µ-XANES at the S-K edge and hard/soft XRF analyses of ancient biosignatures in Early Archaean cherts from Barberton, South Africa. A. Hubert[1,2], A. Simionovici[2], L. Lemelle[3], F. Westall[1], B. Cavalazzi[4], J.N.-Rouzaud[5], C. Ramboz[6], [1]Centre de Biophysique moléculaire-CNRS-OSUC, Orléans, France (frances.westall@cnrs-orleans.fr), [2]ISTE-Grenoble, France, [3]ENS-Lyon, France, [4]Univ. Johannesburg, South Africa, [5]ISTO-CNRS-Orléans, France, [6]ENS-Géologie, paris, France..

Introduction: One of the main objectives of a sample return mission from Mars is the *in situ* search for biosignatures [1]. Reliable identification of traces of life in very ancient rocks requires a wide range of evidence that includes: (1) information on the nature of the degraded organic molecules that constituted the former life forms, (2) evidence of metabolic activity, and (3) eventually morphological traces of the fossilised life forms [2-4]. Methods developed for the study of ancient traces of terrestrial life can be adapted to the search for extraterrestrial life. We here describe nanoscale *in situ* analysis of molecular and elemental signatures associated with a previously well-characterised, 3.3 Ga-old microbial mat from the Barberton Greenstone Belt [4,5]. This is a photosynthetic microbial mat that was first calcified and then hydrothermally-silicified as it was living. Although it is unlikely that photosynthetic microorganisms developped on Mars 3], calcification related to sulphur (not sulphate) reducing bacteria activity could have occurred in the vicinity of high biomass production, for instance around hydrothermal vents.

Methods: For this study we cut thin vertical FIB slices 3 µm thick though the mat. We used X-ray Fluorescence spectrometry (XRF) and X-ray Absorption Near-Edge Structure spectroscopy (XANES) of submicrometric resolution at the European Synchrotron Radiation Facility (ESRF) of Grenoble [4]. We focused on sulphur (S) and calcium (Ca) phases as representative of sulphur reducing bacteria activity and carbonate precipitation.

Results: The first set of XRF analyses was made at low energy: 2.5 keV to be more sensitive to the sulphur phase. Coupled with XANES analyses at the S-K edge, they allowed us to identify and localise two different phases of sulphur: an inorganic phase (sulphate, Fig. 1a) and an organic phase (thiophene, Fig. 1b).

A second set of analyses was made at higher energy: 17,4 keV in order to detect heavier elements, such as the Ca. This showed a spatial overlap between the distribution of organic S and Ca (Fig. 2) indicating a potentially common phase. Indeed, high resolution TEM study of other FIB slices of the microbial mat [4] documented the precipitation of the carbonate phase (aragonite) onto the organic matrix of the silicified mat.

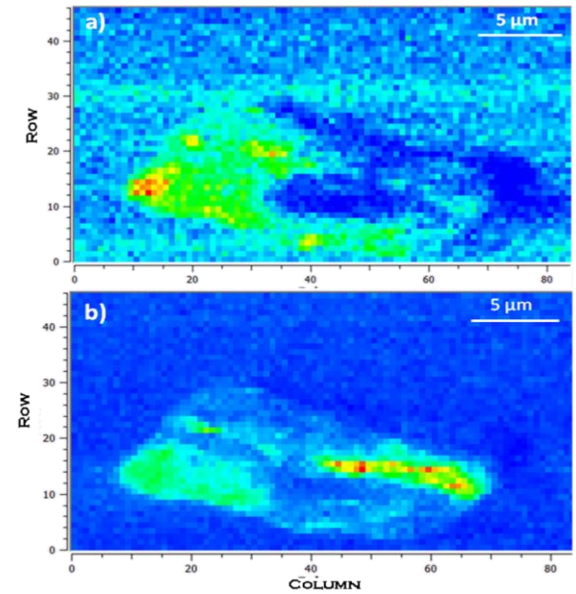

Figure 1. Spatial distribution of the S phases: a) sulfates map at E = 2,482 keV; b) organic S map at E = 2,474 keV.

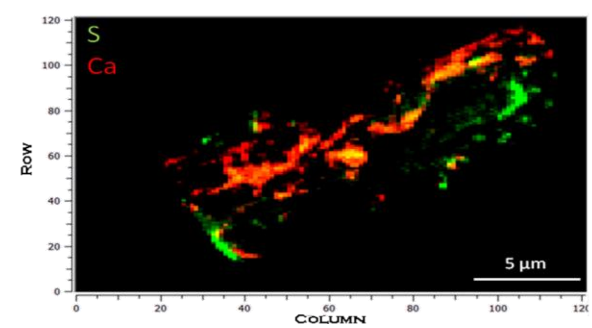

Figure 2. Compared distributions of S (green) and Ca (red). E = 17,4 keV. The overlapping distributions are orange.

Discussion and conclusions: Sulphur, an important bioelement, was detected in both an organic and inorganic phase on a nanometer-scale in this 3.3 Ga-old microbial mat. Thiophene is an organic molecule linked to the reduction of organic matter by biogenic processes [6] but can also be found in abiogenic meteoritic organic matter. Its direct association with the Ca phase aragonite, however, suggests a calcification process guided by sulphur reducing bacteria with the precipitation of crystallites of carbonate on the S-rich organic matrix.

Our study underlines the necessity of using nanoscale *in situ* analyses in the study of ancient biosignatures, as well a pluridisciplinary approach since it was only with HR-TEM that we were able to accurately identify the carbonate phase and to determine the critical association with the degraded organic matter of the microbial mat.

As noted in the introduction, such calcification could occur in hydrothermal settings where anaerobic biomass is (relatively) high. Tentative evidence of hydrothermal activity has been detected on Mars [7] and hydrothermal materials are amongst those proposed for sample return and the search for martian life.

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