



GeoRaman 2020

14th International GeoRaman conferences
Book of Abstracts



Bilbao, Basque Country, Nov. 2-5, 2020

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Universidad del País Vasco Euskal Herriko Unibertsitatea

University of The Basque Country

Abstracts



GeoRaman 2020

14th International GeoRaman conferences

O. Gómez¹, J.A. Carrero², L.A. Fernández³
Editors

IBeA Research Group, University of The Basque Country
Organizing Committee of GeoRaman 2020

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Foreword

The main aim of this congress is to provide a scientific forum to present and promote the use of analytical techniques in the field of Geosciences. This series of conferences has a tradition since 1986, starting in Paris, and has since then been held in multiple cities in Europe, USA, and Australia.

The GeoRaman 2020 conference scope covers all scientific aspects where Raman spectroscopy and geology meet. GeoRaman has served as an important meeting point for scientists from different area of knowledge, to present their studies, participate in scientist discussions and find collaborative partners. Starting this year, several space agencies are going to launch missions to Mars in which for the first time Raman spectroscopy is going to be present (Perseverance and Rosalind Franklin rovers).

The meeting is focused on different aspects:

- Raman Spectroscopy for Materials Science
- Raman Spectroscopy under Extreme Conditions
- Raman Spectroscopy for Cultural Heritage and Archeology
- Raman Spectroscopy for Environmental Sciences
- Raman Spectroscopy for Earth Sciences
- Raman Spectroscopy for Planetary Science and Space Exploration
- Raman Spectroscopy for Extraterrestrial Materials, Astrobiology, and Paleobiology
- Raman techniques and Relevant Instrumentations (LIBS, IR, Vis-NIR, etc.)

The total number of contributors in this GeoRaman 2020 was about 70 researchers and professionals from all around the world.

All their contributions are collected in this Book of Abstracts. Moreover, the works showing a clear analytical advance (not just “novelty”) will have the chance of being published in a Special Issue of ***Journal of Raman Spectroscopy*** after the standard peer review process.

Kepa Castro and Zongcheng Ling, Nov 2020

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THE SUBMARINE VOLCANOS OF THE BASQUE CANTABRIAN BASIN (BISCAY, SPAIN): UNDERSTANDING MARS THROUGH THE EARTH

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The study of terrestrial Martian analogues has become a very important field for the planetary exploration, since the understanding of the processes that happened in the Earth could help in the comprehension of those that could have happened on Mars. Therefore, they could be useful in the process to know the history of the neighboring planet. In the next Martian missions carried out by NASA and ESA, Jezero crater and Oxia Planum will be the landing sites respectively.

In this sense, the Basque Cantabrian Basin (Biscay, Spain) has different examples of emplacements with submarine volcanic origin that were formed during the Late Cretaceous times [1] that could be analogues to some volcanic areas described in the Mars landing sites. Some of these examples, such as Meñakoz and Armintza outcrops, are nowadays in contact with the seawater. Others, such as Fruiz and Enekuri locations, are in the inland part of the basin and without contact with the sea for a million years after the land emerging processes. These last outcrops were analysed in this research work using Raman and visible near-infrared spectroscopies due to their implementation in the mentioned missions. Some of the found minerals are common for all the emplacements, such as albite, which is thought to be the original mineral from which others arise. This mineral is reported to be present in Martian meteorites [2] and, in general, plagioclases are one of the dominant minerals in the Martian crust [3]. An example of the latter minerals, also found in all the emplacements, are chlorites, which are phyllosilicates formed by hydrothermal alteration and, as phyllosilicates, may be present in some areas of the Jezero Crater and Oxia Planum sites. However, minerals such as diopside or titanite have been found only in Fruiz and Enekuri and not in Meñakoz nor Armintza, demonstrating how different geochemical conditions in which these emplacements are located produced different formation mechanisms. Moreover, differences between Fruiz (manganese oxides, Figure 1.a) and Enekuri (zeolites, Figure 1.b) were also identified, which show that even in similar geological environments, mineralogical differences appear. Therefore, this fact would be very important for the study of Martian surface since different processes that are happening in the Earth could be similar to those observed on Mars.

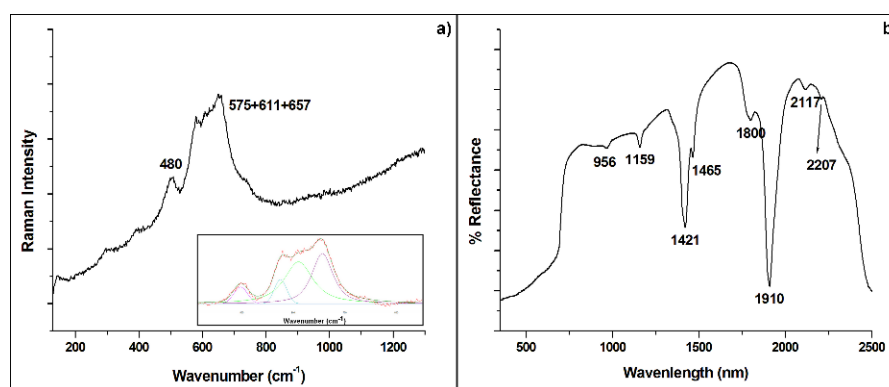


Figure 1: a) Raman spectrum of manganese oxides observed in Fruiz and b) VNIR spectrum of analcime (zeolite) observed in Enekuri

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EXOMARS/RLS: RAMAN SEMI-QUANTIFICATION ON MARS?

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The ESA/ExoMars missions is scheduled to be launched in 2022. The *Rosalind Franklin* rover will drill the Martian surface down to a depth of 2 meters, thus accessing rock samples that have been sheltered from UV radiation and other alteration processes. After crushing, powdered materials will be delivered to the analytical laboratory of the rover where spectroscopic (RLS [1], MicrOmega) and chromatographic (MOMA) analysis will be carried out.

Knowing that 1) vast areas of the selected landing site (Oxia Planum) are covered by Amazonian lava flows, and 2) the mineralogical composition of Martian primary rocks shown compositional trends with time [2], the detailed mineralogical study of unaltered igneous rocks could help deepening our understanding of the geological and environmental evolution of Mars. Raman spectroscopy may play a key role in the achievement of this scientific goal. Indeed, beside effectively detecting the mineralogical heterogeneities of Martian analogues, preliminary studies suggest that the chemometric analysis of RLS data sets could be used to estimate the relative concentration ratio of their main mineral phases [3].

Following this research line, the present work seeks to evaluate if igneous rocks detected at Oxia Planum could be effectively classified by combining qualitative and semi-quantitative analysis of RLS data. To do so, the RLS ExoMars Simulator was first used to analyze a wide collection of feldspar, olivine and pyroxene minerals detected on Mars. After spectra comparison, the most representative phases of each mineral group, (labradorite, forsterite and augite, respectively) were selected and mixed at different concentration ratio. Laboratory samples were analyzed through the RLS ExoMars simulator by emulating the operational constraint of the RLS flight model (20-39 spectra per sample). Through a univariate analysis of the collected data, RLS-dedicated calibration curves were generated by calculating the intensity ratio between the main peaks of olivine ($\sim 855\text{ cm}^{-1}$) pyroxene ($\sim 660\text{ cm}^{-1}$) and feldspar ($\sim 505\text{ cm}^{-1}$) with respect to their total intensity. Predictive equations were then used to semi-quantify the main mineral phases from well characterized terrestrial analogues. By comparison with XRD reference data, the results obtained in this work strengthen the idea that, by combining qualitative and semi-quantitative information, RLS data sets could be effectively used to classify igneous rocks on Mars.

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EXOFIT FIELD TRIALS: EXPERIENCE LEARNED FROM THE USE OF RLS QUALIFICATION MODEL AND REPRESENTATIVE PROTOTYPES

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The ESA/Roscosmos ExoMars mission to Mars is scheduled to be launched in 2022. Seeking to prepare the ExoMars operation team to manage the engineering and scientific challenges arising from the *Rosalind Franklin* rover soon operating at Oxia Planum, a rover prototype equipped with representative ExoMars navigation and analytical systems was recently used in two mission simulations (ExoFit trials)

The first field test was carried out in Tabernas (Spain), a desertic area characterized by the presence of clays, partially altered sedimentary rocks and efflorescence salts. The second ExoFit trial was performed in the Atacama Desert (Chile), in a sandy flat land displaying diorite-boulders, clays patches and evaporites.

The Raman Laser Simulator (RLS) team participated in both simulations: portable spectrometers were used to determine the mineralogical composition of subsoil samples collected by the rover-drill and to investigate the possible presence of biomarkers. In-situ analysis were carried out by means of the RAD 1 system (Raman Demonstrator), which is a portable spectrometer that follows the same geometrical concept and spectral characteristics of the RLS flight model (FM). In the case of Tabernas trial, additional analysis were performed using the RLS qualification model (EQM2).

Prior to analysis, geological samples were crushed and sieved to replicate the granulometry of the powdered material produced by the ExoMars crusher. After flattening, from 8 to 10 spots were analyzed.

From each site, two cores were drilled and analyzed. On one side, the main mineralogical phases detected in the first Atacama core are quartz and calcium carbonate. In addition to those, the mineralogy of the second core also includes hematite and calcium sulphate.

On the other side, RAD 1 spectra gathered from Almeria core-samples confirmed the presence of quartz as main mineralogical phase. However, peaks of medium intensity at 146 and 1086 cm^{-1} were also observed, confirming the detection of rutile and calcium carbonate respectively. The same samples were further characterized by means of the RLS-EQM2 system: beside confirming the detection of the abovementioned mineral phases, additional Raman biomarkers-related peaks were also found.

Even though deeper Raman analysis of ExoFit samples need to be performed, preliminary results provide solid clues about the role Raman spectroscopy could play in the fulfillment of the ExoMars mission objectives.

MINERALOGICAL AND CHEMICAL CHARACTERIZATION AT THE MACRO-SCALE BY AUTOMATED MULTI-ANALYTICAL APPROACH

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In intrusive igneous rocks, ocelli facies are well-known concerning felsic and intermediate complexes, but less documented in undersaturated alkaline intrusions. Few micro- to macro descriptions were provided in alkaline-carbonatite complex. Textural, mineralogical and chemical information combined with spatially-resolved major and trace element content in such ocelli texture can give us clue for documenting immiscibility processes.

An amazing macroscopic ocellar texture from the Crevier intrusion (CAI) (Greenville Province, Québec, Canada) [1] was analyzed by Raman spectroscopy. Several thousands of Raman spectra were acquired using a portable spectrometer that was not originally dedicated to mapping (RaPort, Enhanced Spectroscopy). It was set in an automated bench that can accept various portable instruments (XRF, FTIR, VNIR-SWIR, LIBS). The scanning of the sample was done on a surface of $6 \times 8 \text{ cm}^2$ with a step of 1 mm (4780 spectra). The data were then massively processed using different software: baseline subtraction and normalization (LabSpec6, Horiba), mineral identification (RPIRS [2]), and then false-color mapping (PyMca, ESRF). The results were fully validated by comparison with micro-XRF map (Figure 1), demonstrating that fine mineralogical identification of complex sample is feasible using portable Raman spectrometer.

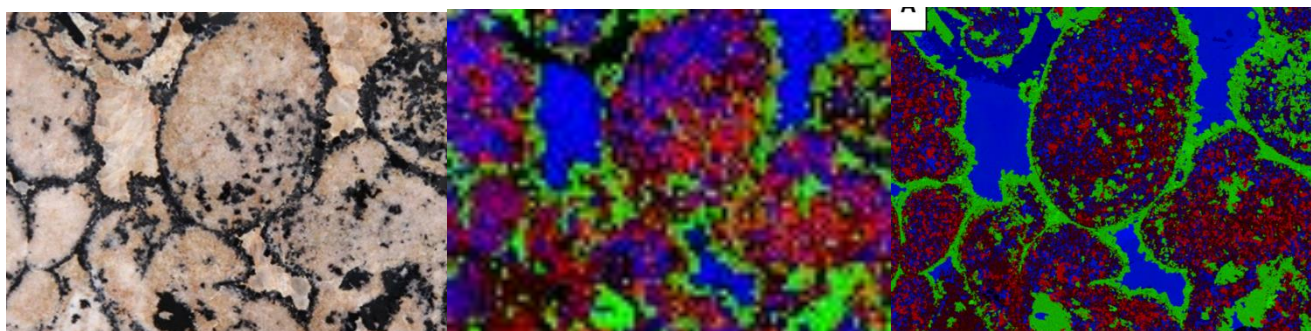


Figure 1: Left: sample photography. center: Raman map with green: nepheline; blue: carbonate; red: albite. Right: micro-XRF map with green: Fe; blue: Ca; red: Al. Image size = 8 cm × 6 cm

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CHARACTERIZATION LATE MEDIEVAL AGES GLAZED POTTERY (XIV-XV CENTURIES) OF VEGA POTTERY WORKSHOP (BURGOS, SPAIN)

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This work focuses on the Raman characterization of middle age glazed pottery from a pottery workshop in Burgos (north of Spain). The analysed pottery includes glazes from the same workshop that operated from 14th to 16th centuries. During the excavation a workshop structure with two ovens and a water system to transport water from the river were found. The study aims is outlining the production technology of the glazed pottery.

Ten colours of glazes have been established, with colours varying from honey to yellow, from yellow to green and from green to honey. The association of pieces to a colour is not always simple issue, since colours gradations are frequent on the same surface. Besides overfiring produces important colours alterations often making difficult colours attribution.

Microstructure, chemical and mineralogical features indicate different ways of glaze manufacture. Most of the times lead-rich compound flux was applied on the unfired ceramic, but sometimes was applied after the firing. To achieve glazes of different colours chromophore elements such as zinc, copper or iron were used. Glazes final colours are due to composition mixture of both ceramic body and slipware (Figure 1). Vega pottery glazes composition varies between 31% and 56%wt of lead, and when a chromophore element are present varies between 3.5 and 6.5% of iron, from 2% to 5 %wt of zinc or up to 2%wt of copper.

Raman spectra are characteristic of lead glazes with low polymerization rate indicating low firing temperatures <700 °C [1]. However, Raman measurements taken on glazes of overfired ceramics provided also low temperatures. Polymerization index (PI) [1] show a good correlation with the lead content of the glazes (Figure 2). Thus this index it is more dependent on the glazed composition than on the firing temperature contrary to what stated Colomban et al. [1].

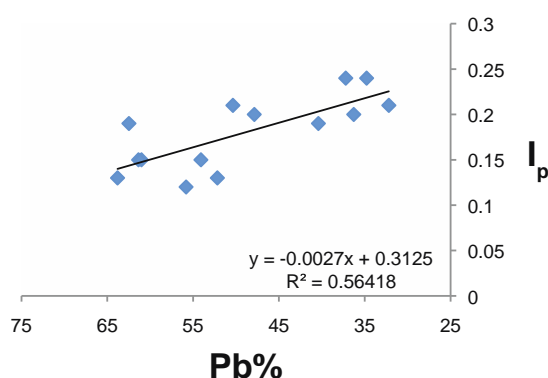


Figure 1: Left) Detail of glazed colour variation on a white slip jar. Right) Scattergram of polymerization index (I_p) vs lead content of glazes

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THERMODYNAMIC BEHAVIOR OF SULFUR AND NITROGEN SYSTEMS AT HIGH PRESSURE AND HIGH TEMPERATURE: AN EXPERIMENTAL/RAMAN COUPLED APPROACH

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The greenhouse effect is the natural mechanism of warming up the Earth's surface. Greenhouse gases include mainly water vapor, carbon dioxide, methane, and nitrous oxide. Human activities have enhanced the level of greenhouse gases in the atmosphere causing serious environmental problems and contributing to a high Earth temperature. One of the main highlighted approaches to control this emission is CO₂ sequestration, capture and storage (CCS). When CO₂ is captured, impurities including SO_x, NO_x, Ar are collected along depending on the industrial sources of fumes [1]. NO and SO₂ are both known for having high reactivity as acids and oxidizing agents when solubilized in water. Their reactions with rocks, completion/downhole equipment and reservoir are important to be studied and modeled. Undertaking research on these gases will help to assess the short, medium and long term of geological storage. SO_x-NO_x systems are not well described beyond high pressures and temperatures. Thus, thermodynamic data necessary for geochemical modeling are missing.

This project proposes to acquire new thermodynamic data on H₂O / (SO_x-NO_x) / salt systems at high pressure (up to 600 bar) and high temperature (up to 200 °C). Data acquisition is based on Raman spectrometry, fused silica capillaries and Monte-Carlo molecular simulations which are carried out to determine additional solubility data and improve knowledge of the thermodynamic behavior of these systems.

The experimental system allows the observation of the different phases and the characterization of the volume ratio and the chemical composition of the SO₂/H₂O or NO/H₂O systems under storage conditions [2]. A silica capillary tube was sealed at one end before being connected to a secure gas loading line located in a securitized fume cupboard. The tube is then filled with pure SO₂ or NO or with a binary system containing an aqueous phase (water or brine). Gas was captured by cold trap by immersing the capillary in liquid nitrogen. Capillary tubes were then sealed at the other end to obtain a Fused Silica Capillary Capsule (FSCC) or connected to a pressurization device (High Pressure Optical Cell) thanks to a high-pressure valve. FSCCs containing solutions at known concentrations of dissolved NO_x and SO_x species were also prepared for calibration. Raman spectra were acquired as a function of temperature by setting the capillary on a heating-cooling stage (Linkam CAP500).

Raman spectra of SO₂ and NO were recorded individually and in the presence of water at different pressures and temperatures up to the critical parameters of both species. The evolution of the different spectral parameters (peak position, peak area, peak intensity, etc...) was studied at different pressures and temperatures to obtain solubility parameters. Also, an evaluation of the compositions and possible reactions that might occur at storage conditions were investigated especially when applied to gas mixtures in the presence of water.

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DETECTING MICROBIAL PIGMENTS FROM GYPSUM USING RAMAN SPECTROSCOPY: FROM FIELD PROSPECTION TO LABORATORY STUDIES

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Terrestrial detection of biomarkers in various mineral matrices using Raman spectrometers including field deploying of miniature instrumentation in Mars-analogue sites can be seen as a training for next Martian missions. In fact, both the European Space Agency (Exomars) and North American Space Agency (Mars 2020) robotic rovers will include Raman spectrometers. Feasibility of detecting biomarkers of extremophilic cyanobacteria and algae (pigments, osmotic solutes and lipids) using Raman microspectrometry was reviewed previously [1]. Here the idea is to show - firstly how portable Raman instrumentation permits to detect carotenoids fast and onsite under field conditions. Secondly, laboratory microspectrometric investigations allow to obtain more detailed information about spatial distribution of pigments originating from microorganisms.

Macrocrystalline gypsum layers and aggregates are well-known from Tertiary series in Sicily and Eastern Poland. In Southern Sicily gypsum sediments accumulated during Messinian crisis (Late Miocene) are outcropping and were investigated near Scala dei Turchi, Torre Salsa and Siculiana Marina. Polish Tertiary (Badenian, Middle Miocene) examples of gypsum colonisations of decimetre to meter long outcropping crystals were studied near Chotel Czerwony, Skorocice and Chwalowice. Miniature portable Raman spectrometers equipped with green lasers allowing resonance Raman signals of carotenoids are evaluated here. Possibilities of collecting spectra of carotenoids under non-resonant conditions using a portable sequentially shifted Raman spectrometer (832 and 1064 nm lasers) are shown as well. Observed shifts of positions of Raman features of carotenoids between gypsum samples (and sites) are discussed and critically evaluated. In addition, acquired data are compared to data obtained through laboratory Raman microspectrometric investigations.

Selected zones of microbial colonisations of few types of gypsum are described from the point of view of the presence of algae and cyanobacteria. Pigments are detected through conventional Raman microspectrometric measurements. Carotenoids were documented in major part of samples (common Raman bands at around 1525, 1157, and 1004 cm^{-1}). Additionally, Raman spectra of other pigments were recorded in several zones using near infrared excitation (785 nm): chlorophyll (1151, 1327, 1287, 1184, 917, and 745 cm^{-1}), scytonemin (1593, 1152, 1438, and 1173 cm^{-1}) and phycobiliproteins (1633, 1584, 1371, 1236, 813, and 667 cm^{-1}). Portable instrumentation permits detection of carotenoids in gypsum fast and onsite under field conditions. Raman microspectrometric investigations of colonisations allow to gather detailed information about pigment distribution in micrometric zones of gypsum samples.

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EVALUATION OF CARBONIFICATION OF COALS USING PORTABLE RAMAN SPECTROMETER

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The ability of fast but reliable analyses of carbonaceous matter of coals and other sedimentary rocks using miniaturized Raman spectrometers can have significant impact in different fields. A speedy in situ discrimination among the coals of different maturity can be quite useful in the mining industry or prospection. In astrobiological research, the detection of carbonaceous matter remnants in the sedimentary rocks for example on Mars could be one of the significant discoveries of the future Mars exploration missions' rovers equipped with miniaturized Raman spectrometers.

Raman microspectroscopy has been used to describe structural state of carbonaceous materials by observing and calculating of parameters of G and D bands representing vibrations within or at the boundaries of the planar rings of carbon atoms. Since the degree of maturity of coals is positively correlated with increased structural ordering of carbonaceous matter in coals, Raman microspectroscopy was shown to be an effective tool for estimation of maturity of coal (coal rank) [1] and maturity of kerogen in shales [2].

In contrast, only a few studies reported investigations of different types of carbonaceous matter using portable Raman spectrometers in the past. However, both the study of carbonaceous matter in stromatolite or black shale [3] or analyses of samples of kerogen, shungite or anthracite [4] were performed using the near infrared 785 nm excitation or sequentially-shifted excitation in the infrared region, respectively. These studies reported spectra of lower quality and deformation of D and G bands was also observed. In the current investigation, a portable Raman spectrometer equipped with a 532 nm excitation was used for analyses of more than 50 samples of coals with types ranging from lignite to anthracite. Additional samples including graphite, shungite, asphaltite, carbonaceous matter of stromatolite were also included for comparison purposes. Good quality Raman spectra recorded on almost all the samples enabled to use spectroscopic parameters of D and G bands located at around 1350 and 1580 cm^{-1} . Such parameters include ratios of intensities (I_d/I_g), widths and band positions of both bands. These parameters allowed to evaluate the degree of maturity (carbonification) of analyzed coal samples. It was demonstrated that miniaturized Raman spectrometer equipped with an appropriate excitation can provide a fast and reliable analyzes of samples rich in organic/carbonaceous matter.

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FAST *IN SITU* ANALYSES OF CAROTENOIDS WITHIN NATURAL BIOCOLONISATIONS ON WALLS OF CONVENT OF CHRIST IN TOMAR AND THE CATHEDRAL OF ÉVORA (PORTUGAL) USING THREE PORTABLE RAMAN SPECTROMETERS

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Sometimes building stones or plasters of historical monuments show a pinkish-orange hue. These might originate from minerals or their alteration products within building materials or from microbial growth on the walls. In the latter case, it may be related to the presence of carotenoid pigments produced by microorganisms. An *in situ* measurement campaign was conducted to analyse this pinkish-orange phenomenon occurring locally but extensively on the walls of two world heritage monuments in Portugal: the Convent of Christ in Tomar and the Cathedral of Évora. A number of Raman spectra were recorded *in situ* by using one portable suitcase-sized and two portable handheld spectrometers equipped with green (532 nm) excitation and the results are compared. Obtained Raman spectra confirm the presence of carotenoids within pinkish-orange coloured altered patches on the stone and mortar substrates of the structures. The resonance Raman effect of the green laser is ideal for fast analyses of carotenoids on historical building stones, mortars or plasters. When comparing the different spectra from the different sites, as recorded with the different spectrometers, all Raman spectral features are very similar. Based on direct spectroscopic analysis of carotenoids, it is not possible to identify or discriminate different bacterial species that might be present at the sites. Consequently, in a second stage, samples of microbial colonisations were obtained and bacterial strains were cultivated and Raman spectra of pigments from these cultures were evaluated. The spectra are dominated by two sharp bands at *ca.* 1510-1520 and 1150 cm^{-1} , while often a medium to strong band is also observed at *ca.* 1000 cm^{-1} . These bands are assigned to the $\nu_1(\text{C}=\text{C})$ and $\nu_2(\text{C}-\text{C})$ stretching vibrations and the $\rho(\text{C}-\text{CH}_3)$ deformations, respectively. Minor variation in wavenumber positions of Raman bands in spectra obtained with different instruments on the same zones are discussed, and might be explained by the combination of the heterogeneity of the samples and the instrumental differences. The technical performance, user experience during analyses and limits for using portable instrumentation for unambiguous discrimination of carotenoids are considered as well.

NEW CALIBRATION DATA FOR DETERMINATION OF PVX PROPERTIES OF BINARY AND TERNARY CO₂-CH₄-N₂ MIXTURES BY RAMAN SPECTROSCOPY. APPLICATION TO NATURAL FLUID INCLUSIONS

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Natural fluid inclusions (FIs) filled by geological fluids and trapped within minerals during or after crystal growth are known as the most reliable relict of actual paleofluids. CO₂, CH₄ and N₂ are the most common gaseous species omnipresent in a large variety of geological fluids. Investigating FIs is, therefore, an unavoidable step to provide key information for reconstructing the P-T history and for a better understanding of the geological processes.

Raman spectroscopy is known as the best-suited alternative method to microthermometry for the investigation of natural FIs because it can provide simultaneously non-destructive qualitative and possible quantitative analyses after specific calibrations. The relative Raman scattering cross-section (RRSCS) and the pressure- or density-induced vibration frequency shift of the Raman bands of gases such as CO₂, CH₄ and N₂ were intensively studied since the 1980s [1]. However, most of the RRSCS and calibration data were only calculated for pure components or at low pressure (density). Ignoring the composition effect upon the Raman quantitative analyses can lead to considerable errors, especially when applied to the geological fluids containing generally several substances at elevated pressure. The experimental data of Seitz et al. revealed the variation trend of CO₂ and CH₄ Raman signal with composition change, but no accurate calibration was given [2-3].

The present work's aims are (i) to reevaluate the RRSCS of CO₂ and CH₄ (relative to that of N₂), and (2) to provide new and accurate calibration data for multi-component quantitative analyses of binary and ternary CO₂-CH₄-N₂ mixtures at any concentration. The Raman in-situ analyses were performed using a high-pressure optical cell (HPOC) system [4], a fused silica transparent capillary [5] and a heating-cooling stage (Linkam CAP500[®]). From the experimental data, the pressure-induced Raman shift of the ν_1 band of CH₄ as a function of composition was interpreted at the molecular level based on intermolecular interaction changes using the Lennard-Jones potential approximation. Several calibration equations fitted from experimental data collected at 22 and 32 °C and over 5-600 bars were provided [6-7]. The uncertainties on composition, pressure and density are about ~0.5 mol%, <20 bars and <0.02 g·cm⁻³, respectively. Since each calibration equation was fitted for a specific pressure (density)-composition range and the uncertainty calculation is quite cumbersome, a computer program was also developed to facilitate the use of our calibration data. The calibration data was successfully applied to natural fluid inclusions from different zones of Central Alps, Switzerland, and compared with microthermometry for validation.

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RAMAN SPECTROSCOPY OF EMERALDS FROM LATE 19th CENTURY

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A cross shaped pendant made around the end of 19th was recently loaned from Einsiedeln Abbey (Switzerland) to the collection centre of the Swiss National Museum for research purposes. The exact date the item was donated to the Abbey by the Italian Cardinal Mariano Rampolla del Tindaro (1843-1913) is still unknown. For security reasons, the item cannot be moved outside collections centre and it can be studied solely using non-destructive methods available at the centre's premises as well as mobile instruments. The cross was difficult to handle and potential dismantling of different pieces was excluded.

Nineteen green homogeneously coloured gems were mounted with a closed back on the about 10 cm long cross pendant. Cuts and shapes of the green stones were studied macroscopically and under optical microscope (up to 80x) when possible. Green gems' reaction under long-wave (365 nm) and short-wave (254 nm) 3 Watt UV lamps. Raman spectra were carried out using excitation wavelengths of 532 nm (Nd:YAG laser), 633 nm (He:Ne laser) and 785 nm (diode laser).

Studied green gems were faceted in square to rectangular shapes ranging from 3 to 9 mm. All stones were inert under UV lamps. They all present main band at around 1068 cm⁻¹, using 532 nm laser, which is due to Si-O and/or Be-O stretching in beryl [1-5]. The spectra present high luminescence above 2000 cm⁻¹. With the laser at 785 nm, bands OH related bands were apparent, all samples presented a band at 3608 cm⁻¹ and a weak around 3598 cm⁻¹. This is characteristic of low alkali content emeralds, such as some emeralds from Colombia, Afghanistan, Brazil, Russia and Nigeria [2, 5]. All samples presented inclusions under microscope, mainly multiphase with jagged outlines similar to those observed in natural emeralds from some mines in Colombia, Afghanistan, China and Zambia [6]. Combination of spectroscopic and microscopic results lead us to Colombia as the most probable source of these emeralds. However, further research with additional non-destructive methods would be needed to confirm this geographic origin.

Acknowledgements: The authors would like to thank the Collection Centre of the Swiss National Museum (Affoltern am Albis) and Einsiedeln Abbey for the collaboration during this project.

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RLS ROUTINE OPERATIONS CONCEPT ON MARS SURFACE

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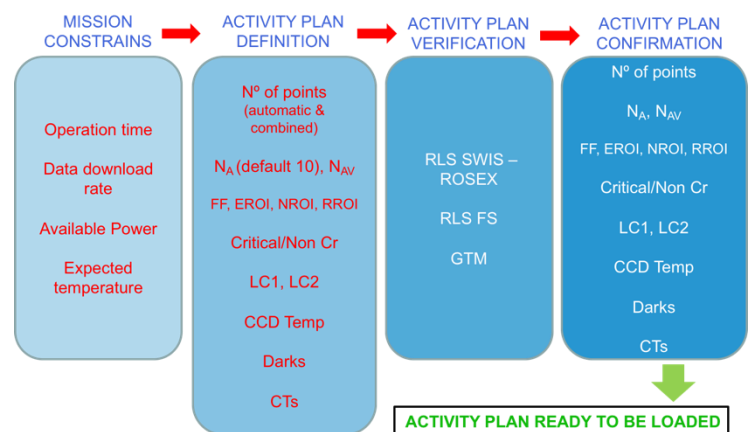
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The Raman Laser Spectrometer (RLS) [1] is one of the instruments being part of the Pasteur analytical suite on board the Rover module of the second ExoMars mission, now planned to be launched in 2022. It will perform Raman spectroscopy on Mars samples acquired by the Rover's drill at surface and sub-surface level. RLS supports two operation modes: automatic standalone mode, where the sample is analyzed at fixed equally-spaced positions from one end to the other, and combined science mode, looking for specific positions previously selected by MicrOmega as potentially interesting points for RLS [2].

Two operational processes will manage the surface mission operations after the egress for the Rover as a whole, the Strategic and Tactical planning. The first will identify the most interesting science objectives, and supervise continuously that all operation activities are addressed to accomplish the mission objectives, while the second will focus on the daily mission activities. Both processes will be performed in parallel by scientist and engineers from instruments and platform subsystems in a well established agile and coordinated way, since there will be few hours since telemetry from last executed activities reception for assessment, until new activities have to be uplinked to the Rover.

RLS, taking into account the Rover operations context with its boundaries and constraints, has defined its own operation [3] based on short-term response and supporting in-situ and remote operations. Specific software tools have been designed to obtain a first quasi-automatic data assessment and, also, to support further science and engineering data analysis without so a strict timeline.

RLS ground models, including the one in the Rover GTM, will be used to support operations at ROCC level. For RLS specific operations, the RLS team counts with a complete Ground Testing Framework able to command [3] the RLS flight spare model (FS), allowing activity plans validation or deep investigation of anomalies during operations on Mars with a fully representative hardware.



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RAMAN SPECTRA OF CYANOBACTERIA IN ROCK FROM NB -REE TOMTOR DEPOSIT, RUSSIA

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Samples of rock from the Tomtor Nb - REE deposit (Russia) [1] have been investigated by Raman micro-spectroscopy using visible 532 nm wavelength excitation. Raman spectra of different samples of this rock confirm their composition as calcites and other carbonates such as rhodochrosite and mixed solid solution phases (Ca, Mn, Fe, Mg, Ba, Sr, REE)(CO₃). Raman spectra of apatite, goethite, hematite, and sulfides were also obtained. An association between cyanobacteria and the phosphates has been noted. Cyanobacteria exhibited Raman modes at 1517 cm⁻¹ and 1138 cm⁻¹ which are characteristic of pre-resonance spectra of carotenoids, namely the stretching modes of the -C=C- and -C-C- bonds, respectively (Fig.1). Laser-induced photoluminescence of REE and Mn²⁺, obtained as an analytical artifact in the Raman spectra, has been observed in most cases with significant spectral intensity. The luminescence emission of Mn²⁺, Sm³⁺, Eu³⁺, Pr³⁺, Ho³⁺, Er³⁺ in the spectra of the apatite-containing samples obtained with 532 nm excitation can be attributed both to apatite and to other mineral phases with a low concentration which contain these elemental ions. The results obtained in this study allowed us to confirm that the biogenic presence of the cyanobacterial mat had a significant impact on the formation of the unique Nb-REE Tomtor deposit.

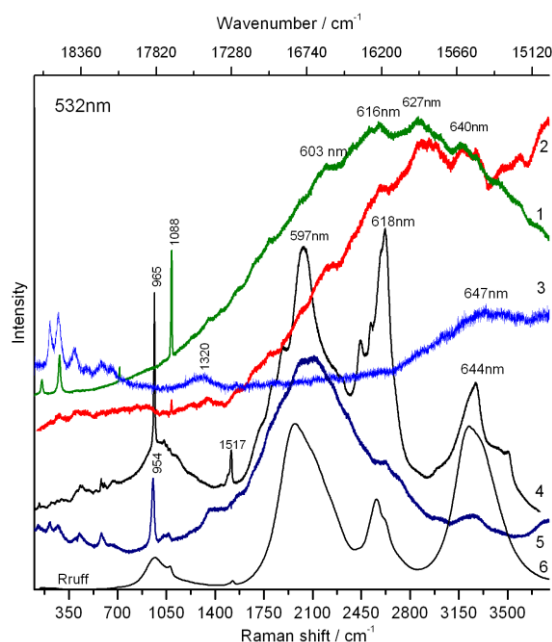


Figure 1: Raman spectra of Tomtor samples: calcite (curve 1); rhodochrosite (curve 2), hematite (curve 3), apatite (curve 4); apatite and barrio-oligite (curve 5); burbankite RRuff ID: R050646 (curve 6).

Acknowledgements: The partial support of the Russian Science Foundation, project No. 18-17-00120, is gratefully acknowledged.

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RHEOLOGICAL PROPERTIES OF CALCALKALINE RHYOLITES ASSESSED THROUGH BOSON PEAK ANALYSIS.

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Colossal eruptions of Super-Volcanoes are considered to be the engines for both extinctions and for rebirths of the life on the planet Earth. These catastrophic events are rare and their triggering mechanisms are largely unpredictable. Their eruptive products mainly consist of calcalkaline rhyolites and show a switch of the eruptive behavior from effusive to explosive in a narrow compositional zone. This excludes significant contribution from water content or crystallinity. In this talk, I will present a thorough study of six synthetic anhydrous analogs mimicking the composition of Yellowstone, (the most dangerous and active Super-Volcano on Earth). The samples are glassy rhyolites containing an alkali ratio ($K\#$) of c.a. 0.5, show an increase in viscosity (measured at c.a. 850°C) of two orders of magnitude as network modifier cations slightly exceed the charge balancer ones. In order to shed light on the structural state of these rhyolitic glasses we analyze the Boson Peak (BP). The BP position (ω_{BP}) shifts toward higher values of ω as the not tetrahedrally coordinated cations exceed the tetrahedrally coordinated ones. In other words, the lower is the glass polymerization, the higher is the ω_{BP} and less viscous the melt. Indeed, the existence of a scaling law of the rhyolite's Boson Peak is proved for $0.40 < K\# < 0.49$ and is linearly correlated with viscosity. This behavior could be ascribed to a different distribution of the collective modes (tetrahedra rotation) in the system. Contrary, mismatch on the BP scaling could be due to a different scale of the heterogeneities (observed for higher $K\#$ c.a. 0.77) and treated with higher scaling factor. This is the reason why we exploit Raman spectroscopy not only as a tool for solving the structural uncertainties of the amorphous volcanic products, but also to discriminate rheological properties of multicomponent melts and magmas with similar chemical composition.

AN END-TO-END GROUND TESTING FRAMEWORK FOR EXOMARS RAMAN LASER SPECTROMETER (RLS) INSTRUMENT

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The Raman Laser Spectrometer (RLS) [1] is one of the Pasteur Payload instruments belonging to the analytical suite onboard the ExoMars' Rosalind Franklin Rover Module that will perform Raman spectroscopy on Mars subsurface samples for a definitive identification and characterization of minerals and biomarkers [2] so that the question of whether life has ever existed on Mars could be addressed.

In order to validate the instrument behavior and performances, support the instrument functional integration, verify the on-board SW and simulate the real RLS operation in Mars, it became necessary to develop a versatile and full automated system. For this purpose, a powerful ground-testing framework has been implemented including electrical and logical emulation of the Rover's On-Board Computer (OBC) interface with RLS [3].

The system is driven by specifically developed scripts which provide a real-time verification of all the telemetries that will be generated during Mars operation. These are checked against expected results, generating automated reports and notifying alarms and warning events to analysis operators in case of any detected anomaly. It also provides capabilities to post-process and evaluate the engineering housekeeping and science telemetries. Its architecture is depicted in Figure 1.

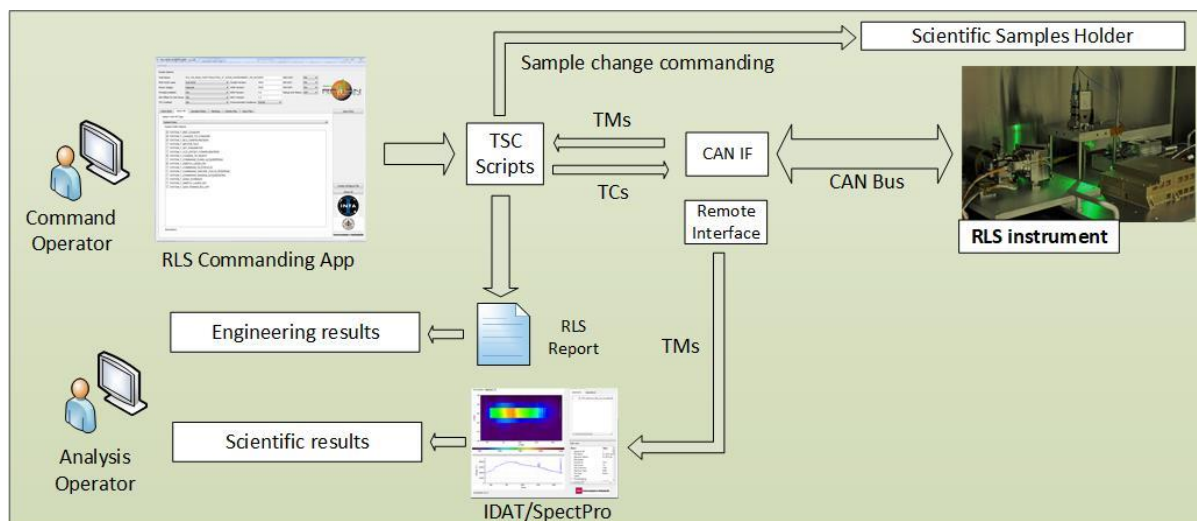


Figure 1: RLS Ground Testing Framework architecture.

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AN AUTONOMOUS CONTROL SOFTWARE FOR EXOMARS RLS INSTRUMENT TO PERFORM IN-SITU ANALYSIS OF RAMAN SPECTRA AT MARS SURFACE

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The Raman Laser Spectrometer (RLS) is one of the three key scientific instruments included in the Analytical Laboratory Drawer (ALD) in the ExoMars 2022 Rover mission which will analyze sub-surface samples on Mars [1]. It will make use of Raman spectroscopy to directly measure the molecular composition of the Martian samples with the final aim of searching for signatures of past or present life on the planet [2].

In order to obtain the maximum scientific performance at the Mars surface while optimizing the limited operation opportunities for RLS, according to the Rover Reference Surface Mission, and solving the engineering difficulties intrinsic to space instrumentation, the RLS team has developed an advanced embedded software that provides an automated control of all RLS subsystems as well as post-processing capabilities to perform prompt in-situ analysis of Raman spectra [3, 4].

Developed for a custom space electronics system, with challenging constraints in terms of execution memory, data storage or power consumption, the RLS control software is capable of safely commanding and controlling all RLS critical elements, such as the optical head focusing mechanism, the CCD imager, both excitation laser sources (redundant), or their corresponding thermal control subsystems, under the severe conditions of the Martian environment. In addition, it also includes the logic to perform automated Raman acquisitions and apply post-processing algorithms [3, 4] to adapt the acquisition to the sample spot under analysis, by avoiding signal saturation, minimizing fluorescence background, removing undesired spikes due to Cosmic Ray impacts and by calculating the acquisition times to maximize the signal-to-noise ratio of the acquired spectra.

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PRELIMINARY RAMAN STUDIES OF MARTIAN NAKHLITE NWA 10720

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Northwest Africa (NWA) 10720 is a martian nakhlite meteorite and was found as freshly broken stone of 1015 g near the border region of Western Sahara in 2015 [1]. This work reports preliminary Raman characterization on mineralogies, petrography, and geochemistry to understand its petrogenetic history.

Nakhlite NWA 10720 is clinopyroxenites with 65.4 vol.% clinopyroxene, 10.2 vol.% feldspar, 19.0 vol.% olivine, and 5.3 vol.% oxide/sulfide via Raman point-counting measurements ($\sim 200 \mu\text{m}$), exhibiting the high percentage of augite similar to potential paired meteorites [2].

Optical image of NWA 10720 exhibits an ophitic texture (Figure 1a and 1b), composed of major euhedral clinopyroxene ($\text{En}_{31.2-42.7}\text{Fs}_{22.7-46.9}\text{Wo}_{25.8-37.0}$) which show igneous zoning with Fe-rich rims, euhedral to anhedral fayalitic olivine ($\text{Fo}_{19.5-47.8}$) with heterogenous composition (Figure 1e), and plagioclase with accessory minerals (Figure 1f). No maskelynite was observed, indicating moderate shock metamorphism. Feldspar commonly occupies interstices between augite grains. Melt veins are variable in size and crosscut the section in random orientations. The average Mg# of pyroxene is 55.7 compared with average Mg# (38.1) of olivine (Figure 1c and 1f), revealing the fractional crystallization processes via the variable mineralogies and compositions consistent with the provenance of nakhlites [3].

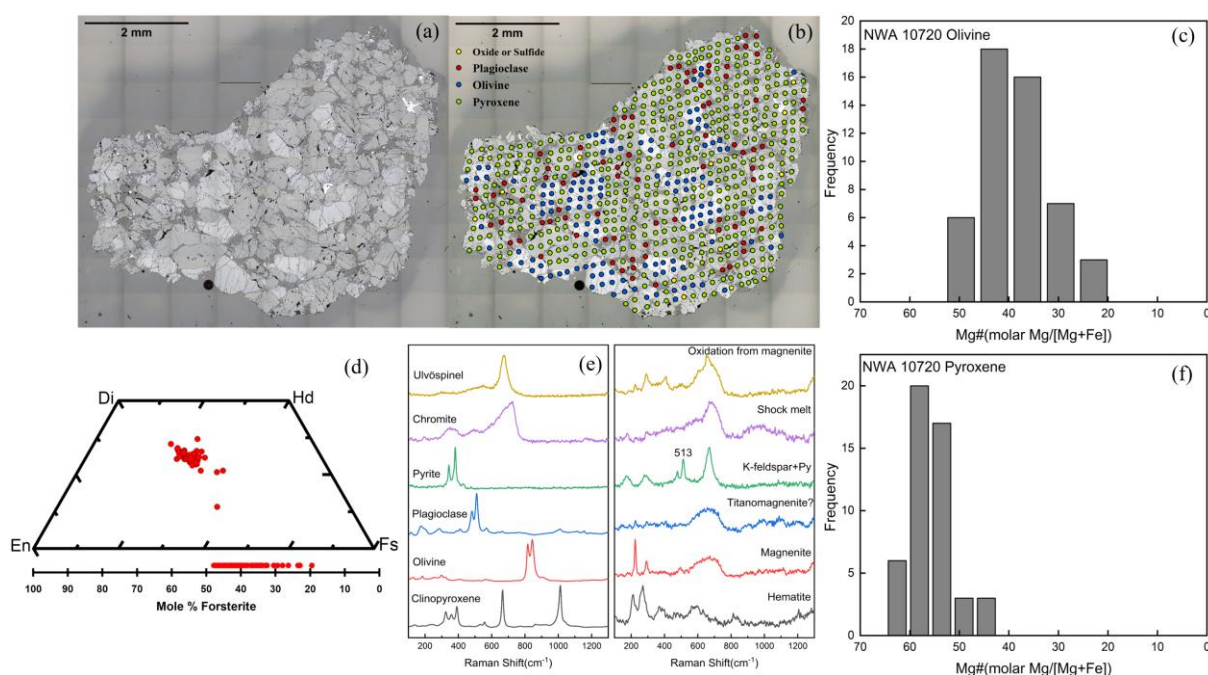


Figure 1: (a) and (b) Optical image of NWA 10720. (c) and (f) Mg# frequency distributions of pyroxene, olivine from Raman analyses. (d) Pyroxene and olivine compositions. (e) Phases identified and their Raman spectra.

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FINDING OF EPIGENETIC ARAGONITE IN THE DEEPEST MANTLE XENOLITHS: SIGNIFICANCE FOR MANTLE METASOMATIC PROCESSES

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Silicate metasomatism events in the upper mantle is considered as ordinary in the Earth's history, but many indirect evidences also point to the important role of carbonate-rich melts in the mantle modifications. However, findings of carbonates are very rare in mantle xenoliths [1]. Here we report the first finding of aragonite in the mantle xenoliths from kimberlites. Aragonite was identified among interstitial minerals in xenoliths of sheared garnet peridotite from Udachnaya kimberlite pipe (Siberian craton). This type of xenoliths are the deepest mantle rocks derived from 180–230 km depth. According to experimental data, aragonite is a high-pressure polymorph of CaCO_3 , which is stable at upper mantle pressures and temperatures [2]. Thereby aragonite is used as indicator of high P-T parameters in petrological studies [3]. Calcium carbonate in mantle xenoliths was identified initially by composition using scanning electron microscopy. Then Raman spectroscopy was applied to determine CaCO_3 polymorph. Both polymorphs of the CaCO_3 , aragonite and calcite, are characterized by main strong Raman band at 1086 cm^{-1} and medium band at 283 cm^{-1} . However, aragonite may has additional medium and weak Raman bands at 143, 153, 161, 181, 191, 207, 273, 702, 706 and 1462 cm^{-1} (Fig. 1), whereas calcite has two medium bands at 156 and 713 cm^{-1} and one weak band at 1436 cm^{-1} . The presence of aragonite in the deepest mantle xenoliths is direct evidence of existence of carbonatite or carbonate-rich melts in the deep mantle (>230 km) near lithosphere basement of ancient cratons. Such melts can percolate through the upper mantle rocks and should inevitably modify their mineralogy and trace element budgets of individual minerals. Alkali-rich primitive kimberlite melts are a good candidate on the role of mantle metasomatic agents for such type of mantle rocks.

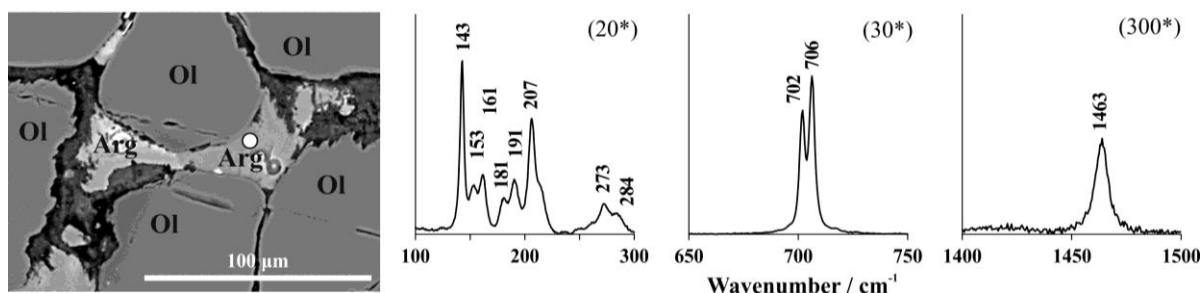


Figure 1: BSE-image of the sheared garnet peridotite with rock-forming olivine (Ol) and Raman spectrum of interstitial aragonite (Arg) in fingerprint regions; the circle indicates point of the Raman spectrum. Relative scaling (*) is given with respect to the strong band at 1086 cm^{-1} .

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MELT INCLUSIONS IN MANTLE XENOLITH FROM BULTFONTEIN KIMBERLITE PIPE, SOUTH AFRICA

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Primary composition of kimberlite melt is poorly constrained because kimberlites ubiquitously contaminated by xenogenic material and altered by post-emplacement hydrothermal processes. Recent study of unique unaltered xenoliths of sheared garnet peridotites (SGP) from Udachnaya-East kimberlite pipe (Siberian craton) discovered melt inclusions in olivine [1, 2]. This type of xenoliths represents the deepest mantle rocks derived from the base of lithosphere (180–230 km depths). The melt inclusions were interpreted to be snapshots of the most primitive (i.e., close-to-primary) kimberlite melt that were infiltrated into SGP. Alkali carbonates, halides and sulphates were found among daughter phases in these melt inclusions indicating that the primary kimberlite melt was alkali-carbonatitic in composition [1, 2]. We studied melt inclusions in olivine from one SGP xenolith from another kimberlite locality, Bultfontein pipe (Kaapvaal craton, South Africa), using a confocal Raman microprobe system Horiba Jobin Yvon LabRAM HR800 equipped with a 532-nm laser. The melt inclusions in studied sample (Fig. 1a) are texturally similar to those in the Udachnaya-East SGP. However, they are less abundant than in the Udachnaya-East SGP, because olivine grains are extremely serpentinized. Raman spectroscopy revealed that unexposed inclusions in the Bultfontein SGP contain calcite CaCO_3 , dolomite $\text{CaMg}(\text{CO}_3)_2$, shortite $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$, nyerereite $(\text{Na},\text{K})_2\text{Ca}(\text{CO}_3)_2$ (Fig. 1b), eitelite $\text{Na}_2\text{Mg}(\text{CO}_3)_2$, northupite $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$ and bradleyite $\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)$. This daughter minerals assemblage, containing alkali carbonates, is similar to the mineralogy of the melt inclusions in the Udachnaya-East SGP. Therefore, conclusion about alkali-carbonatitic composition of primary kimberlite melt is true not only for the Udachnaya-East kimberlites and could be extended to other kimberlites.

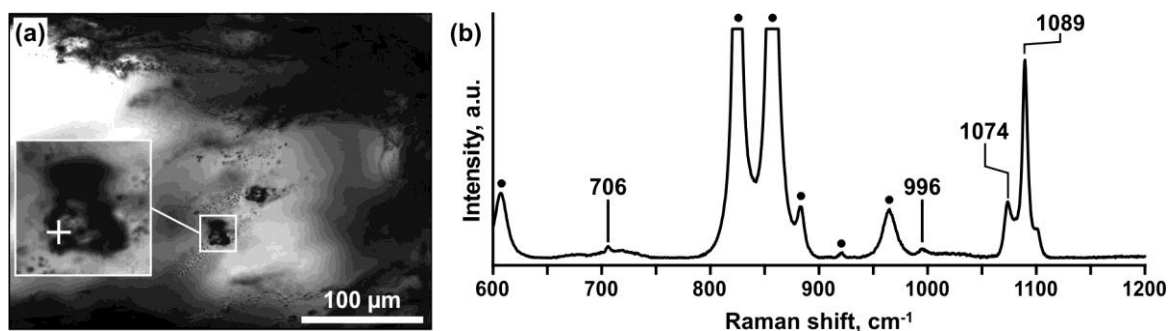


Figure 1: (a) Melt inclusions in olivine of peridotite xenolith from Bultfontein pipe. White cross indicates point for Raman spectrum in pallet (b). (b) Raman spectrum of a daughter phase within inclusion. Numbers and black circles label peaks of nyerereite (for reference see Fig. 12 in [3]) and host olivine, respectively.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (grant No. 20-35-70058).

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SPECTROSCOPIC STUDIES OF IRON (OXYHYDR)OXIDES RELEVANT TO MARS

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Iron (oxyhydr)oxides were predicted to be globally distributed on Mars, a red planet in our solar system, by telescopic studies [1]. Ferric oxides that have also had been identified from the Martian meteorite and Mars orbit remote sensing are dominated in the last era (the siderikian) of Mars [2,3]. They are thought to form from a slow superficial weathering of iron salts such as ferric sulfate. The types of iron oxides include goethite (α -FeOOH), akaganéite (β -FeOOH), lepidocrocite (γ -FeOOH), hematite (α -Fe₂O₃), ferrihydrite (5Fe₂O₃·9H₂O), magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), schwertmannite (Fe₈O₈(OH)₆(SO₄)·nH₂O), etc. It is necessary to obtain a comprehensive spectral database of iron oxides to interpret datasets from missions in the future, such as NASA Mars 2020 and China's first Mar Mission, etc.

To avoid any ambiguous detections, comprehensive analytical instrument development is required. Raman spectroscopy is one of the promising planetary spectroscopy techniques especially for explorations of mineralogies and biomarkers on Mars [4,5]. It could either be used *in situ* or remotely to identify the type of ferric (oxyhydr) oxides. We have synthesized the ferric (oxyhydr)oxides, such as akaganéite, goethite, magnetite, and their solid solutions, starting from ferric sulfates or ferric chloride. X-ray Diffraction (XRD) and Raman methods are employed to perform the structural and spectroscopic characterizations of the martian analog samples. The goal of this study is to acquire critical spectroscopic and mineralogic information for their potential martian utilizations (phase identifications, environmental condition constraint for Mars).

Figure 1 shows the Raman spectra of goethite, akaganéite and XRD pattern of the magnetite that we synthesized in the laboratory. The mid-infrared and visible near-infrared spectra are also acquired for the spectral database. We found that, although iron (oxyhydr)oxides produce relatively weak Raman signals comparing to other silicate minerals, their phases can be readily identified from their characteristic Raman spectral patterns.

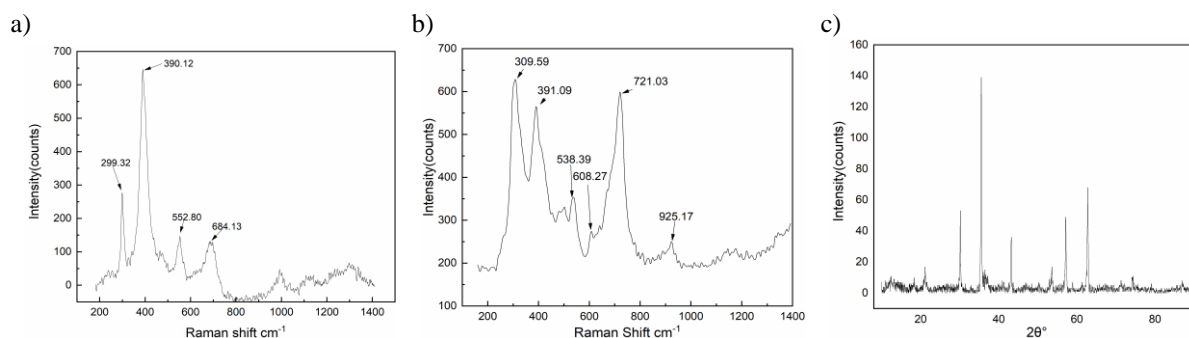


Figure 1: a. Raman spectra of goethite (α -FeOOH). b. Raman spectra of akaganéite (β -FeOOH). c. XRD pattern of the Magnetite.

Acknowledgments: The fundings are from the National Natural Science Foundation of China (U1931211, 11941001, 41972322) and the Natural Science Foundation of Shandong Province (ZR2019MD008).

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SPECTROSCOPIC CHARACTERIZATIONS OF SYNTHESIZED MANGANESE OXIDES RELEVANT TO MARS

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Manganese (Mn) (hydr)oxides within the veins of the sedimentary rocks of Gale and Endeavour craters have been found by Opportunity and Curiosity rovers [1-2], indicating the existence of the amount of liquid water at the surface or subsurface on ancient Mars. However, precipitating and concentrating Mn in rocks and sediments require high-potential oxidants to oxidize Mn to insoluble, high-valence oxides, revealing that Mn (hydr)oxides can provide unique constraint about the redox condition of the water body on Mars. The observation of rovers identified the limited manganese oxides at the local outcrops and within the veins hosted rocks on Mars but the indistinguishable types of Mn oxides from the mixtures, possibly owing to the lack of systematic laboratory spectroscopy. In this work, a variety of Mn oxides were synthesized by the hydrothermal method using Teflon-lined stainless autoclave. The structural and spectral characterizations of Mn oxides were systematically performed to establish the spectral database of manganese oxides, including XRD, Raman, MIR, VNIR, LIBS. Compared to the natural Mn oxides, samples synthesized in the laboratory have a good purity that can be regarded as standards of Mn oxides.

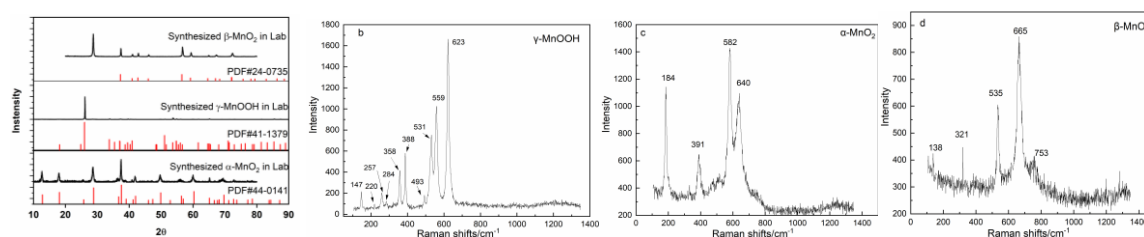


Figure 1: XRD and Raman spectra of γ -MnOOH, α -MnO₂, and β -MnO₂

The identification of the γ -MnOOH, α - and β -MnO₂ have been performed by XRD (Figure 1a). The Raman spectra of γ -MnOOH, α - and β -MnO₂ were obtained (Figures 1b, 1c, and 1d). Raman spectra of γ -MnOOH exhibit five strong peaks located at 623, 559, 531, 388, 358 cm⁻¹. As for α -MnO₂, the two main peaks around 582 and 640 cm⁻¹ have been observed in our spectral range, attributed to the Mn-O vibration[3] in α -MnO₂. The Raman spectra of β -MnO₂ is characterized by two sharp peaks at 535 and 665 cm⁻¹, owing to the stretching mode of the MnO₆ octahedra [4]. The characteristic XRD pattern and Raman spectra of α - and β -MnO₂, γ -MnOOH confirm the homogeneity of samples with good crystallinity, thus those datasets would be helpful for future Mars in-situ explorations.

Acknowledgments: The authors thank the supports from the National Natural Science Foundation of China (U1931211, 11941001, 41972322) and the Natural Science Foundation of Shandong Province (ZR2019MD008).

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PIGMENTS AND FIRING TEMPERATURES OF GLASS BEADS FOUND AT THE VACCAEI NECROPOLIS OF PINTIA (S. IV-I BC)

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The archaeological site of Pintia (Padilla de Duero, Valladolid, Spain) has provided a priceless global picture of the Vaccaei culture, who inhabited the sedimentary plains of the Duero river for a few centuries (s. IV-I BC). In particular, Pintia preserves the only Vaccaei cemetery known, the necropolis of "Las Ruedas", which has been studied for almost 40 years. The large number of well-preserved graves found in the necropolis, together with the diverse trousseaus and viatic offerings found in them, suggest the relevance of the funerary rituals in the ancient Vaccaei culture.

Among other items recovered from the graves, Pintia highlights as the most important archaeological site in the interior of the Iberian Peninsula in terms of the number of glass beads found, currently over six hundred pieces. As glass pieces were highly appreciated goods in the Protohistory of the Iberian Peninsula, their broad presence suggests the relevance of the Vaccaei culture in its time. Moreover, no evidence has been found about the local production of such pieces, being probably a testimony of the commercial and political relationships with other cultures.

After more than two thousand years, several of these glass beads are exceptionally well-preserved, showing intense colors or even elaborated polychrome (Figure 1). A representative set of these pieces have been studied by Raman spectroscopy, carried out in microscopic mode, in order to identify the pigments employed to achieve such colors (e.g., Massicot, CaSb_2O_6), as well as to obtain information about the glass production technology (i.e., the firing temperature). The information about the pigments provided by the Raman spectra of the glass beads was complemented by energy-dispersive X-ray (EDX) microanalysis and X-ray Fluorescence (XRF).

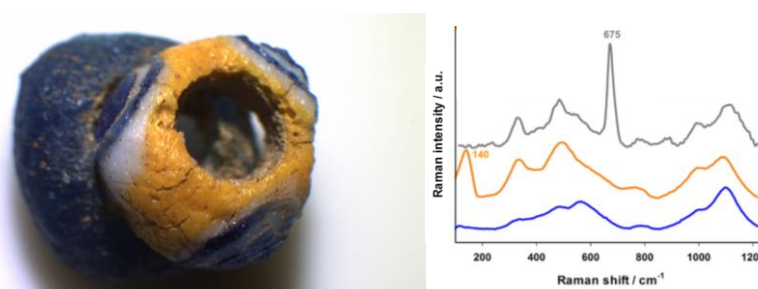


Figure 1: Polychrome glass bead found in the necropolis of Las Ruedas (Pintia, Padilla de Duero, Spain) and Raman spectra of the regions with a different color (the grey line is assigned to the white color).

ORIGIN AND PARTICULARITIES OF THE PORTUGUESE NATIONAL TREASURE “O DESTERRADO”: A RAMAN STUDY

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“O Desterrado” (which could be translated as “The Banished”) is a masterpiece by Antonio Soares Dos Reis (1847-1889). This sculpture in marble was created in 1872 in Rome (Italy), and then moved to Portugal, where is currently preserved in the Museo Nacional de Soares Dos Reis (Porto, Portugal). Although it is a national treasure of Portugal, there are several questions some alterations of unknown provenance in the texture or color of the sculpture.

In particular, the sculpture presents a yellowish color in the left leg and foot, which has been told to be related to some ancient tradition or art students of touching these parts of the sculpture. In addition, some small regions of the sculpture present white surfaces with a particular texture, which could have been an intentional effect created by the artist.

A detailed in-situ Raman spectroscopy study has been recently performed on this sculpture, with the aim to provide answers to these unsolved questions, by identifying the composition and characteristics of the marble, as well as of the visible alterations. The Raman spectra of the marble proved that its features are compatible with those of the Statuary Venato Carrara marble, presenting dark streaks with organic matter in which it is possible to found pyrite crystals. Moreover, the metamorphism temperatures determined for the sculpture are in good agreement with those of the region of the Apuan Alps. Regarding the alterations, Raman analysis has demonstrated that the yellowish color of the left leg is not related to the composition of the marble (i.e., it is not associated with a streak), while the degraded white surfaces present calcium phosphates, which sometimes are found on Carrara marble.

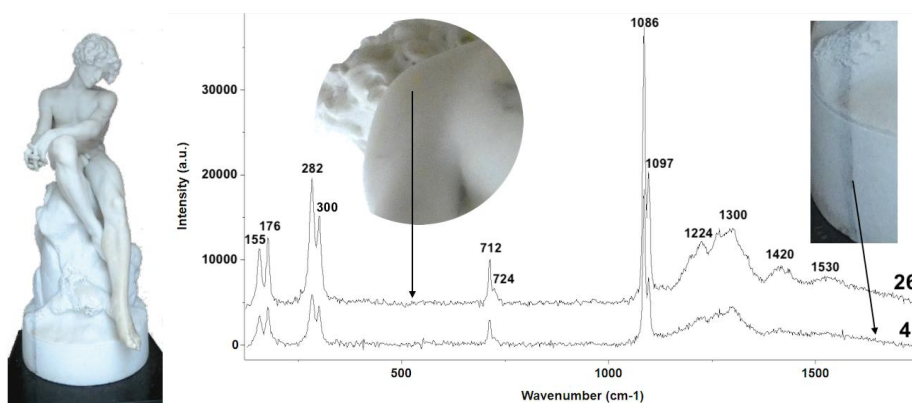


Figure 1: Photography of “O Desterrado” and Raman spectra of some marble streaks.

LABORATORY SPECTROSCOPIC STUDIES OF K-H₃O-NA ALUNITE SOLID SOLUTIONS RELEVANT TO MARS

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Alunites ((K, Na, H₃O)Al₃(SO₄)₂(OH)₆) are part of alunite super group with rhombohedral (R3m) symmetry [1]. K-bearing alunite has been identified in several craters located in the Noachian highlands of the Terra Sirenum region (30°S, 158°W) of Mars based on remotely acquired CRISM datasets, indicating acidic (pH < 3), sulfurous waters at the time of its formation [2, 3, 4]. However, detailed chemical compositions of alunite solid solutions are still ambiguous for Mars remote sensing and in-situ spectroscopic studies, which may lead to incomplete phase identifications and inaccuracy of evaluating local hydro-thermal conditions.

In this study, we synthesized 21 alunite solid solutions with different K-Na-H₃O contents and 3 alunite endmember under hydrothermal conditions in autoclaves at an incubator chamber at 145 °C for 48 hours. The exact chemical compositions (Fig. 1 a) were obtained by SEM-EDS (FEI Nova NanoSEM 450). Raman spectra were collected with inVia[®] Raman System (Renishaw Company). Raman features (Fig. 1 b) show systematic variations with Na-number (Na/(K+Na+H₃O)×100%) in alunite (e.g. Raman features at ~1085 cm⁻¹), which can be used to predict alunite compositions using Raman spectra (e.g., SuperCam) in combination with a geochemical modeling method to better understand past water-rock interactions on Mars. In addition, the mid-infrared and visible near infrared spectral datasets of these solid-solution samples were also collected for their future applications in Mars data analysis.

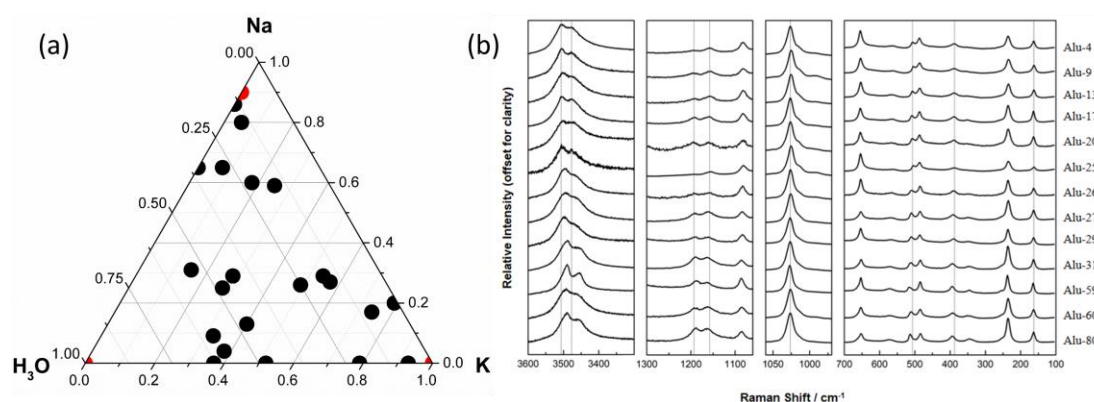


Figure 1: (a) Compositions of synthesized alunite samples. (b) Raman spectra of alunite solid solutions with Na, K and H₃O content (Alu-4 meaning 4% Na content in alunite).

Acknowledgments: The fundings are from the National Natural Science Foundation of China (U1931211, 11941001, 41972322) and the Natural Science Foundation of Shandong Province (ZR2019MD008).

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RAMAN SPECTROSCOPY STUDY OF DYPINGITE, NESQUEHONITE AND ARAGONITE FROM OBNAZHENNAYA KIMBERLITE PIPE

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The Obnazhennaya pipe is unique among kimberlites of the Siberian Craton (Russia), since it is a 20 meter in height crag located in the river valley. Thus, the kimberlite body of the Obnazhennaya pipe constantly interacts with precipitation. Kimberlite melts, as well as rocks, are initially enriched in the CO₂ component, reflected in the presence of various carbonates. Mg-H₂O-rich carbonates, dypingite (Mg₅(CO₃)₄(OH)₂•5H₂O) and nesquehonite (MgCO₃•3H₂O), to the best of our knowledge, are identified for the first time in these rocks. The assemblages of serpentine ((Mg,Fe)₆[Si₄O₁₀](OH)₈) + dypingite + aragonite (CaCO₃) was found around the rock-forming olivine grains ((Mg,Fe)₂SiO₄) within the kimberlite body, while dypingite + nesquehonite forms a white coating or small (up to 5 mm) stalactites on the surface of the crag. Dypingite is characterized by main strong Raman band (RB) at 1120 cm⁻¹ and medium RBs at 147, 184, 202, 232, 247, 725 and 760 cm⁻¹. Nesquehonite has one strong RB at 1100 cm⁻¹ and medium RBs at 119, 167, 187, 199 and 228 cm⁻¹. Aragonite was identified by strong RB at 1085 cm⁻¹ and medium/weak RBs at 152, 180, 190, 205, 701, 706 and 1462 cm⁻¹ (Fig. 1). C–O isotopic composition is δ¹³C_{PDB}=2‰ and δ¹⁸O_{SMOW}=20‰ for the dypingite + aragonite assemblages and δ¹³C_{PDB}=12‰ and δ¹⁸O_{SMOW}=27‰ for the dypingite + nesquehonite assemblages, which indicates the non-mantle nature of carbon and oxygen in the studied carbonates. Source of water (magmatic vs external) for serpentinization of kimberlite rocks as well as the initial water content in kimberlite melts are debatable issues [1, 2, 3]. In the case of the Obnazhennaya, it can be argued that the serpentinization of these rocks and the formation of the studied carbonates occur in present time at temperatures < 50 °C, when CO₂-rich atmospheric water penetrate through the rock and interacts with mantle olivine. During serpentinization of olivine some water is spent on the formation of serpentine, with the release of Mg and its admission into residual fluid. Thus, during the formation of very unusual for kimberlites carbonates, such as dypingite, nesquehonite and aragonite, some of the constituent elements (Mg, Ca) have mantle nature whereas others (C, O) are of external origin.

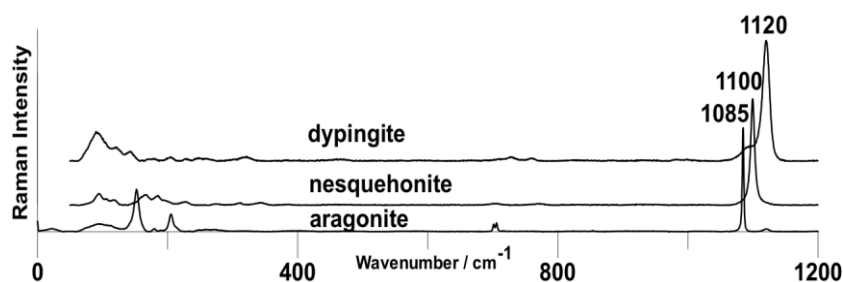


Figure 1: Representative Raman spectra of the carbonates.

Acknowledgments: This work was supported by the Russian Science Foundation (grant No. 18-77-10062).

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IDENTIFICATION OF MINERALS IN KELYPHITE AROUND GARNET IN KIMBERLITE-BORNE XENOLITHS USING RAMAN SPECTROSCOPY

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Garnet grains in mantle xenoliths from kimberlites are ubiquitously surrounded by a kelyphitic rim. The kelyphite mostly consists of extra-fine mineral grains (<5 μm). It leads to ambiguous identification of minerals in the kelyphite by electron probe microanalyses both WDS and EDS. However, correct information on the phase composition of the kelyphite is of key importance for revealing its genesis. Confocal Raman spectroscopy is useful for identification of constituting phases of the kelyphitic rim.

We examined the kelyphite around garnet in unaltered xenolith of sheared lherzolite from the Udachnaya-East kimberlite pipe (Siberian Craton) [1]. Raman spectra were collected by a Horiba Jobin Yvon LabRAM HR800 Raman system equipped with a 532 nm laser.

Minerals in the kelyphite were identified by comparing of obtained spectra with literature dataset [2-6]. The kelyphite is composed of the eight minerals (Fig. 1): enstatite (En), clinopyroxene (diopside (Di) or augite (Aug)), spinel (chromite-spinel solid solution (Chr-Spl)), pargasite (Prg), phlogopite (Phl), sodalite (Sdl), olivine (Ol) and rare garnet relics. Raman spectra of the garnet relics and the garnet rim are similar. Olivine is forsterite (Mg# = 81.9) according to Raman evaluation method [6].

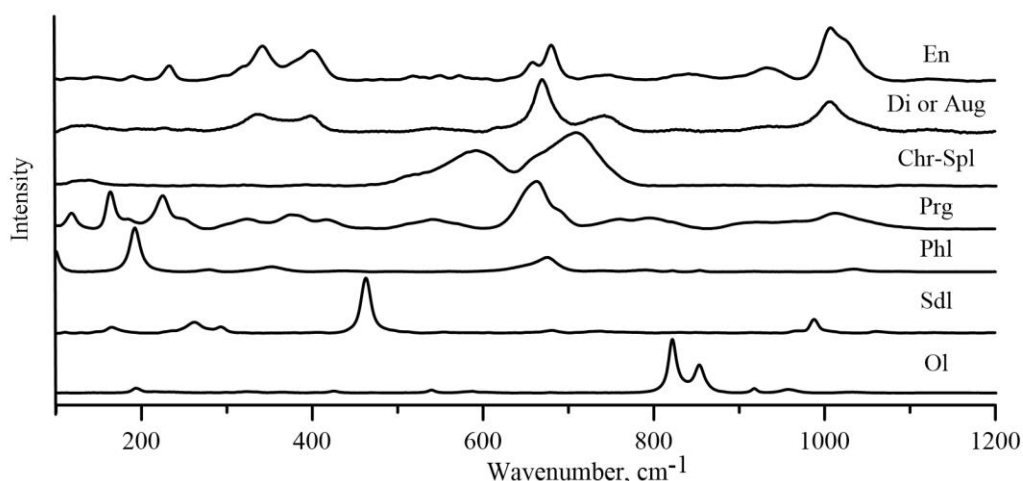


Figure 1: Representative Raman spectra of the kelyphite-forming minerals.

Our results confirm the mineral assemblage of the kelyphite described in previous works and reveal that the kelyphite in unaltered xenoliths does not contain chlorite and serpentine. The latter indicates that chlorite and serpentine are secondary minerals in the kelyphite and crystallized during post-magmatic alteration of kimberlites and their mantle xenoliths.

Acknowledgments: This work was supported by the Russian Science Foundation (grant No. 18-77-10062).

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A REMOTE RAMAN SYSTEM FOR PLANETARY MATERIAL STUDIES IN SHANDONG UNIVERSITY

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As a powerful vibrational spectroscopic technique, Raman spectroscopy has been widely used in the terrestrial and planetary sample analysis in laboratory owing to its advantages in quick and non-destructive analysis on the mineralogy and mineral chemistries of rocky and/or soil samples. For planetary explorations, Raman spectroscopy also exhibit great potentials like sharp and non-overlapping peaks for unambiguous phase identification, rapid analysis with no sample preparations, low-mass and robust behavior, etc. Until now, several Raman systems have been proposed for either in-situ or remote detections on planetary surface for lander's or rover's exploration missions of Moon, Mars, Venus, Europa, asteroids etc. Specifically, three Raman payloads are ready to exploration Mars (e.g., RLS on ESA's ExoMars and SuperCam and SHERLOC on NASA's Mars 2020) [1-3].

Remote Raman spectroscopy can detect and identify the minerals and organics at the distance from several meters to hundreds of meters [4]. In this work, a Remote Raman system that has been built for planetary material studies in Shandong University. In this system, a compact Nd: YAG Q-switched laser source (Beamtech Optronics Co, Ltd Dawa-200 Laser, 1064 nm, 0~232 mJ/pulse, 0~20 Hz, pulse width 9 ns, central laser spot divergence ~1 mrad, diameter ~6 mm) is used to generate 532 nm green laser by a harmonic generation of 1064 nm laser with a doubling crystal. The laser spot diameter on the sample is about 1.5 cm at a distance of ~4 meters. Raman signal is collected by the telescope and focused on a fiber probe by a convex lens. The Notch filter is used to remove the 532 nm Rayleigh scattering laser in the spectrometer. With this remote Raman system, several minerals and organic materials such as Calcite, Quartz, Olivine, Plagioclase, K-feldspar, and Ethanol have been measured. The Raman spectral patterns demonstrate "fingerprints" spectra for their phase identifications as well as structural analysis.

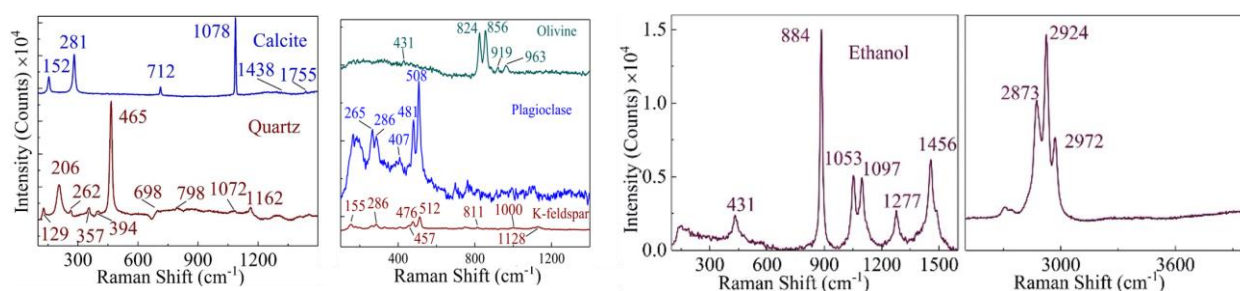


Figure 1: The Raman spectra of Calcite, Quartz, Olivine, Plagioclase, K-feldspar, and Ethanol

Acknowledgments: The authors thank the supports from the National Natural Science Foundation of China (U1931211, 11941001, 41972322) and the Natural Science Foundation of Shandong Province (ZR2019MD008).

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IN SITU RAMAN MONITORING OF GLYCINE-MGSO₄ 5H₂O UNDER MARTIAN SIMULATED CONDITIONS

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Minerals can catalyze, concentrate and protect molecules under harsh planetary conditions, among them, we are interested in Glycine-metal(II)sulfates compounds due to two main reasons. 1) This molecule contains glycine in its structure which is an amino acid, and therefore one of the basic “Building Blocks” to form proteins. 2) Its structure can contain water molecules which, as other salts, are a plausible medium to storage water.

Therefore, the aim of this work is to study Glycine-MgSO₄ 5H₂O salt, under Mars simulated conditions (99% CO₂ and 0.6% H₂O at a pressure of 7mbar) at the laboratory by using *in situ* Raman spectroscopy inside the Planetary Atmospheres and Surfaces Chamber (PASC), a dedicated planetary simulation chamber (see Figure 1.A) [1]. Mg has been chosen as a metal due to its abundance on Mars as a water soluble sulfates [2]. Our goal here is, in one hand to study the chemical evolution of this particular molecule under Mars planetary simulated conditions by *in situ* Raman spectroscopy and on the other hand to provide quality Raman spectra of compounds to help with its possible detection on Mars for the upcoming planetary missions.

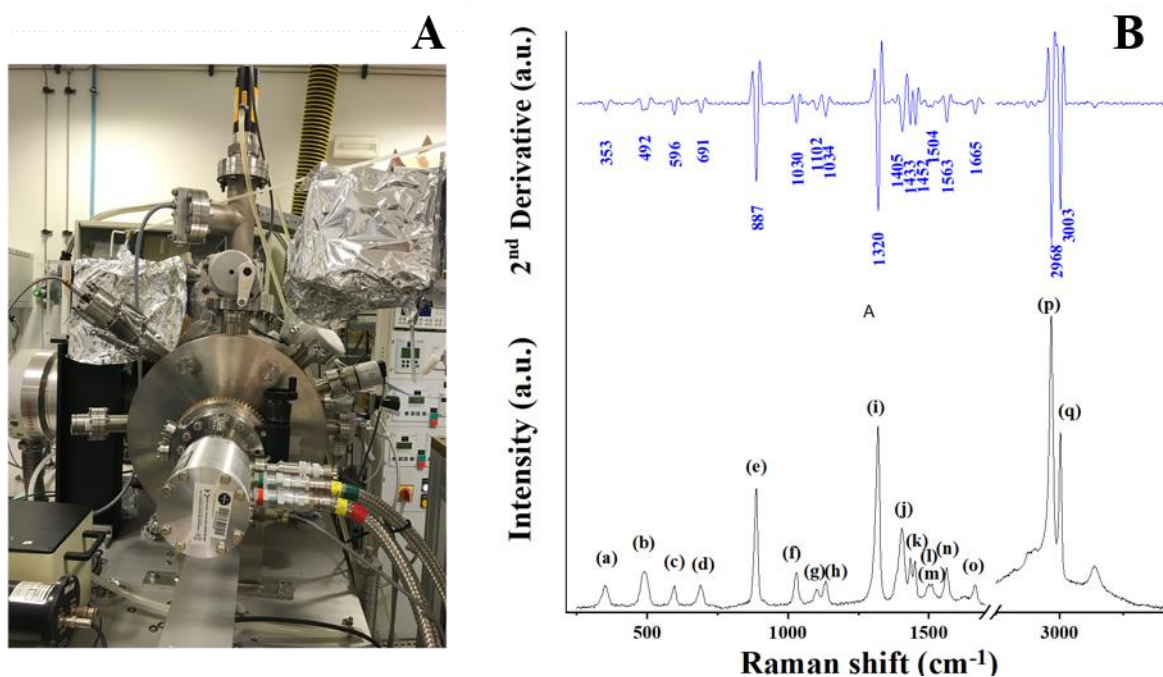


Figure 1: A. Imagen the the Planetary Atmospheres and Surfaces Chamber (PASC), B) Raman spectrum of GlyMgSO₄ 5H₂O.

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RLS SAMPLE ACQUISITION POSITION VERIFICATION WITH THE EXOMARS ALD QM AND RLS EQM

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Raman Laser Spectrometer (RLS) is one of the three key analytic instruments of the ExoMars mission Pasteur Payload, within the ESA's Aurora Exploration Programme. Installed in the Analytical Laboratory Drawer (ALD) of the ExoMars 2022 Rover, RLS will analyze sub-surface samples on Mars to determine its molecular composition [1].

The RLS operational scenario considers the Raman analysis on powder samples [2] and will be carried out with the internal optical head (iOH) located on the top of the sample distribution mechanism (SPDS), inside the ALD (UCZ). The iOH provides an optical I/F with the ALD and the unobstructed field of view allows direct sample observation through an optical window which prevents contamination from the iOH to the UCZ.

The powder sample is presented in front of the iOH using the SPDS refillable container (RC). The Raman iOH focuses the RLS laser light on the sample and performs the scan of the entire surface following an imaginary line, created by the relative movement of the SPDS. The SPDS moves the sample (x, y) underneath the iOH, whose actuator (± 1 mm range) moves the IOH optical path (z) to reach the accurate acquisition position that allows effective Raman operation (5 μ m resolution). The Acquisition position is obtained when the volume irradiated by the excitation is optimized to maximize the Raman scattering intensity.

In our system, the sample reference surface (Z=0 position), is ideally on the top of the sample surface. The sampling drilling (grain size) and flattening methods (ALD) provides an uncertainty over the acquisition position but always ensuring the sample in the RC is inside the focusing range for RLS situated at $\pm \Delta$ μ m from the sample surface. The main parameters defining the RLS system measurement geometry are the working distance, standoff distance from the iOH optical lens to the sample and the acquisition position, offset distance from Z=0.

The final sample topography obtained after SPDS drilling and flattening processes is verified in representative end to end tests using RLS instrument to retrieve the sample roughness information. The ALD QM representative samples are crushed by the Drill and stored in the dosing station. The dosing station transports the powder to the RC which is finally flattened before sample presentation to RLS. The SPDS moves the sample in steps of 200-400 μ m scanning a big area of the sample and RLS EQM performs AF and Raman image acquisitions in every spot to determine the real acquisition position.

In this work we present the results of the SPDS flattening performance and the nominal sample acquisition position (RLS actuator default position), based on the RLS acquired data.

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RLS - THE EXOMARS 2022 RAMAN INSTRUMENT: DESIGN AND OPERATION HERITAGE FOR FUTURE PLANETARY MISSIONS

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The Raman Laser Spectrometer (RLS) [1] is one of three analytical instruments located within the Rover ALD (Analytical Laboratory Drawer) on the ExoMars 2022 mission. Purely devoted to mission scientific purposes, it will use Raman spectroscopy to analyse some selected surface and sub-surface samples obtained with the Rover Drill (capable of reaching up to 2m in depth) and crushed before being presented by a carousel mechanism to the suite of laboratory instruments. The RLS will characterize the mineral phases that result from water-related processes and will help to determine the water/geochemical environment as a function of depth in the shallow subsurface. The instrument will also be able to detect organic compounds and will aid the ExoMars rover's search for signs of life through its ability to identify biochemical molecules and mineral bio-products.

After the RLS Instrument flight model (FM) was delivered for integration into ESA's Rosalind Franklin Rover in December 2018, a number of instrument level tests were performed - both during the Rover level testing and characterization campaign and during the flight spare model (FS) test campaign (an instrument installed at INTA facilities that is identical to the FM). During these processes several important lessons were learned about optimum instrument design that could be applicable to similar Raman instruments planned for future planetary exploration missions, whether for lunar rover missions, the exploration of Phobos (e.g. RAX for MMX) [2] or the exploration of icy moons orbiting outer planets.

The main aspects of instrument development that will be discussed include: spectrometer design, laser design and excitation capabilities, sample handling and preparation (including contamination avoidance) and, in particular, how Raman spectroscopy could be combined with other analytical techniques on-board future space mission payloads. Besides, several aspects of instrument operation are also analyzed, such as: science operating modes (i.e. interactions with other instruments like RLS & MicrOmega [3], or implementation of automatic sample scanning modes), optimization algorithms [4] taking into account mission constraints (e.g. power, downlink rate, time) and on board processing and calibration. All of these critical aspects of functionality of the ready to fly RLS instrument, could be important for helping to define the operation, size and design of future mission instruments.

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RAX – RAMAN SPECTROMETER FOR PHOBOS IN-SITU EXPLORATION

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Phobos occupies a unique position in the exploration of the Solar System. It is a low-gravity object inside the gravity well of Mars. The origin of Phobos as well as Deimos, are uncertain and studying both provides insights into the formation of the inner Solar System, including the terrestrial planets [1]. Gaining knowledge about the origin, evolution, and formation of Solar System bodies is the main objective of the Martian Moons eXploration (MMX) mission and the accompanying rover mission.

The MMX mission to be launched 2024 by the Japan Aerospace Exploration Agency (JAXA) will conduct remote sensing observations of both Mars moons, Phobos and Deimos. It will carry out in-situ measurements and return samples from the surface of Phobos [2] back to Earth. A rover provided by DLR/CNES will be deployed on Phobos and perform scientific measurements on the surface including Raman spectroscopy with an instrument - RAX (RAMAN spectrometer for MMX) - developed by DLR, INTA/UVA and JAXA/UT/Rikkyo [3]. RAX is a compact, low-mass Raman instrument with a volume of approximately 81x98x125 mm³ and a mass of less than 1.4 kg. In-situ Raman spectroscopy will provide information about Phobos' mineralogical and geochemical composition of the Phobos surface [4]. The RAX data will support the characterization of a potential landing site for the MMX spacecraft and the selection of samples for the return to Earth. The comparison with measurements on returned samples in laboratories on Earth allows more detailed analyses and provides the most unambiguous means to distinguish among the different hypotheses about the moons' origin. The RAX measurements will be compared with Raman measurements obtained from the RLS instrument during the ExoMars mission, to provide evidence for the Martian or non-Martian origin of the surface minerals of Phobos.

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SALT SOLUTIONS STUDY BASED ON RLS-LIKE DATA. AN APPROACH TO EUROPA

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Jupiter's satellite Europa is one of the most interesting planetary bodies in the Solar System for astrobiology. In the following years NASA and ESA will increase their efforts in the study of the Jovian system. Europa Lander mission includes a Raman instrument as recommended payload, that could allow detection of organics but also a characterization of their context, the salty frozen surface. The aim of this work is to evaluate the capabilities of a hypothetical Raman instrument, that would analyze molten ice, in the calculation of its salinity through the analysis of several brines, in order to find an automated process to implement in the mission. For this, several solutions with different concentration of different salts (magnesium chloride and sulfate) have been made, including solutions of both salts.

Parting from a band model of pure water, which has two clearly distinguishable areas. The bending band at $1500\text{-}1800\text{cm}^{-1}$ is not considered in this study, since it disappears with salinity. Therefore, we will only focus on the main band located between $2800\text{-}3800\text{cm}^{-1}$, where a theoretical five-band model is used [1].

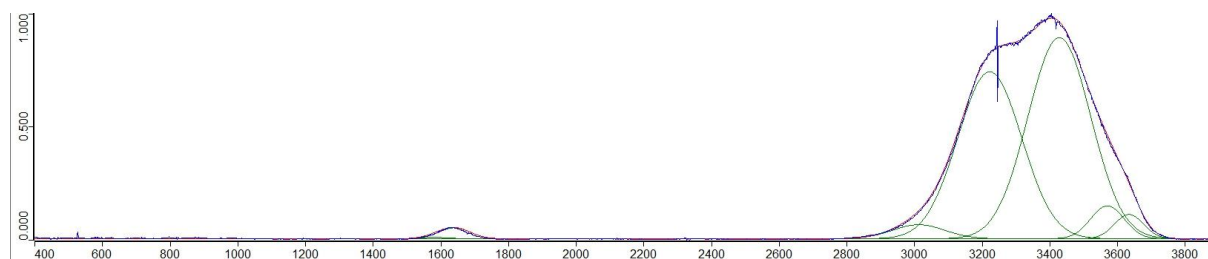


Figure 1: Raman water bands

Since sulfate presents a band at $930\text{-}1030\text{ cm}^{-1}$, a direct detection and quantification can be done based on sulfate Raman features. This is much more complicated when we have salts with no Raman features, that are only detected by their influence in the main bands of water, as chlorides. Studies indicate the influence of ionic concentration in the individual bands of water [2,3], but also the size of the ions in play can introduce different distortions. From the band model of water, the parameters can be modified for each concentration in order to obtain a relationship that relates to salt content. With this, there is enough knowledge to determine the concentration of a chloride in pure solutions. This work evaluates also if the variations in the water bands in a sulfate-chloride solution can describe the content of the “invisible” member in the mixture, which is a situation closer to what is expected in Europa.

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AUTOMATIC IDENTIFICATION OF CARBONATES BASED IN RAMAN-LIBS COMBINATION

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Raman-LIBS is a combination with great potential for planetary exploration. RLS instrument in Exomars started as a combined instrument, SuperCam, already a reality, will carry this combination in Mars2020 mission [1]. The present work evaluates the power of combination of these two techniques for automatic identification of different Ca-Mg-Fe carbonates of relevance for Mars [2].

While Raman is sensitive to structure, LIBS is sensitive to elemental composition, in carbonates identification this means that the first could tell us the presence of carbonates, but differences in spectroscopic features of different carbonates could be subtle. The second could never tell if the different elements are arranged in a carbonate and its structure, distinguishing polymorphs. Combination of both can provide all the information needed for an accurate identification of carbonates or mixtures. Different algorithms and methods are evaluated in this work based on data collected by our group's standoff Raman-LIBS system, using different setups, including SuperCam like collection parameters.

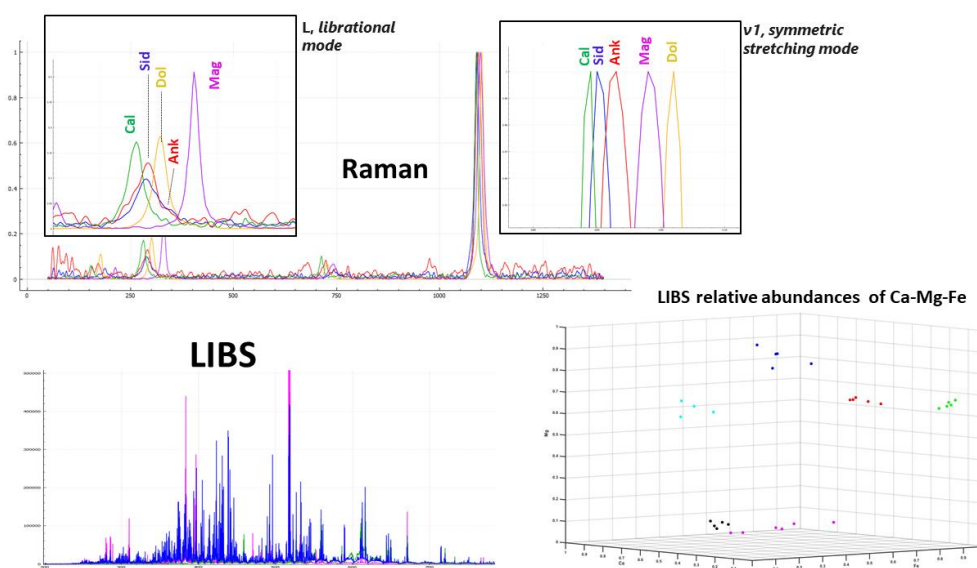


Figure 1: Spectroscopic features of different carbonates for both techniques

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RAMAN SPECTRA OF MARKOVKA CHONDRITE (H4)

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Markovka chondrite (H4) under investigation was a small fragment 1x2x5 cm – part of the large meteorite fall at 1967 near Markovka village, east Siberia. It was stone rain of fragmented chondrite body with the size ca. 1 m as whole. Relative fresh and unweathered sample allows us to collect detailed Raman spectra of mineral phases with Witec Alpha 300 System, DLR. Assuming an onion shell model [1] for the Markovka's parent body we obtain constraints for its size and interiors conditions.

Raman spectra (presented on Fig. 1) contain lines as of main silicate groups (olivine, pyroxene, etc.) as Fe-oxides (maghemite, goethite, etc.). Measurements of the characteristic line shift provide important information concerning chemical content and deformation state of the H4 rocks. But, most remarkable is existing of carbonates – namely, aragonite (CaCO₃). It is high-pressure polymorph of calcite and, according its phase diagram, is stable starting 3 kbars, only [3]. With mean density of chondrites as 3-4 g/cm³, such pressure is possible for body with radius ca. 400 km. Current accretion models suppose quite short time interval of ca. 1-2 Mio. years (since CAI formation) and planetesimals with limited size ca. 50-200 km (in radius). Markovka provides new constraints on evolution processes at the early Solar system and worth for the further detailed mineralogical and geochemical analysis.

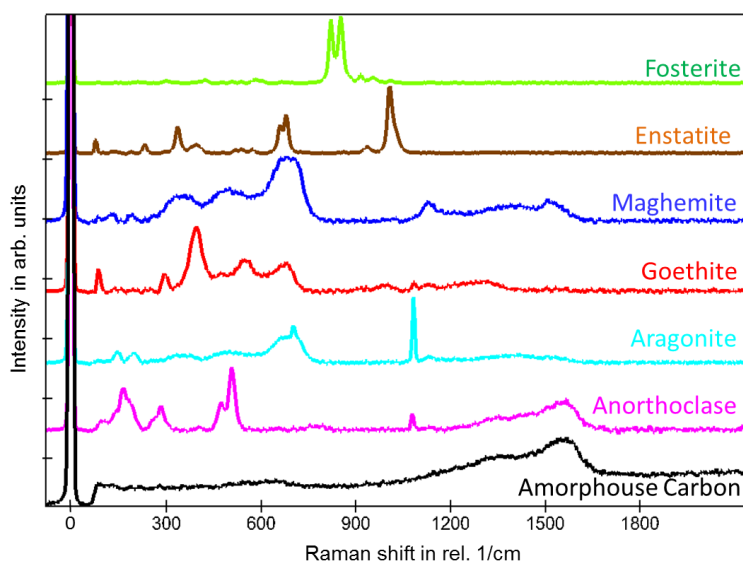


Figure 1: Raman spectra of mineral phases of Markovka (H4) meteorite

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RAMAN STUDY OF THE DARKENING OF POMPEIAN CINNABAR

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Red cinnabar (α -HgS), called *κιννάβαρι* by Theophrastus of Eresos and *minium* by Pliny the Elder and Vitruvius [1], was one of the most expensive pigments employed in the most lavish Roman mural paintings. However, the vivid red hue of this mineral is prone to blacken, as stated by Vitruvius, who did not encourage its use in open spaces, exposed to sun- and moonlight. Prominent examples of this cinnabar darkening are to be found in the Casa della Farnesina (Rome) or the Villa dei Misteri (Pompeii), while this process happens in a lesser dramatic scale in several locations, which sometimes remain unnoticed by non-expert visual inspections. Some cinnabar decorations from the mural paintings of the Archaeological Park of Pompeii are nowadays almost completely blackened, disrupting the correct transfer of the colour used by the Roman painters to the visitors. This is the case of the cinnabar decoration from the south wall of the room G in the House of the Gilded Cupids (Regio VI, 16, 7).

In this work, the darkening products on the surface of cinnabar wall paintings of the Archaeological Park of Pompeii have been evaluated by Raman spectroscopy. This approach combines the micro-analysis of samples embedded as cross-sections and the in-situ measurements performed with portable Raman instrumentation.

The selected samples belong to the House of Marcus Lucretius (Regio IX, 5, 3) and the House of Ariadne (Regio VII, 4, 31/51). Interestingly, the House of Marcus Lucretius presented a deposit where earlier detached mural decorations (2nd Pompeian style) had previously been abandoned and buried. Thus, 2nd and 4th style samples, the latter exposed to the 79 CE eruption, have been subjected to Raman spectroscopy. On the other hand, all the samples pertaining to the House of Ariadne have suffered the influence of the volcanic eruption and the modern environmental exposure after the excavations of the 19th century. Finally, the in-situ analyses were executed at the House of Ariadne and the House of the Gilded Cupids.

The results point out to diverse degradation pathways: from dark coatings of MnO₂ [2], triggered by biological activity during the burial, to the presence of mercury-chlorine compounds and gypsum in the environmentally exposed surfaces [3].

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RAMAN MAPPING OF COMPLEX MINERAL ASSEMBLAGES: APPLICATION ON PEGMATITIC PHOSPHATES PARAGENESIS

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Phosphate minerals form an important component of numerous geological and biological systems. In geological systems, phosphates occur nearly in all rock types, being particularly abundant in sedimentary (i.e. phosphorite) and magmatic rocks. In the latter, pegmatites are highlighted for their vast and exceptionally rich phosphate mineralogy [1]. Pegmatitic phosphates crystallize in various environments, and changes in environmental conditions during crystallization are reflected on the formation sequence of these minerals, termed paragenesis. Raman imaging is able to detect those mineralogical changes in complex assemblages with high spatial resolution [2], successfully determining the paragenesis. Raman spectroscopy is more advantageous than conventional methods because it requires little sample preparation, it is non-destructive, and it is capable of identifying hydrated minerals and phases composed of light elements (e.g. H, Li). This study applies state-of-the-art Raman imaging techniques to define the paragenetic sequencing of complex phosphate mineral assemblages in the Buranga rare-metal pegmatite, a P-Li-Nb-Ta-rich magmatic rock located in Western Rwanda. The Buranga dyke was chosen for the development of the Raman mapping methodology of complex mineral paragenesis because it hosts more than 50 individual phosphate species, often with complex intergrowth or replacement textures [3]. Our results show the replacement of primary amblygonite $[\text{LiAl}(\text{PO}_4)\text{F}]$ by secondary montebrosite $[\text{LiAl}(\text{PO}_4)\text{OH}]$. Mapping of the OH-stretching peak position around 3360 cm^{-1} and the peak width identifies the mineral phases, illustrates their spatial relations, and allows to estimate the distribution of fluorine within the sample. We also investigate the replacement textures of phosphate minerals in a complex assemblage. Each observed phase has unique spectral features that allow their identification and classification in the Raman maps. The sequence trolleite $[\text{Al}_4(\text{PO}_4)_3(\text{OH})_3]$ + rosemaryite $[\square\text{Na}(\text{Mn}^{2+},\text{Fe}^{2+})\text{Fe}^{3+}\text{Al}(\text{PO}_4)_3]$ \rightarrow lazulite-scorzalite $[(\text{Mg},\text{Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2]$ \rightarrow samuelsonite $[\text{Ca}_9(\text{Fe},\text{Mn})_4\text{Al}_2(\text{PO}_4)_{10}(\text{OH})_2]$ \rightarrow wardite $[\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$ is proposed for this assemblage. Analysis of Raman maps show that the Buranga pegmatite experienced a progressive hydration process during cooling, followed by internal remobilization of elements, such as F, Li, Na, and Ca. Our data confirm that phosphates in complex mineral assemblages can (1) be straightforwardly analysed by Raman mapping, (2) record the evolution of the magmatic host rock, and (3) be used as proxies for pegmatite formation.

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RAMAN SIGNATURE OF PHOSPHATE MINERALS: A NEW SPECTRAL LIBRARY

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The main disadvantage of Raman spectroscopy in mineralogical studies is the lack of extensive and public spectral libraries. The development of online databases, such as the RRUFF project^[1], certainly shows the potential of Raman analysis for routine applications. However, many complex and accessory phases, such as phosphate minerals, still require a comprehensive library offering good quality spectra. Phosphates form an important component of numerous geological and biological systems, and their application in geological studies has been historically significant^[2-3]. To overcome the issue of fragmented databases, a phosphate Raman spectral library was developed using samples from KU Leuven's Bosman mineral collection, a historical collection identified by mineralogical studies of Professor Herman Bosman. This study applies state-of-the-art Raman analyses to obtain high-quality spectra of common to rare phosphate minerals, mostly from samples of the minerals' type-localities. Spectra of phosphate minerals can be divided into three domains: 1) high wavenumber region (1300-4000 cm^{-1}) representing vibrations of water and hydroxyl molecules; 2) medium wavenumber region (250-1300 cm^{-1}) representing internal modes of the main oxyanions (PO_4 , AlO_n , FeO_6 , MnO_6 , etc.); and 3) low wavenumber region ($<250 \text{ cm}^{-1}$), usually related with crystalline lattice modes or metal-oxygen modes of the interstitial cations^[4]. A combination of literature data review and our results show that phosphate group [PO_4] modes are represented by an in-plane bending (ν_2) from 350 to 500 cm^{-1} , an out-of-plane bending (ν_4) from 500 to 650 cm^{-1} , a symmetric stretching (ν_1) from 930 to 1000 cm^{-1} , and an asymmetric stretching (ν_3) from 1000 to 1150 cm^{-1} . The H_2O molecule stretching vibrations occur from 3000 to 3400 cm^{-1} and bending from 1600 to 1700 cm^{-1} . The OH group normal modes usually occur at high wavenumbers, and are represented by a stretching vibration of the molecule from 3300 to 3600 cm^{-1} and bending vibrations at 800-830 cm^{-1} . Stretching vibrations of the [AlO_n] octahedron are found from 600 to 900 cm^{-1} . The assignment of bands below 500 cm^{-1} is most difficult as several vibrations of [MO_6], [AlO_n], [PO_4], and lattice vibrations can be superimposed in this region. Unknown phosphate minerals can be identified when compared with our database, considering that good quality spectra are acquired, *i.e.* where the main spectral features are easily recognized.

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POMPEIAN CINNABAR: ORIGIN AND CHEMICAL MONITORING OF ITS MANUFACTURE BY μ -RAMAN AND ELEMENTAL ANALYSIS

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Cinnabar red pigment has been found in archaeological sites since the Neolithic, frequently applied to mural paintings or ceramics, as well as in burials and symbolic contexts. Several mining sources are known to have been exploited throughout the world but few of them were already active since the Roman time. One of the most important deposits is located in Spain, in the mining district of Almadén (Ciudad Real, Spain) [1]. This site was already known and widely used as testified by Pliny the Elder in *Naturalis Historia* [2]. However, the preparation of the pigment was not straightforwardly conducted in Hispania. According to Vitruvius, it took place in Rome, between the Temples of Flora and Quirinus, and consisted of repeatedly grinding, washing and heating the mineral until obtaining a fine, pure powder [3].

To conduct this work, two objectives were established: (i) to assess possible differences in the mineralogical/chemical composition of cinnabar ores from different locations inside the Almadén mining district, (ii) to confirm the potential use of the mineral from Almadén in the production of the Pompeian cinnabar.

To achieve the first objective, the usefulness of Raman spectroscopy against other techniques such as X-ray diffraction and ED-XRF spectrometry has been evaluated. Principal Component Analysis (PCA) has been also applied for the data analysis to identify possible differences in the composition of the mineral ores according to the sampling location inside Almadén mining district. For the second one, a multianalytical methodology, which comprises the use of not only the previous techniques but also isotopic studies, has been applied to verify the source/origin of the mineral used to prepare the Pompeian cinnabar in the Roman time. Apart from the mineral specimens of Almadén, cinnabar used on Pompeian wall paintings and the raw pigment itself recovered in its original container in the excavations of the archaeological site of Pompeii have been considered in this study.

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BENCHTOP AND PORTABLE RAMAN SPECTROSCOPY FOR THE STUDY OF PATAGONIAN (ARGENTINA) ROCK ART MURALS

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Raman spectroscopy was chosen as a first choice technique for the analysis of paintings from rock shelters situated in Patagonia, Argentina. The starting point of this research is dated back in 2014 where samples from rock art shelters were analyzed with micro-Raman spectroscopy. [1]. Two years later the first portable Raman spectroscopy campaign was realized [2,3] underlining the importance of identifying the materials and degradation products of rock murals non-invasively and non-destructively.

Focusing on the rock art murals situated in the steppes of the Chubut province, a multi-instrumental Raman approach was applied on their colorful surfaces. Raman data were collected with benchtop and portable Raman spectrometers revealing the major components of the white, black, yellow, red, green etc. figures of the rock panels of the shelters. Moreover, special attention was given on the degradation products and processes affecting the rock murals, posing serious risks on the preservation of these outstanding works of art.

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IN SITU RAMAN SPECTROSCOPY: A VALUABLE TOOL FOR THE ANALYSIS OF ARTWORK FROM PISA AND FLORENCE (ITALY)

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Portable Raman spectroscopy has been growing in importance in the last years in different scientific fields ^[1], thanks to the *in situ* and direct characterization of the artefacts. The new instruments immersed in the market are lighter, relatively easy to move, more sensitive and with a simplified interface with make them user friendly. Technological developments minimised the total packaging of the spectrometers, with the possibility to carry new investigations on valuable and ancient objects without even moving them from their museum environment or, even, to have a first *in situ* characterization during archaeological or restauration campaigns.^[2] The highly automatized Raman spectrometer Bravo by Bruker® with sequentially shifted excitation technology is one of those new instruments.

State-of-the-art mobile instruments were used during an *in situ* campaign carried out in Pisa and Florence (Italy), on a set of different artefacts, provided a large set of data in order to in-deep evaluate the potential and limits of several instruments. The analysed materials included stone and glass mosaics from an on-going archaeological excavation ^[3], some building artefacts and pigment traces on statues recently recovered in the “Museo dell’Opera del Duomo di Pisa”.

For the comparison, the dispersive i-Raman®EX, by BwTek, equipped with a 1064nm laser has been used for a more complete interpretation of the materials used. Some of the materials, such as calcium carbonate (CaCO₃), quartz (SiO₂) and gypsum (CaSO₄·2H₂O) were easily detected by both instruments, but in some other cases, such as the carbon black identification, required a more careful analysis to be completely characterized.

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RAMAN FINGERPRINT SPECTROSCOPY OF HYDROGEN PEROXIDE AND ITS IN-SITU DETECTION FOR FUTURE MARS EXPLORATION

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Potential applications

Small amounts of gaseous H_2O_2 occur naturally in the air on Earth and beyond. H_2O_2 is inferred on Moon, Mars and Jupiter's satellites. Gaseous H_2O_2 was detected in the Martian atmosphere [1] and supposed on the surface and even under subsurface of Martian regolith. The Martian surface is oxidizing. And, H_2O_2 is one of important oxidizing components for this oxidizing environment. Raman spectroscopy has many advantages for trace analysis with highly specific selectivity and stand-off work pattern which was successfully selected as scientific payload for Martian surface exploration by NASA and ESA. The existence of H_2O_2 on Martian atmosphere and surface should have an effect on the Martian minerals, organic and living matters. Therefore, it is of great significance for H_2O_2 detection on Martian surface. In this work, the spectral feature of H_2O_2 (both under room temperature and low temperature) was recorded by a fiber Raman spectrometer, and detection limit of (LOD) H_2O_2 mixed with the simulated Martian soils was analyzed. Our results show that H_2O_2 has remarkable Raman spectral features different from that of the associated mineral and H_2O (Fig.1). H_2O_2 can be easily detected with high LOD of 400 ppm. The Raman spectral signatures and the decomposition feature of H_2O_2 under low temperature and UV radiation will also be reported.

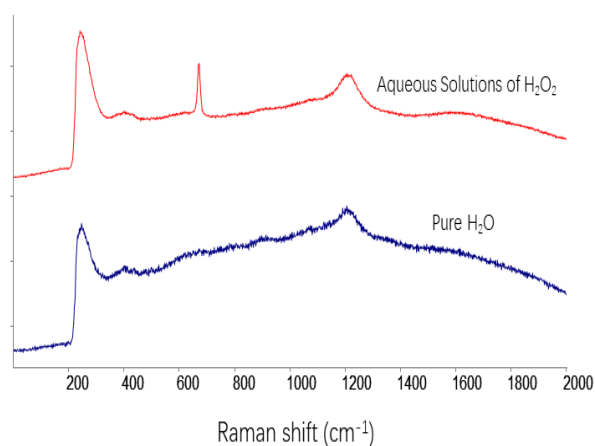


Figure 1: The Raman fingerprint of H_2O and aqueous solution of H_2O_2 (Concentration: 1%)

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SPECTRAL ANALYSIS OF OXIA PLANUM ANALOGUE SAMPLES FROM CAITHNESS, SCOTLAND

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As part of the ExoMars Surface Science & Rover Operations preparatory activities [1, 2], the various instrument teams have been involved in a series of field studies in order to optimize the design and operation of the instruments. Most recently, members of the PanCam and Raman Laser Spectrometer (RLS) teams collected analogue samples from a number of geologically relevant sites in Caithness, Scotland. The region was specifically selected as it provides a similar geological context to that likely to be interrogated by the ExoMars rover when it lands on Mars in 2023 in the region of Oxia Planum.

The field location in Caithness is an ancient Lacustrine deposit/region [3] that incorporates geological structures, estimated to be from the lower Devonian to Jurassic ages. These structures are identified as being possible analogues to the geological structures and processes that are known to be present at the Oxia Planum landing site (i.e. based on observations previously made by orbiters [4]). 10 samples were collected for subsequent analysis with laboratory based, flight representative instruments. These include both the RLS prototype at the University of Leicester (built in order to optimize the design and development of the RLS camera system [5]) and the RLS Flight Spare system (a fully flight representative instrument located at INTA, Madrid). The analogue collection includes samples from the lower Devonian age (in which sandstone, epidote, and granite are readily identifiable), a sample from the middle Devonian age (which incorporates pyrite and sulphate evaporates), and a quartz-rich sandstone from the upper Devonian age. In combination, the analogue sample set provides a clear indication of the capability of the instrument to identify and characterize materials that are of particular geological interest at Oxia Planum (see example set in Figure 1).

Here, we present a summary of the spectra acquired from the analogue sample set using the two flight-like instruments and comment on the overall scientific capability of the RLS instrument when characterizing materials similar in nature to those likely to be found at Oxia Planum. We also discuss how well the geological context of the landing site region can be understood when complementary data from other instruments on the ExoMars rover (such as PanCam, CLUPI and MicroOmega) are combined with the spectral information obtained with the RLS instrument.



Figure 1: An example collection of the samples and geological structures identified for analysis with the ExoMars RLS prototype at University of Leicester.

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EXOMARS PREPARATION: CHARACTERISING NAKHLA METEOR ANALOGUES USING THE RAMAN LASER SPECTROMETER SIMULATOR

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The scientific aims of ESA's ExoMars rover mission are to investigate and characterise the geology, water environment and habitability of the Martian surface (and sub-surface) in search for biological signatures and mineralogical evidence of processes associated with life [1]. The Raman Laser Spectrometer (RLS) within the rover's Analytical Laboratory Drawer will play a key role in achieving the mission aims: it was specifically designed to identify organic compounds and mineral phases linked with water-rock interaction [2].

As part of the mission preparation, the instrument teams have been investigating and characterising the response of the RLS and its sensitivity limits to key target materials. Carbonaceous materials- in particular those containing reduced carbon- are of significant interest: simple reduced carbon structures are expected to be present on the Martian surface as a result of volcanic erosion, meteor bombardment or as a product of ancient biological processes [3]. Veinlets of carbonaceous matter have been observed in Nakhla meteorites and have been highlighted as evidence for reduced carbon on Mars [4]. In addition to the reduced carbon content, the similarities between the meteorite composition and the material expected at Oxia Planum make Nakhlite meteorites and their analogues ideal for assessing the performance of the RLS instrument.

Here we present the Raman analysis of a Nakhla meteorite analogue sample recovered from an area of ancient carbon-bearing lava flow in the UK using the RLS Simulator, located at the Centre de Astrobiologia [5]. The basaltic sample contains a large quantity of embedded carbonaceous material (analogous to Nakhrites), thought to be thermally altered from shales [6]. The sample was exposed to additional thermal stress through the use of projectile impact [7]. We present the full sample characterisation, and highlight the spectral signatures associated with geological thermal maturity processes and impact stresses. We discuss how thermal history and shock impacts of a sample might affect the Raman spectra observed, review the level to which such signatures can be identified by a flight representative instrument, and hence infer how the performance of the RLS during mission operations.

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RAMAN SPECTROSCOPY IN EXTREME ENVIRONMENTS

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Raman spectrometers are now routinely proposed as key analytical instruments in the baseline payload designs of most planetary exploration missions [1,2,3,4,5]. Alongside other analytical instruments (e.g. LIBS, XRF and XRD that are sensitive to elemental/mineralogical components), the powerful (and largely non-destructive) molecular spectroscopy technique is acknowledged as being ideally suited for completing the comprehensive characterisation of planetary surface samples [6,7]. With careful selection of the excitation wavelength(s), typical spectrometer designs are sensitive to a very broad range of key minerals and organic compounds [8,9,10]. Following two decades of investment by various space agencies [2,11], the TRL of baseline spectrometer systems is relatively high, with a wide range of technically capable, low mass, low power designs readily available [12,13]. Recent instrument development work has focused on improving the autonomous operation of such spectrometers (i.e. by developing sophisticated sample scanning algorithms, optimising data acquisition modes and improving auto focus and thermal stabilization systems). Other key areas of development include:

improving thermal and mechanical robustness so that instruments can operate precisely across a broad range of challenging environments (e.g. very low temperatures for Europa lander missions, very high temperatures for Venus and very high levels of radiation in the vicinity of Jupiter), and

optimising radiometric models so that sampling strategies and instrument design trade-off studies can be adequately informed [14,15].

Here, we present initial results from two separate instrument design studies that were performed in preparation for anticipated future mission opportunities (one for a Europa lander and one for a lunar lander). In particular, we report on laboratory measurements obtained with two prototype camera systems (one based on a recently developed CMOS sensor and one on a traditional CCD sensor) that were developed for the unique challenges associated with these missions, and also focus on the development of radiometric modelling software that specifically accounts for the high levels of radiation expected on Europa. Camera system performance is described in terms of the primary scientific goals of each mission and we highlight the overall spectral capability of each instrument design using appropriately selected analogue samples.

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RADIATION AND RAMAN SPECTROSCOPY: THE UNIQUE CHALLENGES ON EUROPA

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Three different Raman Spectrometers will be deployed on two separate space missions in the next few years (Raman Laser Spectrometer on ESA's ExoMars Rover [1], and SHERLOC and SuperCam on NASA's Mars2020 [2]). The molecular spectroscopy technique is considered to be an ideal analytical tool for identifying signs of past and present life and has recently become a highly ranked instrument on a number of future planetary exploration payloads due to recent technology developments. Raman spectrometers are considered to be particularly suitable for missions to Europa. A recent NASA Europa lander mission study report proposes that a vibrational spectroscopy instrument be included as a baseline instrument in order to assess habitability and identify potential bio-signatures by confirming molecular composition of the surface [3]. There are a number of environmental challenges associated with Europa missions that are significantly different to those anticipated for a mission to Mars. Two aspects of the Europa environment need to be carefully considered: extreme low temperatures and extreme high radiation levels (eg. protons, electrons and ions) [4]. Radiation is the most significant challenge for the design and development of a Raman instrument as key subsystems can be significantly damaged due to the interaction of the high-energy particles with sensitive components (eg. detectors and optics). The scientific performance of the instrument will be significantly compromised if steps are not taken to ensure robust components are selected or appropriate mitigation strategies used. Samples extracted from Europa are expected to be radiation processed for extraction depths up to 10cm. This results in modifications to spectra that need to be carefully accounted for with sufficient preparatory work before instrument designs are completed and operating modes finalised.

Here we define an analogue sample set for optimising an instrument for a mission to Europa. This includes hydrated salts (e.g. hydrated magnesium/sodium sulphates) and minerals associated with biological processes that can be used to inform optimum design and operation of a Raman spectrometer [5]. The samples have been carefully selected to encapsulate key science goals of recent mission proposals and incorporate samples with the most challenging spectral requirements (e.g. distinguishing between similar materials that exhibit small changes in band position or shape, even after accounting for the impact of radiation damage/processing). We also present results from a series of radiation exposures, performed to understand the impact of the harsh environment on both spectrometer subsystems and samples, particularly in terms of the instrument's ability to meet future mission science goals.

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UV BIOMA: A RAMAN AND A LASER-INDUCED FLUORESCENCE INSTRUMENT FOR IN SITU ANALYSIS OF VENUS

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Some chemicals that could be relevant for life processes are found in Venus upper planet atmosphere (H_2S , OCS , SO_2 , NH_4Cl , NH_2COOH and H_2O). Moreover, the atmosphere instability and the reason for the high ultraviolet (UV) heterogeneous absorption between 320 and 400 nm on the top cloud layer and mesosphere (~ 40-70 Km) are unknown phenomena's reported in the literature. These two scientific questions, could be studied and probably solved by using small Ultraviolet (UV) Raman and fluorescence instruments mounted in a CubeSat mission send to Venus.

Several planetary mission are currently using compact Raman devices to perform planetary science. The most well-known example is the NASA 2020 mission to Mars. The mission counts with the SuperCam instrument, to perform 7 m distance Raman analysis; but also, with the Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC) Raman device installed in a robotic arm to perform proximity measurements. In this last case, the Raman uses a 248.6 nm laser emission (1) Similarly, ESA is planning to send in 2022 the ExoMars mission, which counts as well with Raman capabilities (2).

Our purpose is to show the possibility of developing new a lander/planner probe device that includes a multi-channel tuneable emitting laser, a receiving telescope and a multi spectral device to study the ultraviolet and visible. The goal of the mission will be to analyse emission and absorption of UV light in Venus atmosphere, and the possible presence of organic compounds, these by Raman spectroscopy.

These developments would be of direct application also in future missions in which the analysis of the composition of the surface or of the material in suspension in the atmosphere of Venus

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RAMAN SPECTROSCOPIC STUDY OF SODIUM SILICATE SOLUTIONS FOR GEOPOLYMER PRODUCTION

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A set of sodium silicate solutions was investigated by means of Raman spectroscopy (532 nm), as they are used as alkaline activators in geopolymer production.

The general formula for soluble silicates is: $R\text{SiO}_2/M_2\text{O}$, where M is an alkali element and R is the molar ratio. Dilution and addition of alkalis change the molar ratio and pH. The result is known as waterglass ($R\text{SiO}_2 \cdot yM_2\text{O} \cdot n\text{H}_2\text{O}$). The availability of soluble silica affects workability, setting, and mechanical strength of the geopolymer, as it modifies both gel composition and the microstructure.

A higher silica concentration and higher R determine a greater polymerization of silicatic species in solution. Moreover, high pH values are requested for the geopolymerization to occur. To clarify the behavior of silicatic species, useful for this reaction to take place, different solutions were tested by Raman spectroscopy, varying R and pH.

Raman spectroscopy is suitable for characterizing the Si-O network, as band positions and their relative intensities are related to the connectivity of silicatic species, allowing to differentiate the contribution of monomers and different oligomers (Figure 1).

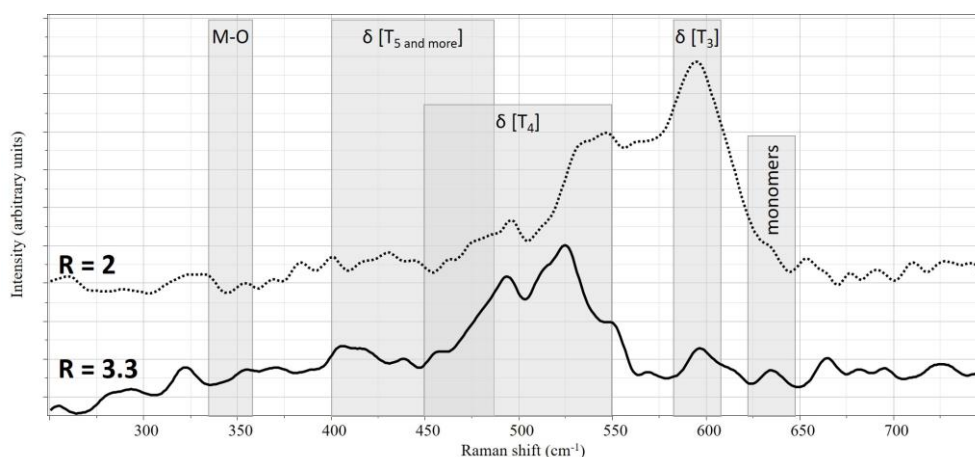


Figure 1: Bending region of the silicatic network of sodium silicate solutions at different R values. The reference positions are based on [1].

Acknowledgements: The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione "Cultural Heritage" CUP E66C18000380005).

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IN SITU AND LABORATORY RAMAN SPECTROSCOPY FOR THE STUDY OF ROMAN PIGMENTS ON WALL PAINTINGS AND POLYCHROME SCULPTURES (LATERAN AND PALATINE AREAS, ROME)

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In the last decade, Raman spectroscopy has been widely employed for the investigation of Roman polychromies, both on walls and on sculptures [1-4], thanks to its suitability in the detection of pigments, non-invasiveness, and allowing also in situ analyses. Archaeometric campaigns were carried out in Rome with portable Raman spectroscopy, coupled with complementary techniques such as X-ray Fluorescence (XRF) and/or Fourier Transform Infrared Spectroscopy (FTIR) and, where necessary, integrated with laboratory Raman analyses. The objects of investigation went from wall painting fragments of a villa in the Lateran area (second half of 1st c. BC-2nd c. AD), to the recently discovered Sphinx Room pertaining to Nero's Domus Aurea, to polychrome traces on marble sculptures discovered on the Palatine Hill and kept at Museo Palatino and Museo Nazionale Romano. In situ Raman results proved valuable to give overall information on the highest number of spots as possible, notwithstanding, it must be remarked that filter noise, fluorescence and photoluminescence can hinder Raman features identification: micro-sampling and laboratory instrumentation with different excitation wavelengths helped overcoming one or more of these drawbacks.



Figure 1: the pigments subjected to Raman analyses, belonging to a), Lateran painted fragments, b) Domus Aurea Sphinx Room wall paintings and c) polychrome traces on a marble sculpture from Palatine Hill.

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SUITABILITY OF RAMAN SPECTROSCOPY FOR THE STUDY OF ALKALI ACTIVATED MATERIALS: PROS AND CONS.

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Alkali activated materials (AAMs) are inorganic polymeric materials obtained by mixing of solid aluminosilicate precursors with an alkaline solution (NaOH and Na₂SiO₃ mixed in various ratios) [1, 2]. This new class of aluminosilicate materials has emerged as a greener alternative to traditional concrete, for large-scale as well as for niche applications, such as conservation and restoration of built heritage [3, 4].

In this work we apply Raman spectroscopy both to Sicilian aluminosilicate precursors (volcanic ash, volcanic soils, clayey sediments and waste ceramics) and to the respective AAMs [5-7], in order to have an insight into the geopolymerization process from a molecular point of view.

In the field of vibrational spectroscopy, Raman is much less employed in the literature with respect to Fourier Transform Infrared (FTIR) for the above-mentioned purpose. Our aim is to highlight the advantages and drawbacks of a Raman approach to the comparison of the raw materials employed and the respective AAMs. Raman analyses during the first hours of geopolymerization were also carried out on the clayey sediments-based products.

The preliminary results are differentiated according to the employed precursors, mainly exhibiting spectra relative to crystalline phases; on the other hand, the band width may be indicative of the crystallization degree of the newly formed aluminosilicate gel.

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PORTABLE RAMAN APPLICATIONS ON SICILIAN ZEOLITES (ITALY)

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Zeolites are present in numerous outcrops of vulcanites of different ages in Sicily (Italy). Some of these outcrops are important because they represent the ideal genesis conditions of some of these minerals. At this purpose, a group of zeolites, coming from areas of the Ionian coast and Palagonia village of Eastern Sicily was investigated by means Raman Spectroscopy. In the geological record, these areas have been influenced by intense volcanic events which produced mineralization of hydrothermal origin [1,2].

Sicilian zeolite samples were analyzed *in situ* using mobile Raman apparatus, directly on the outcrops of Aci Castello and the nearby Lachea Island (Fig.1) or in the local collections where they are preserved. The same samples have been then analysed using laboratory micro-Raman in order to compare the results and identify the zeolite species. In particular, the fixed instruments were a Jasco NRS-3100 micro-Raman and a Horiba LabRam while the portable ones were DeltaNu (Operating at 785 nm) and an EnSpectr Raport (operating at 532 nm). The strength and weakness points of each instrument have been highlighted. Generally, the Raman spectra of zeolites are often affected by a broad fluorescence, making them of difficult interpretation [3,4]. However, satisfying results were obtained with micro-Raman discerning zeolites of different group, such as natrolite, chabazite and phillipsite. The use of portable instruments demonstrated the possibility to obtain identification of zeolites and related minerals (as analcime) in difficult environment (e.g. in full sun, far from power supply, in places hard to reach).



Figure 1: In Situ Raman experiments at Lachea Island (Eastern Sicily).

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RAMAN SPECTROSCOPIC STUDIES OF DONWILHELMSITE IN SHOCK MELT POCKETS WITHIN THE LUNAR METEORITE OUED AWLITIS 001

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In meteorites, microscopic zones of shock melt mirror pressure and temperature regimes similar to those prevailing in the Earth's mantle [1,2]. In hundred micrometer sized shock melt zones the pressure-temperature-time path allows for the formation and preservation of mantle minerals, minerals that are otherwise naturally inaccessible at the Earth's surface [1,2].

On polished thick sections or slabs of meteorites, those zones of shock melt containing potential high pressure phases can be recognized using reflected light optical microscopy aided by the use of immersion oil, as minerals and glass display intense brightness contrast. The composition and structure of glasses and minerals can be studied by Raman spectroscopy.

The Raman spectrum of donwilhelmsite and the surrounding glass is displayed in Fig. 1. The position of the broad band centered around either 975 cm^{-1} or 1015 cm^{-1} indicates the relative abundances of non-bridging Si-O than Al-O tetrahedral, the band position increases with decreasing non-bridging Al-O tetrahedral [4,5]. The absence of Raman features in the $\sim 800 \text{ cm}^{-1}$ spectral region typical for SiO_2 glass shows that the glass is not dissociated in phases such as CaO, CaSiO_3 or SiO_2 . An incomplete crystallization sequence can explain the absence of stishovite. The new high-pressure mineral donwilhelmsite crystallized in shock melt zones, roughly anorthositic in composition, in the feldspatic lunar meteorite Oued Awlitis 001 [3].

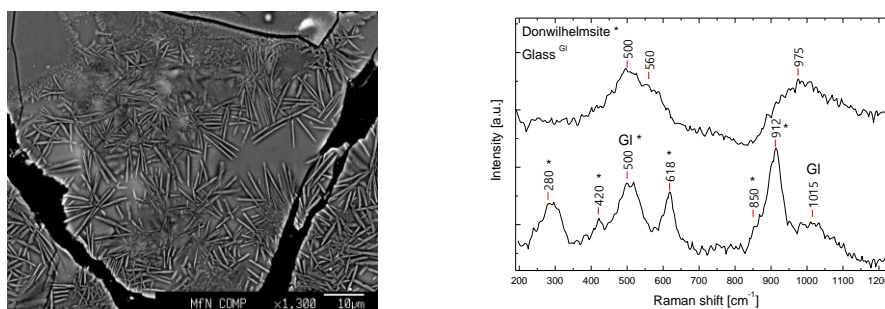


Figure 1: Backscattered electron image of donwilhelmsite in a shock melt pocket within Oued Awlitis 001 (left). Raman spectra of glass and of donwilhelmsite with glass. (right)

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RAMAN SPECTROSCOPY IN VOLCANOLOGICAL SCIENCES

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One of the central goals of modern volcanology is to understand the physics and chemistry of processes that operate during transport, storage and eruption of magmas. These endeavors include both forensic reconstructions of pre-historic volcanic eruptions and real-time analysis of active volcanic systems. From the microscopic to the macroscopic scale, magmatic and volcanic processes are primarily governed by the physical and chemical properties of the melt. These properties of the melt are, themselves, highly transient because of cooling, differentiation, assimilation, mixing, and volatile exsolution that commonly attend transport and eruption. Volcanic glasses are particularly informative in that they represent the quenched melt fractions of magmas at the time of eruption. These natural glasses can be investigated in the laboratory to track the transient evolution of volcanic systems. Lab-based tools and techniques, for example, can be used to estimate the compositions and thermochemical properties of volcanic glasses as well as the presence of crystal from the nano-scale and the presence of volatiles and, thus, can inform on pre- and syn-eruptive magma conditions. Such data can contribute to long and short-term hazard planning at active volcanic centers. Here we explore and review some of the latest ideas and applications of Raman spectroscopy to the volcanological sciences and examine the potential for Raman spectral analysis to be used as a field based aid to volcano monitoring via in situ studies of proximal deposits and; perhaps; in remote sensing campaigns.

RAMAN SPECTROSCOPY STUDY OF REE MINERALS FROM LATERITES OF MOUNT WELD REE DEPOSIT, WESTERN AUSTRALIA

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Among critical metals Rare Earth elements (REEs) are irreplaceable for their role as materials of magnets (e. g. for wind turbines, electric cars), data storage devices, high-performance ceramics, batteries for hybrid cars etc. (i.e. [1]). Mount Weld deposit in Western Australia, one of the world's richest REE deposits (average ore grade 13.8% Σ REEO [2]), is located in carbonatite-related supergene laterite. Previous studies suggest that weathering process is responsible for the concentration of REEOs [3]. Little detailed information of mineral phases concentrating REEs in Mount Weld deposit is available so far. The ores of the deposit contain abundant fine-grained REE minerals, which difficult to distinguish from compositional data along. We present the first characterisation of REE minerals from high grade ore from Mount Weld deposit by Raman spectroscopy combined with in-situ LA-ICP-MS and SEM data.

Sample of high REE ore is a white-yellow laterite contains of large, (up to 0.5 cm) euhedral porphyroblasts of monazite in a fine grained matrix of REE minerals. The fibrous REE phosphate occurring in the "tree root" structures was identified as rhabdophane (LREE)PO₄•(H₂O) by Raman spectroscopy as it has a spectra similar to the one of monazite with PO₄ band at 983 cm⁻¹, compare to 972 cm⁻¹ for monazite and also 470 cm⁻¹ (463 cm⁻¹ for monazite) moreover rhabdophane unlike monazite has also a series of peaks at H₂O field (between 2838 and 3085 cm⁻¹). These results for PO₄ band are consistent with spectroscopic data [4] for both monazite and rhabdophane. Raman spectroscopy allowed to identify the inclusions of mineral cerianite, (Ce⁴⁺)O₂, in monazite and the spectra are characterised by prominent Raman peaks at 175 cm⁻¹, 465 cm⁻¹, 973 cm⁻¹ and 1060 cm⁻¹. These results are consistent with the SEM response and also can be compared with [5] and [6] who have observed Raman bands at 184 cm⁻¹, 449 cm⁻¹, 571 cm⁻¹; and 465 cm⁻¹, 570 cm⁻¹ for natural and synthetic cerianite respectively. McBride and coauthors [5] interpreted appearance of 570 cm⁻¹ peak when concentration of O²⁻ vacancies rises in a crystal due to substitution of Ce⁴⁺ instead of LREE³⁺. The non-stoichiometric compositions of Ce oxide phase could be another reason for the Raman peak shifts. The results of this study demonstrate that Raman spectroscopy is a powerful method for identification of fine-grained REE minerals in laterite of a REE deposit. Nominally, cerianite consists of Ce⁴⁺ oxide however the synthetic Ce oxide is known to be composed of Ce³⁺ and Ce⁴⁺ in non-stoichiometric proportions. Our results suggest that natural cerianite also could be a mixture of different Ce oxides and therefore record the conditions of formation of REE deposits.

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SIMULATION OF METHANE RAMAN SPECTRA FOR NATURAL GAS ANALYSIS

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One of the promising applications of Raman spectroscopy is the analysis of natural gas composition [1]. Compared to conventional gas chromatography, Raman gas analyzers are capable for *in situ* analysis, including reservoirs using the fiber probes [2]. However, for this method improvement, it is necessary to develop methods to derive concentrations of species with high accuracy. As is known, the main component of natural gas is methane (50-95%). In this regard, the analysis of the natural gas composition is related to determination of the concentrations of its components against the background of the methane spectrum [3]. However, with pressure variation, the methane spectrum changes significantly (half-widths and line shifts). Neglecting these changes leads to an error in measuring the concentrations of other components. Thus, to take into account changes in the spectral characteristics of methane, it is necessary to simulate its spectrum at different pressures.

In this work, Raman spectra of the methane ν_2 band (1535 cm^{-1}) were recorded in the pressure range of 1-50 atm using a high-resolution spectrometer with a spectral resolution of $<0.5\text{ cm}^{-1}$. From these spectra, the spectral characteristics of the individual lines (intensity, wavenumber, and broadening coefficient) of the methane spectrum were determined. Verification of these characteristics was carried out by comparing the simulated spectra with the experimental ones, obtained on a high-sensitivity Raman spectrometer (resolution $\sim 8\text{ cm}^{-1}$), which can be used to measure the composition of natural gas. As a result, good agreement was achieved (see Fig. 1). The data obtained can also be used to derive the pressure of methane-bearing media.

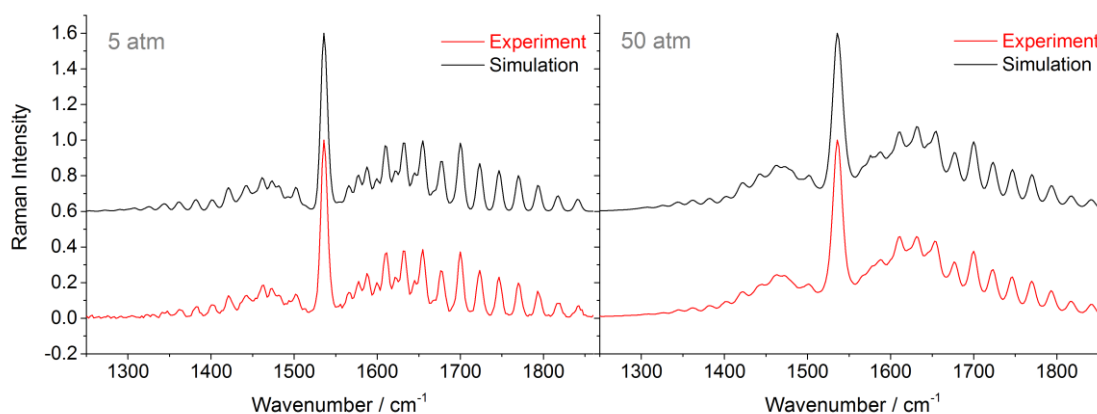


Figure 1: Experimental and simulated Raman spectra of $^{12}\text{CH}_4$ near 1500 cm^{-1} .

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THE ROMAN MOSAIC TESSERAE FROM VILLA SAN PANCRAZIO (TAORMINA, ITALY): EDXRF AND RAMAN SPECTROSCOPY ANALYSES FOR MANUFACTURING ASSESSMENT

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The excavation works of Villa San Pancrazio (Taormina, Italy) are bringing to light a vast, multi-layered, Roman-Imperial residential quarter featuring luxurious dwellings decorated with wall paintings and mosaic floors, pointing it out as one of the most extensive and significant archaeological sites of the city [1]. The stylistic and iconographic studies of the polychrome and black and white mosaics suggest a dating to the Middle Imperial period, during the II century A.D.

Accordingly, the present work aims to provide a contribution for the assessment of the mosaics manufacturing technology through the analyses of the raw materials employed. For that purpose, a micro-destructive multi-analytical methodology, mainly based on the combination of energy dispersive X-ray fluorescence (EDXRF) and Raman spectroscopy, was used to characterize a wide selection of stone, ceramic and glass tesserae collected from different mosaics. In addition, semi-quantitative elemental data obtained for the black and white samples coming from the bichromatic mosaics were explored by means of Principal Component Analysis (PCA).

The investigations provided interesting information about the natural lithotypes used, local and imported, and how artificial materials, i.e. ceramics, transparent and opaque glasses, were produced. Accordingly, the significant technical and qualitative level of the residences mosaic systems was ascertained, revealing the owners high socio-economic profile, and also yielding important clues on the economical and cultural exchanges with other areas of Italy and the Roman Empire.

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HIGH RESOLUTION METHANE RAMAN SPECTRUM IN THE RANGE OF 2900-2940 cm^{-1} AS A FUNCTION OF PRESSURE

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Methane is the main component of natural gas and can often be found in fluid inclusions. Based on the spectral characteristics (shift and half-width) of its most intense ν_1 Raman band (2917 cm^{-1}) contactless pressure evaluation is possible. In this regard, it is very important to determine the relationships between these spectral characteristics and pressure correctly. However, in the available data [1–3], there is significant discrepancy ($>1 \text{ cm}^{-1}$) in the pressure dependence of ν_1 band.

In this work, we studied the methane spectra in the pressure range of 1-100 atm in the spectral range of 2900-2940 cm^{-1} (see Fig. 1) using a high-resolution Raman spectrometer ($<0.5 \text{ cm}^{-1}$). Taking into account the high intensity of the spectra, wavenumber calibration was performed by individual vibrational-rotational lines of the ν_3 band (3020 cm^{-1}). The data obtained made it possible to find the most reliable results of other authors. In addition, we observed a pressure-induced Raman band in the analyzed range at first time. This band contributes to the half-width of the ν_1 band and can lead to a significant error in measurement of the concentration of the $^{13}\text{CH}_4$ isotopologue.

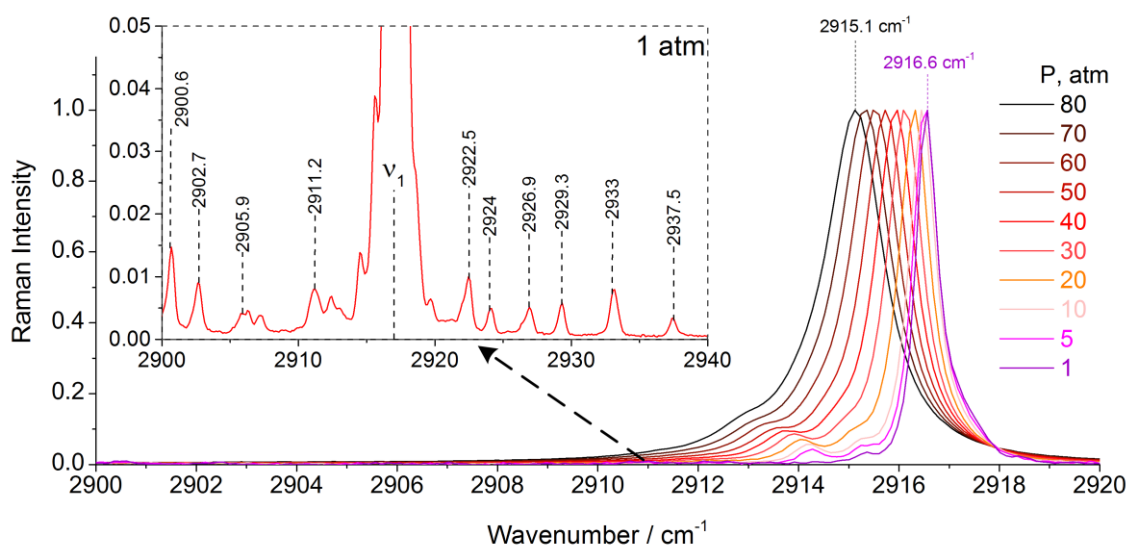


Figure 1: Raman spectra of methane near 2917 cm^{-1} at different pressure. Inset shows magnified area of the spectrum at 1 atm near baseline.

Acknowledgements: This work was supported by the Russian Science Foundation (grant № 19-77-10046).

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EXTRATERRESTRIAL ORGANIC CARBON IN NWA 5508 CHONDRITE: PEAK METAMORPHIC TEMPERATURE DETERMINATION BASED ON FIRST-ORDER RAMAN MODES

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Chondrites provide important clues on the metamorphism in their parent bodies and conditions in early solar system. Determining absolute temperatures of chondrites is a difficult work since there is no consensus on underlying mechanisms of metamorphism in their parent bodies. The least altered meteorites are known to be those of type 3. The CV3 chondrites are of interest to study due to their refractory inclusions. A more precise evaluation of the metamorphic grade would supply better information on the origin and primitiveness of these inclusions. Among spectroscopic methods, Raman spectroscopy leads to a structural characterization of organic matter [1] and certain minerals [2,3] in meteorites. Here, we studied NWA 5508 carbonaceous chondrite (CV3) by Renishaw InVia Raman spectrometer equipped with 532 nm excitation line. Raman spectra were recorded between 220-2100 cm^{-1} . Peak metamorphic temperatures (PMTs) were suggested for Leoville (~ 250 °C), Vigarano, Mokoia, Kaba, Efremovka (300–400 °C), Grosnaja (~ 500 °C), Axtell and Allende (550–600 °C) [1,4]. Up to our knowledge, no PMT was assigned to NWA 5508, yet. By using Raman spectroscopy, we assigned PMT between 436-518 °C to NWA 5508 based on Busemann's and Cody's works [5,6]. No noticeable thermal stress was observed since Full Width at Half Maximum at ~ 1345 cm^{-1} exhibits a relatively broad profile that might be an indication of weakly graphitized carbon [7,8].

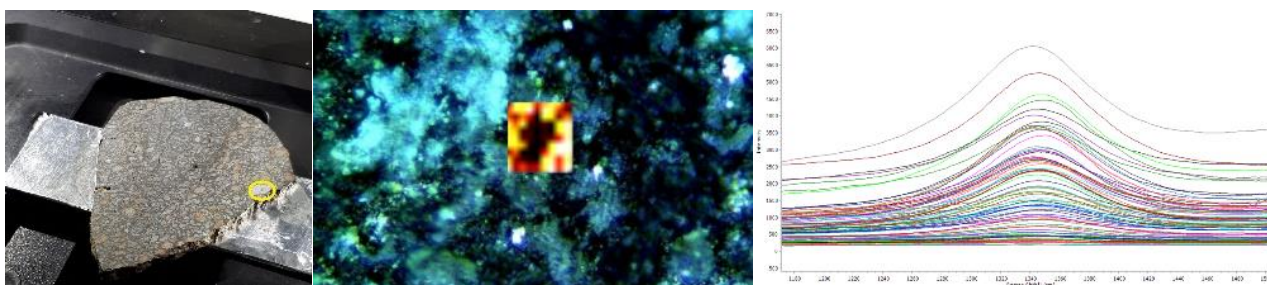


Figure 1: NWA 5508 sample in spectrometer (left), Raman mapping and spectra (middle and right).

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CHAIN SIZE DEPENDENT RAMAN SPECTRA OF A RECENTLY DISCOVERED METEORITIC ASTRO-ORGANOMETALLIC COMPOUND AT 130 K AS IN MARTIAN CLIMATE

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This work has connection to the astrobiologically relevant chemical class that may form Grignard-type reagent compounds. Although CHNOS groups in meteorites were thoroughly discussed, there is still a huge gap for investigation of CHOMg compounds. These compounds and their potential relation to thermal history in meteorites might extend our knowledge of carbon speciation at molecular level in meteorites and their parent bodies. A recently discovered astro-organometallic compound [1-3], C_{16} -dihydroxymagnesium carboxylate (DHMC) anion ($C_{16}H_{33}MgO_4$), was investigated to reveal theoretical Raman spectra at 130 K which stands for approximate minimum Martian temperature. Here, we built 5 to 13 carbon containing chains of DHMC for electronic structure computations and Raman spectra were computed based on Hartree-Fock theory with 3-21G basis set as implemented in Gaussian 09 software [4]. We found that Raman peaks observed at around 17 cm^{-1} shifted to 12 cm^{-1} . After 8-carbon member chain addition, there is a significant shift towards 1170 cm^{-1} from 1130 cm^{-1} accompanied by a slight shift at 1220 cm^{-1} to 1231 cm^{-1} . This peak might be evaluated as the most sensitive peak in terms of determining chain-size effect for DHMC at 130 K in Martian conditions. All these peaks are clear evidence of carbon chain elongation. We can conclude that all theoretical spectral efforts will eventually help upcoming planetary missions by integrating Raman spectral libraries into on-board Raman spectrometers.

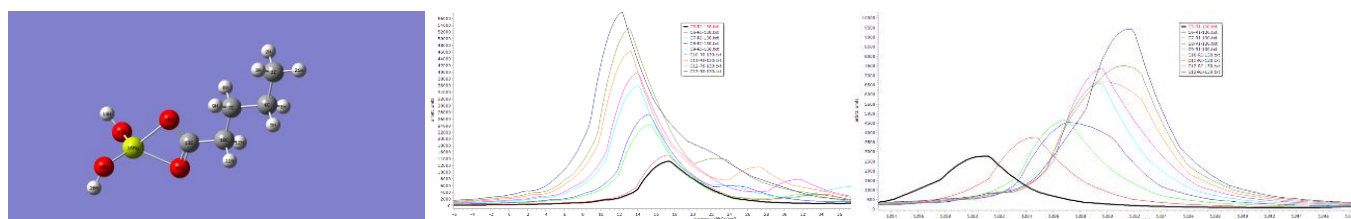


Figure 1: DHMC, 5-carbon chain (left) and corresponding chain size dependent Raman spectra of selected Raman bands (middle and right).

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NATURE OF DISORDERED GRAPHITE IN THE KOKCHETAV UHPM ROCKS: RAMAN AND FIB-TEM STUDY

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Ultrahigh pressure (UHP) terrains are unique geological objects for the reconstruction of the global cycle of different elements, including carbon. The tourmaline and zircon are well known very rigid and chemically resistant minerals in metamorphic rocks [1]. Here we present the possible scenario of disordered graphite formation in the Kokchetav UHP rocks revealed by Raman-spectroscopy and high-resolution transmission electron microscopy (TEM) on cross-section foil cut using focused ion beam (FIB).

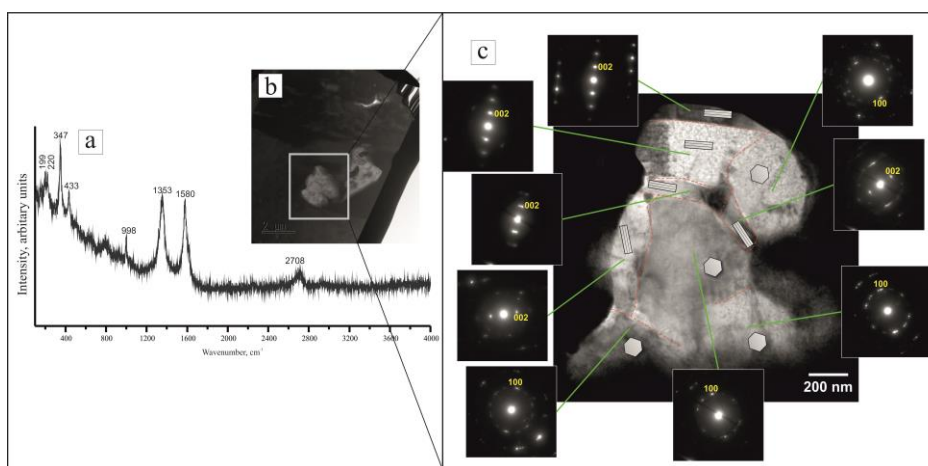


Figure 1: (a) Raman spectrum of graphite inclusion in zircon showing low degree of graphite crystallinity; (b) - Transmission electron microscopy bright field low-magnification images showing location of inclusion in zircon. TEM images of polycrystalline graphite aggregates in zircon. (c) Low- magnification bright-field image. SAED pattern of different region clearly indicates that the grain is highly-ordered polycrystalline graphite aggregate.

Raman band (at $\sim 1350\text{ cm}^{-1}$) assigned to disordered graphite was detected in graphite coexisting with diamond and pure graphite aggregates. This coexistence of diamond and graphite are commonly interpreted as partial graphitization of diamond. Recent experiments on diamond graphitization revealed that the transformation proceed via intermediate metastable phase of a linear hydrocarbon [2]. Lack of this phase of linear hydrocarbon in our study indicates that partial diamond graphitization is not predominant mechanism of disordered graphite formation in UHPM rocks. Raman-spectrum of graphite with significant disordered patterns may be the result of different orientation of graphite crystallites (up to 8 nm in size), which according to high resolution TEM studies are perfectly ordered. Thus crystallization of these graphite crystallites occurs from the supersaturated fluid/melt.

Acknowledgments: This study was supported by Russian Science Foundation grant №18-17-00186.

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RAMAN SPECTROSCOPIC AND PL STUDY OF DIAMOND CRYSTALS FROM DIFFERENT TOURMALINES FROM THE KUMDY-KOL UHPM ROCKS (KOKCHETAV MASSIF, NORTHERN KAZAKHSTAN)

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Diamond and coesite are the most popular mineral-indicators for identification of the ultrahigh pressure metamorphic conditions diamond and coesite subfacies, respectively [1]. Findings of diamond inclusions exclusively in K-bearing tourmaline (maruyamaite) [2,3] with unusual isotopic boron composition [4,5] from the Kokchetav massif (Northern Kazakhstan) stimulated the experimental study of the origin this unusual tourmaline, which demonstrates that the ultrapotassic fluid and high pressure are prerequisite for crystallization of maruyamaite[6,7]. Recently diamond inclusions were detected in schorl-uvite tourmaline from garnet-clinopyroxene rocks. Diamonds occurring as inclusions in maruyamaite are skeletal crystals up to 10 microns in size. Very rare octahedral crystals (up to 20 microns) were detected as inclusions K-bearing tourmaline with K₂O content as high as 1.4 wt.%, which cannot be classified as maruyamaite [8]. Diamond inclusions in schorl-uvite tourmaline are larger in size (up to 200 microns) and no regularities were detected in their spatial distribution within the tourmaline crystals. K₂O contents in schorl-uvite tourmaline are below 0.1 wt %, indicating it's crystallization from boron-rich, but K-poor fluid. If the diamond crystallization in these two different rocks types proceeds from UHPM boron-rich fluids we can expect the boron defects in diamond structure. Our previous Raman spectroscopic studies of metamorphic diamond clearly demonstrate that Raman spectroscopy can be used for discrimination of diamond from different rock types [9–11]. Here, we report the Raman spectroscopic and PL study of the diamond inclusions in different type of tourmaline, occurring within the Kumdy-Kol microdiamond deposit. This study was supported by RSF 18-17-00186.

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VALIDATION OF THE SUPERCAM-RAMAN FOR NASA'S MARS2020 MISSION: TESTS AND COMPARISON WITH LABORATORY RESULTS

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Raman spectroscopy is one of the analytical techniques of the instrument SuperCam, onboard NASA's Mars 2020 Perseverance rover. SuperCam will be able to perform remotely Raman, LIBS, luminescence and VISIR spectroscopies, as well as capturing sound with a microphone and acquiring remote micro-images [1]. To validate the performance of the SuperCam-Raman spectrometer described elsewhere [2], several rock samples were prepared and tested first at the laboratory with (a) a benchtop inVia-Raman instrument (Renishaw) and (b) a portable-Raman device (BWTek); then (c) with the Flight Model-Body Unit / Engineering Qualification Model-Mast Unit (FM-BU/EQM-MU) setup at Los Alamos National Laboratory (LANL), and finally (d) with the SuperCam's Flight Model (FM) configuration (after the thermomechanical tests of the rover). The results from the four setups were then compared.

Clinoptilolite, kaolinite, ilmenite, quartz, orthoclase, opal, serpentine, gypsum and white calcite were the rock samples tested. Figure 1 shows the comparison of the two spectra for the white calcite obtained with the (FM)-SuperCam-Raman and inVia. The (FM)-SuperCam-Raman shows a similar spectrum than the (FM-BU/EQM-MU) SuperCam-Raman, as well as those obtained with the portable-Raman and the reference inVia-Raman spectrometers. The results from both SuperCam-Raman setups were very accurate for most of the minerals, having comparable signal-to-noise ratios to the laboratory instruments. The SuperCam-Raman was not only accurate regarding the bands positions, but also regarding the relative intensities of the bands, 0.40:0.11:1 for the inVia and 0.44:0.11:1 for the (FM)-SuperCam-Raman, for the 282, 712 and 1086 cm^{-1} bands shown in Figure 1.

The inter and intraday reproducibility of SuperCam-Raman was checked using the average numbers of the main bands of calcite, gypsum, apatite, quartz and talc collected during the LANL calibration campaign. For all the tested minerals the relative standard deviation (RSD) of the main band position was lower than 1%.

Moreover, the validated SuperCam-Raman is able to differentiate between polymorphs of the same compound or minerals from the same mineral group with similar spectra.

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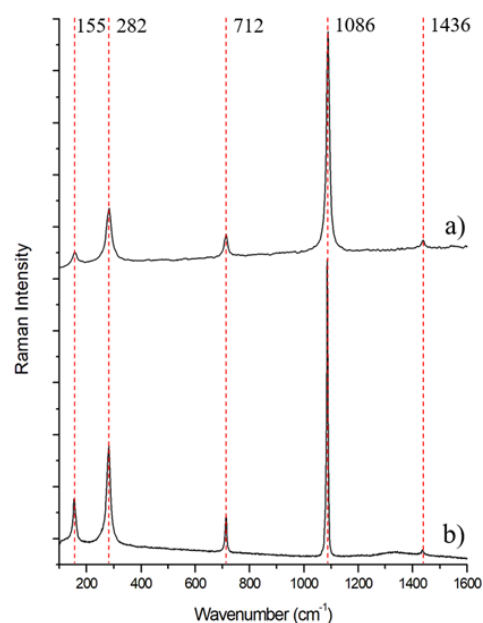


Figure 1. Calcite spectra of the same slab obtained with a) SuperCam and b) inVia

RAMAN STUDY OF OIL SPOT GLAZE PRODUCED IN LINFEN KILNS (SHANXI PROVINCE, AD 1115-1368)

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Jian wares from Fujian province (China) are very famous for their lustrous black glaze that exhibits unique colored patterns, which were very appreciated during the Song period, in particular the silvery “Oil Spot” patterns (OS). It was shown that the highly reflective nature of these OS came from a 2D periodic array of micro sized ε -Fe₂O₃ crystals [1], a rare metastable polymorph of Fe₂O₃ with unique magnetic properties. Since this discovery, this interesting phase has been identified in several types of Chinese ancient ceramics.

In this study we focus on the OS ware produced in the Linfen kilns complex (Shanxi province) [2], which were also famous and highly demand during the Jin and Yuan period. These OS are characterized of high gloss black glaze with brown spot of several microns. The investigations revealed (Fig.1) that a large number of reddish-brown snowflake shapes spots are homogeneously distributed on the surface of black glaze in contrary to Jian wares for which the oil spots are more heterogeneously distributed. But more interesting micro-Raman showed that the crystals in oil spots are only hematite (α -Fe₂O₃). The ε -Fe₂O₃ phase was only found in surrounding black glaze. The formation of reddish-brown oil spots of Linfen productions is very original and Raman spectroscopy combined to SEM-EDS is powerful way to study it. Interesting information concerning the manufacturing process was deduced as well as new data about the ε -Fe₂O₃ nucleation and growth.

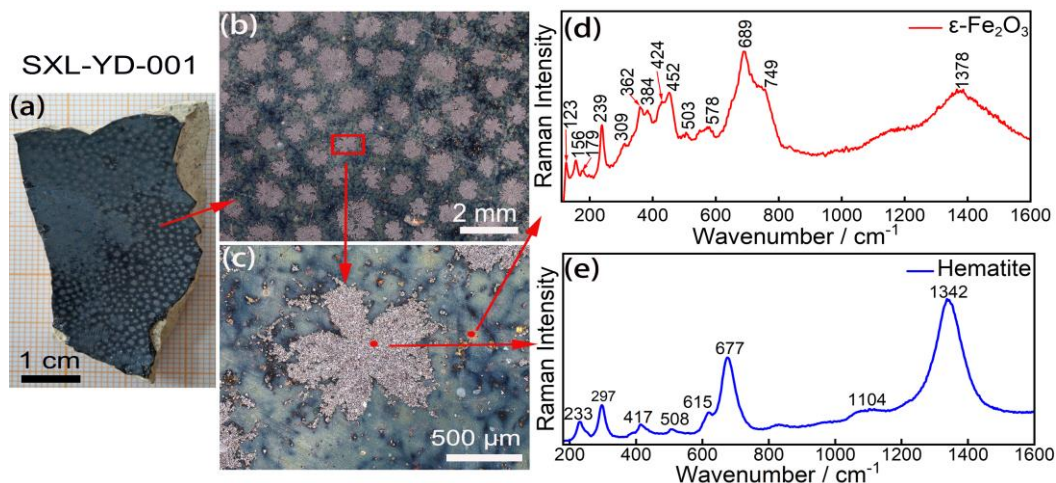


Figure 1: (a) Photo of a fragment excavated from Linfen kilns; (b) and (c) magnified optical images; Raman spectra collected in the oil spot pattern (d) and in glass matrix (e).

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ORIGINAL AND ALTERATION MINERAL PHASES IN THE NWA10628 MARTIAN SHERGOTTITE DETERMINED BY X-RAY FLUORESCENCE AND RAMAN MICRO-SPECTROSCOPY

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North West Africa 10628 (NWA 10628) is a shergottite found in Tindouf (Algeria) in 2014 for which there is no new information apart from Meteoritical Bulletin. The mineral phases present in NWA 10628 were investigated by non-destructive techniques, micro Energy Dispersive X-ray Fluorescence imaging (μ -ED-XRF) for the distribution of chemical elements on the surface, and micro-Raman spectroscopy and imaging (μ -Raman) for minerals in the bulk and fractures.

The matrix is dominated by pyroxenes, mainly as augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆) and diopside (CaMgSi₂O₆). Olivine and feldspars appeared as small crystals all along the matrix. Merrillite (Ca₉NaMg(PO₄)₇) was found as the highest crystals in inclusions. As whitlockite (Ca₉NaMg(PO₄)₆(HPO₄)) transforms to merrillite by high temperature/pressure we suggest that merrillite came from whitlockite in the ejection of meteorite from Mars. Gypsum (CaSO₄·2H₂O) was found by Raman spectroscopy in two areas of NWA 10628, as small crystals in the bulk and as apparently amorphous deposits in fractures. For gypsum in fractures, we consider its presence as sign of terrestrial weathering, because most of the times it appeared with calcite (CaCO₃), another neomineral coming from terrestrial weathering. For calcium sulfate crystals in the bulk, we mostly observed gypsum and anhydrite (CaSO₄) in the Raman spectra, maybe due to a partial dehydration of gypsum by the high pressure/temperature in the ejection of the rock.

Pyrite and marcasite (FeS₂ polymorphs) were observed by Raman spectroscopy, as well as their oxidation products (terrestrial weathering) goethite (α -FeO(OH)) and rozenite (FeSO₄·4H₂O). The appearance of hematite (Fe₂O₃), magnetite (Fe₃O₄), ilmenite (FeTiO₃) and anatase (TiO₂) suggested that ulvospinel (Fe₂TiO₄) was the precursor in Mars because ulvospinel can transform to ilmenite by pressure (ejection from Mars) and later on, ilmenite in magnetite/hematite and anatase by oxidative weathering in Earth.

RAMAN SPECTROSCOPY OF NANOMATERIALS SYNTHESIZED ON A CHINGA METEORITE

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Currently, scientists are interested in whether there are carbon nanotubes in space [1]. This research focuses on the synthesis of multiwalled carbon nanotubes (MWCNTs) and hematite nanowhiskers using an extraterrestrial substrate. The synthesis was carried out by catalytic pyrolysis of ethanol using CVDomna commercial equipment for carbon nanotube growth. A sample of Chinga meteorite (ataxite, ungrouped) [2] was used as a substrate.

The sample was prepared using standard metallographic procedures including polishing and etching with 1 wt. % nital for 5 minutes. The synthesis was carried out with CVDomna at 600°C and a pressure of 15 kPa for 10 minutes using a vapor-gas mixture of air and ethanol. The analysis of synthesized nanomaterials was carried out using the Zeiss Sigma VP scanning electron microscope and the LabRAM HR Evolution Raman microscope. The lateral resolution was 1-2 μm, and the excitation wavelength was 488 nm. Spectra were collected by means of backscattering geometry.

The Chinga contained submicroscopic duplex plessite and acicular kamacite spindles with its enveloping high-nickel taenite rim [2, 3]. After the synthesis on the surface of the duplex plessite, MWCNTs prevailed. Its diameters were 15-32 nm, average – 20 nm. The Raman spectra include two sharp peaks D (~1350 cm⁻¹, FWHM is 113.8 cm⁻¹), which correspond to a disorder mode, and G (~1580 cm⁻¹, FWHM is 75.9 cm⁻¹), which was a tangential mode [4]. The higher the I_D/I_G intensity ratio and the greater the FWHM of these peaks indicates the higher disorder in MWCNTs. The I_D/I_G is 1.13. These parameters, moreover, mean that MWCNTs were curved.

On the taenite surface, thin nanowhiskers of Fe₂O₃ were formed. Their diameters are 11-21 nm, average – 16 nm. The MWCNTs were synthesized on the kamacite surface. Diameters are the same as for MWCNTs on the plessite surface and the FWHM of D and G peaks are 98.8 cm⁻¹ and 77.6 cm⁻¹ correspondingly, the I_D/I_G is 1.17.

The fine-grained structure of duplex plessite and kamacite made it possible to synthesize MWCNTs with an average diameter of 20 nm; a disordering of MWCNTs is high. The taenite areas do not lead to the formation of MWCNTs, but hematite nanowhiskers were synthesized under the proposed conditions.

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PORTABLE RAMAN SPECTROSCOPY AND CLASSICAL GEMOLOGY FOR THE IDENTIFICATION OF BLUE GEMS

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Even though classical gemology remains a powerful tool for assessing unmounted gems in trade and in jewellers' collections, such an approach is hardly applicable to mounted ones, or museum objects. In the last decade, Raman spectroscopy has been used for routine investigation for gemological purposes, being fast, non-destructive and non-invasive. The availability of portable instrumentations further expanded the potentialities of such an approach, either as complementary or alternative to the classical one based on observation, refractive index, specific gravity, etc. This research follows previous works on red gemstones [1] and emeralds [2], and the comparison between portable and laboratory equipments in the study of blue gems [3]. In this study, we further assess the capability of a portable Raman spectrometer (i-Raman by BWTEK, 785nm laser) to characterize blue gemstones representative of the current fashion and trade, supplied by private jewelers. The obtained results allowed a complete characterization of the studied gems and showed potentialities and drawbacks of such a portable Raman spectrometer for their characterization.

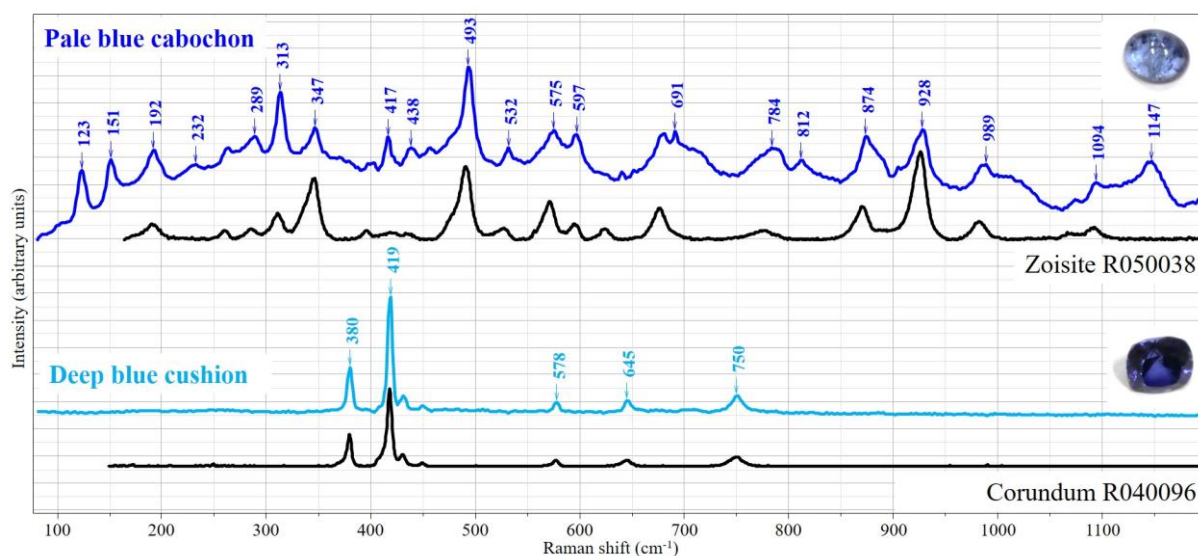


Figure 1: Raman spectra of two of the unmounted gems studied by classical gemology and Raman spectroscopy, and references from the RRUFF databases.

Acknowledgments: The jewelers Dr. Ugo Longobardo and Dr. Salvatore Salini are acknowledged for providing the samples used in this study.

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SULFATE COATING OF OLIVINE GRAINS IN THE RBT 04262 MARTIAN SHERGOTTITE AS PROOF OF THE TERRESTRIAL OR MARS WEATHERING

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The Roberts Massif (RBT) 04262 Mars meteorite [1] was found in the Roberts Massif (Antarctica) and was collected by the 2004-2005 ANSMET (Antarctic Search for Meteorites) expedition [2]. It was initially classified as olivine-phyric shergottite, but later, Mikouchi et al. [3] argued that RBT 04262 was a lherzolitic shergottite.

In this work, the RBT 04262 Martian shergottite was analyzed point-by-point as well as in Raman imaging modes using the InVia confocal micro-Raman spectrometer (Renishaw, UK). It is provided with 785 and 532 nm excitation lasers and a CCD detector.

According to the Raman results, olivine and pyroxene were the predominant compounds of the sample. Olivine was identified by its most characteristic Raman bands at 820 and 850 cm^{-1} [4], whereas the orthopyroxene was detected by its distinctive Raman bands between 300-400, 650-700 and 980-1020 cm^{-1} [5]. Other secondary minerals were also found, such as chromite (685 cm^{-1}), merrillite (974 and 958 cm^{-1}), gypsum (1008 cm^{-1}) and epsomite (986 cm^{-1}) [4].



Figure 1 : High Resolution Raman images of (A) Olivine, (B) Pyroxene, (C) Epsomite and (D) Gypsum along the RBT 04262 Mars meteorite.

Even if the detected sulfates have been previously detected on Mars surface, their distribution covering the olivine grains (Figure 1) indicate that they are weathering products. This weathering can be due to two different reactions. On the one hand, at Martian temperatures as low as -60 °C, the H_2SO_4 aerosols react with the surface of the olivine grains producing sulfate minerals [6]. On the other hand, they could be also produced by the reaction between the terrestrial water that entered across the cracks during its stay on Earth and the olivine grains. Therefore, the origin of the minerals is not clear but considering their distribution it can be assured that they were formed by weathering.

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SPACE WEATHERING SIMULATION ON MINERALS AND THEIR MIXTURES FOR SPACE APPLICATION

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Raman spectroscopy is an excellent tool to perform petrological and mineralogical investigations in a fast way, both of terrestrial and extraterrestrial rocks. Therefore, Raman spectrometers have been developed for operation on planetary surfaces, e.g. the Raman Laser Spectrometer (RLS) on board ESA's ExoMars2022 [1] and, under development, the RAX (RAman spectrometer for MMX) [2] for the Martian Moons eXploation mission (MMX) [3].

To study the influence of micrometeorite bombardment on atmosphereless bodies as one trigger of space weathering (SW) [4] we investigated olivine (Fo₉₁) and pyroxene (En₈₇) as well as their mixtures with Raman spectroscopy. SW is simulated by laser irradiation. The laser experiments were done with an excimer laser system (ArF UV laser; wavelength 193 nm) at the Physikalisches Institut in Münster.

We examined the irradiated as well the non-irradiated part of pressed pellets (Fig. 1) of the pure minerals and their mixtures with a confocal Raman microscope Witec alpha300R system operated with laser excitation wavelength of 532 nm. As a first result, we found that the analyzed irradiated samples contain a disproportionately high amount of pyroxene compared to the original ratio. This can be a hint for congruent melting of olivine [5].

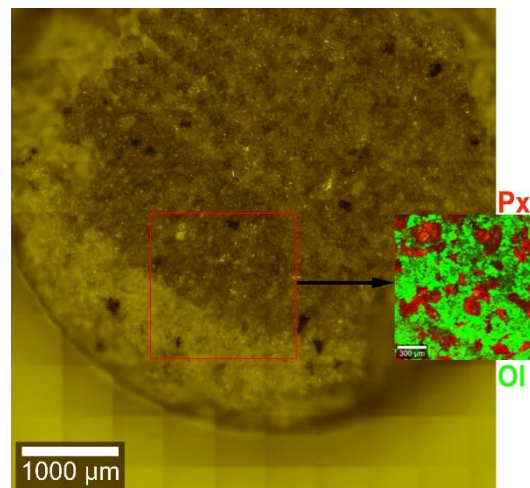


Figure 1: Investigated pellet with the ration of 85 % olivine and 15 % pyroxene. The irradiated region is dark in the middle of the pellet surrounded by unirradiated material. The red square marked the area investigated with Raman spectroscopy. The result of the Raman scan is shown on the right (green: olivine, red: pyroxene).

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SPECTROSCOPIC INVESTIGATION OF WALL PAINTINGS IN THE ALHAMBRA: DECORATIONS WITH RED BRICKS

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The Alhambra Monumental Ensemble (Granada, Spain) is currently the only preserved palatine city of the medieval Islamic period. It constitutes the best example of Nasrid art in its architecture and decorative aspects. In this work, we focus on the study of one of the most unknown decorations: wall paintings imitating red bricks. They are found in many different locations within the Alhambra, including both exterior and interior walls and vaults. We have considered locations (see Figure 1) from different periods to gain information about their characteristics in terms of materials, execution techniques and conservation state. They have been studied combining a non-invasive methodology using portable equipment (X-ray fluorescence (XRF) and Raman spectroscopy) with complementary studies on selected samples (SEM-EDX, Raman and FTIR microspectroscopy).



Figure 1: Map of the Alhambra Monumental Ensemble showing the study sites

The red color of the rectangles imitating bricks was always due to hematite ($\alpha\text{-Fe}_2\text{O}_3$), as revealed by its characteristic Raman bands. Considering XRF results and the abundance of red ochre in the region the use of a natural pigment could be hypothesized. The red pigment was applied over a white finishing layer, which acted also as the edge lines between the false bricks. The chemical composition of the white areas was different depending on the locations. Lime (CaCO_3) mortar and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) plaster were found. Evidences of material alterations (i.e. calcium oxalate in the form of weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and of different interventions were also found in some locations. These results will provide insight on the historical significance of such decorations in the Alhambra monument and it will also be useful to carry out adequate posterior restoration or conservation works.

CHARACTERIZATION OF MICROPLASTICS FROM SURFACE WATER OF ATTICA, GREECE, BY MEANS OF M-RAMAN SPECTROSCOPY

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Environmental geochemistry constitutes a major field of application of μ -Raman spectroscopy (μ -RS) in geosciences. From inorganic to organic, and biological contaminants, in soil, water, and air μ -RS is a useful tool in their characterization. In the last decade, μ -RS has been rapidly gaining ground in the analysis of microplastics (MPs) [1].

In this work, surface water from the southeastern part of Attica, towards the Erasinos river basin that flows into the Southern Evoikos Gulf, were tested for MPs by means of optical microscopy and μ -RS. Specifically, two samples were collected in August 2020, near the river mouth of the Erasinos river in Vravra (Sample D1 freshwater from the river approx. 1km from the coastline, Sample D3 sea water with significant freshwater input at the immediate exit of the river towards the sea). Samples were stored in 1lt glass bottles and were filtered using a vacuum pump for extracting the microplastics. Cellulose filters were applied and then samples were dried at room temperature covered with Petri glass dishes. Non-destructive Raman study was performed on the MPs on the filters employing a Renishaw inVia Reflex micro-Raman. The 785 nm excitation wavelength laser was used to acquire Raman spectra in the spectral range 100–4000 cm^{-1} . Two different types of MPs were identified (Fig. 1); polyethylene terephthalate (PPT) in the sample D1, documented by the double peaks at 1616 cm^{-1} and 1729 cm^{-1} (ν CH) [1], and polypropylene (PP) in the sample D3, documented by the distinctive peak at 1296 cm^{-1} (ν CH) [2].

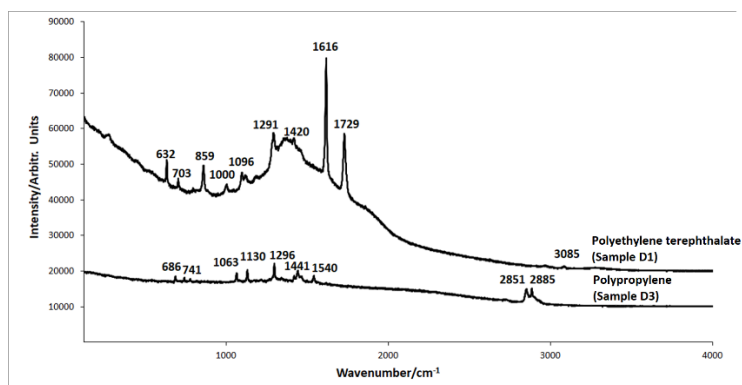


Figure 1: Raman spectra of Polyethylene terephthalate (sample D1) and Polypropylene (sample D3)

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MICRO-RAMAN STUDY OF CESANITE IN CHLORIDE SEGREGATIONS FROM UDACHNAYA-EAST KIMBERLITES

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Cesante has been found in only three places to date and are limited to a geothermal field. In this study we report cesante with remarkably similar associated minerals in quite different site – at the rims of chloride segregations in kimberlites of Udachnaya-East pipe. Challenges of micro-Raman identification of cesante are associated with its low water content. Raman spectrum under standard conditions does not detect water bands and may lead to misidentification. In cesante formula $[Ca_{1+x}Na_{4-x}(SO_4)_3(OH)_{x(1-x)}H_2O]$, 'water' occurs as molecular water and as structurally bound hydroxyl incorporated in mineral structures [1]. Cesante contain appreciable structural water (2.9 wt%), however, there is no reported Raman spectra of cesante in the region $2800-3800\text{ cm}^{-1}$. We conducted long-term (one hour) accumulations of Raman spectra to prove the presence of hydrated H_2O and OH group.

The Raman spectrum of cesante is shown in fig.1B. Most of the absorption bands can be referred to modes involving $[SO_4]^{2-}$ ions. The broad band at 3244 cm^{-1} is due to hydrated water. The 3554 cm^{-1} band, typical of structural OH, is very faint and interfered with by the H_2O band. We used deconvolution to clarify peak positions of molecular water and structural hydroxyl.

The study aims to find out the source of the Na-Cl-S-enrichment in the Udachnaya-East pipe, which are highly discussed [2].

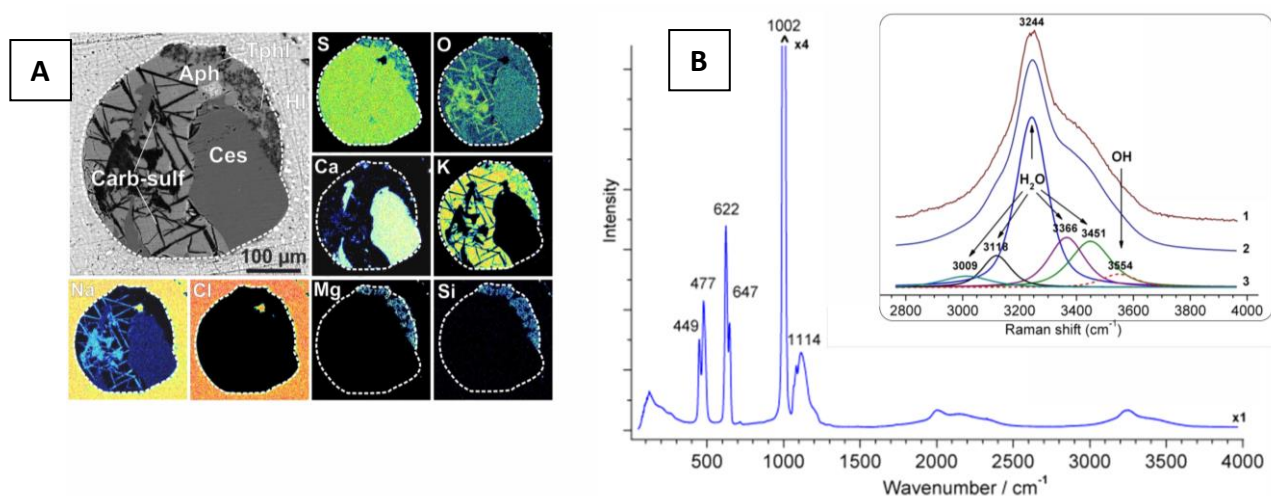


Figure 1: A- SEM images showing morphology and composition of sulphate-rich inclusions in halite from chloride segregations of Udachnaya-East kimberlites: Aph-aphtitalite, Ces-cesante, Tphl-tetraflgopite, HI-halite; B-Raman spectrum of cesante daughter mineral within sulfate melt inclusion. Inset: Raman spectrum deconvolution for cesante in the $2800-3800\text{ cm}^{-1}$ spectral region: 1- the experimental spectrum; 2- the entire simulate spectrum, 3- curve fitting.

Acknowledgement: This work is partly supported by Russian Foundation for Basic Research (grant 18-05-00682).

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MULTI-ANALYTICAL APPROACH TO THE STUDY OF MECCA GILDING TECHNIQUE

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Meccatura is a type of historical gilding technique, which consists in the application of a coloured varnish on burnished metal surfaces (silver or tin foil) with the aim to both imitate the golden surface and to protect the silver from tarnishing [1]. Since the medieval period in Europe, it has been applied in paintings, carved wood altarpieces, frames, polychrome sculptures and decorated leather. There is a variety of mecca historical recipes, which report on different organic substances, e.g. siccativ oils, resins (sandarc, colophony, shellac etc.), organic dyes (saffron, dragon's blood, gommagutta, aloe etc.), plasticizers (beeswax or carnauba), often unknown, subject to degradation phenomena and past interventions [1-3]. More recently, the classical *mecca* has been substituted with mixtures of synthetic colourants charged with pigments and inert materials. Due the complexity of present materials, this represents an analytical challenge for heritage scientists and conservators. With more attention dedicated to the traditional gilding techniques, available scientific results on the *meccatura* are rather fragmentary, being part of a larger multi-analytical study on decorated artworks. This paper focuses on *meccatura* research issues, outlines the gaps in their scientific study and proposes methodologies to overcome them. In specific, the limitations and contribution of the advanced non-invasive spectroscopic techniques such as Raman and Surface-Enhanced Raman Spectroscopy techniques are discussed and supported by complementary spectroscopic and non-spectroscopic methods [4-8]. The paper also compares the role of these currently available non-invasive analytical techniques to the study of historical and modern glaze recipes and single organic components, their alteration and ageing, in comparison with the traditional analytical methods.

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SERS IDENTIFICATION OF NATURAL YELLOW DYES IN PROTEINACEOUS FIBRES USING AG-AGAR NANOCOMPOSITE

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Before the synthetic dyes era, dyers and painters obtained yellow dyes, for textile and lake production, from natural sources such as weld, saffron, and turmeric. The main disadvantage of these colourants is their high light-sensitivity. Natural yellow dyes have a very similar chemical composition that in many cases varies only in the proportion of the main components [1]. Their identification is of particular interest for the study of textiles; it helps to understand the original colour of artefacts and to establish informed preventive conservation strategies.

There is a lack of investigations regarding the characterization of yellow dyes using SERS due to its complexity. The majority of yellow dyes used in cultural heritage have a reduced water solubility that limits the interaction between the dye molecule and the nanoparticles (NPs). Researchers noticed differences between FT-Raman and SERS spectra from several components of flavonoid dyes because the molecules, in particular OH reactive groups, interact with the NPs [2-4].

Weld was identified in silk samples using an on-fibre non-hydrolysed method with Ag photo-reduced NPs. However, the authors found differences among the standard and the obtained SERS spectra attributed to impurities and interaction of the dye with NPs [4]. To solve the water solubility problem and reduce sample contamination due to NPs colloids Cesarotto et al. [4] applied UV-LA-SERS method for studying yellow lakes, but the method requires sample pre-treatment using HF vapours. O-safranin was studied with Ag NPs using Raman, resonance Raman and SERS. The experimental results, compared with DFT calculations, suggest a minor effect of the interaction between the molecule and the NPs on the resulting spectra [5].

This work aims to characterize different natural yellow dyes in proteinaceous fibres in a non-destructive way using the Ag-Agar method. We tested a selection of solvents to set-up a tailored protocol for the extraction of the dye and its absorption into the gel system before the SERS analysis. Mock-ups were prepared dyeing silk and wool fibres and were artificially aged in order to identify changes in the molecule due to degradation of dye.

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SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS): EXTRACTIONLESS NON-HYDROLYSIS METHOD FOR THE DETECTION OF RED LAKE PIGMENTS IN PAINTINGS

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Lake pigments - widely used for their intense, brilliant color - were obtained by precipitation or adsorption of the organic dye onto a powdered inorganic substrate, exploiting the formation of a complex between the organic molecules and a metal cation (commonly Al³⁺) [1-2].

Identification of mostly diffused red organic lakes is of fundamental importance for the study of their manufacturing technology and to their conservation/long-term preservation but this poses an analytical challenge. The poor specificity and sensibility but also the invasiveness of conventional methods applied to organic compounds limits the characterization of this kind of substances [3-4]. To circumvent these problems, recent studies have focused on the application of surface-enhanced Raman scattering (SERS) to the identification of organic colorants in works of art. The noble-metal SERS substrate not only provides enhanced Raman signals but also quenches the fluorescence generated by many organic colorants [4-5].

Usually, chemical analysis of lake pigments is performed by detaching small samples from the artifacts. Some authors treated the samples with acids (e.g., HF [6], HCl [7]) to hydrolyse the bonds between the dye molecules and the inorganic substrate and to promote the dye adsorption onto the SERS substrate, according to an extractionless hydrolysis approach. In other case, dyes are removed from the solid sample with a solvent employing an extractive approach [7]. An alternative approach could be the use of active gels [8-9] or laser ablation [10] to remove the dyes from the painting layers and to deposit them onto the SERS substrate [11].

The goal of this work is to develop an extractionless non-hydrolysis approach that employing silver colloidal pastes applied to the study of dyes in painting layers mounted in cross sections, that shows great potential for the unambiguous identification of red dyes – and their degradation pathways - applied in different media on a variety of substrates. Moreover, it is necessary to deepen the knowledge about the mechanisms of pigment-nanoparticle/organic dye-metal cation interactions and improved spectral libraries of known and deliberately aged paint samples.

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PHONON ANHARMONICITY OF ORTHOPHOSPHATES LnPO_4 (La, Ce, Nd) AND NATURAL MONAZITE ACCORDING TO T-DEPENDENT RAMAN SPECTROSCOPY

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Natural Th,U-bearing monazite is widely used as a geochronometer; monazite-like orthophosphates are promising matrices for the immobilization of radioactive waste. The high radiation stability of these materials is assumed to be due to the low critical amorphization temperature. However, it can be expected that the ability to become amorphous is determined primarily by the dynamics of the crystal lattice. In this work, the lattice dynamics of natural monazite from pegmatites (Urals) in the initial state (radiation dose $D_\alpha = 2.2 \cdot 10^{19}$ α -decays/g) and after annealing (1200°C, 100h, $D_\alpha \approx 0$), and also a number of synthetic orthophosphates LnPO_4 (Ln = La, Ce, Nd), were investigated by the temperature dependent Raman spectroscopy. The spectra of LnPO_4 (Fig. 1a) and monazite correspond well to the monoclinic structure, sp.gr. $P2_1/n$. The Raman shift of the A_{1g}/B_{1g} mode of symmetric stretching vibrations $\nu_1(\text{PO}_4)$ increases in the series $\text{La} \rightarrow \text{Ce} \rightarrow \text{Nd}$ [1]; the position and the width (FWHM) of ν_1 in the initial and annealed monazite reflect its radiation and chemical disordering [2-3] (Fig. 1b).

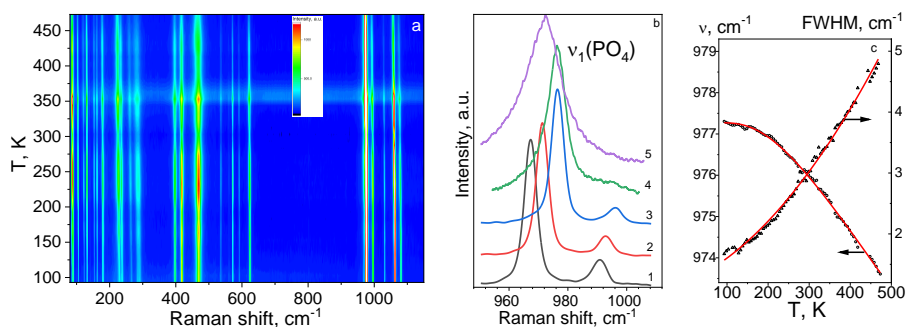


Figure 1: 2D-map of T-dependent Raman spectra of NdPO_4 (a); the segment of the spectra (293 K) of LnPO_4 (Ln=La, Ce, Nd) (1-3) and monazite before (4) and after (5) annealing (b); T-dependences of the ν_1 mode position and FWHM in NdPO_4 and their approximation (red lines) within the model [5] (c).

The T-dependences of the Raman shift and FWHM (Fig. 1c) are nonlinear at $T < \sim 230$ -350 K, and they are sensitive to the type of Ln and D_α . The $(d\nu/dT)_P$ values for ν_1 decrease in the series $\text{La} \rightarrow \text{Ce} \rightarrow \text{Nd}$. The implicit (quasi-harmonic) and explicit (phonon interaction) contributions to the anharmonicity of vibrations are revealed. The lattice dynamics are analyzed taking into account the change in the electronic structure of the P-O and Ln-O sublattices with an increase in the atomic number of Ln [4] and radiation disordering.

Acknowledgement: This work was supported by RFBR grants 18-05-01153 and 20-05-00403.

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ORGANIC COMPOUNDS DETECTION IN GEOLOGIC SAMPLES BY RAMAN IMAGE AND RAMAN-SEM-EDS COMBINATION

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The identification of organic compounds by spectroscopic techniques is becoming a necessary challenge considering the upcoming Mars missions carrying out by rovers with several spectroscopic techniques.

In the special case of organic compounds, Raman microscopy has shown good results in their identification and characterization [1]. However, this task in real samples is not easy as the concentration of these compounds in rocks is very low, and the biggest drawback of this technique is its Limit of Detection (LOD). In contrast, this technique does not involve sample consumption, which results very interesting to preserve the precious Martian returning samples for further analysis. Considering this, Raman imaging and combination of Raman spectroscopy with SEM-EDS will be very useful for this aim, as they can analyse large rock surfaces at micrometric scale.

The best results arose using the 514 nm laser for Raman analyses. Raman imaging performed using a step between measurement points of the same size of the laser spot resulted very successful (Figure 1).

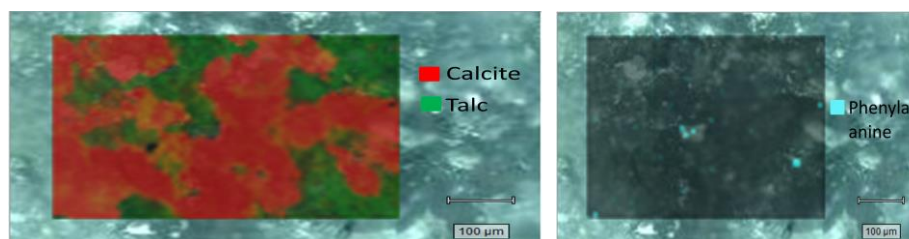


Figure 1: Phenylalanine found by Raman imaging in a stromatolite.

Finally, the combination of Raman spectroscopy and SEM-EDS gave also a good output. The employed methodology consisted on performing an EDS mapping in a certain region of the samples and identifying carbon rich areas. Then, by means of a Raman probe that is introduced in the SEM vacuum chamber, those C-rich areas were analyzed molecularly.

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DEVELOPMENT OF A PORTABLE DEEP-ULTRAVIOLET EXCITATION (248.6 nm) RAMAN SPECTROSCOPY SYSTEM

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Raman spectroscopy has very high chemical specificity and measures the vibrational energy of molecular bonds. However, Raman scattering is an inherently weak process. To compensate for it, highly sensitive two or three stage cooled detectors are used which demands more energy input, larger footprint and cost. Samples and optical components also generate fluorescence background signal during measurements, lowering the signal to noise ratio (SNR) and reducing the sensitivity of the technique. Fluorescence background and large footprint are the major bottlenecks in the translation of Raman technology to the field.

We have designed and developed a portable Raman spectroscopy system that uses deep ultraviolet (Deep-UV) excitation of 248.6 nm wavelength. Since the fluorescence background from most samples is not generated before the 260 nm wavelength, the main advantage of our system is that it can acquire spectra in the fingerprint region, which are potentially fluorescence background free and have high SNR. To minimize the interference from Rayleigh scattered light, and further increase of sensitivity, we have deployed orthogonal geometry in the excitation and collection optical trains. This separation of excitation and collection optical paths also allows for flexibility in the desired spatial resolution. Our Deep-UV Raman system uses a low footprint and single stage cooled miniature spectrometer. Fig. 1 shows the Raman spectrum of diamond, which we suggest to use as the calibration sample. The spectral resolution estimated by FWHM of diamond Raman peak was $\sim 22 \text{ cm}^{-1}$.

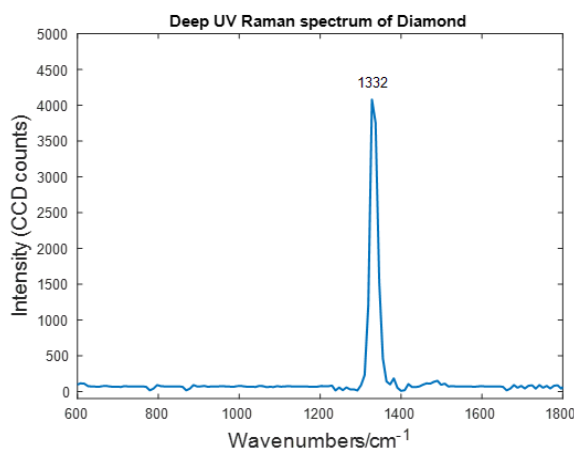


Figure 1: Deep UV Raman spectrum acquired from the calibration sample: Diamond

Currently work is in progress to acquire Deep-UV resonance Raman spectra from samples having molecular electronic transitions near the excitation wavelength. This will result in an important sensitivity increase, improved spectral resolution, low cost and smaller footprint.

UNEXPECTED COMPOUNDS IN THE BRICKS AND COMMERCIAL MORTARS OF A BUILT HERITAGE CONSTRUCTION FROM 1918: THE INFLUENCE OF INDUSTRIAL PORT ACTIVITIES

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In this work Raman spectroscopy and X-ray diffraction were applied for the diagnostic study of some commercial mortars, belonging to different company, applied on the walls of Punta Begoña Galleries, an historical building located in a coastal environment (Basque Country, Northern Spain) with industrial activity. In addition to mortar essays, even historical bricks were analysed, which showed a strong deterioration process, visible in the form of cracks and loss of material caused by the presence of salt efflorescences. In both cases the molecular and mineralogical analyses were carried out to study the conservation state of brick and mortars exposed to the environmental stressors. The presence of the degradation compounds was studied considering the orientation of the materials inside the building. Among the decay products, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was identified in a higher number of samples of the mortar together with sodium nitrate (nitratine, NaNO_3) in minor amount. In some mortar samples a biodeterioration processes was identified by the presence of calcium oxalates whewellita ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and wedellita ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) as a results of secretion of microorganisms. In addition, Raman analyses all the mortar samples showed the presence of the xanthophyll carotenoid astaxanthin, which can be used as a bioindicator of pollution level because it appears as the first xanthophyll in highly contaminated areas [1]. On the other hand, in the historical bricks, in addition to beta-carotene astaxanthin and gypsum, the presence of niter (KNO_3) was also detected. The obtained results were extremely useful to understand the deterioration processes in order to study the atmospheric impact in modern material in these aggressive environments in a short time period (a year and a half after their application) as well as the analyses on brick demonstrated the negative influence of the marine aerosol and industrial activity over the years.

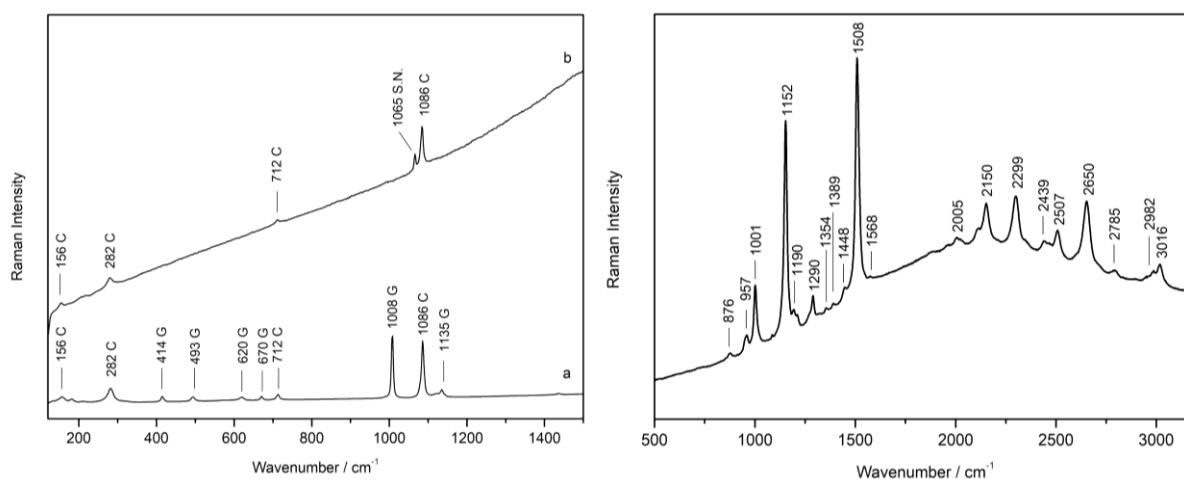


Figure 1: Raman spectrum of nitratine (S.N.) plus calcite (C) (a) and gypsum (G) plus calcite (C) (b) on the left and Raman spectrum of astaxanthin on the right.

UNDERSTANDING THE EXOMARS RLS INSTRUMENT

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The flight model (FM) of the Raman instrument for the ExoMars 2022 mission, the Raman Laser Spectrometer (RLS) [1], has been delivered to ESA and is already integrated in the Rosalind Franklin rover. Given the schedule constraints imposed by the project for the delivery of the flight model, the available slot for its characterization back in 2018 lacked the sufficient time for an in-depth scientific test campaign. Happily, some tests with the integrated instrument were carried out profiting from the assembly and integration tests of the Analytical Laboratory Drawer (ALD) of the rover, and the system tests of the rover itself.

In addition, the RLS flight spare (FS) model was integrated and setup at INTA, replicating the exact same characteristics as the actual FM. Thus, this model is being used to thoroughly characterize and understand the instrument performance by performing several tests with different sets of samples and operational conditions, with the funded expectation that the lessons learned with this model will be applicable to the FM.

All in all, in this work we will discuss the results from the tests performed with the RLS FM and FS, which have provided a good understanding of the instrument analytical performances. This includes studying aspects such as 1- the spatial cross-registration between the RLS and MicrOmega instruments, which will allow the analysis, on the same position, of interesting spots on the sample; 2- the detection of traces of contamination in crossed analysis between RLS and MOMA in the MOMA calibration target; 3- the determination of the instrument performances, understanding how they might be affected by the environmental parameters such as temperature or vacuum; 4- the optimization of the acquisition parameters of the instrument as a trade-off between spectral quality and operational limits such as bandwidth, power or time; and 5- the identification and quantification capabilities of the instrument based on the analysis of mineral samples relevant to the Oxia Planum mineralogy.



Figure 1: The RLS Flight Model

The objective of this work is to provide the scientific community with an overview of the instrument performances in order to know what can be expected from the instrument, to facilitate the best possible scientific return during the operation on Mars.

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RLS SPECTRA ACQUISITION OPTIMIZATION WITH THE FLIGHT SPARE

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The flight Raman instrument for the ExoMars 2022 mission, the Raman Laser Spectrometer (RLS) [1], was delivered and is already integrated in the *Rosalind Franklin* rover. In parallel, the RLS flight spare (FS) model is being used at INTA facilities to thoroughly characterize and understand the instrument performance, as well as to optimize the scientific return of the flight instrument through a proper parameterization.

The optimization and characterization of the instrument can be focused in usually interconnected aspects such as working temperature, detector temperature, vacuum level, laser power and spectral stability, thermal control PID parameters, temperature range and stabilization times, detector offset or gain, and the many system parameters of the instrument which define the operational behavior of the instrument application software.

Concretely, in this work we present the experiments and analysis centered in the optimization of the spectra acquisition algorithms implemented onboard the RLS instrument. Few parameters govern the performance of the acquisition algorithms of the instrument. The developed algorithms provide the instrument with the capability to automatically or programmatically (from ground) adjust the acquisition parameters, such as the fluorescence quenching time, integration time, number of accumulations, or detection and removal of cosmic rays that might impair the acquisition [2].

The RLS instrument features an automated integration time (t_i) calculation algorithm, which allows optimizing this time for every spot in the sample. However, due to several reasons, the number of accumulations (n_a) has to be established from ground as a system parameter, so it will be the same for all the samples and spots obtained during one operational cycle (sol). It has been reported [2] that, for constant total acquisition times ($t_i \cdot n_a$) in instruments such as RLS, the signal to noise ratio (SNR) of a spectrum increases more by maximizing t_i , than by maximizing n_a . This is in agreement with the implementation performed on the onboard software of RLS. Thus, the present study is centered in the characterization of the optimal number of accumulations (which is configurable from ground) for the RLS operation.

Several samples with different emission efficiencies (diamond, calcite, serpentine and vermiculite), have been analyzed with the RLS FS, acquiring high number of acquisition parameters. The data has been processed to establish the spectral quality (measured as the SNR) as a function of the number of accumulations. In the conference we will present the results from this study and address the necessary trade-off between the onboard parameters which are affected by, or impact on, the configuration value of n_a . E.g. the operation time, data budget and bandwidth, laser life and spectral quality. This discussion will be used to take a decision as to how to parameterize the flight instrument for Martian operation.

[1] Rull, F. et al. The Raman Laser Spectrometer for the ExoMars Rover Mission to Mars. *Astrobiology* 17, 627–654 (2017).

[2] Lopez-Reyes, G. & Rull Pérez, F. A method for the automated Raman spectra acquisition. *J. Raman Spectrosc.* 48, (2017).

LASER POWER AND THERMAL INCREASE ON SAMPLES DURING RAMAN SPECTROSCOPY ANALYSES

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Many types of Raman spectroscopy systems are used in various domains, from micro-Raman to remote Raman. Nevertheless, among the common specifications of any present system is the use of a laser as monochromatic light source. The setting of the laser power is thus a universal problem for any Raman spectroscopist to find a compromise between the signal intensity and the risk of thermal alteration of the sample. In many studies, authors simply mention that “the laser power was set to n mW in order to prevent sample from any damage”; however, this information does not address the problem of thermal increase induced by the laser since this depends on many factors (laser wavelength, optics, sample...). Thus, this study identifies the different parameters to consider and proposes simple protocols to optimize the analyses.

Among the parameters to consider are:

- **The instrumental optical path.** Between the exit point of the laser and the sample, the light passes through different lenses, windows and optical fibers, and is reflected on mirrors and other reflecting surfaces. During its travel, the light is thus partly absorbed and deviated, and only a part of the initial power finally arrives at the sample.

- **The focusing system.** One of the most important parameters is the laser spot size. Indeed, the smaller the spot, the more important the surface power density.

- **The duration.** Before reaching thermal equilibrium, the longer the sample is exposed to the laser, the higher the temperature increases. Since Raman spectrum can now be acquired in a few tens of millisecond, the effect of heating is thus generally limited. This is in particular the case during Raman imaging. Thus, it is better to consider surface energy density rather than surface power density.

- **The sample itself.** The physical properties of the sample are the most important things to consider. These include optical absorption coefficients (depending on the laser wavelength), thermal conductivity and surface roughness. All these parameters will modify what is finally the key unit to consider: the energy density.

These considerations have consequences on the way to carry out Raman measurements. For instance, we demonstrated that powdered samples are more sensitive to thermal alteration than massive samples, but that this effect can be compensated by changing the optics [1].

During this presentation, a series of simple experiments to estimate the different key parameters will be presented and procedures to circumvent some issues will be proposed.

[1] F. Foucher, G. Lopez-Reyes, N. Bost, F. R. Pérez, P. Rüßmann, F. Westall. J. Raman Spectrosc. 44, 2013, 916-925.

STRUCTURAL EVOLUTION OF MATERIAL UNDER PROTON IRRADIATION MONITORED BY RAMAN SPECTROSCOPY

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Organic molecules are prime targets for the search for life on other planetary bodies in the Solar System. Understanding their preservation potential and detectability after ionic irradiation, with fluencies potentially representing those received for several millions to billions of years at Mars or in interplanetary space, is a crucial goal for astrobiological research.

In order to be able to perform *in situ* characterization of such organic molecules under ionic irradiation in the near future, a feasibility experiment was performed with polymer test samples to validate the optical configuration and the irradiation chamber geometry.

We will present a Raman *in situ* investigation of the evolution of a series of polymers during proton irradiation. To achieve this goal, a new type of Raman optical probe was designed, which documented that proton irradiation (with a final fluence of $3 \cdot 10^{14}$ at.cm⁻²) leads to an increase in the background level of the signal, potentially explained by the amorphization of the materials.

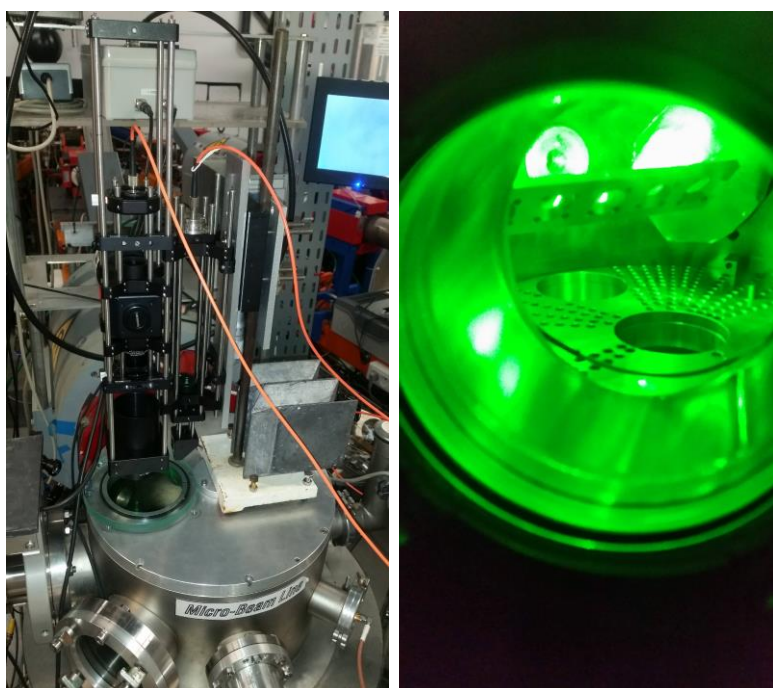


Figure 1: Raman probe and optical window (left) and view inside the irradiation chamber (right).

HIGH PRESSURE – HIGH TEMPERATURE PLATFORM FOR IN SITU RAMAN STUDIES

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In order to better understand complex Earth (volcanic/magmatic systems and associated hazards, geothermal activity, ...) and Material Science (glass and ceramic fabrication, clean energy production, ...) processes as well as to improve related thermodynamic models, it is necessary to acquire experimental data in situ, in real extreme conditions. Consequently, the main goal of PLANEX project is the development of a high pressure – high temperature analytical platform that allows to measure in situ physical/structural/chemical properties of various materials such as molten silicates, salts, carbonates, oxides, hydrous fluids and gases, etc.. The research axis based on Raman scattering appears as a crucial part of the Planex's platform. This spectroscopic technique allows us to determine - as a function of temperature, pressure and time - the structural and dynamics modifications of main silicate network ($50\text{-}1200\text{ cm}^{-1}$) and of various (volatile) species such as H_2O , CO_2 , S, etc. ($1000\text{-}6000\text{ cm}^{-1}$). Moreover, it provides the opportunity to track nucleation and crystallisation processes.

The high temperature – high pressure Raman device is presented in Fig. 1 The high resolution is coupled, through the home-made Raman probe, to the so called transparent Internally Heated Pressure Vessels (IHPVs) equipped with three sapphire windows and inner sapphire sample container. The actual design equipped with two excitation wavelengths: 355 nm and 532 nm allows to record in situ Raman spectra up to 1200°C and under 2000 bar. The very first Raman scattering results will be discussed.

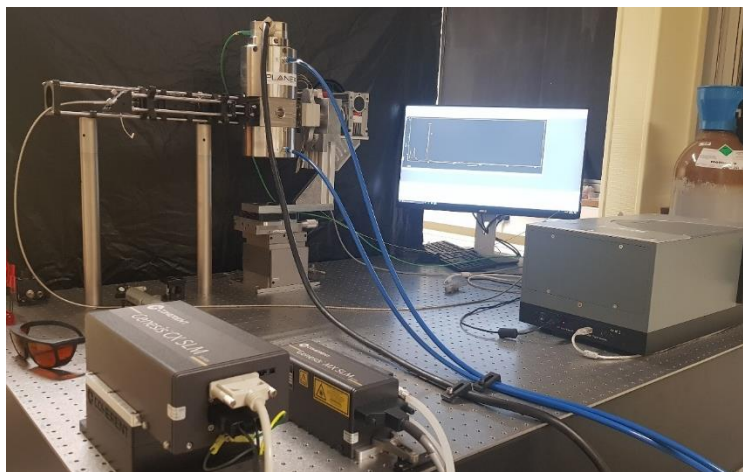


Figure 1: High pressure-high temperature PLANEX's platform for in situ Raman analysis

FEASIBILITY OF RAMAN OPTICAL ACTIVITY FOR DETECTING AND DISCRIMINATING CHIRALITY FOR PLANETARY SCIENCE INSTRUMENTATION

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Amino acids and carbohydrates, as individual compounds, can be formed abiotically and have been identified in a variety of extraterrestrial materials. Therefore, in these cases, it is not merely the presence, but rather the chirality of these molecules that is indicative of biological origin. Biologically synthesized materials on Earth are composed of L- and D-enantiomers of amino acids and carbohydrates, respectively. To date, no spacecraft-based Raman spectrometer has the capability to distinguish between enantiomers of these compounds. While there is only one commercial-off-the-shelf (cots) Raman optical activity (ROA) spectrometer available, surprisingly however, no research has been undertaken to ascertain the feasibility of this technology for the capability of biosignature detection in astrobiology and planetary science. Therefore, for the first time, this proposed effort would undertake a feasibility study to establish if ROA would afford the discrimination of the chirality of amino acids and carbohydrates in astrobiologically relevant simulant samples.

Firstly, this research will investigate if ROA can distinguish between the D- and L-enantiomers of a collection of amino acids and carbohydrates most commonly found in biology and meteorites. Common amino acids that most frequently occur in abiotic and biotic samples include glycine, alanine, glutamic acids, aspartic acid, leucine, serine, and valine, and likewise, common carbohydrates include glucose and fructose. Subsequently, a database of amino acid and carbohydrate chirality relevant for astrobiology would be constructed. Then, the limit of detection would be determined by serial dilution of the D- and L-enantiomers of the above compounds in water, then likewise for saline solutions relevant for Europa, such as, NaCl, KCl, MgCl, MgSO₄, and Na₂Mg(SO₄)₂. To further test the feasibility of this technique, mixtures of Raman active substances, amino acids, and carbohydrates would be analyzed to determine the strength of chiral signatures. To facilitate this, statistical methods such as chemometrics would be employed to discriminate characteristic chirality signals and further determine enantiomeric ratios.

With the discovery of water-ice and a subsurface liquid ocean on Europa and Enceladeus, measurement of chirality is becoming a highly desirable capability for search for life centric missions. To this end, NASA is currently investigating a potential Europa lander mission, and instrument and technologies relevant to such a mission are also especially of interest.

Acknowledgments: CPM and WJBD thank NASA PICASSO grant 80NSSC20K1093 for funding.

RESONANCE RAMAN AND POLARIZED RAMAN SCATTERING OF SINGLE-CRYSTAL HEMATITE

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Hematite is a well-known iron sesquioxide ($\alpha\text{-Fe}_2\text{O}_3$) with a corundum-type ($\alpha\text{-Al}_2\text{O}_3$) structure consisting only of (Fe^{3+}O_6) octahedra, that crystallizes in the trigonal D_{3d}^6 space group ($R\bar{3}c$, No 167 rhombohedral symmetry), which is an n-type semiconductor with 2.1 eV band gap. Interestingly, previous work has demonstrated that the Raman spectra collected on hematite nanoparticles undergo an intensity enhancement, due to a dependence on excitation energy. Above all, the bands at ca. 660 and ca. 1320 cm^{-1} , which are assigned as the 1LO and 2LO modes, respectively, experience the strongest intensity enhancement, which has been attributed to resonance Raman scattering when excited with excitation energy at or close to the band gap. However, the resonance Raman scattering mechanism is not clear, and further has not been explained. To this end, we have undertaken studies to examine the excitation energy dependence and polarized Raman scattering on a pure single-crystal of hematite to gain a better understanding of the resonance enhancement mechanism for the 1LO and 2LO modes. Resonance enhancement mechanisms giving rise to LO phonons in semiconductors can be attributed to the Deformation Potential (DP) or Fröhlich Interactions (FI) scattering. The DP and FI contributions that give rise to the LO phonon scattering in semiconductors are distinguishable due to their contrasting polarization selection rules:

$$\mathcal{R}_{DP}^{LO} = \begin{pmatrix} 0 & \alpha_{DP} & 0 \\ \alpha_{DP} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathcal{R}_F^{LO} = \begin{pmatrix} \alpha_F & 0 & 0 \\ 0 & \alpha_F & 0 \\ 0 & 0 & \alpha_F \end{pmatrix}$$

It can be observed in the above polarizability tensors, that the FI tensor is diagonal so that the contribution of LO phonons attributed to FI scattering will solely be present for parallel-parallel polarized incident and scattered light, $e_i \parallel e_s$, for the α_{xx} and α_{yy} configuration geometries. While consequently, the DP tensor shows that the contribution of LO phonons attributed to DP scattering will be present in spectra collected in cross-polarized $e_i \perp e_s$ geometries, that is, α_{xy} and α_{yx} configurations. Here, employing these selection rules, we conducted the following polarization Raman scattering measurements: $(XX)\bar{Z}$, $Z(XY)\bar{Z}$, $Z(YY)\bar{Z}$, and $Z(YX)\bar{Z}$ on the basal facet $\{0001\}$ of single-crystal hematite to distinguish between DP (dipole-allowed) and FI (dipole-forbidden) scattering. Our polarization experiments strongly suggest that the Fröhlich LO phonon interaction dominates the Raman scattering over the weaker DP contribution. Furthermore, polarization experiments collected using the following geometries $Z(X'X')\bar{Z}$ and $Z(Y'Y')\bar{Z}$ demonstrate that the interference between dipole-allowed and dipole-forbidden Raman scattering is constructive for LO phonons in these configurations. Therefore, we attribute the mechanism of resonance Raman scattering of the 1LO and 2LO modes in the Raman spectrum of hematite due to contributions from FI and DP process.

COMPARISON BETWEEN RAMAN, CATHODOLUMINESCENCE AND EDS MAPPING IN A Ca-Al INCLUSION IN RENAZZO CR2 CHONDRITE: THE POTENTIAL OF RAMAN INDUCED FLUORESCENCE AS A MAPPING TOOL

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Fluorescence has a bad reputation among Raman spectroscopist, as it conceals the most interesting Raman signal, often making impossible to detect any information from the studied sample.

Here we present an investigation with the aim to take advantage of the fluorescence signal in the analysis of a Ca-Al inclusion (CAI) in the CR2 Renazzo carbonaceous chondrite. Carbonaceous chondrites are among the most pristine object in the solar system, representing early aggregates which escaped subsequent metamorphism and shock. Due to long term exposure to cosmic radiation they often show defect induced fluorescence. Within the chondrite, Ca-Al rich inclusions represent the earliest products of condensation of the solar nebula. The studied sample, coming from the Mineralogical Museum of the University of Parma, was investigated by mapping Raman peaks, fluorescence signal, optical and spectroscopic cathodoluminescence and SEM-EDS emission of the major elements. The Raman spectrum was measured by 473 and 632 nm laser sources.

Among the mineral phases in the CAI, anorthite shows a blue cathodoluminescence signal, revealed in the cathodoluminescence spectrum as a broad peak at 440 nm. The Raman spectrum shows two hardly discernible peaks of the doublet at 485-505 cm^{-1} , and a high fluorescence emission, in which we find a structured peak at 690 nm, and a broader one at 740 nm. The shape and position of the peak at 690 nm reminds the emission of Cr^{3+} , which however was not found in anorthite at the resolution of the electron microscope (0.1 wt%). Calcite shows an orange cathodoluminescence, due to an emission at 610 nm, related likely to Mn^{2+} exchanged with Ca. Also, in calcite fluorescence is present in the Raman analysis, with a broad peak at 760 nm. Pyroxene does not show cathodoluminescence, and fluorescence from a broad peak at 760 nm makes useless the Raman signal; however, due to its higher emission the peak at 760 nm can be used to map the pyroxene distribution.

Combined mapping by Raman peaks and fluorescence, cathodoluminescence and SEM-EDS showed that spinel and melilite are primary phases, with accretion of anorthite and pyroxene as Wark-Lovering rims, and subsequent alteration in two stages, first with formation of sodalite, and then with the growth of interstitial calcite.

This work outlines the potential of mapping using the fluorescence induced during Raman analysis, giving complementary information to the relations between the different minerals.

MULTI-TECHNIQUE AND NONDESTRUCTIVE INVESTIGATION OF ROMAN FINDS AND LOMBARD JEWELRY COLLECTION FROM LODI VECCHIO (LOMBARDIA, ITALY)

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Roman objects and a Lombard treasure, in form of grave goods, were analyzed in the frame of an investigation campaign on archaeological findings in Lodi Vecchio (North of Italy), using different archaeometric techniques. An analysis of the local history, from the 1st to the end of the 6th century, in Roman and Lombard times was conducted through the study of different artifacts (coins, jewels, pigments etc.) and materials (minerals, metal, glass etc.). They reflect and depict the art, architecture and culture typical of that two cultures, whose testimonies are found in this archeological site. The findings were analysed *in situ* using portable instrumentation: Raman spectroscopy with two different excitation wavelengths (785 and 532 nm), and X-ray fluorescence (XRF). Wall-paintings pigments and mortars were analyzed in laboratory with micro-Raman spectroscopy, micro-FTIR, polarizing microscopy and x-ray diffraction (XRD). The goal was the complete characterization of gemmological materials findings (metals, gemstones and glasses) to catalogue the Lombard treasure for its exhibition in the *Laus Pompeia* Museum (Lodi Vecchio, Italy) and to better defining the previous classification, sometimes changing the attribution of gems.

Results show the presence of quartz, chalcedony and other more precious minerals and stones like lapis lazuli. The investigation on the artist's palette showed presence of expensive Roman pigments (e.g. cinnabar) which suggests wealthy commissioners. Interesting results emerged from the analysis of mortars and plasters. In previous petrographic studies it is assessed that sediments from the Adda catchment are characterised by quartz, feldspars and metamorphic lithic grains derived from the Austroalpine and Southalpine tectonic units of the Central Alps, with common metamorphic rock fragments and serpentine-schist lithic grains. The identification of abundant feldspars and minerals belonging to the serpentine group suggests that the sands used for Roman object come from the paleo-Adda river. Moreover, the analyses of the golden pendants, realized with the cloisonné technique, underline the amazing talent of Lombard goldsmiths. The Raman spectra of the red stones present in the pendants show typical signals of garnets with very similar composition for all the stones (around 70% almandine and 30% pyrope) suggesting a common provenance. Among them, a red fragment, cut to imitate a garnet, is identified as a "fake" as its spectrum shows the characteristic glass features. Two Lombard drinking glass horns, rare archaeological findings in Italy, were also analysed. The results suggest that the Lombard grave and its findings could have belonged to a rich family, buried in the most significant place of the town, near the Episcopal palace and cathedral. Combining a molecular technique (Raman spectroscopy) and an elementary technique (XRF) in portable modes, it was possible to characterize all the materials (amorphous as well as crystalline). This work highlights the advantage of using complementary and non-destructive portable techniques for the study of high-value Archeological objects which cannot be moved or transported to a lab. Using two Raman instruments with two different laser wavelengths showed that the 532 nm laser yielded for these materials (in particular silicate gems) superior results, compared to 785 nm.

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CALCITE-ARAGONITE ALTERNATING LAYERS IN RECENT MINERAL SPRING PISOLITHS FROM CORUND, ROMANIA

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Recent concretionary spherical grains also known as pisoliths, discovered in carbonate deposits from Snail Hill natural reserve from Corund, Romania are described. Similar structures have been described occurring at the surface, formed in pools originated from mineral springs, thermal or not [1], [2].

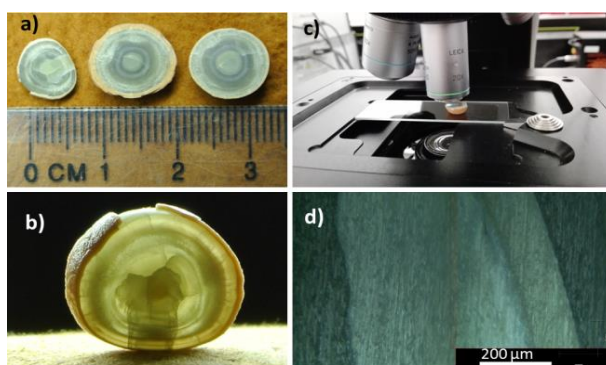


Figure 1: Cross sections of pisoliths (a, b) revealing their concentric carbonate layers occurrence and the reddish-brown outer crust; c) the direct characterization approach via micro-Raman spectroscopy; d) micrograph taken at the Raman microscope showing the clear demarcation of the concentric layers.

Their spectacular cross-section structure as multi-layers carbonate minerals is described using multi-laser Raman micro-spectroscopy and X-ray diffraction data. The pisoliths core revealed typical calcite signal randomly alternating with amorphous carbonate while their outermost spherical layer under the crust showed clear aragonite polymorph. Excitation with 442 nm line (UV-Raman) revealed additional G and D bands characteristic for the biomass-derived carbon material. These bands were absent in Raman spectra obtained with 532, 632.8 or 785 nm excitation, due to the increased Raman background, which is also an indicative of existent biological-derived carbon. These results are discussed considering other author's similar results [3] regarding the biogenic carbonates in stromatolites. Due to the Mg/Ca ratio and the alkalinity of the dripping water, the comparison with proto-Aragonite and monoclinic-Aragonite [4] - as precursor stages of the metastable aragonites - is discussed. raised the question of are discussed

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