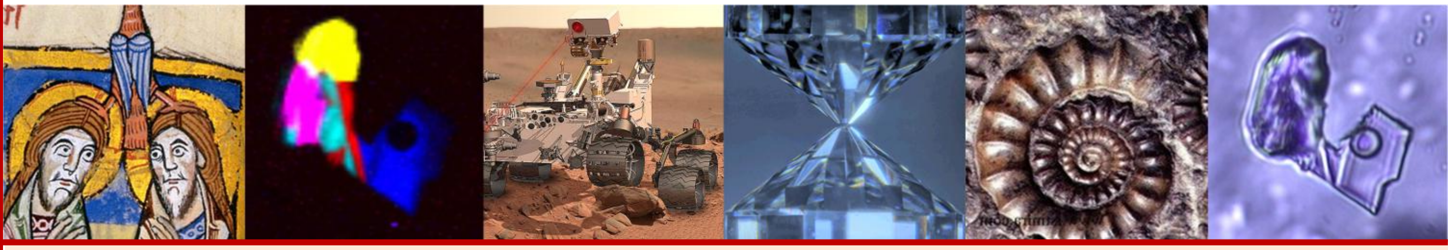

XII International Conference

GeoRAMAN – 2016

Novosibirsk, Russia, June 9-15, 2016

ABSTRACT VOLUME

Raman Spectroscopy

Environmental Sciences Carbonaceous Materials

Materials Science Earth Sciences Pigments Study

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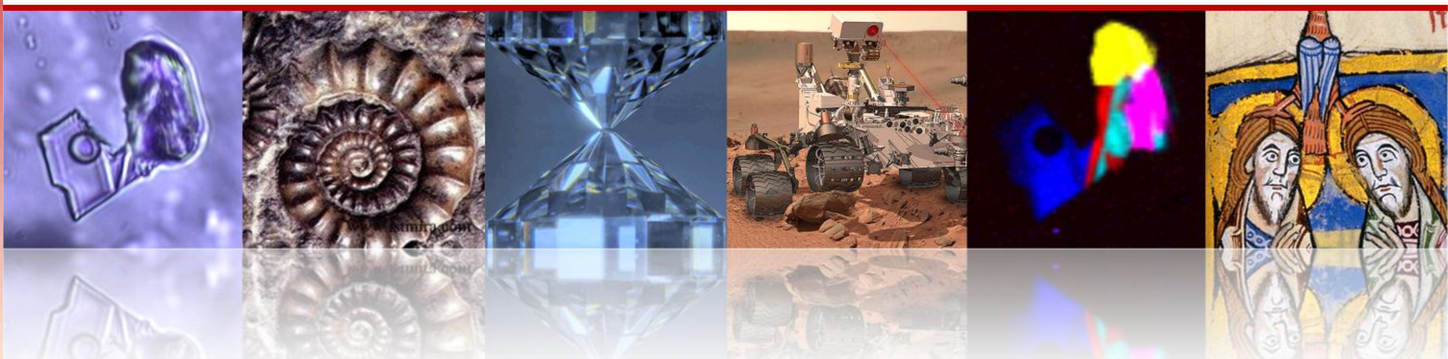

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Russian Academy of Sciences
V.S. Sobolev Institute of Geology and Mineralogy

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ORAL PRESENTATIONS

Temperature-dependent polarized Raman spectra of rare-earth trifluoride crystals

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The trifluoride crystals with rare-earth metal ions with the general formula *Re*F$_3$ (*Re* = Pr, Nd, La, Ce) have a trigonal structure of tysonite, space group *P-3c1*. *Re*F$_3$ have become the subject of research interest due to current applications in fiberoptics, fluorescent lamps, as an active medium of solid-state lasers and scintillators [1,2]. The structure of crystals under study remains stable from 300K up to the melting point [2]. In this work, we applied the Raman spectroscopy to study of *Re*F$_3$ crystals at low temperature. The aim of this study is to investigate possible structural changes associated with phase transitions or anion disordering.

Raman spectra were collected using the polarized radiation of a 488 and 514 nm Ar+ laser in the wavenumber region between 10 and 700 cm^{-1}. The spectra were recorded on the Horiba Jobin Yvon T64000 spectrometer. The temperature studies were performed using the ARS CS204–X1.SS closed cycle helium cryostat in the temperature range of 150–400K.

The polarized Raman spectra from oriented *Re*F$_3$ single crystals were measured and the symmetry of all observed phonon lines was determined. The number of observed lines is an agreement with the Raman selection rules. Obtained spectra were compared with the results of the lattice dynamics simulation within the semi-empirical model. The Grüneisen parameters have been calculated for some zone center modes.

The temperature behavior of the Raman lines does not provide evidence for phonon anomalies associated with structural phase transitions.

Acknowledgements: The reported study was funded by RFBR according to the research project No. 16-32-00351 mol_a. and partly by the “Krasnoyarsky regional fund of scientific support and scientific-technical activity”.

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Raman and infrared spectroscopic characterization of Gd-doped MnS

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Sulfides $Me_xMn_{1-x}S$ (Me = 3d metal or Me = Re) are promising materials for the study of systems with metal-insulator phase transitions. Such solid solutions provide good possibility for studying the influence of cation-substitution-induced electron doping onto the optical properties of the materials. We investigated the Raman and IR spectra of new solid solution $Gd_xMn_{1-x}S$ for the three compositions with x = 0.04, 0.1 and 0.2. The program package LADY was used to perform lattice dynamics simulation of $Gd_xMn_{1-x}S$ crystals. The best agreement between experimental values of atomic vibrations and the calculated ones was obtained using the Rigid Ion Model. Raman spectra were excited by an argon ion laser (514.5 nm) with 5 mW output power. IR spectra for the compositions x = 0.1 and 0.2 show two absorption peaks, which are consistent with the simulated TO and LO modes. Raman spectrum for all tested compounds should be absent in case of ideal Fm3m structure. However, experimental Raman spectrum is found to exhibit several well-observable lines in the frequency range from 50 to 700 cm^{-1}. The high-frequency part of the spectrum (above 500 cm^{-1}) contains lines apparently due to the vibration of the molecular groups Mn_2O_3 and Mn_3O_4 formed under exposure of samples by laser radiation. The region 400-500 cm^{-1} in the Raman spectra is presented by peaks related to the vibrations of sulfur atoms in α - S8 phase [1]. Due to the violation of the translational symmetry, a manifestation of phonons from G, X, L, and W points of Brillouin zone is possible. On the basis of the calculations of lattice dynamics and dispersion curves for all phonon branches in Brillouin zone points noted above, experimental Raman lines were completely assigned. Vibrational spectra for the composition x = 0.04 are markedly different from those for compositions x = 0.1 and 0.2, which indicates that the compound $Gd_xMn_{1-x}S$ with x = 0.04 has differing structure; probably, this sample contains two phases [2].

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Study of phase transitions in ferroborate crystals with structure of huntite mineral

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Multiferroic materials showing the coexistence of at least two ferroic orders ((anti)ferroelectric, (anti)ferromagnetic and (anti)ferroelasticity) are expected to find potential applications in many devices. Amongst these properties the coexistence of ferroelectricity and ferromagnetism is highly desired. Besides their coexistence, of utmost importance is a strong coupling between the two ferroic orders. In multiferroic materials, the coupling interaction between the different order parameters can produce additional functionalities. The application of multiferroics will make possible to significantly enlarge the functional possibilities of spintronics.

Crystals of the RFe3(BO3)4 family (R is rare earth ion) with huntite mineral structure were reported to possess multiferroic features, demonstrating both structural and magnetic phase transitions [1 – 4], where transition points may be varied by rare earth composition. In this work we used Raman spectroscopy to study $Ho_{1-x}Nd_xFe_3(BO_3)_4$ (x = 0, 0.25, 0.5, 0.75) single crystals.

Raman measurements on $HoFe_3(BO_3)$ crystal were carried out at pressures up to 7 GPa and at temperatures up to 680 K by using a diamond anvil cell in order to determine the pressure–temperature phase diagram. From the changes in the Raman spectrum at the phase transition, the stability regions of phases I, II were investigated (Figure 1). After reaching 675 K and 2.5 GPa Raman spectra lines disappear and formation of a new crystalline form was discovered. This form persists ambient condition after removing high pressure and temperature.

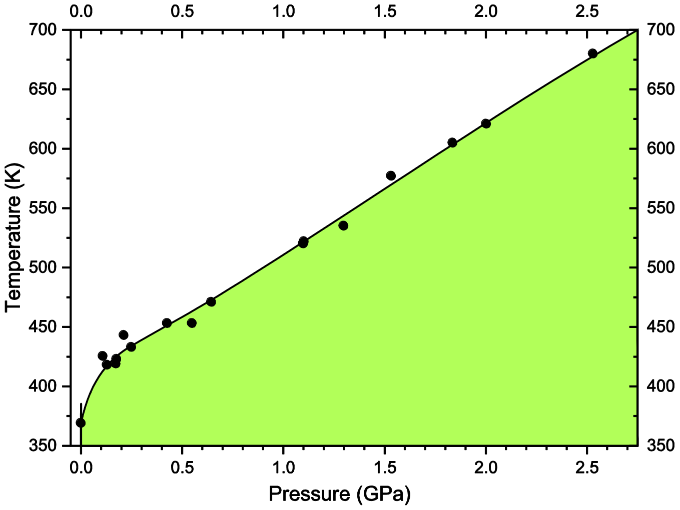

Figure 1. Pressure–temperature phase diagram in $HoFe_3(BO_3)_4$

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Raman spectroscopy of diamonds implanted with helium ions

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It took more than half a century since then, as the ion implantation was formed as an independent field of science and technology. Fundamental research and development in recent years in the field of ion implantation are mainly for doping semiconductors and metals implantation forced introduction means of various chemical elements in polymers, ceramics and composites.

In this paper, implantation accelerated to an energy of 40 keV singly charged ions He^+ was carried out at a specialized installation: ion-beam accelerator ILU-3 at room temperature in a vacuum under 10^{-5} Torr. The radiation dose ranged from 1.0×10^{16} to 7.4×10^{16} ions / cm^2 at an ion current density constant 1.5 - 5.0 mA/cm^2.

The samples for the research were the natural cut diamonds (diamonds) from the Yakut deposits. There were implanted helium 4 faceted diamond and held 21 series of ion implantation. With minimal doses diamonds acquired a amber-yellow color, with maximum doses became black. Colored or Stained implanted diamonds are referred to as the fancy type.

The study of crystal-chemical characteristics of the implanted diamond was carried out on IR - spectrometer VERTEX 70 with a module for the study of Raman scattering light RAM II. This laser was used to excite the system: Nd: YAG and diode-pumped, air-cooled. Shooting range is 100 - 3700 cm^{-1}. All experimental studies implanted samples were carried out at room temperature.

The Raman spectrum of the colorless diamond was fixed as the parent line at 1332 cm^{-1}. The Raman spectrum of fancy yellow diamond produced by implanting helium ions with dose of 1.0 x 10^{16} ions/cm^2 for 5 minutes was detected as the line head at 1332 cm^{-1}. The Raman spectrum of the diamond fancy black obtained by implantation of helium ions with a dose of 7.4 x 10^{16} ions/cm^2 in the head line at 1332 cm^{-1} but also there was broad line of low intensity detected for 1 hour duration of implantation in the range of 1200-1600 cm^{-1}.

From the above interpretation of Raman spectra of colorless diamonds can be implanted and to draw certain conclusions. The intensity of the line head 1332 cm^{-1} practically unchanged in all three samples. The emergence of a broad line in the Raman spectra in the region of 1200-1600 cm^{-1} with a maximum at 1366 cm^{-1} according to the literature is observed in graphite with a significant disordering of the lattice. This allows the state in diamond formation during ion implantation of carbon clusters with sp^2 – hybridization, ion beam impact on the crystal structure of natural diamonds leads to the formation of new carbon clusters.

Parent line 1332 cm^{-1} in the Raman spectrum is a kind of "calling card" of the diamond, the criterion of its purity and quality. The impurities, inclusions, internal stress in the crystal, the presence of segregated phases or disordered, such as graphite lead to smearing of the peak and a shift in wavelength, the appearance of additional lines in broad spectrum. Quantitatively it is expressed by FWHM - factor (Full Width at Half Maximum) - width of the Raman peak at its half-height. From the interpretation of Raman spectra of the studied diamond FWHM-factor of the head line is 1332 cm^{-1} for the colorless diamond – 3,409 cm^{-1}, yellow diamond with the implantation dose of 1.0×10^{16} ions / cm^2 – 3,315 cm^{-1}, and for the black diamond implantation with a dose of 7.4 x 10^{16} ions/cm^2 – 3,054 cm^{-1}. This fact indicates that in the process of ion implantation of nitrogen centers are destroyed is determined and streamlining of the diamond crystal structure.

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Micro-Raman investigation of elastic properties of diphenylalanine nanotubes

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Piezoelectric micro- and nanotubes of diphenylalanine ($C_{18}H_{20}N_2O_3$, FF) are considered as an advanced material for developing new biocompatible sensors, coatings, piezoelectric elements for medical equipment etc. [1-3]. Special interest was attracted to its remarkably rigid structure (Young modulus is up to 27 GPa [3,4]). In this work, components of the elasticity tensor and Young moduli of the nanotubes were determined by the analysis of Raman spectra. Obtained values are in line with those from direct measurements by nanoindentation.

FF molecules in water rich solution [5] form helical nanotubes filled by water molecules via self-assembly process. Then individual nanotubes bond together and form microtubes, which can be considered as a hexagonal crystal. Such system can be described by simple mass-in-mass scheme. Effective frequency of FF microtubes lattice vibrations can be calculated as a weighted mean over the low-frequency region in Raman spectrum. All of these allow identifying 4 independent elastic tensor components tubes FF, which are consistent with *ab-initio* calculations [6], and estimate Young modulus. Obtained value was found to be 16.77 GPa. Direct measurements of Young modulus showed two average values of 9 and 23 GPa. The first value is close to 8.75 GPa calculated in [6] using *ab-initio* calculation in empty FF nanotube, whereas the second value is close to that obtained from Raman measurements in the context of the proposed model. Thus, water in the nanochannel cores of the nanotubes essentially increases the Young modulus of the tubes.

The equipment of the Ural Center for Shared Use «Modern Nanotechnology», Ural Federal University has been used. The research was made possible in part by the grant of the President of Russian Federation for young scientists (Contract 14.Y30.15.6554-MK) and by the Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006).

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Raman spectroscopic study of cracking and hydrolysis of propane, C_3H_8, in fused silica capillary capsules between 300 and 400 °C

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Hydrocarbon gases in deep sedimentary basins have unusually high concentrations of CH_4 (>95 mol%) and low concentrations of C_2H_6, C_3H_8, and higher hydrocarbons (C_2+). Based on experimental work [1] this may be caused by reduction-oxidation (redox) reactions of the gases with water, transition metal bearing minerals, and/or sulfur. In geologic environments with limited redox reactivity the importance of water alone as a reactant is unknown. We conducted isothermal experiments on C_3H_8, with or without water, in fused silica capillary capsules [2] at temperatures (T) between 300 and 400 °C for durations up to 322 hours, evaluating reaction progress with Raman spectroscopy at room T before and after heating. After an initial experiment some samples were reheated to the same T for total durations up to 821 hours. Consumption of water was monitored by calculating the changes in relative volumes of the vapor, aqueous, and C_3H_8 liquid phases from the length of the phases in the capillary. Reactions of C_3H_8 without water produced a small amount of CH_4, reaching a steady state after about 100 hours of heating at $T<360$ ºC. At higher T, steady state was not observed because fluorescence from products of coking reactions obscured the Raman spectra. Reactions with water appear to be largely hydrolysis, generating a CH_4-rich vapor phase and methanol and ethanol in the aqueous phase. At fixed T, Raman spectra showed that concentrations of alcohols increased steadily with time as water was consumed. Highly oxidized carboxylic acids or CO_2 were not present in any experiments. Published work [1] with C_2+ gases, water, and iron-bearing mineral buffers showed that C_2+ hydrocarbons are oxidized in a sequence starting with conversion to alkenes, then alcohols, ketones, and ending with carboxylic acids and CO_2. However, in the absence of redox reactive minerals, our observations show that the reactions between propane and water are relatively limited, forming alcohols without further oxidation to propanoic or ethanoic acid and/or CO_2. This observation suggests that during deep burial hydrocarbon gases may be more stable in iron-poor reservoirs like quartz arenites or carbonate grainstones than in mudstones or arkoses that are rich in redox reactive iron-bearing siliciclastic and diagenetic minerals.

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Remote Raman characterization of high temperature fumarolic minerals

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In the frame of the study of the dynamic of active volcanic environment, minerals are nice probes of the chemistry involved in fresh lava flows. Raman spectroscopy is a nice tool for their characterization and on GeoRaman 2014 we presented field characterization of secondary minerals growing at the surface and in lava tubes of fresh lava flow [1, 2]. Nevertheless, due to the high temperatures linked to volcanic activity, the study of the first steps of lava cooling and weathering needs of remote Raman setups and procedures dedicated to high temperature targets. Currently, we are working on the development of such setup and in this paper we present recent results of field Stokes and Anti-Stokes Raman characterization of medium temperature minerals performed in the hostile fumaroles activity of Solfatara (Phlegraean fields, Naples, Italia).

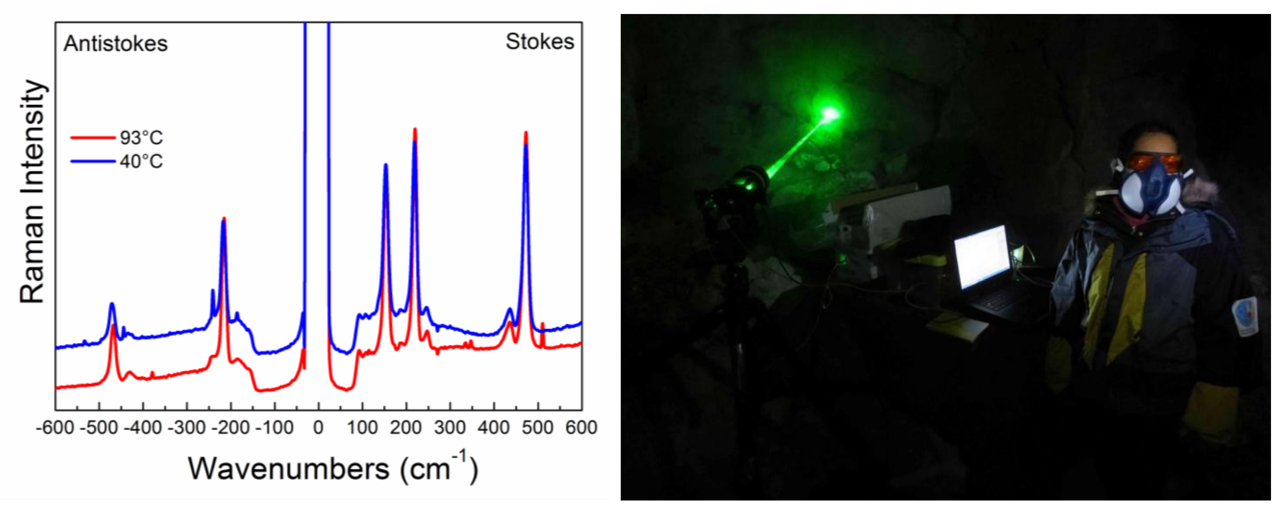

Figure 1. Left : Remote Antistokes & Stokes Raman spectra of Sulfur at 40 and 93°C. Right : picture of the Remote measurement in the fumaroles of Solfatara.

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Raman study of thaumasite and its decomposition at simultaneously high *P-T* parameters

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Thaumasite $Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$ is extraordinary mineral that possibly plays particular role in silicate-sulfate-carbonate balance of the Earth's interiors. High pressure behavior of thaumasite was studied only in He medium at room *T* [1]. We present Raman spectroscopy study of thaumasite compressed in water at simultaneously high *P-T* conditions up to ~300 °C and ~2 GPa, in order to elucidate possible non-quenchable states (polymorphism, overhydration, reversible amorphization and dehydration), as well as its decomposition. Raman bands of thaumasite diminish in intensity and widen in the range of 200-300 °C (Fig. 1). Thaumasite crystals are partly dissolved in water. After the release of high *P-T*, strong band at 991 cm^{-1} shifts to 985 cm^{-1}, corresponding to partly disordered thaumasite. The stability range of thaumasite is extended up to ~250 °C at ~2 GPa. At 300 °C and ~2 GPa, thaumasite is decomposed to aragonite, gypsum and partly amorphous silicate within 30 min.

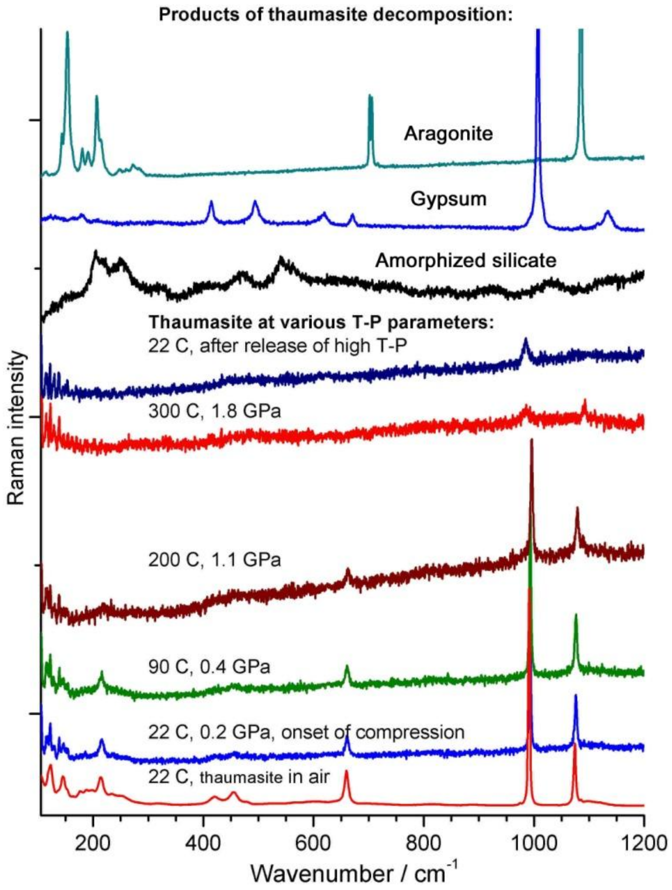

Figure 1. In-situ and ex-situ Raman spectra of thaumasite, compressed in water at high P-T parameters, and the products of its decomposition.

This work was supported by the Russian Foundation for Basic Research (projects No. 14-05-00616 and 15-55-45070-IND) and the Russian Science Foundation (project No. 15-17-30012).

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Pressure-induced phase transitions of vaterite, a metastable phase of $CaCO_3$

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Vaterite, a metastable phase of $CaCO_3$, is a rare mineral occurring as biominerals and abiogenic origins. Behavior of vaterite at high pressure will give us an insight on phase transformation of metastable materials. While pressure responses of calcite and aragonite have been intensively investigated for a long time, nothing is understood on pressure-response of vaterite. In this study, we have observed Raman spectra and X-ray diffraction (XRD) patterns of vaterite at high pressure using diamond anvil cells (DACs). Vaterite was synthesized by mixing two aqueous solutions, $CaCl_2$ (60 mM) and $NaHCO_3$ (60 mM) at 30°C. The mixed solution was filtrated using a membrane filter with a pore size of 0.45 μm, washed by pure water, and dried at about 130 °C.

High-pressure experiments were conducted at room temperature using DACs with flat culet diamond anvils of 600 μm in diameter. Helium gas was loaded in a sample chamber as pressure transmitting medium to achieve a quasi-hydrostatic high-pressure condition. Raman spectra of vaterite were obtained using a micro-Raman spectrometer consisting of a 50-cm single polychromator (500 is, Chromex), an optical microscope (BX60, Olympus Optical Co. Ltd.), a Si-based CCD with 1024x128 pixcels (DU-401A-BR_DD, Andor Technology) in a frequency region from 150 cm-1 to 1500 cm^{-1} including the lattice modes and stretching mode of calcium carbonate. Angle-dispersive XRD experiments were conducted at a synchrotron beamline (BL-18C), Photon Factory, KEK.

Raman spectra of vaterite exhibited two strong Raman bands at 1075 and 1091 cm^{-1} attributable to the symmetric stretching vibration (ν_1) of carbonate ion. With increasing pressure, the peak positions of ν_1 band upshifted. Moreover, the band shape of ν_1 changed drastically at high pressure. The discontinuous changes were observed at 5.0 and 7.7 GPa and a new additional peak component was observed at 8.6 GPa. These changes are consistent with results observed from XRD at high pressure. These observations suggest the phase transformation of vaterite to the high-pressure phases which are independent from published high-pressure phases of $CaCO_3$. After decompression to ambient pressure, vaterite partially transformed to calcite. In the presentation, we will discuss the pathway of the phase transformations of vaterite.

High-pressure evolution of encaged hydrocarbons in natural clathrasils

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Naturally occurring gas-bearing clathrasils provide evidence for the participation of microporous silicates in hydrocarbons transport within the Earth's crust, which is also connected to the gas storage problem. It is therefore important to characterize their high-pressure behavior with the emphasis on the state of the guest molecules and their possible role in the structure evolution, as well as on pressure stability limits of these compounds.

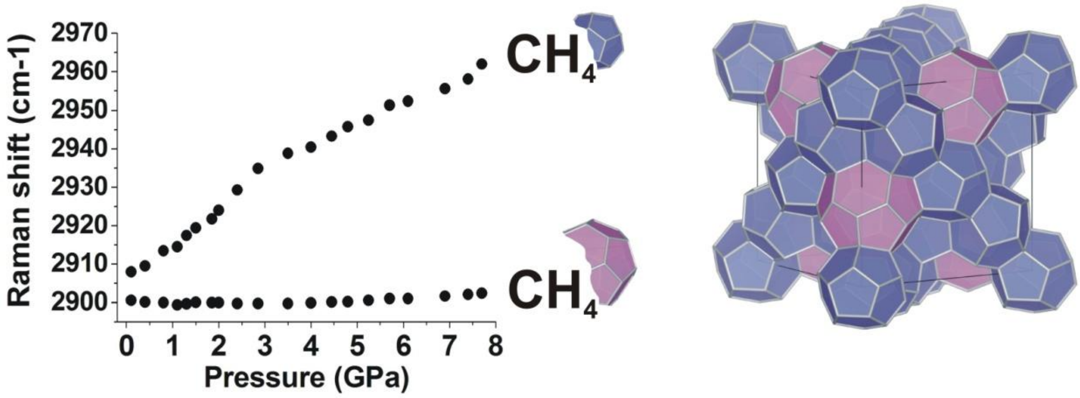

Figure 1. The pressure shift of C-H stretching modes of methane encaged in small (violet) and large (pink) cavities of chibaite (left) and the framework structure of chibaite (right).

We present a comparative high-pressure spectroscopic study of two natural clathrasils, melanophlogite $46SiO_2 \cdot 8X$ (X = CH_4, N_2, CO_2) (MEP framework isotypic to cubic gas hydrate sI) and chibaite $136SiO_2 \cdot 24X$ (X = CH_4, C_2H_6, C_3H_8, C_4H_{10}) (MTN framework isotypic to cubic gas hydrate sII) [1,2]. Different ν/P trends observed for the C-H stretching modes of methane in melanophlogite and chibaite (Fig. 1) are discussed in terms of the "small / large cage" proportion in MEP and MTN framework.

This work is supported by Russian Foundation for Basic Research [grant #15-55-45070].

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Raman spectra and lattice dynamics simulation of the elpasolite crystals at high pressure: comparative analysis

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Elpasolite, one of the rare fluorine minerals, was first found in the “Pikes Peak region”, El Paso County, Colorado, USA (1885). It can be found also in Italy, Greenland, Ukraine and Russia. Single crystal samples of $Rb_2KB^{(2)}F_6$ ($B^{(2)}$ = *In, Sc, Tb, Ho, Dy*) and Rb_2NaYF_6 were synthesized in laboratory of Crystal Physics, Kirensky Institute of Physics, Krasnoyarsk, Russia. These crystals belong to the perovskite-like crystals with the elpasolite structure $A_2B^{(1)}B^{(2)}X_6$ (*A* and *B* are metal or rare-earth metal cations, or more complex molecular ions and *X* are oxygen or halogen anions, high symmetry phase space group *Fm*3*m*, $Z = 4$), which are extensively studied due to their wide variety of distorted structures and exciting complex sequences of phase transitions [1]. The aim of this work is to study structural phase transitions and lattice dynamics (LD) of perovskite-like crystals in the wide pressure range by Raman spectroscopy and semi-empirical LD simulation.

Raman spectra were collected using the polarized radiation of a 514.5nm Ar^+ laser (Spectra-Physics Stabilite 2017) power 15mW on the sample in the wavenumber region between 10 and 1200 cm^{-1}. The spectra in the 180° geometry were recorded on a Horiba Jobin Yvon T64000 spectrometer. High-pressure experiments were performed in a diamond anvil cell EasyLab µscope DAC–HT(G). To perform LD simulation of investigated compounds the program package LADY was used. So called “hybrid model” [2] was used. This model is a combination of valence force field (VFF) and “rigid-ion” models (RIM).

In the pressure range of 0.9 – 1.0 GPa additional lines become visible in the Raman spectra of Rb_2KInF_6 and Rb_2KScF_6 crystals. Lattice instability induced by soft phonon mode condensation found at 0.9 GPa for Rb_2KInF_6 and at 1.0 GPa for Rb_2KScF_6, that soft mode is associated with displacements of four fluorine atoms from $B^{(2)}F_6$ octahedrons only and corresponds to the rotation of the octahedron as a whole around four-hold axis. Experimental Raman spectra of Rb_2NaYF_6 is typical for the high symmetry cubic phase of elpasolites under pressure up to 4.33 GPa, numerical simulation shows the absence of phase transition up to 10GPa.

Acknowledgements: The reported study was funded by RFBR according to the research project No. 16-02-00102 A and 16-32-00351 mol_a.

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Raman microspectrometric study of pigments in melanized fungi from the hyperarid Atacama Desert gypsum crust

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Melanins are a group of dark biological pigments that are synthesized by a variety of organisms and play several important roles in the protection against harmful effects like UV-radiation and free radicals. Different types of melanin were described from several organisms. Melanins are found in bird feathers, animal and human hair and skin, sepia ink, or inside of microorganisms such as some bacteria and fungi, but significant structural differences as well as not yet fully understood mechanisms of function put melanins in a unique position among the natural pigments [1].

A new, unusual microbial community composed of eukaryotic algae and fungi colonizing the interior of gypsum crust were discovered in the hyperarid core of the Atacama Desert. This area is characterized by extreme environmental conditions and is considered as a Martian analogue site. Previously, endolithic colonization of halite and gypsum crusts was investigated by imaging and spectroscopic methods [2]. Here an attempt is made to better understand blackish zones of fungal and algal colonization embedded within gypsum crust using Raman microspectrometry.

Microbial communities were located near the surface in the pores of the gypsum crust samples. Raman spectra of pigments were acquired directly on samples of gypsum crust, as well as on the prepared thin sections of the rock. Spectroscopic signatures of several pigments were detected using several excitations wavelengths (445, 514, 633, 780, 785 nm). Most importantly, Raman spectra of black-pigmented colonization share characteristics of melanin as described in the literature: two broad bands located at wavenumbers around 1600 and 1350 cm^{-1}. Careful selection of excitation wavelength as well as laser power settings was required to minimize fluorescence and other adverse phenomena and to record the usable Raman spectra of melanins. Spectroscopic evidence for other pigments in microbial zones are also discussed such as carotenoid pigments of algae.

These finding are important because melanins are regarded also as pigments of relevance in the fossilized samples in the geological record. Therefore a question arises whether melanins should be considered among suitable biomarkers in astrobiological research.

Acknowledgments: grant CGL2013-42509P.

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Miniature Raman spectrometers for field analysis of microbial pigments: recent achievements and perspectives for planetary applications

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Pigments of microorganisms can frequently be detected not only using sophisticated Raman microspectrometers but also by miniaturized Raman devices under field conditions. This possibility has important consequences for areas like geobiology and exobiology. In the case of carotenoids Resonance Raman signals can generally be collected when exciting targets using nowadays common 514 or 532 nm diode lasers [1, 2]. Carotenoids are main photosynthetic and protective pigments from microorganisms from several groups. β-Carotene is known from cyanobacteria and common in algae. Bacterioruberin, common in Archaea, was repeatedly detected and easily discriminated from other carotenoids due to its longer polyenic chain. Torulene and γ-carotene were found as pigments of some yeasts. The presence of astaxanthin can be documented in common mesophilic algae (i.e. *Haematococcus pluvialis*) but also on high mountains in high UV exposed zones in snow algae (i.e. *Chlamydomonas* cf. *nivalis*). Experience from laboratory and *in situ* field measurements is discussed as well as the analytical limits of the small portable Raman instruments. Comparison is made between investigations of microorganisms from pure cultures versus complex native matrices of colonized crusts, endoliths, crystal inclusions. The application of miniature Raman instruments as well as flight prototypes in areas of microbal survival under extreme conditions is an important stage to prepare for the successful deployment of this kind of instrumentation in the context of forthcoming astrobiological missions to Mars.

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Applications of Raman spectroscopy in art and archaeology: challenges and opportunities

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In archaeometrical research, one wants to balance the risk on damage of the artefact with the amount of information that is gained from the analysis. Different approaches are possible, including the use of several complimentary techniques (rising the information content) and the use of *in situ* non-destructive approaches.

Raman spectroscopy has grown to a well-established method in archaeometry. Indeed, the method has numerous advantageous methods that come in very useful in this research area. These favourable properties include, amongst others, the ability to record spectra of inorganic as well as organic molecules, the speed of analysis, and the possibility to identify unknown materials by comparing them with previously recorded reference spectra (‘fingerprinting’). Also, the very small spectral footprint allows us to record spectra of single pigment grains, or from a single paint layer, when analysing cross-sections of embedded samples. Moreover, Raman spectroscopy can be considered as a non-destructive approach, considered the laser power is kept sufficiently low. When mobile or portable instrumentation is used, this allows us to perform *in situ* investigations of precious objects.

Where Raman spectroscopy is able to provide molecular information on the samples, it can be combined with X-Ray fluorescence analysis (XRF), which yields the elemental composition of the sample. Thus complementary information is obtained, what allows us to obtain a more complete view on the artefact composition. Where this approach might seem straightforward, there are some pitfalls, which have to be taken into account.

This approach will be illustrated with several examples from our daily practice in Archaeometrical research.

Identification of the pigments for smoked mural by confocal micro-Raman spectroscopy

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The development of non-invasive analytical methods is of widespread interest to the fields of conservation science, providing chemical insight into the materials used to create painted works of art, which can, for example, inform decisions about their restoration and preservation, or help discern original works from forgeries. There are a large number of ancient murals in Mogao Grottoes in Dunhuang museum, northwest China, which are World Cultural Heritage. However, a large portion of these murals have been damaged by smudging more or less during the early 20th century. The protection of these ancient murals is to obtain information on original pigments, color and other related materials etc. In this work, we report on the results of the spectroscopic analysis for imitated smoking mural from Cave 71 in Mogao Grottoes. Confocal micro-Raman spectroscopy and its depth scan have been proposed to carry out the recognition of the pigments used in drawing for the smoked murals. Five main pigments (black, red, green, blue and white) used in the imitated mural are analyzed before and after smoking. The results show that, before smoking, five main pigments on the murals can be distinguished easily and keep the same with original pigments. After smoking, the mural is covered by a layer of sootiness and the resolution of the paint is reduced obviously. However, nearly all of the pigments have still been detected successfully till the paint has totally been covered, except for the red pigment. With increasing the smoking time, the red pigment is more and more difficult to explore due to the destruction of smoking treatment. The smoking process is mainly the accumulation of amorphous carbon. Confocal micro-Raman spectroscopy and its depth scan can provide an important approach for the identification of the original pigments for smoked murals in "Mogao grottoes" in Dunhuang museum. This research has great significance for the restoration of ancient mural and the insight of the mural's history in Dunhuang Mogao grottoes, China.

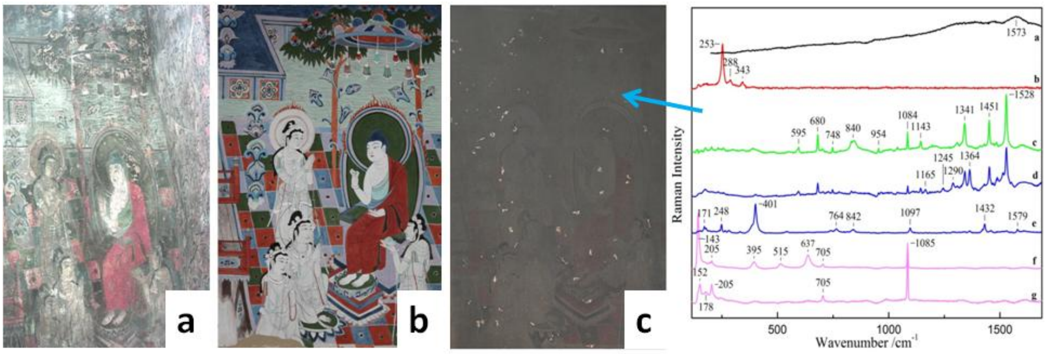

Figure 1 Photos of the mural "MaitreyaJingbian" in the cave 71th in Mogao Grotto (a), the imitative mural (b), the smoked one (c) and the corresponding Raman spectra.

Raman spectroscopy characterization of secondary phases of spent nuclear fuel

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The performance assessment of the deep geological disposal for spent nuclear fuel (SNF) as a final storage requires stability studies to ensure the nuclear waste integrity under the so called repository conditions. It is widely accepted that after such long times the barriers that protect the waste will be breached and SNF will be in contact with the storage surrounding water [1]. The matrix of the SNF composed by uranium dioxide, UO_2, will be leached by groundwater and then, depending on the environmental storage conditions some of the fission products and actinides contents in the SNF will be released to the external repository barriers and finally, in the worst case, it will migrate to the biosphere [2].

This corrosion process is described primarily via the oxidation of U(IV) to U(VI) and then, the formation of alteration products, usually containing UO_2^{2+} in their crystal structures and named secondary phases [3]. The characterization studies of these phases are a great challenge due to the radiotoxicity of these materials, what complicates its handling.

In the last years, Raman spectroscopy has been used to analyze different secondary phases [4], due to the features of this technique, which meets the safe conditions requirement for working with radioactive substances. In this work, we present a detailed study of different secondary phases formed under repository conditions using Raman spectroscopy as a main technique.

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Identification of inorganic and organic inclusions in the Vostok Lake ice with Raman spectroscopy

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The investigation of inclusions entrapped into the accretion ice of the subglacial Lake Vostok in Antarctica [1] gives an insight into former times of the Antarctic history. Terrestrial (of biological and geologically-mineralogical origin) as well as extraterrestrial (meteorites) materials are hermetically embedded in the Vostok ice core and give information about the conditions and events on Earth at former times. Confocal Raman spectroscopy is well suited for the analysis of the inclusions without melting the ice and, therefore, preventing undesirable contamination with present-day material. It is a nondestructive method for material identification with depth resolving capability. It permits a locally precise statement about the chemical-mineralogical composition and allows the context information preservation of several side by side inclusions.

Here, we want to show first results of our Raman measurements of the inclusion in the Vostok lake ice sample 5G-3 3607-4 (3607 m depth, age is in the range 20-40 kyr). Our study shows that Raman spectroscopy is a very useful method for the exploration of inclusions entrapped into lattice of any natural mono-crystalline ice. As Raman spectroscopy is already planned to be applied in upcoming missions in space research (ExoMars [2], Mars 2020 [3, 4, 5], icy moons) a co-operation of the space science community with the Antarctica-Lake Vostok community is suggested to test the space instrumentation under the extreme environment and conditions of the Lake Vostok.

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[5] Clegg S.M. *et al.* (2015) 46th LPSC (The Woodlands, Texas, USA), Abstract No.2781

Determination of manganese oxides of economic and environmental interest by Raman spectroscopy

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Manganese oxides form numerous and ubiquitous mineral species, and some of these are frequently enriched in elements like Li, Co, Ni, Cu, Fe, Zn [1]. These minerals are sometimes called “wads” or “psilomelane” and appear as fine-grained dark crusts, nodules or concretions. They were described in many places around the world, from the oxidized horizon of large ore deposits in (New-Caledonia, DRCongo, Cameroon,…) to the large manganese nodules fields of the deep oceans floors. Understanding of their complex and highly variable compositions can provide insights on the environment (geo-bio-chemical) that led to their formation and the type and abundance of elements scavenged in their structures [2].

In this study we investigate a series of complex and often poorly crystalized manganese oxides, hardly identifiable by classical XRD techniques. Using carefully selected instrumentation parameters to avoid sample degradation, and an custom semi-automated curve-fitting algorithm, we make a systematic classification of the Raman spectral signature on common manganese oxide species. The investigated sample includes layered manganese oxides (asbolane, buserite, birnessite, lithiophorite, vernadite, chalcophanite, feitknechtite) and “tunnel” structured manganese oxide (pyrolusite, todorokite, hollandite and ramsdellite). Many of these oxides have similar structural features, namely the MnO_6 octahedral units building the layers framework, but show a great diversity of structural defects and physico-chemical variability. By comparing with SEM-EDS data, we then propose correlations of specific Raman shifts and peaks intensities with the respective chemical content of the studied samples. This work is then applied to a first tentative phase identification and classification on a selected batch of manganese nodules collected in the Atlantic and Pacific ocean floors.

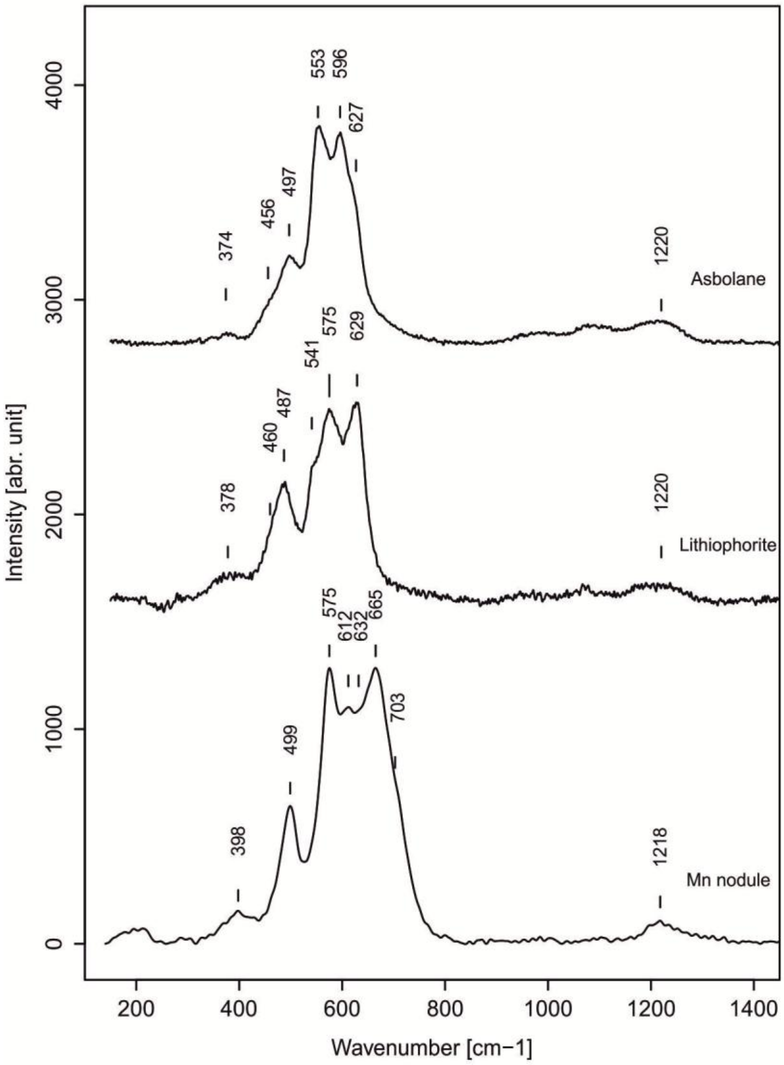

Figure 1. Example of manganese layered oxide Raman signatures (asbolane and lithiophorite) and a probable tunnel-like manganese phase (ex: todorokite) on a deep-see manganese nodule (532nm laser source, 0.2mW power (exit of the laser box), 50x1000µm slit, 5x100s acquisition)

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Detection of biosignatures in silicified rocks using Raman spectroscopic mapping

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Potential microfossils dating back to the Noachian on Mars (-4.5 to -3.5 Ga) may have been silicified by hydrothermal fluids and could thus be very similar to the oldest traces of life found on Earth in cherts from Australia and South Africa (3.5 Ga old) [1-2]. Due to the small size and simple shapes of these microbial remains, their biotic origin and syngenecity is often difficult to demonstrate and requires sophisticated instrumentation [2]. The detection and resolution limitations of space qualified instruments will make this demonstration all the more complicated on Mars during future *in situ* missions [3]. In this context and in view of the fact that Raman spectrometers will be part of the future ExoMars 2018 and Mars 2020 mission payloads, we have made a study of the potential of Raman spectroscopy to detect possible biosignatures that could be observed on Mars. In particular, we used the mapping mode to highlight variations in the mineral matrix and carbonaceous matter signals associated with silicified microorganisms, mainly originating from the 800 My old Draken formation, Svalbard. We were able to detect opaline silica directly associated with carbonaceous matter [4]. If this metastable mineral normally converts to quartz, we showed that this conversion has been inhibited by the carbonaceous matter within which the opal precipitated. We were also able to demonstrate that this association could be considered as a good biosignature. Interestingly, the Raman maps also document very fine variations in the spectrum of the carbonaceous matter. In particular, the distribution of the intensity ratios of the two main carbon peaks of the spectrum are directly associated with the microfossil shape. We interpret this non-random distribution as a consequence of compositional variations in the precursor components [5]. Using abiotic bacteriomorph structures, we were able to demonstrate that such variations are intimately linked to the biotic origin of the structure. These features could be helpful to detect potential traces of life in Martian rocks.

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Raman spectroscopic analysis of anthropogenic and volcanic ashes

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In this study we present the Raman microspectroscopic characterization and comparison of anthropogenic ash (i.e. coal/biomass-fired power plant) and volcanic ash particles. Cluster analysis has been performed on the data, in order to get information on the main constituents that comprise the ashes. For the anthropogenic ashes, the majority of the Raman spectra are characteristic of glassy phases exhibiting broad bands. Minerals typically found in coal ashes, such as quartz, rutile, coal and calcite [1] have also been identified (Fig. 1a). The volcanic ash particles exhibit characteristic Raman bands (broad bands from ~ 200 to ~ 1100 cm^{-1}) typical for plagioclase feldspars (anorthite) and pyroxene (augite) minerals [2,3] (Fig.1b). An overview on the differences and similarities between anthropogenic and volcanic ashes is of interest because these types of materials are seen as pollutants from an atmospheric point of view and, also they are regarded as resources by particular industry branches.

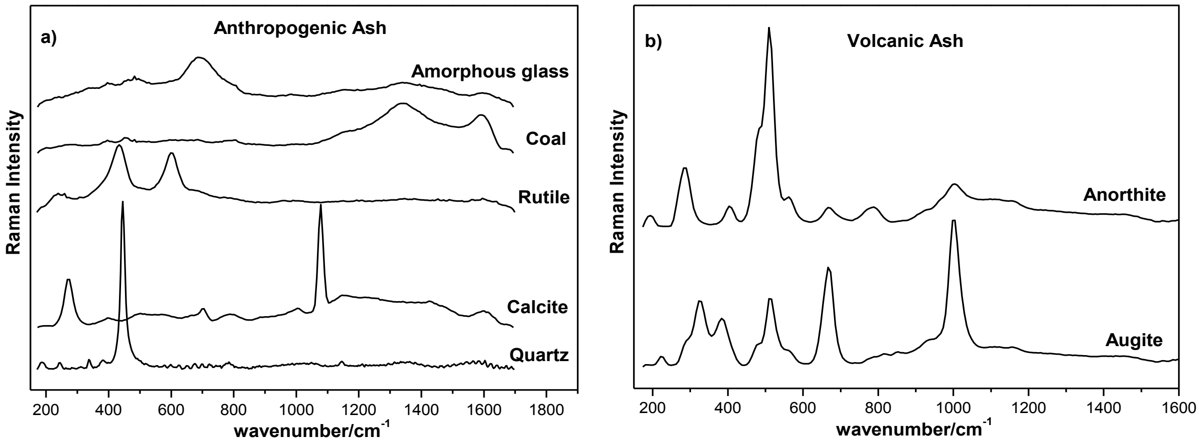

Figure 1. Recorded Raman spectra of the main constituents found in ashes

Acknowledgements: Funded by Deutsches Zentrum für Luft- und Raumfahrt (grant nr. 50QX1301)

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Raman spectroscopy in the Arctic and Antarctic: habitability and biosignature preservation in cold springs and paleolakes

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In July 2015 we carried out in-situ Raman investigations at three perennial springs and one paleospring site located at Axel Heiberg Island in the Canadian High Arctic (Fig. 1). At nearly 80° N, these springs are located in a region of thick, continuous permafrost. From the springs we collected samples of well-developed travertine, icing pastes and nearby salt deposits resulting from efflorescence. Concurrent with sample collection, we deployed a Raman spectrometer and an IR reflectance spectrometer for in-situ measurements at the four sites. We recorded 100+ Raman spectra and 50+ IR reflectance spectra on those sites. We identified gypsum, iron sulfates, kerogens, elemental sulfur, organics, halite, hydrated, iron sulfates, and thenardite. These results are helping us evaluate the potential of spring deposits as high-priority targets for the search for life on Mars.

In November 2015 we travelled to Lake Untersee in the mountains of Queen Maud Land, Antarctica (Fig. 2) to continue a series of studies aimed at understanding the lake ecosystem, its sedimentary history, local climate, and to begin detailed investigations of a paleo-basin located to the east of the lake. At these sites we deployed a Raman spectrometer, IR reflectance spectrometer, and an X-ray diffraction/fluorescence (XRD/XRF) spectrometer for in-situ measurements. Our investigations include studies of the physical and biogeochemical characteristics of the lake, deposition and preservation of biomarkers, and the use of in-situ analytical techniques to identify organic signatures within a mineralogical context while developing synergistic operational concepts for in-situ analyses in paleolakes analog to early or present Mars.

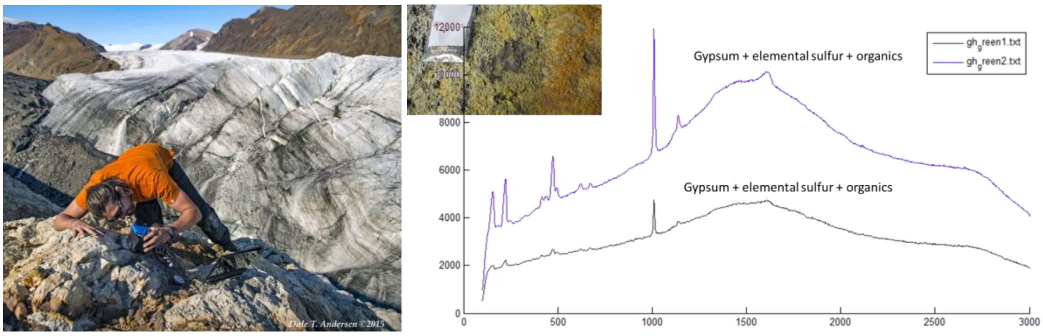

Fig. 1. In-situ analyses and Raman spectra of Axel Heiberg paleosprings.

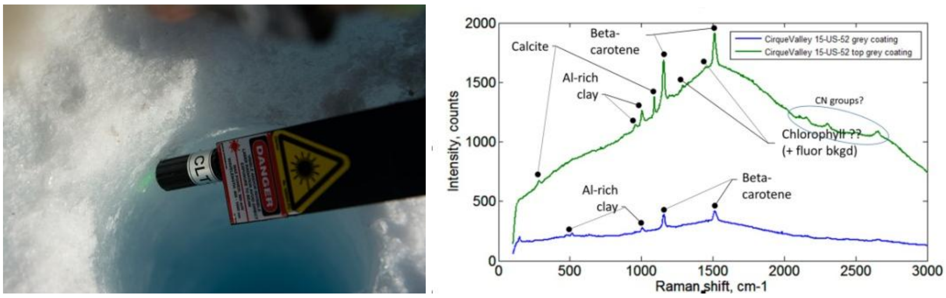

Fig. 2. In-situ analyses and Raman spectra of Untersee glacier ice and paleolake deposits.

BIOMEX on EXPOSE-R2: preservation of cyanobacterial Raman biosignatures after Martian ground-based simulation exposure

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The space mission EXPOSE-R2 successfully concluded last February a 15-month exposure of four astrobiology experiments on the outside of the International Space Station. Among them, the BIOMEX (BIOlogy and Mars EXperiment) experiment aims at investigating the endurance of extremophiles and stability of biomolecules under space and Mars-like conditions in the presence of Martian mineral analogues [1]. The preservation and evolution of Raman biosignatures under such conditions is of particular interest for guiding future search-for-life missions to Mars (and other bodies) carrying Raman spectrometers (such as the Raman Laser Spectrometer instrument aboard the future ExoMars rover). Cyanobacterial photoprotective pigments (namely carotenoids) have been classified as high priority targets for biomolecule detection on Mars and therefore used as biosignature models due to their stability and easy identification by Raman spectroscopy [2]. We report here on their preservation potential after ground-based Martian simulations performed in preparation of the BIOMEX experiment and the return of the space exposed samples. As model organisms, cyanobacteria of the genus *Chroococcidiopsis* were used due to their well-known relevance in astrobiology tasks dealing with the search for life on Mars and future space applications [3]. *Chroococcidiopsis* cells mixed with two Martian mineral analogues (phyllosilicatic and sulfatic Mars regolith simulants) were exposed to high UV irradiation combined or not with a Martian simulated atmosphere and consecutively analyzed with a 532nm Raman microscope at 1mW laser power (as proposed for the RLS instrument on ExoMars). Carotenoids showed high preservation potentials and were detectable after simulations of the real space exposure mission: 500MJ/m^2 of full UV (200-400nm) irradiation and Martian simulated atmosphere [4]. Data gathered during the ground-based simulations will contribute to interpret future results from space experiments and guide our search for life on Mars and other bodies of interest.

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High-pressure minerals in L6 chondrite Dhofar 922

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Dhofar 922 is L6 ordinary chondrite (found in Oman, February 6, 2003). The major constituent minerals of the host-rock are olivine ($Fa_{25,3}$), orthopyroxene ($En_{77}Fs_{21,5}Wo_{1,5}$), clinopyroxene ($En_{47.4}Fs_{7.7}Wo_{44.9}$), plagioclase (maskelynite) ($Ab_{86.6}An_{9.8}Or_{3.5}$), chromite, troilite and Fe- Ni metal. The host-rock is cut by the network of the shock-melt veins (SMVs). The SMVs are filled with fragments of the host-rock embedded in a fine-grained silicate-troilite-metal matrix. Dhofar 922 meteorite contains relatively large blue ringwoodite grains with a size up to 100 μm. They were described in [1]. The fine-grain majorite-pyrope and tiny magnesiowüstite aggregates were also identified. The estimation of high-pressure minerals formation in the SMV is 22-30 GPa [1]. We characterized high-pressure minerals, wadsleyite, ringwoodite ($Fa_{34.9}$) and majorite–pyrope ($Na_{0.08}Ca_{0.15}Mg_{3.00}Mn_{0.01}Fe_{0.04}Cr_{0.03}Al_{0.33}Si_{3.81}O_{12}$) by Raman spectroscopy and also identified jadeite ($Ab_{84.7}An_{12.7}Or_{2.6}$) (Fig. 1). Jadeite forms by albite dissociation reaction: albite = jadeite + silica at pressures above 3 GPa and temperature 1000 ^oC. The field stability of jadeite is 3–19 GPa. Jadeite transforms to high-pressure polymorph lingunite at pressures above 19 GPa. Lingunite was not found in present study. We suggest, that jadeite in the Dhofar 922 forms during reverse transition of lingunite upon decompression stage at 19 GPa.

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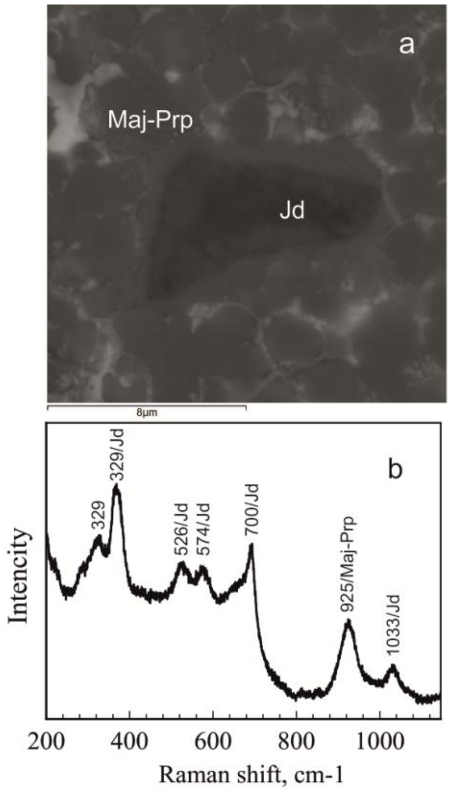

*Figure 1. (**a**) BSE image of jadeite (Jd) and majorite-pyrope (Maj-Prp); (**b**) Raman spectrum from jadeite grain.*

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Standoff spatial heterodyne Raman spectrometer for mineralogical analysis

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Raman spectroscopy is ideally suited for planetary exploration, because Raman spectra are very useful for mineralogical measurements as well as to measure organic and inorganic biomarkers [1]. The traditional grating based dispersive monochromators require very narrow entrance slits thus limiting light throughput. Recently, we developed a new type of Fourier transform (FT) Raman spectrometer; the spatial heterodyne Raman spectrometer (SHRS) [2], which provides high spectral resolution in a very small system without limiting light throughout. In this work we present results of time-resolved Raman measurements on a number of minerals including silicates, carbonates, sulfates with the SHRS using a pulsed 532 nm laser source.

Figure 1 shows the SHRS Raman spectra of (a) forsterite (Fo)-rich olivine (18 mJ/pulse) and (b) calcite ($CaCO_3$) (10 mJ/pulse) measured with 532 nm pulsed laser excitation operating at 100 Hz along with respective interferograms. The Raman fingerprint lines in the doublet of the olivine at 823.7, and 855 cm^{-1} are well resolved (Fig. 1a). Similarly the fingerprint Raman lines of calcite at 154 and 281 cm^{-1} corresponding to the lattice modes are clearly seen in Fig. 1b along with the strong line at 1085 cm^{-1} of carbonate ions, $\nu_1(CO_3^{2-})$. These sharp Raman lines positively identify these minerals.

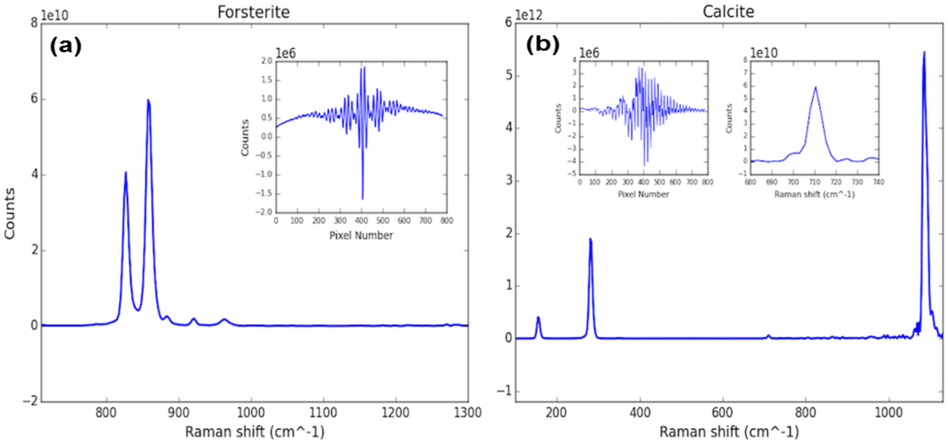

Figure 1. SHRS Raman spectra of (a) forsterite (Mg_2SiO_4)-rich olivine, and (b) $CaCO_3$ (calcite) at standoff distance of 70 cm. Spectrum (a) was acquired with gratings set at Littrow angle corresponding to 552.7 nm wavelength and Spectra (b) was acquired with gratings set at Littrow angle corresponding to 532 nm wavelength.

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Raman spectroscopy used for the determination of organic matter in Libyan Desert Glasses and Darwin Glasses

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Libyan Desert Glasses (LDGs) and Darwin Glasses (DGs) are impact glasses formed when an extraterrestrial body (meteorite, asteroid or comet) impacted on the Earth in the Western Desert of Egypt (near the Libyan border, Africa) and in Tasmania (Australia) respectively. Although the identification of inorganic mineral phases has been vastly studied, less attention has been pay to the organic matter trapped in those impact glasses. The presence of organic compounds in the impact glasses can offer information about the area when they were formed, about the extraterrestrial body impacting on Earth as well as on the terrestrial weathering processes affecting the nature of the compounds found in these bodies. In this work Raman spectroscopy was employed as a non-destructive technique to detect organic matter in both LDG and DG samples, allowing us to detect the characteristics Raman bands corresponding to different Polycyclic Aromatic Hydrocarbons (PAHs) and oxalates. This information has not been reported so far, only the detection of organic components has been studied in DGs by Pyrolysis gas chromatography mass spectrometry (Py-GCMS), a destructive analytical technique [1]. The occurrence of PAHs has not been reported in the literature in LDGs and DGs. The presence of oxalates in LDGs indicates the possible existence of biological activity around the LDGs, since oxalates salts could be formed by reaction of metals with the oxalic acid excreted from fungi, lichens and plants [2]. Finally, those identifications were corroborated by Py-GCMS and later through Ionic Chromatography and GC-MS in extracts obtained by leaching with Milli-Q water. Thus, it was concluded that Raman spectroscopy is a superb technique to measure organic compounds in impact glasses such as LDGs and DGs without destruction of the samples.

Acknowledgements: L. Gomez-Nubla is grateful to the University of the Basque Country (UPV/EHU) for her post-doctoral contract. Moreover, this work has been financially supported by the project "Development of the Raman instrument for the ESA Mission Exomars2018: Science support, equipment testing and operation support" (ref. ESP2014-56138-C3-2-R) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

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Raman spectroscopic studies of K-Na alunite solid solutions relevant to Mars

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Alunite ((K, Na, H_3O)$Al_3(SO_4)_2(OH)_6$), as a common ferric sulfate mineral on Earth, has recently been suggested to be present on Mars by remote sensing studies [1]. The detailed investigations of mineral chemistries and corresponding Raman spectroscopic features for alunite (and jarosite) solid solutions are essential for their potential in-situ discoveries on Mars by the forthcoming Raman payloads aboard ExoMars and Mars 2020 [2,3]. Previous work has focused on the B site (Fe/Al) substitutions of alunite-jarosite solid solutions [4], here we examine Raman spectral features of the K-Na (A site) alunite solid solutions with intent to quantitatively correlate the chemical variations with their typical Raman peak positions. Five alunite minerals with different K-number (molecular 100×K/(K+Na), acquired by ICP-MS) are hydrothermally synthesized. As shown in Figure 1, the major Raman peak positions of K-Na alunite solid solutions show systematic variations in concert with their K-numbers, which are applicable for chemical estimations using future Raman payloads.

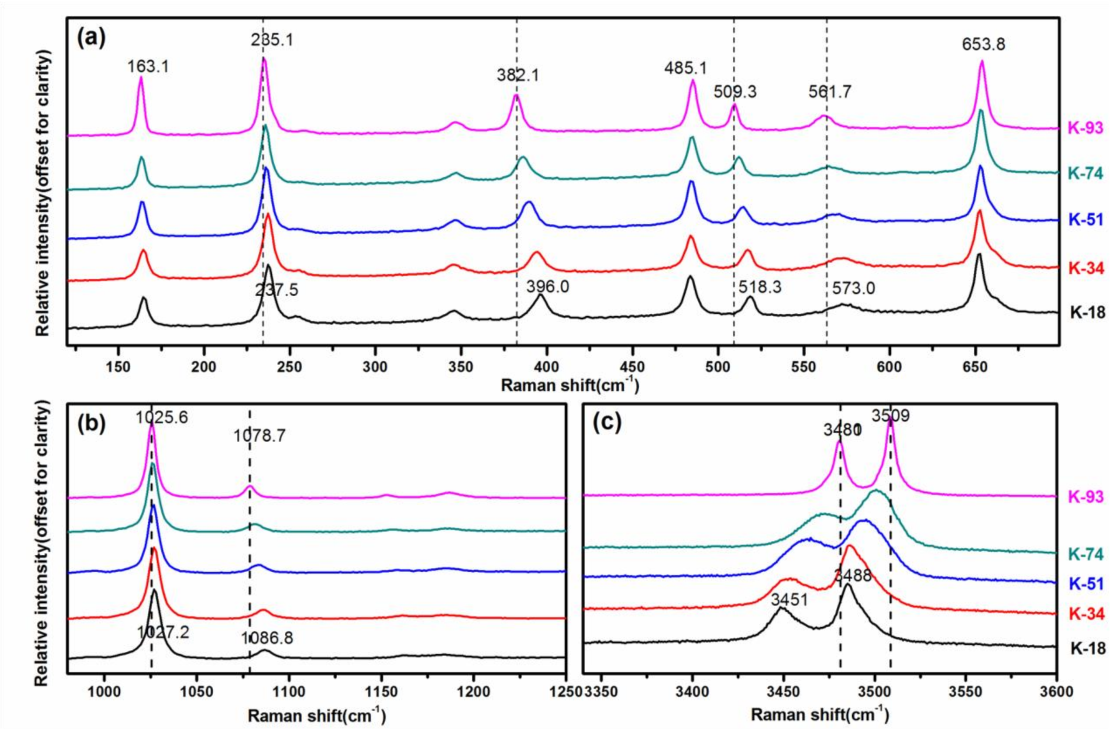

Figure 1. Raman spectra of five synthetic K-Na alunite solid solutions with different K-numbers.

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Broad spectrum of high-pressure phases in L6 chondrites Dhofar 717 and 864

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Dhofar 717 (6 g) and Dhofar 864 (1233 g) are among wide range of L6 chondrites found in Oman in 2001-2002. They were studied in details by secondary electron microscopy and Raman spectroscopy. The host-rock minerals are olivine (Fo_{25-26}), orthopyroxene ($En_{77}Fs_{21.5}Wo_{1.5}$), clinopyroxene ($En_{47}Fs_8Wo_{45}$), plagioclase ($Ab_{83}An_9Or_8$), chromite, apatitle, troilite and Fe- Ni metal. The host-rock is cut by the abundant shock-melt veins (SMVs). The SMVs contains fragments of host-rock mineral grains and aggregates, most of which has been transformed to high-pressure phases. High-pressure minerals are also abundant in the vicinity of the SMVs. Olivine close to the veins is transformed to wadsleyite and ringwoodite, whereas inside the SMVs it is totally replaced by wadsleyite-ringwoodite aggregates. The SMV background is presented by fine-grained majorite, ringwoodite and metallic phases. Plagioclase grains are transformed to jadeite-linguinite aggregates, however most of them are presented by pure fine-grained jadeite. Some jadeites are rimmed by high-Ca majorite. Orthopyroxene is transformed to majorite, akimotoite and vitrified Mg-perovskite. At the same time detailed identification of bridgmanite is not clear from the Raman spectra and need to be confirmed in further studies. Apatite inside the SMVs is also replaced by fine-grained aggregates, however, identification of phases in these aggregates by Raman spectroscopy is difficult. Broad range of high-pressure minerals indicates heavy shocked conditions for studied meteorites with relevant pressures above 20-25 GPa. Textural observation indicates melting structures of olivine and plagioclase and may correspond to the temperatures above 2500 K.

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Raman detection of bacteria and β-carotene in a mineral background

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In our Solar System, Mars is considered one of the prime candidates to have spawned life. Although the current climate on Mars is very harsh, the planet is believed to have been much more habitable in the past. Any possible current life on Mars must be able to withstand the extreme drought, radiation levels and temperature swings. Earth has examples of organisms that fit this profile, such as *D. Radiodurans* [1], hence terrestrial habitats that host extremophiles are readily studied.

Due to current payload constraints, many complex analytical techniques are not feasible on missions to Mars' surface. The ExoMars 2018 rover will be equipped with a Raman spectrometer. This spectrometer has some potential to detect biosignatures, but it is more focused on the characterisation of the mineralogy of individual habitats. This work focuses on assessing the next generation space instrumentation for life detection using carotenoids, a widely accepted proxy for biosignatures [2]. To obtain an increase in specificity and SNR, we are optimising the excitation wavelength for resonance Raman spectroscopy (RRS).

Due to the high radiation levels on Mars, it is expected that any present life would reside beneath the surface, hence β-carotene and various bacteria were measured embedded in different mineral environments. We report two scenarios: 1. living organisms behind a several millimetre thick surface; 2. living organisms deeper below the surface. In the first case, time-resolved Raman spectroscopy can help us to 'look through' translucent minerals. Previous research has already shown that it is possible to detect Raman signal of *D. Radiodurans* through a translucent mineral layer of several millimetres thick [3]. For the second scenario, measurements will have to be performed on samples obtained by drilling up to a few metres deep. In this case, life could be hidden anywhere in the sample. As a proxy for such samples, we measure spectra from different mixtures of β-carotene or bacteria with minerals of different composition and varying grain sizes. We vary bacteria/carotene concentrations to quantify our detection limits and optimise our set-up for the detection of biomarkers. Our goals are to optimise our own set-up for the detection of biomarkers in a mineral environment and to develop methods that could be used to detect possible life on Mars. The results of our research will add to the preparation for future Mars missions and can increase our chances of detecting life on Mars.

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Shock metamorphism of chondrites and other meteorites: application of micro-Raman spectroscopy

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We have studied high pressure minerals in L, LL and H-chondrites, Martian and Lunar Meteorites, and other meteorites. In order to study these high pressure minerals micro-Raman spectroscopy provides a non-destructive powerful tool to identify the high pressure mineral spices. In this paper, we will show the results of our micro-Raman spectroscopic studies combined with the other techniques such as SEM-EDS, TEM, Synchrotron X-ray diffraction, and EPMA.

Minerals recording shock histories are silica minerals such as crystobalite, tridymite, and quartz, feldspar, olivine, and pyroxenes. We can identify coesite, stishovite, and seifertite as the high pressure polymorphs of silica minerals, maskelynite, jadeite, and hollandite as the high pressure forms of albite, wadsleyite, ringwoodite, and a mixture of ferropericlase and bridgmanite as high pressure phases of olivine, and majorite, akimotoite, and bridgmanite as high pressure polymorphs of pyroxene. These high pressure phases are the indicators of the shock pressure

Two typical textures are observed in the high pressure phases in shocked meteorites, showing those in solid state transformation and crystal growth from melts formed by shock events. We show the two typical textures observed in these high pressure minerals and estimate the formation conditions of these high pressure minerals. These textures in meteorites show similarity with those of the static high pressure experiments and they are different from those observed in shock experiments. The characteristic textures are caused by long durations of the shock events due to large scale impacts in meteorites.

Based on speciation and textural observations of these high pressure minerals, we discuss the nature of the shock events in various meteorites such as L, LL, H chondites, Ureilite, and Lunar and Martian meteorites.

Raman analysis of the NWA 6148 Martian meteorite: olivine characterization and its differences with other nakhlites

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The NWA 6148 meteorite was found in the region of Northwest Africa and is one of the 15 Martian meteorites catalogued as nakhlites. They were formed in Mars from basaltic magma, leading to flows or shallow intrusions. Due to their scarcity, their study is essential and provides relevant information about Mars' surface composition and potential environments for life. However, even if their study could result crucial, there are almost no studies about this nakhlite and there is a lack of knowledge about meteorite NWA 6148. In this work a sample of 0.246 g of the NWA 6148 meteorite was analyzed by two Raman spectrometers (with 785 nm and 532 nm excitation laser).

Regarding Raman data, among others, augite, olivine and calcite were found in the meteorite (Fig. 1). In this work, the two main olivine bands were found in the range of 817–820 cm^{-1} and 841–847 cm^{-1}. According to the study of Takashi Mouri et al. [1] those wavenumber ranges mean that the composition of the olivines found vary from Fo_{30}–Fa_{70} to Fo_{55}–Fa_{45} (Fo: %Mg content; Fa: %Fe content). This variation of the metal proportions in the olivine leads to think that there are different types of olivines in the meteorite, which in most of the detected cases differ from the ones found in literature [2]. Regarding the calcite, it was stated by Hicks et al. [3] that it appears in other nakhlites found in desert environments due to weathering in desert zones.

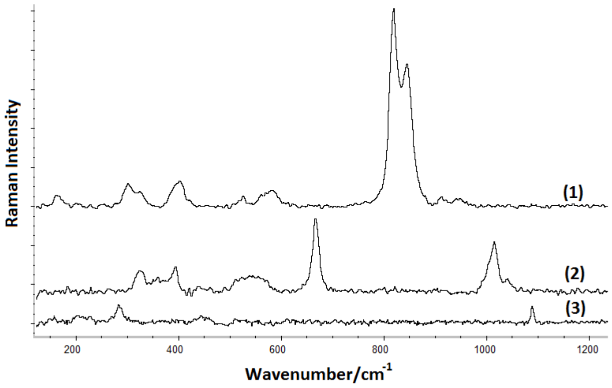

Figure 1. Raman spectra of olivine (1), augite (2) and calcite (3).

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Definitive and comprehensive mineralogy for a Venus Landing Mission

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A Venus landing mission is long over-due, which was categorized very high in NASA Decadal Survey for New Frontier Program [1]. Venus has the youngest surface built through relatively recent volcanic activities, and a dense atmosphere of high pressure and high temperature near the surface. Venus would have the most interesting atmosphere-surface interactions. These characters make *the mineralogy of the surface of Venus to be "the single most fundamental question"* faced by any future Venus landing mission [2, 3, 4].

A Raman system for *in situ* measurements (with highly condensed laser beam and line scan capability) on a Venus lander could provide finger-print spectra of silicates, carbonates, sulfates, phosphates, oxides, sulfides, hydroxides, etc. for definitive mineral phase identifications with high Raman efficiency. In addition, the Raman peaks of minerals are very sharp and non-overlapping in the spectra of mineral mixtures (rocks and regolith), thus the phase ID can be made by direct inspection of raw spectra.

Furthermore, a Raman system working in visible spectral range allows the laser beam and Raman photon collection through a transparent window (fused silica or sapphire). This character will enable Raman measurements to be made behind a window in a Venus lander. The Venus surface/subsurface samples could be delivered onto that window from outside. In addition, it only takes 10 s to < 1 minute to obtain a Raman spectrum. During a 2-4 hours Venus landing mission, it will collects several hundred Raman spectra from Venus samples

An *in situ* Raman system, Compact Integrated Raman Spectrometer (CIRS) supported by NASA MatISSE program, has very high technical Readiness Level (TRL 5-6). It uses the simplest, the most mature and effective techniques, i.e. continuous wave, low power 532 nm laser, optics in visible spectral range (532-676 nm), and conventional CCD. In addition, it has been demonstrated being capable [5-16] to provide three types of science information on the analyzed samples: *(1) Complete Mineral ID; (2) Mineral chemistry; (3) rock characterization.* Scientifically and technically, CIRS is ready for a Venus landing mission that will provide crucial information for the building of an understanding on Venus origin, history, and surface-atmosphere interactions.

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Shifted excitation Raman differentiated spectroscopy for planetary surface exploration

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Raman spectroscopy probes fundamental vibrations of molecules that produce finger-print spectral patterns with sharp peaks. Raman spectra can be acquired non-invasively, non-destructively and fast, thus is suitable for landed surface explorations on planetary bodies [1-27]. On the other hand, Raman scattering phenomenon is intrinsically weak. It requires carefully crafted optical configurations with high Raman efficiency and robust optical-electronic-mechanical engineering, in order to provide the necessary science performances during a robotic planetary mission. In terrestrial geological applications, a major threat has been the fluorescence interference that appearing in some terrestrial rocks and regolith samples.

Supported by NASA-MatISSE program (NNX13AM22G), we conducted three sets of studies to address the potential fluorescence issues for planetary applications. They are: (1) to evaluate the fluorescent properties of a broad range of extraterrestrial materials and their potential threat to cw-green-Raman for planetary application [28]; (2) to compare Raman signal strengths, generated by five laser wavelengths (785, 633, 532, 442, 325 nm), from a set of major rock-forming minerals and typical bio-markers [29]; (3) to develop SERDS technology against potential fluorescence interferences.

SERDS is a methodology based upon the wavelength change of Raman signals vs. non-wavelength change of fluorescence signals, when changing the excitation laser wavelength. Technically, the SERDS function has been successfully realized in the development of Compact Integrated Raman Spectrometer (CIRS) at JPL We report here the validation of SERDS application on natural rocks (Fig. 2-3).

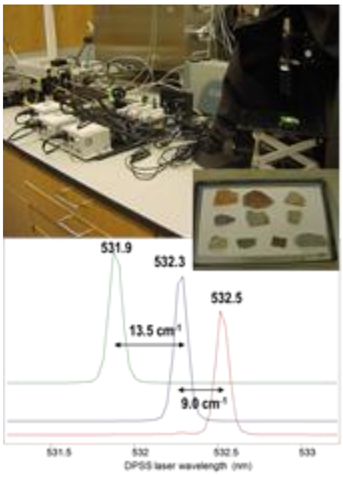

Fig 2. SERDS experiment setup at WUSTL

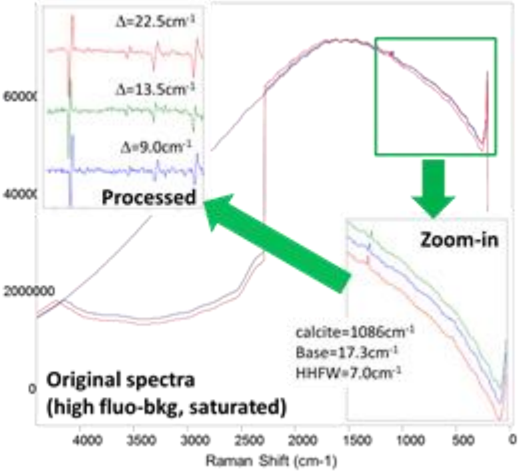

Fig 3. SERDS measurements and data process of rock AKB

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Spectral features of crichtonite series minerals from preferentially oriented inclusions in pyropes from mantle xenoliths of Yakutian kimberlites (Russia)

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Crichtonite series minerals (CSMs) are one of mantle accessories found in kimberlites, mantle xenoliths as well as inclusions in diamonds [1-2]. They are also known as preferentially oriented inclusions in pyropic garnets [3-5]. CSMs are complex oxides with a formula $^{XII}A^{VI}B^{VI}C_{18}{}^{IV}T_2O_{38}$, where **A** = Sr, Pb, Ca, Na, K, REE, Ba, U; **B** = Mn, Y, REE, U, Zr, Fe; **C** = Ti, Fe, Cr, Nb, V, Mn; **T** = Fe, Mg, Zn. Along with EMP and XRD analyses they may be successfully identified with micro-Raman spectroscopy. In this study we represent data on spectral features of CSMs of mantle origin on the example of those included in garnets together with exsolved rutile, ilmenite, pyroxenes, olivine, chromite from peridotite and pyroxenite mantle xenoliths from kimberlites of Yakutia (Obnazhennya, Udachnaya, Mir). Raman technique takes an opportunity to find CSMs that are not covered and to estimate their composition and homogeneity at one grain and one sample.

The main bands are 132, 146, 315, 430, 450, 694, 721, 806, 833 cm^{-1}. They correspond to oxygen–cation bonds vibrations with Ti–O and Zr–O ones dominated. The impact from large ion and different rare earth element cations from the A position usually shifts modes. Thus, when considering CSM's Raman spectra, it is better to evaluate mode interrelation and intensity as a whole than tracing the precise peak position.

We have measured CSMs with 532, 488 and 785 nm excitation wavelength and found no evidence of CSM disruption under laser in our samples as it was defined in experimental work [6]. One of special features of CSM's Raman spectra is that they have low intensity compared to other minerals (like silicates, rutile etc). In that case detector properties are meaningful.

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Fluid composition and low oxygen potential of mantle magmas produced by non - destructed methods of study fluid inclusions.

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The composition and PT - parameters of volatiles in rocks play crucial role in speciation, transport and deposition of ore components. Early investigations of fluid inclusions in mantle minerals showed dominating role of CO_2. Recent studies have shown that the fluids may have more complex composition within the system COHNS (CO_2, N_2, H_2O, H_2S) [1-3]. We stuided primary fluid inclusions in olivine and matrix glass in the Fe-Ni alloy - bearing high-magnesium basalts of West Greenland (Disko island) by thermobarometry, Raman and IR spectroscopy.

Raman spectra of fluid inclusion are shown in fig.1. The solid phase in inclusions are represented by high quality graphite (peaks 1361, 1582, 2715, 3254 cm^{-1}, note very low I(D)/I(G) ratio); the fluid phase contains CO_2 (1284, 1387 cm^{-1}), N_2 (2329 cm^{-1}) and CH_4 (2917 cm^{-1}). A small broad peak at 3334 cm^{-1} is likely H_2O in accordance with thermobarometry and IR spectroscopy data.

The entrapment pressure estimated from homogenization temperature of the melt inclusions and calculated density of CO_2 in fluid [4] is about 0.5 GPa. The crystallization of the Disko basalts occurred at low oxygen potential, which is suggested by the presence of native Fe-Ni in sulfide bodies.

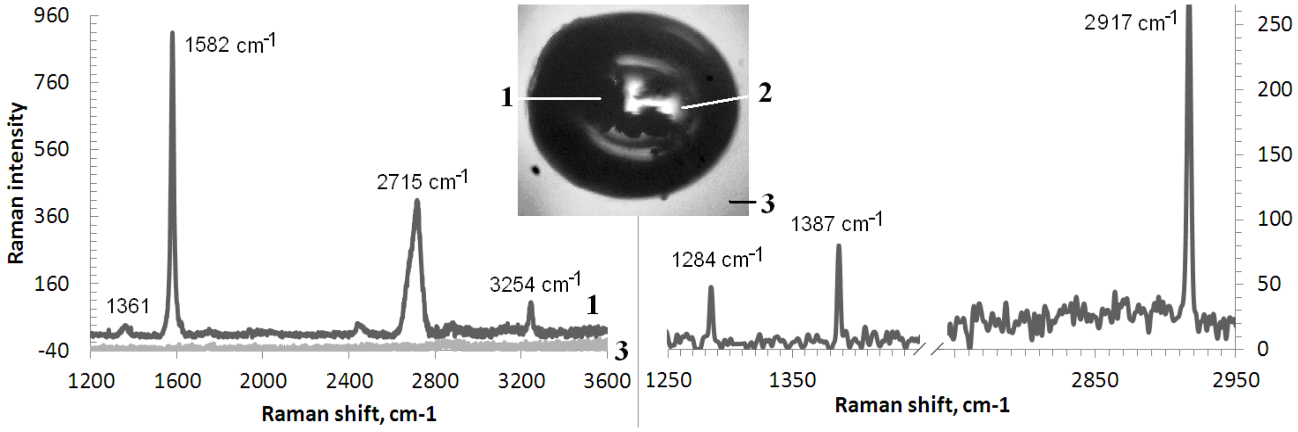

Figure 1. Raman spectra of fluid inclusion in glass (island Disko, West Greenland).

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Determination of the chemical composition of plagioclases by Raman spectroscopy

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Plagioclases are framework silicates occurring in planetary crusts; they can be described as a solid solution ranging from the Na-endmember, albite ($NaAlSi_3O_8$), to the Ca-endmember, anorthite ($CaAl_2Si_2O_8$), in which the Si:Al ratio varies. The investigation of their chemical composition is a key-point to understand the petrologic evolution of the parent rocks. In this work, we propose Raman spectroscopy as a procedure to gain chemical information from plagioclases. The major problem in plagioclases is their mixing behaviour which is complicated by the various compositional-driven phase transitions and by the Al,Si ordering. The most comprehensive Raman investigation on feldspars [1] led to a classification of the major structural types without a detailed study of the changes of the Raman features within the plagioclase composition. We performed Raman investigation on a series of well characterized plagioclases, previously analysed by PXRD, TEM, FTIR spectroscopy and calorimetry. The samples consist of 20 homogeneous purified natural, low structural state plagioclases, showing the highest degree of Al,Si order possible for each composition, which ranges from An_0 to An_{100}. The suggested protocol is composed of two steps: first, the wavenumber difference between the two major peaks of the plagioclases is measured to roughly establish the symmetry of the investigated mineral; second, the chemical composition of the unknown plagioclase is estimated from the two calibration equations obtained by fitting the peak linewidths of the most intense Raman band. We point out that the relationship between composition and linewidth can be correctly obtained only for low structural plagioclases with a degree of order not far from the studied references. The method has been tested on three different plagioclase crystals from a volcano and two meteorites: the compositions evaluated by Raman data are in good agreement with the chemical analyses.

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Quantification of gas concentrations in fluid inclusions

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The study of geological fluids is of first importance to understand heat and matter flows in the Earth crust, for example to elucidate the conditions of transport and deposition of metals. Raman spectroscopy is a popular technique to study fluid inclusions, because it provides localized, non-destructive, and fast analysis. The knowledge of the gas phase composition of fluid inclusions has many applications, in ore genesis or basin studies.

Molar fractions can be determined by Raman spectroscopy, knowing the Relative Differential Raman Scattering Cross Sections (σ_i) of each gas [1-4]. The values of σ_i of the gases commonly found in fluid inclusions were determined in 1972-1973 [5-6]. More recently, some studies pointed out a possible effect of pressure and gas mixture composition on these values [1,2,7,8]. Despite that, the σ_i were never re-evaluated. Because the ranges of validity of the different σ_i remain unknown, the uncertainty on molar fractions in the gas phase of fluid inclusions is unknown. As a result, the interpretation of the fluid in terms of PT or fO_2 is only approximated. In the present study, mixtures of known compositions are prepared and loaded in a new High Pressure Optical Cell [9] dedicated to gas studies. The effect of the composition of different mixtures of N_2-CO_2-CH_4 and pressure from 1 to 300 bars on σ_i is evaluated. Gas phase composition of CO_2-CH_4 fluid inclusions are determined by Raman spectroscopy and compared to values obtained by the observation of phase transitions during microthermometric experiments.

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Raman spectroscopy of gem quality variscite and metavariscite

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The dimorphous aluminum phosphates (Al[PO$_4$]-2H$_2$O) variscite and metavariscite (orthorhombic and monoclinic respectively) are used as gems [1-3]. Moreover, variscite has been described in carvings and ornaments of Neolithic period [2,4-6]. Variscite and metavariscite can be transparent to translucent to opaque with a color from green (sometimes bluish) to white to yellow to brown. Translucent to opaque varieties (cryptocrystalline) can cause misidentification with green turquoise, chrysoprase and a variety of other lesser known gem materials [2,3,5,6]. Raman spectroscopy has been applied for the identification of various phosphates of these mineral groups [7] as well as presented in online databases [8]. However, the published spectra can differ from sample to sample (see again [7] and [8]). For the present study, a series of gem quality transparent (single crystal) and translucent (cryptocrystalline) variscite and metavariscite was investigated using Raman spectroscopy. All samples present the main vibration bands at the region from 990 to 1050 cm^{-1} due to PO$_4$ symmetric stretching vibrations. The exact positions of the variscite and metavariscite Raman bands are slightly different. It is also observed that translucent samples present broader bands compared to the transparent samples. This is probably due to the size of crystals as well as the possible presence of other minerals in the translucent varieties of variscite and metavariscite. Bands broadening, possibly due to crystals size was also observed in turquoise [9]. Spectra on translucent samples were also acquired with a mobile Raman spectrometer; mineral identification could be sometimes difficult, only based on such spectra.

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Spatial heterodyne Raman spectroscopy for mineral detection

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Spatial heterodyne Raman spectroscopy (SHRS) is a new type of Raman spectroscopic detection technique with the characteristics of high optical throughout, high spectral resolution, and no moving parts. The concept of SHRS was first proposed by Dr. Nathaniel R. Gomer and Dr. S. Michael Angel et al. [1, 2]. SHRS is very suitable for the planetary exploration missions, which can be used to the analysis of minerals and find biomarkers maybe exist on the surface of planetary [1]. The authors have applied the technique to standoff Raman spectroscopic detection, analyzed the main characteristics, including spectral resolution, bandpass and signal to noise (SNR) of standoff SHRS. Some Raman spectra of natural rocks have been achieved at a distance of about 10 m (detected spectra can be seen in Fig.1). The detection ability of 2-dimensional (2D) SHRS is also analyzed through experiments [3]. Although 2D SHRS has a lower SNR than 1D SHRS, the authors think it can be also used to detect minerals with strong Raman scattering to achieve a broader spectral band. A prototype of SHRS-LIBS combined detection system is also under designing. The prototype can be used to detect Stokes and anti-Stokes Raman peaks together. By adjusting the power or point size of laser, LIBS spectra can be detected too. The authors hope that the prototype can be built in the year of 2017.

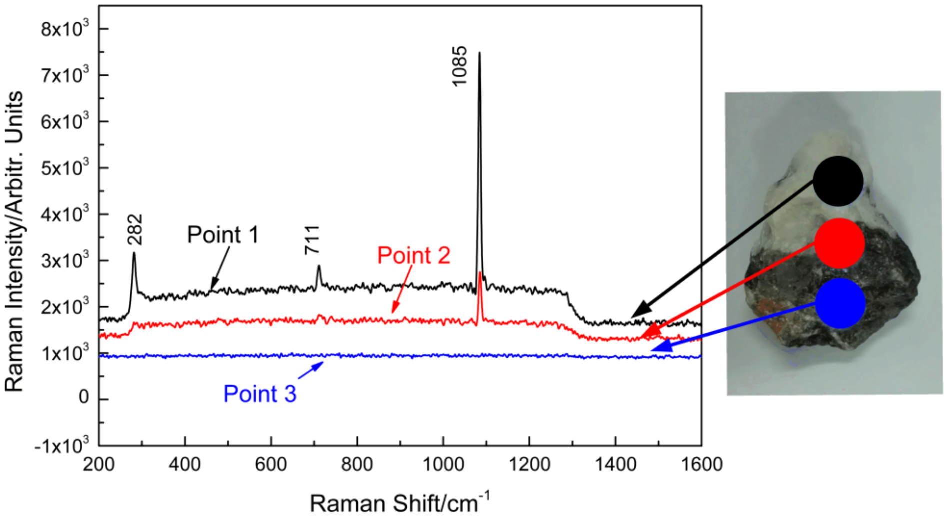

Figure 1. The detected spectra of a natural rock using standoff SHRS at a distance of 10 m.

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Field identification of minerals at burning coal heaps using miniature Raman spectrometers

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Coal fires and burning coal heaps represent unique mineralogical settings with occurrence of mineral phases which are otherwise very rare, highly unstable and/or cannot be formed under low-temperature conditions. Combination of combustion process, temperature up to 1000 °C and exposure to the aggressive gases lead to the extensive alteration of tailing and production of new mineral phases encrusting gas vents and fissures [1]. Many of these minerals are also produced around volcanic fumaroles and in areas of geothermal activity [2]. Here, our main interest lies in the study of minerals originating from gas interactions called “sublimates” (NH_4-halides like sal ammoniac, sulfates like mascagnite, org. compounds like kladnoite) and alteration products (anhydrous/hydrated sulfates of ammonia, Fe, Al, Mg, Ca, K and Na) closely related to the fumaroles. Previously, miniaturized Raman spectrometers were repeatedly and successfully used to identify secondary minerals, notably sulfates [3], carbonates [4], or even organic minerals [5]. Currently, we test small Raman instruments for the field identification of gas vent minerals both under controlled laboratory conditions and outdoors at several heaps in Central Europe (mainly in the Czech Republic: Heřmanice, Ostrava, and Zastávka, Brno). Due to common instability of the phases, attention is made to proceed fast after sampling to collect structural (powder XRD) and Raman spectroscopic data. Sulfur, sal ammoniac, mascagnite are easily discriminated using laboratory microspectrometer. Unambiguous discrimination of ammoniojarosite, efremovite and some others can sometimes be challenging. Our ultimate goal is the application of miniature Raman instruments for the reliable and unambiguous identification of minerals surrounding fumaroles at burning coal heaps. Performances of a miniature Raman spectrometer (785 nm excitation) to detect sal ammoniac, mascagnite, sabieite and efremovite under field conditions at Heřmanice heap in Ostrava are reported.

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Raman study of $FeSiO_3$ pyroxene polymorphs across the displacive phase transitions

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Along the join of $(Mg,Fe)SiO_3$ pyroxene, two different types of displacive transitions observed in orthorhombic and monoclinic symmetries at high pressure, i.e. Pbca ↔ HP-type $P2_1/c$ ↔ HP-type Pbca [1,2] and $P2_1/c$ ↔ C2/c [3]. Previous elastic velocity studies indicted the acoustic mode behavior in both types of displacive transition being different; the former transition is a ferroelastic transition and induces the elasticic velocity softening [4,5] and the latter gives the change of the pressure derivatives of elastic velocity across the transition [6]. It's desired to investigate the Raman mode (optic mode) behavior across these transitions.

In this study, the $FeSiO_3$ pyroxene polymorphs were employed to investigate the behavior of Raman modes across the phase transitions. Raman patterns of orthorhombic (opx) and low-pressure monoclinic (LP-cpx) were collected in the frequency range of 100 to 1200 cm^{-1} and up to the pressure of ~20 GPa. Compared opx and LP-cpx at ambient conditions, both of Raman patterns showed highly similarity. Upon compression, the Raman patterns of both pyroxene polymorphs started showing difference as soon as reaching the phase transition. We observed some general features in the transitions of ortho- and clino- $(Mg,Fe)SiO_3$ at 650-700 and ~1000 cm^{-1}, which they are related to the structure changes of SiO_3 chains across the phase transitions. In clino LP- HP transition, the minor mode softening observed under pressure as the computational study predicted [7]. The anomalous mode behaviors observed in the series of phase transitions in ortho-pyroxene may be related to the ferroelastic transition. The details will be presented in the meeting.

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Evolution of rock-forming media in diamond-bearing gneisses from the Kokchetav massif

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Fluid or melt inclusions in minerals, formed at ultra-high pressure (UHP) conditions, provide an information on processes which occur in deeply subducted crust [1]. UHP gneisses of the Kokchetav complex were metamorphosed within diamond stability field at 1000 ˚C and 6-7 GPa [2] and experienced extensive partial melting [3].

Raman spectra were obtained by Laser Raman spectrometer LabRam HR800 (Horiba Jobin Yvon), using a 532 nm at 15 mW (laser spot size of about 0.8 µm).

Diamond-bearing gneiss (sample 108a-117) was collected in the Barchi-Kol area. It is composed of Grt, Qz, Mu, Bt, Pl and Kfs. Accessory minerals are represented by Cpx, Zrn, Dia, Gr, Ap, Tit, Cal, Mnz, Py, Cpy, Py and Dum. Grt porphyroblasts reach up to 3 mm in size. Zrn were identified in matrix and as the inclusions in Grt porphyroblasts. Dia side by side with CO_2 and CO_2+H_2O inclusions occur within Zrn grains. Neither CO_2 inclusions, nor Dia was detected in Grt porphyroblasts. Cores of garnet porphyroblasts contain multiphase solid inclusions (MSI) and aqueous fluid inclusions. Bt, Chl, Qz, Ap, Phe, Ph, Vrm, Cal, Mnz and Gr were identified as the minerals of MSI by means of SEM analysis and Raman spectroscopy. Fluid inclusions contain liquid water and H_2O vapor with no traces of CO_2, N_2 or CH_4. Fluid inclusions are spatially close and even interconnected with a polyphase inclusions.

Presence of microdiamonds inclusions in Zrn testify for the UHP formation of Zrn. CO_2 inclusions in Zrn closely coexisting with microdiamonds reveal that diamond formed at moderately oxidized conditions during peak of metamorphism. MSI represent trapped melts and presence of Mnz in MSI suggests high temperature of formation, likely at conditions close to the peak [4]. Consequent crystallization and necking of the melt inclusions resulted in the formation of fluid and multiphase inclusions in garnet porphyroblasts. The absence of CO_2 peaks in Raman spectra of fluid and polyphase inclusions in Grt suggest that amount of CO_2 dissolved in hydrous melt was insignificant and melt formed at reduced conditions.

This study was supported by a grant from the Russian Science Foundation (RSF 15-17-30012).

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Raman spectra of natural sorbents – cationic and anionic clays

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The layered silicates, namely nontronites [1] – high Fe smectites, and anionic clays – hydrotalcites [2] of different origin have been studied by Raman spectroscopy together with the complex of physical chemical methods. The purpose of this study was to perform a comparative analysis of their composition, structure, and properties. We recorded Raman spectra for only some from studied samples, such, only for the nontronite from the Salair Ridge weathering crust (fig.1). For nontronites contain the large amount of microelements from the bottom sediments of the Okhotsk Sea [3] our attempt to recorder Raman spectra was unsuccessful. Obviously, the symmetry of minerals can be refined by the methods of vibrational spectroscopy [4]. For example, nontronite (fig. 1) because the proposed either monoclinic (*C2/m* or C2) or triclinic PI space groups have vibrational bands that do not coincide in the IR and Raman spectra in the first case but do coincide in the second and third cases. Such coincidences have not been observed for the vibrational spectra of nontronite, and this fact is in favor of the *C2/m* symmetry. The possibilities of the method have been demonstrated by the example of mineral iowaite (hydrotalcite group) crystallizing in trigonal system.

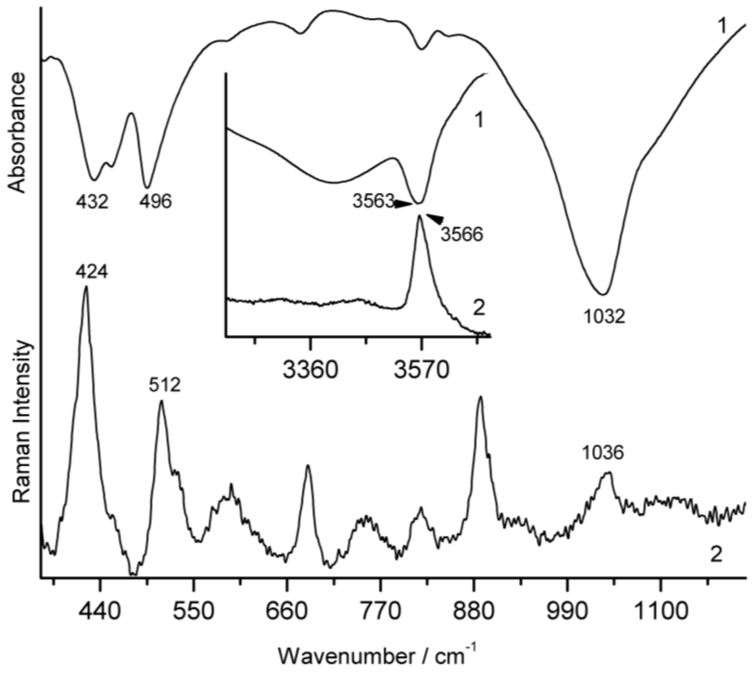

Figure 1. An infrared(1) and Raman (2) spectra of Salair nontronite

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Dynamic properties of zircon with different degrees of radiation damage as studied by temperature-dependent Raman spectroscopy

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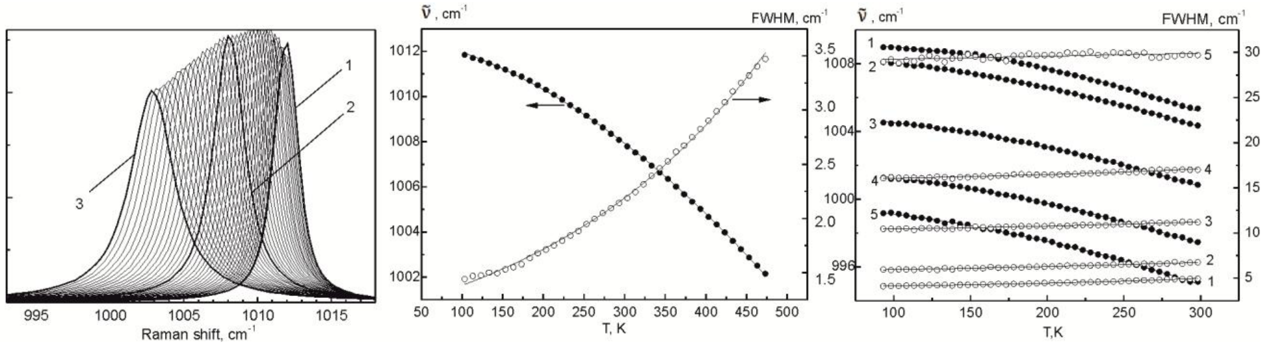
Lattice dynamics at the atomic level governs the response of minerals to external influences (e.g. T, P, α-dose), and it is important for the understanding of mineral-transformation mechanisms. The effect of structural disorder on dynamic properties has been studied by T-dependent Raman spectroscopy for some natural U- and Th-containing zircon samples, including a highly crystalline specimen from the Mud Tank carbonatite, Australia (at T = 93–473 K), and mildly to severely radiation-damaged zircon gems from Sri Lanka (at T = 93–293 K). The T-dependences of the positions ($\tilde{\nu}$) and widths (FWHM) of the nine most intensive Raman lines were measured. The relationships of shifts (1–9 cm^{-1}) and broadenings (1–6 cm^{-1}) of Raman lines and the symmetry of normal modes were analyzed, and the isobaric-mode Gruneisen parameters were determined. The external libration R(SiO$_4$) near 356 cm^{-1} (E$_g$ mode) is characterized by the strongest downshift and broadening whereas the internal ν_2(SiO$_4$) vibration near 266 cm^{-1} (B$_{2g}$ mode) is characterized by a small temperature-induced upshift. The T-dependences of Raman parameters are non-linear (fig.1). Low-T approximation limits of Raman-shift and FWHM values were estimated [e.g. they are 1012.4 and 0.8 cm^{-1}, respectively, for the ν_3(SiO$_4$) band in Mud Tank zircon]. Lattice-dynamic properties of zircon are discussed in terms of the combined effect of radiation damage and thermal factors.



a *b* *c*

Figure 1. Temperature-dependent Raman spectra (632.8 nm excitation) showing the ν_3(SiO$_4$) band of the Mud Tank zircon: 1 - 93K, 2 - 293K, 3 - 473K (a); T-dependences position and FWHM of the ν_3(SiO$_4$) band in the Mud Tank sample (b) and in Sri Lankan zircon gems: 1–5 – samples with different degree of radiation damage (c). Circles – experiment, lines – approximation (b,c).

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Raman imaging of disordered graphite in coesite inclusions in kyanite from the Kokchetav diamond-bearing gneisses

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The evolution of carbonaceous material during the deep subduction is very disputable theme now. With increasing PT-conditions organic matter underwent different stages of evolution and the end points of these changes are graphite or diamond crystals. There are several geothermometers based on the degree of graphite crystallinity [1]. The Raman imaging of the intergrowth of graphite and coesite inclusions in kyanite porphyroblasts from diamond-bearing gneisses from Kokchetav massif (Northern Kazakhstan) was the main aim of the study. These gneisses consist of large kyanite and garnet porphyroblasts in quartz-biotite-phengite-K-feldspar matrix. Accessory minerals are rutile, zircon, apatite, graphite and UHP relics – diamond and coesite. The Raman imaging of intact inclusions is the most informative and unrestrictive method for detailed study of mineral relations even within the small inclusions (5-10 µm). Raman imaging was performed by alpha - WITec Raman system equipped with a 488 nm laser and a 100X NA0.9 objective. Raman imaging reveals that in addition to well-ordered graphite flakes, which can be observed with optical microscope, there are tiny disordered graphite inclusions within the coesite inclusions in kyanite porphyroblasts. In most cases graphite was found at the quartz-coesite interface (Fig. 1). There are two main models for origin of disordered graphite: (i) diamond graphitization and (ii) crystallization from COH-fluid [2-3]. In our case well-ordered graphite has euhedral shape, thus the model of diamond graphitization for graphite formation can be excluded. It is likely that major part of graphite crystallization occurred near the peak of metamorphic conditions from COH-fluid. Some of this COH-fluid was entrapped by SiO_2 inclusions. It is well known that the degree of coesite-quartz transition is controlled by fluid amount [4]. The coesite-to-quartz transformation is accompanied by significant volume increase and it produces strong radial crack pattern, which may promote the leakage of fluid and precipitation of disordered graphite.

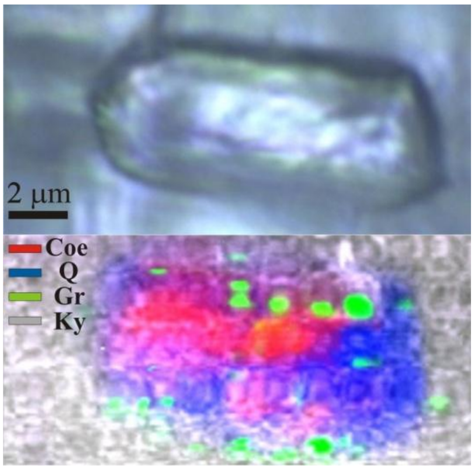

Figure 1. Raman map for coesite inclusion from kyanite Gr-rich core.

This study was supported by a grant from the Russian Science Foundation (RSF 15-17-30012).

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In situ discovery of moissanite in eclogitic rocks of the Kola region, Russia

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Numerous relicts of the Archaean eclogites and eclogitic rocks have been defined in the northern part of the Belomorian Province, Fennoscandian Shield [1 and references therein]. Two types of moissanite mineralization have been found in the least altered lens of eclogitic rocks of the Kokh-ozero area. The Raman spectroscopy has been used to study moissanite inclusions in host minerals (Almega XR ThermoScientific spectrometer, the Institute of Geology of Karelian Research Centre of the Russian Academy of Sciences).

The first type of moissanite presents euhedral semi-transparent crystals up to 20 µm in orthoclase grains (Fig. 1a). Characteristic modes of moissanite and orthoclase have been well showed in the Raman spectra (Fig. 1b).

The second type of moissanite forms intergrowths with diamond and graphite in clinopyroxen grains (Fig. 1c). Characteristic modes of moissanite, diamond, graphite and clinopyroxen have been well showed in the Raman spectra (Fig. 1d).

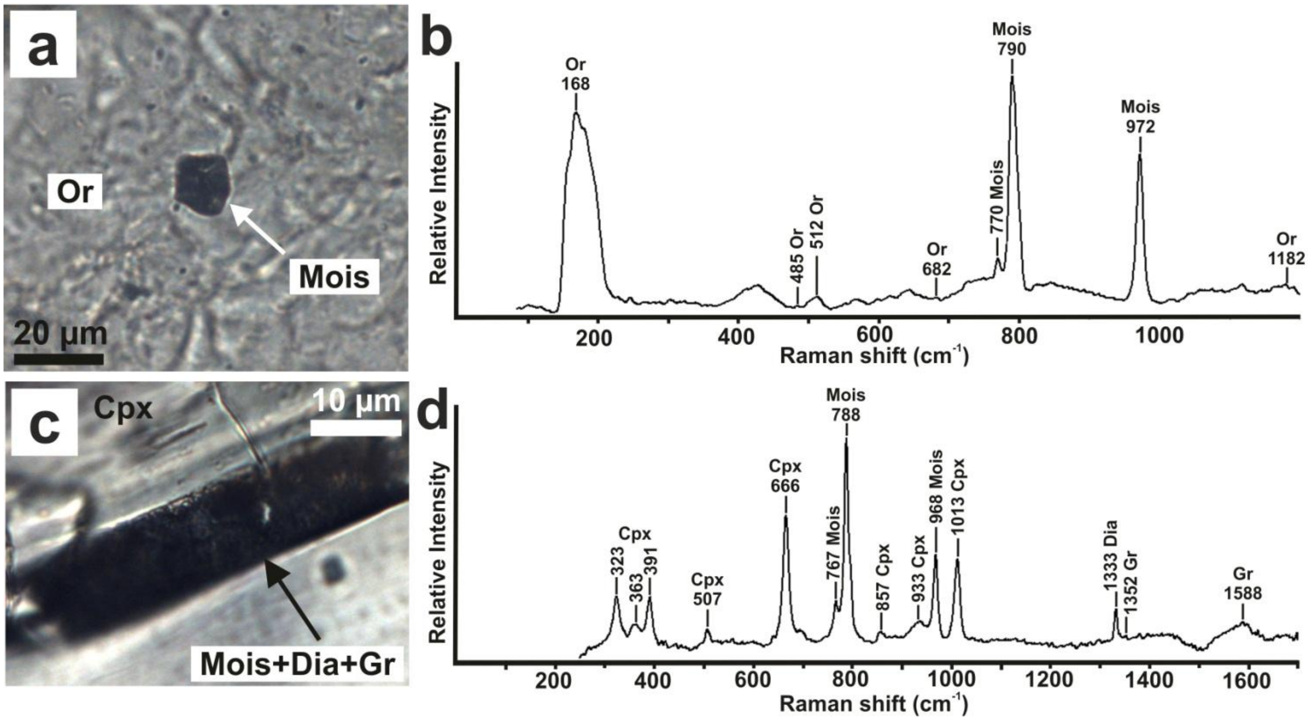

Figure 1. Moissanite (Mois) in eclogitic rocks. (a) Moissanite inclusion in orthoclase (Or); (b) the representative Raman spectrum of moissanite and orthoclase; (c) intergrowth of moissanite, diamond (Dia) and graphite (Gr) in clinopyroxene (Cpx); (d) the representative Raman sperctrum of moissanite, diamond, graphite and clinopyroxene.

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Phonon confinement in radiation-damaged zircon

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Widths (FWHMs) of Raman bands of crystals reflect the average size of the domains possessing translational order. Disruptions in the translational periodicity (e.g. by grain boundaries, dislocations, point defects etc.) distort Raman bands due to a reduction of the average phonon coherence length, commonly referred to as phonon confinement [1]. The observable (asymmetric) band broadening and change in band positions depend on phonon dispersion properties (e.g. [2]).

The dependence of the Raman FWHM of the $\nu_3(SiO_4)$ (B_{1g}) mode is well established in ion-irradiated zircon (e.g. [3]). New results for naturally self-irradiated zircon suggest that crystalline domain sizes decrease very rapidly with increasing dose [4], and may reach very small dimensions at irradiation levels where Raman band broadening is readily observed in zircon (Figure 1). The estimated domain sizes indicate that the phonon coherence lengths decrease to tens of nanometres already at very little broadening relative to crystalline zircon [5], giving rise to phonon confinement effects.

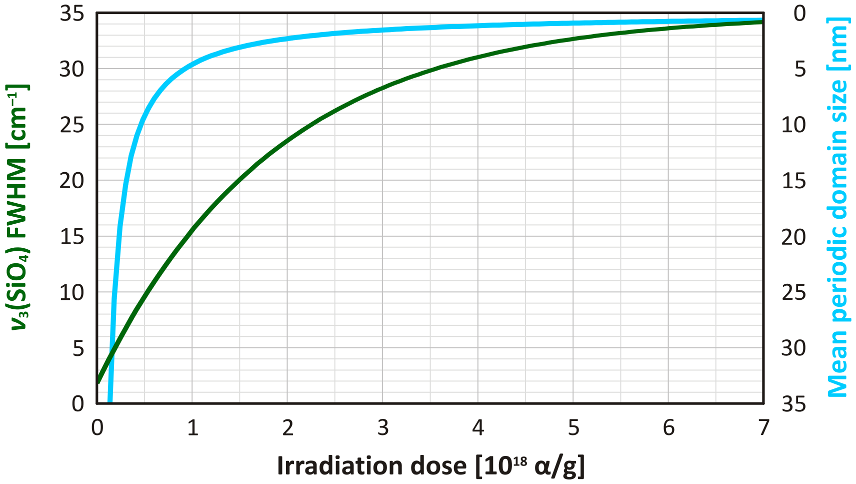

Figure 1. Raman band broadening (dark green, modified after [6]) and estimated crystalline domain sizes (light blue, after [4]) as a function of alpha dose.

Acknowledgments: This project has been supported by OTKA grant PD116183 to T.V. and FWF grant P24448–N19 to L.N.

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Classification of minerals using Raman and near-infrared reflectance spectroscopy

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The rock/mineral type and its distribution provide key clue on the geological origin and environmental changes of Mars. Therefore, the measurement and discrimination of martian rock/minerals is great helpful to understand those processes. As multi-component, in-situ, and rapid techniques, Raman and NIR spectroscopy are powerful and widely used for mineral/rock classification [1,2] in the field and even planetary exploration.

In this work, both Raman and NIR spectral features of several martian key silicates, carbonates and sulfates were investigated. And the distinguishing capacity of those two spectroscopic techniques was analyzed and compared.

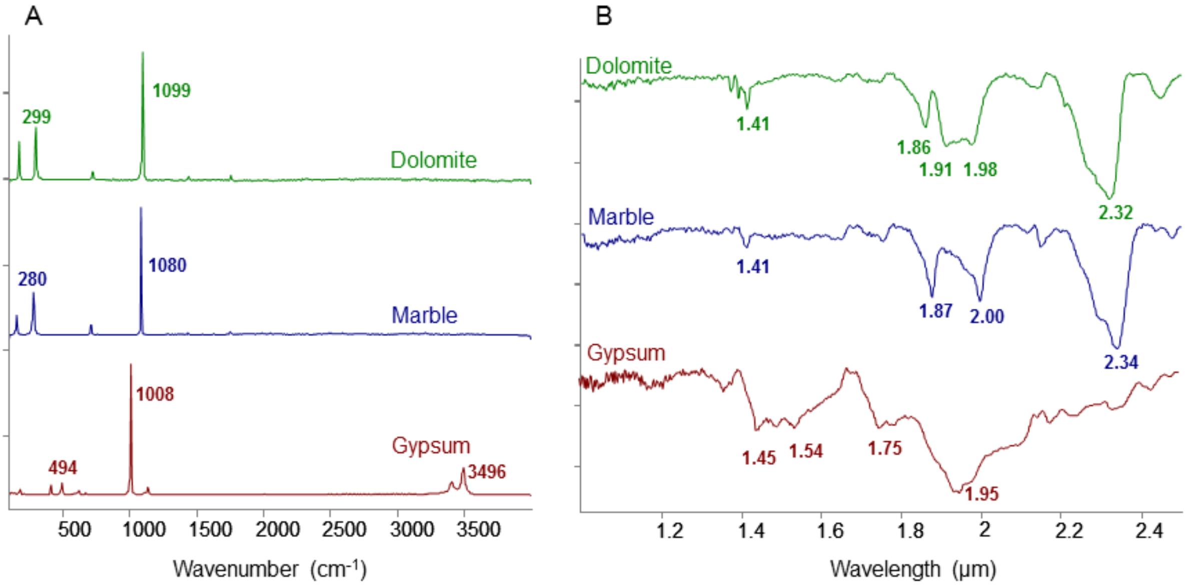

Figure 1. The Raman and NIR reflectance spectra of dolomite, marble and gypsum

As seen in Figure1, Raman scattering produces sharp, narrow lines beyond NIR spectral features which will be much helpful to identify minerals. Next, a Raman and NIR spectral database of main martian minerals will be built, and some chemometrics methods (such as PCA, PLS-DA, ANN, SVM) will be used to make prediction model of mineral classifications.

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Raman observation of the SiO_2 phases in natural diamonds

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The SiO_2 is not characteristic for peridotitic rocks in the upper mantle, but it occurs there only as phase (quartz or coesite) of metabasic (eclogitic) association. These phases may rarely be found in mantle xenoliths but commonly as syngenetic inclusion in natural diamonds. In the present study we have analyzed inclusions of SiO_2 phases in upper mantle and sublithospheric diamonds from alluvial placers of northeastern Siberian craton and Juina Province (Brasil) to identify residual strains and possible phase transitions.

Inclusions of SiO_2 have been found in several diamonds from alluvial placers of northeastern Siberian craton. All these inclusions have been identified as coesite by Raman micro-spectroscopy. In three diamonds, coesite is associated with garnets of eclogitic paragenesis with high grossular component (16-24 mol.%). All inclusions of coesite have low concentration of impurities, except one diamond, where coesite contains 1.13 wt% FeO. Micro-Raman measurements on an intact inclusion of remnant vibrational band shifts give a maximum confining pressure ~3.5 GPa.

In many cases the SiO_2 inclusions in diamonds from Juina Province form assemblages with typical inclusions of superdeep metabasic minerals: Maj–Gt, CaSi–Pv, and CaTiSi–Pv. Such assemblages suggest that the SiO_2 phases were possibly trapped as stishovite at a pressure of more than 8-10 GPa. The inclusions in most diamonds consist only of SiO_2, with no significant admixtures. The SiO_2 phase in some inclusions coexists with microblocks of the Al_2SiO_5 phase. No reliable evidences for the presence of stishovite have been reported at present time. Considerable strain which is observed by EBSD and Raman spectroscopy for some inclusions of the SiO_2 and combined SiO_2 + Al_2SiO_5 phases in diamonds from Juina Province suggests that they were formed in the sublithospheric mantle, in metabasic substrates, and these phases were initially trapped as stishovite or Al-stishovite.

Annihilation of the carbon deposition in refractory materials: catalysis of the Boudouard reaction by iron minerals

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Carbon deposition on refractory products is well known and dread by refractory suppliers and users. This deposition causes premature degradation of refractory linings, which operate under reducing atmosphere (carbon monoxide) [1]. The mechanism of CO decomposition into solid carbon has been studied for long time and is called the Boudouard reaction: $2CO \rightarrow CO_2 + C_{(solid)}$. In this study, we report *in situ* Raman investigations of the carbon deposition on iron and iron oxides at 600°C under reducing conditions ($CO + H_2$ mixture, Fig. 1). The annihilation of the Boudouard appears to be favoured by the presence of other iron minerals (e.g. pyrite and pyrrhotite). The evolutions of mineralogical phases, under reducing conditions, are observed using *in situ* Raman spectroscopy. For these experiments an original instrumental device was developed to control the temperature, the gas mixture flow directly under the Raman probe.

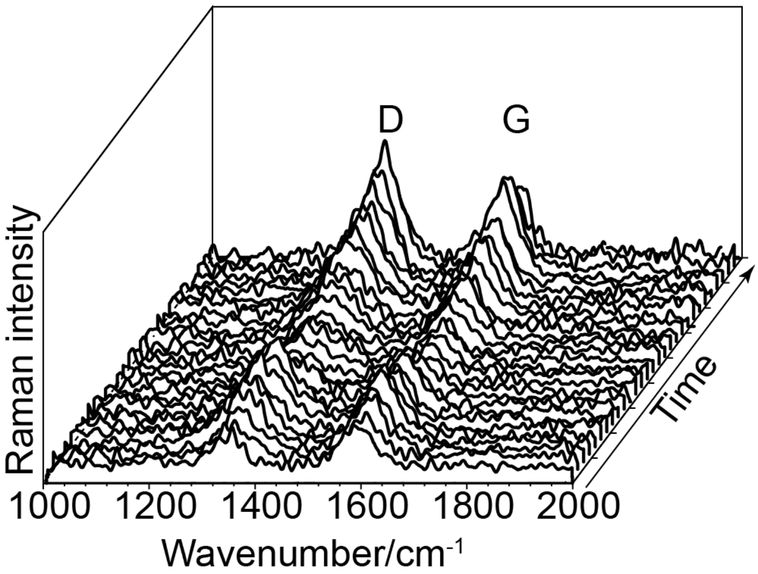

Figure 1. Evolution of Raman spectra recorded over 30 minutes at 600°C with Fe_2O_3< 5 µm precursor with 5% H_2 + 95% CO mixture.

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Primary hydrocarbons inclusions in garnet from the schists of Romashkino oil and gas field

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Despite the many arguments of the organic theory of the oil origin, a number of experimental studies allows for the possibility of the deep recharge of oil and gas fields [1]. Giant Romashkino oil and gas field in the South-Tatar arch of the Volga-Ural province is an example of these fields. Recent studies show a common deep source of hydrocarbon generation for oil deposits and natural bitumen in the region [2]. Here we studied the primary fluid inclusions in garnet from the crystalline basement schists of Romashkino oil and gas field by Raman and IR spectroscopy. A study of Raman spectra revealed the presence of polyphase hydrocarbons in inclusions. Four clear peaks were observed in the Raman spectra of fluid inclusions: 2867, 2921, 3006 and 3065 cm^{-1} (Fig. 1). The presence of the Raman modes in the range of 3000 - 3100 cm^{-1} indicates C-H stretching of aromatic compounds [3]. Two peaks at 2867 and 2921 cm^{-1} correspond to C-H stretching of aliphatic compounds [3]. We observed four peaks in IR spectra at 2885, 2959, 3041 and 3074 cm^{-1}, which also correspond to the frequencies of C-H stretching. Polyphase hydrocarbon inclusions in garnet from the basement rocks of the South Tatar arch suggest possible association of oil and gas source with deep fluids. However, they can also be connected with Archean organic materials in the studied rocks.

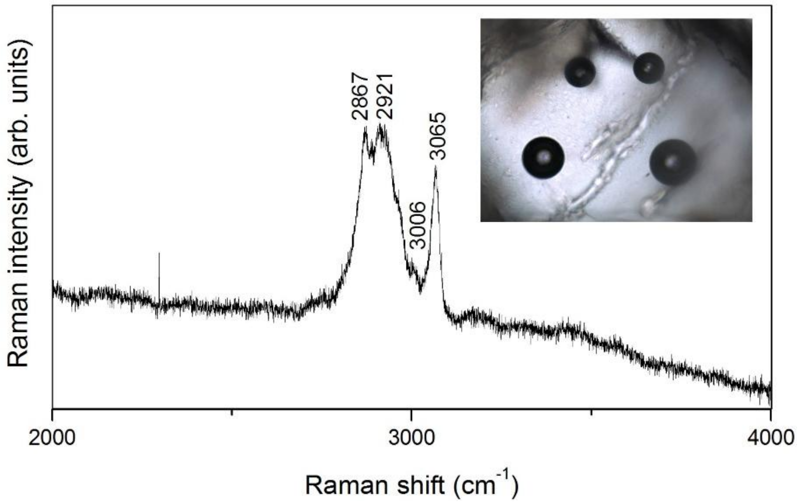

Figure 1. Raman spectra of polyphase hydrocarbon inclusions in the garnet from the schists of Romashkino oil and gas field

The work is supported by Russian Science Foundation RSF (No 15-17-30012) and Ministry of Education and Science of Russian Federation (project No 14.B25.31.0032).

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Raman spectroscopy of carbonaceous and oxide phases in impact-melted zones of Elga meteorite

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The Elga meteorite was found in 1959 in the basin of river Elga, Yakutia. It belongs to type IIE fine-grained octahedrites with rounded silicate inclusions. Detailed petrographic and mineralogical analyses showed existence of five petrologic types of silicate inclusions embedded into Fe-Ni metal matrix [1]. Several features, such as injection and liquid immiscibility structures, relict minerals and structural relationships between the silicate inclusions and metal, indicate that primary inclusions were melted during several (at least two) impact events.

A fragment (~12x9 cm) was sectioned from peripheral part of the meteorite. It contains rounded irregularly shaped silicate inclusion connected to a zigzag vein, which are related to the impact events. Partial melting and subsequent recrystallisation related to the first event caused formation of complex schreibersite-oxide rims at the metal-silicate boundaries. In the brecciated rims and in melt pockets inside the silicate a suite of unusual carbonaceous fragments were observed. Microprobe, Raman and FIB-assisted TEM revealed three principal associations: siderite-phosphide, siderite-oxides and oxides-carbon. The oxides are mostly Fe-Ni spinels of the magnetite-trevorite series. Reliable determination of the carbonaceous phase using Raman spectroscopy alone in not possible, since weakness of the signal prevented multiwavelength spectroscopic investigation. A tentative assignment to poorly ordered sp2 carbon is supported by EELS results.

Siderite and sp^2 carbon were not observed in other IIE meteorites. In general, siderite ($FeCO_3$) occurs very rarely in meteorites and is found only in Martian meteorites; sp^2 carbon is relatively common for carbonaceous chondrites and for martian meteorites. In Elga the carbonaceous phases are associated exclusively with the oxide rims at the metal-silicate interface, whereas in the other types of meteorites they are present in the silicate matrix. In Elga the carbonaceous phases are related to processes of shock metamorphism.

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Quantitative determination of the natural gas composition with Raman spectroscopy and chemometric methods

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The application of Raman spectroscopy in oil and gas industry can by effective tool for determination of unconventional reservoir fluid composition [1]. A description of a prototype system based on spontaneous Raman scattering spectroscopy developed for qualitative and quantitative analysis of natural gas is presented [2]. The work discuss influence of temperature (from 20°C to 100°C), pressure (from 14,7 PSI to 5000PSI) and density to Raman spectra which are use for natural gas composition calculation [3-5]. Chemometric methods are applied for percentage content determination [6].

Acknowledgments: The work was performed with financial suport from the *National Centre for Research and Development* and industrial partners, project no.: BG1/IRES/13 and from the *European Institute of Innovation & Technology* KIC – UNGASLAB.

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An experimental study on the kinetics of structural evolution of natural carbonaceous material to graphite

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The structural evolution of carbonaceous material (CM) to graphite using micro-Raman spectroscopy is widely used as a thermal indicator in metamorphic terrains. However, the process strictly depends not only on the peak temperature but also lithostatic pressure, tectonic deformation, fluid activity and catalytic effects during metamorphism. Such complex processes make it difficult to understand the natural structural evolution of CM, and proper assessments of these factors have been seldom achieved. Therefore, it is essential to consider a fundamental kinetic model for natural graphitization under geological timescales and crustal *P-T* regimes.

We report here new experimental kinetic study on the structural evolution of CM to graphite at various temperatures (1000 to 1450 °C) under a pressure of 1GPa for various durations (10 min to 115 h). Natural CMs extracted from sedimentary rocks in the Shimanto accretionary complex and the Hidaka metamorphic belt, Japan, transformed its morphology and crystallinity with increasing temperature and duration of experiments. Based on the area ratio (D1+D4 / G+D2+D3 bands) obtained by micro-Raman spectroscopy, we assessed the kinetics of graphitization using three differnt methods, a power rate model, a Johnson-Mehl-Avrami-Kolmogorov (JMAK) model and a superposition method. The effective activation energies for graphitization between 258 and 339 kJ mol^{-1}at 1GPa were obtained, which were much lower than those previously reported (~ 1000 kJ mol^{-1}). Summarizing the previous studies and our results between 0.1 and 1000 MPa, we found that the effective activation energies systematically decrease as a function of pressure. Based on the experimental results in this study, the sigmoid functions obtained from the time–temperature relations can be extrapolated to low-temperature conditions at 1 GPa. Our kinetic model using the area ratio predicts that CM undergoing metamorphism for about 1 m.y. will begin to crystallize at ~ 340 °C, and will transform to graphite at over ~ 590 °C. Thus, natural graphitization undergoes a much faster transformation than reported in previous studies at 1atm and could be explored in laboratory experiments using natural precursor materials under pressure conditions and time spans that reflect natural conditions in the Earth's crust.

Raman spectrum of hydrocarbons mixture at the Earth crust pressure and temperature

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The existence of crude oil and natural gas deposits at the depth, exceeding conventional “oil window” could not be explained by the concept of biotic origin of petroleum. The main source for such deposits could be the deep fluid from the asthenosphere, according to the concept of abiogenic origin of hydrocarbons. This fluid migrates up to the surface and forms oil and gas deposits in any kind of rock and in any kind of structural position of the Earth crust [1]. So, the crude oil and natural gas deposits should exist on the depth much deeper than the “oil window” and hydrocarbons should be stable at the Earth crust thermobaric conditions.

To check this hypothesis, the stability of synthetic oil was investigated at the Earth’s crust thermobaric conditions (up to 450ºC and 1.4 GPa). The experiments were carried out in Diamond Anvil Cells (DAC) with the internal resistive heating. Raman spectroscopy with a green Ar+-laser (514.5 nm) was used for *in situ* analysis of the petroleum composition. Ruby and Sm:YAG Raman shifts were the controllers of temperature and pressure inside the sample [2,3]. The sample of the synthetic oil was kept at the extreme thermobaric conditions: 320 °C and 0,7 GPa (3 hours), 420 °C and 1,1 GPa (3 hours), 450 °C and 1,4 GPa (12 hours). After the experiment the Raman spectrum of the sample were compared to the spectra of the sample before the experiment. The comparison showed no changes in the sample’s composition after the experiment. This fact demonstrates the stability of hydrocarbons at the Earth crust thermobaric conditions (at the depth down to 50 km [4]). Obtained data may broaden the knowledge about the the generation, structure, size and location of the world oil and gas potential resources.

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Infrared Raman spectroscopy of graphitic and cubic B-C-N materials

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Raman spectroscopy is commonly used for characterization in chemistry and materials science because vibrational information is very specific for the chemical bonds in molecules. Visible Raman spectroscopy has already been applied to characterization of graphitic phases containing nitrogen phases, however, the strong fluorescence and photoluminescence that accompany visible Raman excitation of graphitic phases limit the sensitivity that these Raman excitation wavelengths are able to achieve [1,2]. Here, we report the use of near-infrared (NIR, 830 nm) light to excite Raman scattering from the samples of the graphitic and cubic BCN phases (g-B-C-N and c-B-C-N). It is demonstrated that NIR Raman spectra of g-BC2N phase are similar to that of graphite containing D (1350 cm-1) and G (1589 cm-1) bands, however there is a shift the position of the D band of the g-BC2N to the lower frequency range (1290-130 cm-1). Similar shift was predicted for graphitic BC phases, but was never detected [3].

UV and visible Raman scattering spectra of a superhard phase, cubic BC2N, have been measured already [2]. The Raman band at 1326 cm-1 was attributed to the longitudinal optical (LO) mode of cubic BC2N. This study reveals that NIR Raman spectra of cubic B-C-N phases contain three main peaks centered around 1000, 1077 and 1310 cm-1, which is in line with theoretical predictions [4]. In summary, this study demonstrates that the use of the NIR Raman scattering allows identification of the cubic and graphitic B-C-N phases.

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POSTER PRESENTATIONS

SEM-EDS and Raman SCA (Structural and Chemical Analyzer) methodology for the analysis of Martian meteorites

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Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDS) and Raman spectroscopy combination in the new SCA (Structural and Chemical Analyzer) instrument is a novelty technique based on the simultaneous elemental, molecular and structural analysis of the samples. Raman SCA device allows performing Raman analysis in the exactly same micrometric area analyzed by SEM-EDS. For this work, a Renishaw InVia Raman spectrometer was used provided with a 514 and 785 nm laser, coupled to an SEM-EDS device (Zeiss-Oxford).

This device is really useful for the analysis of Martian meteorites since apart from the molecular and elemental characterization, it is possible to evaluate the distribution of both elements and molecules. In this way, homogeneity analysis can be performed. Moreover, the time of analysis is saved because all these analyses are performed at the same moment.

The EET 79001 shergottite meteorite was studied to fulfill the lack of information about it. It was seen that the composition of the studied specimen was very heterogenic, determining augite ($(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$) and olivine as the most common compounds. Olivine appeared as large inclusions (around 1.5 mm). Besides, chromite inclusions were also detected with variable size, dispersed in the augite matrix. Apart from that, calcium phosphate was detected, but scarcely.

The distribution of elements and therefore, compounds, is crucial for the comprehension of the formation and weathering process suffered by meteorites and SEM-EDS-SCA device is one of the most suitable technique for accomplishing this aim.

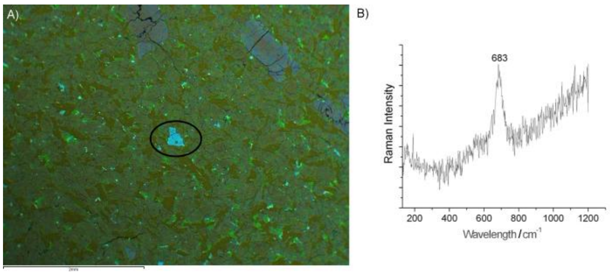

Figure 1. A) SEM-EDS false color image of the EET 79001 surface. B) Raman spectra obtained in the blue inclusion of A) image.

Acknowledgements: US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center. This work has been financially supported by the project “Development of the Raman instrument for the ESA Mission Exomars2018: Science support, equipment testing and operation support” (ref. ESP2014-56138-C3-2-R) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

Combined micro-spectroscopic techniques and LA-ICP-MS analyses for the characterization of ferruginous cements in temperate latitude beachrocks subjected to anthropogenic pressure

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Beachrock formations preserve the environmental conditions in which the sedimentary units where formed [1]. Few beachrock locations present high amounts of slag, anthropogenic artifacts attesting the impact of human actions on the coastal systems [2]. This work has studied an unusual temperate latitude beachrock (Tunelboka cove, Nerbioi-Ibaizabal estuary, North of Spain), which retains the legacy of a heavy anthropogenic environmental disturbance. Indeed, the units contain iron-rich solid wastes derived from metallurgical activities, constituting early diagenetic ferruginous cements that never have been studied. Such cements have been analysed by different Raman Spectroscopic techniques (MRS, imaging and SCA), assisted by SEM-EDS and LA-ICP-MS.

The EDS analyses showed Fe and O as the major elements. The LA-ICP-MS analyses revealed the existence of Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Pb and even La, Ce, U. The MRS, Raman imaging and SCA revealed mixtures of Fe^{2+}/ Fe^{3+} oxides like limonite, hematite, magnetite, magnesioferrite ($MgFe_2O_4$), lepidocrocite and goethite. Sporadically, the iron oxides were found encompassing calcite, aragonite, gypsum and siliciclastic mineral phases.

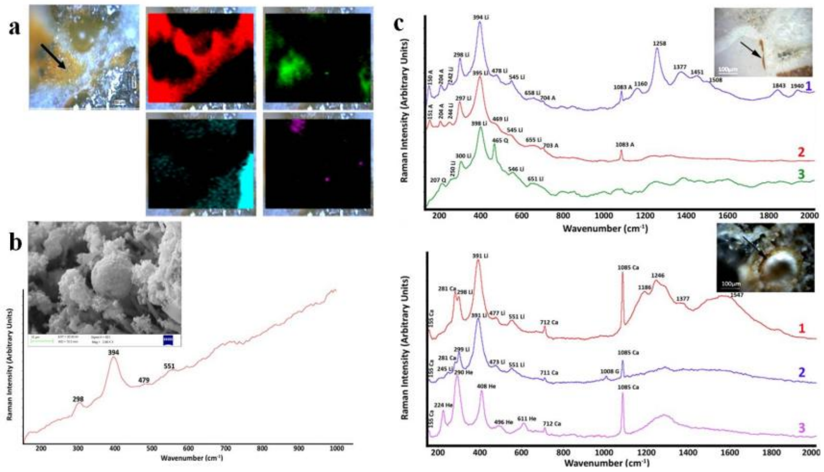

Figure 1. a) Raman Imaging, b) SEM-Raman SCA and c) MRS analyses of ferruginous cements.

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Raman spectroscopy of olivine inclusions in diamonds from Yakutian kimberlites

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Olivine occurs quite often in diamond and is one of the most common inclusions. Olivine Raman spectrum has a characteristic set of two intense lines around 825 cm^{-1} (K_1) and 857 cm^{-1} (K_2) corresponding to lattice vibration.

The study of inclusions in diamonds was carried out on confocal Raman microscope, RENISHAW company inVia, equipped with a software package Wire 3. The excitation of lattice vibrations was carried out using a laser with a wavelength of 532 nm, the diffraction grating 1200 I/mm was chosen and a CCD detector. Raman spectrometer had a resolution of 1-2 cm^{-1}. The accuracy of the wave number is not less than 0.5 cm^{-1} and calibrated using a standard of monocrystalline silicon. Spectra were recorded using x50, x20 lenses (Leica, Germany).

Olivine inclusions of 100 diamonds from 13 kimberlite pipes of Yakutia were investigated. The position of the major peaks K_1 and K_2 in the Raman spectra of olivine identified about 825 and 857 cm^{-1}. Using the results of the definition of K_1 and K_2 in the Raman spectra the Mg-number of olivine inclusions (Mg #) in diamonds from kimberlite pipes Yakutia was calculated.

Distribution according to Mg# of olivine inclusions in diamonds from kimberlite pipes Yakutia is bimodal with two high peaks of forsterite minal on 90.0-95.0 and 80.0-85.0.

So-called “residual pressure” in diamonds was defined using the values of lines shifts in the Raman spectra recorded for olivine inclusions within the diamond. The most intense bands of SiO_4-group stretching vibrations in the olivine spectrum were observed as a doublet with peaks near 825 and 857 cm^{-1} which have a pressure on the shear rate 2.81 ± 0.09 and 2.69 ± 0.12 cm^{-1} / GPa. It is found that the value of the residual pressure in diamonds ranges from 0 to 1.8 GPa.

Comparative analysis of the Raman spectra of olivine inclusions in diamonds from kimberlite pipes of Yakutian province shows that combination of Mg# and residual pressure for different pipes has a specific character. So for olivine inclusions in diamonds from Komsomolskaya-Magnitnaya kimberlite pipe, one can note the higher value of Mg and residual pressure, in the case for those of Aikhal pipe parameter data performance is noticeably lower.

Thus, the using of Raman spectroscopy for investigation of inclusions in diamonds permits to identify not only the mineral but also gives a possibility obtaining the value of its chemical composition and residual pressure. The study shows that diamonds with inclusions of olivine with a higher fayalite minal prevalence may confirm their relatively late crystallization in comparison with crystals that contain relatively higher magnesian olivine inclusions. Data on the high residual pressure in diamonds with high Mg# olivine inclusions may indicate the deep level of their origin.

Solubility and dissolution mechanism of 1,2-dichlorobenzene in subcritical water investigated in a fused silica capillary reactor by *in situ* Raman spectroscopy

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The solubility of 1,2-dichlorobenzene in subcritical water was measured using an optically transparent fused silica capillary reactor (FSCR). The total dissolution process of 1,2-dichlorobenzene in subcritical water were observed under microscope and recorded using digital camera. The solution uniformity of 1,2-dichlorobenzene during dissolution was confirmed by Raman spectroscopy. The solubility of 1,2-dichlorobenzene increased linearly with temperature increasing in the range of 257 to 294 °C. The dissolution mechanism of 1,2-dichlorobenzene in subcritical water is investigated through analysis the Raman spectra of 1,2-dichlorobenzene and water during the dissolution process in the FSCR.

Raman analysis of paintings: comparison between different excitation wavelengths in mobile systems.

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Mobile Raman spectrometers can be very powerful tools for the non-desturctive *in-situ* investigation of artworks that cannot be moved to laboratories, because of their size or their value. A major limitation of most portable instruments is the use of a single laser line, usually chosen between the very common 532 nm generated by a doubled Nd:YAG laser and the 785 nm line of a diode laser. The presence of a second laser line could help in case a strong fluorescence overwhelms the Raman signal.

Recently, we had the opportunity to study some important paintings present in Sicily. The first are the wall paintings of Sala Vaccarini at the Libraries "Civica and A. Ursino Recupero", part of the 16th century monumental complex of Benedictine Monastery in Catania. The second, are a group a few paintings from the Italian master Caravaggio (1571-1610) and from his disciples, present in the Regional Museum of Messina.

We had the opportunity to use at the same time a dual laser mobile Raman, EZRAMAN-I-DUAL Raman system (EnwaveOptronics, Irvine CA, USA), equipped with a 785 nm and a 532 nm lines, and a single laser mobile Raman from B&W Tek Inc. (i-Raman EX) equipped with a NIR source, at 1064 nm, very useful to reduce fluorescence.

Despite the very strong fluorescence, probably related to the presence of varnish, the use of different laser lines allowed to identify most of the main pigments in the oil paintings of Caravaggio and disciples. A larger number of pigments were identified in the wall paintings of Sala Vaccarini, with both instruments. Different sources identified different pigments. The various laser lines showed their different behavior during the analysis: lower fluorescence was induced by the source with the longest wavelength (at 1064 nm) but the measurements required a slightly longer time due to low scattering efficiency at high wavelengths. The highest efficiency could be reached by the lowest wavelength one (532 nm), but usually the induced fluorescence was too high to produce useful results. A good compromise was represented by the 785 nm line, whose increase in efficiency respect to the 1064 line is balanced by a worse fluorescence background.

Acknowledgements**:** Some of the results here presented are part of the Master degree thesis of Dr. Luca Grioli. The authors thank the director, Dr. Caterina Di Giacomo, Dr. Donatella Spagnolo and Dr. Gioacchino Barbera of Museo Regionale Interdisciplinare di Messina, and Dr. Francesco Nicola Neri of Superintendence of Cultural Heritage of Catania, for allowing our analyses and for their assistance during the experimental work.

Micro-Raman characterization of glaucophane

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Glaucophane is a sodic amphibole, whose name in Greel means “blue appearing”. Is a typical component of the “blue schists”, whose colour depends on the presence of this mineral. Pure glaucophane has an ideal formula $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$. Actually, it is difficult to find a pure term, because of the frequent substitutions (in particular Fe^{2+} for Mg and Fe^{3+} for Al). Glaucophane forms a series with ferroglaucophane $Na_2Fe^{2+}{}_3Al_2Si_8O_{22}(OH)_2$ and magnesioriebeckite $Na_2Mg_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$.

In this work, the relationship between the chemical composition and the Raman spectra of glaucophane is investigate.

18 natural samples, mostly coming from Alps, have been studied. The first part of the characterization was carried out by SEM-EDS, in order to have the elemental composition of the crystals in different points of each sample. Non-polarized micro-Raman spectra have been obtained on the same points with a Horiba Jobin-Yvon LabRam apparatus exiting at 473.1 and 632.8 nm.

As for other amphiboles (e.g. the actinolite-tremolite series, previoulsly studied), in the the high-wavenumber range, the OH-stretching peaks changes in number (1 to 4) and relative intensity, according to the composition. A simple model is presented to estimate the $Mg/(Mg+Fe^{2+})$ molar ratio from the areas of the OH stretching peaks.

At lower wavenumbers (150-1300 cm-1), the main Raman feature, at nearly 670 cm^{-1}, attributed to the $Si-O_b-Si$ symmetric stretching, show a splitting increasing with the relative amount of Mg. Even the splitting can be used to estimate the $Mg/(Mg+Fe^{2+})$ ratio.

Analyzing the glaucophane crystals with the same orientation respect the laser polarization, is possible to correlate the relative intensity of the peaks around ~980 cm^{-1} and ~1040 cm^{-1}, attributed to the Si-Ob-Si asymmetric stretching, with the $Al/(Al^{VI}+Fe^{3+})$ ratio.

The combination of the proposed methods allow, in fast and non-destructive way, to identify the composition of the glaucophane crystals along the join glaucophane-ferroglaucophane, estimating the $Mg/(Mg+Fe^{2+})$ ratio, and along the join glaucophane-Mg-riebeckite, estimating the $Al/(Al^{VI}+Fe^{3+})$ ratio.

High-pressure Raman spectroscopy of silicate and germanate Ca-clinopyroxenes

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Ca-rich clinopyroxenes are considered as major constituents of the Earth mantle. For this reason, they have been subjected to several experiments aimed to describe their thermal and compressional behaviors, in order to model the elastic properties of the mantle. However, little is known about the pressure-induced changes in the Raman spectra of Ca-rich clinopyroxenes. .All the samples of this study have *C*2/*c* space group and general formula $Ca^{2+}M1T_2O_6$, where M1 is populated by Mg^{2+} or Co^{2+}, and the T site by Ge^{4+} or Si^{4+}. They are all synthetic except for Si diopside. An ETH-type diamond anvil cell (DAC) was used for the high-pressure experiments. The crystalline samples were placed in the gasket hole along with some ruby chips for pressure measurements (by the ruby-fluorescence method). Methanol:ethanol = 4:1 mixture was used as hydrostatic pressure-transmitting fluid. Room and high-pressure Raman spectra were collected (exciting at 473.1 nm) up to 7.6 GPa for silicates and to 8.27 GPa for germanates, in compression and decompression, using a Jobin-Yvon Horiba LabRam Raman spectrometer.

The high-pressure Raman experiments showed no phase transition within the *P*-ranges investigated, as all peak positions vary linearly as a function of pressure. Our data confirm the previous experimental findings on Si-diopside [Chopelas et al., 2000]. In all the investigated samples, all the Raman peaks shift upon compression, but the major changes in wavenumber are attributed to the bending and stretching modes of the tetrahedral chains (*i.e.*, the building units of the pyroxene structure). Upon compression, the kinking angle between tetrahedra decreases and the wavenumber of the bending mode increases [Lambruschi et al., 2015]. Among the samples, Ge-pyroxenes show the higher *P*-induced peak-position shifts, being more compressible than the corresponding silicates.

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Raman spectroscopy of carbonaceous material from high-carbon rocks from Paleoproterozoic Soanlahty Formation, Ladoga district

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The Raman spectra of 15 samples of high-carbon rocks (up to 60 wt.% C) from the Soanlahty Formation metamorphosed in a higher-grade greenschist-facies ($P<3$ kbar) were obtained using the 532 nm excitation laser wavelength. There are the G (graphite) band at 1582 cm^{-1} and some defect bands on the first-order region. The main defect band D1 at 1352 cm-1, D2 which makes a shoulder on the G band have been detected within all the samples. Both bands attribute to in-plane defects. The D1/G intensity ratio is usually less than 1.0. On the second-order region we focused on the S1 peak at~2700 cm^{-1}. It is known that this band is very sensitive to structural changes along the C axes. The splitting of S1 peak indicates the appearance of a three-dimensional ordering in the structure of the carbonaceous material. We divided all the Raman spectra into two types: with a symmetrical (or lightly asymmetrical) and an asymmetrical profile of the S1 band. Very broad and weak bands: the D3 at ~1500 cm^{-1} and the D4 at ~1245 cm^{-1} mostly appear on the Raman spectra of the first type. These bands have been attributed to defects outside the plane aromatic layers such as tetrahedral and amorphous carbon. It can be assumed that the interlayer defects mostly prevent the formation of three-dimensional order. The G and D1 peak width, center positions of the G, D1, D2 bands and the D1/(G+D1+D2) area ratio are nearly identical for the both types. The Raman parameters (the D1/G intensity ratio, the D2/G intensity ratio) reveal a higher degree of structural organization of the second type carbonaceous material which can be considered as graphite. Using Raman carbonaceous material geothermometer [1], we defined that three-dimensional structure of carbon in the Soanlahty Formation could have been formed at around 450 to 480^{o}C.

The carbonaceous matter from the high-carbon rocks which have pelitomorphic massive texture demonstrates both types of Raman spectrum. Furthermore, some spectra with the D1/G intensity ratio more than 1.0 have been obtained. But we found only crystallized graphite in strained high-carbon rocks or along schistosity planes in massive ones. The rocks are usually recrystallized along the strain zones. It can be supposed that shear stress and fluids have affected the progress graphitization of carbonaceous material.

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Spectroscopic properties of carbon nanotubes filled with mercury (I) chloride

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Carbon nanotubes (CNT) present an impressive group of graphitic structures having many remarkable electronic, chemical, and mechanical properties. They are particularly interesting for the nanomaterials research in order to develop substances with predefined properties oriented towards specific technological applications. In this work the modification of CNT by intercalation of mercury chloride was studied by spectroscopic methods.

Single-walled (SWNT) and multi-walled (MWNT) CNT filled with the crystals of mercury (I) chloride were obtained for the first time in the melt of CNT+$HgCl_2$ mixture at 290^{o}C. Structural and electron properties of filled CNT were studied by TEM, Raman spectroscopy, X-ray photoelectron spectroscopy and NEXAFS. The obtained data indicate that the reaction between CNT carbon and mercury (II) chloride occurred to produce Hg_2Cl_2 molecules regularly arranged inside CNT. The model of Hg_2Cl_2 molecular stacking in CNT (Fig. 1) was suggested, such that the nanotube axis is perpendicular to the plane (001) of the crystal.

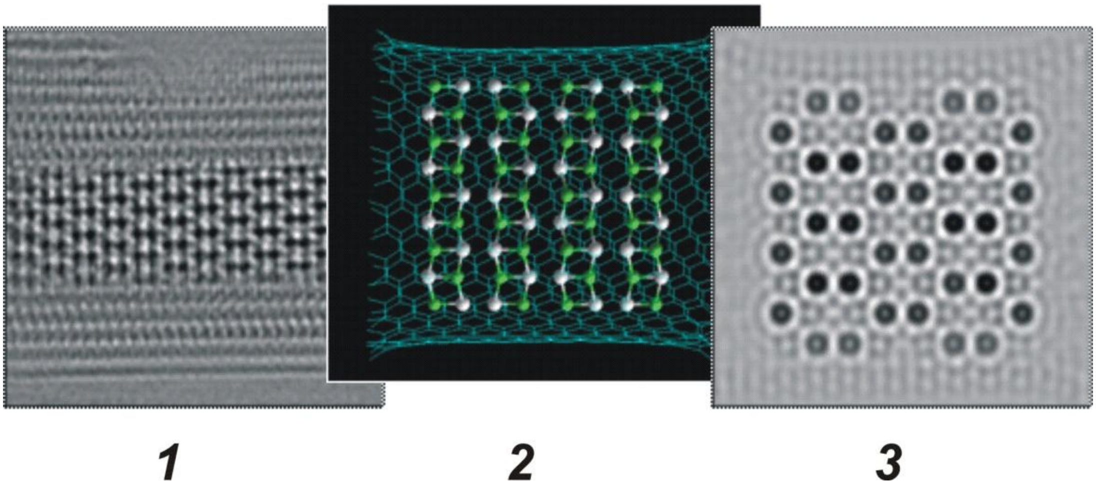

Figure 1. TEM photo (1), the structure model (2) and modeled diffraction image (3) of CNT filled with Hg_2Cl_2.

The spectroscopic examination of the obtained samples indicates the charge-transfer between the atoms of CNT and mercury (I) chloride, in agreement with the previous studies of CNT filled with heavy metal halides [1].

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Alteration of Raman spectra of micron-sized solid particles induced by laser irradiation

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The Raman Laser Spectrometer (RLS) is an instrument on board of the future ESA ExoMars mission [1]. It will analyze crushed to micron-sized powder samples in a low pressure Martian atmosphere. Such micron-sized (poly)crystalline solid particles might be heated by laser irradiation during the Raman measurements [2]. Here, we report on the laser-induced alteration of Raman spectra of such particles. Raman spectra of the rock forming minerals olivine and pyroxene were collected with different laser intensities and at different ambient temperatures. We compared their behavior with Raman spectra taken from well investigated crystalline silicon particles of the same size range [3]. Our analyses indicate that laser-induced heating results in a broadening and shifting of characteristic Raman lines at the Stokes and anti-Stokes spectral regions. For elementary crystalline silicon particles with median sizes below 250 µm a significant local temperature increase and relevant changes in Raman spectra were observed. In comparison, significantly weaker laser-induced Raman spectral changes were noticed in the chemically and structurally more complex and more transparent rock-forming silicate minerals, even for lower grain sizes. Thus, it can be stated that laser power densities that will be realized in the RLS ExoMars instrument [4] should cause only low heating effects and, thus, negligible frequency shifts of the major Raman lines in common silicate minerals such as olivine and pyroxene.

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Micro-Raman and multidisciplinary characterization of Bronze Age pottery from *terramare* settlements in Northern Italy

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Ceramics of Santa Rosa in Poviglio, Reggio Emilia, Northern Italy, dating to the Middle and Late Bronze Age (XVI-XVII century BC) have been studied through a multi-disciplinary approach: radiography, X-rays fluorescence spectroscopy and μ-Raman spectroscopy. The study allowed to focus on the manufacturing technique and to obtain chemical and mineralogical information.

Radiographic analysis revealed a production of familiar type with the use of colombino technique for all tested samples, excluding the loops that have been modeled separately and applied on the body at a later time. No major compositional variations in the ceramics were found by X-rays fluorescence, apart from the calcium content.

The micro-Raman measurements on the surface revealed in almost all the samples anatase, hematite, quartz, calcite and feldspars, suggesting that the ceramics were fired at a temperature between 800 and 900 °C.

The abundant hematite implies a reducing cooking environment, even if the presence of magnetite indicates incomplete phase transformations, probably due to too short cooking times or firing in not totally controlled atmosphere, as common in open-air or pit furnaces.

Raman spectra reveal ubiquitous amorphous carbon, related to an incomplete combustion of the organic material, present in the clay, or due to the use of wood as a fuel, in direct contact with ceramics.

The results give further insight in the pottery production of terramare settlements in the central Po valley, in Emilia-Romagna, Northern Italy.

Micro-Raman spectroscopy of melt inclusions in sapphires

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Introduction: Sapphire deposits are widespread throughout Southeast Asia and Africa [1, 2]. The Nezametnoye deposit is recognized as one of the most prospective placer deposits of sapphire in Russia. Research of primary inclusions in sapphires makes it possible to obtain accurate information on the condition of mineral crystallization. The aim of this paper was to determine the composition of primary inclusions in sapphires by micro-Raman-spectroscopy.

Materials and methods: Sapphires contained melt inclusions, mineral inclusions, and fluid inclusions. Primary melt inclusions in samples composed of transparent glass and gas bubbles, and sometimes contained one or more mineral phases.

Primary melt inclusions were analyzed by Raman spectroscopy using a Horiba LABRAM HR 800 spectrometer coupled with a Si-based CCD (charge-coupled device) detector and a Melles Griot 514 nm Ar^+ green laser. These analyses were performed at the Primorye Shared Analytical Center for Local Elemental and Isotope Analysis, Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS, Vladivostok).

Results and Discussion: Primary melt inclusions consist of carbon dioxide with peaks 1284 and 1385 cm^{-1}, transparent glass and mineral phase of ilmenite with peak at 680 cm^{-1}. Methane has not found. Secondary fluid inclusions are presented by single-phase inclusions that contain carbon dioxide as liquid or gas and have peaks 1284 and 1385 cm^{-1}.

Early researchers who examined glasses with primary heated melt inclusions have concluded that the source of the sapphires was the rare-metal pegmatite, greisens, and metasomatites associated with the Mesozoic granitoid bodies underlining this deposit.

Mineral phases of ilmenite in the primary melt inclusions show that the process of the corundum formation is more complicated and requires further investigations.

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The Raman and visible near-infrared spectral mixing effects of jarosite endmembers and solid solutions

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Jarosite ($KFe_3(SO_4)_2(OH)_6$), has been identified on Mars by Mössbauer spectrometer aboard Opportunity rover [1] and Na-jarosite and H_3O-jarosite were also suggested to exist on Mars [2,3]. Some recent work has been done on the spectral variations caused by the sodium substitution of postassium or the iron substitution of aluminum [4,5]. Here we focuse on the vibrational (Raman) and visible near-infrared (VNIS) spectral mixing effects between different volume ratios of three jarosite end-memebers (K, Na, H_3O-jarosite) and their corresponding solid solutions (K-Na, K-H_3O, Na-H_3O jarosite solid solutions) with intent to quantitative characterize their differences and spectral mixing effects, which are invaluable for their potential in-situ (by Raman) and remote sensing detections (by VNIS). Three jarosite end-members and five jarosite solid solutions with different alkali molecular ratio (i.e. K-number=100×K/(K+Na+H_3O), Na-number=100×K/(K+Na+H_3O)) detected by ICP-MS and SEM-EDS) are hydrothermally synthesized in 140 °C. Figure 1 shows the preliminary work of Raman characterizations of jarosite end-members and jarosite solid solutions, whose Raman spectral features are key information for their mineral identifications using future Raman payloads (e.g. ExoMars 2018 and Mars 2020).

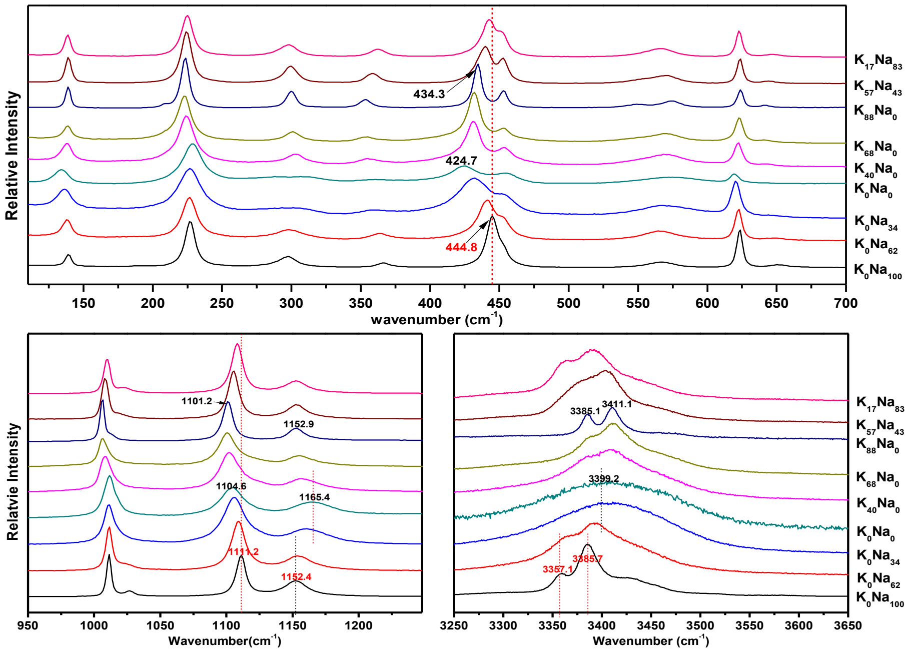

Figure 1. Raman spectra of synthetic jarosite end-members and solid solutions with different alkali ratios.

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Raman spectroscopy of hydrothermal and weathered shungites

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Raman spectroscopy is widely used to characterize the structural ordering of carbonaceous matter (CM). Numerous studies have been focused on change of the CM structural ordering in metamorphic processes unlike the CM transformation during weathering. We studied the CM from sedimentary-volcanic Precambrian rocks of the Zaonega Formation in the Onega Basin, Karelia, Russia (shungite), experienced metamorphic transformation and weathering.

The Raman spectra for studied shungites are consistent with poorly ordered CM. Two types of unweathered shungites with different structural ordering were distinguished on the basis of spectral differences. The most abundant shungite has the relatively low structural order because of high parameter $R1=I_{D1}/I_G=1.4$, D1 band with FWHM = 56 cm^{-1} and D3 and D4 bands in the absence of D2 band. In the second-order region it is characterized by bands 2695 cm^{-1} и 2940 cm^{-1} with low and equal intensities ($I_{2700}/I_{2900}=0.94$). Another type is more ordered shungite, that is characterized by lower parameter R1 =0.72, and the D1 band width is closed to the most abundant shungite. The peak decomposition demonstrates the presence of D2 band, typical for more ordered CM, D3 and D4 bands have low intensities. Additional arguments to the higher degree of structural ordering of this shungite are the spectral differences in the second-order region which include the intensity increase of band at about 2700 cm^{-1} ($I_{2700}/I_{2900}=2$). These data correspond to the increasing of interlayer ordering. Applying the Raman CM geothermometer, as proposed by [1], the metamorphic temperatures were determined to be around 420 °C for the shungite, in contrast to the most abundant shungite with estimated temperatures of 340 °C. So the shungite is believed to be hydrothermally altered. Similar changes were observed in the model heating of primary shungite upto the temperature 500 °C in air.

Weathered shungites, forming on the surface of the both shungite types, have the lowest degree of structural ordering. It is supported by the increasing of D1 band width up to 75 cm^{-1} and disappearance of bands in the second-order regions, though the intensity of D1 band is lower than that of G band. Scattering of spectral parameters for weathered shungites is significant, indicating the high shungite heterogeneity, as compared with unweathered shungites. It might be caused by the occurrence of shungites of various degree of weathering. Thus the Raman spectra of unweathered and weathered shungite display the changes in intralayer and interlayer structural ordering.

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Carotenoid found in fluid inclusions of ancient halite: evidence from Raman spectra

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As some evaporites were found on Mars, to discover the potential of life (or microorganisms) and organic matters in evaporate sedimentary environment has been a hot spot for exploration on Mars. Previous studies indicated that halophilic algae and prokaryote are contained in high salinity ecosystem [1, 2, 3]. In this study, we performed petrologic and Raman spectroscopic analyses on fluid inclusions in ancient halitecollected from Chaka Salt Lake, west of China. Through observation under microscope, results show that some microorganism or organic fragment material (showing green rounded or subcircular grains) were trapped in primary fluid inclusions (Fig. 1). According to previous studies [1, 2, 3], under optimal growth conditions, dunaliella algae are typically green from chlorophyll pigments in their chloroplasts. So, it indicates that the green rounded materials in fluid inclusions are dunaliella algae. These green spots were identified by Raman spectroscopy. Experimental results show that there appear obvious Raman bands at 1010 cm^{-1}, 1160 cm^{-1} and 1525 cm^{-1} respectively, as shown in Fig. 1. Comparing to the results of Winters et al. [2] and Marshall et al. [4], it can be confirmed that the three Raman bands are carotenoid pigments of dunaliella. Our study confirms that fluid inclusions in halite are good containers for preservation of ancient bacteria or organic matters, and Raman spectroscopy has good potential to identify halophilic archaea in fluid inclusions. Based on these two points, it is promising for finding more information of ancient living beings on Mars or old samples on Earth.

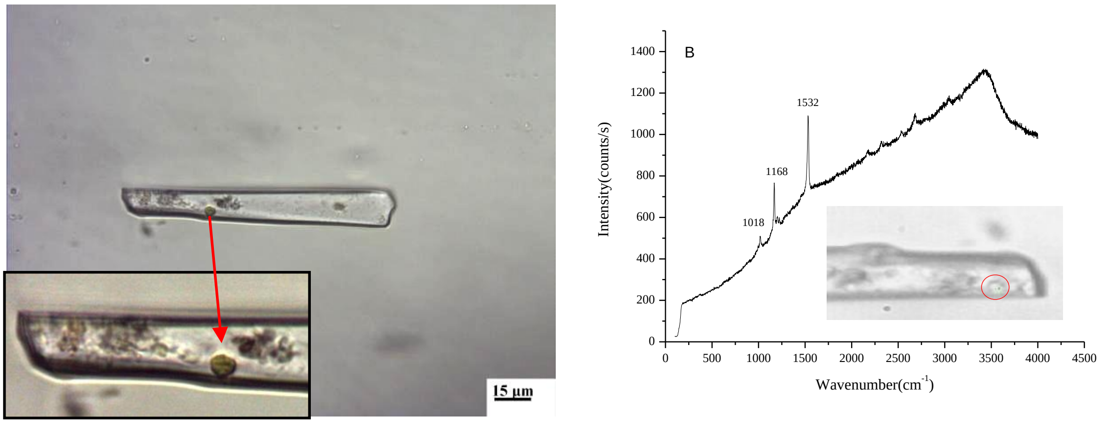

Figure 1. Micrographs and Raman spectra of dunaliella algae in fluid inclusion

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Phonon spectra of rare earth pyrochlores $R_2Ti_2O_7$ (R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu): ab initio calculations

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Ab initio calculations of crystal structure and phonon spectra of rare earth pyrochlores $R_2Ti_2O_7$ (R = Gd-Lu) have been done. The frequencies and irreps of phonon mode have been defined at Γ point. For R = Tb, Tm, Yb similar calculations were executed for the first time. The hydrostatic pressure influence upon phonon spectrum of $Gd_2Ti_2O_7$ up to 35 GPa have been investigated. Results of the calculations are in good according with the available experimental data.

In this work calculations of the phonon spectra of rare earth titanates $R_2Ti_2O_7$ have been done within MO LKAO approach in the CRYSTAL09 program [1]. Hybrid functionalities DFT B3LYP and PBE0 have been used.

It is shown that it is possible to receive the good description of structural, dynamic and elastic properties of the crystal lattice of $R_2Ti_2O_7$, having included 4*f* shell of rare earth ion in pseudopotential.

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Raman (532 and 785 nm) study of glass beads from the Kongo Central province, Democratic Republic of Congo (DRC)

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Glass beads play a significant role in the KongoKing project, as they are ubiquitous in funerary contexts, and are thought to be of European manufacture. Typological comparison with European productions suggested specific production centers (Venice, Amsterdam, Germany, etc.). However, European beads in Western Central Africa have yet to be studied from the chemical point of view. Therefore, in order to better understand the technological know-how in use in glass making workshops in Europe, some non-destructive analysis were performed. Raman spectroscopic investigation, as well as handheld X-ray fluorescence (hXRF) analysis and chemometrics were successfully applied to a first set of glass beads from the elite burial site in Kindoki [1]. A new set of samples from other sites in the surrounding underwent non-destructive chemical research, similar to the one described above. By applying the same analytical protocol to the two sets of beads will contribute to a better comparison between these samples.

A non-destructive, multi-technique approach, is used, which allows for a full characterization of the glass, in terms of matrix (stabilizers, flux, etc.) and colour/opacity. In fact, Raman spectra of glassy materials contain reliable information regarding the glass network itself, as the effect of cations other than Si affect the angles and bond lengths, producing shifts and different relative intensity ratios of the silicatic network vibrations [2, 3]. Moreover, crystalline phases affecting the colour and transparency of glass can be successfully identified using this technique. On the other hand, hXRF analysis can clarify the chemical nature of some colourants (e.g. the detection of elemental Co in blue glasses) and, when coupled with chemometrics, groups of similar beads can be established. So far, no chemical analysis were performed on Western central African archaeological materials, therefore the comparison will be limited. Finally, this information will be included into archaeological typological catalogues and will provide additional information on trading routes and cultural processes taking place between Europe and the Kongo Kingdom during the last five centuries.

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Raman spectroscopy application in the study of fluidal graphitic mineralization

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Raman spectroscopy has become the most widely used tool to study carbonaceous matter (CM) and natural samples from a variety of geological settings [1-6].

The aim of this work was estimating of temperature conditions of carbonaceous metasomatites formation in fault zones (South-Eastern Siberia, Russia) through study of ordering degree of natural fluidal graphitic carbon by detail analysis of high resolution Raman spectroscopy data [7].

The ordering degree of the naturally heterogeneous CM is estimated by the relative area of the graphitic carbon defect band (R2 ratio) with Beyssac`s Raman geothermometer [6]. The calculation of temperature formation of metasomatic CM was performed by Beyssac`s formula $T\ ^\circ C = -445 \times R2 + 641$. Temperature can be estimated with accuracy ± 50 °C in the temperature range of 330–650 °C [6].

Analysis of the calculations shows that the formation of the most ordered CM metasomatic of the Tunkinskii fault ($R2 = 0.14–0.15$) was formed at the range 450–580 °C. CM metasomatites of the Ospinsko–Kitoiskii ultrabasic massif are characterized by heterogeneity of ordering. The temperatures of their formation are estimated within 360–500 °C. The wide range of R2 values (0.37–0.68) of CM of vein bodies points to quite wide temperature variations in local conditions, which are limited by the fault sizes. Samples from metamorphic carbonaceous schists of the Ospinskaya and Toltinskaya formations are characterized by a low degree of CM structural ordering with R2 variations from 0.46 to 0.58 corresponding to the narrow temperature range of 380–430 °C of graphitic carbon formation.

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Martian analogue samples, their Raman biosignatures, and degradation by the cosmic radiation environment

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The success of an astrobiological search campaign on Mars, or other planetary bodies in the solar system, relies upon the reliable detection of biosignatures of past or present microbial life. Spectroscopic techniques are ideally suited for triaging targets potentially containing biosignatures, which can be confirmed by supporting instrumentation. Here we discuss the complementary use of Raman and FTIR spectroscopy for the detection of biosignatures of microbial life colonising a diverse sample set collected from martian analogue sites around the world, including the Mojave desert, the Atacama desert and the Antarctic Dry Valleys [1]. Results are presented on the Raman and FTIR spectroscopic characterization of these martian analogue samples, both in terms of the mineralogical context and the detectable biosignatures. Raman spectroscopy is sensitive to specific biological pigments including carotenoids, chlorophyll and scytonemin, and FTIR reveals the presence of more generic cellular organic molecules including fatty acids, polysaccharides and proteins. A further key consideration in the detectability of past or present microbial life on Mars is the degree to which these Raman biosignatures will have been degraded by the long-term bombardment of the martian surface (and penetrating into the subsurface) by the energetic particle radiation of the unshielded cosmic ray flux [2,3,4,5,6].

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The mineralogical composition of the rocks deposit “Elovoe” (Northern Khakassia)

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The field “Elovoe” is located in the northern part of the gold-bearing of Saralinskiy district within Yuzikskogo ore field. The area of “Elovoe” field is 29.1 km^2. The administrative area is included in the Ordzhonikidze district of the Khakassia Republic [1]. The geological and structurally deposit area is confined to volcanic formations Sargainskogo graben (D1) in the west contact [2] and the carbonate deposits of Yuzikskoy brachyanticline (V) [1].

Mineralogical and petrographic studies revealed the basis of 35 samples from three wells and 10 thin sections. For the purpose to show the variety and mineral content of the rocks involved in the geological structure of the area some samples were selected. According to the results of petrographic data revealed the following: volcanics of basic and intermediate composition (metadolerity and metaandesites), metasomatic rocks, calcareous breccias with effusive filler, marbled limestone, breccia effusive with chlorite–carbonate cement, tufoalevrolity metasomatic and calcareous sandstones participate in the geological structure of the deposit “Elovoe”. Cracks are also observed in separation of carbonaceous matter, orpiment, realgar.

Samples are of endogenous (hydrothermal–metasomatic) and exogenous (oxidation zone) origin. Hydrothermal–metasomatic mineralization are associated with change of host rocks: potassium metasomatism, albitization, silicification, propylitization, listvenitization, beresitization [1]. Primary and secondary sulphide oxidized ores in mineralogical composition are distinguished. The metasomatic oxidation zone as a result of supergene processes are turned into clay–like rock, composed of hydromica 50 – 60 %, 30 – 35 % quartz, limonite 5 – 10 %, jarosite, kaolinite and are the products of the zone of quartz–hydromica supergene leaching. Hub gold are pyrite, carbonaceous matter. Gold finely disperses to 0.2 mm in the ore [1].

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Raman spectroscopy – a tool for evaluation of shock metamorphism and semi-quantification of mineral phases from chondritic meteorites

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Chondritic meteorites of varying chemical and petrologic types (LL3 – L5 – L6) with S5 – S6 shock grades have been studied to evaluate relative amount of shock metamorphism and to estimate X_{Mg} of olivine and pyroxene from Raman spectral parameters. These chondritic meteorites are essentially composed of olivine + orthopyroxene + Na-plagioclase ± clinopyroxene ± apatite ± merrillite + opaque minerals (including magnetite, chromite, troilite, kamacite and taenite). The shock features in chondrites have been identified by the presence of high pressure polymorphs of olivine like wadsleyite (~ 917 cm^{-1}) and ringwoodite (~ 797 cm^{-1} and 844 cm^{-1}), transformation of plagioclase to maskelynite and development of pyroxene glass due to high intensity impact induced shock deformation. The presence of extraterrestrial diamond polytypes (like 6H, 8H, B-C phase; size ~ 1-3 μm) in chondritic meteorites was determined from characteristic Raman peaks at 1308 cm^{-1}, 1314 cm^{-1}, 1315 cm^{-1}, 1332 cm^{-1}, 1359 cm^{-1} 1360 cm^{-1}, 1504 cm^{-1} and 1585 cm^{-1} respectively. These indicate an escalation of impact shock pressure ~ 18 - 45 GPa [1]. The Raman spectra of chondritic olivine and pyroxene systematically vary within a certain limit depending on the chemical composition and crystal structure of the phases and can be useful to determine the chemical composition of mineral phases in a semi-quantitative way. The two dominant Raman stretching vibration modes of olivine at ~ 820 cm^{-1} (κ_{1}) and ~ 856 cm^{-1} (κ_{2}) with $\omega = \kappa_1 - \kappa_2$ has been used as an index for semi-quantification of X_{Mg}, which increases with increase in ω values. Correlations have been made between Raman peak positions (820 cm^{-1} and 856 cm^{-1}) and X_{Mg} of olivine [2] to obtain a second degree polynomial equation which broadly shows fair degree of accuracy when compared to analyzed EPMA data in terms of semi-quantification of X_{Mg} in olivine ($^{Ol}X_{Mg}$). The Raman spectral peaks of pyroxene (mostly orthopyroxene at ~ 340, 660, 680 and 1014 cm^{-1}) when compared with $^{Opx}X_{Mg}$ as derived from mineral chemistry show systematic lowering of Raman peak values with decreasing $^{Opx}X_{Mg}$. Thus, this concept of Raman spectroscopy can be used in unmanned planetary surface exploration missions to determine the mineral chemical compositions.

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Portable Raman spectroscopy applied to verifying jade and quantifying its jadeite content in Olmec ceremonial stone axes from El Manatí, Veracruz, Mexico

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The El Manatí archaeological site in Veracruz State, Mexico, is famous for its deposits of ceremonial stone axes and beads from the Olmec culture (1300 - 1000 BC). A DeltaNu "Inspector" portable Raman spectrometer was carried from the *Muséum-MNHN-Paris* to the El Manatí archive at the *Centro-INAH-Veracruz* for a remote analytical operation for *non-destructive* hand-held physico-chemical analysis in order to try to identify some of the minerals present (*without* having any thin sections available). The key points of interest were: which objects, if any, contain the high-pressure minerals jadeite or omphacite and, if so, then with what mol. % Jd {jadeite : inosilicate $NaAlSi_2O_6$} in the solid-solution jadeite-diopside-hedenbergite which is that of jadeite-jade. The mol. % is obtainable semi-quantitatively from the Raman spectral wavenumber of the Si-O-Si vibration band. With no sample treatment of any kind, 93 Raman spectra were obtained directly from 41 fine-grained ceremonial stone axes or beads of greatest potential interest. The qualities of the mineral identifications were extremely variable from "excellent" to "poor". Jadeite provided most of the better identifications as its Raman signal is relatively strong and its wavenumbers well-known. Jadeite (95 mol. % Jd down to 75 mol. % Jd) was discovered, with confidence, in 13 axes and 4 beads, omphacite in 3 axes and 2 beads, and diopside-hedenbergite in 8 axes. Other minerals established, or only suggested from poorer spectra, include quartz, albitic plagioclase, serpentine, zoisite, dolomite and semi-amorphous carbon (from burning). Garnet was not found in these 41 artefacts, but it is known in some other axes from Mesoamerica that are, or probably are, eclogites. These results provide important mineralogical information for archaeologists studying rock-types used in Mesoamerican cultures. However they do not, of course, indicate any particular provenance of the high-pressure jade source rocks and it will be very difficult to advance in that search without making some thin sections and making detailed conventional petrological studies to try to recognise some locality-dependent distinguishing criteria. Rare occurrences of eclogite, omphacitite and/or jadeitite are known "nearby" in Mexico, Guatemala [1-2], Cuba and the Dominican Republic.

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Raman spectroscopic study of carbonate of $(Na,K)_2Ca(CO_3)_2$ solid solution

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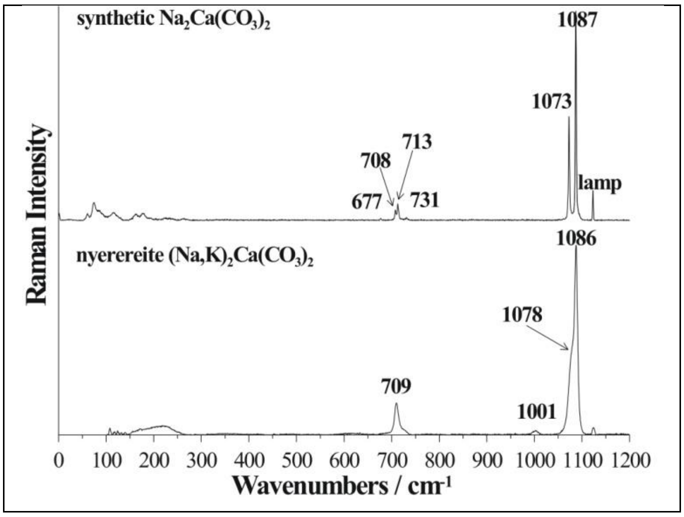
Nyerereite $(Na,K)_2Ca(CO_3)_2$ is a rare alkali-bearing carbonate, which is not stable in contact with the atmosphere. Nyerereite is very important for magmatic petrology, because can be used as indicator of mantle melts composition. Nyerereite in natural samples appears exclusively as micro-scale phases within crystalline inclusions and daughter phase in melt inclusions of different rocks minerals, except those from the Oldoinyo Lengai modern natrocarbonatites, where this mineral occurs as major rock-forming phase. Pure end-member $Na_2Ca(CO_3)_2$ was not identified in nature and nyerereite always contains some impurities of K, Sr, Ba, S, P, F, and Cl. The identification problems of nyerereite with small sizes by WDS and EDS analyses are well known. Non destructive Raman spectroscopic study can solve the problem of identification of this mineral. Here we present the results of Raman spectroscopic investigation of well-studied samples of synthetic pure $Na_2Ca(CO_3)_2$ (space group $P2_1ca$, commensurately modulated structure [1]) and nyerereite (space group $Cmc2_1$, incommensurately modulated structure [2]).



Synthetic phase has strong bands occurring at 1087 and 1073, medium bands at 713 and 708, weak bands at 731 and 677 cm^{-1} assigned to the $(CO_3)^{2-}$ vibration. Nyerereite has strong band occurring at 1086, with a weak shoulder at 1078, a medium band at 709 cm^{-1} assigned to the $(CO_3)^{2-}$ vibration and a weak band at 1001 cm^{-1} assigned to the $(SO_4)^{2-}$ vibration (Figure). Thus, the incorporation of large cations (K, Sr, Ba up to 0.4 afpu, K_2O up to 7.5 wt.%) and other anionic groups in nyerereite leads to: (i) incommensurately modulated structure; (ii) smaller number of Raman bands assigned to the $(CO_3)^{2-}$ vibration, but another vibration bands (e.g. $(SO_4)^{2-}$) may be present.

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Raman spectroscopy as a tool to determine the shock pressure and temperature conditions suffered by Libyan Desert Glasses

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Libyan Desert Glass (LDG) is a 28.5 million years old melt product found in the Western Desert of Egypt. The formation of this impact glass is still unknown. Fortunately, Raman spectroscopy could be a very valuable tool for the determination of the formation conditions of these mysterious materials. Actually, Raman spectroscopy is able to detect changes in the structure of molecules due to pressure and temperature variations. With this aim, several samples of LDG specimens have been analysed by means of Raman spectroscopy (785 nm and 514 nm wavelength lasers) with 1 cm^{-1} spectral resolution, checking the displacements on Raman bands due to pressure and temperature variations during the formation of LDGs.

Regarding the glassy matrix spectra, it was possible to obtain the temperature at which the melt was subjected following the polymerization index (I_p) developed by Colomban et al. [1]. Moreover, different types of anhydrite (A-I and A-II) and displaced quartz spectra were detected in the same samples that lead to think that samples experienced different temperature (300-1180ºC) and pressure (26 GPa) conditions until its definitive cooling.

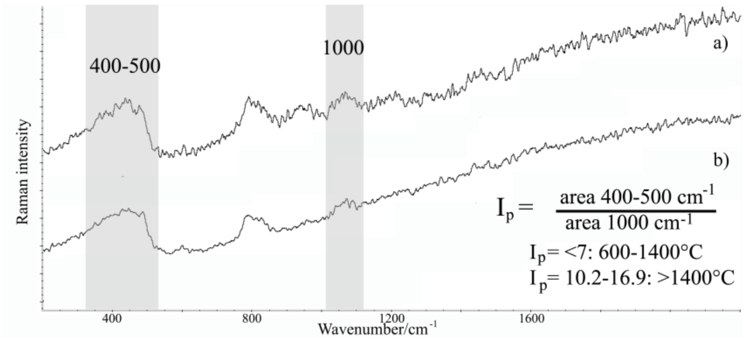

Figure 1. Raman spectra of LDG glassy matrix with their temperature formation following Colomban et al. index. a) 600-1400ºC, b) >1400ºC.

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Raman study of phengite at *P-T* conditions modeling cold slab subduction

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Phengite $K(Al,Mg)_2(OH)_2 (Si,Al)_4O_{10}$ is potassium dioctahedral mica. Its structure is similar to that of muscovite, but with high content of Mg. Phengite as water transporter is among the most deep hydrated minerals in subducting slabs [1].

We present Raman study of phengite compressed in water medium at simultaneously high *P-T* conditions up to 500 °C and 12.2 GPa, in order to model its behavior at conditions of cold slab subduction and to detect possible non-quenchable states (polymorphism, amorphization and dehydration). Raman spectra of phengite exhibit high stability up to maximal *P-T* parameters used (Fig. 1). Its Raman bands slightly decrease in intensity and widen in the range of 300-500 °C. Monotonous *P*-dependences of the wavenumbers of strong bands at 263, 703 and 3612 cm^{-1} (the last is O-H stretching mode) prove that no transitions are available at high *P-T*. According to the data [1], phengite can transform to K-hollandite at $P>10$ GPa, $T>500$ °C, however, we did not observe this transformation that could be caused by small time (~4 h) in our experiment or different composition of phengite samples. Thus, our in-situ experiments prove highly baric and temperature stability and absence non-quenchable transitions of phengite.

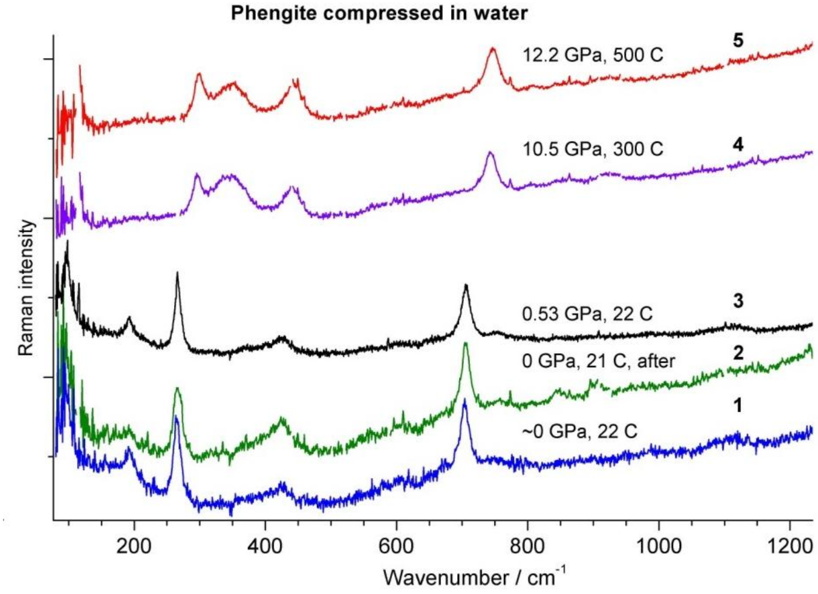

Figure 1. In-situ Raman spectra of phengite compressed in water at high P-T parameters.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (projects No. 14-05-00616 and 15-55-45070-IND) and the Russian Science Foundation (project No. 15-17-30012).

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Determination of Raman spectrum of lonsdaleite in Popigai impactites

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The vibrational spectrum of lonsdaleite, having thetrahedral coordination of carbon atoms, that is the relative to diamond, is still puzzle because no single-crystalline samples are available. There are only nano-sized aggregates of natural or synthetic origin [1].

Experimental Raman spectrum of lonsdaleite in Popigai impactites is recorded, using 325 nm exciting line, and extracted from diamond-lonsdaleite aggregate Raman spectra. This experimental spectrum is compared with *ab-initio* calculated Raman spectrum of lonsdaleite, determined with CASTEP program package (Fig. 1).

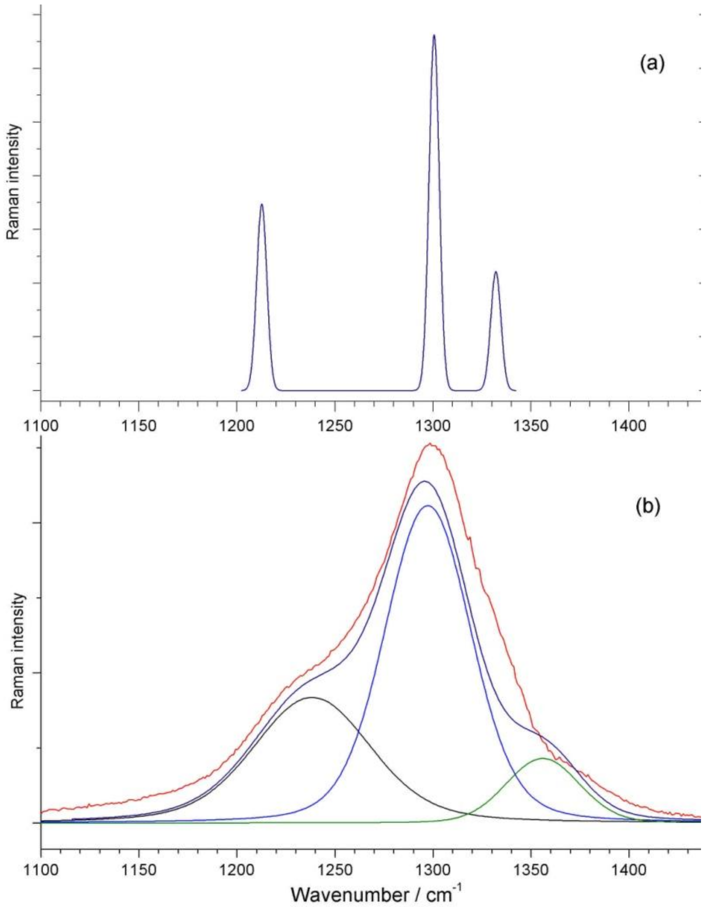

Figure 1. The ab-initio calculated Raman spectrum (a) and experimental Raman spectrum of lonsdaleite recorded from Popigai impactite (nano-aggregate of 28% lonsdaleite - 72% diamond, where the last spectrum is subtracted) (b).

Acknowledgments: This work was supported by Russian Science Foundation (project No. 15-17-30012).

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The challenges of Raman spectroscopy for discrimination between chloride minerals in natural inclusions – example from the Siberian igneous province

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Raman spectroscopy is well accepted as a prime analytical technique for identification of daughter minerals in inclusions, allowing to constrain the composition of ore-forming paleofluids. Reference spectra of several hydrated chlorides and anhydrous complex chlorides are now reported [1, 2]. Here we present comparison of Raman data from natural inclusions with spectra of reference and discuss the difficulties in identifying of Ca- and Fe-bearing daughter minerals. The samples were taken from Siberian LIP: 1) the contact zone of dolerite sill with evaporites, 2) halite-magnetite rock from volcanogenic deposit.

Fluid inclusion studies on the metamorphosed halite (*Lena-Tunguskaya province*) revealed the presence of both hydrates and anhydrous chlorides. Raman spectra are typical of $CaCl_2$-hydrates, and the position of peaks match with the experimentally determined spectra [2]. Fluid evolution of *Korshunovsk Fe-ore deposit* have been studied using inclusions in different minerals, related to several stages of magnetite formation. Raman spectroscopic study of inclusions in halite detected that spectra of hydrates do not fit with any reference spectra [1, 2]. Inclusions in apatite and forsterite without liquid water at room temperatures commonly contain along with chlorides uknown OH-bearing minerals (3570 cm^{-1}) with strong peak at 66 cm^{-1} in inclusions in apatite and with main peak at 690 cm^{-1} in forsterite. The Raman spectra are different to spectra of Fe-K-bearing chloride daughter minerals from salt melt inclusions from diorite-hosted porphyry gold deposit Biely Vrch, thus the presence of $KFeCl_3$, NaK_3FeCl_6 (rinneite) and K_2FeCl_6 can be excluded [3]. Raman analyzes revealed complex composition of salt melt inclusions from magmatic-hydrothermal environments. Numerous phases can be expected from relevant diagrams. Chemical synthesis of $CaFeCl_5$, $MgFe_2Cl_8$ and $KCaCl_3 \cdot 2H_2O$ can be most helpful in identification of unknown phases.

Acknowledgments: This work was supported by grant RFBR 15-05-09345.

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The differentiation of Raman spectra of salts using multivariate data analysis

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Raman spectrometers are planned to be used for future planetary missions, for example to Mars. One challenge is to detect and identify various types of salt. Salts lower the freezing point of water and, therefore, support the existence of liquid water which is a necessary condition for the presence of life on Earth.

In this study we investigated 14 different salt types using confocal Raman spectroscopy. These salts (NaCl, KCl, NaBr, NaI, LiCl, Na_2SO_4, K_2SO_4, $CaSO_4{\cdot}2H_2O$, $MgSO_4{\cdot}H_2O$, $MgSO_4{\cdot}7H_2O$, $Fe_2(SO_4)_3{\cdot}xH_2O$, $CaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$ and $FeCl_3{\cdot}6H_2O$), among others, were chosen according to their possible extraterrestrial occurrence mainly regarding Mars [1, 2 and references therein] and the icy moons Europa [3, 4] and Enceladus [5, 6].

Most of the samples could be clearly distinguished by their major and minor Raman bands, whereby the identification of diatomic salts was challenging because only some Raman lines with poor signal-to-noise ratio could be seen in the low relative wavenumber region.

Additionally, the identification of the salt samples was done by applying multivariate data analysis, in particular Principal Components Analysis (PCA). Using this method we developed different models which are well suited for the differentiation and identification of the examined salt. An objective criterion to determine the separability of the clusters of the PCA and, therefore, the quality of the models is realized by applying the cluster analysis [7]. Therein, the probabilities for distinguishing clusters representing different salts were calculated. A high degree of separation between the different clusters was achieved.

On the basis of these results, it can be concluded that Raman spectroscopy combined with PCA and cluster analysis is an appropriate method to detect and identify various types of salt. For that reason, the next step would be to investigate frozen salt solutions which may exist on Mars and the icy moons mentioned above.

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Raman and magnetic analysis of natural terrestrial glasses

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Several years ago we have started to develop an extended database on the Raman Spectroscopy signature of natural terrestrial, but also meteoritic glasses [1]. Background of this project were our first studies on a Belize glass sample, but also the findings of the Mars Phoenix mission, namely numerous in part highly magnetic spherules of still unclear origin and formation [2,3]. The most important outcome after that first step was the clear requirement of an extended database based on a selected set of properties of natural glasses: magnetic signature of natural glasses was never investigated systematically, and we decided to significantly extend in parallel our existing database on Raman Spectroscopical characteristics. The focus of this contribution is a first step towards a database of the Raman spectroscopic and the magnetic signature of natural glasses. Amongst others, the following types of natural glasses are under investigation in our project:

Tectitic, impact, volcanic and seismo-tectonic glasses, fulgurites and frictionites / hyalomylonites. Meteoritic glasses such as from shock veins are also taken into consideration [4].

A Horiba Xplora Integrated confocal LASER micro Raman system is used for our studies (mostly the 532 nm LASER). Magnetic susceptibility is investigated mainly by KLY3 of AGICO Comp., and SM30 and SM100 instruments of ZH instruments, both Czech Republic.

The Raman spectra of all investigated natural silica-rich (extra-) terrestrial glasses are characterized by the following typical features:

- Generally quite noisy signal showing more or less high background
- High fluorescence background at higher wave numbers (from about 1000 1/cm)
- Two broad bands centred around 450-600 1/cm and 850-1100 1/cm

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Raman analysis of Hayabusa / Itokawa returned particles

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The JAXA Hayabusa mission successfully returned particles of the asteroid Itokawa in 2010. The recovered particles have been first studied by the preliminary examination (PE) team and the obtained results are providing significant and unique information about the formation and evolution of meteorite parent bodies [1, and publications in this issue]. The particles revealed that their mineral compositions and oxygen isotopes are close to those of equilibrated LL chondrites [1].

After the PE, the samples have been distributed by JAXA as international AO study and our team received 4 new and 3 PE particles. We have performed detailed mineralogical and crystallographic studies on these particles [2,3]. Here we report results of our investigations by Raman Spectroscopy on three selected Itokawa particles.

A Horiba Xplora Integrated Confocal LASER micro Raman system was used for our studies, used LASER wavelengths were 532/638 nm. Three particles have been selected for our Raman-analyses, the following phases could be identified by high-resolution mapping:

RA-QD02-0036: olivine, plagioclase, troilite, chromite and a whitlockite-merrillite phase. The sharp and well developed Raman pattern of the plagioclase indicate a low shock stage of S1-2.

RA-QD02-0041: olivine and plagioclase. This particle is generally characterized by a very high fluorescence background. The plagioclase Raman pattern indicate a quite low shock stage.

RA-QD02-0133-01: olivine and plagioclase, we could not detect any other phase. Shock stage was estimated as similar to the other two particles.

The Raman spectroscopy analyses generally produced spectra are of high quality. These findings point to very fresh sample material collected from asteroid Itokawa without any significant weathering or alteration effects. The phase compositions confirm the PE results (LL 5).

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Raman spectra of impact zircons in the Jarva-Varaka structure of the Kola Peninsula

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Zircon crystals from aluminous gneisses of the Monchegorsk region (Kola Peninsula) were studied by means of Raman spectroscopy (Raman spectrometer HORIBA LabRAM HR 800) in the SPbU Resource “Geomodel” centre. Studied gneisses are hosts for the Jarva-Varaka layered massif of the Monchegorsky ore district [1]. Zircon crystals showed variation of Raman spectra from the core part of crystals with typical zircon Raman pattern to complete absence of spectral bands in the marginal parts and rims (Fig. 1). There was also a transition zone between cores and marginal parts of crystals, where the Raman spectrum is "blurred". Mineral inclusions in zircon rims (Pl and Sill-Ky) also have no Raman spectra. Such pattern may be associated with the transformation of crystalline zircon (and mineral inclusions in it) to diaplectic glass under the influence of shock metamorphism, since the Jarva-Varaka massif according to geological and geochemical data is compared with the Sudbury structure, for which impact origin is assumed.

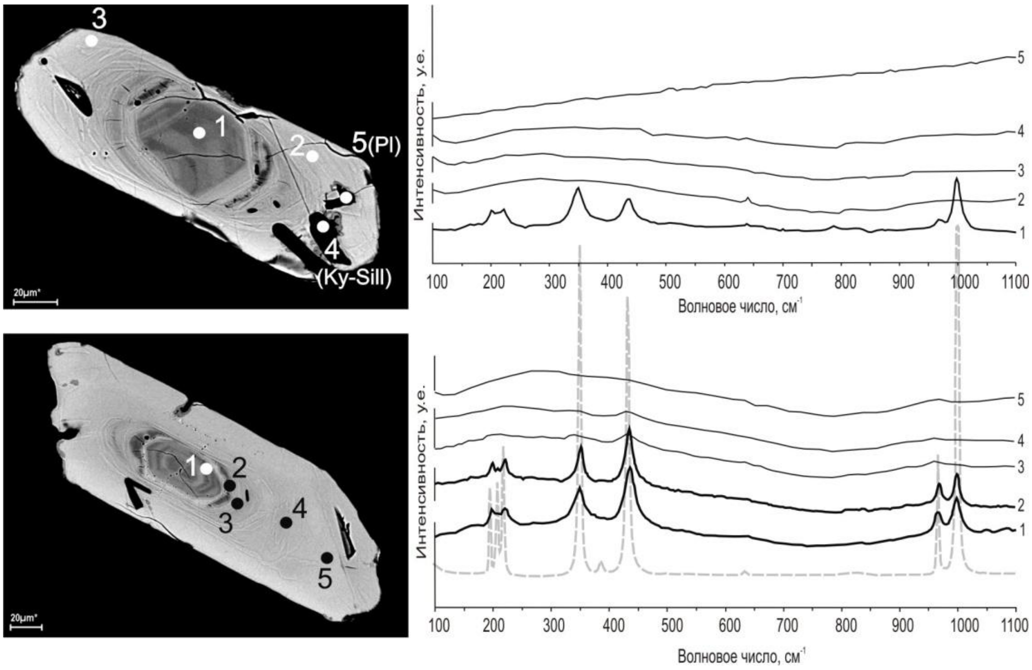

Figure 1. Raman spectra for zircon domains and mineral inclusions (Pl, Sill-Ky) from aluminous gneisses – hosts for Jarva-Varaka massif (Monchegorsk ore districts). Gray dotted line show spectrum of crystalline zircon.

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Raman mode frequencies in 3C-SiC

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In the present work, mode Raman frequency and its pressure as well as temperature variation in 3C-SiC are reported using density functional perturbation theory as implemented in Quantum ESPRESSO package [1]. The calculated frequencies match well with available experimental results [2]. Further, phonon frequencies along major symmetry directions are also reported along with their pressure variation, based on which it is observed that softening of phonon modes is responsible for pressure induced structural phase transition from zinc blend to rock salt type structure.

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IR-determination of water abundance in eclogite xenoliths, kimberlite pipe Udachnaya, Yakutia

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Water plays a key role in evolution and dynamic of the Earth. Water could change physical and chemical properties of mantle minerals, or the part of the mantle, for instance, the effect on mineral deformation and its impact on mantle rheology [1]. Kimberlites are one of the most important objects for research because they carry mantle xenoliths to the surface. Although, the mantle contains small amounts of eclogites, this rocks are the valuble components in the processing of the material between the crust and upper mantle of the Earth (e.g., subduction and exhumation of ultrahigh-pressure metamorphic rocks).

We have studied representative collection of the 25 relatively fresh xenoliths of eclogites. The studied eclogites are bimineralic and contain 40-70 % clinopyroxene (Cpx) and 30-60 % garnet (Grt). Cpx and Grt show wide range of compositions. Clinopyroxenes are characterized by Na_2O (1.66 – 7 mas.%) and Al_2O_3 (1.9 – 15.26 mas.%) contents and Mg#=73 - 91.9. In garnets almandine component varies from 19 to 48%, pyrope component - from 21 to 72%, grossular component - from 8 to 33%. All eclogites are divided into three groups by classification scheme of [2], based on MgO and Na_2O contents in Cpx.

The water in eclogites is mainly stored in omphacite (4-99 ppm); garnets do not contain measurable OH. Taking into account the volume rations of mineral phases in the studied xenoliths, the water contents in eclogites vary over narrow ranges from 2 to 55 ppm. We obtained no correlation between water concentration and temperature, pressure or composition of the rock. Low amounts of water in eclogites may be related to hydration during subduction or partial melting of the rock before kimberlite ascent. Our results confirm limited water transfer in subducted slab which closely associated with intense dehydratation process.

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Minerals of Fe in oxidation zone of massive sulfide ore - identification by Raman spectroscopy

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Pyrrhotite massive sulfide ore in Bragino site, South Pechenga structural zone, the Kola region in oxidation zone subjected intensely to secondary mineralization. Secondary minerals are represented by oxides: goethite, lepidocrocite, magnetite and iron sulfates: melanterite and rozenite. One of the reliable methods of identification of this minerals is Raman spectroscopy. Our research of this mineral were carried out on Raman spectrometer Almega XR ThermoScientific, Olympus VH51 microscope, 100x lens, laser 532 nm at the Institute of Geology of Karelian Research Centre of Russian Academy of Sciences.

Goethite α-FeO(OH) formed by marcasite, pyrite and pyrrhotite as veinlets and kidney in massive sulfide ore (Figure 1). It is homogeneous in composition, contains various fragments and relics of enclosing rocks. In goethite are marked euhedral crystals and veinlets of magnetite, confirmed by Raman spectra and chemical analysis.

Lepidocrocite γ-FeO(OH) forms tabular individuals which coalesce into bundles and rosettes on goethite crusts and fills the voids in goethite veinlets. Mineral is homogeneous in composition.

Melanterite $Fe(SO_4)•7H_2O$ forms in the early hours when massive sulfide ore is exposed to contact with water, in the form of tabular transparent, sometimes bluish, crystal. In the process of dehydration melanterite completely replaced by **rozenite $Fe(SO_4)•4H_2O$** within days.

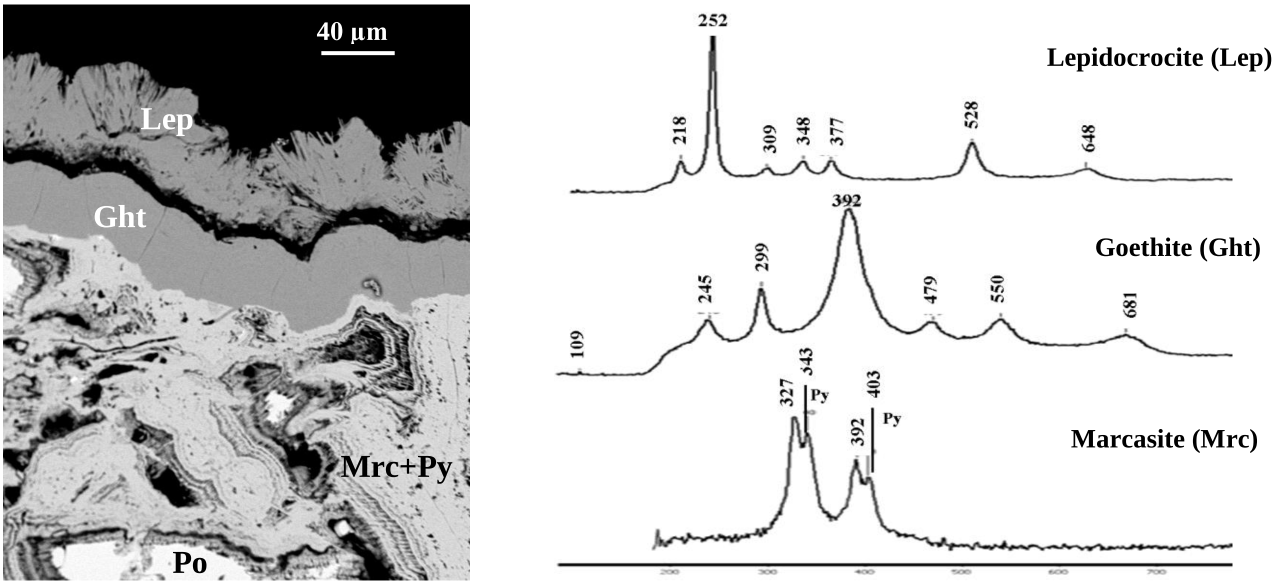

Figure 1. Morphology of precipitates of minerals in oxidation zone (left, BSE images) and corresponding them Raman-spectra (right). Po – pyrrhotite.

Effect of modifier cation on multialkali germanate glasses structure

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Germanate systems can be considered as high-pressure structural analogues of silicate melts, because the coordination number of germanium atom can be not only four, but five and six. System K_2O-Li_2O-GeO_2 was studied by Raman spectroscopy to detect anionic motifs, which are connected polialkali effect: extremes on the physicochemical properties dependence on the composition in oxide systems with several modifier cations.

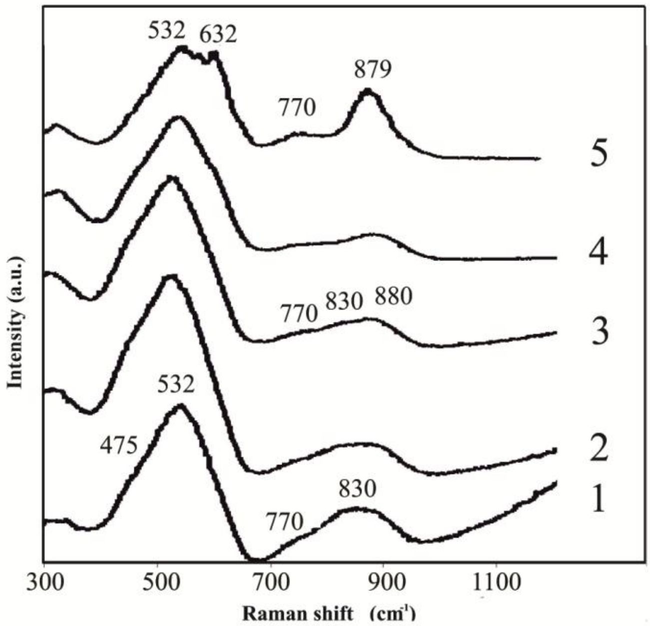

Figure 1. Raman spectra of glasses $xK_2O(20-x)Li_2O-80GeO_2$, where x = 0, 5, 10, 15, 20 mol. % (1-5, correspondingly).

Figure 1 shows that the glass 1 structure consists mainly of three-membered rings, consisting of germanium-oxygen tetrahedra GeO_4 (band 532 cm^{-1}). A weak shoulder near 475 cm^{-1} corresponds to the presence of a small amount of Ge (V). Glass 5 structure also consists mainly of three-membered rings, the low-band (632 cm^{-1}) indicates the presence of Ge (VI). The high-frequency region of the spectra is characterized by bands 770 cm^{-1} and 880 cm^{-1} (TO-LO-doublet) and 830 cm^{-1} and 879 cm^{-1} (Q^3 (Li^+) and Q^3 (K^+), respectively). It has been found that the replacement of Li^+ to K^+ in the lithium tetragermanate glass occurs first increase the amount of Ge (V) on the background of disappearance of non-bridging oxygen atoms associated with lithium cations. Further substitution leads to formation of Ge (VI) followed by appearance of non-bridging oxygen atoms coordinating potassium cations. Thus, there is a non-statistical distribution of modifier cations in the tetragermanate glasses: lithium cations with equal opportunities occupy energetically favorable position near Ge (V), whereas potassium cations prefer Ge (VI) environment.

Compositional analysis of shale gas by Raman spectroscopy and its application for *in-situ* measurements

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At the beginning of the 21st century shale gas production accounted 1% of natural gas production in U.S., whereas in 2010, this share increased to 20% and it is still growing. Shale revolution also reached Poland when U.S. Department of Energy announced in 2011 and 2013 that shale gas recoverable resources in Poland amount to 5.3 Tcm and 4.1 Tcm respectively [1,2].

These optimistic forecasts began development in unconventional natural gas exploration in Poland and development of new measurement methods for analysis and evaluation of natural gas composition (including shale gas). Development of conventional and unconventional natural gas reservoir management includes continuous monitoring of hydrocarbon exploitation processes and its impact on the reservoir and environment. Raman spectroscopy, which allows identification of gases (methane, ethane, propane and other gases i.e. nitrogen, hydrogen sulfide) and other chemicals can be very promising for application of providing quick, non-invasive, nondestructive and quantitative analysis [3-4].

The composition of natural gas often includes heavier hydrocarbons which change the thermodynamic properties of the mixture. This causes formation of a two-phase system under certain conditions of pressure and temperature. Correct identification of natural gas composition using Raman spectroscopy for two-phase system is a technical challenge [5-6].

Acknowledgments: The authors would like to acknowledge financial support from the *National Centre for Research and Development* and industrial partners, project no.: BG1/IRES/13 and from the *European Institute of Innovation & Technology* KIC – UNGASLAB.

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A Raman spectroscopy high-pressure study of crystalline nucleobases and their cocrystals

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Nucleobases are cyclic nitrogen-containing structures, based on purine or pyrimidine ring. They are found in DNA and RNA structures, where they are responsible for holding two nucleic acid strings together by hydrogen bonding, ensuring the complementarity of nucleotides. It is the nucleobases that encode the genetic information in their sequence, which is then translated into proteins.

Even though their great significance and presence in nature, there is little direct experimental information of their crystalline structure and properties of the complementary base pairs. [1] This is mainly because of the difficult crystal growth conditions, resulting in small size and instability of the crystals. Since the crystal size was insufficient to measure under laboratory X-ray diffractometer, spectroscopic analysis had to be implemented.

We decided to use Raman spectroscopy to characterise topological structures of adenine, uracil and adenine/uracil complex. Raman spectroscopy has been proven to be the best option to determine inter- and intramolecular interactions of these compounds because of its nondestructive nature and sensitivity to H-bonds, the crucial element in the base pair structures. Moreover, the compactness of Raman spectroscopy ensured comfortable handling and simultaneous measurement of all three crystals at on step of certain pressure. In our experiments we coupled Raman spectroscopy with high pressure, in order to determine the structures stability with respect to hydrostatic compression and to compare the compressibility of structures of individual nucleotides with that of a crystal built by their complementary dimers.

Crystals were compressed in an Almax-Boehler diamond anvil cell in paraffin oil as hydrostatic medium. Raman spectra were measured using a Horiba Raman microscope at step size of 0.5 GPa to 5 GPa.

The results showed no phase transitions, indicating a remarkable stability of the structures, not very common for crystals of biological molecules. The compressibility of single- and two-component crystals and the shifts of vibrational bands related to hydrogen-bonded interactions in the structure have been compared. Whether this robustness of the hydrogen-bonded molecular clusters of nucleotides is contributing to the evolutionary reason for the occurrence of nucleobases in nucleic acids, can be debated.

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The stability of pyrophyllite in water up to 100 kbar / 450^{o}C

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Recent experimental studies revealed a number of hydrous silicate phases that can potentially play a role in water transport from outer geospheres to the mantle [1]. Among them, a high-pressure hydrous modification of talc, so-called 10 Å phase $Mg_3Si_4O_{10}(OH)_2•H_2O$, is of special significance because its stability is intermediate between the minerals of oceanic peridotites (serpentine, talc, chlorite) and deep-seated silicates [2]. In peridotite systems this phase can accumulate an appreciable amount of aluminum [3]; the influence of Al onto the stability of 10 Å phase has not been studied. In this respect, it is interesting whether an Al-analogue of 10 Å phase can be formed through the reaction of pyrophyllite with water at high *P*, *T*.

The H*P*/H*T* Raman spectroscopic study revealed no hydration of pyrophyllite up to 100 kbar and 450^{o}C. At that, the Raman bands of pyrophyllite become weaker at 100 kbar, but the spectrum is fully restored after the pressure release. The obtained data extend substantially the upper pressure limit of pyrophyllite stability as compared to the available calculation data (20 kbar / 440^{o}C [4]) and indicate a stabilizing role of aluminum in the structure of layer silicates. The absence of pressure-induced hydration in pyrophyllite, in contrast to that observed in talc at 40-70 kbar/500^{o}C [2], can probably be related with the difference in the local structure environment of hydroxyl groups in these minerals. The formation of hydrogen bonds between structural hydroxyls and H_2O molecules [5] seems to be essential for intercalation of water into hydrophobic structures like talc and is apparently prohibited in pyrophillite.

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Automated and self-regulated Raman spectra acquisition for space exploration: ExoMars RLS instrument

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The RLS instrument on board ESA-Roscosmos 2018 ExoMars mission will be equipped with a set of algorithmic tools to automatically optimize the acquisition parameters taking into account the onboard available time and resources. This will provide a self-regulated and unsupervised method for the acquisition of spectra, dealing with fluorescence and cosmic rays, and calculating the spectra SNR, integration time (t_i) and number of accumulations (n_a). To design and develop the algorithms, many samples were analyzed with the RLS ExoMars Simulator, a 532nm Raman spectrometer with a 3-axis positioning system to emulate the operational framework of the Exomars rover [1, 2].

The general algorithm flowchart calculates the following parameters sequentially, on a short-time reference spectrum acquired by RLS: 1-saturation avoidance, 2-fluorescence detection and quenching, 3-detection and removal of cosmic rays, 4-onboard calculation of spectral SNR and 5-calculation of final t_i and n_a. Then, the final spectrum with the calculated parameters will be acquired by RLS.

Saturation avoidance, as well as fluorescence and cosmic ray removal (steps 1, 2 and 3, respectively) are needed to ensure the quality of the reference spectra that will be used for the calculation of the acquisition parameters in steps 4 and 5. After ensuring the no-saturation of the spectrum (step 1), the fluorescence detection and removal algorithm (step 2) will reduce the background of the spectrum. This will be done by illuminating with the laser for a time calculated depending on the sample under study (based on the decreasing rate of the background). Cosmic rays (step 3) will be detected and removed by comparison of consecutively acquired spectra. SNR calculation for onboard operations (step 4) is a low-computation algorithm for the calculation of the spectral quality of a spectrum. The SNR value will be used as a parameter of the acquisition parameters adjustment algorithms. Finally, the adjustment of t_i and n_a is performed based on the optimization of the overall operation time with a spectral-quality-based method.

In addition to the intrinsic advantages of automated Raman acquisition, our proposal for the automation of RLS will potentially save a lot of time during Raman acquisitions without compromising the spectral quality of the results. This approach can in principle be used for the automation of any Raman spectrometer.

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Biogeological analysis of desert varnish using portable and confocal Raman spectrometers in preparation for Mars missions

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In 2018 and for the first time, a Raman spectrometer will be utilized to study the composition of the first two meter of Mars' surface when the ExoMars rover is launched [1]. Raman spectrometers have the capability to detect geological substances constituting the rocky surface of Mars (inorganic molecules and inorganic molecular ions). The nature of rocks on the surface of Mars will provide information about the habitability of the planet. In addition, Raman instruments have the ability to detect potential biological-derivative substances, often referred to as biomarkers (organic molecules originating from extent or extinct living organisms). In preparation for ExoMars, studying the detection capability of miniaturized Raman spectrometers is essential, in particular for instruments developed for space missions (compromised by the associated challenging constraints such as minimal power budget, mass budget, data budget and overall envelope). It is important to address that capacity on both lab synthetic samples and natural terrestrial analogues samples.

We present here a comparison of the capability of a number of Raman spectrometer designs/configurations to describe the habitability of desert varnish samples [2] which are mineral coatings comprising clay, iron oxide and manganese oxide [3]. They are often associated with living organisms in many stable extreme environments on Earth. Desert varnish are recognized as terrestrial analogue samples for the martian surface and similar mineral formation have been recently identified on Mars [4]. In particular, we will compare spectral data recorded with benchtop instruments and miniaturized spectrometers with operating modes similar to the future ExoMars Raman Laser Spectrometer. We will discuss important instrumental parameters such as the excitation wavelength, the number of spectra recorded per sample and selection of optimal operating modes, in particular in the context of the detection of biomarkers dispersed within a specific geological matrix.

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Raman and EPR study of shock-wave effects on crystalline quartz

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The experimental determination of properties of crystalline solids at high pressures is of increasing importance [1]. The present investigations aims at quantitative and qualitative assessment of structural deformations in shock-wave treated natural quartz crystals using Raman and EPR spectroscopy. The plates of quartz crystals were cut and put in the cell that has undergone the explosion loading with pressures from 9 GPa to 34 GPa. Raman bands of quartz diminish in intensity and widen with increasing shock pressure that proves the increasing disordering (Fig. 1). In the pressure range of 25-34 GPa, amorphization of quartz is observed. The EPR spectra of the quartz samples were collected before and after treatment at different pressures. Then the same samples have been irradiated with dose of 2 MRad from ^{60}Co source. The intensity of EPR signal associated with Al impurity show complex behavior in dependence on the shock treatment. The intensity of well-known E' centers is increased with the shock pressures up to 34 GPa when the abrupt diminishing and broadening of the E' line is observed (Fig. 2).

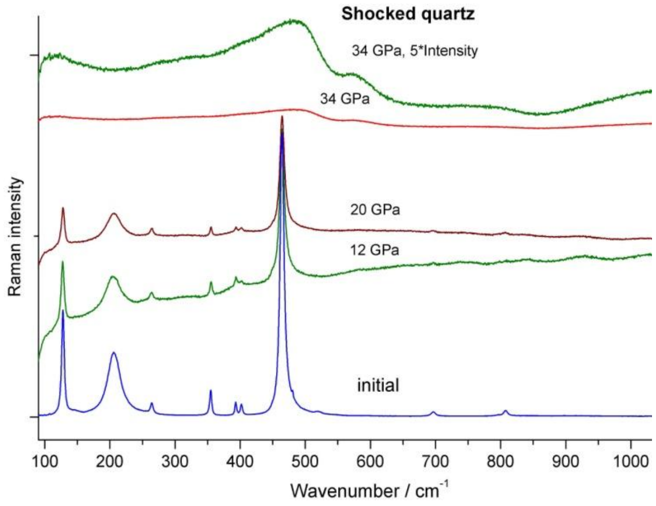

Figure 1. Raman spectra of quartz samples treated by shock-wave loading.

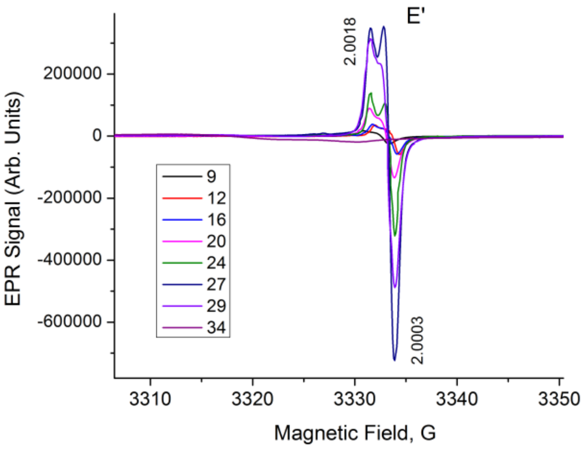

Figure 2. EPR spectra of E' centers treated by shock-wave loading (pressure is measured in GPa).

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Raman characterization of carbonaceous matter and apatite from phosphate-rich Paleoproterozoic rocks in the Zaonega Formation

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One of the most ancient records of biological phosphate processing are the Paleoproterozoic (2.06 – 1.98 Ga) organic-rich sedimentary rocks containing several P-rich layers of the Zaonega Formation in the Onega Basin, Karelia, Russia. Geochemical characteristics and morphological features of P-rich layers in the Zaonega Formation are considered to be the result of sulphur-bacteria activities [1]. We used Raman spectroscopy to study the carbonaceous matter and apatites, forming the P-rich layers, in order to find the additional arguments of their biological origin. Two types of carbonaceous matter were identified by means of Raman spectroscopy. The Raman spectra of both CM types are consistent with poorly ordered carbonaceous matter with two intensive bands G (~ 1580 cm $^{-1}$) and D1 (~ 1350 cm $^{-1}$) in first-order region, but each of them has with some important spectral differences. The primary CM occurs in the P-rich layers, forming lenses and nodules together with apatite and dolomite, and is more ordered than the migrational CM, observed both in the P-rich layers and matrix dolostones. Primary CM is characterized by R1=1.0. Its Raman spectra have narrower D1-band (FWMH=48 – 51 cm $^{-1}$), clearly display D2-band and relatively high intensive peak at 2700 cm $^{-1}$. More disoredered migrational CM is characterized by R1=1.5, wider D1-band (FWMH=65 – 70 cm $^{-1}$) and low intensive bands in second-order region. Appling the RS thermometer, proposed by [2], the metamorphic alteration temperatures of primary and migrative CM would be roughly determined ~390 and 340 °C correspondingly. These temperatures are consistent with greenschist facies overprinting occurred during the 1.89-1.79 Ga Svecofennian orogeny. Raman spectra of phosphates are consistent with spectrum of fluorapatite. The position (964 cm^{-1}) and width (FWMH = 8 cm $^{-1}$) of phosphate symmetric stretching (ν_1-$PO_4{}^{3-}$), which is sensitive to variations in apatite chemistry, correspond to the diagenetically altered apatite. It is also supported by rather high Crystalinity Index C_{Raman}=0.49 and $C_{X\text{-}ray}$=1.3, calculated using Raman [3] and X-ray diffraction data correspondingly. Thus, characteristics of the Raman spectra give additional argument for biogenic origin of phosphorus as well as organic matter found in the Paleoproterozoic rocks of Zaonega Formation.

Acknowledgments: Russian Foundation for Basic Research supported this work (project 15-05-08705 A).

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Raman spectroscopic study of mineralogy “non-fresh” salty kimberlites from Udachnaya pipe

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The presence of alkali carbonates, sulfates and halides in the Udachnaya East (UE) kimberlite pipe provide unique opportunity to study the composition and evolution of kimberlite magma [1,2]. Findings of NaCl in some hydrothermally altered kimberlites lead to confusion about origin of the kimberlites [2]. In this paper we focus on Raman spectroscopic study of mineralogy of hydrothermally altered (“non-fresh”) kimberlites. The mineral assemblage in this type of kimberlite is dominated by serpentine, halite, calcite, iowaite, barite, celestine and hibbingite. This mineral association has never been reported for ultra-fresh salty kimberlites. Thus presence of these minerals can be a diagnostic feature of “non-fresh” salty kimberlites.

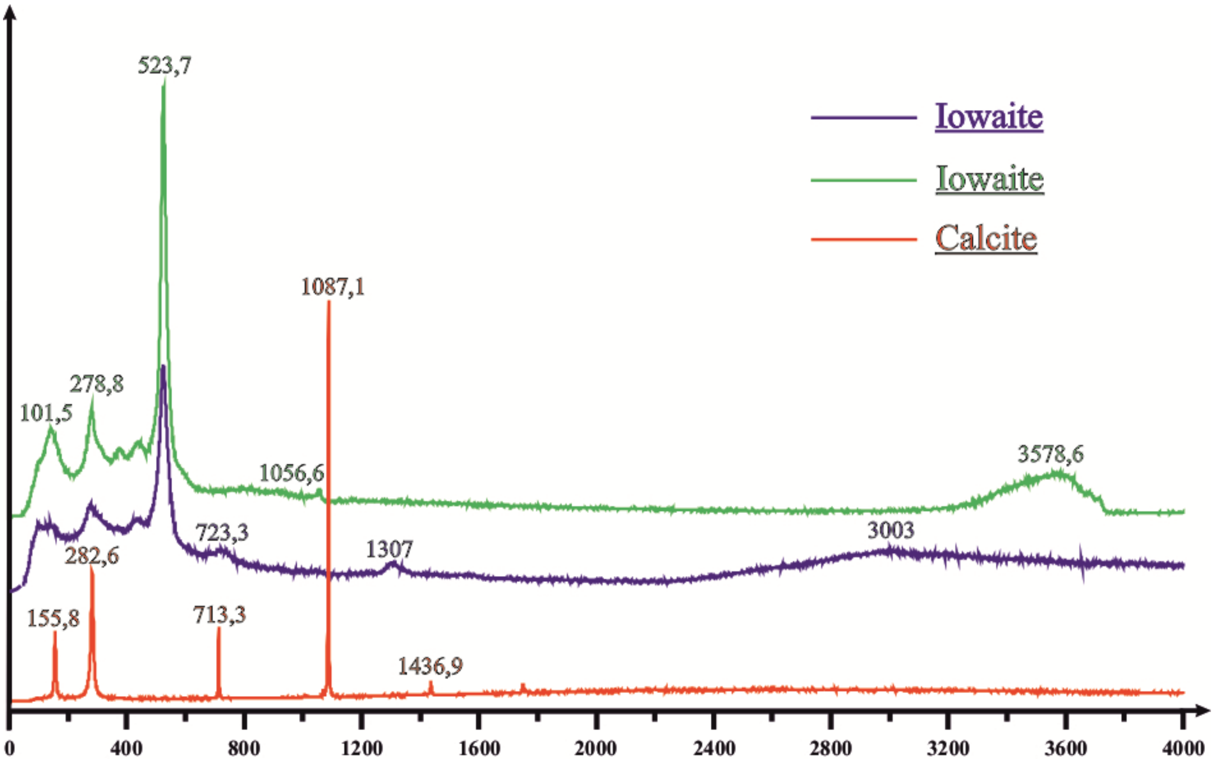

Figure 1. A representative Raman spectrum of calcite and iowaite from salts nodules in kimberlites.

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Peculiarities of natural graphites: Raman spectroscopy data

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The interest to the studies of rocks with a high carbonization degree is connected with the determination of the conditions for mobilization, transport and re-deposition (in different forms) of primarily scattered magmatic carbon. The present work deals with the studies of graphite in different genesis carbon-containing rocks. The first and second-order Raman spectra have been correlated with changes in the structure of graphite of the multifarious mormorphological types. For ore formation processes and in the development of genetic models for ore deposits, the key parameter is the temperature. Metamorphic temperatures can be evaluated using formulae that involve the ratios between the areas under the Raman bands due to defects and under a graphitic band. Raman spectra of disordered carbonateous materials normally have a more complex apperance, and they differ both from the Raman spectra of graphite contained in magmatic rocks [1, 2]. The established correlation between the bandwidths of the D1- and G-bands in different types of rock, namely magmatic one (Talnakh, Russia), marble (Baikal, Russia), carbon-silicon shale stratum (Oka zone of Eastern Saiyan, Russia), black shale (Malomyur, Sukhoi Log, Russia), ultramafic rocks obtained from ophiolites (Ospa, Eastern Saiyan, Russia) and others is shown in Fig. 1. It has been shown that the graphite is substantially varied in their structural-order both in samples obtained from the same deposit and, to a greater extent, in samples obtained from the rock of different types.

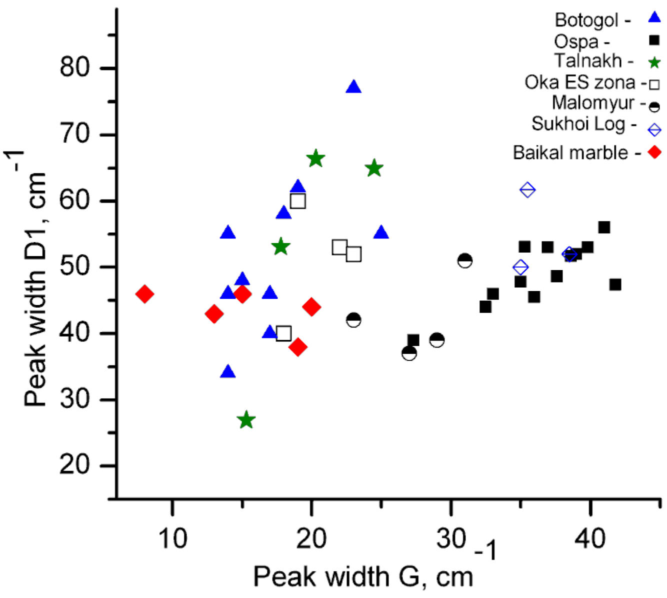

Figure 1. Correlation between the peak width of the D1 band and the peak width of the G band for samples from different rocks

Acknowledgments: The partial support of the RFBR Foundation with grants No. 14-05- 00734a is gratefully acknowledged.

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Raman spectroscopy of the minerals in different Chelyabinsk LL5 meteorite lithologies

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Raman spectroscopy is a recent useful method in the Earth sciences and it is also applied in studies of extraterrestrial materials. Light lithology of the Chelyabinsk chondrite was an initial material, whereas dark-colored and impact melt lithologies were formed during subsequent shock events generated by impacts in the space. The investigation of the chemical composition, strain, stress, as well as their distribution within the minerals of different lithologies is currently important [1-3]. This work presents investigations of the main mineral phases in the ordinary chondrite Chelyabinsk LL5 by Raman spectroscopy and electron microprobe analysis. We compared the spectral characteristics of minerals such as olivine $(Fe,Mg)_2SiO_4$, pyroxene $(Fe,Mg)SiO_3$, chromite $(FeCr_2O_4)$ and troilite (FeS) in a light-colored lithology (LCL), dark-colored lithology (DCL) and impact melt lithology (IML) (Fig.1). The silicate matrix is mostly composed of rock-forming olivine (forsterite) and pyroxene (enstatite) minerals. Chromite $FeCr_2O_4$ inclusions were observed as individual grains in the LCL and as ideally faceted crystals in the IML. Troilite grains were found both as individual inclusions in silicate matrix and as assemblages together with metal grains in all lithologies, while troilite shock-melted veins were observed in the DCL only.

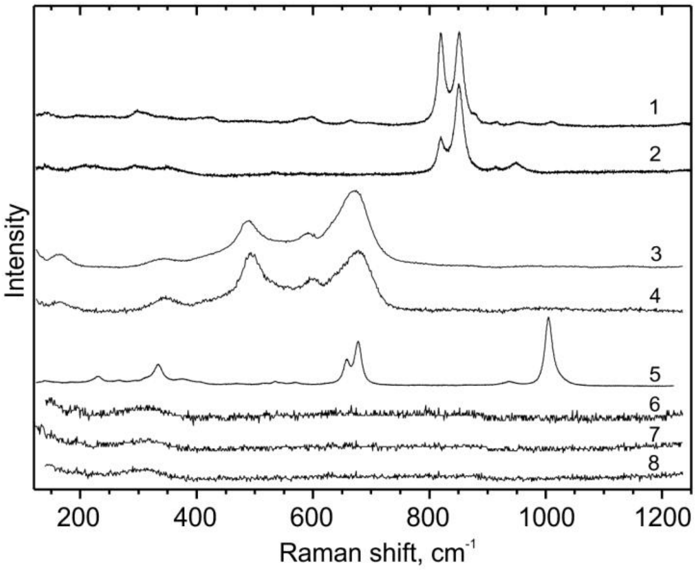

Figure 1. Raman spectra of olivine (1 - DCL, 2 - IML), chromite (3 - LCL, 4 - IML), enstatite (5 - IML), and troilite (6 - LCL, 7 - DCL, 8 - IML) in the Chelyabinsk LL5.

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Graphite in mantle of Central Aldan superterrane of Siberian craton: *in situ* micro-Raman characterization

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Mineral inclusions in mantle-derived lherzolitic Cr-pyropes from alkaline diatremes of Chompolo field (Central Aldan superterrane of Siberian craton) were studied using micro-Raman spectroscopy. The nine graphite inclusions (1-25 micron) were identified in three garnet crystals (samples: s21, 1n11, s124) (Fig 1a). Other mineral inclusions coexisting with graphite in these garnets are represented by forsterite, diopside, phlogopite, amphibole, rutile, Cr-spinel, Mg-ilmenite, apatite, chalcopyrite, magnesite, and Zr-Ba-mineral of crichtonite series. The order-disorder relations of graphite inclusions are shown on Fig 1b. The first two spectra demonstrate D1 and D2 bands, which are typically observed in disordered graphite [1]. Sample s124 contains three ordered and one disordered graphite inclusions. The maximum overpressure of 2.2 GPa for s124d sample has been estimated assuming a pressure dependence of the G-band upshift (1589.4 cm^{-1}) [2]. Inclusion assemblage in studied garnets is similar to that in mantle-derived pyropes from Navajo Volcanic Field [3]. The magnesite, phlogopite, amphibole, rutile, apatite, magnesite, and Zr-Ba-mineral inclusions strongly suggest an episode of metasomatism by carbon-rich agent in the lithospheric mantle of Central Aldan superterrane, contemporaneous with the formation of graphite inclusions and host pyropes.

This work was supported by grants from the RFBR (15-05-04885 and 16-35-60052 mol_a_dk).

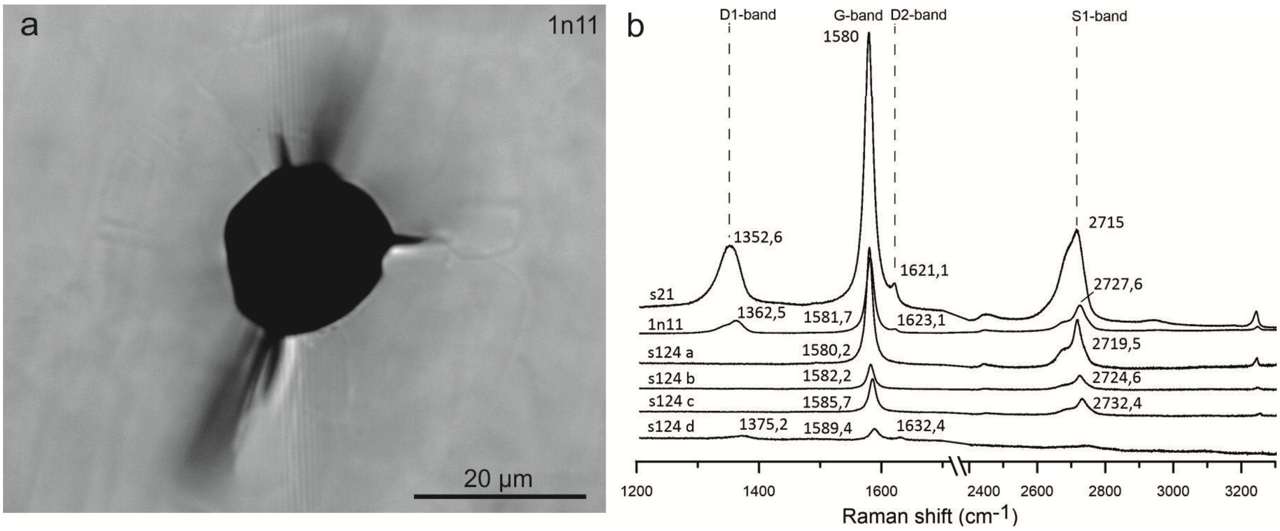

Figure 1. Microphoto (a) and Raman spectra (b) of graphite inclusions enclosed in Cr-pyropes.

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Strontium and barium aluminosilicates: from glass to melt

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Natural magmatic processes (volcanic eruptions, melt (un)mixing, magma differentiation, fractional crystallization etc.) as well as technological processes of glass, ceramics and glass-ceramics production pass the stage of a molten state. Being the most common compounds found in the nature and widely used in the glass industry, aluminosilicates have been studied for decades. Even though glass is a good approximation of liquids at high temperature there are not many structural studies in molten state, mainly due to technical difficulties. In this work we will investigate strontium and barium aluminosilicates which received only little attention.

By means of Raman spectroscopy we investigated the structure at medium range order of strontium and barium aluminosilicates. The compositions studied lie between peralkaline and peraluminous fields, and silica content varies in a wide range. Spectra were acquired from ambient to high temperatures and then deconvoluted in order to obtain information on Qn species distribution. High temperature in these experiments was achieved with a micro-heating device using Pt-Ir10% or Pt-Ir20% wires (temperatures up to 1700 °C) [1].

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Rare zirconium minerals in kimberlites of Yakutia

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Rare minerals of zirconium – kimzeyite and calzirtite, are identified in groundmass of kimberlites from Manchary pipe, Khompu-May field (Central Yakutia). Kimzeyite composes grains (size up to 30 mm), having relatively uniform composition, but idiomorphic zonal grains are found sometimes (Table). Calzirite (Table) occurs as xenomorphic gains (size less than 15 mkm). Compositions of single grains are uniform.

Chemical composition of kimzeyite (1) calzirtite (2) of kimberlites from Manchary pipe

Oxides	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	ZrO_2	Sum
1(center)	13,5	8,3	5,7	12,7	1,3	27,1	30,8	99,5
1(margin)	25,3	8,9	4,7	14,7	2,6	34,3	8,7	99,3
2		14,7		0,8		13,4	70,5	99,4

Diagnostics of minerals is confirmed at INTEGRA SPECTRA measuring system (NT-MDT company, Zelenograd) in Arctic Innovation Center, North-Eastern Federal University, Yakutsk (Fig. 1). Some differences in low frequency part of spectrum can be explained by different content of impurities in minerals.

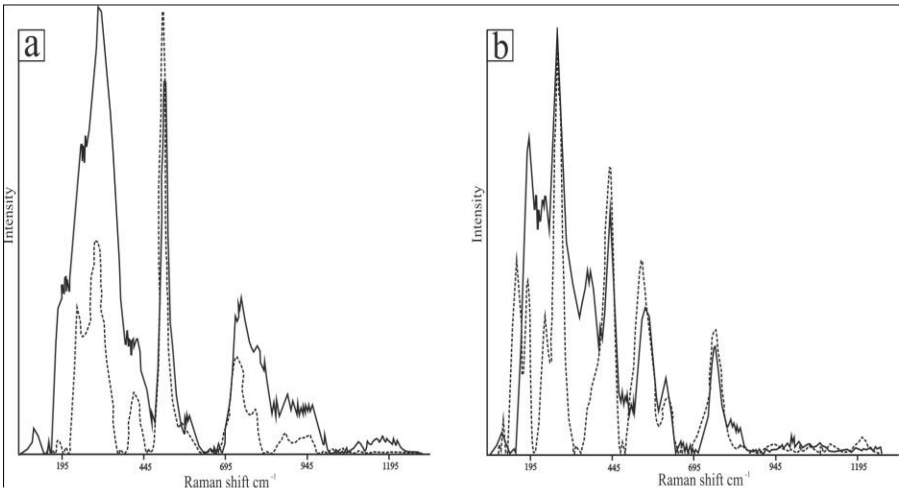

Figure 1. Raman spectra (a) – kimzeyite, (b) – calzirtite. Solid line shows spectra of minerals of porphyritic kimberlites from Manchary pipe, dotted line shows spectra of minerals from data base of RRUFF Project.

Thus, kimzeyite and calzirtite-rare minerals of zirconium, are diagnosed in kimberlite rocks of Yakutian kimberlite province for the first time. This allows to suggest that, kimberlite rocks of Khompu-May field are geochemically specific.

Raman gas analyzer of natural gas

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The determination of natural gas components is important for enterprises of gas industry, since the economic efficiency of these enterprises depends in many respects on the natural gas composition. At present the main method of determining its chemical composition is gas chromatography; however, the Raman spectroscopy gas analysis has a number of significant advantages. Among them are relatively quick results of gas analysis, simultaneous monitoring of all molecular compounds (including sulfur compounds and water vapors) whose content exceeds the sensitivity threshold of the equipment and the absence of expendable materials and complicated procedure of sample preparation [1, 2]. In the present work, a high-sensitivity model of the Raman gas analyzer of natural gas developed by us is described together with its operating principle. Results of its approbation on a real natural gas samples with different chemical composition are presented. A comparison of the data obtained with the results of chromatographic analysis demonstrates their good agreement. It is experimentally established that the developed Raman gas analyzer can reliably determine the content of all molecular natural gas components whose content exceeds 0.005% for 100 s.

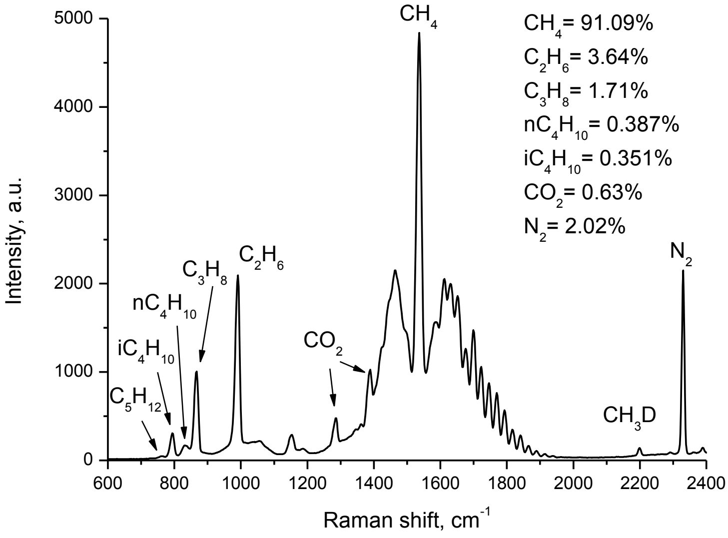

Figure 1. Raman spectrum of the natural gas

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A novel approach to single out Raman scattering spectra from laser induced fluorescence in thermally sensitive materials

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Raman spectrometry offers many advantages for the study of geological and archaeological materials. Our current research tries to address the two main issues that limit a more widespread or routine application: sample laser-induced fluorescence and/or thermal alteration.

In low maturity organic matter, or in certain minerals, fluorescence is typically used as a general denominator for a significant and broad emission of the sample under laser excitation. Using a non-gated Raman instrument, like most commercially available equipment, this phenomenon competes with the Raman scattering and can dominate a spectrum almost completely, making the extraction of the actual Raman signature impossible using spectral processing techniques alone. Prolonged irradiation can reduce fluorescence (photo-bleaching effect) (ex: Panzer et al. 2012), but not always yields useable spectra, especially on thermally sensitive materials.

In this study, we reconstruct the Raman spectra of fluorescent prone and thermally sensitive material such as organic matter, clays and cobalt oxides (see Burlet et al. 2011) subjected to structural or chemical changes during irradiation with a continuous laser source (532 and 785nm) in a confocal Raman microscope setup (Bruker Senterra). The novel method we propose consists in discretising the photo-bleaching operation into several hundreds of short-duration measurements (down to 1s) using an automated set-up. While the broad component of the spectrum progressively reduces, we show that it is possible to track the evolution of the fluorescence and Raman signal with a dedicated regression and correlation algorithm. Our method shows that it is then possible to separate the two signals and correct the non-fluorescent part of each individually measured spectrum back to that of the initial measurement, thus allowing for a near full correction of the laser-induced thermal maturation effect.

The preliminary results are very promising, and indicate that characteristic Raman spectra can be isolated even when fluorescence makes up over 95% of the spectrum. Further test are currently conducted to confirm these initial findings.

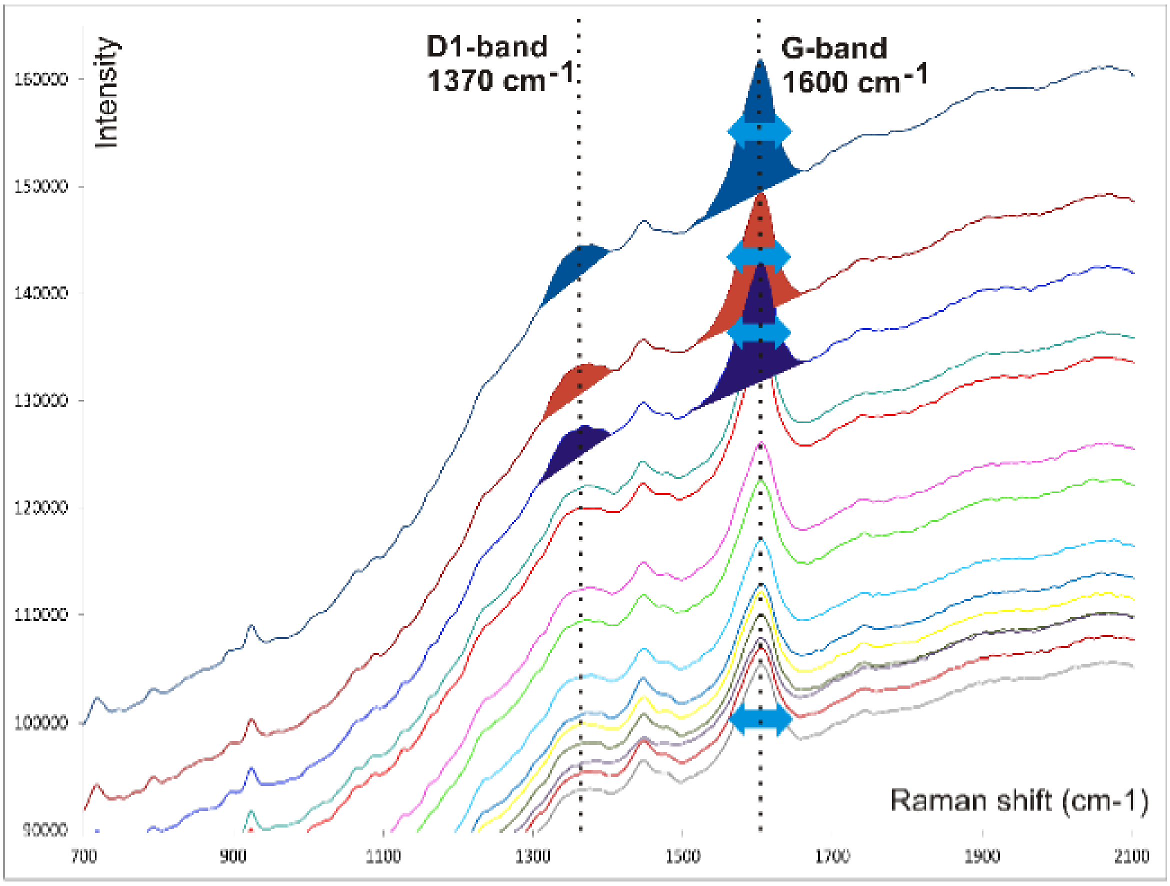

Figure 1. Typical reduction of fluorescence in low-mature bitumen during repeated measurements, accompanied by less obvious shifts in the typical D and G bands due to increasing thermal maturation.

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The first Raman data for the Cr-glagolevite and unknown Na-Mg-rich phyllosilicate from the Pt-rich chromitite of the Nizhny Tagil massif, Urals

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The mafic silicates in the PGM-rich chromitites of the Ural-Alaskan-type intrusions are enriched in chromium and alkalis. Chromian glagolevite is one of the typical Na-rich low temperature phyllosilicate in chromitite. It intergrows with chromite, PGM and other silicates, indicating their low temperature origin. Glagolevite was discovered in the metasomatic skarns of the Kovdor alkaline-ultrabasic complex in the Kola Peninsula [1]. Its chromian rich varieties were described approximately at the same time in platinum-bearing chromitites of the Nizhny Tagil massif [2]. Just recently an extremely Na-Mg-rich unknown phyllosilicate was discovered in Pt-rich chromitites in association with serpentine and glagolevite. These minerals were not found in dunite host, therefore it reflects an alkaline-rich composition of the ore-forming system. Glagolevite and unknown Na-Mg-rich silicate are similar to chlorite due to their optical properties and can't be recognized without X-ray microprobe analysis. We present the first results of Raman investigations of Cr-glagolevite and unknown Na-Mg-rich phyllosilicate which can be used for mineral identification (Fig.1) and included in international databases.

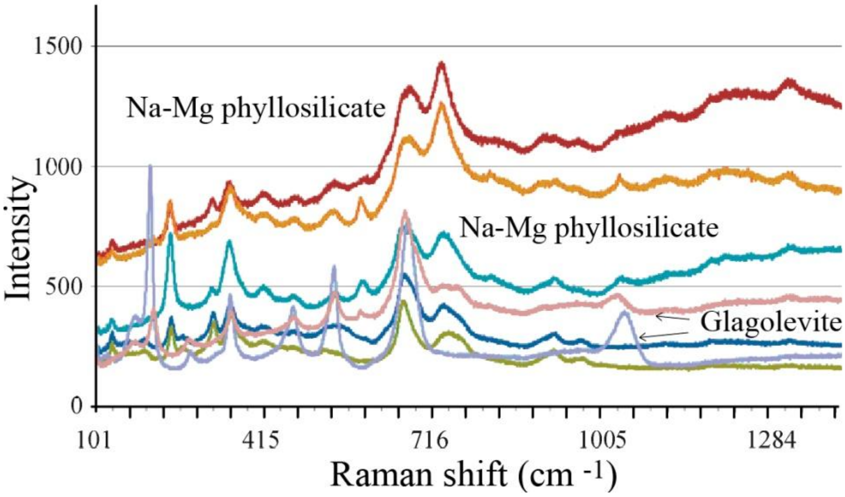

Figure 1. Raman spectra of Cr-glagolevite and unknown Na-Mg-rich phyllosilicate from the Pt-rich chromitites of the Nizhny Tagil massif, Urals.

***Acknowledgments*: The study is supported by RFBR 16-3-05-00508, UB of RAS 15-18-5-34 and Russian Science Foundation grant No. 16-17-10283.**

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Raman identification of mineral inclusions in specific rounded diamonds from the placers of northeastern Siberiam Platform

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The northeastern part of the Siberian platform is a unique region in terms of kimberlite occurrences. Numerous kimberlite pipes discovered within this region are extremely poorly diamondiferous or non-diamondiferous. However about 70% of the diamond placer deposits of the Siberian platform are concentrated here. The primary sources of the diamonds are having not been discovered yet. The crystals dark gray to black in color with specific rounded morphology (variety V [1]) are one of the dominant groups of diamonds in these placers.

Mineral inclusions are extremely rare in the diamonds of variety V. In the present study some inclusions of Cpx's (omphacite, diopside and jadeite), Coe, Grt, Kfs, and Kya have been identified by Raman spectroscopy (Fig. 1).

This specific set of mineral inclusions in the V variety diamonds indicate that they crystallized in a broadly eclogitic or metapelitic chemical environment. Major-element compositions determined by EDS in inclusions of Grt's show considerable heterogeneity. The Cpx's also show a continuous range from diopside to omphacite (up to 'pure' jadeite) which illustrates that the 'calc-silicate' inclusion suite is simply an end-member component of a broader range of compositions.

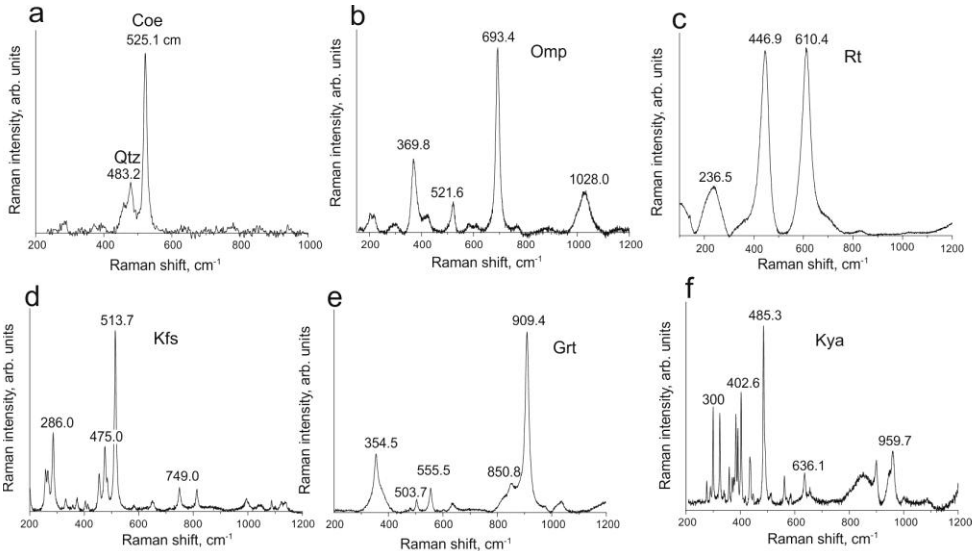

Figure 1. Raman spectra of inclusions in the diamonds of variety V. a – Coe + Qtz, b – Omp, c – Rt, d – Kfs, e – Grt, f – Kya.

This study was partially supported by RFBR (№ 16-05-00614).

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Pressure-induced shift of nyerereite Raman bands: a diamond anvil cell study up to 7 GPa

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Rare mineral nyerereite, $Na_2Ca(CO_3)_2$, was first found in 1963 in Ol Doinyo Lengai natrocarbonatite lava. A particular interest nyerereite attracted as an inclusion phase in mantle minerals (diamonds and olivines from kimberlites) [1]. As Raman spectroscopy is the main tool for analysis of such inclusions and residual pressure measurements, an important task is to find relation between position of nyerereite Raman bands and pressure.

We measured Raman spectra of nyerereite from Ol Doinyo Lengai up to 7 GPa using a diamond anvil cell and silicone oil as a quasi-hydrostatic pressure-transmitting medium (Fig. 1a). The $v_4(CO_3^{2-})$ (710 cm^{-1}) and $v_1(CO_3^{2-})$ (1078 and 1087 cm^{-1}) bands of nyerereite demonstrated blue shift under pressure with parameter dv/dP of 1.26, 2.88 and 3.36 cm^{-1}/GPa, accordingly (Fig. 1b).

The obtained results demonstrates an absence of pressure-induced phase transformations in nyerereite up to 7 GPa, and give a calibration for residual pressure measurements in nyerereite-containg inclusions.

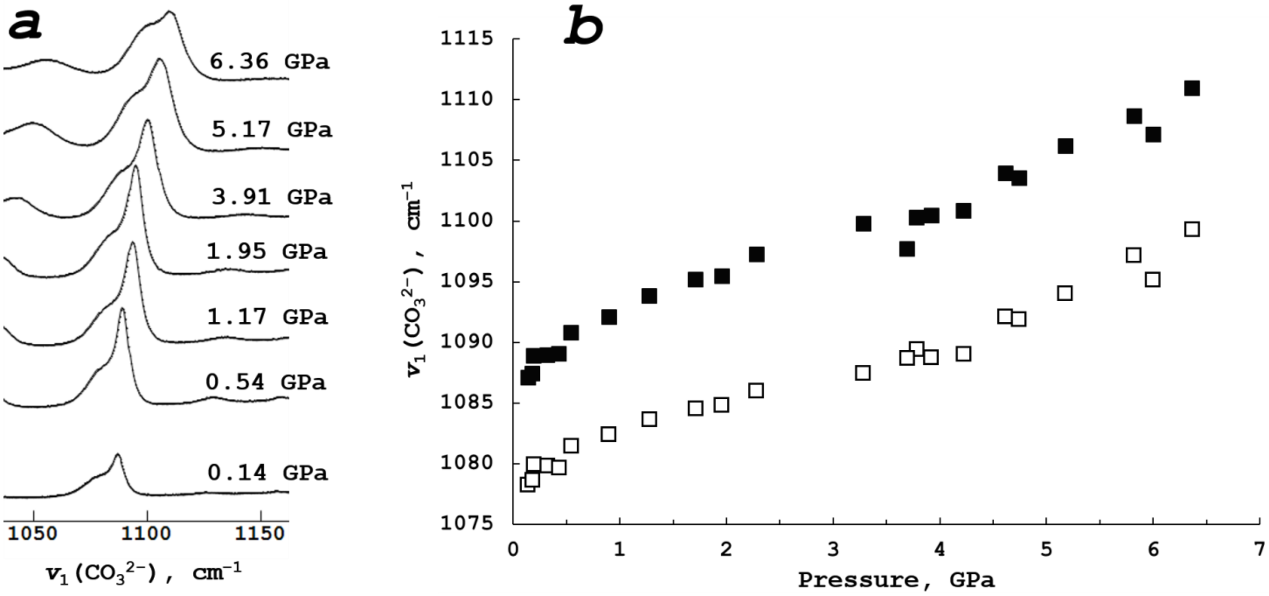

Figure 1. Behavior of nyerereite $v_1(CO_3^{2-})$ band under high pressure (a); pressure-induced shift of nyerereite $v_1(CO_3^{2-})$ band (b).

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The first use of portable Raman instrumentation for the *in situ* study of prehistoric rock paintings in North Patagonian sites

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Archaeometrical studies in North Patagonia (Argentina) reveals useful information about the materials used by the population that inhabited the area. This region has been considered as a transit zone between population groups from the mountains and others located in the Patagonian steppe. In the archaeological sites of North Patagonia lithic materials, pottery, rock art as well as paintings or engravings on rocks, leather, textiles, etc. are commonly found.

In the current project, a measurement campaign was organized to study prehistoric rock paintings *in situ*, in order to investigate the materials and the sources of the materials from the hunter-gatherer populations, inside their own environment. Portable Raman instrumentation was used to identify components and pigments, as well as possible products of degradation on site. Recently, mobile Raman instrumentation was employed for the direct analysis of rock art in Spain, France, and South-Africa. Until now, portable Raman analysis for the investigation of North Patagonian rock painting sites, is not reported before.

This research aims to identify the different materials used, and thus try to establish relationships over time. The distinction between clay like materials and natural rocks will provide valuable information for the manufacturing technique and production process of the inhabitants and will determine the local "palette" of native population. Comparison with many archaeological sites within North Patagonia will be made. Finally, the study of the degradation processes of these materials will give valuable information for a better preservation of the remains in the archaeological sites.

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The degradation of Mn in CorTen steel affected by acid rain

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CorTen steel is a type of weathering steel which is widely used in outdoor structures because it has a special resistance against the atmospheric corrosion through the formation of a protective layer. This layer is formed due to the reaction of some alloy elements with the atmosphere. However, the material could not fulfill its function properly depending on the environment in which the steel is exposed. [1].

In the present work, the effect of the acid rain, characteristic of some polluted atmospheres, was studied. For this aim, some pieces of CorTen steel were immersed in synthetic acid rain. Then, these pieces were analyzed by Raman spectroscopy in order to identify which corrosion and degradation products were present in the protective layer. For this analysis, an InnoRam B&WTEK (MicroBeam) Raman spectrometer was employed using a 785 nm laser.

The results showed that the main components were iron oxides and oxyhydroxides, as it was expected. However, apart from those iron phases some manganese compounds were also detected. On the one hand, a manganese oxide with its main Raman band at 580 cm^{-1} (Figure 1) was identified. On the other hand, a manganese sulfate was also found in the steel surface through its main Raman band at 1024 cm^{-1}. This element is used as alloy element in CorTen steel to enhance its hardness, consequently if a sulfate is formed due to the reaction of the material with acid rain, manganese will be leached, due to its solubility. Therefore, this process could involve a loss of the mentioned property.

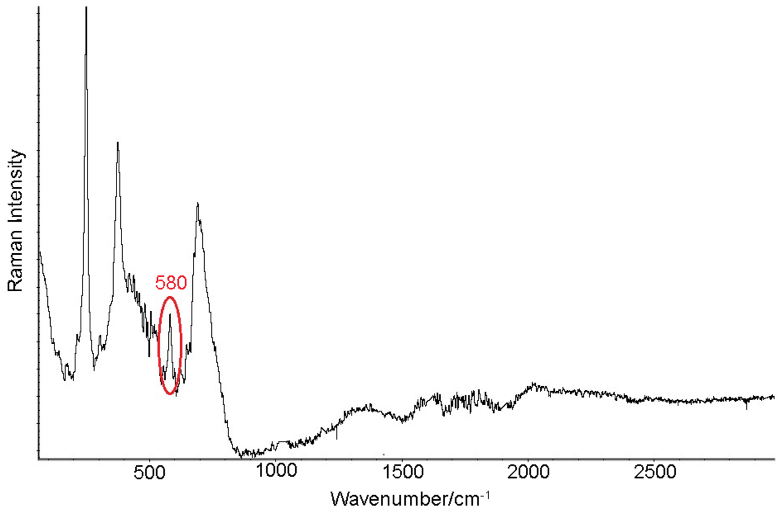

Figure 1. Raman spectra of iron oxides and manganese oxide (580 cm^{-1}).

Acknowledgements**:** This work was financially supported by the project DISILICA-1930 from the Spanish Ministry of Economy and Competitiveness (MINECO) (ref. BIA2014-59124-P) and the European Regional Development Fund (FEDER).

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Characterization and differentiation of schwertmannite and akaganeite group compounds by Raman spectroscopy: implications for space exploration

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Schwertmannite is a relatively recent described mineral [1]. It is located in evaporite acidic environments. It has been considered a precursor in the formation processes of jarosite group which gives special relevance in the study of the processes that have taken place in the formation of this mineral in places like Mars.

Furthermore, structural studies have been made on this mineral have linked structure with oxides of the akaganeite-group. That is why it is interesting to study whether these compounds can be identified and differentiated by Raman spectroscopy.

The main difficulty encountered when analyze these materials is their low crystallinity, as they are mostly amorphous materials with a large volume of water in its structure which makes them highly thermolabile and therefore degradable under the action of the laser.

For this study, we have been synthesized several compounds under controlled conditions and analyzed by Raman spectroscopy, and assigned and compared, such as bands on the Fe-O vibrations such as those relating to the anions trapped in the structure such as sulfate.

As mentioned, these analyzes are critical of the upcoming planetary exploration missions, including Mars, as they will carry instruments of analysis by Raman spectroscopy as are RLS of Exomars'18 and SuperCam of Mars2020.

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Analysis of the influence of composition and origin of jarosite group compounds on the Raman spectra

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The jarosite group, has been extensively studied from many points of view, both in its genesis and its structural elucidation, its relationship to environmental aspects as AMD or even its presence in offworlders materials.

At the same time, they were often characterized by various techniques, including Raman spectroscopy [1-2] providing separate information about structure, composition, reactivity, etc.

For this work we have been collected both natural geochemical samples of different origins as synthetically prepared samples under controlled conditions.

By Raman spectroscopy we found significant differences about the structure and origin. Also we found significant differences not only when there are complete substitutions of cations but even in partial replacements.

These results are of great relevance and application, not just for the pure analysis of samples but also to establish hypotheses about possible mechanisms of formation.

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Amorphous zinc borate as a low-cost standard for baseline correction in Raman spectra

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Some of the samples we deal with in Raman analyses are good scatterers, transparent or semi-transparent, and present low fluorescence and for these samples Raman signals are usually intense and easy to detect since the intensity of the signals is higher than the distortions introduced by the instrument. In this case baseline correction is an easy process, even unnecessary in some cases. There are some other samples that make things much harder for baseline correction. In these conditions it is frequent to face low quality spectra, with low intensity Raman signals, sometimes weaker than the parasite signals of the baseline. Other times only the instrument introduces distortions in the spectrum. In this situations a good baseline correction is essential to obtain a representative Raman spectrum of the analyzed sample.

The solution of this problem starts with the search of a sample that shows a Raman spectrum similar to NIST SRM standards that could be used as reference for baseline correction [1-3]. We started evaluating different borates and borosilicates, and finally selected a thermally processed zin borate that presented a high luminescence, useful for the purposes of baseline correction. This substance is then used in a similar way as you may use a NIST SRM, but just for baseline correction purposes. Results are presented in terms of SNR evaluation using the mentioned substance, that seems to be a good option, cheap to find and easy to prepare in great amounts. In our case we evaluated this material as candidate to be part of the calibration unit of both, Exomars RLS and Mars 2020 Supercam, although at this moment it is no longer considered to be part of the CU in either one of them because of technical reasons.

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Micro-Raman application in gemology: identification of sapphire heat treatment

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Abstract. Detection of sapphire heat treatment is in prime interest for gemological laboratories. Non-destructive Raman microspectroscopy is perfectly suited for gemological investigation of inclusions and its alteration after multi-stage heat treatment process. We performed heat treatment experiments on sapphire and two geuda crystals coming from Tanzania and Sri-Lanka. The Tanzanian sapphire were heated step by step at 400°C, 800°C, 1200°C, 1600°C and 1700°C in oxidizing conditions. Gueda crystals were heat treated at 1650^0C in reducing conditions.

Results. *Zircon inclusions.* The Tanzanian sapphire contained abundant zircon inclusions. With the increasing of heating temperature (1200^0C and above) zircon Raman lines underwent modification and became more apparent, FWHMs of the Raman peaks became significant lower. For example, the average ν_3 FWHMs for 18 zircon inclusions were 10.8-9.7 cm^{-1} (1200^0C), 10.2-9.3 (1600^0C), 9.8-8.9 (1700^0C). In contrast, the average ν_3 FWHMs for unheated zircon inclusions were 12.3-16.4. In addition, the characteristic zircon Raman peaks of all heated inclusions (1600-1700^0C) were shifted to higher wavenumbers. Moreover zircon inclusions Raman spectra after 1600-1700°C annealing showed partial zircon destruction and additional peaks. At 1700^0C a doublet were observed at 179 cm^{-1} and 191 cm^{-1} consistent with the Raman spectrum for baddeleyite. Thus, at 1700^0C zircon inclusions showed evidence of decomposition [3].

Fluid inclusions. Milky white geuda samples after applied heat treatment (1650^0C) changed its color to blue. Untreated samples contained numerous two-phase fluid inclusions with liquid CO_2 (1387 and 1282 cm^{-1}). Typical for Sri-Lanka sapphires [1] fluid inclusions with diaspore and graphite were also observed. Graphite inclusions showed only one narrow G (E_{2g}) band at 1580 cm^{-1} indicating crystalline well-ordered graphite [2].

After the heat treatment experiment CO_2-diaspore inclusions were not fixed in Raman spectra. Graphite inclusions demonstrated two broad bands 1355 (D) and 1578 (G) cm^{-1} in Raman spectra consistent with disordered graphite [2].

Conclusion. Multi-step annealing experiments with corundum coming along with micro-Raman spectroscopy investigation of inclusions can gain valuable analytical data. This information allows improving of the heat treatment identification methods for rubies and sapphires.

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A combined micro-Raman and standoff Raman spectroscopic study of feldspars

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Micro-Raman and telescopic Raman spectroscopy has been shown an effective tool for mineralogical analysis. Motivation of the present work is to determine Raman fingerprints of various well characterized natural feldspar minerals by analyzing their Raman spectra with both micro-Raman and standoff instruments employing near infrared, visible and UV lasers.

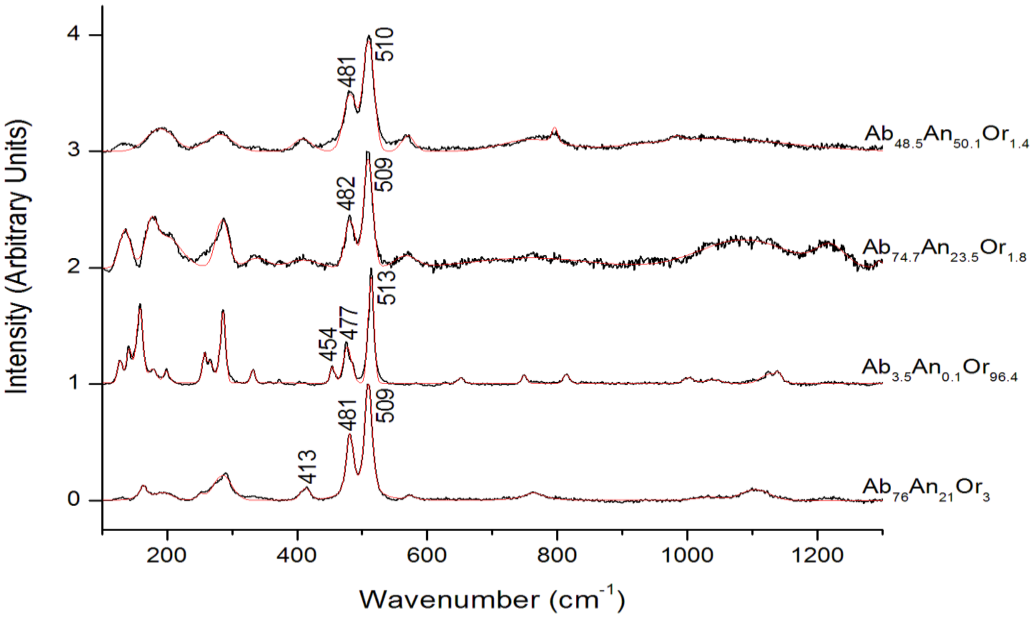

Figure 1. Micro-Raman spectra of ternary feldspars measured with 514.5 nm laser excitation

Figure 1 shows the micro-Raman spectra of a number of natural feldspar minerals. The compositions of these minerals were measured with electron microprobe and are marked in Fig. 1. It is evident from Fig. 1 that the variation in the fractions of albite (Ab, $NaAlSi_3O_8$), anorthite (An, $CaAl_2Si_2O_8$) and orthoclase (Or, $KAlSi_3O_8$) components of the feldspars affects the positions of symmetric stretching modes of four-membered rings of TO_4 tetrahedra in the 450-520 cm^{-1} region [1-2]. The positions and line widths of the anti-symmetric T-O-T stretching modes in the 950-1300 cm^{-1} region are also affected by Al content and the Si-Al ordering in these feldspars. Similar results were obtained with standoff Raman spectrometers with samples at 10 to 17 m distance using both 532 and 266-nm laser excitations. Potential use of standoff Raman spectroscopy for identifying the feldspar minerals on planetary surfaces will be discussed.

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Raman spectroscopic study of accessory minerals of diamond-bearing and diamond-free kyanite gneisses from the UHPM Kokchetav massif

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Accessory minerals (AM) are very important in UHP-rocks, because they are the host minerals for many elements and they control the behaviour the trace elements during partial melting [1]. Here we present the Raman spectroscopic study results of AM from kyanite gneisses (Kokchetav massif) (Raman wavelength 532 nm). Ky gneisses consist of large kyanite (Ky) and garnet porphyroblasts, biotite, phengite, K-feldspar, graphite, relicts of UHP-phases – coesite and diamond. Zircon (Zrn), rutile (Rt), apatite (Ap), allanite (All), magnetite, monazite (Mnz), pyrite and barite are very abundant AM in this type of rocks. In All and Mnz the average La_2O_3, Ce_2O_3, Nd_2O_3 contents are 2.71, 5.97, 2.46 and 15, 28.5 and 10.8 wt.% respectively. According to experimental studies [2-3], Ap, Mnz and All have wide stability field, however on the retrograde stage Mnz can be replaced by All and Ap by the reaction: $Mnz+fluid+Ca^{2+} \rightarrow All+Ap$. The association Mnz+All+Ap was observed in diamond-bearing gneisses as inclusions in kyanite together with diamonds (Fig. 1). It is likely that there were several generations for AM: monazite that formed at the prograde part of PT-path and which are products of Mnz breakdown. The Mnz lamellae (5-8 µm) were identified in Ap, only from diamond-free gneisses. It is likely that these lamellae was formed on the retrograde stage from the LREE-rich Ap through the reaction: $Ap(LREE) \rightarrow Ap+Mnz+Fluid$. The presence of monazite at peak conditions might be a reason why kyanite gneisses did not experience intensive depletion in LREE and Th [4], which is evident in garnet-biotite gneisses [1].

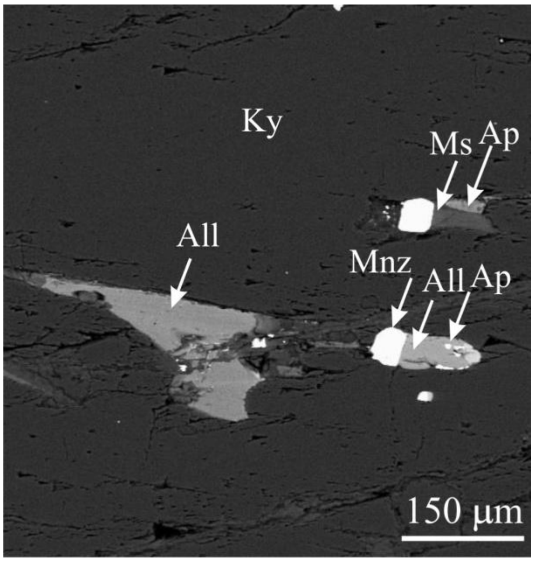

Figure 1. AM in kyanite

This study was supported by a grant from the Russian Science Foundation (RSF 15-17-30012).

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Ab initio simulations and experimental Raman Spectra of Mg_2SiO_4 forsterite to simulate Mars surface environmental conditions

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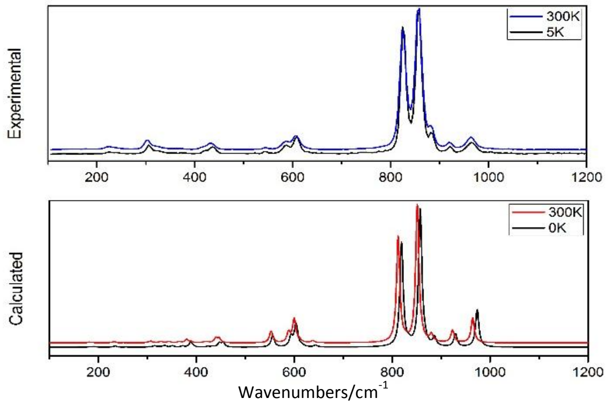
In order to study the possible response of Raman spectra to the different environmental conditions occurring on Mars surface, *ab initio* simulations of Raman spectra of Mg_2SiO_4 forsterite have been computed from first principles, employing the hybrid Hamiltonian WC1LYP [1,2] by means of CRYSTAL14 code [3].

To do so full Raman spectra have been calculated at 0K and at 300K. Simulations have been compared with experimental Raman spectra taken on a natural sample of forsterite [4], carried out with the same environmental conditions at the Institute of Planetary Research, DLR in Berlin.

A very good agreement with the experimental data, in both environmental situations, allowed assignments of Raman features to specific vibrational modes. Moreover, a quantum mechanical mass substitution of ^{56}Fe for ^{24}Mg in the M1 and M2 sites has been performed. The aim is to relate the major experimental peaks, not only to specific structural features but also to link them to the occurring Raman shifts due to temperature and composition.



The results will provide new clues to improve the interpretation of data acquired during the 2018 ExoMars mission, which will carry on board a Raman Laser Spectrometer (RLS) [5].

Figure 1. Raman spectra at different environmental situations experimental and calculated.

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Raman spectra at different temperatures and structure of δ-BiB_3O_6 Crystal

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Phase diagram of Bi_2O_3-B_2O_3 system had been studied intensively in sixties [1], and crystals of bismuth triborate BiB_3O_6 were synthesized among them for the first time. This crystal attracted special interest of several scientific groups in the last years due to its high optical nonlinearity, that provide wide practical applications for it as an active medium in systems of optical frequencies transformations. For a long time only one α-phase was known for this composition, but six new phases of BiB_3O_6 have been found in the recent years [2]. However only α-phase is investigated in details up to now. Its structure is built of chains of [BO_3] triangles and [BO_4] tetrahedrons in 1:2 ratio. First principles simulations of its electronic structure showed that [BO_4] tetrahedrons provide the main part of optical nonlinearity. Among other phases of BiB_3O_6 only γ and δ include [BO_4] tetrahedrons exclusively; and centrosymmetrical γ phase is of scanty interest for nonlinear optics, while structure of δ phase ($Pca2_1$, $Z = 4$) looks more attractive for such applications. Still physical properties of this phase have been studied rather poorly, and its vibrational spectra at different temperatures has never been investigated up to now. In this work we have performed such measurements.

To obtain Raman spectra Ar+ polarized radiation at 514.5 nm were used as an excitation (Spectra-Physics Stabilite 2017, 100 mW output, 15 mW at the sample). Spectra in 180° geometry were obtained with Horiba – Jobin Yvon T64000 spectrometer in 10 to 1600 cm^{-1} range. Their temperature dependence within 8–300 K range was investigated with ASR Closed Cycle Cryostat CS204-X1.SS.

Raman spectra of δ-BiB_3O_6 phase has been obtained and their symmetry interpretation has been performed. Experimental data are compared with results of empirical lattice dynamics simulations for δ and α phases of BiB_3O_6, performed within LADY software [3]; special optimization software has been designed to determine empirical parameters of the model, taking into account lattice stability conditions. Using such models experimental Raman lines have been assigned to structural units vibrations and stability of these BiB_3O_6 phases are compared.

Acknowledgements: This work has been partially supported by RFBR (grant 15-42-04347, 16-32-00351), the Ministry of Education and Science of Russian Federation and Krasnoyarsk regional fund of scientific and technical activity.

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Raman spectroscopy of olivine inclusions in diamonds from Yakutia

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New data on the study of residual pressure in olivine inclusions in diamonds from pipes Aikhal, Udachnaya and placers of Ebelyakh river are presented.

Analysis of stressed inclusions in diamonds using Raman micro-spectroscopy was carried out, taking into account that, chemical composition of inclusions of one mineral in the volume of host mineral is the same.

The most intensive bands of stretching vibrations SiO4-groups in olivine spectrum were observed as a doublet with maximums about 825 and 857 cm^{-1}, which has significant shift rate on pressure 2.81±0.09 and 2.69±0.12 cm^{-1}/GPa, that is presented as increased values of band frequencies in stress inclusions stressed inclusions. Analysis of Raman spectra showed that, these bands had maximum shift on frequency for inclusion in sample 2004 from pipe Aikhal: 826.14 and 857.17 cm^{-1}. This doublet was used for determination of residual pressure P_i in olivine inclusion, and frequencies for zero pressure were identified experimentally on Raman spectra of olivine inclusion, brought to the surface: ~823.47 and 855.71 cm^{-1}. Raman spectra, obtained from olivine inclusion in sample 2004, gave maximum shift to each doublet band for value $\Delta\nu$=2.67±0.2 and 1.46±0.2 cm^{-1}, that corresponds to inner residual pressure in inclusion P_i=0.41±0.05 GPa calculated from formulas of the works [1, 2]. According to [1] this residual pressure in inclusion helps in evaluating pressure of diamond crystallization, which, according to our calculations, is at least P_f =4.8±0.5 GPa at model temperature of its growth 1200 °C.

Comparative analysis of Raman spectra of olivine inclusions in diamonds from placers of Ebelyakh river on inclusions, contained in diamond and then brought to the surface, showed that, frequency shifts are insignificant for any band of the doublet $\Delta\nu=\pm0.3$ cm^{-1} (~822.9 -823.5 cm^{-1} and 855.4-855.7 cm^{-1}) and it is impossible to calculate pressure of diamond crystallization in this case. According to data of the study of olivine inclusion in diamond crystal from kimberlite pipe Udachnaya, it follows that importance of frequency shift for 856 cm^{-1} band may vary within the limits $\pm$0.5 cm^{-1} in stability field P-T conditions of diamond on carbon phase diagram [3].

Calculated values in comparison with obtained values for olivine inclusions in kimberlite diamonds indicate that, olivines in placer diamonds are in less stress conditions, and perhaps, these values directly depend on structural orientation of olivines in diamond [4].

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Raman mapping of stressed chromite inclusion in diamond

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Raman mapping of stressed chromite inclusion in kimberlite diamond is presented. Raman measurements were carried out with Renishaw inVia (UK) spectrometer, using 532-nm exciting laser line of 1 mW power. The plane of Raman image (Fig. 1) corresponds to the middle cross section of inclusion and diamond field around this inclusion. Red color in Fig. 1 corresponds to the wavenumber of diamond Raman band of 1333.34 cm^{-1}, whereas black color represents the value of 1331.5 cm^{-1}. The reasons of stressed state are discussed: joint origin of inclusion-diamond at high *P*-*T* conditions; non-isotropic compression of diamond; effect of impurities etc. Stressed diamond field accounted from inclusion centre has radial and azimuthal directions. Note that azimuthal dependence of the stress is more noticeable and contrast. We assume that the origin of this strong azimuthal stress is due to different compression of diamond crystal, detected by Raman shift rate 2.2 cm^{-1}/GPa along [111] and 0.7 cm^{-1}/GPa along [001] according to ref. [1]. Both directions in some projection can form the angle that differs from 90° that could explain the azimuthal stressed field observed in Fig.1. Additional complex stress perturbation is evoked by cracks in diamond. Internal pressure in inclusion is estimated as ~0.8 GPa.

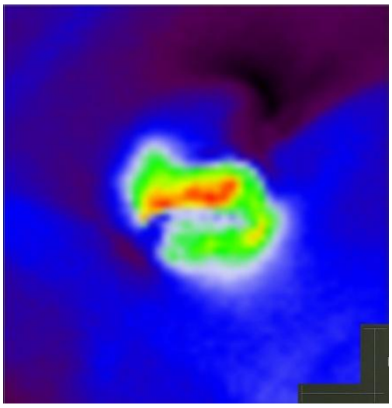

Figure 1. Raman image of stressed chromite inclusion in diamond. Scale bar along x-y in the corner corresponds to 50 μm. Signal of each point is collected from volume 5x5x5 μm^3.

This work was supported by Russian Science Foundation (project No. 15-17-30012).

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The combined use of Raman spectroscopy and XRF spectroscopy for the investigation of decorative Belgian wall tiles

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Since centuries floors and walls are decorated in the most diverse ways to give them a more comfortable and beautiful appearance. In the 19th century, new industrial techniques are introduced for the production of the tiles and since then, many production centres are established in Belgium and Northern France. In the 20th century, the production of decorative Belgian wall tiles comes to a head. On the one hand, tiles are still produced for their practical nature, but on the other hand, complete tile panels are designed and made down to size for the decoration of facades, porches and interiors. These wonderful creations can be admired to this very day in different buildings all over the world.

A marking at the back of the tiles shows by which manufacturer the tiles are produced. Identification of the manufacturer by looking at the front and thus based on their decoration and colours is still impossible. In this research, a new method based on chemical analysis is developed to discriminate different tile manufacturers. Therefore, a selection of Belgian wall tiles, dating from 1900 – 1930 and produced by four different manufacturers, are investigated. Raman and X-Ray Fluorescence analysis are performed on the body and the glazes of the tiles, to obtain a unique fingerprint of each group of tiles. Combining these chemical analyses with chemometrical data analysis methods, chemical markers for each manufacturer are identified.

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Laser alteration of iron sulfides in various environmental conditions

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Upcoming lander missions to planetary bodies require new innovative techniques for *in situ* investigation of their surfaces and near surface materials. In recent years, Raman spectroscopy has successfully been proposed for planetary missions. For example, the Raman Laser Spectrometer (RLS) [1] of the joint ESA and Roscosmos mission ExoMars will for the first time in space identify minerals and organic compounds in Martian surface rocks and soils.

In preparation of space missions, the goal of our present study is to investigate iron sulfides with respect to their possible response to relevant environmental conditions. Iron sulfides are chosen because they are widely disseminated on the Martian surface; they might also be present in the rocks of Jupiter's satellites Ganymede and Callisto, as well as on the lunar surface. In addition, they are present in almost all meteorites [2,3]. Since on Earth in ambient air iron sulfides are very sensitive to laser irradiation, it is necessary to know how these minerals react under conditions that are similar to space or Martian environments [4]. Therefore, a proper investigation mode needs to be developed. Additionally, analyses in vacuum, at different temperatures, and Raman excitation with varying laser power produce a comprehensive Raman database for upcoming missions, e.g., RLS onboard of Exo-Mars [5].

For this study, we selected the iron di-sulfides pyrite, marcasite, and chalcopyrite, as well as the iron sulfides troilite and pyrrhotite. The spectra were taken with various laser power and in various environmental conditions that included ambient air, vacuum down to 10^{-6} mbar, 8 mbar CO_2 atmosphere, and temperatures ranging between room temperature and ~ 10 K, resembling those on Mars, as well as on the Moon, on asteroids, and beyond. We found that Raman spectra of different iron di-sulfides are stable under these different environmental conditions and with increasing laser power. In contrast, iron sulfides are very sensitive to the laser power in ambient air and convert into hematite and magnetite. However, most important for space missions, no effects were found with increasing laser power in vacuum. In addition, a CO_2 atmosphere does not affect the spectra of the investigated minerals, a finding particularly important for missions to Mars, including ExoMars.

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Raman spectra of natural phlogopites of different ages

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The influence of pressure on the diffusion of argon in the mantle conditions may be significant. For an Ar-Ar dating study of the samples, an assessment of pressure effect on the mechanism of bleeding an argon from mica at high temperatures and pressure is important and problematically [1-3]. Phlogopite micas of different geological ages, from the deposits located in Russia (Aldan and Slyudyanka) and Tadzikistan (Kuhi Lal) have been investigated by micro-Raman spectroscopy using a wavelength of 532 nm (2.33 eV) of a Nd:YAG laser. The purpose of the present study is an investigation of the characteristics of micas by micro Raman spectroscopy together with infrared spectroscopy, X-Ray powder diffraction, SEM methods before and after treatment. It has been shown that the chemical composition, structure and spectroscopic properties of phlogopites from different deposits do not have the signs of recrystallization, solid state transformations, and melting after treatments up to 3GPa, and 1000°C (2 h) and the hydroxyl-stretching band shift is negligible (Fig 1b). The behavior of all samples is fully reversible on decompression. A comparative analysis of other methods used for the structural characterization of micas shows that Raman measurements can be performed in a relatively fast, nondestructive procedure for samples *in situ* using thin sections of samples.

The partial support of the RFBR Foundation No.15-35-20267 is gratefully acknowledged.

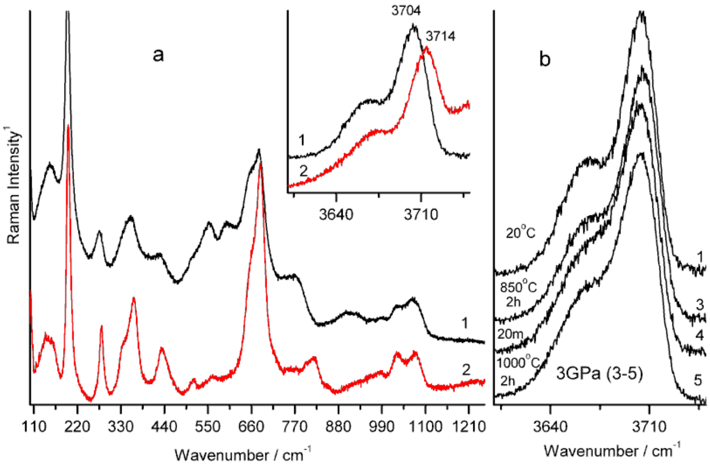

Figure 1. Raman spectra of Aldan-1927±12Ma (1) and Kuhi Lal -7.7±0.7 Ma *(2) phlogopites (a); Raman spectra in region of OH stretching vibrations (b) after the treatment of Aldan sampls at 3GPa 850 °C 2h (3), and 1000 °C 20 min (4) and 2h (5).*

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Categorizing of organic polyiodides according to theoretical and experimental Raman data

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Polyiodides I_n^{x-} are widely used in electronic devices, water disinfection and crystal engineering. Conducting, optical and bacteriostatic properties depend on the features of polyiodide-anions spacial organization and are closely connected with the processes of iodine adsorption, storage and release from the crystalline state. Raman spectroscopy is one of the most informative tools to analyze properties of I–I bonds and intermolecular interactions. Analysis of experimental and theoretic Raman spectra of oriented single crystal in this work is used to localize chains and layers of polyiodide-anions in bulk crystal as a preliminary step for further anisotropic measurements.

In this work we demonstrate the possibilities of experimental and theoretic Raman spectra in the understanding of intermolecular interactions with iodine participation, localization of polyiodide chains and layers in bulk crystals, identification of polyiodide subunits in anions of complex structure, observation of iodine loss processes [1].

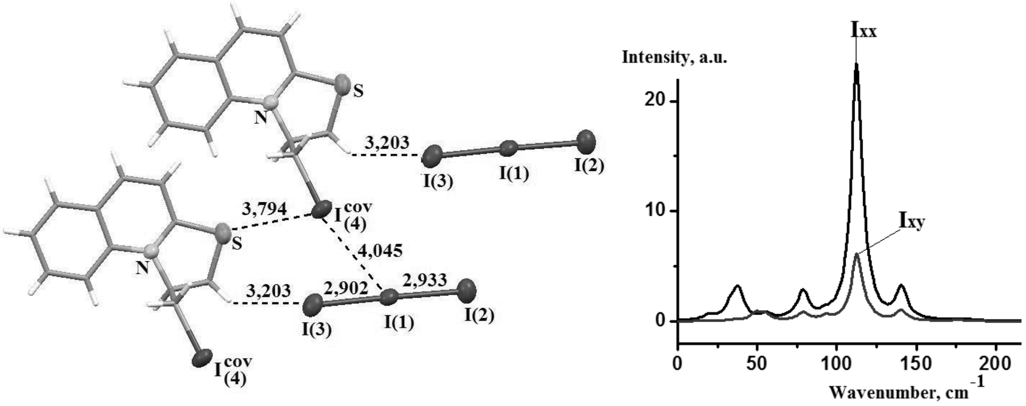

Figure 1. Fragment of crystal structure (left) and theoretic polarized spectra of thiazoloquinolinium triiodide I_3^- (right); agreement with experiment in the triiodide stretching vibration value is 3 cm^{-1}

Good agreement of obtained theoretical spectra in crystalline state (3D periodic Kohn-Sham calculations in Crystal14) allowed us to use these data to solve a row of cases concerning interpretation of nontypical experimental spectra [2], spectral properties of unstable under laser explosion polyiodides, comparison of theoretic spectra in specific directions with experimental polarized spectra, analyzing theoretic polarizability tensors. This work has been supported by the Ministry of Education and Science of the Russian Federation GZ 729.

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[2] Bartashevich E.V. *et al.* (2016) *Acta Crystallographica C* **72**, 341.

High-pressure polymorphism of chlorpropamide: multiple routes

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Studies of polymorphic molecular crystals are important for the basics of high-pressure science, and are related to phenomena, which are common for molecular solid-state chemistry and experimental mineralogy. For a compound prone to polymorphism, it is not possible to predict which phase will be formed at a selected (T, P) point based solely on a thermodynamic phase diagram. Instead, there exists a complex interplay of nucleation and growth kinetics, alongside thermodynamics, that lead to these unpredictable results. This phenomenon is exemplified on the high pressure polymorphism of chlorpropamide. An antidiabetic drug, chlorpropamide (4-chloro-N-(propylamino-carbonyl)benzenesulfonamide, $C_{10}H_{13}ClN_2O_3S$), is particularly prone to polymorphism. In addition to the commercially available α-polymorph, which is the thermodynamically stable form under ambient conditions, four other polymorphs (β-, γ-, δ-, ε-) can be preserved indefinitely long under ambient conditions. At 0.1-0.5 GPa in a pentane-isopentane mixture, the β-polymorph of chlorpropamide was shown to transform into the γ-polymorph if present in the cell alone. In contrast, transformation to a mixture of the γ- and δ-polymorphs is observed if the δ-polymorph (alone or with the α-form) is added. Within the pressure range 2.4 – 3.3 GPa the α-, and δ-polymorphs undergo further phase transitions yielding different novel high-pressure phases.

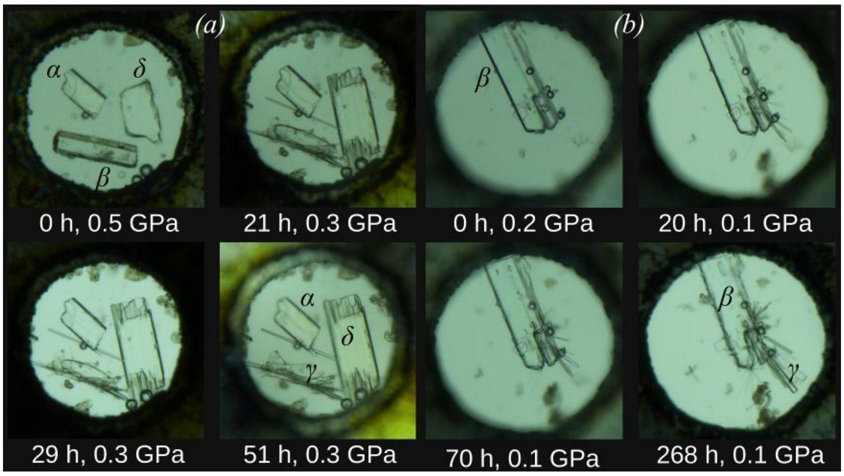

Figure 1. The crystals of α-, β-, δ-polymorphs of chlorpropamide in DAC at different time moments. The growth of new needle-shaped crystals (γ-polymorph) and growth of δ-polymorph are clearly seen in the presence of α-, and δ-phases (a), whereas only the recrystallysation of β- into the γ-polymorph is clearly seen if the β-phase is present alone (b)

The work was supported by a grant from RSF (14-13-00834).

Raman spectra of mendipite: an ab initio study

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Natural mineral mendipite (lead oxychloride $Pb_3O_2Cl_2$) is a promising material possessing specific physicochemical properties [1]. Although there are reliable data on the crystalline structure of $Pb_3O_2Cl_2$, obtained by X-ray analysis [2], information on its phonon spectra are fragmentary, and the interpretation of the vibration bands presented in literature is presumptive [3].

In our previous study [4] were performed ab initio calculations of the crystal structure and the phonon spectrum of $Pb_3O_2Cl_2$ in the framework of LCAO approach are performed by the Hartree–Fock method and in the framework of the density functional theory with the use of hybrid functionals. The calculations were performed by the CRYSTAL code, destined for periodic systems. The results of calculations made it possible to interpret the experimental vibration spectra and reveal silent modes, which do not manifest themselves in these spectra but influence a crystal's optical properties.

In present study additionally were performed calculations of Raman spectra intensities of polycrystalline powders (total intensity, parallel polarization, perpendicular polarization), spectra of single crystals in each inequivalent polarization direction: *xx*, *xy*, *xz*, *yy*, *yz*, *zz*. Comparison with the available experimental data is presented in Figure 1.

As seen, the calculation is well reproduced the vibration frequencies and obtained mostly correct qualitative estimation of intensities.

Spectra of single crystal in inequvivalent polarization directions *xx*, *xy*, *xz*, *yy*, *yz* and *zz* presented in Figure 2.

Intensities of polycrystalline powders considering parallel and perpendicular polarizations showed in Figure 3.

This work was supported by the Russian Foundation for Basic Research, project no. 15-03-00368a.

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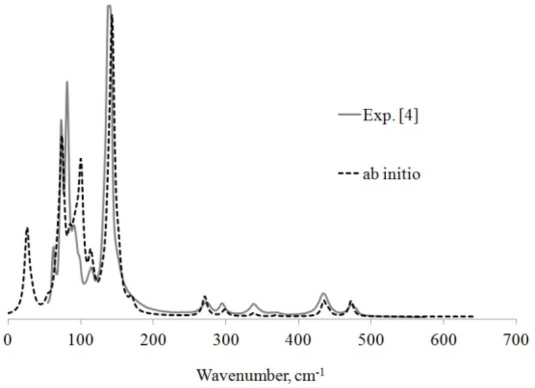

Figure 1. Comparing experimental and calculated Raman spectra for polycrystalline powder.

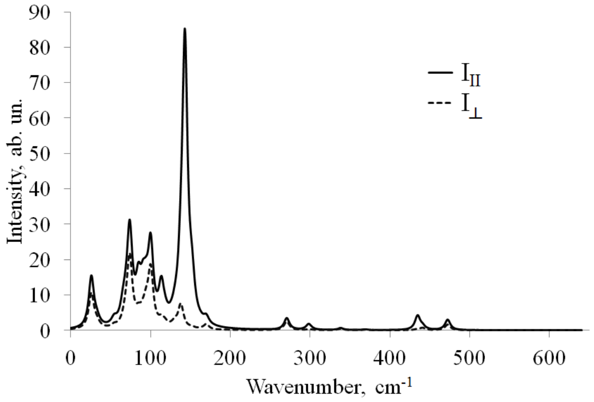

Figure 3. Spectrum with parallel and perpendicular polarization.

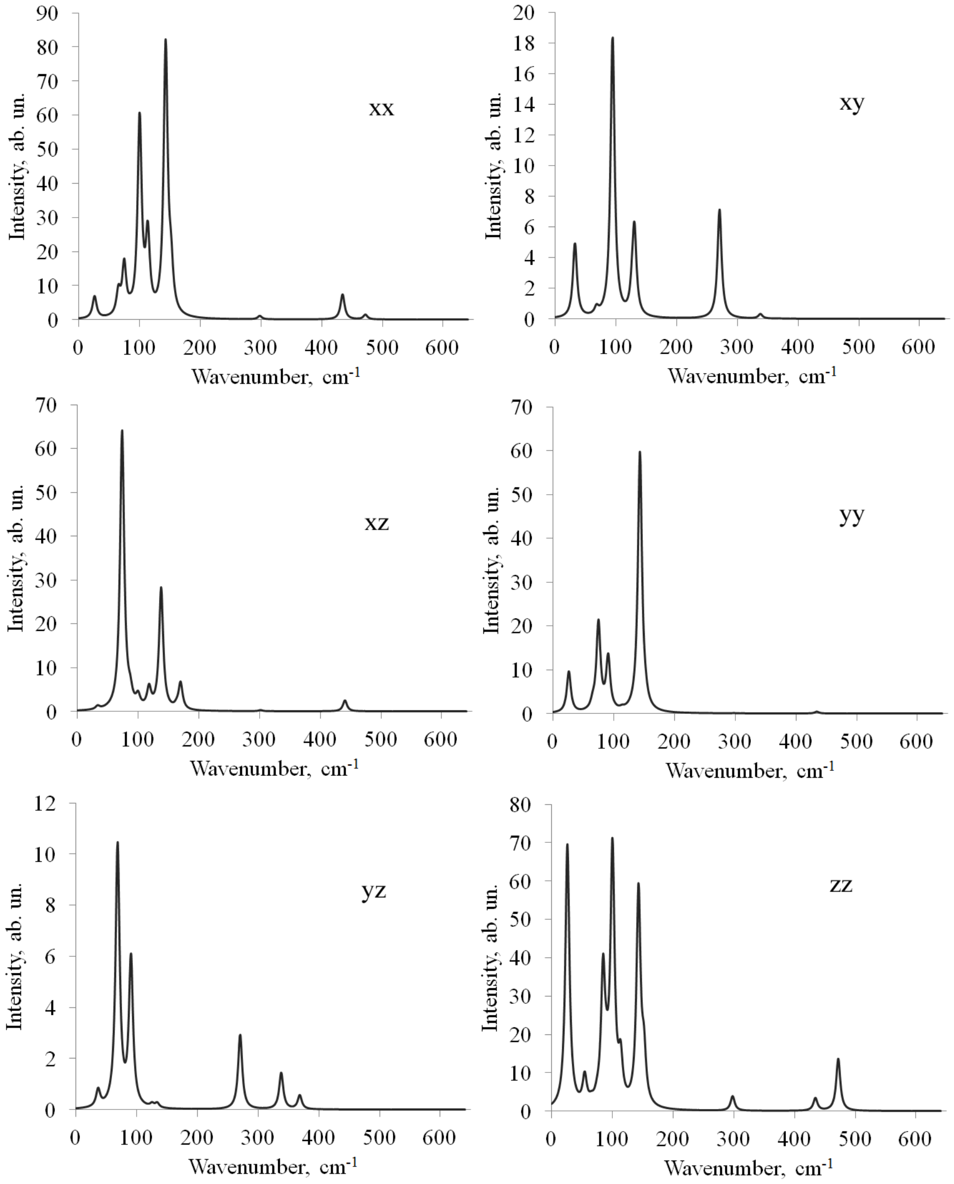

Figure 2. Spectra of single crystal in inequvivalent polarization directions.

High-uranium heterogeneous zircons: Raman, photoluminescence spectroscopy and U–Th–Pb dating by EPMA analysis

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The U–Th–Pb isotope system in zircon may be disturbed, e.g. by the secondary loss of radiogenic lead. Recognition of such alteration is crucial for the interpretation of geochronology results, particularly for chemical dating by electron probe micro-analyzer (EPMA). In the present project, high-U zircon samples from granite pegmatites, Middle Urals, Russia, were studied.

The structural and chemical heterogeneity of samples was characterized by EPMA, including JPD analysis of BSE, CL, O K_α, and U M_β images [1], and Raman and photoluminescence (PL) spectroscopy. We found a high-U interior region (U up to 10.2 wt.%) without obvious indicators of alteration (*Fig.1a*). This zone has stoichiometric composition and its Raman spectrum is similar to that of amorphous $ZrSiO_4$ [2]. Also, we have detected altered zones with lower U concentration that are not stoichiometric and contain non-formula elements such as Ca, Al, and Fe. Its Raman spectrum shows a band near 760–810 cm^{-1} which is not typical of zircon (*Fig.1c*); we assign it to the symmetric stretching of $(UO_2)^{2+}$ groups [3]. This assignment is supported by the intense uranyl-related PL observed. The EPMA age of 245.8±2.2 Ma agrees reasonably well with previous results.

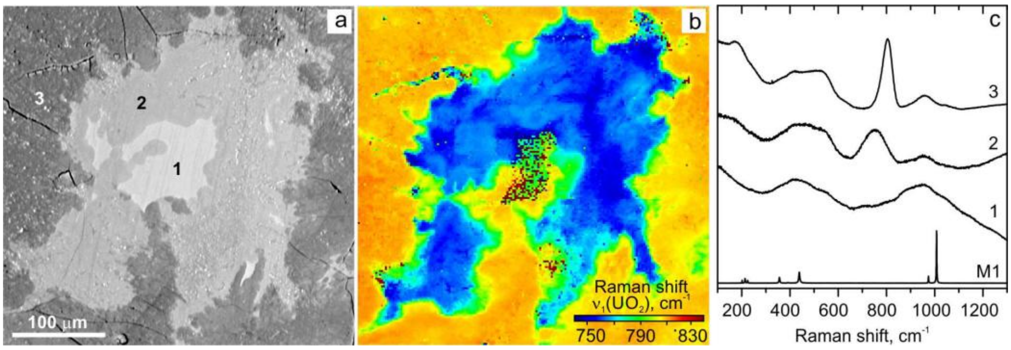

Figure 1. Heterogeneous high-U zircon from the Aduiskii Massif. (a) BSE-image; (b) Raman map visualizing the position of the $(UO_2)^{2+}$ Raman band; (c) Raman spectra obtained in zones 1 (high-U, stoichiometric), 2 (altered), 3(altered), and from kimberlite reference zircon M1.

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Raman study of phase transitions in diphenylalanine nanotubes

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Piezoelectric micro- and nanotubes of diphenylalanine ($C_{18}H_{20}N_2O_3$, FF) are considered as an advanced material for developing new biocompatible sensors, coatings, piezoelectric elements for medical equipment etc. [1,2]. Self-assembling and thermal behaviour of FF micro- and nanotubes is intensively discussed in the literature, and several mechanisms are proposed [3,4]. An irreversible loss of piezoelectric response and second harmonic generation happened around 150°C has been attributed to the phase transition from hexagonal $P6_1$ group to orthorhombic Pbca [5] and irreversible FF cyclization [6]. The detailed study of this process has not been investigated until now.

Micro- and nanotubes of diphenylalanine were prepared by dissolving the FF peptide (Bachem AG) in 1,1,1,3,3,3-hexafluoro-2-propanol at a concentration of 100 mg/mL. The stock solution was diluted by deionized water to final FF concentration of 2 mg/mL. Measurements of Raman spectra were carried out using confocal Raman microscope Alpha 300AR (WiTec GmbH).

Typical Raman spectrum of FF nanotubes consists of two regions: (1) from 10 to 375 cm^{-1} corresponds to lattice vibrations, (2) from 375 to 3250 cm^{-1} corresponds to vibrations of various functional groups. Lattice vibrations of FF nanotubes are characterized by an effective frequency, which is obtained by calculation of the weighted mean over low-frequency spectral region.

Temperature dependence of the effective frequency has two pronounced features at T=100°C and T=140°C. Variations of water-dependent spectral line at 1032 cm^{-1} show, that first feature can be attributed to water evaporation from the nanotubes. The second feature is associated with irreversible structural change of individual FF molecules. Analysis of the spectral lines of certain characteristic vibrations showed rotation of phenyl rings in the molecules [5], and decay of carboxylic and amino groups. The observed effects indicate the cyclization process.

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