# *IN SITU* SEARCH FOR TRACES OF LIFE IN EXTRATERRESTRIAL SAMPLES USING X-RAY SPECTROMICROSCOPY AT THE SULFUR K-EDGE.

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**Introduction:** Extraterrestrial sample return missions have been undertaken (Stardust and Genesis) and are being planned for Mars (Mars Sample Return, 2025). One of the major objectives of the latter is the search for traces of life. It will be important to start searching for traces of life during the preliminary examination stages while returned samples are still stored in their original container in order to determine the quarantine level constraints and to decide on an optimal analytical strategy. *In situ* X-ray fluorescence using synchrotron microbeams and the derived imaging techniques are among the essential tools to be used during preliminary examination stages [1].

Sulfur is a major element in cells and in sedimentary organic matter. It plays an important role in the formation and preservation of fossil organic matter. Its fluorescence photons are more penetrative than those of the other major biological elements (C, H, O, N, P) and X-ray absorption near edge spectroscopy (XANES) at the S K-edge can distinguish sulfur speciation (8 redox states) in organic [2,3] and inorganic compounds [4]. However, few *in situ* microfluorescence studies at the S K-edge [5] have been done in comparison to carbon K-edge. Two selected case studies exemplify the relevance of micro-X-ray fluorescence (XRF) at the S K edge performed at the ID21 beamline of the ESRF to search for traces of life in extraterrestrial samples.

**Experimental method:** The Scanning X-ray Microscope (SXM) of the ID21 beamline of the ESRF is decribed in [6]. At the sulfur K-edge, the SXM provides an energy resolution of 0.2 eV and a 0.3 μm probe size with a flux of up to $10^9$ ph/s. Fine tuning energy of the incident beam in the 2.46 and 2.5 keV range allows recording of XANES spectra and hyperspectral fluorescence images.

**X-ray spectromicroscopy at the S K-edge on micrometer grains in "Stardust" keystones:** Stardust fragments captured in silica-aerogel keystone are unique returned samples. S Kα line fluorescence maps and S K-edge XANES could be made *in situ* within this material on the terminal particles and on their tracks. Sulfides were the only mineral group found [7]. Mapping the entire tracks was shown to be the only method to determine the total mass of the major elements of a cometary grain [8]. Due to significant absorption of S Kα line fluorescence, sulfur abundance quantitation needs further analytical developments, even though exceptional materials were used in the design of the containment gel. This implies that the search for other major elements of biological interest requires the extraction of the samples from their containment material, possibly in an SXM chamber constructed in accordance with quarantine requirements.

**X-ray spectromicroscopy at the S K-edge on micrometer Neoproterozoic cells in a silica matrix:** The kerogeneous cell walls of microfossils embedded in cherts were mapped using S Kα line fluorescence and analysed by S K-edge XANES [9]. Millimeter-sized surfaces were explored at the μm scale by juxtaposition of field of views < 100 $\mu m^2$. The first step in the analysis is the establishment of a systematic inventory of the positions of internal reference marks (topological and surface composition irregularities). This is done by mapping major elements, such as Fe and Si, with Kα line fluorescence. The second step involves quantitation of S by XRF from S Kα line fluorescence maps of $\mu m^2$ zones. For the studied confinment conditions, the minimum detection limit reached for S is inferior to 300 ppm. XANES showed that sulfur in the walls is most likely contained in heterocyclic organic compounds, such as thiophenes. This identification opens up discussions related to the biological origin of the organic matter and of its preservation.

**Conclusions:** These studies show that X-ray spectromicroscopy at the S K-edge allows identification of organic S-bearing compounds within micrometer-sized silica matrices. Silica, as a fossilising matrix may have been important on Noachian Mars as it was on early Earth. Indeed, amorphous hydrothermal silica has recently been discovered on the planet [10]. This method is also a unique nondestructive technique that can be implemented in a SXM allowing millimeter-sized grains and millimetric exploration of natural surfaces with micrometer-scale resolution that is necessary in the search for traces of life in rare materials.

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