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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:** Characterization and imaging of bio-geochemical markers from extreme environments (deep sea hydroothermal vents and Archaean metasediments)	**Experiment number**: ME-401
Beamline:	**Date of experiment**: from: June 2002 to: December 2002	**Date of report**: 10 April 2003
Shifts:	**Local contact(s)**: S. bohic, A. Simionovici, A. Somogyi, J. Susini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

P. Philippot*[1], J. Cauzid*[1,2], J. Foriel*[1], B. Ménez*[1], N. Thébaud*[1]

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Report:

The aim of Long Term Project ME-401 is to perform a variety of instrumental developments and experiments dedicated to the imaging and quantitative analysis of minute (µm-scale) and delicate (fluid inclusions, living and fossil microbial filaments, biogenic markers) objects trapped in natural (complex) rock samples. To date, much effort has been devoted to the study of fluid inclusions because, besides their geological interest, they can be considered as relatively simple analogues pertaining to the evaluation of the important parameters involved in quantitative analysis. Important factors to be considered in quantitative simulation and that can be evaluated experimentally using fluid inclusions include their morphology (spherical to ovoid), the occurrence of water or anhydrous phases in the liquid, solid and vapour state, and their location in quartz (SiO_2), a chemically "clean" and transparent host mineral that facilitates X–ray spectra deconvolution and permits optical measurements of the inclusion depth and size. Quantitative analysis of individual fluid inclusions forms the core of the work of Jean Cauzid, a PhD student under the co-supervision of P. Philippot, A. Simionovici and A. Somogyi and co-financed by the ESRF and the CNRS. Satellite to this approach is a variety of investigations devoted at exploring the significance of fluid, microbe and mineral interactions in hydrothermal systems from modern deep sea environment (black smokers, metal sulfide deposits) and in very ancient fossil systems of Archaean age (i.e., 3.5 billion years old hydrothermal system of North Pole, western Australia), which could provide clues to understanding life origin on Earth.

Quantitative analysis and chemical imaging of fluid inclusions were performed on ID22 using X-ray micro-fluorescence, fluo-tomography and phase contrast tomography. With regards to more complex systems involving fluid and microbial interactions, a combination of different techniques including X-ray micro-fluorescence (ID22), X-ray absorption near-edge spectroscopy (ID21) and infrared microspectroscopy (SA5, LURE) was used. We benefited of 24 shifts on ID22 for semester 2002-I, and of 15 shifts (ID 22) and 9 shifts (ID21) for semester 2002-II. Because Jean Cauzid started his PhD in October 2002, we asked to move half of

the shifts of the semester 2002-I to 2002-II. Accordingly, with the exception of 12 shifts performed in June 2002, most of the experiments for the first year of the project were performed in November and December 2002.

TIMETABLE for 2002

	Experiments ID 22	Shifts	Experiments ID 21	Shifts
2002-I	June 2002	12		
2002-II	November 2002	15	November 2002	9
	December 2002 (moved from 2002-I)	12		

Experiments and instrumental developments on ID22

KB mirrors. A major evolution of the instrumental environment on ID22 concerns the installation of a crossed mirror system based on a Kirkpatrick Baez (KB) design during summer 2002 (this development was performed by the beamline scientists, not our group, but we performed a variety of comparative tests during our experiments). This system ensures the focusing of monochromatized X-rays at different incident energy (6 to 17 keV), with a spatial resolution of 2 x 3 μm^2 at a flux of about 1 to 3 10^{11} ph/s. Compared to the previous setup utilizing Compound Refractive Lenses (CRL) and Fresnel Zone Plate (FZP), KB mirrors resulted in optimizing the spatial resolution by a factor of 3 and increasing the flux intensity by one order of magnitude. This new KB environment literally revolutionized our perception of fluid inclusion analysis!

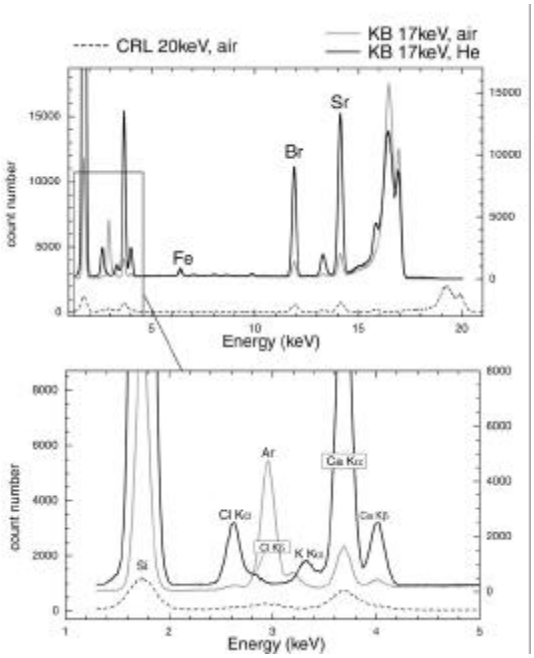

Figure 1. Typical X-ray spectra obtained on the same fluid inclusion of composition close to seawater. Hatched spectrum was obtained using a CRL at 20 keV in air. Plain spectra were obtained using KB mirrors at 17 keV in air (light line) and using a helium chamber (black line).

As an example, Figure 1 shows three fluorescence X-ray spectra of the same fluid inclusion obtained in June 2002 using a CRL and in November 2002 using the KB either in air or using a He chamber (see below). The fluid inclusion analyzed is about 10 µm large and contains a fluid phase with composition close to that of seawater. Results show a sensitivity increase by a factor of 3 coupled with a reduction of time acquisition by a factor of 4 (typically 300 s against 1200 s using a CRL). A positive consequence of this achievement is that we can now perform a sufficiently large number of precise analyses in a reasonnable amount of time, which is prerequisite to all approaches dealing with natural systems. A negative consequence, however, is that most of the data performed in June 2002 using the CRL display such a low count rate compared to the data obtained using the KB setup that we decided to redo the same analysis during the November experiment.

Helium chamber. One of the first task of Jean Cauzid was to install a helium chamber along the beam path in order to reduce the effects of air absorption and X-ray diffusion. This in turn increased the detection limits of light and heavy elements owing to reduced X-ray absorption of soft X-rays and increased signal over background ratio (see Figure1). The first prototype has been used during November and December 2002 experiments. A second generation chamber is under construction.

Quatitative analysis. An important effort has been devoted at improving the interface for the acquisition and quantification of trace element concentrations of single fluid inclusions. A preliminary version of a software developed by Jean Cauzid is currently tested on the data obtained during November and December

experiments. Ideally, we aim at developing a software for on-line data treatment so as to permit evaluating the results during the measurements. In order to test experimentally the effects of the different factors involved in the quantification procedure (fluid inclusion depth and thickness, fluid inclusion geometry, samples thickness, angle of penetration of the incident and fluorescent beams, detector efficiency…), a variety of analysis on microcapillaries and synthetic fluid inclusions coupled with fluo-tomography reconstruction will be performed this semester.

High energy tests at 35 keV. Part of the December 2002 experiment was devoted at testing a new high energy lens that ensured focusing of 35 keV monochromatized X-rays. The lens used was designed by the group of Christian David at the Paul Scherrer Institut. The main interest was to evaluate to which extend heavy elements of major geochemical interests such as iodine could be investigated for their K lines rather then their L lines, the later overlaping with the K lines of the light to medium Z elements (typically around 3-5 keV). With regards to fluid inclusion analysis, iodine is of particular interest as it is commonly used together with bromine and chlorine in geochemical modeling of hydrologic processes. A large variety of geological samples of different origin have been investigated (deep-crustal phlogopite containing up to 7 weigth% Cl from the Norwegian Caledonides, glass inclusions trapped in olivine from the Mt Etna volcanoe, high-salinity inclusions from Dabieshan (China) and Alpine high-presure rocks, low-salinity inclusion fluids from the North Pole Archaean hydrothermal system (Australia), and H_2O-CO_2 inclusion fluids from gold deposits of Portugal, Italy, Australia, France, USA and Columbia. Halogen (Cl, Br, I) contents have been succesfully characterized in the suite of briny inclusions from the Alps and Dabieshan using the lens at 35 keV and the KB mirrors at 17 keV during the same experiment. In other samples, iodine was either too diluted (below the ppm) to be analyzed or concentrated in specific, yet unidentified areas. Nevertheless, these results show the feasibility of developing high-energy X-ray micro-fluorescence analyses on ID 22, hence opening new avenues of research in the future.

Experiments on ID2I, ID22 and SA5 (LURE)

The aim of the experiment performed in November 2002 on ID21 was to characterize the spatial distribution at a µm-scale of the different oxidation states of sulfur in individual living and fossil microbial filaments. In both types of fossil and contemporary filaments, the occurrence of three main sulfur species (sulfate, sulfide and SH-radicals) showing heterogeneous distribution that underline the cytoplasm of individual cells in the case of the present-day filament, suggests that the original microorganisms were actively metabolizing sulfur. These results were published in the 2002 ESRF Highligths. In order to complement the micro-XANES analysis on ID21, the filaments were investigated for their trace element composition using ID 22 (December 2002) and their organic matter content using SA5 (micro-infrared spectroscopy beamline at LURE). Results show the presence of a variety of trace elements including Se and Th in the living filament and the occurrence of CH-radicals and amides in both types of filaments. This clearly implies that the sulfur redox distribution observed at the filament scale was indeed related to microbial activity. These results show the large potential of combining high-resolution synchrotron techniques for extracting unequivocal bio-geochemical information from complex natural matrices, which in turn could be used to track remnant of “life” in Archaean and extraterrestrial material.

Publications relating to the Long Term Project ME 401 performed on beamlines ID22 and ID21

Foriel V., Philippot P., Cauzid, J., Susini J., Dumas P., Khodja H, Ménez, B., Somogyi, A., Moreira D., Fouquet Y. and Lopez-Garcia P. High resolution synchrotron-based imaging of sulfur oxidation states in individual microfossils and contemporary microbial filaments. Geochim. Cosmochim. Acta, in review

and Bohic S. (2003) Trace element content and distribution in a single fluid inclusion from Dunbar Oil Field, North Sea. Journal de Physique IV in press.

Foriel V., Philippot P., Banks D., Rey P., Cauzid, J., Somogyi, A., 2003. Composition of 3.5 Gyr seawater at North Pole Dome, Western Australia, implications for life in Archaean shallow waters. Submited to Chemical Geology.

Philippot P., Foriel V., J., Susini J., Khodja H, Grassineau N., Fouquet, Y. 2003. High-resolution imaging of sulfur-redox state in individual microfossils. Journal de Physique IV, in press

Philippot P., Foriel V., Cauzid, J., Susini J., Ménez, B., Somogyi, A. 2003 Imaging sulfur-metabolising activities in individual filamentous bacteria and microfossils. Highlights ESRF 2002, 85-87.

Other Publications relating to work performed on beamline ID22

Ménez B., Simionovici A., Philippot P., Bohic, S., Gibert, A, Chukalina M., 2001. Insight to X-ray fluorescence micro-tomography of an individual fluid inclusion using a third generation synchrotron light source. NIM B 181 (1-4), 749-754

Ménez B., Philippot P., Bonnin-Mosbah M., Simionovici A., Gibert, F., 2002. Analysis of individual fluid inclusions using synchrotron X-ray fluorescence microprobe: progress towards calibration of trace elements. Geochimica et Cosmochimica Acta, 66, 561-576.

Philippot P., Ménez B., A. Simionovici, Cuney, M., Chabiron, A., Snigirev A., 2000. X-ray imaging of uranium in a single inclusion. Terra Nova, 12, pp. 84 – 89

Philippot P., Ménez B., Drakopoulos, M., A. Simionovici, Snigirev A., Snigireva I., 2001. Mapping trace-metal (Cu, Zn, As) distribution in a single fluid inclusion using a 3rd generation synchrotron light source. Chem. Geol., 173, 151-158.

Sanchez-Valle C., Martinez I., Daniel I., Philippot P., Bohic S., Simionovici A., 2003. Dissolution of strontianite at high P-T conditions: an *in situ* Synchrotron X-ray fluorescence study. Chemical Geology in press.

Vanko, D., Mosbah, M., Philippot P., Roedder, E. and Sutton, S., 2001, Fluids inclusions in quartz from oceanic hydrothermal specimens and the Bingham, Utah, Porphyry-Cu deposit: A study with PIXE and SXRF.Chem. Geol., 173, 227-238.

Master and PhD students involved in experiments using synchrotron radiation at the ESRF

Cauzid, J. Geochemistry and X-ray imaging of trapped fluids from fossil hydrothermal systems : Instrumental developments. PhD Thesis, co-tutelle between ESRF and Institut de Physique du Globe de Paris, Defense planned end of 2005.

Foriel, J., 2000. La géochimie des fluides inclus appliquée à la compartimentation des réservoirs pétroliers, MSc, Institut de Physique du Globe de Paris, 29 pp.

Foriel, J. Caractérisation des relations entre comportement des halogènes (Cl, Br et I), concentration des U, Ni…) et activité organique dans l'océan archéen. PhD Thesis, Institut de Physique du Globe de Paris. Defense planned end of 2003.

Molinari, D., 2001. Elements traces dans les fluides de haute pression : contraintes sur le pétrogénèse des magmas d'arc insulaire. MSc., Institut de Physique du Globe de Paris, 30 pp.

Thébaud, N. Geodynamics of triple point junction : Relationship between deformation, thermal structure, fluid circulation processes and mineralisation. PhD Thesis, co-tutelle between Université Paris 6 and Sydney School of Geosciences. Defense planned end of 2004.