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Detection of biosignatures in silicified rocks using Raman spectroscopy

F. Foucher and F. Westall
Centre de Biophysique Moléculaire, CNRS, Orléans, France,(frederic.foucher@cnrs-orleans.fr / Fax: +33-2-38631517)

Abstract

In this study, we demonstrate the usefulness of Raman spectroscopy, and in particular Raman mapping, as a very powerful tool for the study of both organic matter and minerals associated with silicified biological remains. Our investigations concern silicified organic matter, microorganisms and biological remains of various origins and ages, from the metacherts of Isua, Greenland, 3.8 Ga, to silicified wood from the Petrified Forest National Park, Arizona, USA, 225 Ma.

1. Introduction

The payload of the ExoMars mission (ESA/Roscosmos) will comprise a Raman spectrometer as part of its instrument suite to help detection of possible traces of life. Potential microfossils dating back to the Noachien 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]. However, due to the subtlety of these traces, their detection $insitu$ on Mars will be relatively difficult and probably based on indirect evidence such as biominerals. Here, we show biosignatures potentially detectable on Mars using Raman spectroscopy.

2. Materials and methods

The Raman spectrometer used (WITec Alpha500 RA) allows compositional 2D mapping from the micrometric to centimetric scale, with up to 160 000 spectra/image. The confocality of the system permits micrometric spot size and 3D mapping using stacking process. It is equipped with two laser wavelengths, green Nd:YAD frequency doubled laser at 532 nm and near IR laser diode at 785 nm.

All the analyses were made on 30 μm thick polished thin sections.

3. Results

The analysed areas were chosen in order to observe the carbonaceous matter and the associated minerals as seen in Fig. 1.

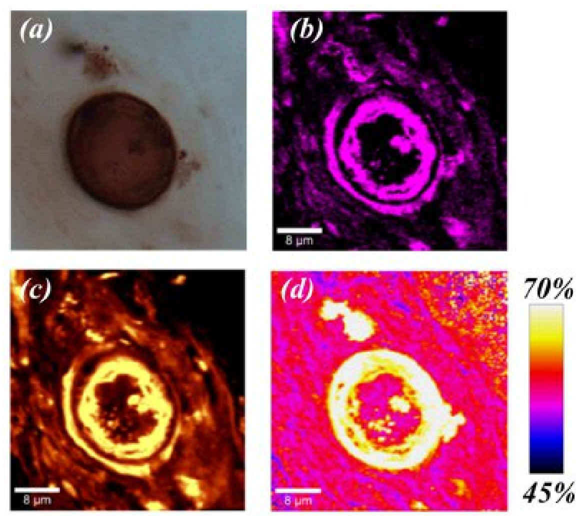

Figure 1: Microfossil from the Draken formation, Svalbard, 800 Ma. (a) Microscopic optical view and Raman map of (b) opaline silica, (c) carbonaceous matter and (d) ratio of the two main peak intensities of the carbonaceous matter spectrum D/G.

These minerals include opaline silica, titanium dioxide (anatase), pyrite or hydroxyapatite. Opaline silica is metastable and normally converts to quartz but, in poorly metamorphosed rocks, such as cherts from the Draken formation, Svalbard, -800 Ma, conversion has been inhibited by the kerogen matrix within which the opal precipitated (Fig. 1b). Both anatase and pyrite may be formed abiogenically but their intimate association with the remnains of microorganisms suggests a link between the diagenesis of the dead organisms and the precipitation of these minerals. Interestingly, the Raman maps also document very fine variations in the spectrum of the carbonaceous matter in relation to the biological remains. In particular, the ratio D/G of the two main peaks of the spectrum (disordered or graphite peaks, respectively) is directly associated with the microbial remains as seen in Fig. 1d.

4. Summary and Conclusions

Raman mapping permits identification of certain characteristics of the organic and mineral signature directly as a function of the microfossils studied. Moreover, trace phases, such as opal, or rare, sparsely disseminated mineral phases are more likely to be identified in mapping mode compared to spot analysis mode.

References

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