



Micro-Raman study of Precambrian Permineralized Cells from the Draken Formation.

Frédéric Foucher and Frances Westall

CNRS, Centre de Biophysique Moléculaire, Orléans Cedex, France (frédéric.foucher@cnrs-orleans.fr)

The study of ancient bacterial remains is relatively difficult due to their simple shape and their small size. The morphology of the observed structure is not sufficient to establish its biogenicity and complementary analyses are necessary using high resolution instrumentation, such as elemental analyses by EDX or SIMS, mineral mapping by Raman/IR, or HR-SEM/TEM. Most of this equipment is heavy and the analyses therefore need to be carried out in laboratory. Although some instruments have been miniaturized, their resolution is limited. This is a limiting factor in the search for past life on Mars in the next missions (e.g. MSL, 2011; ExoMars/MAX-C, ESA/NASA 2018). One of the miniaturized instruments is the Raman spectrometer. Laboratory studies have shown the value of Raman spectroscopy (point analyses and mapping) for studying fossil bacteria. Permineralised microbial cells contain both organic and mineral components and may be associated with biominerals. Organic components and minerals can be identified by Raman spectroscopy on the micrometric scale.

With this in mind, *in situ* non-destructive micro-RAMAN analyses were carried out on carbonaceous-walled microfossils from the Precambrian (700-800 Ma) Draken Formation, Spitsbergen (Svalbard). The well preserved (silicified) microfossils come from cherty lenses in a dolomite-dominated conglomerate formed in a tropical tidal flat/lagoonal setting (Swett and Knoll, 1985; Fairchild et al., 1991; Labrot, 2006). The microbiota consists of microbial mats of filamentous cyanobacteria in which the remains of various planktonic microorganisms can be observed. The Raman spectrometer used (WITec Alpha500 RA) allows compositional 2D/3D mapping of the fossilized microorganisms with a sub-micrometric resolution. In this way it was possible to document the presence of very tiny crystals (less than 1 μm) of titanium dioxide (anatase), pyrite and hydroxyapatite within the carbonaceous permineralized walls of the microfossils. The formation of these minerals, in particular hydroxyapatite, is associated with microbial activity. Moreover, microcrystalline silica (opal) is associated with the fossil cells. Previously it had been hypothesised that the silicification of the lenses containing the microbial mats was secondary replacement of carbonate. However, our new finding demonstrates that the microorganisms had been primarily silicified. This explains the excellent preservation of the fossils. Indeed, experiments to artificially silicify microorganisms demonstrated the precipitation of microcrystalline silica (opal) on the membrane of bacteria (Westall et al., 1995). Normally opal recrystallises to alpha quartz with time but, in this case, recrystallisation has been arrested, probably because the presence of organic matter on the nanocrystal surfaces inhibited them from continued growth. A similar observation were made on 1.9 Ga old silicified microbes from the Gunflint formation using TEM (Moreau and Sharp, 2004). The Raman signature of opal associated with carbonaceous matter of a certain structural complexity could be a potential biosignature on Mars especially since Raman spectroscopy is the only space-adapted technique capable of distinguishing opal in a quartz matrix.

References:

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