VERTICAL GEOCHEMICAL PROFILING ACROSS A 3.33 GA MICROBIAL MAT FROM BARBERTON. F. Westall[1], L. Lemelle[2], A. Simionovici[3] G. Southam[4], L. LacLean[4], M. Salomé[5], S. Wirick[6], J. Toporksi[7], A. Jauss[8].. [1]Centre de Biophysique Moléculaire-CNRS and Université d'Orléans, 45071 Orléans cedex 2, France (westall@cnrs-orleans.fr). [2] Université de Lyon, CNRS, UMR5570 Laboratoire des Sciences de la Terre, USR3010 Laboratoire Joliot-Curie, Ecole Normale Supérieure de Lyon, Lyon, France.[3] Observatoire des Sciences de l'Univers de Grenoble, Lab. Géophysique Interne & Tectonophysique, Maison des Geosciences, BP 53 38041 Grenoble Cedex 9, France. [4]Department of Earth Sciences, University of Western Ontario, 1151 Richmond St, London, Ontario, CANADA N6A 5B7.[5] ID21 Beamline, European Synchrotron Radiation Facility (ESRF), 6 rue J. Horowitz, F-38043 Grenoble Cedex, France. [6]National Synchrotron Light Source, Brookhaven National Laboratory, P.O. Box 5000, Bldg. 725B Upton, NY 11973-5000, USA. [7]WITec Wissenschaftliche Instrumente und Technologie GmbH, Hörvelsinger Weg 6, D-89081 Ulm, Germany

Introduction: Similarities in the habitable characteristics of early Earth and early Mars [1,2] 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 in depth structural and geochemical investigations on a superbly preserved anoxygenic photosynthetic microbial mat that formed at the surface of exposed littoral sediments from the Onverwacht Group (3.47-3.33 Ga; [3]). The relatively large size of the three dimensional structure (~5 mm^2) permits multiple, complementary analyses on one and the same structure and allows nano-scale analysis that provides the kind of information obtainable on living mats by nanoprobes.

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 Absorbance Fine Structure, NEXAFS) species. XANES at the sulfur K-edge has been used to document S bound to biogenic organic molecules (thiol and alkyl-monosulfide) in recent prokaryotic cells. *Eschericia coli* cells [4], in recent microbial contamination of the Tatahouine meteorite [5], in recent microfossils on hydrothermal chimneys [6] and in 800 My-old microfossils from the Draken Formation, Spitzbergen [7].

Materals and methods. The Josefsdal Chert is a small 3.33 Ga exposure in the Msauli River Valley of the Barberton Greenstone Belt, South Africa. It represents a sequence of biolaminites (sedimentary texture formed by the stacking of microbial mats at the sediment surface in a beach/mudflat environment)[8] formed in a littoral mudflat environment (biolaminites have been described from the Late Archaean by [9]). The biolaminites are characterized by alternating whitish detrital layers and kerogen-rich black layers. Very early silicification has preserved the fine, wavy textures of the black laminae. Since deposition and silicification, the chert has undergone uppermost prehnite/pumpellyite to lowermost greenschist metamorphism and is chemically and structurally well-preserved.

One freshly exposed surface of the chert broke open along the plane of weakness represented by one of the microbial mats that had been coated with silica [3]. The 1-5 μm thick mat is formed by 0.25 μm thick filaments that are tens of microns in length. The filaments are streamlined and overturned by water flow but internal layers as well as the top layer are coated with evaporite mineral pseudomorphs (aragonite, gypsum, high Mg calcite, a halide) testifying to intermittent desiccation (desiccation racks also occur in the mat).

FIB thin (900 nm) and thick (3 μm) sections were made in a number of locations across the mat for high resolution TEM-STEM+EDX study and high resolution SEM + EDX and synchrotron study, 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.

Results: The high resolution electron microscope studies show that, although the mat morphology is structurally superbly preserved at the surface by a silica coat, all the organic matter beneath the surface is degraded, resulting in an amorphous to reticulate texture that is reminiscent of kopara (cf. [10]). Small detrital particles are embedded within the mat. Whereas the lower part of the mat has been micritised (the reticulate, polymer-like texture still preserved), the upper layer immediately below the silicified surface is kerogen. The whole thickness of the mat was subsequenttly impregnated by silica. Micritisation of the lower part of the mat is confirmed by the EDX and synchrotron mapping that document the presence of $CaCO_3$ with trace amounts of Fe, Mg.

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. 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.

Discussion: The first surprise provided by this sample was the degree of nanoscale structural and geochemical variability preserved within this 3.33 Ga microbial mat. The similarity between the lower micritised part and the upper, “kopara”-like parts of the mat to structures found in modern photosynthesising mats is astounding (Note that this mat is indeed endogenous and syngenous with the formation of the sediment; it is not a later infiltration or artifact [3]). The primary producing organisms responsible for the growth of the mat were the filaments, probably anoxygenic photosynthesisers. However, the presence of reduced S and sulphate within the bulk of the mat points to the possibility of co-existence of heterotrophic microorganisms, such as sulphur-reducing bacteria (SRBs) [7]. Micritisation of part of the mat, a typical by-product of SRB activity in modern photosynthesising microbial mats (e.g. [11]), supports the presence of SRBs. Indeed, a small colony of rod to vibroid-shaped organisms silicified adjacent to the filamentous mat may represent these microorganisms.

Previous carbon isotope analyses produced two values [3]: a bulk sample had a $\delta^{13}C$ value of -22.7 ± 0.1‰ (0.01 wt% C) whereas a sample from a kerogen-rich layer had a $\delta^{13}C$ value of – 26.8 ± 0.1‰ (layer 0.07 wt%). Given the limitations of the analytical techniques used, these values are necessarily a mix of the isotopic ratios produced by the community of microorganisms living in the mat. However, more inforamtion on the community can be provided by the XANES K-edge S analyses that may point to the presence of SRBs within the bulk of the degraded organic matter beneath the active mat surface.

An important component of biofilms and microbial mats is the extracellular polysaccharides [12]. The peaks picked up in the NEXAFS study are related to different C-containing functional groups, most likely polysaccharides [13].

Conclusions:

This is the first nanometer-scale profiling of an Early Archaean microbial mat. On the level an of an individual mat, it demonstrates that anaerobic photosynthetic microorganisms were the primary producers of the mats and that other heterotrophs, probably 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 the structures, as well as provide more information about the metabolic strategies of the microorganisms that formed them.

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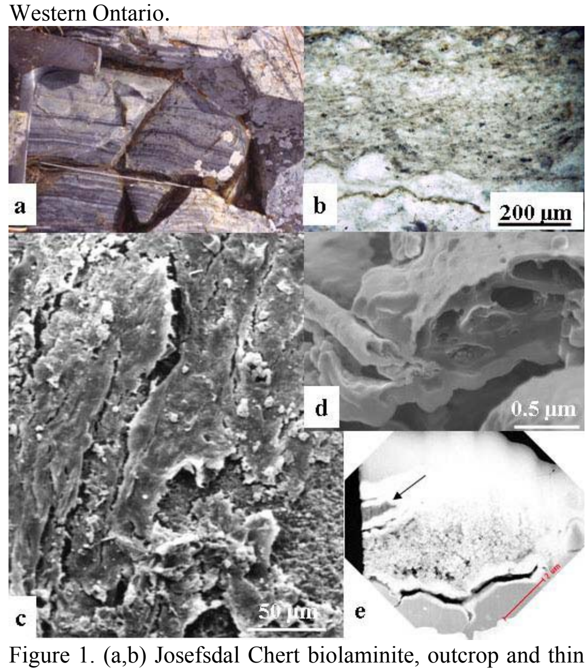

Figure 1. (a,b) Josefsdal Chert biolaminite, outcrop and thin section. (c) SEM view of the 3-D preservation of a microbial mat. (d) FIB cut through part of the mat showing the “kopara”-like internal texture. (e) STEM image showing the lower micritised and upper kerogen (arrow) parts of the mat.