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Vertical geochemical profile across a 3.33 Ga microbial mat from the Barberton Greenstone Belt.

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Similarities in the habitable characteristics of early Earth and early Mars encourage hypotheses of an independent appearance of life on Mars. Silicified volcanic sands and silts deposited in littoral environments on the early Archaean Earth therefore serve as ideal analogues for sediments deposited on Noachian Mars, when the environmental conditions on the planet were more clement and conducive to life. The traces of life they contain may also be representative of Noachian age martian life, if it ever appeared. Investigations of the geochemical characteristics of such ancient microfossils and biosignatures are therefore of relevance to understanding what kinds of biogenic traces may remain in Noachian rocks, as well as to future studies of traces of martian life in returned samples.

We are making nanometric scale analysis structural and geochemical investigations on a superbly preserved, anoxygenic photosynthetic microbial mat that formed at the surface of exposed, biolaminated littoral sediments (Josefdal Chert, 3.33 Ga [1,2]).

Particularly innovative on material of this age are the synchrotron studies on the sulphur (X-ray Absorption Near Edge Spectroscopy, XANES) and carbon (Near Edge X-ray Absorbtion Fine Structure, NEXAFS) species. XANES at the sulfur K-edge has previously been used to document S bound to recent biogenic organic molecules [3-5] and in 800 My-old microfossils [6].

FIB thin (900 nm) and thick (3 μm) sections across the filamentous microbial mat were made in a number of locations for high resolution TEM-STEM+EDX, SEM+EDX and synchrotron studies, respectively. Raman spectrometry was also performed on the same FIB sections. The Raman analyses were made at WITEC, Ulm, Germany. The synchrotron investigations on FIB sections included (1) X-ray mapping of elements Mg to Fe, XANES at the S K-edge on the Scanning X-ray microscope of the ID21 beamline of the European Synchrotron Facility, Grenoble, and (2) NEXAFS on the carbon species at the National Synchrotron Light Source, Brookhaven..

The mat surface is perfectly preserved but the organic matter beneath the surface is degraded, resulting in an amorphous to reticulate texture that is reminiscent of kopara. Whereas the lower part of the mat has been micritised (Ca, Fe, Mg), the upper layer immediately below the silicified surface is kerogen. *In situ* imaging by X-ray microscopy coupled with XANES analyses at the Sulfur K-edge shows predominantly SO_4 (white line peak at 2482.5eV) in the micritised layer, and organic S (white line peak at 2474eV) associated with the kerogeneous layer formed immediately beneath the upper silicified filaments. XRF analysis of the sulphur documents about 0.1% S in the kerogenous layer. NEXAFS of the kerogen-rich area produced 3 individual peaks (284.5, 286, 287.4-290 eV) that can be related to a number of extracellular polymer components [7]. The Raman spectrum showed that the carbon component of the FIB section exhibited both the D and the G peaks of carbonaceous material that is relatively mature, i.e. in accordance with the degree of metamorphism of the Josefsdal Chert.

This is the first nanometer-scale profiling of an Early Archaean microbial mat. On the level of an individual mat, it demonstrates that anaerobic photosynthetic microorganisms were the primary producers of the mats and that probably other heterotrophs, such as SRBs, were responsible for the very early diagenetic degradation of the organic matter and its lithification (micritisation). Synchrotron studies (XANES and NEXAFS) were instrumental to the fine-scale profiling that has been accomplished on this pristinely-preserved mat. On the basis of this investigation, similar studies of less well preserved ancient materials (and eventually martian materials) will help elucidate the biogenicity of the structures, as well as provide more information about the metabolic strategies of the microorganisms that formed them.

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