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Raman characterization of PTAL samples and their relevance to ExoMars-related studies

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Planetary terrestrial analogue library (PTAL) project

Funded by the European Research Council through the H2020-Compet-2015 programme (grant 687302), the Planetary terrestrial analogue library (PTAL) project (Figure 1) will deliver to scientific community an extended multi spectral database of terrestrial analogues materials that were selected based on their congruence to well-known Martian geological and environmental contexts.

Figure 1: QR code providing direct access to the PTAL website.

In detail, the PTAL project aims at providing future users with: 1) complementary Raman, NIR (near infrared spectroscopy), LIBS (Laser-induced breakdown spectroscopy) and XRD (X-ray diffractometry) data gathered from over 100 samples by using both commercial and dedicated spacecraft instrumentation, 2) analytical results obtained from artificial samples replicating Martian protoliths composition and altered under controlled physical-chemical conditions. 3) direct access to a dedicated software (SpectPro) for the refined interpretation of PTAL spectroscopic data, and 4) physical access to analogues samples and synthesized materials.

Raman analysis of PTAL samples

The whole set of Raman data feeding the PTAL database was gathered using two different systems. On one side, a laboratory spectrometer was manually employed to collect between 15 and 30 spectra from the most interesting spots of each sample. The instrument is composed of the following commercial components: a Research Electro-Optics LSRP-3501 excitation laser (Helium-Neon) emitting at 633 nm, a KOSI Holospec1.8i spectrometer, an Andor DV420A-OE-130 CCD detector and a Nikon Eclipse E600 microscope (objectives of 5x, 10x, 20x, 50x and 100x). On the other side further Raman analysis were carried out by means of the so-called RLS ExoMars Simulator, which is considered one of the most reliable tools to effectively emulate the scientific outcome that will be potentially produced by ExoMars/ Raman Laser Spectrometer (RLS) [1] on Mars. The instrument is composed of a BWN-532 excitation laser (B&WTek) emitting at 532 nm, a BTC162 high resolution TE Cooled CCD Array spectrometer (B&WTek) and an optical head (B&WTek) with a long WD objective of 50x. The vertical and horizontal positioners coupled to the RLS ExoMars Simulator have been designed to emulate the original Sample Preparation and Distribution System (SPDS) of the ExoMars rover. Furthermore, the operations and algorithms carried out by the instrument to autonomously obtain high quality spectra (i.e. integration time/number of accumulations selection and signal to noise ratio optimization) are the ones designed for the RLS on Mars [3]. By means of the RLS ExoMars Simulator, 40 analysis were performed on each sample by simulating the operational conditions required by the Analytical Laboratory Drawer (ALD) of the ExoMars rover. Mineralogical data obtained from the interpretation of the over 4500 spectra collected to feed the PTAL database are summarized in the work of M. Veneranda et al (2019) [2].

Relevance of PTAL samples to ExoMars-related studies

To obtain physical access to PTAL samples offers the unique opportunity to combine the data contained in the PTAL library with further analysis in the laboratory. As proved in the work summarized below, this helps the RLS science team in optimizing the scientific outcome that could derive from the ExoMars rover mission.

Olivine Fo/Fa ratio estimation

According to remote CRISM data olivine represents, together with clino-pyroxene and Fe/Mg vermiculite, one of the major mineral phases of the selected landing site of the ExoMars rover (Oxia Planum). Olivine can be described as a solid solution between forsterite (Fo, Mg2SiO4) and fayalite (Fa, Fe2SiO4) end members. Considering that the Fo/Fa ratio affects both the position of Raman vibrational modes, the wavelength shifts of the main doublet around 820 and 850 cm^{-1} has been deeply studied to formulate empiric equations for Fo/Fa ratio estimations [4]. However, the equations published to date cannot be applied to RLS data since the multiple restrictions to be considered during the development of instruments for space applications makes the RLS to have a lower spectral resolution (6-10 cm^{-1}) than the laboratory spectrometers employed in the referenced works (1 cm^{-1}). To overcome this issue, Erica group researchers are developing Fo/Fa semi-quantification equation that perfectly adapts to the spectral performances of the RLS and the operational modes to be followed on Mars. For this purpose, the whole set of data included in the PTAL database were first evaluated to identify olivine-bearing rocks having different Fo/Fa ratios. After obtaining physical access to the selected PTAL analogues, in-depth Raman analysis were performed by means of the RLS ExoMars Simulator by following the ExoMars operational mode. As suggested by the obtained results, the RLS ExoMars simulator can detect several secondary peaks between 700 and 1000 cm^{-1} (which can be attributed to the internal stretching vibration modes of SiO_4) even when the olivine content in the sample is below 5%. Considering that the exact position of these peaks varies according to the Fo/Fa ratio of the sample under analysis, the additional information provided by their shifting can be used to increase the reliability of the RLS-dedicated Fo/Fa semi-quantification equation. Based on the results obtained to date, this strategy allows to more accurately estimate the Fo/Fa ratio from data emulating the RLS spectra that will soon be gathered on Mars.

Future advances

The RLS science team will soon have access to the spare model of the RLS system, which is now being assembled by INTA. The RLS spare model will become the best spectroscopic tool to simulate on earth the analytical results that the RLS will obtain on Mars. By analyzing an extended set of olivine samples (including PTAL analogues), the instrument will be employed to optimize the proposed equation and obtaining a semi-quantification method that perfectly adapts to spectral response and operational modes of the RLS on Mars. In this way it will be possible to optimize the scientific outcome deriving from the interpretation of RLS data collected on Mars.

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