

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The present study focuses on the analysis of palaeo-pollutions and the sedimentary environments in which they were trapped in the Roman *Portus* harbor. *Portus* received heavy-metals pollution both from local foundries, fulling, and tanning and from distal upstream development in Rome. Rome wastewaters, which accounted for up to 3 percent of the total Tiber discharge, were forwarded to *Portus* through a network of canals (*Canale Romano* and *Canale Trasverso*) connecting the river to the sea. In this manner, harbor basins accumulated both allochthonous and autochthonous heavy metals.

We determined major and trace element concentrations as well as Pb isotope compositions in a high-resolution set of samples from sediment cores recovered in the *Portus* area. Principal component analysis of elements that are less prone to the influence of human activities, such as Ca, Mg, Mn, Zr, K, Al, Ti, Na, Sr, and Mn, was used in conjunction with metallic elements to break down the sedimentary load into local and regional components.

The record of Pb concentrations and isotopic compositions reveals an overall general trend on which other signatures are superimposed. The geochemical background of the Tiber catchment (24.7-26.2 ppm Pb and $^{206}Pb/^{207}Pb \sim 1.198$) represents geologically young (model age T_m <50 Ma) Pb derived from natural runoff over young sediments and volcanics in the Latium. From the 1st century AD to the end of the roman period, the harbor regime evolved from a dominant fluvial (enriched in Al, Ti, Mg, K, and Zr) to a more marine influence (high Ca/Mg, Na/Al, Sr, and $CaCO_3$) in the upper part of the harbor unit. "Imperial" Pb (90.5-35.4 ppm Pb and $^{206}Pb/^{207}Pb \sim 1.187-1.192$) requiring the prevalence of Hercynian (T_m >200 Ma) Pb, probably imported from central or northern Europe, gets progressively diluted with time. The transition from the roman to the medieval period is characterized by a closed environment (high Ca/Mg, Na/Al, Sr, and $CaCO_3$) with a spike of unradiogenic $^{206}Pb/^{207}Pb$ (~ 1.184). Either an alluvial plug formed, which blocked fresh water entry into the harbor from the *Canale Trasverso*, or the harbor burned, causing melting of the ancient waterworks. Finally, the upper part of the sediment cores consists of overflow deposits enriched in Al, Ti, K, Mg, and Mn associated with the return of the pre-anthropogenic geological background (18.9-28.2 ppm Pb and $^{206}Pb/^{207}Pb \sim 1.196-1.201$). In this post-roman sedimentary unit pollution signatures shift to a mix of heavy metals dominated by Co, Cr, Ni, and Zn, whereas during the roman period elements such as Pb, As, Fe, Cu, and Sn were predominant.

The fractionation of Lithium isotopes during continental weathering: clues from the Amazon and Mackenzie rivers

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Numerous studies on river systems have shown that Lithium isotopes are fractionated during chemical weathering as ^6Li is preferentially retained in solid secondary phases whereas dissolved fractions are enriched in ^7Li. In this study we investigate the Li isotope composition of Suspended Particulate Matter (SPM) and bedload transported in two of the largest world river systems having drastically differing climate conditions: Amazon and Mackenzie rivers. In order to separate the effects of hydrodynamic sorting and chemical weathering, Li isotope were measured along river depth profiles to capture all the SPM grain size variability.

We find that Li content and isotope composition display a strong variability in relation with grain size within a single water column in both Amazon and Mackenzie Rivers. Li content in SPM increases by a factor up to 3 from coarse (river bed) to fine (channel surface) particles, ranging from 30 to 90 ppm. All bedloads and SPM samples have Li/Al molar ratios higher that of the mean Upper Continental Crust (UCC), despite the fact that 10 to 20% of total Li in both rivers is transported in the dissolved load.

River sediments Li isotopic composition (δ^7Li) ranges between -3.5 to 5‰ and displays an inverse relationship with grain size. δ^7Li is also well correlated (R^2>0.9) to the weathering index Na/Al, further illustrating the fact that weathering products are isotopically fractionated toward low light δ^7Li values. Amazon river-sediments δ^7Li values are more than 1‰ lower than those of the Mackenzie for a given Na/Al value. We interpret these relationships between Li content, δ^7Li, Na/Al and grain size as a binary mixing between a coarse-grained, relatively Li-poor, high δ^7Li component ($\delta^7Li \sim 5‰$) and a fine end-member having low δ^7Li and high Li concentrations. The low δ^7Li value of the fine component could be the result of either present day light-Li co-precipitation/adsorption into secondary minerals or of the recycling of fine-grained silicate sedimentary rocks or a combination of both processes. These results have important implications for establishing global mass budgets of erosion and for using lithium concentrations and isotopes as a tracer of sedimentary recycling.

Li isotopes fractionation during lower crustal magmatic segragation.

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Introduction

Kerguelen basalts contain abundant mantle xenoliths, including mantle peridotites and deep magmatic segregates equilibrated in the granulite facies [1]. Lithium chemical and isotopic distribution were measured in two-pyroxene granulites in using the Cameca IMS 1270 Ion probe at CRPG, in order to define their signature and describe the Li behavior during the lower crust formation process.

Samples description

The studied xenoliths display close mineralogical compositions, bearing Mg81-92 Al-diopside, Mg-78-93 enstatite and labradorite or bytownite. Spinel and garnet are observed in 2 of them, and they all are type II xenoliths [1,2]. The xenoliths range along a regular magmatic cristallisation trend, with decreasing Mg content.

Li and δ^7Li distribution

On the whole rock scale the Li contents increase from 1,5 up to 9 ppm, following the cristallisation trend with the Li content increasing during the cristallisation. At the sample scale Li contents is higher in Cpx compared to Opx and to plag, with a ratio Opx/Cpx of 0.8-0.9 and a ratio Plag/Cpx of 0.2-1. At the grain scale, Li displays an homogeneous distribution in most minerals, at the exception of few depleted or enriched Cpx rims.

The δ^7Li values measured on Cpx and Opx range in between -9 and +20, normalized to lsvec . The Cpx Li depleted rims display enriched δ^7Li values, associated to Li diffusion isotopic fractionation. Most xenoliths display relatively homogenous δ^7Li distibution, with only few per mil scatters, and only one Li poor xenolith display δ^7Li values scattered on a large range, from -9 to +14. A general observation is that Cpx display higher δ^7Li values than Opx (+2 to +3 ‰), and that the values are more scattered in Opx than in Cpx. There is positive correlation between the Li contents and the δ^7Li values, both at the mineral and whole rock scales, pointing out a melt-mineral isotopic fractionation for Li, with the melt being enriched in ^{7}Li compared to the residue.

Conclusions

The bulk value for these granulite samples is in agreement with a direct derivation from the mantle (5-8 ppm, $d^7Li≈+5$), but at the sample scale, Li content and Li isotopic composition is strongly dependent on the melt-solid fractionation during crystallization in the granulite facies. The large scatter observed on the Li poor sample could result from the partial re-equilibration of this early formed granulite with late enriched fluid.

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Understanding Archean weathering using silicon isotopes and Ge/Si ratios

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Weathering conditions in the Mesoarchean are poorly constrained. Recent studies have shown that neoformation of secondary clay minerals are associated with large Si isotope and Ge/Si fractionation in response to desilication processes and the weathering degree [1, 2, 3, 4]. Here, we present the first application of these weathering proxies on a 2.95 Ga paleosol profile and coeval shales. The paleosol is developed on andesite and shows a well defined mineralogical and chemical differentiation. δ^{30}Si values are lighter (down to -0.44‰) and Ge/Si values higher (up to 3.2μmol/mol) than parental andesite values (-0.14‰ and 2.1μmol/mol, respectively). Such trends support the formation of secondary minerals that preferentially incorporate light Si isotopes and Ge relative to Si, as observed during modern weathering [1, 2, 3, 4, 5]. However, less pronounced fractionation relative to modern soils with neoformation of kaolinite can be potentially explained by mineralogical control on δ^{30}Si with the formation of Fe-rich smectite, reported with heavier Si isotope composition than kaolinite [6]. In contrast, the top of the paleoprofile shows a return to heavier δ^{30}Si values (up to -0.11‰) and lower Ge/Si ratios (down to 1.1μmol/mol). This may be explained by a preferential release of light Si isotopes and Ge during partial dissolution of Fe-rich smectite to form kaolinite. This transformation is thought to have been governed by drainage conditions with fast drainage favoring kaolinite, implying moderate rainfall and/or poor-drainage conditions during weathering. In addition, we demonstrate that the combination of δ^{30}Si and Ge/Si tracers in 2.95 Ga Archean shales can reflect the relative proportions of primary rocks and secondary minerals. Moreover, a kaolin-rich or -poor nature of secondary clays can be evaluated. Therefore, combining δ^{30}Si and Ge/Si ratio as paleoweathering tracers opens new perspectives in quantifying Archean superficial weathering dynamics with potentially important paleoclimatic implications.

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[5] Lugolobi et al., (2010) *Geochim. Cosmochim. Acta* **74**, 1294-1308.
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Late Cretaceous rapid arc growth in the Arequipa area of southern Peru

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During the Late Cretaceous and Paleocene, intense magmatic activity along the Toquepala arc resulted in the building of a continuous relief along the Peruvian margin. This arc growth coincided with the only known significant uplift along coastal southern Peru [1] and can thus be considered to have been a major factor in this uplift.

Our study has focused on a batholith segment extending in the Arequipa area over 60x40 km for a ≥7 km thickness. We confirm that granitoids were emplaced mainly between 90 and 60 Ma, into the Proterozoic basement, a dominantly mafic Liassic (200-175 Ma) plutonic suite, and Jurassic strata. The Late Cretaceous–Paleocene suite consists of numerous plutons, dykes and sills with compositions varying from gabbro to granite.

We analysed trace elements, and Sr and Nd isotopic ratios on a collection of 100 samples principally located along 3 cross-sections of the batholith. The obtained geochemical compositions are in good agreement with data available from the literature [2]. Given the large lithological range, covering a wide spectrum of chemical compositions, Rb-Sr systematics was used to identify two magmatic suites. Samples represent either the Liassic or the Late Cretaceous-Paleocene suite, which are easily distinguished in a Rb-Sr isochron plot. Samples plotting along the 60 Ma isochron were separated and their measured $^{87}Sr/^{86}Sr$ isotopic ratios were used to determine LLD (liquid lines of descent) for gabbro-granite series within the batholith. Using $^{87}Sr/^{86}Sr_m$ as an indirect proxy for fractional crystallization, we propose a simple but powerful method to estimate the nature and compositions of primitive magmas in a plutonic environment.

These results are critical to estimating crustal growth and thickening in the Arequipa area. They will also be analysed in terms of magmatic flux for a better understanding of the mantle vs. crustal contribution to Andean arc magmatism.

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Unravelling glacial sediment provenance through soil chemistry in the north of Ireland.

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Background and method.

Reconstructing palaeo-ice sheets provides important information on how they respond to and drive climatic changes over long timescales. Traditional approaches to reconstructing palaeo-ice sheets rely heavily on geomorphological evidence. However, recent work on ribbed moraines [1] and drumlins [2], which are used to reconstruct ice flow direction, major ice flow pathways and drainage conduits, indicates that using geomorphology alone can potentially produce misleading results if small areas are investigated. Furthermore, ascertaining ice flow direction in regions where no bedforming events have occurred can present difficulties. An alternative approach to investigating former ice flow direction is to use geochemistry to determine glacial sediment provenance, from which transport direction can then be established.

This study presents results from the first regional geochemical investigation of glacial sediment provenance in Ireland using soils developed in areas of till superficial geology. The soil samples were gathered as part of Geological Survey of Northern Ireland's Tellus survey [3] which collected soil samples at a density of 1 sample per 2km^2 accross all of Northern Ireland. The Tellus samples were supplemented by an additional 81 samples taken at a density of approximately 1 sample per 4km^2 around the margins of the Tellus survey where no previous sampling had occurred. Bulk geochemistry was determined by X-ray Fluorescence from which 28 lithophile and rare earth elements were selected. Principal Component Analysis (PCA) was then applied to these elements using 3917 soil samples from across the entire region. PCA is a variable reduction procedure that allows groups of elements to be identified, and is used here to infer underlying till geochemistry. Since till geochemistry is a product of its parent materials, the PCA groupings can aid identification of the original bedrock source and thus the sediment provenance and ice transport direction.

Results and conclusion.

The results show that most till deposits in the study area are closely related to local bedrock, with changes of geochemical composition occurring across lithological boundaries. This suggests that the majority of tills have been locally derived and that till transport in this sector of the British-Irish Ice Sheet was low, with rapid comminution and low evacuation rates of entrained debris.

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Controls on seawater ^{231}Pa, ^{230}Th and ^{232}Th concentrations along the flow path of major deep-water masses in the Southwest Atlantic

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12b. Pa and Th distributions in the ocean: controlling mechanisms

Pa-231 and ^{230}Th are naturally occurring radionuclides in the ocean, produced through the α-decay of dissolved U. Once produced, the two radionuclides are adsorbed onto particles and removed from seawater as the particles settle to the sediment. Due to its higher particle reactivity, ^{230}Th is readily removed from seawater once produced, while less particle-reactive ^{231}Pa can be advected by deep ocean circulation to high-productivity areas to be subsequently removed. Therefore, a fractionation between ^{231}Pa and ^{230}Th takes place in seawater, making the ^{231}Pa/^{230}Th ratio a potential water-mass proxy to reconstruct past ocean circulation. However, factors such as particle flux and composition also play a part in the oceanic distribution of ^{231}Pa and ^{230}Th. To make use of ^{231}Pa/^{230}Th as a paleo-circulation tracer therefore requires a thorough understanding of the controls on the distribution of the two nuclides in seawater. Despite a growing knowledge of water-column ^{231}Pa and ^{230}Th concentrations, rather little is known about the distribution of the nuclides in the South Atlantic Ocean. This basin has recently been the focus of down-core ^{231}Pa/^{230}Th records [1], but is characterised by a more complex pattern of deep-water circulation than the North Atlantic, with multiple water masses flowing in different directions.

In this study, we present high-resolution dissolved ^{231}Pa, ^{230}Th and ^{232}Th data for twelve profiles in the Southwest Atlantic collected during GEOTRACES cruise GA02s (JC057) in March, 2011. The data capture all the main Atlantic water masses along their meridional flow paths and cross a gradient of productivity and dust input. Concentrations of dissolved ^{230}Th range from 0.0060~1.27 dpm/1000l and show a nearly linear increase with increasing water depth as a result of reversible scavenging process [2]. Concentrations of dissolved ^{231}Pa range from 0.0094~0.37 dpm/1000l and show an increase with depth in the upper water column with more variable concentrations at depth. ^{231}Pa/^{230}Th ratios characterise the three deep water-masses (AAIW, NADW, AABW) and show an evolution along flow paths. There is, however, also an obvious decrease in ^{231}Pa/^{230}Th near the equator, potentially due to higher productivity in this region. We will discuss the impact of these observations on the use of ^{231}Pa/^{230}Th to assess past ocean circulation. Concentrations of ^{232}Th are low but appear to provide information about detrital inputs to the region from dust and from the Rio Plata.

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Applications of XRF analysis in lithogeochemical anomaly prospecting

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X-ray fluorescence (XRF) can be used directly to analyze contents of ore-forming elements in a gold mine and other characteristic indicator elements such as Zn, Cu, Pb, As, Sb, Fe, etc. in the field. It will make contributes to delineate the favorable areas for mineralization of gold mine, and quickly obtain the location and distributional pattern of gold mine geochemical halo.

Due to the polytropism of geological samples and the differences of analytical methods, the results of chemical analysis are quite different from the results of XRF analysis. As a result, specific standard samples corresponding to each kind of elements are requested in different lithology for each mine. And then the standard curve of best sample linear can be made.

Dashui Gold Deposit in Maqu, Gansu, which was found in west Qinling mountain area, is a type of gold deposits with unique mineralization. On the basis of geochemical exploration and actual situation of the deposit, the representative 3530 m and 3490 m middle sections of No.103 exploration line of Dashui Gold Deposit were selected for measuring. The measuring device is CIT-3000SMP. The design spacing is 3 m, and the analyzing time is 120 seconds per point. Five limestone and six diorite porphyrite samples with chemical analysis results had been used to fit standard curves and establish standard database respectively by the linear fit of the peak area and contents combining with the inverse computation of software. Then multi-element analyses had been down on the survey middle sections to delicate the favorable areas for mineralization of gold mine, and quickly obtain the location and distributional pattern of gold mine geochemical halo. The results demonstrate that:

1. Au, As, Cu, Fe, Mn, Ag, Sb, Ti, Sr, etc. appear high strength anomalies on the known middle sections, meaning that they can be treated as the indicating elements for Dashui Gold Deposit.

2. There is a high anomaly area in and near the contact zones of diorite porphyrite and hematite limestone of known ore body in 3490 m middle section. The width of the anomaly is about 33m. Combining with the geological situations of other middle sections, this area is delineated as level one prospective area. This area might be formed by the combination of two narrow gold veins, and it connects with other ore veins of the higher and lower middle sections.

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CALCIUM ISOTOPES: KEYSTONE FOR UNDERSTANDING ISOTOPIC FRACTIONATION AND PLANETARY MATERIAL PROCESSES

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Non-traditional elements like Ca, Mg, Li, Fe, Mo and others have proven to be valuable for assessing the mechanisms and magnitude of non-equilibrium isotopic fractionation processes. These so-called kinetic effects are important not only for low-temperature processes, but also for hydrothermal and magmatic conditions. Theory and experiments are progressing rapidly and are leading to a new level of understanding and a roadmap for further experimental work. This presentation will focus mainly on Ca isotopes, but the principles and effects are applicable to other elements. With respect to mineral growth from aqueous solution, the essential insight is that equilibrium growth can occur only if the molecular exchange fluxes at the mineral-solution interface are large in comparison to the rate of growth. For typical minerals growing at Earth surface temperature, this is unlikely to be the case, the consequence being that the kinetics of the forward reaction strongly influence isotopic fractionation, causing precipitated solids to be enriched in light isotopes. A rough estimate of surface exchange fluxes can be derived from mineral dissolution rates, but more detailed ion-by-ion growth models can be used to develop a more comprehensive description of the forward and backward reaction rates. For calcite, not only solution oversaturation, but also the $Ca:CO_3$ ion ratio in solution can strongly affect both growth rate and Ca isotopic fractionation. Ionic strength and other aspects of solution composition also modify isotopic fractionation, and analogous models can account for trace element partitioning as well. Preliminary data suggest that Ca isotopic fractionation in calcite and epidote also occurs at hydrothermal temperatures of 150 to 400C, with fractionation factors similar in magnitude to those for calcite at 25C. In magmatic systems, isotopic fractionation can be deduced by both chemical diffusion and thermal gradients in silicate liquids. The magnitude of Ca isotopic fractionation due to chemical diffusion has been shown to be dependent on silicate liquid composition, with high-Si, high-viscosity liquids producing larger fractionations than low-Si liquids. Diffusion in the solar nebula is probably responsible for some Ca isotopic variations observed in carbonaceous chondrites. Both phenocrysts in magmas and nebular condensates are likely to have kinetic fractionation effects if they grow under transport-limited or high oversaturation conditions. Current efforts are directed at experimental testing of model predictions, and modeling the coupling between growth inhibition/catalysis and isotopic fractionation.

A comparison of shale weathering rates inferred from catchment solute mass balance versus soil profile chemistry at Plynlimon, Wales

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In an effort to quantify the influence of climate on shale weathering rates, a transect of study sites has been established on Silurian shales along a climatic gradient in the northern hemisphere as part of the Susquehana Shale Hills Critical Zone Observatory, PA (USA). The coldest and most northerly site of this transect is the Hafren watershed in the headwaters of the River Severn, at Plynlimon, Wales, UK. The watershed, which is approximately 24 km from the west Wales coast, has an area of 357 ha and is 70% covered by Sitka spruce plantation forestry. The watershed has been extensively studied with continuous measurements of precipitation and runoff since 1968 and weekly monitoring of rain and stream water chemistry since 1983. These data provide an ideal opportunity to compare weathering rates derived from watershed mass balance to those derived from soil geochemical profiles. Annual solute mass balances over the past 25 years were determined by subtracting stream output fluxes from precipitation input fluxes using Cl as a conservative tracer. Annual mass balance estimates for dissolved elements such as Si are relatively consistent over time (mean value 23.2 ± 0.7 kg Si ha^{-1} yr^{-1}) while those of Na are more variable (mean value 2.69 ± 1.2 kg Na ha^{-1} yr^{-1}) and show influence of variations in sea salt input. Area-weighted release rates of Mg (mean value 5.36 ± 0.3 kg ha^{-1} yr^{-1}) are indicative of weathering rates of the dominant shale minerals illite and chlorite. Weathering rates were also estimated from soil geochemical profiles, where elemental depletions relative to parent shale chemistry were used to calculate a weathering rate over the last 10 ka. Mg release estimates from soil ridgetop samples (5.16 kg Mg ha^{-1} yr^{-1}) are in close agreement with the watershed mass balance calculations. Conversely, the estimated Si weathering flux derived from soil profiles of 6.6 kg ha^{-1} yr^{-1} is much smaller than the watershed mass balance flux estimate. This may imply that the watershed mass balance estimates for Si are influenced not only by weathering processes in the augerable regolith but also in the fragmented shale bedrock underlying the soil profile. Si cycling through the Sitka spruce trees must also be evaluated. The weathering rates obtained from the two methods at Plynlimon will be placed in context with our observations for the overall shale climosequence, where weathering rate estimates at the other locations are restricted to geochemical profiles alone.

Distribution of GDGTs in tropical sediments from Guadeloupe (French West Indies): implications for application of MBT/CBT and TEX$_{86}$ proxies

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Glycerol dialkyl glycerol tetraethers (GDGTs) are lipids of high molecular weight present in membranes of Archaea and some bacteria. Archaeal membranes are composed predominantly of isoprenoid GDGTs, with acyclic or ring-containg biphytanyl chains. The amount of isoprenoid GDGTs with cyclopentyl moieties was shown to increase with water temperature and variations in surface water temperature can be determined via the TEX$_{86}$ proxy. Recently, another type of GDGTs, with branched instead of isoprenoid alkyl chains, has been discovered in peat. Branched GDGTs were suggested to be produced in soils by still unknown bacteria. The degree of methylation of branched GDGTs, expressed in the MBT, was shown to depend on air temperature and to a lesser extent on soil pH, whereas the relative abundance of cyclopentyl rings of branched GDGTs, expressed in the CBT, was related to soil pH. The MBT/CBT proxies are increasingly used as paleoclimate proxies. The aim of this study was to investigate the distribution of GDGTs in tropical sediments from Guadeloupe (French West Indies). Surficial sediment samples were collected in four coastal water ponds: two located in Grande-Terre and two in a smaller island named La Désirade, 10 km east from Grande-Terre. GDGTs either present as core lipids (CLs; presumed of fossil origin) or derived from intact polar lipids (IPLs; markers for living cells) were analysed. Interestingly, the distribution of archaeal and bacterial GDGTs differed between the four sites, as shown by the higher values of the TEX$_{86}$ and MBT in sediments from La Désirade than in those from Grande-Terre. These differences were also reflected in the TEX$_{86}$- and MBT/CBT-derived temperatures. Temperature estimates derived from GDGTs present in La Désirade sediments were consistent with temperature recorded in the area (annual air temperature 26 °C), whereas temperature estimates derived from Grande-Terre sediments were much lower than expected values. The variability in archaeal GDGT distribution between the four water ponds might be due to different archaeal communities between Grande-Terre and La Désirade. Bacterial GDGTs seem to be essentially derived from surrounding soils in La Désirade. In contrast, in Grande-Terre, a substantial proportion of bacterial GDGTs might be produced in the water pond in addition to being produced in surrounding soils, as revealed by the high relative abundance of bacterial IPLs vs. CLs downcore. Our results suggest that caution should be exercised when interpreting MBT/CBT-derived temperatures in aquatic environments, as they might be largely biased by in situ microbial production.

Weathering of voclanics and the geological carbon cycle

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Weathering and volcanic rocks

Weathering rates in granitic and cratonic terranes have been well studied, yet information on weathering in volcanic terranes remains sparse. Available data suggest that mafic – intermediate volcanic terranes play a disproportionately large role in the carbon cycle. They have high abundances of Ca and Mg silicates, the weathering of which results in much greater CO_2 consumption rates than the weathering of the alkali silicates typical of continental crust, which is an inefficient CO_2 sink. They also have mineralogy and texture that weather much faster than those typical of most cratonic terranes. Additionally, most active volcanic centers are associated with arcs and hotspots that are adjacent to oceans where marine moisture and orographic effects can lead to high runoff and erosion rates, and many of the active island arcs today are located in the wet tropics. All of these features suggest that weathering and CO_2 consumption rates of volcanics should be high. While there are relatively few published data from streams draining active arcs that permit estimation of CO2 consumption rates, there is growing evidence to support the hypothesis that arc weathering is an important CO2 sink [1, 2]

The contribution of arc terranes to global weathering budgets is poorly known in part because rivers in these settings tend to be small and have not been sampled systematically (or in most cases at all) for geochemical purposes. Unlike major continental regions, where a single large river can give information about a large fraction of both the continental surface and total runoff, island arcs are a type of "non-point source" problem. Many smaller streams deliver large loads per unit basin area, and the aggregate flux can be quite large, but no one stream samples a large region.

The srtontium isotope ratios of arc and hot spot weathering is low, reversing the common relationship beteen silicate weathreing and changes in seawater 87Sr/86Sr. Changes in the rates of arc weatheirng can be important drivers of the long term carbon cycle

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Open-system behavior of U-series in carbonates: what we can learn from old limestones

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Conventional U/Th age determination assumes closed-system behavior. This criterion is violated in most Pleistocene fossil corals as evidenced by unreliable ages, ^{226}Ra offsets with respect to radioactive equilibrium with parent ^{234}U, as well as variable initial coral ^{234}U/^{238}U ratio, that are in most case substantially higher than that of modern seawater. The source of excess ^{234}U (and ^{230}Th) in fossil corals and its relationship to U-series age determinations remains an open issue in U-Th geochronology. Many investigators [2,3] consider that open-system behavior results from an enhanced alpha-recoil mobility of U-series nuclides (^{230}Th, ^{234}Th and consequently ^{234}U).

The premise of this study is that alpha-recoil-related processes evoked for open-system behavior of fossil corals, should also be active in "old" carbonates. Here we illustrate this issue with precise and accurate measurements of ^{234}U/^{238}U ratios in borehole core samples from deep, low-permeability Mesozoic formations of the Paris basin, France [3]. The initial objective of the study was to investigate the behavior of naturally occurring uranium isotopes as a means to assess the long-term safety of radioactive waste disposal in a clayey formation of Callovo-Oxfordian age targeted by the French Agency for nuclear waste management (ANDRA). Special attention was paid to U-series disequilibria within over- and underlying Mesozoic carbonate formations. All samples associated with pressure-dissolution features (stylolites) depicted systematic ^{234}U/^{238}U disequilibria at the centimetric scale, thus illustrating some uranium mobility during the last 2 Ma. This finding illustrates an unusual and unexpected mechanism of uranium remobilisation implying relocation and fractionation processes, since U was supposed to be practically immobile under the reducing conditions and low porosity and permeability characterizing the host sedimentary formations. We intend to discuss here the mechanisms responsible for uranium mobility in such deep sedimentary rocks and will make a comparison with mechanisms that have been proposed to drive U mobility in fossil corals.

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Impact of remediation design on arsenic leaching from historic gold mine tailings

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Secondary As minerals can reduce metal(loid) mobility in mine wastes, but may dissolve under changing geochemical conditions during or after remediation. The objective of this study is to optimize remediation strategies for As-bearing tailings from abandoned gold mines in Nova Scotia. A logical clean up plan at these publicly accessible sites would be to place a cover on the tailings, a method often successful at limiting sulphide oxidation and thus, preventing acid production and metal(loid) release. However, due to the heterogeneous nature of these strongly weathered mine wastes, this may lead to dissolution of some As-bearing minerals and an influx of As to local waters. The challenge of remediating such tailings lies in the different Eh-pH niches in which Fe-arsenates (oxidizing, acidic), Ca-Fe-arsenates (oxidizing, alkaline), and sulfides (reducing) are stable. Since these mine wastes are mineralogically complex and associated with variable pH and redox conditions, a one-size-fits-all remediation approach will be difficult to achieve.

To assess the geochemical changes induced by various remediation scenarios, the following options have been tested: (1) unremediated tailings in the field, (2) unremediated tailings in the lab, (3) a simulated limestone cover, (4) a simulated vegetative cover, and (5) a soil cover. For scenario 1, four field bins were filled with one of each tailings end member (hardpan tailings, oxic surface tailings, wetland tailings, or high Ca/As tailings). Leachate from the bins was sampled bi-weekly for two years. Scenarios 2-4 involved a set of three columns per tailings end member that were leached weekly with one of three input solutions: synthetic rainwater, synthetic rainwater equilibrated with $CaCO_3$, or a weak organic acid solution, respectively. Scenario 5 consisted of one column of each tailings end member topped with a 30-cm-thick soil cover that was leached with synthetic rainwater.

Results from Scenarios 1-4 show the As mineralogy in the tailings is the primary control on As mobility. Under field conditions, both hardpan and wetland tailings produced acidic, metal(loid)-rich drainage over time, and only the high Ca/As tailings remained near-neutral throughout the tests. In the lab, column leachates for a given tailings end member showed similar pH values and concentrations of sulphate, As and Fe despite the range in input solution pH (from 4.6 to 10). The scenarios tested so far have not proven to be effective mitigation strategies against As leaching. Reducing water and oxygen availability may be the best way to minimize As release and prevent acid generation.

Stablization of mercury in riverbank sediments of the South River, Virginia (U.S.A.)

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Metal-bearing sediment particles from eroding riverbanks can be an ongoing source of bioavailable mercury (Hg) to aquatic ecosystems. Hyporheic zones in particular can be important sources of both inorganic and organic-complexed Hg, which can be rapidly transported to adjacent surface waters. The objective of this study was to investigate the release and treatment of dissolved and particle-bound Hg in water derived from the riverbank sediments of the South River, Virginia. A profile of sediment was collected along a riverbank. Samples were characterized to assess the potential for Hg release as both dissolved and particulate forms. A series of resuspension experiments was conducted to simulate erosion of the riverbanks into the river. Mechanisms controlling transport of Hg during a riverbank inundation event were evaluated through column leaching experiments, which were conducted under variable flow conditions. Carbon-based amendments were applied in batch experiments to limit the release of Hg from sediment containing either 70 mg kg^{-1} or 280 mg kg^{-1} of Hg. Continuous flow-through column experiments were conducted to evaluate the potential for treatment of both dissolved and particulate Hg under transport conditions.

Elevated concentrations of Hg were observed in the river water during the resuspension experiments. The highest concentrations of Hg released (up to 80 μg L^{-1}) were observed for sediment samples collected from near the top of the riverbank profile. Mercury release during the resuspension experiments showed a non-linear response as the mass of sediment was increased, suggesting a possible solubility control on aqueous Hg concentrations. In column experiments, Hg concentrations in the in the 0.45 μm-filtered fraction of the effluent varied from 0.15 μg L^{-1} for samples collected from the base of the riverbank to 8 μg L^{-1} for samples collected from the top of the riverbank. Filter size-fractionation of water column effluent suggested approximately 50% of the leached Hg was present in the dissolved phase, with the remainder in particulate form.

Results from batch and column experiments indicated that the addition of reactive media resulted in lower aqueous concentrations of Hg. The co-blending of carbon-based adsorbent to sediments resulted in decreases in aqueous Hg ranging from 43 to 89% in the South River water. The adsorption of Hg ranged from 32 to 202 ng Hg per g reactive material. Decreases of 98% of Hg in column effluent were observed following 35 pore volumes of flow, and 91% after 100 pore volumes of flow. Results from laboratory-based experiments indicated that the addition of reactive media resulted in lower concentrations of both dissolved and particulate Hg in the river water. The potential application of carbon-based amendments to the riverbank sediment may be an alternative approach to reduce Hg flux in the South River.

Use of stable (HOCN) and radiogenic (Sr) isotopes to determine the geographic provenance and traceability of artisanal cheeses of Quebec, Canada.

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Analysis of stable isotopes has often been used to determine the traceability of different food products [1]. The light stable isotope ratios in dairy products such as cheese can provide information for tracing geographical origin [4]. The province of Quebec is Canada's largest cheese producer and artisanal cheeses are becoming a larger part of this market. In this context, we selected artisanal cheeses from six different regions of the province of Quebec to study the applicability of light stables isotopes and radiogenic isotope (Sr) ratios as descriminants to provide geographic traceability.

The cheese samples were analysed for light stable isotope ratios (HOCN) which are mainly influenced by altitude, distance from the sea, use of fertilizer, rainfall, food type, temperature, longitude and latitude [2,3,6]. The Sr isotope analyses are indicative of the geology of the type of substrate of the grazing areas [5]. Prelininary results yeild ^{87}Sr/^{86}Sr ratios that vary from 0.70978 to 0.71347 for both winter and summer cheeses. These values reflect soils composed largely of glacial tills derived from either the Canadian Shield or Appalachain Orogen. Furthermore, we observed a direct correlation of the ^{87}Sr/^{86}Sr ratios of cheese, milk and soil from the grazing area. Stable isotope δD values vary beteween -107.57‰ to -56.38‰, and δ^{18}O beteween -18,64 ‰ to -6,45‰ for both winter and summer cheeses. Water and milk δD and δ^{18}O results are similar to chesse results but with and enrichment in δ^{18}O values. Stable isotope δ^{13}C values vary between -27.12‰ to -21.40‰ and δ^{15}N beteween 4.66‰ and 6.21‰ wich is representative of C$_3$ plant CO$_2$ fixation. These results allow us to conclude that the use of stable and radiogenic isotopes can provide geographical provenance and traceability of the artisanal cheese of Quebec.

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The climate sensitivity of oceanic oxygen

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The warming of Earth's climate is expected to lead to a widespread loss of oxygen from the ocean, exacerbating the localized effects of coastal eutrophication. The mechanisms responsible for climate-forced deoxygenation – changes in gas solubility, ventilation of the ocean interior, and respiration of organic matter – are spatially heterogeneous, so the susceptibility to oxygen loss varies greatly among water masses. Moreover, the wide range of time scales involved in the adjustment of the oceanic oxygen distribution, coupled with the presence of strong internally generated variability greatly complicate the detection and attribution of trends. This talk will synthesize the current evidence for and understanding of changes in oceanic oxygen from model simulations, modern ocean observations, and the geologic record. A central conclusion is that the low latitude ocean, where the biological constraints from low oxygen are most profound, are also intrinsically most sensitive to climatic perturbations. Given the long transit times from thermocline outcrops to the tropical oxygen minimum zones, the response of oxygen in those regions to climate warming must either be slow to arrive, or else driven by local rather than remote climate trends. This suggests that if an expansion of the tropical oxygen minimum is already underway, its climatic origin is likely to be found in tropical winds rather than high latitude stratification. The major uncertainties and implications for ecosystems and biogeochemical cycles will also be discussed.

Benthic nitrogen fluxes and denitrification in Bering Sea shelf sediments.

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Abstract

Benthic-pelagic coupling is hypothesized to be quite strong in the in the highly Bering Sea shelf ecosystem and primary production of the system is thought to be nitrogen limited[1]. Nevertheless, sedimentary denitrification and benthic nutrient fluxes and their seasonal trends are poorly characterized. Through the Bering Sea Ecosystem Study (BEST) program, we measured benthic fluxes of N_2 and dissolved inorganic nitrogen species, the extent of coupled nitrification/denitrification, and the water column nitrate deficit (using N**[2]) on the Bering Sea shelf in the spring and summer 2009 – 2010. We found that sedimentary denitrification is widespread over the shelf and is fuelled mostly through coupled nitrification/denitrification, the net balance of sedimentary DIN flux is negligible over the shelf, and that water column N** varies widely according to season and year. In the summer, N** appeared to be strongly affected by non-Redfieldian uptake of inorganic nutrients by phytoplankton in the spring bloom; in the winter, N** was strongly affected by sedimentary denitrification. Our findings indicate that the estimate of total N loss in the Bering Sea shelf should be revised upwards by at least 50% to 5.2 – 6.2 Tg N y^{-1}. In addition sediments appear not to be a large source of remineralized nutrients for primary production over the shelf, hence sedimentary denitrification exacerbates N-limitation of the ecosystem.

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Kinetic Monte-Carlo: a tool to investigate the corrosion of glasses

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Monte-Carlo modeling

The Monte-Carlo modeling of the corrosion of glasses by water makes it possible taking into account both the chemical reactivity at the atomic level and the morphology of the altered surface film at the mesoscopic scale. The method was mainly applied to borosilicates in relation to the durability of the nuclear waste confinement glasses. The effect of substituting silica for more (B, Na) or less (Al, Zr) oxides was studied [1, 2].

The model leads to three major predictions. First, the initial dissolution rate is controlled by the surface area of the porous layer produced by the departure of the most soluble oxides. Second, the corrosion blocking that frequently occurs in static conditions is due to the restructuring of the altered film, which leads to the densification of the external layers and to the closure of the pores (Fig 1). Third, the presence of insoluble oxides in the glass composition paradoxically increases the degree of corrosion, since it prevents the layer reconstruction.
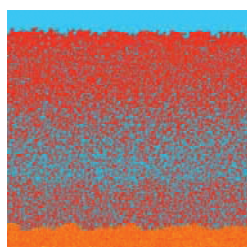

Figure 1: Cross section of the reorganized gel showing the densification of the external layers and the closure of the pores [3].

Experimental studies

All these predictions were broadly confirmed by experimental studies of the kinetics of corrosion and by the characterization of the corroded films by various techniques including NMR, gas adsorption and spatially resolved mass spectroscopy [3, 4]. Especially, the gel reconstruction was probed by small angle X-ray scattering and the porosity closure was evidenced by neutron scattering with solvent index matching. An inverse correlation between the initial dissolution rate and the final degree of corrosion was demonstrated both as a function of pH, and glass composition when silica is replaced by zirconia, or Na_2O by CaO [4].

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Continental growth through the sedimentary reservoir: Hf in zircon & Nd in shales records

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~7% of the present-day exposed crust consists of rocks of Archean age, yet models of continental growth suggest that 20-100% of the present-day volume of the continental crust had formed by 2.5 Ga ago [e.g. 1]. These models rely on understanding the balance between the generation of new crust and the reworking of old crust, and how these have changed with time. For that purpose, the variations in radiogenic isotope ratios in detrital rocks and minerals are a key archive.

We considered two different approaches to model the growth of the continental crust: (i) the variation of Nd isotopes in continental shales with various deposition ages, which requires a correction of the bias induced by preferential erosion of younger rocks through an erosion parameter 'K' [2-3]; and (ii) the variations in U-Pb, Hf and O isotopes in detrital zircons sampled worldwide. These two approaches independently suggest that the continental crust appears to have been generated continuously, but with a marked decrease in the continental growth rate at ~3 Ga. The >4 Ga to ~3 Ga period is characterised by relatively high net rates of continental growth (~3.0 $km^3.a^{-1}$), which are similar to the rates at which new crust is generated, and destroyed, at the present time [4]. Net growth rates are much lower since 3 Ga (~0.8 $km^3.a^{-1}$), which may be attributed to higher rates of destruction of continental crust. The inflexion in the continental growth curve at ~3 Ga indicates a change in the way the crust was generated and preserved. This change may be linked to onset of subduction-driven plate tectonics and discrete subduction zones.

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Improved analytical method for determination of Mg isotopes: Application to seawater and natural carbonates

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Magnesium isotopes are a powerful tracer of low temperature geochemical processes [1, 2]. However, widespread application of Mg isotopes in geochemical studies is limited due to the relative amount of Mg required for high precision measurements, high procedural blanks, artificial fractionation induced by chromatographic methods, and low matrix tolerance [1, 2]. The improved method for Mg isotope ratio (δ^{25}Mg & δ^{26}Mg) determination has low mass consumption (5 ng-Mg) with high precision ($\pm$ 0.1‰, 2s) and high matrix tolerance using Neptune® MC-ICP-MS. A single step chromatographic method is used to quantitatively (100.0% $\pm$ 0.2%) separate Mg from matrix elements with low blanks and no column induced fractionations. Quantitative separation of other matrix elements (Li, Na, Ca, and Sr) was also achieved with > 99% recovery (Fig. 1). This procedure is optimal for natural carbonates and seawater samples with high matrix loads.

Preliminary MC-ICP-MS analyses of CAM1, DSM3, and seawater fall in the published range (Δ^{25}Mg$_{Cam1}$ and Δ^{26}Mg$_{Cam1}$ relative to DSM3 are 1.47‰ and 2.67‰, respectively) (Fig. 2). Internal reproducibility ranges from 0.029‰ to 0.144‰ / AMU (1σ, n=105), while external reproducibility obtained on pure Mg solutions is 0.009‰ / AMU (1σ). These new analytical methods will be used to investigate relationships between $^{7/6}$Li, $^{(26/25)/24}$Mg, and $^{(88/87)/86}$Sr ratios in natural carbonates to asses their viability as indicators of weathering and endmember mixing in carbonate systems.
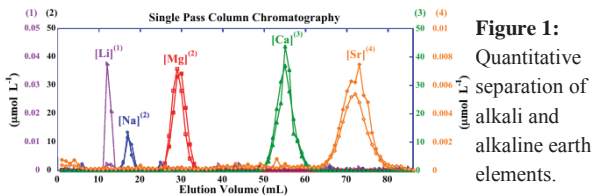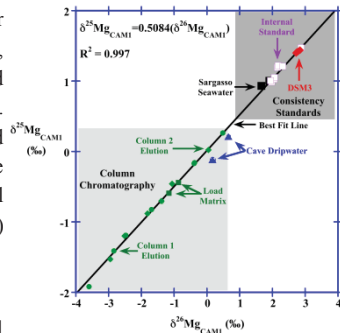

Figure 1: Quantitative separation of alkali and alkaline earth elements.

Figure 2: δ^{25}Mg vs. δ^{26}Mg for elution matrices, seawater, cave dripwater, DSM3, and internal isotope standards. Error bars (2σ) are contained within data symbols. The slope of the best-fit line through all data is δ^{25}Mg = 0.5084 (δ^{26}Mg) R^2 = 0.997.

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Effect of Nanoparticles on the Displacement Pattern of CO$_2$ Injection in Porous Media

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Introduction

The patterns that emerge from a displacement process depend greatly on the mobility ratio between displaced and displacing phases. When a less viscous fluid (e.g. CO$_2$) displaces a more viscous fluid (e.g. brine) the displacing fluid fingers through the porous media, causing it to travel faster and longer distances. Spontaneous formation of foam during the displacement may be an effective solution to stabilize the displacement. Surface treated nanoparticles have been shown to stabilize CO$_2$ in water foam by adhering to the surface of CO$_2$ bubbles and preventing their coalescence [1]. However, the large adhesion energy suggests that mechanical work must be applied to bring the nanoparticles from bulk phases to the CO$_2$-water interface [2]; Co-injection of CO$_2$ and nanoparticle solution at high rates is known to provide sufficient energy. Here, we study the foam formation during a fluid/fluid displacement at low shear rate.

Methodology

In order to capture the efficiency of the nanoparticle foam flood, we inject CO$_2$ and CO$_2$ analogue fluids into sandstone cores preloaded with either brine or brine with suspended nanoparticles. We use CT scanning to measure the saturation profile and flow pattern during a displacement, and pressure transducers to measure the overall mobility.

Results and Conclusion

Even at small flow rates (low shear rate) the presence of nanoparticles acts to control the CO$_2$ mobility. The displacement front is more spatially uniform and breaks through later in the presence of nanoparticles compared to displacements without nanoparticles (Fig. 1). Pressure measurements during the displacement are consistent with generation of a viscous phase such as an emulsion. These observations suggest that nanoparticle stabilized emulsion is formed during the displacement which acts to suppress the viscous instability. We argue that generation of droplets of CO$_2$ occurs at the leading edge of all drainage displacements; however, the droplets are preserved only in the presence of nanoparticles.
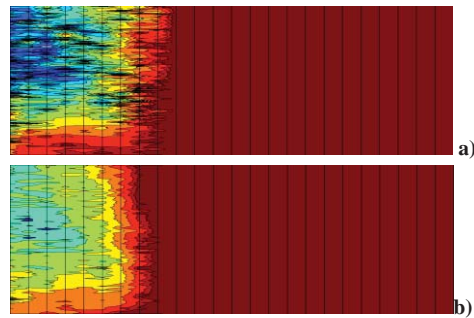

Figure1. Side view of the Boise sandstone core after injection of 0.10 PV of octane, a) without nanoparticle, b) with nanoparticle

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MELT ROCK REACTION IN THE MANTLE AND ACCRETION OF THE LOWER CRUST AT SLOW SPREADING RIDGES

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Introduction

Primitive olivine cumulates; dunite, troctolite, and olivine gabbro associated with mantle peridotite are common features of oceanic core complexes away from fracture zones. They are broadly interpreted as from the crust-mantle transition zone, formed where melt transport focused beneath a 2nd order ridge segment. Mapping at Kane Megamullion on the MAR shows local magmatic centers may form anywhere beneath a ridge segment: existing for several hundred thousand years before magmatism focused elsewhere [1].

Olivine-rich troctolites form by melt-rock reaction with the mantle, in a sequential reaction between peridotite and migrating melt, forming first dunite, then troctolite, then olivine gabbro. This occurs due to solidification-by-reaction between melt and the mantle [2]. Such reactions may continue in the lower crust until olivine is eliminated. Ol-rich troctolites in IODP Hole U1309D appear to have this origin [3-5]. Rafting of troctolites to higher levels likely due to tectonic rollover wgeb the lower crust supports a shear stress at low magmatic budgets. Thus a portion of the lower crust may be hybridized mantle.

Ol-rich troctolites also occur within a mantle section at Godzilla Megamullion in the Parece Vela Basin [3]. They include both Ol-rich (Ol > 60 vol.%) and plagioclase-rich (Pl > 60 vol.%) troctolites. The latter likely formed by local dissolution of a plagioclase matrix, and crystallization of olivine, Cpx and new plagioclase by melt produced by mixing high-MgO melt residual to Ol-troctolites formation with melt crystallizing cumulus plagioclase in a melt transport conduit.

We find olivine nickel contents can constrain the formation environment of Ol-rich rocks in the lower crust and mantle, the nature of the formation process, and the magma budget. Comparison to the nickel contents of other troctolite and gabbro occurrences in oceanic and ophiolite settings reveals a set of relationships generally consistent with our interpretations. Notably, the olivine gabbros from the 1500-m Hole 735B Atlantis Bank gabbro section have low nickel contents, while those from the 1400-m Hole U1309D Atlantis Massif gabbro section have high nickel. This is consistent with less-reacted infiltrating melt at the latter, strongly supporting the idea that U1309D represents a deeper section of the lower crust near the crust-mantle transition, while the former have been shown to represent the dike-gabbro transition and underlying gabbros.

Godzilla troctolites and gabbros have clear similarities to EPR troctolites and gabbro segregations drilled in dunites crosscutting mantle peridotites at Site 895 at Hess Deep. These represent multi-stage crystallization of stagnant melts in conduits beneath the EPR. Thus, it appears that the processes that formed the Godzilla troctolites occur beneath ocean rises across the spreading rate spectrum.

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THIN CRUST OVER THE MARION RISE: MELTING A HETEROGENOUS MANTLE FROM BENEATH GONDWANA

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The Marion Rise stretches ~ 3100 km along the SWIR from its shoalest point at 850 m, 250-km north of Marion Island, to 5600-m just west of the Rodriguez TJ. By any measure it has essentially the same relief as the Icelandic/Reykjanes Rise, but is twice as long. Cut by numerous large-offset transforms, which would likely dam sub-axial asthenospheric flow, it is unlikely that the rise can be supported by a mantle plume beneath the Marion Hotspot. The hotspot, however, traces back to the Karoo volcanic event at 185 Ma near the time of the breakup of Gondwana, and formation of the SWIR. Hence the mantle substrate beneath the SWIR likely comes from beneath southern Africa, representing the residue of the Karoo event.

We compiled new and existing data on SWIR dredge and dive samples, and find that large peridotite exposures occur throughout, including the Marion Rise crest. In the absence of significant gabbro representative of a lower crustal section, and the presence of near-amagmatic spreading segments along the rise, we conclude that the crust over the Marion Rise, in sharp contrast to the Reykjanes Ridge, is relatively thin and discontinuous. At the same time, analysis of peridotite spinel shows a systematic increase in mantle depletion up the Marion Rise correlating to the composition of spatially associated basalts and ridge depth. Hence the degree of mantle depletion increases towards the rise crest. In the absence of significantly thicker crust, this must be in large part the consequence of an earlier mantle melting event – presumably coinciding with the Karoo volcanism – but possibly including a yet earlier mantle depletion.

This, then, provides an explanation for the Marion Rise other than a simple thermal anomaly attributable to sub-axial asthenospheric flow fed from a mantle plume beneath the Marion Hotspot. Harzburgite in the garnet stability field is significantly less dense than lherzolite, and hence the systematically higher degree of mantle melting required by the Marion Rise basalts and peridotites likely reflects a major density anomaly beneath the SWIR centered on Marion Island 250 km to the south. Thus the Marion Rise may exist due to an isostatic response to an earlier mantle depletion event predating the present day volcanism.

Basalts isotopic compositions along the Marion Rise are highly variable, reflecting a heterogenous mantle consistent with interactions and entrainment of a heterogeneous continental lithosphere and crust in the asthenosphere as Africa migrated northward during the opening of the SW Indiaan Ridge [1-3].

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Thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature

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Polycyclic aromatic hydrocarbons, including monomethylated phenanthrenes (MP), are common components of bitumen associated with sediment-hosted ore deposits. Their relative abundances are often interpreted as indicators of thermal maturity and hence may help constrain models for the transport and deposition of metals sharing a genetic history with the organic compounds. A high degree of thermal maturation yields products in chemical equilibrium [1], but a lack of thermodynamic data for aqueous MP at high temperature has precluded a quantitative interpretation of their origin in hydrothermal settings. Values for the standard molal Gibbs energy and enthalpy, entropy, and heat capacity were generated for aqueous phenanthrene and the MP isomers methylated at the 1-, 2-, 3-, 4- and 9-positions on the phenanthrene structure. These values were derived from reported thermodynamic properties of the crystalline compounds [2], their solubilities and enthalpies of solution, and relative properties of the MP isomers from quantum chemical simulations [3] at 25 °C. Preliminary extrapolations to higher temperature were carried out using a constant heat capacity difference between the isomers. At 25 °C, 2-MP is highly favored over 1-MP. With increasing temperature, however, the difference in stability between the two diminishes, eventually crossing over to higher stability of 1-MP at temperatures greater than ~400 °C. The calculated equilibrium ratios of 2-MP to 1-MP (MPR) are consistent with two independent constraints: (1) maximum reported values for mature source rocks (~160 °C), and (2) MPR observed in Archaean rocks exposed to temperatures of 200–300 °C [4].

These comparisons indicate that relative abundances of methylphenanthrenes can be used to infer thermal conditions and sources of bitumen found in ores and host rock. At the Here's Your Chance (HYC) Pb-Zn-Ag deposit (McArthur River, Northern Territory, Australia) bitumen in the ore zones has a lower MPR than unmineralized shale samples. The range of values in the bitumen associated with the ore is consistent with temperatures of isomeric equilibration of ~350–400 °C. The source of MP, therefore, could reasonably have been a hot brine that cooled as it reached the ore zone. The offset in the relative abundances of MP between the ore and shale layers suggests a different degree of interaction of the brine with these layers. Since phenanthrene has a higher average oxidation state of carbon than its methylated counterparts, consideration of their relative abundances in a thermodynamic framework could place constraints on redox conditions in the ore-forming system.

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The possible role of crystal conduction and inter-particle electron transfer in Fe-oxide phase transformation and growth

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A series of anerobic experiments have been conducted to study the mechanism of Fe^{2+}-mediated ferrihydrite transformation. At pH 6.5 and 7 and in the presence of 5 mM dissolved $Fe(II)Cl_2$, freshly formed, 2-line ferrihydrite rapidly exchanges isotopes with Fe^{2+} in solution (75% equilibration within 10 minutes). During the first 2-3 hours of reaction, X-ray pair distribution function (PDF) analysis and transmission electron microscopy shows evidence of increasing size of ferrihydrite particles and coherent scattering domains, but minor or no mineral transformation. After this lag phase, more rapid transformation commences to major end-phases lepidocrocite (pH 6.5) and magnetite (pH 7).

Extensive isotope exchange for ferrihydrite without significant phase transformation indicates that interfacial electron transfer and crystal conduction leads to oxidation of adsorbed Fe(II), resulting in Fe(III)-oxide growth, and reductive dissolution of Fe(III) at a different site, similar to what was initially observed for hematite [1]. In contrast to the lag phase observed for 2-line ferrihydrite, transformation of 6-line ferrihydrite to magnetite commences immediately at pH 7. More rapid conversion of larger and presumably less soluble ferrihydrite is inconsistent with recrystallisation by classical dissolution/reprecipitation. Rather, it suggests solid state transformation with magnetite nuclei forming either inside the ferrihydrite or at its surface.

With X-ray diffraction, materials subjected to ultrasonification during reaction display much weaker Bragg peaks from goethite, lepidocrocite and magnetite than those observed from material synthesised in regular experiments and the coherent scattering domains of the phases are smaller in PDF. This indicates that particle contact enhances crystal growth. Such a feature could reflect growth by 1) oriented attachment, which has been observed for ferrihydrite conversion to goethite [e.g. 2], or 2) electronic coupling between crystals, leading to Fe^{2+} electron donation and crystal growth on one particle, then transfer of the electron to an adjacent particle where interfacial reduction and dissolution occur.

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The role of fluids in the monazite record during successive partial melting events: a textural, chemical and in situ dating study in Grt-Ky gneisses of the Central Rhodope (Bulgaria, Greece)

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Monazite is considered to be resistant to diffusive Pb loss at high temperatures and thus, it is particularly adapted to record various stages during a sequence of high-temperature geological events. This study focuses on Grt-Ky gneisses from the lower part of the metamorphic pile in the central part of the Rhodope Metamorphic Complex, in the areas of Chepelare (Bulgaria) and Sidironero (Greece). The outcrops of both regions have experienced a polycyclic evolution during Alpine times, with at least two stages of high temperature metamorphism. According to P-T estimates, the first event involved granulite facies dehydration melting that produced peritectic garnet and kyanite together with a K-rich melt. The second event relates to widespread fluid-assisted partial melting. The latter is well known in adjacent rocks, where it is dated at ~36-50 Ma, but is poorly expressed in our samples, which well preserve the early granulite facies assemblages. Monazite is present in all samples, included in early porphyroblasts such as garnet and kyanite or in the matrix. Matrix monazites are associated with white mica, rutile and biotite (Greek part) and sillimanite and biotite (Bulgarian part). Matrix monazite grains show fluid-assisted dissolution-recrystallisation features with pronounced Y-zoning correlated to age domains. Y-poor domains, dated by LA-ICPMS method (^{208}Pb/^{232}Th ages) between 130 and 155 Ma, represent the largest part of each grain, while Y-rich domains, dated between 40 and 50 Ma, occur either as thin discontinuous rims (< 15 μm) or as small single grains surrounding the Mesozoic grains or filling white mica cleavages. The low P and REE-content of the surrounding minerals suggests that the Cenozoic domains essentially crystallized at the expense of the Mesozoic domains. In addition, garnet being the Y-richest mineral in the samples, its fluid-assisted resorption is the most likely mean to provide Y involved in the Cenozoic domains. The origin of the fluid is not clearly defined: external fluid infiltration or fluid produced by the recrystallisation of H_2O-bearing minerals. Regardless, this fluid interaction was responsible for the partial dissolution of Mesozoic monazite grains, as well as for garnet resorption, and the precipitation of newly-formed Y-rich monazite during mid-Cenozoic times.

Low-*P*, clockwise metamorphism of the Aus granulite terrane, Namibia

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Introduction
Intermediate *P-T* metamorphism has been inferred to indicate the initiation and operation of collisional orogenesis from the Palaeoproterozoic to the present [1]. However, the Precambrian also preserves examples of anomalously hot, likely collisional, orogenies that do not occur in the Phanerozoic. These orogenies are characterised by low-*P*, high-*T* metamorphism, high apparent geotherms and clockwise or anticlockwise *P-T* paths [2], and have been suggested to form during continental back-arc inversion involving juvenile and weak crust [1].

Regional Geology
The Aus granulite terrane of southern Namibia forms part of the Namaqua metamorphic complex that has been metamorphosed and migmatised in a hot orogenic environment during the Kibaran. The terrane consists of older TTG basement gneisses, a high-grade metamorphic supracrustal sequence, and syn-tectonic garnet leucogranite gneisses formed through anatexis of the surrounding rocks. Residual metapelitic rocks preserve assemblages of g-sill-cd-bi-ksp-pl-q-ilm that equilibrated in the presence of silicate melt. Sillimanite mats occur as large, blocky prisms interpreted as pseudomorphs after prograde andalusite. Sillimanite is included in garnet and rimmed by cordierite, indicating consumption of sillimanite to form garnet and cordierite at prograde to near-peak metamorphic conditions.

Results and Conclusions
Pseudosection modelling of metapelitic and metapsammitic residuum compositions constrain peak *P-T* conditions to 825°C and 5.5 kbar. The replacement of sillimanite by garnet-cordierite suggests that the rocks experienced heating with minor decompression to peak metamorphic conditions. The retrograde path likely involved decompression-cooling, as isothermal decompression would have led to the introduction of orthopyroxene, whereas isobaric cooling would have re-introduced sillimanite, neither of which occurred in these rocks. Pseudosections for melt-reintegrated estimates of the protolith composition show that andalusite stability along the prograde path is restricted to *P* below 4 kbar at 550-600°C. This indicates that prograde metamorphism occurred along a high apparent geotherm of 40°C/km, yet the textures suggest that the rocks evolved along a clockwise path at peak *P-T*. Retrogression occurred along a similar geotherm, suggesting that exhumation was slow, and dominantly occurred through erosion, rather than tectonic processes, and that elevated crustal temperatures outlasted the duration of orogeny.

The origin of such a long-lived heat source is enigmatic, particularly as direct evidence for mantle involvement, such as contemporaneous mafic magmatism, is absent. Metamorphism could have involved initial magmatic underplating that led to widespread crustal melting and the redistribution of melt and heat producing elements to higher crustal levels, thereby maintaining an elevated geotherm during the latter stages of orogeny.

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Melt Rheology and Glass Formation

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Melt Rheology

The rheology of molten silicates has been the subject of a century of investigation. Current empirical models for Newtonian melt viscosity are adequate for many applications in petrological and volcanological modelling. Structure-based models have been proposed but no one has delivered yet a complete validation of any of these models.

In detail - potentially in petrologically important detail - the rheology of silicate melts contains a number of features that are not yet sufficiently well modelled. In particular, the high viscosity – high pressure regime of silicate melts will require detailed mapping before the grand conclusions of silicate melt viscosities can be developed.

Glass Formation

The departure of molten silicate from the viscous state forms the central event of explosive volcanism. The glassy products of all eruptions can shed light on the conditions of eruptions themselves. Tracking the path of glass formation in molten silicates has revealed a wide range of phenomena in the petrogenesis of these rocks and many new frontiers await exploration.

Some of the currently identifiable areas of progress in both areas will be reviewed. Some potential next steps will be presented.

Dynamics of organic carbon sedimentation and bottom oxygen and their impact on phosphorus retention in Lake Simcoe: reactive-transport modeling and experimental study.

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Introduction

Lake Simcoe experiences cultural eutrophication associated with point and non-point loading sources. Efforts to reduce total phosphorus (P) inputs to Lake Simcoe since the 1990s, have resulted in significant annual load reductions to the lake [1]. This lake still suffers from excessive growth of filamentous algae, macrophytes, and low hypolymnetic oxygen concentration. Despite a good understanding of the total P budget, our knowledge about the potential for bioavailable P loading from the sediments is limited. The impact of dynamic conditions at sediment–water interface, such as organic carbon flux and oxygen concentration, on phosphorus retention remains unknown. In this study, phosphorus sediment retention in three basins, that experienced distinct sedimentation dynamics, has been investigated experimentally and theoretically. Using diagenetic reaction-transport modeling and sediment core analysis, we investigated the effects that variations in the organic carbon loadings and oxygen bottom concentration, had on the availability of sediment P.

Methods and Results

We performed phosphorus sequential fractionations of sediments during summer stratification and under ice-cover. Phosphorus binding forms have been divided into four operational groups: apatite-bound-P, organic P, inorganic redox-sensitive P (iron-hydro-oxides-bounded) and loosely-bound P, that is in equilibrium with P dissolved in pore water.

The following rank was determined for the P in the sediment apatite-P > organic-P > redox-sensitive-P > loosely bound-P. It was found that the largest amount of P is bound in the sediment as apatite-P, essentially stable in respect to redox conditions. The model results are in agreement with the measured flux of total phosphate to the system and the fractionation data of phosphorus binding forms. A sensitivity analysis was undertaken to identify the most significant parameters, demonstrating that variations in sedimentation rate, and bottom water oxygen concentration, have the largest impact on P diagenesis.

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Chromium isotope fractionation during mobilization and transport in Sukinda Valley, India

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Abstract

The potential of stable chromium (Cr) isotopes as a tracer for the biogeochemical Cr cycle depends on understanding the fractionation Cr isotopes experience. Here we present Cr isotope analyses of different Cr reservoirs to elucidate the Cr isotope fractionation occurring during oxidative weathering in a natural system from Sukinda Valley, India.

Pristine chromite seams show Cr isotope composition similar to mantle inventory rocks [1]. Weathered chromites, highly weathered ultramafic rocks and soils consistently display light Cr isotope composition, indicating that oxidative weathering have preferentially leached and mobilized heavier Cr isotopes. The surface waters display variable Cr isotope signature. However, total dissolved Cr concentration correlate with Cr isotope composition so that high Cr concentration waters (<2.6 mg L^{-1} Cr) show lighter Cr isotope values, possibly reflecting the presence of Cr in colloids, while low Cr concentration waters (>17 μg L^{-1} Cr) have heavier Cr isotope values, reflecting dissolved Cr(VI).

These results show that heavy Cr isotopes are preferentially leached during oxidative weathering. The overall consistency between data indicate that oxidation of Cr(III) to Cr(VI) and subsequent mobilization leads to considerable Cr isotope fractionation, enriching the waters in the heavier isotopes. Contrary, reduction of Cr(VI) during transport enriches the produced solid phases in the lighter isotopes and the remaining solution, in heavier isotopes [2]. The variability of the Cr isotopic composition of natural samples including soil, rock and water samples demonstrates that significant fractionation is associated with Cr biogeochemistry in the environment.

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[2] Ellis et al. (2002), *Science* **295**, 2060-2062.

Pre-eruptive volatile contents of silicate melt inclusions hosted in the Grey Porri Tuffs of Monte dei Porri Volcano, Island of Salina, Aeolian Islands, southern Italy.

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The Aeolian Islands are an arcuate chain of submarine seamounts and volcanic islands, lying just north of Sicily in southern Italy. The eruptive products on the second largest of the islands, Salina, exhibit a wide compositional range, from basaltic lavas to rhyolitic pumice. The eruptions that produced the Grey Porri Tuffs (GPT) during the opening stages of the Monte dei Porri eruption cycle were among the most explosive in the history of the Aeolian Islands. Recent advances in microanalytical techniques permit quantification of the pre-eruptive volatile contents of magmas through analysis of silicate melt inclusions (MI). These data, in turn, provide valuable insights into magma dynamics and evolution, including the role of volatiles in controlling the style of eruption. To this end, lapilli pumice and scoria fragments were collected from the GPT and analyzed to determine the pre-eruptive volatile contents of the magmas as well as their compositional evolution.

Electron Microprobe Analysis (EMPA) of 38 naturally quenched (glassy) MI hosted in olivine, plagioclase and pyroxene define a complicated evolutionary history. Bulk-rock analyses identify the GPT host units as andesitic pumice (SiO_2 59.9 wt %) and high-silica basaltic scoria (SiO_2 53.4 wt%). MI hosted in the GPT pumice unit have basaltic compositions (SiO_2 46.2 wt%) and MI hosted in the scoria unit have basaltic andesite (SiO_2 56 wt%) compositions.

Secondary Ion Mass Spectrometric (SIMS) analysis of 23 inclusions reveals a similar bimodal distribution in volatile contents between the GPT scoria and pumice units. Olivine-hosted MI from the GPT pumice unit have higher average H_2O and S contents (4.53 wt % and 3790 ppm, respectively) compared to olivine-hosted MI from GPT scoria unit (2.7 wt % and 1772 ppm, respectively) but slightly lower F contents (659 ppm in pumice-hosted MI and 875 ppm in scoria-hosted MI). Cl contents are fairly uniform, averaging 3339 ppm in scoria-hosted MI and 3559 ppm in pumice-hosted MI. The higher H_2O contents of MI from the pumices compared to scorias is consistent with more explosive nature of eruptions that produced the pumices, compared to the less-explosive scoria eruptions.

Analysis of several spots within individual, large olivine-hosted MI shows CO_2 abundances of approximately 187-492 ppm in the GPT pumice unit and 233-576 ppm in the scoria unit. If the melt was saturated in CO_2 at the time of MI entrapment, CO_2/H_2O ratios indicate that the olivine in the pumices crystallized at approximately 6.5 km, whereas those in the scorias formed at 4.8-6.2 km.

Black carbon in Arctic snow and sea ice: The big picture through the details

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Overview

Model studies have indicated that black carbon (BC) in snow and sea ice may be producing significant warming in the Arctic and contributing to accelerated sea ice loss. All of these studies indicate that even small concentrations of BC may lead to large climate forcing because positive feedbacks, such as the snow albedo feedback, amplify the initial forcing. However, the magnitude of the forcing reported by different studies varies.

This talk will review our current state of knowledge regarding climate forcing by BC in Arctic snow and sea ice. The range of modeled estimates to date will be presented and reasons for differences between them explored. A recent Arctic-wide measurement study of snow and ice (BC) concentrations and sources will also be presented. This data set can be used to test modeled transport, deposition and in-snow concentration changes. However, the climate impact of BC in the cryosphere also depends strongly other factors such as snow cover, baseline snowpack radiative properties, cloud cover, in-snow redistribution of black carbon, and the presence of other light absorbing constituents. I will review what we know and what we still need to explore in order to understand whether black carbon is making a significant contribution to recent Arctic warming.

Benthic δ^{18}O signature of dense brine from sea ice formation in the North Atlantic

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Abstract

Sea ice is thought to be an important factor for explaining abrupt North Atlantic climate changes during the last ice age. Reconstructing past variations in sea ice cover remains a challenge, in large part because of the complicated and indirect relationships between sea ice proxy indicators and actual sea ice conditions. One approach is to use the idea that the isotopic signature of dense brines produced via salt rejection during the formation of sea ice may be detected in benthic foraminifera records [1]. Brine formation is an active process in the Arctic and Antarctic shelf regions today [2], [3], [4]. In the Southern Ocean in particular, large quantities of dense brines are generated in polynyas and contribute an isotopically light d^{18}O signature to Antarctic Bottom Water [5]. To date, it has been unclear whether North Atlantic and Arctic brines formed from isotopically light surface waters can become dense enough to penetrate to the depth habitats of benthic foraminifera. Storfjorden, located in the southeastern Svalbard Archipelago, is a site of active winter brine formation due to a recurrent polynya. Each winter, dense, brine-enriched waters fill the depressions of the fjord to its sill level and subsequently descend as a gravity current following the bathymetry towards the shelf break [6]. Observations from a September 2000 cruise reveal the presence of cold, salty, brine-enriched seawater sitting in the deepest channels (> 100 m depths) of Storfjorden, with isotopically light d^{18}O values corresponding to the d^{18}O values of the surface water in the region. These results are useful in better characterizing the signature of brine-enriched seawater and brine formation processes, and suggest a way forward for reconstructing sea ice variability from paleoclimate records.

[1] Dokken and Jansen (1999) *Nature* **401**, 458-461. [2] Warren (1981) *Evolution of Physical Oceanography. Scientific Surveys in Honor of Henry Stommel*, 6-41. [3] Fer et al. (2003) *Deep Sea Research I* **50**, 1283-1303. [4] Omar et al. (2005) *The Nordic Seas: An integrated Perspective oceanography, climatology, and modelling* **158**, 177-187. [5] Mackensen (2001)) *Deep Sea Research I* **48**, 1401-1422. [6] Skogseth et al. (2005) *The Nordic Seas: An integrated Perspective oceanography, climatology, and modelling* **158**, 73-88.

Fixation and remediation of trace elements associated with coal fly ash

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Introduction

Fly ash is the dominant component of solid waste produced by coal combustion. Only 38% of the total fly ash generated in 2010 was used for beneficial purposes, primarily due to concerns about potential leaching of trace elements to the environment [1]. In this study, bench-scale batch and column experiments were performed to test treatment methods aimed at reducing the mobility of trace elements associated with coal fly ash.

Results and Conclusions

Chemical fixation of fly ash using a ferrous sulfate (FS) treatment was tested at various solid:liquid ratios for a range of fly ash compositions. The best results were obtained for the 1:30 FS treatment, which successfully reduced the mobility of oxyanion trace elements in all of the fly ash samples studied. Sequential chemical extractions of treated and untreated coal fly ash showed that much of the As, Cr, Mo, Se and V associated with the acidic (Class F) fly ash samples was transferred from mobile to more stable, reducible fractions. Although reduction in trace element mobility was similar for alkaline (Class C) fly ash, FS treatment was less effective in reducing the mobility of As and Se. These elements showed significant reductions in mobility during long-term leaching, suggesting that this treatment method could increase the beneficial use of fly ash.

Older, unlined disposal facilities may serve as sources of trace elements to the environment if meteoric water interacts with the fly ash, creating leachate. Surfactant-modified zeolite (SMZ) has the potential to adsorb both cationic and anionic trace elements from aqueous solutions, but has not previously been tested for remediation of trace elements in fly ash leachate. Bench-scale batch and column experiments were performed to test the ability of SMZ to remediate trace elements in fly ash leachate. Batch experiments showed SMZ affected modest decreases in the concentrations of all oxyanion trace elements in leachate generated from both Class F and Class C fly ash, but was more effective for removal of Cr. Column experiments designed to simulate the use of SMZ as a permeable reactive barrier (PRB) at a CCP disposal facility showed large reductions in leachate trace element concentrations, but indicate that the effective lifetime of a SMZ PRB in the ash disposal environment would be relatively short.

[1] Adams, Thomas H. (2011) *ACAA Press Release*, **Dec. 13, 2011,** 4 pp.

An isotopic record of mercury in San Francisco Bay

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San Francisco (SF) Bay is an urban estuary that has been subjected to extensive pollutant inputs over the past 150 years. Potentially important sources of mercury (Hg) to SF Bay include Hg mining, placer gold mining, agriculture and industrial activity[1]. A previous study of Hg stable isotopes from intertidal surface sediment showed a geographic gradient in $\delta^{202}Hg$ from south (higher $\delta^{202}Hg$) to north (lower $\delta^{202}Hg$)[2]. To constrain background Hg isotopic composition and understand possible changes in Hg sources to SF Bay through time, we analyzed samples from eight dated sediment cores from SF Bay for total Hg concentration (HgT) and Hg isotopic composition. Sediment cores were collected at six open water sites (water depth: 2.3 to 7.8 m) and two wetland locations. At least three sediment intervals (pre-anthropogenic, ~1960, surface) were analyzed from each core. Sediment was also collected downstream of placer gold mines in the Yuba River, CA. HgT was measured by CV-AAS and Hg isotopic composition was determined by CV-MC-ICP-MS.

In all cores analyzed, HgT in pre-anthropogenic sediment is between 39 and 73 ng/g, which is within the range of expected background HgT[3]. In 1960-dated sediment, HgT varies from 239 to 532 ng/g in SF Bay open water cores and is significantly higher in wetland cores (3657 and 4777 ng/g). Surface sediment HgT in the eight cores range from 200 to 640 ng/g. HgT in the sediment derived from gold mine tailings is between 3180 and 6821 ng/g.

In all of the SF Bay cores, the pre-anthropogenic isotopic composition of Hg is similar: $\delta^{202}Hg$ = -1.00‰ (2SD = 0.14, n=6), $\Delta^{201}Hg$ = 0.09‰ (2SD = 0.08, n = 6) and $\Delta^{199}Hg$ = 0.18‰ (2SD = 0.07, n = 6). The 1960-dated sediment in the open water cores show a geographic trend similar to that reported by [2] for intertidal surface sediments: the southernmost location has the highest $\delta^{202}Hg$ (-0.32‰), the south-central locations have lower $\delta^{202}Hg$ (-0.40‰) while further north in San Pablo Bay $\delta^{202}Hg$ is lowest (-0.62‰). In surface sediment, $\delta^{202}Hg$ shows little geographic variation [$\delta^{202}Hg$ = -0.52‰ (2SD = 0.07, n = 6)]. In the sediment derived from gold mine tailings $\delta^{202}Hg$ = -0.57‰ (2SD = 0.21, n=2).

The results demonstrate that the isotopic composition of pre-anthropogenic Hg in SF Bay is different than Hg input from anthropogenic sources. A geographic trend in $\delta^{202}Hg$ is observed in sediment from ~1960, but $\delta^{202}Hg$ of SF Bay open water surface sediment does not vary geographically. It appears that intertidal surface sediments retain an isotopic memory of distinct Hg sources to SF Bay, whereas open water surface sediments have been homogenized, obscuring distinct signals of Hg source.

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Fluid inclusion size, depth and shape: aspects of re-equilibration

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Introduction

In recent decades of fluid inclusion research potential evidences of post-entrapment changes of fluid inclusions have been increasingly noticed. Several studies of re-equilibration experiments have already been published with complex multi-component fluid mixtures. This series lacks experiments with relative simple one-component fluid systems, where the result of alteration processes, such as diffusion, can be directly related to the activity of one fluid component. Specific re-equilibration experiments are currently performed by using pure H_2O and pure D_2O. The interaction of distinct fluid inclusions attributes such as the inclusion depth below the crystal surface, the inclusion size and the inclusion shape appear to be essential for post-entrapment compositional changes.

Performing re-equilibration experiments

For this study pure H_2O fluid inclusions are synthesized in Brazilian quartz crystals which are then exposed to pure D_2O during the re-equilibration process. Fluid properties of D_2O and H_2O are approximately similar, as evidenced with specific equations of state at our experimental conditions. However, diffusion coefficients through quartz will be slightly higher for H_2O than D_2O. Both, synthesis and re-equilibration are carried out under hydrothermal conditions without a pressure gradient. The initial synthesis and the subsequent re-equilibration are performed each at the same experimental conditions.

To clarify the emphases of the above mentioned fluid inclusions attributes two different series of re-equilibration experiments are performed, as examined: **1)** time-dependent series, i.e. different experimental running-times; **2)** temperature-dependent series, i.e. different formation and re-equilibration temperatures.

Results

The gradient in the chemical potential of the entraped H_2O and the external D_2O is a driving force for diffusion of these species through the quartz crystal at constant *P-T* conditions. Fluid inclusion size and depth play an important role in relative short experiments. Fluid inclusion shapes change from irregular to regular and equant in all experiments. The diffusion of H_2O and D_2O increases rapidly between 400 and 500 °C at 337 MPa. At a geological time scale, fluid inclusions in deep rock should re-equilibrate instantanously to new pore-fluid conditions, if the grain that contains these inclusions is completely enclosed by the pore-fluid.

High resolution reservoir age reconstructions from cold-water corals in the North-eastern Atlantic during the Holocene (~ 1700 – 4800 cal yr BP)

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Coupled U-series and radiocarbon dating were performed on cold-water corals (*Lophelia pertusa*) from the North-eastern Atlantic. The coral fragments come from 2 sediment cores (+56-08/929VE and +56-08/930VE with 3.61 m and 5.25 m recovery, respectively) retrieved from shallow inshore coral reefs from the Mingulay Reef Complex (~56°N, 7°W and 120-190 m water depth).

The 40 U-series dates show that coral fragments within the cores are in chronological order and span the mid-late Holocene (1700 - 4800 yr BP). The sediment cores show exceptionally high accumulation rates around 5 - 6 mm yr^{-1} which is higher than those estimated for reefs along the Norwegian shelf (2 - 3 mm yr^{-1}) and an order of magnitude greater than from the coral carbonate mounds of the European continental margin (~ 0.2 mm yr^{-1} for the Holocene).

Reservoir ages were reconstructed from 18 paired U-series and ^{14}C dates measured on the same coral fragments. This high resolution dating, about one analysis every 150 yrs, allows reconstructions of high frequency changes in ventilation and ocean circulation patterns in this region. The reservoir ages estimated range from 240 yrs to 700 yrs with a mean value around 400 years. Our results also suggest cyclic circulation changes in the North-eastern Atlantic: 3 periods, around 2800, 3300 and 3700 yr BP, are characterized by lower values 240, 260 and 290 yr, respectively. One prominent increase of reservoir age is observed at about 3250 yr BP with values reaching 700 yr. The lower reservoir ages are relatively well correlated with lower $\delta^{18}O$ values recorded by planktonic foraminifer *G. bulloides* and reduced coral reef accumulation rates within the Mingulay Reef Complex.

This study suggests that cyclic circulation changes occurred in the North-eastern Atlantic during the mid-late Holocene every 400 - 500 yrs. Further studies with records of similar resolutions would be needed to determine if these changes in reservoir ages are related to local and/or global environmental changes. This study demonstrates that cold-water corals constitute a powerful alternative to provide accurate reservoir ages with unprecedented temporal resolutions.

A clumped isotopes perspective on sea surface temperatures in the Eocene southern high latitudes

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Recent studies of high southern latitude sea surface temperatures during the Eocene Epoch have suggested that very warm temperatures, possibly exceeding 30° C, extended to the Antarctic margin[1,2]. These results could have profound implications for understanding polar amplification of greenhouse warming. However, there are large uncertainties associated with the temperature proxies applied in these studies, due either to unconstrained seawater chemistry (in $\delta^{18}O$ or Mg/Ca) or ambiguity in selecting the appropriate TEX_{86} calibration. Clumped isotopes paleothermomtery is a thermodynamically controlled temperature proxy that does not depend on the isotopic compositions of seawater, and presents a novel opportunity to reduce uncertainties in Eocene SST estimates.

We measured clumped isotopes in Eocene bivalves from two southern high latitude localities: Seymour Island, Antarctica (~65° S paleolatitude) and the South Island of New Zealand (~55° S). Middle to late Eocene (45 to 35 Ma) paleotemperatures at Seymour Island range from 18 to 11°C. Analyses of New Zealand bivalves indicate a temperature decrease from ~26°C to ~20°C between the early and middle Eocene (49 to 40 Ma). These temperature estimates are most consistent with TEX_{86} paleotemperatures from New Zealand and the East Tasman Plateau calculated using the $TEX_{86}L$ calibration[3], supporting the use of this calibration in the Eocene southwest Pacific and possibly other high latitude regions.

Clumped isotope paleotemperatures suggest that New Zealand was approximately 7°C warmer than Seymour Island during the middle Eocene. This difference points either to a sharp meridional temperature gradient or to zonal heterogeneity in southern high latitude SSTs related to different paleocurrent systems influencing the southwest Pacific and southern Atlantic. Paleotemperatures from the East Tasman Plateau suggest that this temperature difference persisted into the late Eocene.[1]

Coupled clumped isotope and $\delta^{18}O$ measurements in bivalves also provide an estimate of the oxygen isotope composition of coastal seawater. At Seymour Island $\delta^{18}O_w$ values are generally within error of the ice free latitude-corrected value of -1.2‰[4]. However a marked decrease to values less than -3‰ around 41 Ma suggests a pronounced hydrologic change. In New Zealand, mean $\delta^{18}O_w$ estimates increase from -1.4‰ in the early Eocene to -0.8‰ in the late Eocene. This shift could suggest an increase in coastal salinity to normal marine conditions, either due to decreased continental runoff or a change in surface paleocurrents.

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[3] Kim et al., (2010) *Geochim. Cosmochim. Acta* **74**, 4639-4674.
[4] Zachos et al., (1994) *Paleooceanography* **9**, 353-387

Refertilisation of the Hawaiian oceanic lithospheric mantle

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A suite of fresh spinel peridotite xenoliths from the Island of Kaula, Hawaii erupted ~3 Ma ago and offer the opportunity to characterise the composition of the oceanic lithosphere and its metasomatic history. Peridotite xenoliths from continental and oceanic lithosphere often indicate early partial melting in which "basaltic" components were removed from the system, followed by varying degrees of metasomatic enrichment in incompatible trace elements.

Depletion of basaltic components in the Kaula samples is well demonstrated by the whole rock major element chemistry. Whole rock MgO wt% ranges from 40.52-45.24 and has strong negative correlations with basaltic components such as Na_2O (0.10-0.33 wt%), CaO (0.69 – 2.41 wt%) and Al_2O_3 (0.78-2.46 wt%) and a positive correlation with Ni (2129-2454 ppm). In particular, the low CaO and Al_2O_3 (<2.5 wt%) indicate relatively refractory compositions, compared with fertile peridotite.

In contrast, trace elements in clinopyroxenes show strong positive correlations between HFSE such as Ti and the HREE. Samples that depart from this trend have elevated LILE contents, in particular Ba (>1 ppm *vs.* an average of 180 ppb) and Pb (>1 ppm *vs* an average of 300 ppb).

The enrichment in trace elements and the relationships between them suggest two distinct types of mantle metasomatism that are possibly related to localised refertilisation of the lithosphere by low degree partial melts of crustal components, within a broader scale metasomatic overprint linked with plume magmatism.

"Natural toxicant" is not an oxymoron. Earth and health scientists need to meet.

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Large parts of Canada may be characterized by natural enrichments in toxicants having a potential to harm health. Originating in bedrock and environmentally re-distributed in air, water, and soil, such toxicants include metals (e.g., Cr, Ni, Cd, Hg), metalloids (e.g.,As), radioactive elements (e.g., Rn, U) and organic compounds (e.g., coal, PACs). Large areas in Alberta, Ontario, New Brunswick, Nova Scotia and Newfoundland with elevated natural arsenic in lake sediments and water. Fluorite elevated in Waterloo, Ontario. Sporatically across Canada areas underlain by chromium and nickel bearing rocks enriching soils and drinking water. Arsenic and uranium in lake sediments (water) on Melville Peninsula in Inuit hunting grounds.

Far from trivial, these naturally occurring toxicants have the potential to cause morbidity (carcinogenic and non-carcinogenic disease) that exceed those that would develop from 'a pack a day' smoking habit.

Despite its potential to inform on the nature and extent of natural toxicants, and their health costs, the earth sciences remain poorly integrated with current approaches to environmental, ecological and human health protection.

All of these toxicants are naturally occurring, present in the environment at levels that will cause harm to human health and despite each toxicant being listed Health Canada's Priority Substance List 1, there is little research in their occurrence. Health officials are not aware they exist, earth scientists are unaware of the implications of their existence. It is time for earth and health scientists to meet.
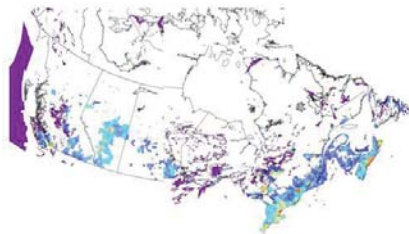

Figure #1: Risk of exposure to nickel and chromium in soil, water, food. Population (2006) of Canada living on rocks that contain chromium and nickel (mafic, ultramafic rocks) . Rocks based on Wheeler's (1997) Scale: 1:7,600,000. Blue, yellow, range polygons delineate census areas (Statistics Canada, 2006).

1. **Wheeler,G.M.,** *1997 Geological Map of. Canada. Geological Survey of Canada*, Map D1860A.
2. **Statistics Canada,** 2006. *Statistics Canada Website*. Census http://www12.statcan.ca/english/census06/reference/dictionary/tables/table1-dictionary.htm Accessed November 20, 2008.

Evidence of ocean acidification viewed by boron isotopes and B/Ca in scleractinian corals

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The monitoring of ocean acidification (seawater pH fall due to rising anthropogenic CO_2 in the atmosphere) is mainly based on three 20-30 years long pH records: ALOHA at Hawaii in the central North Pacific, BATS at Bermuda in the west North Pacific and ESTOC at Canary Islands in the eastern North Atlantic. The current acidification rate of the surface waters deduced from these records is well established at -0.018 ± 0.001 pH-units/yr [1]. This trend is in good agreement with model projections. However the impact of ocean acidification on marine biology and ecosystems, in particular on key marine species such as foraminifera, corals, pteropods, bryozoan and molluscs still remains poorly constrained and further quantification of pH fall and its impact is needed for the high latitudes and the deep environments. While ocean acidification, since the start of the industrial era, was estimated at around -0.07 pH-units for tropical surface waters, the pH decrease since 1870 could reach values higher than 0.15 pH-units at high northern and southern latitudes.

It has been suggested that the isotopic composition of boron trapped in marine biogenic carbonates can be used to infer the pH of the ambient seawater [2]. Since the publication of this pioneering paper, a number of studies have 1) investigated the existing relationship between boron isotopic composition of carbonates (foraminifera, corals) and seawater pH in order to "calibrate" boron isotopes as pH-proxy and 2) used boron isotopes to reconstruct paleo pCO_2 over the Quaternary and further, for the whole Cenozoic. With the development of analytical techniques to measure precisely B-isotopes by MC-ICPMS, intense studies become feasible to precisely quantify ocean acidification over the industrial era using corals.

With the aim to reconstruct the major carbonate chemistry changes of the ocean, we analyzed the B-isotopic composition of long-lived sub-equatorial Pacific surface corals (*Porites* sp.) and Atlantic mid-depth dwelling cold-water corals (*Lophelia pertusa* and *Madrepora oculata*). Boron isotopes were here measured using MC-ICPMS. Our results demonstrate that boron isotopes in scleractinian corals are sensitive to small ambient seawater pH changes and can thus be reliably used to quantify past ocean acidification. The B-isotope results will be discussed together with B/Ca ratios to enlighten the crucial role of temperature in the paleo-pH reconstructions. Finally, a few examples of quantification of the anthropogenic pH fall during the twentieth century will be presented and compared to expected trends for the surface waters of the Pacific Ocean and for the intermediate waters of the North Atlantic. This research was supported by the European integrated project EPOCA and the French INSU/LEFE/CYBER project PHARE.

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The influence of mineralization pathway on composition and isotope signatures in calcite

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Chemical proxy models are based upon the assumption that isotopic signatures and concentrations of minor and trace elements reflect equilibrium fractionation processes that occurred during mineralization. This picture is rooted in the fundamental assumptions of BCF crystal growth theory— a thermodynamic-based model that was derived for step growth at very near equilibrium conditions. However, the applicability of these assumptions are being called into question with the realization that many carbonate biominerals form by non-classical processes. Here, mineralization begins with accumulation of amorphous calcium carbonate (ACC) in a localized environment that subsequently transforms to the crystal/organic composites we know as skeletal structures. It is not yet known 1) if the transformation involves classical microscopic dissolution-repreciptation or an altogether different type of process and 2) the consequences of this process for composition and isotopic signatures.

This study investigates the influence of the ACC to calcite pathway on the Mg content and isotopic signature of calcites. For low solution levels of Mg/Ca, Mg content is insufficient to inhibit step growth and ACC transforms into crystallites of Mg calcites that exhibit the expected linear fractionation with Mg/Ca of initial solutions (0-20 mol% $MgCO_3$). In contrast, when initial Mg levels are above the threshold for step growth, ACC transforms to nanoparticle aggregates of very high Mg calcite (30-50 mol% $MgCO_3$). The Mg content of calcites formed by this process is independent of solution chemistry, without evidence of fractionation. The data suggest mineralization is biased to the alternative pathway when the Mg level in the local environment is too high for significant calcite growth beyond nanoparticle sizes. This pathway is allowed because high levels of supersaturation render thermodynamic barriers to nucleation less significant than the larger kinetic barriers. Thus, the alternative pathway is a consequence of interplays between kinetic and thermodynamic factors.

Parallel experiments used enriched isotope labels (43Ca and 25Mg) to distinguish dissolution-repreciptation from direct conversion during the ACC to calcite transformation. When solution Mg/Ca is low calcite assumes the isotopic label of the growth media consistent with a dissolution-repreciptiation pathway. In contrast, very high Mg calcites that grow from high Mg solutions retain a portion of the ACC isotope signature. This suggests the transformation of high Mg ACC occurs by an alternative pathway that involves a substantial fraction of direct transformation. Collectively our data show that mineralization pathway dramatically affects composition. This type of mechanistic understanding of mineralization processes will be necessary to explain proxy behavior and more accurately reconstruct past environental conditions.

Constraining dehydration rates during regional metamorphism, Townshend Dam, Vermont, U.S.A.

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Progressive dehydration during regional metamorphism can result in pervasive or channelized fluid flow. Given sufficient fluxes, fluid flow may have profound effects on rheological properties of the rock, bulk rock composition, stable and radiogenic isotope compositions, mineralogy, and the kinetics of mineral reactions. Many published studies have used petrologic and stable isotopic data to constrain time-integrated syn-metamorphic fluid fluxes. Here, an integrated geochronologic and thermodynamic anaylsis is used to estimate the dehydration rate and flux during metmorphism of a pelitic schist from Townshend Dam, Vermont.

Microdrilling based on Mn growth zoning, from large (1-3 cm) garnets from one sample, provides information on the rate and duration of garnet growth. Three to six concentric zones (depending on crystal size) of garnet, were sampled for ID-TIMS Sm-Nd geochronology. A partial dissolution procedure was utilized in order to remove inclusion phases from garnet fractions which were analyzed as NdO+ with Ta_2O_5 activation. This yielded clean garnet, with $^{147}Sm/^{144}Nd \leq 3.18$. Garnet-matrix isochron ages of individual garnet zones have been previously reported [1], with the duration of garnet growth across the sample ranging from 5.5 to 11.7 Ma, and an average duration of 7.8 Ma.

Garnet growth may be linked directly to dehydration during regional metamorphism. Thermodynamic analysis of this reaction allows calculation of the stoichiometric ratio between garnet formation and water release. The garnet:water ratio depends on the growth reaction, and the P-T path during growth. In our sample, the average water:garnet molar production ratio is 3.3:1 over the duration of garnet growth. Early garnet growth involves the consumption of chlorite, resulting in initially higher water:garnet ratio. Both thermodynamic and textural analysis have determined that ~ 5.5 vol% garnet was formed during the age span stated above. This equates to a release of 1 wt% (or 2.8 vol%) water during garnet formation, similar to water volumes estimated in previous studies from southeastern Vermont [2]. Using the duration of growth (5.5 to 11.7 Ma), a time-averaged dehydration rate of 1.3 to 2.8 x 10^{-10} moles of water/ cm^3 of rock/ year can be calculated.

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Global-scale changes in Hg cycling during glacial-interglacial transitions

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Abstract

Records of Hg in ice cores from Dome C indicate elevated Hg deposition to Antarctica during cold periods (glacials, stadials) of the Late Quaternary [1, 2]. Hypotheses to explain this phenomenon ultimately center on coincident increases in deposition of soil dust (of South American origin). Vandal et al. [1] suggested dust-driven increases in productivity of the Southern Ocean resulted in increased oceanic Hg^0 evasion, whereas Jitaru et al. [2] argued cold conditions facilitated efficient scavenging of atmospheric Hg onto dust particles. We will present data from additional geologic archives (sediments, ice) that challenge these hypotheses and, further, indicate glacial-interglacial transitions resulted in global-scale changes in Hg cycling. A 40,000-year sediment record from Lake Titicaca (Bolivia/Peru) (corrected for detrital Hg inputs) shows elevated Hg deposition during the Last Glacial Maximum – in remarkable agreement with the extent and timing of the Dome C record. However, there is not enough Hg in the atmosphere and surface ocean even today that could be redistributed to account for the absolute increase in deposition to Lake Titicaca. An additional source of Hg to the system is required, and one possibility is the massive reservoir of Hg in the solid earth. Volcanism was initially dismissed as a source of Hg to Dome C, based on an inadequate amount of non-seasalt sulfate in glacial ice to explain Hg increases [1, 2]. During the Last Glacial Maximum, however, lowered sea level could have acted to depressurize shallow volcanic and hydrothermal systems, encouraging greater activity [3]. Submarine volcanism would add Hg to the ocean, which could later be mobilized to the atmosphere, decoupling it from sulfate and other non-volatile tracers of volcanic activity. We will explore this hypothesis by constraining Hg fluxes from submarine volcanism during glacial and interglacial periods, as well as by comparing the records from Dome C/Lake Titicaca to other Late Quaternary records (reconstructions in progress for GISP-2, Cariaco Basin, Lake Baikal). This work may provide the basis for using Hg as a paleo-proxy of large-scale geophysical/climate change.

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Construction of a Fully Searchable Soils Database Integrating Soil Characterization Data and Whole-Soil Geochemical Data

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Paleopedological studies rely heavily on the use of contemporary soil characterization and whole-soil geochemical data [1, 2, 3]. These soil science resources serve the needs of paleopedologists who reconstruct ancient climate and soil systems using models to relate modern physical/chemical soil characterization data, whole-soil geochemical data, and climate parameters [3, 4, 5]. The (paleo)pedologist currently faces a "data overload" problem due to a number of global and continental-based soil geochemical databases becoming widely available. The overwhelming nature of the available data makes model construction difficult and time-consuming. The emerging field of data analytics addresses the overload problem by providing a systematic process for data acquisition, cleaning, initial analysis and main analysis. We used a data analytics approach to construct the Baylor Paleosol Informatics Cloud (BU-PIC). The BU-PIC uniquely combines: (1) USDA-NRCS pedon data, (2) PRISM-based climate parameters, (3) NLCD land-cover attributes, and (4) published paleosol data. This aggregation of data will allow paleopedologists to upload standardized geochemical data and test and refine soil-derived paleoclimate proxies and paleopedotransfer functions. Although BU-PIC development is in the initial stages of data cleaning, preliminary analysis shows promising results. For example, variations in whole-soil weight % Fe_2O_3 explain approximately 76% of the variance in % Fe_d (pedogenic iron) in all soil horizons spanning 4000 pedons, and variations in whole-soil weight % CaO explain approximately 86% of the variance in $CaCO_3$% in 865 pedons (A and B horizons only, no gypsum). This may be useful for paleopedologists interested in determining the amount of pedogenic iron and pedogenic carbonate within a lithified paleosol. Binning by specific soil orders and soil textural classes suggests that proxies can be improved by separation rather than aggregation seeking "universal" proxies. We believe the success of BU-PIC will rely on building rapport with modern soil scientists while seeking their consultation during the developmental stages. [1] Sheldon, Retallack & Tanaka (2002), *Journal of Geology* 110, 687-696. [2] Driese et al. (2005) *Journal of Sedimentary Research* 75, 339-349. [3] Nordt & Driese (2010), *Geology* 38, 407-410. [4] Nordt & Driese (2010), *American Journal of Science* 310, 37-64. [5] Nordt, Dworkin & Ashley (2011) *GSA Bulletin* 123, 1745-1762.

Towards reconstructing climate and ecosystem for paleoVertisols using bulk geochemistry

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Whole-rock molecular oxides, especially the Chemical Index of Alteration Minus Potassium (CIA-K) have been popularly used in the paleosol community for reconstructing climate, especially mean annual precipitation (MAP) [1, 2]. Initial approaches were universal, aggregating soil geochemical data from widely disparate soil types (e.g., soil orders, soil textural classes, soil ages, etc.). Because CIA-K $(Al_2O_3/(Al_2O_3+CaO+Na_2O)*100)$ is fundamentally an index of clay formation and base loss related to feldspar weathering, it is inappropriate for one soil order that is especially well-represented in the rock record as paleosols, namely, the Vertisols, which are high clay-content soils (typically smectite mineralogy) that have a high shrink-swell potential, and commonly form from alluvium that has been "pre-weathered". Recent advances in developing MAP proxies specific for paleo-Vertisols, such as the new CALMAG index $(Al_2O_3/(Al_2O_3+CaO+MgO)*100)$, have not only improved MAP estimates [3, 4], but have lead to understanding potential use of bulk geochemistry and modern soil characterization data to develop pedotransfer functions for reconstructions of colloidal soil properties such as pH, CEC, Base Saturation, etc. [5]. Carrying this a step further are ecosystem reconstructions of paleosols that evaluate soil conditions influencing net primary productivity using geochemical proxies [6]. Noteworthy is reconstruction of organic C and N in paleo-Vertisols using pedotransfer functions developed using ppm Pb in modern Vertisols [7]. The limits of application of bulk geochemistry to paleosols are as yet unknown, but it is clear that our approach for analyzing separate soil types has merit. We are currently developing a soil database that contains over 1500 US pedon and 6000 soil horizon records that can be queried using different soil wet-chemical and geochemical (whole-soil) parameters to predict specific conditions. Our initial attempts with circa 40 US Vertisol pedons to develop several new proxies specific to paleoVertisols provide more uniform MAP estimates than using CIA-K, as demonstrated by specific examples from Mississippian, Triassic, and K/T boundary paleosols. [1] Sheldon, Retallack & Tanaka (2002), *Journal of Geology* 110, 687-696. [2] Driese et al. (2005) *Journal of Sedimentary Research* 75, 339-349. [3] Nordt & Driese (2010), *Geology* 38, 407-410. [4] Adams, Kraus & Wing (2011) *Palaeo*[3] 309, 358-366. [5] Nordt & Driese (2010), *American Journal of Science* 310, 37-64. [6] Nordt, Dworkin & Ashley (2011) *GSA Bulletin* 123, 1745-1762. [7] Nordt et al. (2012) *Geochimica et Cosmochimica Acta* (accepted).

Wind-driven diurnal variability in freshwater surface microlayer biogeochemistry

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Introduction

Understanding the compositional dynamics of the surface microlayer (SML) at the air-water interface of surface waters is critical because of its role in regulating the exchange of matter between the atmosphere and hydrosphere [1,2]. Temporal variability in SML biogeochemistry is poorly understood, particularly with respect to changing physico-chemical conditions. The objective of this study was to examine the geochemical and microbial composition of the SML and underlying water column (0.5 m depth) in two contrasting freshwater environments (Sunnyside Beach, Lake Ontario, a littoral hard water environment heavily impacted by anthropogenic inputs; Coldspring Lake, a pelagic environment in a small (<1 km²) and relatively pristine soft water lake) over a diurnal timeframe during the summers of 2010 and 2011.
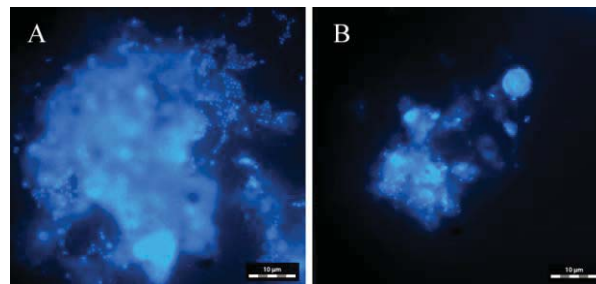

Figure 1: Fragmentation of SML microbial aggregates with increasing wind speed (from A to B, DAPI stained).

Results and Conclusion

Diurnal variability in SML biogeochemistry was closely linked to wind speed in both environments. The visual fragmentation of microbial aggregates (Fig. 1), a reduction in prokaryotic cell numbers, and an increase in dissolved organic carbon accompanied the diurnal transition from relatively quiescent to windy conditions. These changes were not observed at 0.5 m. In both environments, SML enrichment in total particulate matter and particulate iron was negatively correlated with wind speed. Particulate iron decreased in the SML and increased at 0.5m from morning to afternoon with increasing wind speed.

Collectively, these results suggest that particulate matter, including organic carbon and iron, is enriched in the SML under quiescent conditions and undergoes fragmentation over the course of a day in concert with increased wind speed. Further, wind-driven diurnal changes in SML biogeochemistry appear to be (a) conserved between contrasting freshwater environments, and (b) distinct from changes occurring at a depth of 0.5m, highlighting the unique characteristics of the SML.

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Calcium isotope fractionation as a function of solution stoichiometry in groundwater

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While modeling predictions have suggested fluid calcium to carbonate ratio may influence the calcium isotope fractionaton factor as well as the net rate constant during calcite growth, field evidence of the macroscopic effects of solution stochiometry on precipitation rate and isotopic fractionation has been difficult to observe. Here we present some of the first evidence of solution stoichiometry influencing the fractionation in δ^{44}Ca of groundwater in a series of clogged well bores during organic carbon ammended uranium bioremediation of a contaminated aquifer in western Colorado. Secondary mineral formation induced by carbonate alkalinity generated during the bioremediation process lead to substantial permeability reduction in multiple electron-donor injection wells at the field site. These conditions resulted in removal of aqueous calcium from a backrgound concentration of 6mM to >1mM while δ^{44}Ca enrichment ranged from 1‰ to greater than 2.5‰ [Figure 1].
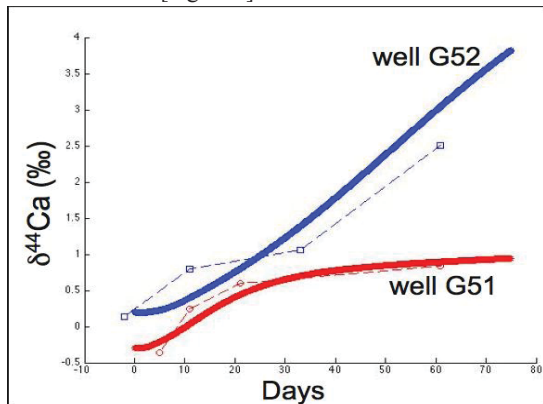

Figure 1: Data and models of δ^{44}Ca fractionation in clogged well bores as a function of time.

The variation observed in δ^{44}Ca between wells is attributed to the difference in carbonate alkalinity generated in each well bore, presenting some of the first field evidence supporting theoretical models of calcium isotope fractionation as a function of fluid $Ca^{2+}:CO_3^{2-}$ ratio. Where the $Ca^{2+}:CO_3^{2-}$ ratio remains >30 the δ^{44}Ca fractionation is accurately modeled by precipitating Ca-40 and Ca-44 as independent species in a TST-style model with carbonate formation calculated as a solid solution [Figure 1 red line]. However reproducing the observed δ^{44}Ca trend where $Ca^{2+}:CO_3^{2-}$ <30 is only accomplished by utilizing a newly developed analytical model for calcium isotope fractionation as a function of solution stoichiometry [Figure 1 blue line].

Constraining late Miocene seawater composition: a multiproxy approach

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The late Miocene (11.61–5.33 Ma) was one of the most climatically stable periods of the past 60 Myr. However, super-imposed on the stable long-term trend, short-term, 40 kyr high-amplitude changes in δ^{18}O are observed that suggest Milankovitch forcing of seawater δ^{18}O composition, temperature, or both. Understanding seawater composition evolution during this time could offer insight into the natural variation of important climate parameters, such as ice volume and sea surface temperatures.

The goal of our study is to reconstruct seawater δ^{18}O composition at different levels in the water column across the late Miocene (3.50-8.50 Ma). The study site is located in the Eastern Equatorial Pacific (Site U1338), and samples were collected during IODP Expediton 321. Understanding temporal changes in Equatorial Pacific seawater temperature and compostion is critical due to the importance of the low-latitude regions for global ocean circulation. Reconstructing $\delta^{18}O_{seawater}$ will be achieved by combining multiple geochemical proxies on benthic and planktic foraminifera. Here we present preliminary δ^{18}O and δ^{13}C data from the benthic foraminifera *Cibicidoides mundulus*. The data's long-term trends reflect global patterns, which implies the site is suitable for a high-resolution seawater composition study. Our ultimate target resolution is 3-4 kyr, which allows resolution of ~20 kyr orbital cycles. As $\delta^{18}O_{calcite}$ from benthic foraminifera is a function of both $\delta^{18}O_{seawater}$ and calcification temperature, the $\delta^{18}O_{calcite}$ will be combined with Mg/Ca and Li/Ca measurements, both temperature proxies, to reconstruct $\delta^{18}O_{seawater}$.

A second component of future work is to reconstruct temporal changes in surface water δ^{18}O and Mg/Ca by combining traditional stable isotope and trace element measurements with a novel proxy called clumped isotopes. The 'clumped isotope themometer' Δ^{47} reflects the amount of rare, heavy stable isotopes ^{13}C and ^{18}O bound together in the carbonate crystal lattice. Δ^{47} shows an inverse relationship with temperature, as more ^{13}C-^{18}O bonding occurs at lower temperature. The initial T-Δ^{47} calibration was based on inorganic calcite, however a recent study has shown that foraminiferal and coccolithophore calcite shows the same T-Δ^{47} relationship and is not affected by 'vital effects'.

We will present initial data comparing Δ^{47} measurements on the fine fraction (predominantly consisting of coccolithophores) to Mg/Ca and δ^{18}O measurements on planktic foraminifera (*Globigerinoides sacculifer*). By measuring Δ^{47} on samples consisting mainly of planktic material, we will be able to deconvolve sea surface temperature from secular changes in Mg/Ca and δ^{18}O seawater values measured in planktic foraminiferal calcite.

Geochemical modeling of lung fluid-mineral interactions: Highlighting fundamental knowledge gaps

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Minerals respired into lungs are known, from a number of epidemiological studies and historical accounts, to have significant human health effects when the dose is high. These health effects often have latency periods of tens of years before symptoms manifest. Geochemists and mineralogists can contribute towards an understanding of how these diseases work in considering mineral interactions in the lung as a fluid-mineral interaction problem. We have performed a series of fluid-mineral interaction models utilizing the Geochemist's Workbench modeling platform, considering thermodynamic, kinetic, and fluid flow parameters towards the dissolution of a set of commonly encountered minerals. Employing rate laws from the literature, we calculated possible residence times of minerals in the lung and found that those times and possible mineral reactions products were sensitive to dose, particle size, lung fluid composiiton, and the flushing rates of fluid across particles in the lung [1].

These calculations bring into light some fundamental parameters that are poorly defined but are important in our ability to define how minerals behave in human lungs over decadal scales. While some reaction rates for minerals are defined in fluids of similar composition to lung fluids [2], many mineral rate laws are not well defined for these conditions. The composition of lung fluid itself is also not well defined with respect to some fundamental chemical speciation, noteably the speciation of phosphorus, and the organic speciation of many key cations for whose activity these calculations of mineral reactivity need to be defined. Additionally the physiological role of fluids flushing past minerals is largely undefined in the human lung, and may have a significant role in the biodurability of minerals.

Within this context as well we can consider how mineral reactivity may be linked to cellular damage and the initiation of fibrotic diseases and cancers. Mineral reactivity can affect cells directly or can affect the biochemical environment cells function in through possible surface reactions that generate reactive molecules (often readicals), sorption of key biomolecules, or changes in the surrounding pysicochemical environment these cells reside in. Some of these reactions may be quite different if we consider the immediate reactivity of a mineral when it enters the lung and becomes whetted by lung fluid v. the reactivity of a mineral and potential secondary minerals forming on dissolution of that mineral over decades. We will discuss the results of our modeling study and what they have brought us to consider about the future state of mineral reactivity and lung fluid interactions.

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Effect of fertilizing soil with Selenium on trace element uptake by kenaf (*Hibiscus cannabinus*)

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Fertilizing food and feed crops with Selenium (Se) fertilizers can result in an increased uptake of Se by the crops, which may be beneficial for humans and animals consuming these crops. However, assessing nutritional quality of Se-enriched crops includes not only studying uptake of Se by the crops, but also how the uptake of other trace elements is affected by fertilizing the soil with Se fertilizer. Therefore, we fertilized three types of soils with two types of Se (Selenate and Selenite, 1 mg Se kg^{-1} added to the soil) and studied the uptake of Se, Cd, Cu, Mn, Ni, Pb, Al, Fe, and Zn by kenaf (*Hibiscus cannabinus*), an indicator plant species for Se, grown on these soils. The three soils were clayey, loamy and sandy, and originally contained 0.50, 0.28 and 0.29 mg Se kg^{-1} dry mass, respectively. Afterwards, we conducted this experiment again on loamy soil using different application doses (0.5, 1, 2 and 4 mg Se kg^{-1} added to the soil).

Applying Selenate resulted in the highest increase of Se concentrations in the crop, with the highest accumulation being obtained on sandy (477 ± 77 mg kg^{-1}) and loamy (518 ± 97 mg kg^{-1}) soil, whereas Selenite performed best on a sandy (107 ± 17 mg kg^{-1}) and a clayey (122 ± 23 mg kg^{-1}) soil. Applying Selenate affects also significantly the concentrations of the other metals in crops grown on the loamy soil, but not in crops grown on the clayey and the sandy soil. When the Se application dose is varied on the loamy soil, Zn is already affected from an application dose of 0.5 mg Se kg^{-1}. The concentration of Al starts to be also affected from 1 mg Se kg^{-1}, and the concentrations of Fe, Mn and Pb also from 2 mg Se kg^{-1}. The Cu concentration is affected from a dose of 4 mg Se kg^{-1} onwards. The Al concentration clearly decreases with increasing application dose of selenite, whereas changes are less clear upon application of selenate. Zn, Pb and Fe concentrations are always reduced when applying selenite. Upon application of selenate, they are also lower than the control concentrations at the lower application doses (until 2 mg Se kg^{-1}), but they are elevated at the highest application dose (from 4 mg Se kg^{-1}). This may be related to reduced plant growth observed when selenate is used at its highest application dose. Mn concentrations are not affected when applying selenite, but they are reduced when applying selenate. Our findings illustrate that different metals respond to Se application in a different way.

Experiments with other crops and other Se fertilizers, including Se nanoparticles, that also focus on effects on Se mobility in the soil and the effects of ageing, are still ongoing. Results of these experiments will also be presented.

EXAFS analysis of crystal chemistry of Ni in a lateritic weathering profile from New Caledonia

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Weathering of ultramafic rocks under tropical conditions in New Caledonia yield lateritic profiles where metals, mainly Ni, are concentrated to economically valuable contents. The vertical distribution of Ni in these lateritic ores was investigated by analysing Ni K-edge EXAFS data along a 64 m depth lateritic weathering profile, to determine the quantitative role of the various minerals on the crystal-chemical behaviour of Ni upon weathering of ultramafic rocks. Three main units were identified from the bottom to the top of the weathering profile, i.e. the bedrock, the saprolite and the laterite. Our results show that Ni is mainly hosted by primary silicate minerals (olivine and serpentine) in the bedrock, while it is mainly incorporated in secondary phyllosilicates and Fe-oxides (goethite) in the saprolite unit, and in goethite within the upper laterite unit. A small part of Ni is also hosted by Mn-oxides at the bottom part of the laterite unit (transition laterite) which is rich in Mn-oxides. Actual modes of association of Ni with all these mineral species yield interesting information about the behaviour of this element during the lateriric differentiation. Ni content and distribution change within the phyllosilicates from the bedrock to the overlying saprolite, suggesting that several generations of these minerals have formed under different weathering conditions. Moreover, the ubiquitous occurrence of Ni-bearing goethite along the studied lateritic regolith emphasizes the major role of this mineral species on Ni speciation at the different weathering stages. This result suggests that Fe-oxides represent the ultimate host for Ni upon tropical weathering of ultramafic rocks in New Caledonia.

Trace metal complexation and dissolution by the triscatecholate siderophore protochelin

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Recent evidence has shown that siderophores, biogenic agents generally viewed as iron uptake agents, may play significant roles in the biogeochemical cycling and biological uptake of metals other than iron. For example, the triscatecholate siderophore protochelin, which is produced by the diazotrophic bacteria *Azotobacter vinelandii*, has been implicated in the uptake of non-ferrous metals [1]. To better understand the effect of catechol siderophores on metal cycling and uptake, we examined the solution chemistry of protochelin, its ability to promote the dissolution of metal oxides, and structure and stability of complexes with environmentally relevant trace metals.

Free protochelin was found to be unstable, decomposing in solution on the timescale of hours to days. Additionally, it is sparingly soluble at pH < 7.5. Electrochemical measurements of protochelin and metal-protochelin complexes revealed a ligand half-wave potential of 200 mV, but no electrochemical activity was observed for the metal centers. These results help to explain patterns in the rates and products of protochelin-promoted dissolution of metal hydroxides.

The structure and reactivity of metal-protochelin complexes was probed by spectroscopic, computational, and chemical methods. The $Fe(III)Proto^{3-}$ complex exhibits a shift in coordination mode at circumneutral to acidic pH, as has been observed for structurally related siderophores [2]. The $Mn(III)Proto^{3-}$ complex was found to have a stability constant approximately three orders of magnitude lower than for $Fe(III)Proto^{3-}$. Cobalt-protochelin complexes undergo redox cycling of Co with concommital siderophore degradation. Structural parameters derived from compuational and spectroscopic methods provide insights into the stability of the metal-protochelin complexes. These results suggest that common metals may affect the biological uptake of metals by protochelin, and that unique properties of the siderophore may affect its dissolution reactivity and the mechanisms of intracellular metal release.

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Multi-scale segmentation of global continental and coastal waters: typological analysis and application to the carbon budget

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Abstract

The coastline of the Earth is over 400 000 km long and about 40% of the world's population lives within 100 km of the coast. Segmentations of the global coastline and their classification into various coastal settings can be derived from a continental perspective based on an analysis of river basin properties (COSCATS) [1], from an estuarine point of view (typology of estuarine systems) [2] or from an oceanic perspective, constructed around a regionalization of the near-shore and distal continental margins (LME) [3]. Here, we present an overview of recent efforts to characterize the whole aquatic continuum using comprehensive geographical units which retain the most important physical characteristics of the land/river, near-shore, and shelf areas.

Geographic and hydrologic parameters such as the surface area, volume and fresh water residence time are calculated for each coastal unit. Next, a multi-scale typological analysis is used to classify river basins, estuaries and continental shelf seas according to climatic, lithologic, morphologic and hydrodynamic criteria of both land and sea.

We combine the different approaches with global databases (GLORICH, GlobalNEWS, SOCAT) to extend the quantification of lateral carbon and nutrient fluxes and establish regional carbon budgets. Applications relate to coastal sciences at local, regional or global scales (e.g., budget calculations, model parameterisations, scaling of local estimates) such as i) GIS-based modeling of carbon routing showing e.g., that 2/3 of the organic carbon delivered by rivers transit through estuarine filters where further processing occurs while the remaining 1/3 directly reaches continental shelf seas, ii) regionalized estimates of the contribution of estuarine systems (small deltas, tidal systems, lagoons, fjords) and continental shelf seas to atmospheric CO_2 exchanges, iii) first steps towards a regionalization of the coastal CH_4 fluxes to the atmosphere.

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Using garnet to record mineralization in a BIF hosted orogenic Au deposit

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The origin of Archean banded-iron formation (BIF) hosted Au deposits are enigmatic and remain highly controversial. Although they are classified as an orogenic Au deposits, the origin of the fluids (magmatic vs. metamorphic) is still in discussion. In an attempt resolve this debate, we present major and minor element compositions of garnet determined by LA-ICP MS and EPMA, from the Musselwhite deposit in the North Caribou greenstone belt, Western Superior Province. The deposit occurs within meta-(chemical) sedimentary rocks, which are enveloped by amphibolite grade mafic to ultramafic rocks. Samples were collected from auriferous garnet -grunerite schist, footwall and hanging wall schist in the mine, as well as auriferous schist from north of Opapimiskan Lake. A sample was also collected from the non-mineralized chemical sedimentary bed that is continuous 24 km from the deposit. Major elements of garnet from mineralized rock show Mn-rich cores (18-25 % Sps component) and Mg (8-15 % Pyp component) and CaO rich rims. The latter is atypical for normal growth zoning in garnet. Mineralized samples show high Eu/Eu* values ranging from 6.34-1.26 in the ore zone in the mine to ~1 to 2.98 from north of Opapimiskan Lake. Low Eu anomalies occur in the non-mineralized sample (Eu/Eu*= 0.706-2.19). The majority of garnet grains show high HREE concentrations with a mean $(Sm/Lu)_{CN}$ value of 1.6 and low LREE (ΣHREE/ΣLREE = 41). Rims of garnet from mineralized samples show large variation in Ni/MgO from ~ 0.14 to 15.5, and Y concentrations from ~ 0.89 to 198 ppm. The high Ni and low MgO are recorded in the core of these grains from the ore zone, whereas their rims show low Ni. Trace element zonation in garnet from the non-mineralized rocks is minor compared to the auriferous samples. The data suggest that garnet growth was contemporaneous with the precipitation of pyrrhotite and chalcopyrite; both sulfides are closely associated with the introduction of Au. Gold-bearing fluid was derived from rocks during metamorphism or extensive alteration of mafic rocks as reflected by variably high Eu/Eu* values and calcic rich rims in the garnet crystals in the mineralized rocks. Results presented here indicate that garnet effectively records the history of hydrothermal activity associated with Au deposits and the data are consistent metamorphic fluid as the principle transporter of Au at Musselwhite.

Linear trend of mid-continent alkaline volcanism, USA: slab-edge focus

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Alkaline volcanism in the mid-continent USA includes a linear zone of Cretaceous-Tertiary kimberlite-carbonatite magmatism. Magmatism along the N40°W linear trend from Louisiana to Alberta occurs at 109-85, 67-64, 55-52, and less than 50 Ma. Magmatism along the southern part of the trend occurred at 109-85 and 67-64 Ma, and magmatism in the north occurred during the last three pulses. In Arkansas, initial Sr-Nd-Hf-Pb isotopic compositions indicate that there were at least two distinct melt sources for alkaline rocks. One end member is characterized by low $^{87}Sr/^{86}Sr$ and high $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$, similar to values of oceanic intraplate basalts interpreted as originating by melting of convecting mantle sources. The other end of the isotopic arrays extends to higher $^{87}Sr/^{86}Sr$, but most clearly lower $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ than seen in most intraplate oceanic basalts. In the north, there are three Sr-Nd isotopic groupings, with latest kimberlite-carbonatite volcanism having the lowest initial $^{87}Sr/^{86}Sr$ and highest initial $^{143}Nd/^{144}Nd$ ratios.

The position of the magmatic track roughly parallel to the western subduction margin of the North American plate, the lack of spatial age progressions of the magmatism that would be consistent with motion of North America over a fixed hot spot, and the presence of Sr-Nd-Hf-Pb isotopic and trace-element compositions that show a temporal evolution from lithospheric to asthenospheric melt-sources, suggest that this linear zone is the surface expression of mantle melting somehow connected to the behavior of the subduction system ~2000 km to the west. We propose that fragmentation of the Farallon and Kula plates, as imaged by tomography beneath North America, opened slab windows parallel to the trench, but well to the east of the convergent margin. These induced sheet-like mantle upwelling along their margins, resulting in small-degree decompression melting that produced highly alkaline magmas.

Tin sorption to magnetite nanoparticles under anoxic conditions

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The long-lived fission product ^{126}Sn is of substantial interest in the context of nuclear waste disposal in deep underground repositories. However, the redox state (di- or tetravalent) under the expected anoxic conditions is still a matter of debate. We therefore investigated sorption and oxidation of Sn(II) in the presence of a typical corrosion product, magnetite ($Fe^{II}Fe^{III}_2O_4$), with a mean particle size of 9.4 nm. In order to simulate waste disposal conditions, the experiments were performed under strictly anoxic conditions in a glovebox at <2 ppm O_2. Macroscopic parameters (pH, Eh, [Sn], [Fe]) were monitored along with redox state and local structure of Sn (X-ray absorption spectroscopy) and Fe (XPS) as a function of time, pH, and surface loading.

Magnetite rapidly sorbed Sn(II), reducing Sn concentration within 0.5 h from 10 to 0.0084 μM. Tin was strongly sorbed by magnetite across a wide pH range from 3 to 9. Reduced sorption at pH <3 is in line with electrostatic repulsion between the positively charged surface of the magnetite nanoparticles (IEP ~6.7) and cationic Sn^{2+} or Sn^{4+} complexes. The reduced sorption at pH > 9 is in line with the transition from $Sn(OH)_2^0$ to the anionic $Sn(OH)_3^-$ which occurs at pH 9. Across the pH range 3-9 and reaction periods ≥1 h, EXAFS-derived sixfold oxygen coordination and XANES edge energy positions of ~29207 eV both indicate the presence of Sn(IV) at the magnetite surface. EXAFS shell fitting as well as Monte Carlo simulations showed formation of edge-sharing complexes of Sn(IV) with FeO_6 octahedra (Sn-Fe distance of 3.15 Å), and formation of corner-sharing complexes with FeO_4 tetrahedra (Sn-Fe distances of 3.60 Å). Even after the longest reaction periods of 1 month, we did not observe incorporation of Sn(IV) into the (compatible) magnetite structure. Also, precipitation of SnO_2 was not observed in spite of supersaturation.

In order to elucidate the reaction pathway, we also studied Fe in solution and at the surface (XPS). Starting with the PZC and increasing with [H$^+$], the magnetite surface released Fe(II) into solution (0.11 g/L at pH 2). After addition of Sn(II), however, [Fe] in solution decreased as a function of Sn loading, in spite of the expected increase of structural Fe(II) due to the coupling to Sn(II) oxidation. This suggests a re-adsorption and possible re-precipitation of Fe(II) at the magnetite surface. Nevertheless, Fe(II) again re-dissolved as a function of time at low pH. With XPS we were not able to detect an adequate increase of the Fe(II)/Fe(III) ratio at the surface, supporting an electron redistribution between bulk and surface Fe centers.

In conclusion, our study demonstrates that Sn is strongly retained by magnetite across a wide pH range, forming stable surfaces complexes and stabilising the magnetite surface against dissolution.

Development of (U-Th)/He geochronology of columbite ores

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Goal

Columbite-tantalite (called also as 'coltan') belongs to the most important source minerals of high-tech elements [1]. Its genesis is mainly connected to granitic pegmatites ranging from the Archean to the Cenozoic. The major- and trace element pattern, and the formation age (typically determined by different techniques of U-Pb geochronology) [2] are used for understanding the development of the deposits, and also as diagnostic tools in provenance studies of ores. We aim to develop a double-dating procedure combining columbite U/Pb geochronology with (U-Th)/He thermochronology.

First He measurements - indications of high closure temperature

In order to avoid effects from zoning of the samples we used air-abraded multi-grain aliquots for dating. Our experiments support that the crystal lattice of columbite is tight, i.e. He is not leaking. The degassing tests were performed in an IR-laser-heated full-metal helium extraction line at the GÖochronology Laboratory. The duration and temperature needed for the complete gas release indicate that the closure temperature of columbite is higher than 250 °C. This temperature is considerably higher than the He closure temperatures of commonly used minerals like apatite ($\sim$ 60-70 °C; e.g. [3]), however, considerably lower than the closure temperature of the U-Pb geochronometer in zircon or in other oxides. Consequently, He-thermochronology of columbite can provide constraints to the post-emplacement thermal evolution and erosion history of the deposits. In consequence, the double-dating of columbite is thought to provide useful fingerprints for the provenance studies of ores.

Digestion technique

After degassing it is necessary to perform a complete dissolution of the crystals to measure precisely the U, Th and Sm by ICP-MS. In case of Ta, Nb, Fe and Mn rich solutions the precipitation and the adsorptive loss of U is a common problem. By a series of experiments on synthetic and natural columbite solutions we developed a chloride-based digestion technique that keeps the uranium and thorium quantitatively in low acid concentration solutions.

The first columbite (U-Th)/He ages

A well studied columbite specimen from Madagascar yielded a He age of 450 ± 27 Ma, which is slightly younger than its U-Pb TIMS age of 505.4 ± 1.0 Ma. In other pilot samples from African districts, the lag-times between the U-Pb formation and He cooling ages are considerably longer.

[1] Melcher (2008) *SGA News* **23**, 1-14. [2] Smith (2004) *Contrib Mineral Petrol* **147**, 549–564. [3] Farley (2002) *Rev Mineral Geochem* **47**, 819-844.

Enhanced calibration of a new natural gamma radiation technique for quantifying U, Th, and K concentrations in marine sediments

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Determining accurate concentrations of U, Th, and K in marine sediments and rocks is critical for a variety of oceanographic fields such as subseafloor microbiology, paleoceanography, sedimentology and mineralogy, and marine biogeochemistry. Rapid elemental characterization of marine cores will also enhance correlation with downhole geochemical logging. A newly developed natural gamma radiation (NGR) system aboard the Integrated Ocean Drilling Program's (IODP's) *JOIDES Resolution* research vessel provides improved measurement efficiency and lowered background signals to significantly increase the statistical reliability and quality of NGR data [1]. We are developing a combined analytical and modelling technique that converts these high-resolution energy spectra to concentrations with the use of core standards and U/K and Th/K ratios estimated from comparisons to Monte Carlo simulated and experimental spectra.

To further refine the Monte Carlo inversion technique it is critical to calibrate it by comparison to quantitatively measured concentrations of U, Th, and K in the core material. We present results based on the analysis of 38 marine sediment samples from four sites in the South Pacific Gyre recovered during IODP Expedition 329. We analyzed these sediments by ICP-ES and ICP-MS to provide a highly precise and accurate comparative data set. The ICP-ES (for K) and ICP-MS (for U, Th) data were themselves calibrated against international Standard Reference Materials and are both precise and accurate.

Our preliminary results indicate that the NGR technique captured the variability of K concentrations with depth, but systematically underestimated the absolute K concentrations by approximately a factor of two. U and Th NGR concentrations are also seen to deviate from the ICP concentrations, but much of the disparity may be driven by the offset in K concentrations. Since the NGR method calculates U and Th concentrations from U/K and Th/K ratios that are determined from Monte Carlo simulations and experimental data, an improper calibration of K can impact the accuracy of U and Th estimates. Continued improvements of the NGR K concentration calculation are likely to result in more accurate estimates of U and Th concentrations.

Additionally, inconsistencies between the data sets for sediments younger than $\sim$1.5 Myr may arise because the NGR analysis infers U and Th concentrations from the radiation of their daughter products, which can have contrasting chemical behaviour (e.g. adsorptive character) between the different isotopes. We will present our strategies to address these effects, and discuss our efforts to continue development of this evolving new technique.

[1] Vasiliev et al., (2011) *J. of Applied Geophysics* **75**, 455-463.

Microbialite formation in two hypersaline lakes (Bahamas): Insights into organomineralization

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The precipitation of carbonate minerals within a microbial mat (microbialite) results from complex interactions between the microbial communities and the surrounding geochemical environment. This process is referred to as 'organomineralization', and differs from 'biomineralization' (*e.g.*, shells and bones) by lacking genetic control on the mineral product. Organomineralization can be '*active*', when microbial metabolic reactions are responsible for the precipitation through actively changing the saturation index (*"biologically-induced" mineralization*) or '*passive*', when mineralization takes place within a microbial organic matrix, but is induced by environmental reactions (*e.g.*, through degassing or evaporation; *"biologically-influenced" mineralization*). Microbial metabolism can changed the carbonate mineral saturation by acting as an 'alkalinity engine' (changing the total alkalinity and/or the distribution of carbonate species within the total alkalinity) as well as the calcium availability (through Ca-binding capacity of the organic matrix).

Here two cyanobacteria-dominated microbialites that develop in hypersaline environments (Eleuthera and San Salvador Bahamas) are compared with respect to precipitation mechanism. In both lakes, the microbial metabolic activity, the characteristics and turnover of the extracellular organic matter (EOM), and the physicochemical conditions in the water column and sediments were determined to identify the driving forces in microbialite formation. Geochemical modeling indicated an oversaturation with respect to carbonates (including calcite, aragonite and dolomite) in both systems, but these minerals were never found to precipitate at the mat-water interface. This is attributed to the capacity to bind calcium by the EOM in the water column and the upper layer of the microbial mat, inhibiting crystal formation. Therefore, organomineralization within the microbial mat is the consequence of local oversaturation of the EOM binding capacity and/or EOM degradation.

Both microbialites in this study exhibit tight coupling of element cycling and display a stromatolitic lamination, but differ in some mineral features. Notably, isotopic measurements ($\partial^{13}C$ and $\partial^{18}O$) performed on the top carbonate layer (the microbially most active zone) indicate that the precipitate, although resulting from a complex interaction of metabolisms, indicate two opposite isotopic signatures (autotrophic vs. heterotrophic). However, in both systems the early diagenesis of the mineral product (through burial) suggests an increasing influence of heterotophic processes in the mineral precipitation. In the both systems studied here, the organic matrix (EOM) plays a key role in the shaping of the mineral product.

Iron oxide compositional variations in tills along ice-flow paths: Case studies from Sue-Dianne IOCG, and Thompson Ni-Cu deposits, Canada

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Sue-Dianne IOCG deposit

The composition of iron oxides contained in 8 till samples, 0.25-1 mm in size, and five bedrock samples, were selected along a cross-section from up-ice, proximal to, and down-ice from the Cu-Ag-(Au) Sue-Dianne IOCG deposit, Great Bear Magmatic Zone, Northwest Territories, Canada. Iron oxides in tills show the same, but weaker, compositional variations related to the proximity of the deposit than bedrock samples. At and immediately down-ice of the deposit, hematite is the dominant oxide and shows dominant BIF and IOCG chemical signatures in the Ca+Al+Mn vs. Ti+V discriminant diagram. Up-ice and farther down-ice of the deposit, magnetite and titano-magnetite are the dominant oxides and show dominant Kiruna and IOCG signatures (Fig. 1).
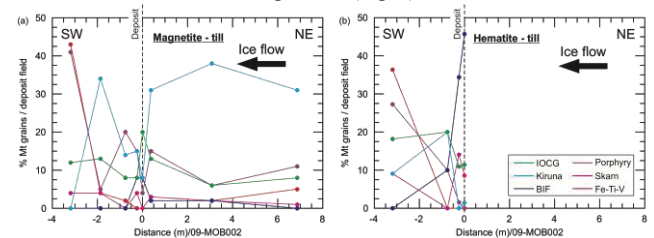

Figure 1: Magnetite and hematite proportion of grains falling in different deposit fields relative to the distance from the Sue-Dianne deposit.

Thompson Ni-Cu deposits

The 0.25-1 mm ferromagnetic fractions of 7 till samples are along a N-S profile along the first direction of ice-flow. In addition, 11 till samples were selected to document a 180 km-long cross-section from the Pikwitonei domain (East) across the Thompson Nickel Belt, Manitoba, Canada, and into the Kisseynew domain (West) along the direction of the last major ice flow movement. The proportions of magnetite having a Ni-Cu deposit signature in the Ni+Cr vs. Si+Mg discriminant diagram increase for at least 2 km to the south of the Pipe Mine along the direction of the first glacial movement, whereas the dispersion of the deposit-derived magnetite to the west is limited during the second glacial movement (Fig. 2)
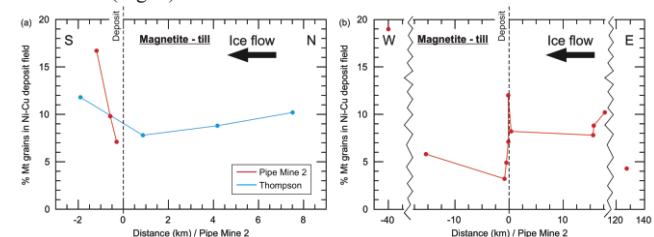

Figure 2: Magnetite proportion of grains falling in the Ni-Cu deposit field relative to the distance from Pipe Mine 2 deposit, Thompson Nickel Belt.

U distribution and speciation in Fe-bearing alteration minerals at the McArthur River U-deposit

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The unconformity-related U-deposits of the Athabasca Basin represent an increasingly important energy resource (18% world's U-reserves) [1] and have been used as natural analogues for the deep geological disposal of radioactive waste products [2]. Since these deposits serve as large-scale natural records of U redox reactions, understanding their formation will contribute to reducing U mobility around contaminated environments. Multiple alteration and uranium mineralization events occurred throughout the basin's history [3] however the role of authigenic, diagenetic and hydrothermal alteration minerals in the reduction of uranium and subsequent precipitation of uraninite is not well understood. Graphite and various other organic compounds have been proposed as possible solid phase reductants [4] but more recent studies suggest the oxidation of Fe in alteration minerals may have played a role in the reduction of U in the Athabasca Basin [5]. In order to better understand the relationship between Fe and U, synchrotron based µXRF and µXAS experiments were conducted on altered and relatively unaltered samples from the McArthur River deposit using the VESPERS beamline at the Canadian Light Source. The distribution of Fe and U as well as other trace elements were determined by collecting µXRF element distribution maps on specific Fe-bearing alteration minerals. XANES and EXAFS spectra were measured on Fe-bearing clay and sulfide minerals, which were selected on the basis of their paragenesis, U concentrations and their proximity to the ore zone. The oxidation states of Fe and U were determined by measuring U LIII and Fe Kα absorption edges and in some cases EXAFS was used to further determine the speciation of U. Results indicate the distribution of U is closely related to that of Fe in proximity to the ore zone but become inversely related with increasing distance away from the ore zone. Variations in the shape of the Fe Kα pre-edge as well as the edge location, measured on similar phases, were attributed to changes in oxidation states. Least altered samples contained abundant reduced Fe and negligible U whereas higher uranium concentrations, and mixed Fe and U oxidation states were observed in altered samples. This study further suggests that Fe-bearing minerals played an important role in the redox processes involved in the formation of the McArthur River U deposit.

[1] Thomas *et al.* (2000) *Geol.Soc.Nevada Symp Proc.,* **1,** 103-126 [2] Burns (1999) *Rev.in Min.*, **38**, 23-90 [3] Alexandre *et al.* (2009) *Mineral. Dep.*, **44**, 41-59 & ref. therein. [4] Kyser *et al.* (1989) *Can.Jour.Earth Sci.,* **26**, 490-498 [5] Alexandre *et al.* (2004) *Tectonics,* **23(5)**

Proton and metal adsorption onto oxidized graphene

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Oxidized graphene is produced from the chemical or mechanical exfoliation of oxidized graphite, and the resulting particles exhibit distinct physical, electrical, and thermal properties ideal for use in advanced materials, sensors, and transistors. The increasing utility of these materials suggests a strong likelihood for current and future environmental releases, and it will be important to understand the interactions between these particles and other environmental constituents. For example, due to a relatively high surface area to mass ratio and the presence of a variety of proton-active function groups, oxidized graphene may significantly influence the partitioning of metals via adsorption in environments where they exist. However, the surface chemistry and reactivity of oxidized graphene are poorly characterized. In order to construct quantitative surface complexation models of the effects of oxidized graphene adsorption on the distribution of metals in geologic systems, stability constants for the important oxidized graphene surface complexes must be determined. Hence, the objective of this study was to evaluate the capacity of oxidized graphene to adsorb protons and metals via potentiometric titrations and batch adsorption studies, respectively. Target metals included Cd, Pb, Ca, and U, and all adsorption studies were conducted over a wide pH range of approximately 2 to 10 in 0.1 M $NaClO_4$ solutions to buffer ionic strength. The potentiometric titration data indicate that oxidized graphene exhibits proton adsorption over a wide range of pH, and the data constrain the pKa values and site concentrations of the binding sites on the oxidized graphene surface. The batch metal adsorption measurements indicated extensive and strong adsorption of metals by oxidized graphene particles, with increasing adsorption with increasing pH. The pH dependence is consistent with measurements of electrochemical surface properties that indicate a more negative ζ-potential at higher pH values. Using the proton-active site concentrations determined from the potentiometric titrations, the metal adsorption data enable us to determine the thermodynamic stability constants for each of the important surface complexes. Through comparison of these stability constants to those for other environmental surfaces, we consider the propensity of oxidized graphene to influence the distribution of metals in natural and engineered systems.

Modeling Nd oceanic cycle in present and past climate, with a focus on the closure of the Panama isthmus during the Miocene.

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The international GEOTRACES program has been organized to study the oceanic processes that control the oceanic distribution of trace elements in the ocean. Nd isotopes measurements represent a promising tracer to study past and present ocean circulation. However the processes that control the distribution of this tracer in the ocean are still not perfectly understood. Modeling represents a unique tool to improve our understanding on this trace element in the ocean. We will present some modeling studies where we have explicitly implemented this tracer in the General circulation model NEMO. The modeling studies has allowed us to progress in our understanding of Nd cycle in the ocean and to investigate the fluxes that dominate the Nd Input in the ocean, and to apprehend the relevant processes that control the internal oceanic cycle. We then show some results from past climate, focusing on the closure of the Panama Isthmus and its impact on the climate and the oceanic circulation during the Miocene.

Using Bulk Paleosol Organic Matter to Reconstruct Atmospheric $\delta^{13}C_{CO2}$

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The carbon isotopic composition of dispersed organic matter in paleosols has the potential to provide two of the input parameters into Cerling's [1] atmospheric pCO_2 paleobarometer equation. These variables are the $\delta^{13}C_{CO2}$ of the atmosphere and the $\delta^{13}C$ of soil respired CO_2. The isotopic composition of marine carbonates has often been used as a proxy for the composition of the atmosphere however, tenuous correlations between marine and terrestrial rocks limits the resolution of resulting atmospheric pCO_2 reconstructions. Additionally, bulk paleosols provide a terrestrial continuum of values for the paleosol barometer as opposed to the sporadic occurrence of coals or charcoal. Therefore, this study investigates the use of dispersed organic matter in paleosols as a record of atmospheric $\delta^{13}CO_2$.

Modern soils have not provided much insight into the likelihood that an atmospheric signal will be preserved in paleosol organic matter. Soil organic matter (SOM) in modern soils typically displays an increase in $\delta^{13}C$ with depth casting doubt on its isotopic reliably in the rock record. The multitude of conflicting theories that have been proposed to explain modern depth trends in $\delta^{13}C$ of SOM [2] may indicate that the modern is not an appropriate analogue for ancient soils. We therefore turn to the rock record for evidence of a preserved atmospheric signal in bulk paleosol organic matter. Only pre-Miocene paleosols are considered in this study to avoid the confounding presence of C_4 plant material which would add an additonal pool of organic matter with its own distinct atmospheric signal. Additionally, none of the studied paleosols exhibit macroscopic evidence of extreme drought conditions, an environmental stress that significantly alters the atmospheric carbon isotope signal preserved in fossil plants.

The successions of stacked paleosols that we have studied (Late Cretaceous/EarlyTertiary in west Texas and Late Triassic in eastern Arizona) have the following characteristics: 1.) Low organic carbon contents (<0.05 wt. %), 2.) No correlation between organic matter abundance and carbon isotopic composition 3.) Carbon isotopic compositions that are similar to modern C_3 plants, 4.) No consistent relationship beween soil depth and $\delta^{13}C$ of SOM, 5.) Presence of temporal trends in the $\delta^{13}C$ of SOM that can be correlated to $\delta^{13}C$ trends in coeval marine carbonates, and 6.) Carbon isotopic compositions that are similar to terrestrial organic matter of the same age from different geographic locations.

Based on these observations, it appears that dispersed organic matter in bulk paleosol samples has the potential to preserve a carbon isotope ratio that reflects the composition of the ancient atmosphere and may be used for quantitative atmospheric reconstructions.

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Constraining tropical climate sensitivity: the need for improved Mg/Ca calibrations

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Abstract

One way to estimate how Earth's average surface temperature will increase with rising greenhouse gas concentrations (Earth system climate sensitivity) is to compare contemporaneous temperature and greenhouse gas concentration data from paleoclimate records. Since numerical models indicate that the tropical climate sensitivity is lower and more tightly constrained than global or high-latitude climate sensitivity, measurements of tropical climate sensitivity can be considered as a lower bound for global climate sensitivity estimates. Here we measure Mg/Ca of surface foraminifera *G. ruber* from ODP Site 871 from the past 800 kyr in the western Pacific warm pool to estimate tropical Pacific equilibrium climate sensitivity to a doubling of greenhouse gas concentrations to be ~4ºC. This tropical SST sensitivity to greenhouse gas forcing is ~1-2 Cº higher than that predicted by climate models of past glacial periods or future warming for the tropical Pacific.

Further, this record of past sea-surface temperature (SST) makes use of the relationship between the Mg/Ca ratio of surface foraminifera and mean annual temperature to estimate past SST. Since high-Mg calcite in modern core-top material preferentially dissolves at water depths as shallow as 1.6 km, well above the lysocline, a correction for such dissolution is necessary. Here we present a new type of dissolution correction for Mg/Ca-based paleotemperature estimation based on a regional core-top calibration from the tropical Pacific [data from 1]. We correct the Mg/Ca data for the loss due to dissolution and then apply the corrected value to the accepted Anand equation [2], since dissolution directly affects the Mg/Ca content of the tests. When applied to existing SST records the new correction decreases the observed glacial-interglacial range of SST. Such a depth-based dissolution equation is especially important for estimating the sensitivity of surface temperatures to changes in radiative forcing, such as atmospheric greenhouse gas concentrations. We recommend such a dissolution correction for all Mg/Ca-based temperature records from open ocean, low productivity sites.

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New U-series isotope data from the Andean backarc indicate shallow melting in the Payún Matrú complex

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Essential differences between magmas in subduction zones and magmas in intraplate or MORB type settings have become apparent with an increasing number of ^{238}U-^{230}Th disequilibria data on recent volcanic rocks. Mid-ocean ridge and ocean island magmas are characterized by enrichment of thorium relative to uranium, whereas magmas related to subduction zones have been shown to vary from ^{230}Th-excess to ^{238}U-excess. In fact, radioactive equilibrium of ^{238}U and ^{230}Th (activity ratios = 1) seems to be a typical feature of many arc magmas, particular in continental arcs. We investigate three volcanic centers located in the main Andean arc and into the backarc system in order to constrain the influence induced by fluids in subduction zones.

The new U-series disequilibria analyses from the Andean backarc system support the OIB-character of the Payún Matru volcano, and the more fluid influenced arc-like character of the Infernillo volcano. Results from Maipo show radioactive equilibrium. For all samples the (^{234}U/^{238}U) ratios are within 1% of secular equilibrium, supporting evidence for the samples being unaffected by significant alteration.

The Infernillo samples plot beneath the equiline with 5-10% excess of ^{238}U. This feature is characteristic of those arcs deviating from equilibrium and is best ascribed a slab-derived fluid enrichment of the mantle source beneath Infernillo. The excess of ^{238}U also requires that the fluid addition occurred within the last 300 ka. In contrast data from the Payún Matru volcano show 5% excess of ^{230}Th, and plot within the ocean island basalt field as defined by literature data. In the case of OIB, partial melting is the main process fractionating Th/U and thus producing the ^{230}Th/^{238}U disequilibria. Analyzed samples are of Holocene age and the relatively low disequilibrium could indicate that melting induced fractionation between U and Th was limited due to shallow melting above the garnet stability field. This is supported by evidence from trace elements (e.g. low Dy/Yb).

Determination of soil organic C species using soft X-ray XANES: normalization & matrix effects

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Soil organic matter (SOM) storage and turnover are affected by the chemical nature and properties of its constituents, particularly the chemical forms of organic C. Synchrotron-based soft X-ray absorption near edge spectroscopy (XANES), probing the atomic and molecular structures of materials, is being used to provide information on the types of C functional groups (e.g., $C=O$, C-OH, R-COOH) in SOM [1]. This type of information is required to fully understand the global C cycle.

Normalization of C K-edge TEY and TFY data has always been a challenge due to the C contamination in soft X-ray beamlines, imparting features into the incident x-ray flux (i.e., Io). The mineral fraction of the soil also contributes to the TEY and TFY signal, in ways not fully understood. Hence, there is concerns that artefacts such as erroneous peaks and/or spectral distortions may be introduced into the C K-edge total electron yield (TEY) and total fluorescent yield (TFY) spectra during the normalization of the raw data and/or into the raw data from the matrix itself (e.g., adsorption saturation), particularly at low soil C content. Both of these could result in incorrect conclusions being reached. To date, no fundamental studies have been conducted that address normalization issues and matric effects in known systems as a function of organic C content, organic functionality and in different matrices.

At the SGM beamline, at the Canadian Light Source, we are studying model systems consisting of varying amounts (50 to <1% (w/w)) of an organic compound with different function groups (e.g., citric acid, phthalic acid, glucose, tannic acid) mixed with a soil constituent (e.g., Al hydroxide, kaolinite, montmorillonite, Fe hydroxide). The organic-matrix mixtures are deposited onto various substrates (e.g., Au coated Si wafers) and TEY and TFY spectra are collected under a variety of conditions such as in the presence and absence of a Ti filter and/or reducing radiation dose rates (C is susceptible to radiation damage at high radiation doze rates and/or in the presence of certain elements such as Cu [2]) by conducting fast scans (20sec) versus normal scans (1500sec). Determination of the appropriate Io using different detection methods such a photodiodes and the collection of TEY and TFY of a variety of substrates such as Au coated Si wafers and C-free matrixes are being explored to normalize the data. From this fundamental approach it is expected that a protocol will be developed that reduces the possibly that artefacts are introduced during the normalization process and/or during the collection of the raw data due to matric effects. Also, the study will provide insight into factors that affect the C detection limit of the soft X-ray. Moreover, this project is part of an initiative to make the SGM beamline a center for Soil Science studies.

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Surface Complexation Models and their Practical Application

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Abstract

While surface complexation theory and models for the description of inorganic ion sorption on mineral surfaces have advanced continuously since the introduction and initial development of these models in the 1970s and 1980s (reviewed in [1]), so too has the practical application of the models. Deployment of surface complexation models to interpret and predict water-mineral partitioning of ions in geochemistry and engineering applications is challenging because of the complexity of these systems, the limitations of the models, the lack of surface complexation databases for all of the minerals of interest, and other factors. The substantial progress in application of surface spectroscopy methods and molecular modeling to increase understanding of the properties of mineral surfaces and the nature of their reactions with ions has been of limited usefulness in constraining surface complexation models [2,3] and has done little to advance their practical application. Of necessity, there is still widespread use of empirical isotherms and distribution coefficients (K_d) to describe and simulate ion sorption processes in field systems. However, surface complexation models have been applied in a variety of contexts to gain insight into the role of sorption reactions in governing the fate and transport of particular ions, and in governing overall system chemistry.

This talk will provide an overview of the development of surface complexation models, and the history of their practical application. Examples from modeling of ion transport in geochemical systems and from contaminant treatment and remediation will be described. The strengths and limitations of the models for practical applications will be examined. Some thoughts about developments needed to advance the practical application of surface complexation models will be offered. The divergence yet complementarity of surface complexation research focused on advancement of basic scientific understanding of mineral-water surface phenomena, and research motivated by practical applications will be discussed.

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