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Biosignatures observed by Raman mapping in silicified materials

F. Foucher (1), F. Westall (1), and A. Knoll (2)

(1) CNRS, Centre de Biophysique Moléculaire, Orléans Cedex, France (frederic.foucher@cnrs-orleans.fr), (2) Department of Organismic and Evolutionary Biology, Harvard University, Botanical Museum, 24 Oxford Street Cambridge, MA 02138, USA

Establishing the biogenicity of ancient microbial remains is relatively difficult due to their simple shape and small size (micrometric-submicrometric). Potential biosignatures that remain in the rocks are related to morphological aspects of the potential microfossils, their chemical composition (carbon and associated elements), and evidence for metabolic activity (elemental isotopic signature, biominerals, corrosion/leaching features). Detection of biosignatures related to each of these microbial characteristics will increase the confidence with which biogenicity can be assigned to an unknown structure.

However, given the small size of the microfossils and the consequent faint organic/geochemical traces, sophisticated instrumentation, such as mass spectrometers, electron microscopes, proton probes, nano-SIMS or even synchrotrons is generally required. 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 and minerals biosignatures. Our investigations concern silicified, carbonaceous-walled microfossils from the Precambrian (700-800 Ma) Draken Formation, Spitsbergen (Svalbard). The microfossils consist of filamentous cyanobacterial mats containing trapped coccoidal planktonic microorganisms. The filaments are generally $\sim$5 μm in width and the coccoidal structures are $\sim$10μm in diameter. The Raman spectrometer used (WITec Alpha500 RA) allows compositional 2D/3D mapping at a sub-micrometric resolution of fossilised microorganisms, whose biogenicity had been previously established on the basis of their morphological characteristics and carbonaceous composition [1]. Complementary features were revealed by the micro-Raman mapping that may aid interpretation of biogenicity in an unknown structure. They included detection of opaline silica, titanium dioxide (anatase), pyrite and hydroxyapatite associated with the microfossils. Opaline silica is metastable and normally converts to quartz but, in this case where the rocks are very poorly metamorphosed, conversion seems to have been inhibited by the kerogen matrix within which the opal precipitated. Both anatase and pyrite may be formed abiogenically but their intimate association with the remnants of microorganisms suggests a link between the diagenesis of the dead organisms and the precipitation of these minerals. Interestingly, the Raman maps of the Draken microfossils also document differences in the D/G peak ratios within a particular microfossil structure.

Thus, we demonstrate that mapping using micro-Raman spectrometry is a rapid method of investigation of potential biosignatures and an excellent complement to other methods of biosignature detection.

Reference:

[1] Knoll, A. H., Swett, K., and Mark, J., 1991, Journal of Paleontology 65, 531-569.