ESRF	**Experiment title:** Characterization and imaging of bio-geochemical markers from extreme environments (deep sea hydrothermal vents and Archaean metasediments)	**Experiment number**: ME-401
Beamline: ID21, ID22	**Date of experiment**: from: June 2002 to: June 2003	**Date of report**: 29 August 2003
Shifts: 75 **(27 left for 2003-II)**	**Local contact(s)**: S. bohic, M. Salomé, A. Simionovici, A. Somogyi, J. Susini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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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.

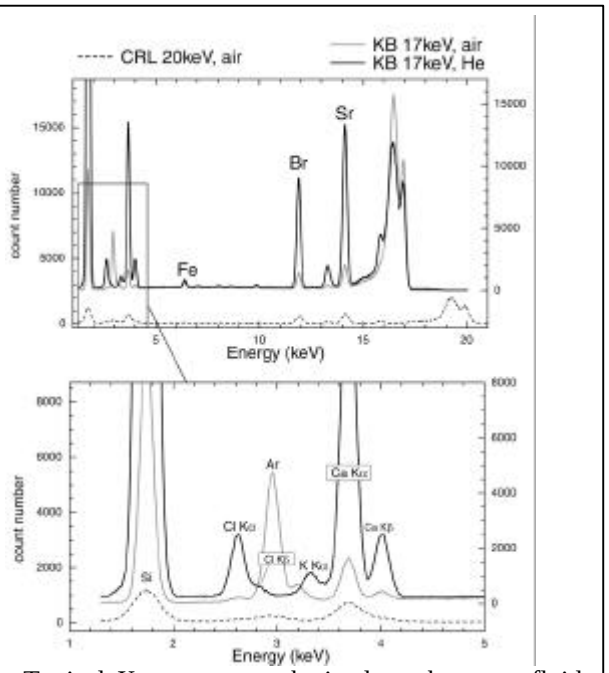
Quantitative analysis and chemical imaging of fluid inclusions were performed on ID22 using X-ray micro-fluorescence, fluo-tomography and phase contrast tomography. With regards to more complex systems involving fluid and microbial interactions, a combination of different techniques including X-ray micro-fluorescence (ID22), X-ray absorption near-edge structure spectroscopy (ID21) and infrared microspectroscopy (SA5, LURE) was used. We benefited of 24 shifts on ID22 for semester 2002-I, 15 shifts for semester 2002-II and 18 shifts for 2003-I and 9x2 shifts on ID21 for semester 2002-II and 2003-I. 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.

*TIMETABLE for 2002 I-II and 2003-I**

	Experiments ID 22	Shifts	Experiments ID 21	Shifts
2002-I	June 2002	12		
2002-II	November 2002	15	November 2002	9
2002-II	December 2002 (moved from 2002-I)	12		
2003-I	June 2003	18	June 2003	9

*18 shifts on ID22 and 9 shifts on ID 21 will be performed current fall 2003

Experiments and instrumental developments on ID22



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

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! 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 scattering. 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 was used during June 2003 experiment. A new generation is currently under construction. This experimental device has already been used by other ESRF users.

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 so far. 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 have been performed during June 2003. Two papers are currently in preparation [1, 2].

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 successfully 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 [9]. 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)

Recent work at the ESRF by the proposers has highlighted the potential for synchrotron X-ray studies of biomarkers in rock samples. This work is pioneering and has received a great deal of interest in the geochemical and microbiological community. Among important experimental breakthrough is the use of combined synchrotron techniques (X-ray micro-fluorescence, X-ray absorption near-edge structure and infrared microspectroscopies) to image the spatial distribution at a µm-scale of a variety of **new** biogenic markers (major and trace elements, C-H and amide radicals, and sulfur-oxidation states) in individual prokaryotic microfossils and in living microbial filaments from deep-sea hydrothermal vents [3, 6, 7, 8]. In both types of fossil and contemporary filaments, the occurrence of CH-radicals, amides, and 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 Highlights and 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. During June 2003 experiment, we performed a series of analysis on the redox state of sulfur in a 6 different prokaryote populations collected in different extreme environments. The results obtained show that not all the population investigated are using sulfur in their metabolism, thus providing a positive control of the interpretation made that what we where dealing with in previous investigations was clearly associated with the metabolism of the microbes and not external contamination (sea water). Apart from these investigations, the first direct constraints on the composition of the Archaean ocean have been obtained by selective analysis of individual fluid inclusions in Archaean basaltic rocks from the Pilbara (Western Australia, 3,500 Myr; [5]). In addition, we have started an comparative study of single fluid analysis from a gold deposit of the Pilbara craton, western Australia (in prep), using SXRF and PIXE analysis using the environmental protocol developed by Chris Ryan at the

Australian CSIRO. This work is part of the PhD study of Nicolas Thébaud in co-tutelle between Sydney and Paris

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

[1] Cauzid, J., Philippot P., Simionovici A., Somogyi A., Foriel J., Menez B., Coupling micro-SRXRF and X-Rays Absorption for quantitative analysis of single fluid inclusions, in prep.

[2] Cauzid, J., Philippot P., Simionovici A., Somogyi A., Galosio B., 2D quantitative mapping of a single fluid inclusion using Synchrotron Radiation X-Rays micro Fluorescence Tomography. in prep

[3] Foriel V., Philippot P., Cauzid, J., Susini J., Dumas P., Khodja H, Ménez, B., Somogyi, A., Moreira D., Fouquet Y. and Lopez-Garcia P. (2003). High resolution synchrotron-based imaging of sulfur oxidation states in individual microfossils and contemporary microbial filaments. Geochim. Cosmochim. Acta, in press

[4] Foriel J., Philippot P., Ménéz B., Simionovici A., and Bohic S. (2003) Trace element content and distribution in a single fluid inclusion from Dunbar Oil Field, North Sea. Journal de Physique IV 104, 385-390..

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

[6] López-García P., Duperron S., Philippot P., Foriel J., Susini J. and Moreira D., (2003), Bacterial diversity in hydrothermal sediment and epsilonproteobacterial dominance in experimental micro-colonisers at the Mid-Atlantic Ridge. Env. Microbiology, in press

[7] 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.

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[9] Philippot P., Molinari D., Cauzid, J, Foriel J., Ménez, B., Somogyi A and Nohammer B (in prep), Cl, Br and I content of HP saline aqueous brines from Dabie Shan and the Alps.

Other publications related to other experiments performed during the last 18 months at the ERSF

[10] Bonnin-Mosbah M., Métrich N., Susini J., Salomé M., Massare D., Ménez B. (2002) Micro X-ray absorption near edge structure at the sulphur and iron K-edges in natural silicate glasses, Spectrochimica Acta, Part B, 57 (4), 711-725.

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[12] Ménez B., Bureau H., Simionovici A., Somogyi A., Massare D., Malavergne V. (2003) In situ SXRF determination of Pb partitioning in Hydrothermal Diamond Anvil Cell, J. Phys. IV, 104, 391.

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[14] Métrich N., Bonnin-Mosbah M., Susini J., Ménez B., Galoisy L. (2002) Presence of sulfite (SIV) in arc magmas: Implications for volcanic sulfur emissions. Geophysical Research Letter, 29, 33/1-33/4.

[15] Métrich N., Susini J., Galoisy L., Calas G., Bonnin-Mosbah M., Ménez B. (2003) X-ray microspectroscopy of sulfur in basaltic glass inclusions. Inference on the volcanic sulfur emissions, J. Phys. IV, 104, 393.-397

[16] Muñoz M., Bureau H., Malavergne V., Ménez B., Wilke M., Schmidt C., Simionovici A., Somogyi A., Farges F. (2003) In Situ Speciation of Nickel in Hydrous Melts Exposed to Extreme Conditions, submitted to Physica Scripta.

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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. 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.

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