

## GEO-RAMAN X<sup>th</sup> MEETING

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**G**eo-Raman meetings started in Paris in 1986 followed by Toulouse (1989) and Nantes (1996). The meeting moved out of France for the first time in 1999 (Valladolid-Spain) and continued a wide international journey, Prague 2002, Hawaii 2004, Granada 2006, Gent 2008 and Sydney 2010. They are focused on the application of Raman Spectroscopy to Earth Sciences from the surface to the deep mantle and to earth materials used in cultural heritage. Such meetings are typically interdisciplinary and allow Earth scientists and Raman spectroscopists to present their latest results obtained in these disciplines and discuss transversally. Raman instrumentation and in situ experimentation are also a part of such meetings since this optical spectroscopy in a huge variety of environment including the exploration of planet of the solar system.

**F**or the first time, an international school supported by the European Mineralogical Union will be held. This is a response to the increasing use of this non-trivial spectroscopy in the different disciplines of Earth sciences facilitated by "plug and play" instruments whereas students in Earth Sciences have rarely the possibility to learn this spectroscopy during their education at the university

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## Evaluation of portable Raman instrumentation for detection of traces of life in rocks – implication for the astrobiological prospecting of Mars

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Raman spectroscopy is considered as one of the key nondestructive analytical techniques to be applied within the robotic exploration of Mars aiming to search for traces of life in the geological record. Here, a series of artificially prepared mixtures of organic or carbonaceous material with rock powders and one natural halite sample with an endolithic colonization dominated by cyanobacteria were analyzed in order to evaluate the possibilities of miniaturized Raman instrumentation to detect the spectral signatures of life. The analysis of powdered geological material aboard the rover vehicle is an important part of the analytical protocol considered for the ExoMars mission.

The mixtures were prepared in defined concentrations with  $\beta$ -carotene, whewellite, shungite and graphite as model compounds representing organic/carbonaceous matter potentially related to the occurrence of microbial life as well as established biomarkers like  $\beta$ -carotene. These compounds were mixed separately with two different powdered rock matrices – gypsum and basaltic rock - in order to estimate the lowest detectable concentration of the particular compound in the matrix and measured by the miniaturized spectrometer system using a 532nm laser wavelength for excitation. Thus eight different two-component systems were studied, each one possessing different concentration levels of the organic/carbonaceous material. The differences between individual compounds as well as the role played by the matrix in its detection were registered. Whewellite was the compound which was detected at the highest content, namely 10 wt.%. Shungite was detected at 0.1 wt.% in both matrices (see figure 1 for example), whereas graphite was detected at 0.1 wt.% in gypsum and at 1 wt.% in basalt. As expected,  $\beta$ -carotene being an excellent Raman scatterer due to its polyenic nature was detected in much lower content in both matrices, benefiting also from an enhancement due to the resonance Raman effect using 532nm excitation wavelength. Nevertheless, a significant difference between the gypsum and basaltic matrices was observed. The limiting content detectable in a gypsum matrix was 0.1 wt. ppm (figure 2), whereas in the basaltic matrix it was 10 wt. ppm.

Natural rock, represented by a halite crust from one of the most extreme environments on Earth – the Atacama Desert (Chile) - was also examined as an example of material which can be considered as a Mars analogue. Miniaturized Raman spectrometers of two different types equipped with 532nm and 785nm lasers for excitation, respectively, were assessed for the detection of microbial biomarkers within this natural halite from the hyperarid region of the Atacama Desert. Measurements were performed directly on the rock as well as on the homogenized, powdered samples prepared from this material – the effect of this sample preparation and excitation wavelength employed in analysis will be compared and discussed. From these results, 532nm excitation is strongly favoured for the analysis of powdered specimens due to its high sensitivity towards carotenoids which therefore dominate the spectra with the possibility of their detection at relatively low concentration levels. For the same reason, this wavelength was a better choice for the detection of carotenoids in direct measurements made on the rock sample. The 785nm excitation on the other hand proved to be more

sensitive towards the detection of the key biomarker scytonemin in zones rich in this organic compound.

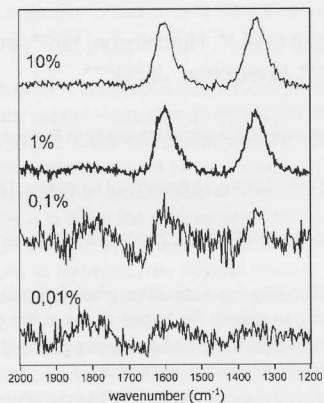


Fig. 1: Shungite bands (D and G bands due to amorphous carbon) as detected at different concentration levels within a gypsum matrix.

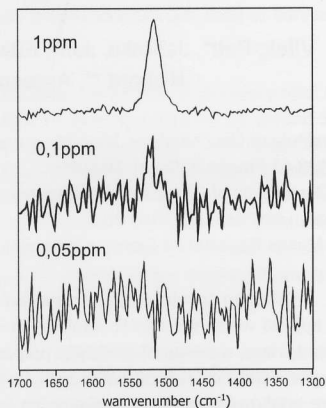


Fig. 2:  $\beta$ -carotene  $\nu_1$ (C=C) band as detected at different concentration levels within a gypsum matrix.