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Detection of biosignatures in silicified rocks using Raman spectroscopy

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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, ranging 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 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]. However, due to the subtlety of these traces, their detection *in situ* on Mars will be relatively difficult and probably based on analysis of the complexity of the organic molecules, or on indirect evidence such as biominerals. Indeed, several minerals are associated with the metabolic activity of life since they are formed or used by living organisms. These biominerals are of great interest for the study of ancient traces of life because, in some circumstances, they are more easily preserved than organic matter with the time . Raman spectroscopy is well-suited to study this kind of association since it is able to analyse both minerals and carbonaceous matter. By using a laser beam focused on an area of interest in a sample, Raman spectroscopy allows identification of the components. However, the detection of potentially interesting phases can be difficult or even impossible at the micrometric scale. Raman mapping is then useful to bring to light features that are ´invisible´.

The aim of this study is to determine if Raman mapping can improve the detection of biominerals and if it can detect changes in the spectrum of carbonaceous matter of biological origin.

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 the stacking process. It is equipped a green Nd:YAD frequency doubled laser at 532 nm.

All the analyses were made on 30 μm thick polished thin sections. The analysed areas were chosen in order to observe the carbonaceous matter and the associated minerals as seen in Fig. 1.

3. Results

Using Raman mapping we were able to detect and identify micrometric mineral phases associated with the biological remains; some of them are potentially of interest as biosignature such as titanium dioxide (anatase), pyrite or hydroxyapatite. Both anatase and pyrite may be formed abiogenically but their intimate association with the remains of microorganisms suggests a link between the diagenesis of the dead organisms and the precipitation of these minerals. Indeed, pyrite is known to be a product of sulphur reducing bacterial degradation of organic matter [3]. We were also able to detect opaline silica associated with carbonaceous matter in poorly metamorphosed rocks [4]. This metastable mineral normally converts to quartz but it is shown that this conversion has been inhibited by the carbonaceous matter within which the opal precipitated (Fig. 1b).

Interestingly, the Raman maps also document very fine variations in the spectrum of the carbonaceous matter in relation to the biological remains structure. In particular, the ratio of intensities of the two main peaks of the spectrum (disordered or graphite peaks) is directly associated with the biological remains as seen in Fig. 1c.

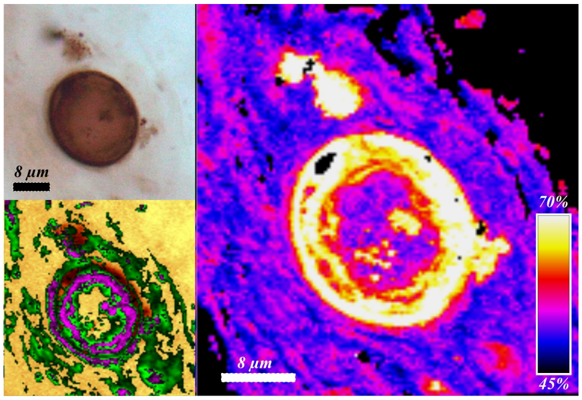

Figure 1: Example of Raman maps of silicified planktonik microorgansims from the 800 Ma old Draken formation. (a) Microscopic optical view, (b) Raman compositional map with the quartz in orange, the carbonaceous matter in green and the opaline silica in purple and (c) ratio of the two main peak intensities of the carbonaceous matter spectrum D/G.

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. Some of these features could be very helpful to detect potential traces of life during upcoming ExoMars mission.

References

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