**RAMAN SPECTROSCOPY AS A KEY TOOL FOR THE DETECTION OF BIOSIGNATURES ON MARS.**
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**Introduction:** Raman spectrometry instruments will be part of the future ExoMars 2020 (the Raman Laser Spectrometer) and Mars 2020 (the SHERLOC and SuperCam instruments) mission payloads. This technique is well-suited for astrobiology and *in situ* space exploration since it is able to detect and identify both organics and minerals. In particular, due to the resonance effect, it is very sensitive to pigments and carbonaceous matter, which could be used as potential biosignatures of present or past life on Mars.

On the other hand, the Raman signal of carbonaceous matter alone is not an unambiguous biosignature. In the absence of optical microscope images of potential microfossils and their mineralogical context (due to the limitations of space instruments), the demonstration of the biogenicity of potential life remnants will be relatively challenging on Mars. In this context, 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, and evaluated the influence of the crushing process used during the ExoMars 2020 mission.

**Materials and methods:** For the detection of biosignatures, a Raman spectrometer (WITec Alpha500 RA) equipped with a green Nd:YAG frequency doubled laser at 532 nm wavelength was used. We focussed our study on silicified microorganisms and carbonaceous matter of various geological ages and from various locations. The analyses were made by Raman mapping on 30 µm thick polished thin sections. Complementary systems were used to test the effect of the crushing process, in particular the ExoMars RLS simulator developed in the Unidad Asociada UVA-CSIC-Centro de Astrobiología, in Valladolid, Spain.

**Results:** *Heterogeneity in the Raman signal of carbonaceous matter.* Interestingly, the Raman maps document very fine variations in the spectra of the carbonaceous matter. In particular, the distribution of the intensity ratios of the two main carbon peaks of the spectrum is directly associated with the microfossil morphology. We interpreted this non-random distribution as a consequence of compositional variations in the precursor components [1].

*Crushing process.* Unfortunately, the Raman mapping technique is not planned during the next missions to Mars. This kind of non-random spatial distribution in the signal of carbonaceous matter would thus not be observed *in situ*. Moreover, during the ExoMars 2020 mission, the analyses will be carried out on crushed samples. When using the laboratory Raman equipment, we observed that the sample crushing process leads to a strong increase in the background level and to a decrease in the signal/noise ratio. Moreover, for certain minerals, the Raman spectra can be modified and this may lead to misinterpretation [2]. Fortunately, using the ExoMars instrument simulator (RLS) these effects appeared to be very limited. On the contary, the mixing of the components in the powder appears to facilitate the detection of minor phases [2,3].

*Opaline silica.* Carbonaceous matter is not the only biosignature of microbial remains detectable using Raman spectroscopy. In particular, some mineral phases associated with biological activity may be preserved through time, some of them potentially of interest as biosignatures, such as hydroxylapatite. More interestingly, we were able to detect opaline silica directly associated with carbonaceous matter [4]. While this metastable mineral normally converts to quartz, we have shown that this conversion can be inhibited by the carbonaceous matter within which the opal precipitated. This association seems to be a reliable biosignature that could be detected even in a crushed sample.

**Summary and Conclusions:** Raman mapping permits the identification of certain biogenic characteristics of silicified microfossils. Although some of them will be difficult to detect *in situ* due to instrumental limitation, others, e.g. the association of opaline silica with carbonaceous matter, could be helpful for detecting potential traces of life in Martian rocks.

**References:** [1] Foucher F. et al. (2015) *J. Raman Spec., 46*, 873-879. [2] Foucher F. et al. (2013) *J. Raman Spec., 44*, 916-925. [3] Lopez-Reyes et al. (2013) *Euro. J. Min., 25*, 721-733. [4] Foucher F. et Westall F. (2013) *Astrobiology, 13:1*, 57-67.

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