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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Imaging sulfur oxidation state of Archaean and modern micro-fossils from submarine hot springs: A clue toward the understanding of the origin of life	**Experiment number**: ME-316
Beamline:	**Date of experiment**: from: 21 November 2001 to: 27 November 2002	**Date of report**: 15 August 02
Shifts:	**Local contact(s)**: J. Susini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Experiment ME-316 aimed at characterizing the oxidation state of sulfur in individual fossilized microfilaments from a black smoker of the East Pacific rise and from a very old hydrothermal system of Archaean age (3.5 billion year old) from the Sulfur Spring Deposit (Western Australia). The main objective was to evaluate if high-resolution micro-XANES analysis at the sulfur edge energy allowed identifying the sulfur redox distribution at a filament scale, which in turn could be interpreted in terms of a biogenic signature inherited from the past activity of sulfur-metabolizing microorganisms.

Central to this approach was to perform analysis of a large variety of standards in order to calibrate the S-edge energy. For this reason, an important part of the beam time has been dedicated to the analysis of pure standard products. These include : S, FeS, FeS_2, $FeSO_4$, $Fe^3{}_2(SO_4)_3$, $Fe_{0.8\text{-}1}S$, CuS, $CuSO_4$ (Cu,Fe)S, $FeCuS_2$, ZnS, (Zn,Fe)S, $ZnSO_4$, $NiSO_4$, $CaSO_4$, methionine, cystine and cysteine.

The structure of the S K absorption edge was scanned in the near edge region. Incident beam energies from 20 eV below the main absorption edge energy of sulfate (2,482 eV for S^{6+}) to 20 eV above the main edge were used. The microscope used a Fresnel zone-plate as a focusing lens and delivered a microbeam of $1\mu m^2$ with a measured photon flux of about 10^8 photon/s.

In order to visualize the internal structure of the microfilament, we mapped out the filaments along their long dimension and then acquired X-ray absorption spectra for each area defined. Figure 1 shows a typical X-ray spectra obtained on a fragment of a filament together with the different maps performed at 2,471 eV (sulfide and/or SH-radicals), 2, 478 eV(sulfide and/or SH-radicals) and 2,482 eV(sulfate). Recognition that the maps at 2,471 and 2,472 eV show different distribution of sulfur species indicates that both sulfide and SH-radicals are present in the filament.

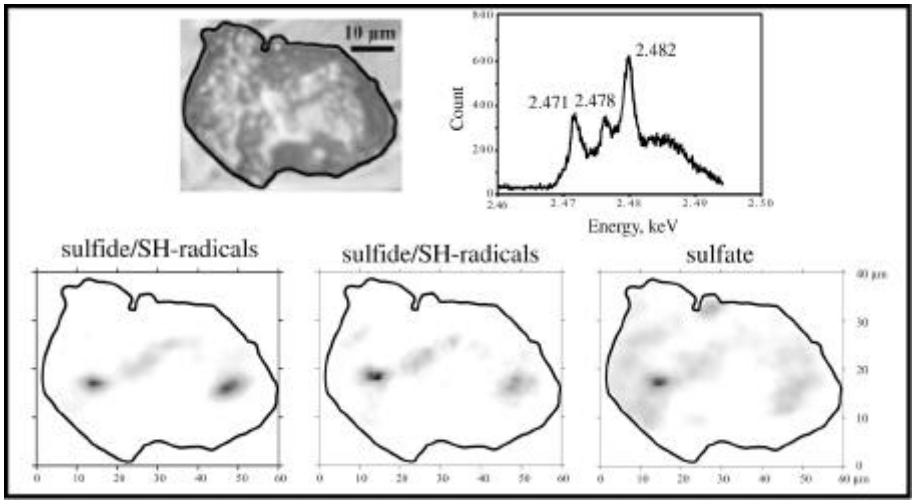

Figure 1. Mico-XANES spectrum of sulfur in a single filament from the East Pacific Rise showing three peaks at 2,482 eV (sulfate), 2,471 and 2,478 eV (sulfide and -SH radicals). Associated maps show the distribution of sulfate, sulfide and SH-radicals withing the microbial filaments shown in inset.

These results suggest that high-resolution microXANES analysis of the oxidation state and local environment of sulfur in individual microfilaments could be used as a new tool for constraining their biogenic origin. With regards to Archaean microfilaments, however, we failed to extract any plausible information in terms of the redox distribution of sulfur because the host matrix contained important content of sulfate (Barite). Our objective in the future ould be to perform the same appraoch described above but on filaments preserved in cherts, which are analogous to the opale coating matrix of the East Pacific Rise filaments.