NATURE AND ANALYSIS OF KEROGEN ASSOCIATED WITH EARLY ARCHAEAN BIOSIGNATURES: LESSONS FOR MARS*.

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Introduction: *In situ* biosignature identification on Mars for MSL and the future ExoMars and Mars 2020 missions is primarily based on the analysis of organic molecules in recognition of the fact that other kinds of biosignatures (morphological, mineralogical) may be difficult to conclusively interpret [1]. However, the preservation of any organic component (abiotic or biogenic) on the surface of Mars is controlled by a number of physico-chemical factors including oxidation and radiation degradation [2] resulting in destruction of at least the labile molecules, although the more refractory components may survive [1].

Present understanding of the habitability of Mars indicates that it was most habitable during the pre-Noachian and Noachian (and possibly earliest Hesperian) periods. Thus, missions such as MSL and ExoMars (also probably Mars 2020) are and will be concerned with evidence of habitability and possible biosignatures in these ancient terrains.

From a microbial point of view, the early habitable, anaerobic volcanic and hydrothermal environments on Mars were very similar to those on the early Earth [3,4]. Study of microbial habitats and their preserved traces in Early Archaean rocks 3.5-3.2 Ga is therefore highly relevant for Mars. The early life forms were anaerobic and included chemotrophs, as well as more evolved phototrophic forms based on sunlight as an energy source [5]. The former in particular are good analogues for possible martian life [1,4]. Their traces are preserved as morphological fossils, organic components, isotopic signatures and biominerals [5]. Of especial relevance for Mars, however, are the carbonaceous biosignatures. Study of the structural and compositional attributes of these biosignature types and their distribution can aid the search for, and understanding of, possible organic biosignatures in martian materials.

**N.B. The study presented here is the result of 10 years of work by a consortium that includes: B. Cavalazzi, F. Foucher, J.N. Rouzaud, S. Derenne, M. Bourbin, A. Verchovsky, V. Pierson, J. Watson, I. Wright, Y. Marrocchi, A. Meibom, S. Mostefaoui, F. Robert, L. Lemelle, A. Simionovici, M. Salomé, G. Southam, L. MacLean, S. Wirik, V. Thiel*.

Early Archaean kerogen: I will be using two formations to illustrate the characteristics of the Early Archaean kerogen carbonaceous and the techniques used to study it. The Kitty's Gap Chert (3.45 Ga) from the Pilbara, Australia, is a fine-grained sediment deposited in a littoral environment that contains silicified colonies of chemotrophic microorganisms coating volcanic detrital grains, as well as the locally-transported fragments of microbial mats [4,6]. The Josefsdal Chert Formation (3.3 Ga) from Barberton, South Africa, has the same sedimentology and was formed in a similar littoral environment. It contains carbonaceous laminae representing either microbial mats or detrital carbonaceous remains. It also contains an exceptionally well-preserved microbial mat [7,8].

Preservation: As noted by [1], a variety of processes influence the fate of organisms through geological time (taphonomy) and what is actually preserved is only a fraction of the total original biomass. In the examples used here, the carbonaceous component of the Early Archaean microorganisms was preserved by rapid silicification, not only of the microorganisms (Fig 1a,b) but also of the surrounding sediments and volcanics (the Early Archaean seawater was saturated in silica to which pervasive, siliceous hydrothermal fluids contributed).

*Biogenicity:*Establishement of the biogenicity of the kerogen is as important in these very ancient terrestrial materials as it would be for martian materials. Structural and compositional characteristics as well as the physical distribution of the kerogen with respect to the matrix sediment are important considerations in this process [9].

Structural characteristics: First order information on the structure of the kerogen is provided by Raman spectroscopy documenting its maturity. Spectra from the Early Archaean cherts show two peaks at 1346 and 1586nm, indicating moderately mature kerogen. The maturity of the kerogen is expressed at the nano-scale by small, more or less parallel-orientated leaflets of a disordered poly-aromatic carbon containing small stacks of fringes ~1 nm long, as revealed by HR-TEM (Fig 1c). These analyses were made on extracted kerogen from the Kitty's Gap Chert and on FIB-sections cut directly into the carbonaceous microbial mat in the Josefsdal Chert.

Compositional characteristics: The <u>molecular composition</u> of the kerogen also reflects its maturity since the biomarker molecules gradually break down with geological time. A variety of methods was used to identify the molecular composition of kerogen in the Josefsdal Chert and in the above-mentioned microbial mat. µ-XANES at the S-k edge and NEXAFS of the FIB sections, ToF-SIMS of the carbonaceous layers in the bulk rock (Fig 1d), and pyrolysis GC-MS of extracted kerogen show that the organic matter consists of polyaromatic fragments, such as thiophene, anthracene or phenanthrene. These moieties are consistent with the nanostructure of the kerogen.

The elemental composition of kerogen in the Josefsdal Chert microbial mat, analysed *in situ* on a FIB-section, is primarily carbon with minor amounts of nitrogen and sulphur (up to 1 %). Trace amounts other elements, such as transition metals Fe, Mn, Ni were detected by µXRF on the same FIB-section.

The isotopic composition of the kerogen in both samples (Kitty's Gap and Josefsdal) was measured by stepped combustion of the isolated kerogen (average of – 25.9 to – 27.8 ‰ for Kitty's Gap; -26.8 ‰ for the carbonaceous layers in the Josefsdal Chert). Preliminary *in situ* analyses of the Josefsdal Chert microbial mat record an average -28.9 ‰ value.

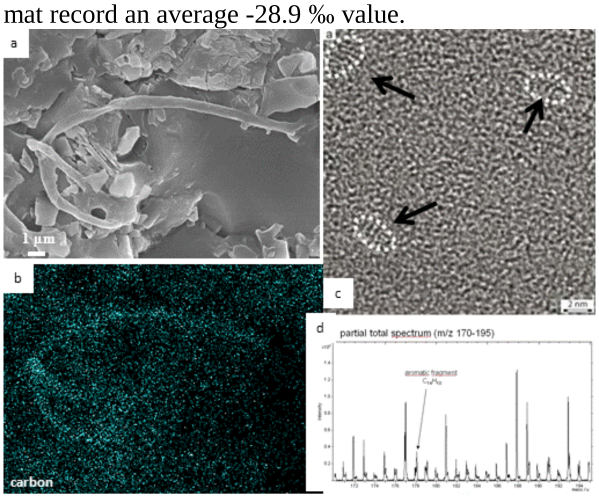

Figure 1. (a,b) Kerogen associated with a microfossil in the Kitty's Gap Chert (3.45 Ga). (c,d) Structure and molecular composition of the aromatic moieties in the kerogen (Josefsdal Chert microbial mat (3.3 Ga).

Distribution of the kerogen: Kerogen in the two samples investigated was distributed in very specific locations with respect to the sedimentary matrix. In the Kitty's Gap sample [4,6], the kerogen occurred as thin films partially coating the 50-200 µm-sized volcanic particles. Optical microscopy showed that the detrital particles often exhibited a dark outline while confocal Raman mapping documented carbon in the form of mature kerogen coating the particles. HR-SEM observation of the volcanic particles *in situ* confirmed this distribution, showing the presence of silicified colonies of microorganisms dotted around the edges of the particles, as well as polymer-filled corrosion tunnels at the particle edges. In the same sample, a sediment surface that had been exposed and then re-submerged by seawater was coated with a thin silicified biofilm consisting of *in situ* microbial cells as well as sedimented detrital fragments of microbial mats.

The microbial mat in the Josefsdal Chert [7,8] sample coats and stabilizes a sedimentary surface. As with the Kitty's Gap Chert, the volcanic particles are often coated with carbon, presumably related to microbial colonization.

Discussion : Relevance for Mars The biogenicity of the kerogen in these cherts was interpreted on the basis of its structure and composition indicating organic molecules that, although highly degraded and no longer containing biomarkers *per se,* still exhibited sufficient complexity to distinguish them from abiogenic molecules. The presence of bioelements, such as N, S, and transition metals in the kerogen was additional confirmation of biogenicity, as was the spatial distribution of the kerogen with respect to specific sedimentary horizons and detrital volcanic particles, as well as to morphological microbial features.

The kerogen in these sediments is significantly mature, consisting of refractory organic molecules. These are the kinds of molecules that would be expected from early martian life, if it existed and if its traces were preserved. Such molecules could survive if sufficiently protected, for example in well-lithified rock. [10] estimated that the combined effects of oxidation and radiation would destroy organic molecules within the upper 1.5 m of the martian regolith. Curiosity has the capability of drilling 10 cm into a rock outcrop, while ExoMars can drill 2m into regolith/soft rock. These depths may offer sufficient protection depending on the lithology of rocks.

Conclusions: The Early Archaean kerogens are good analogues for the carbonaceous remains of possible martian life forms dating back to >3.5 Ga. Their structural and compositional characteristics, as well as their distribution in Mars-analogue volcanic sediments, provide relevant information on what might be found on Mars.

References:

[1] Summons, et al. (2011) *Astrobiology* 11:157-181. [2] Biemann, K. (2007) *PNAS*, 105, 10310–10313. [3] Westall, F. (2005) in.Tokano (Ed.) Water on Mars and Life. Advances in Astrobiology and Biogeophysics, pp. 45–64. [4] Westall, F., et al. (2011). Planet. Space Sci. 59:1093–1106. [5] Westall, F. (2011). in Origins of life, an astrobiology perspective, eds. Gargaud, M. et al. (Cambridge University Press), 391-413[6] Westall, F., et al (2006a). Geol. Soc. Amer. Spec Pub. 405, 105-131. [7] Westall et al., (2006b) Phil. Trans. Roy. Soc. Lond. Series B., 361, 1857–1875. [8] Westall et al. (2011b) Earth Planet. Sci. Lett., 310, 468-479. [9] Westall, F., Cavalazzi, B. (2011) Encyclopedia of Geobiology (Eds.) V. Thiel, J. Reitner, Springer, Berlin, 189-201. [10] Kminek, G., Bada, J. (2006) Earth Planet. Sci. Lett., 245, 1–5.