EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

	Experiment title: Speciation of copper in vapours and brines under magmatic hydrothermal conditions	**Experiment number**: ME714
Beamline: ID22	**Date of experiment**: from: 20-02-2004 to: 24-02-2004	**Date of report**: 6 August 2007
Shifts: 12	**Local contact(s)**: Dr Gema MARTINEZ-CRIADO	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Dr. Joël Brugger	University of Adelaide, Australia
*Dr. Barbara Etschmann	CSIRO Exploration and Mining, Australia
*Dr. Pascal Philippot	Géosciences marines, CNRS-IPGP, Paris-Jussieu
*Dr. Jean Cauzid	Géosciences marines, CNRS-IPGP, Paris-Jussieu
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*Dr. Weihua Liu	CSIRO Exploration and Mining, Australia

Report:

Traditional models for the formation of hydrothermal ore deposits assume that aqueous fluids transported the metals. This view has recently been challenged by new observations showing that gold and copper are preferentially enriched in vapors coexisting with salty aqueous fluids in some important deposits. We aim to measure experimentally the partitioning of Cu, Au and Te between solid, fluid and vapour at temperatures typical for natural ore deposits (350-600˚C). By improving our understanding of metal transport within the Earth's crust, these data will lead to improved models and technologies for exploring and processing base and precious metals.

The experiment had two main objectives:

(1) Proof of concept for the suitably of a new laser-drilled diamond anvil (Fig. 1) for the experimental study of liquid-vapour and solid-vapour partitioning of transition metals in magmatic hydrothermal conditions (i.e. up to 600˚C, 4 kbar).

(2) Obtain the first experimental measurement for liquid vapour partioning of Cu(I) under magmatic-hydrothermal conditions.

We successfully showed that the drilled diamond are suitable of this work (see Figs. 2a,b), and hence fullfilled objective (1). This took about 6 shifts, because of the complexity of the experimental setup, and some issue with scattering from the Cu-contaminated hydrothermal diamond anvil cell (Fig. 2b). A further 3 shifts were lost due to problems with the beam (beam dropped off for 6 hours, and it took about a day to get the monochromator to work reliably again).

After establishing the methodology and measuring a standard copper solution (homogeneous solution with know copper concentration), we loaded the first ‘real’ sample, consisting of water, a NaCl crystal, and a CuCl crystal. Unfortunately, due to a major failure of the experimental set-up, we where not able to collect "real" data under geologically relevant situations. A gas flow controller failed, cutting the supply of the reducing gas that was protecting the heater, the diamond and the Re-gasket. Because the set-up did not allow for optical observation during x-ray collection, we were not aware of the problem. By the time the problem was identified, the electrical system in the cell had been oxidised, and a diamond had broken down probably due to the oxidation of graphite lining the laser-drilled groove. It would have taken 24 hours to replace the diamond and electrical system, but we had only 24 hours of beam-time left at that stage. We spent the remaining time collecting XANES spectra of standard Cu(I) and Cu(II) solutions loaded in capillaries.

This was our first contact with a 3rd generator beam-line, and the first opportunity to test a complex piece of equipment. We have established the soundness of the approach, and plan to improve the design to ensure success at the next experiment. In particular, we have built a second cell (cost ~AU$25,000), to minimise sample loading time and to suppress the risk associated with a major failure of a cell. We are also working on using a nuclear microprobe to perform preliminary experiments.

In 2004 we had the opportunity to use the large volume X-ray absorption cell developped by Jean-Louis Hazemann and his team at FAME (exp. ME1137), and we have shifted our emphasis towards collecting high quality x-ray absorption data using this cell to understand Cu speciation in brines and low-density supercritical fluids. Based on this understanding, we plan to revisit the hydrothermal diamond anvil cell technology in near future.

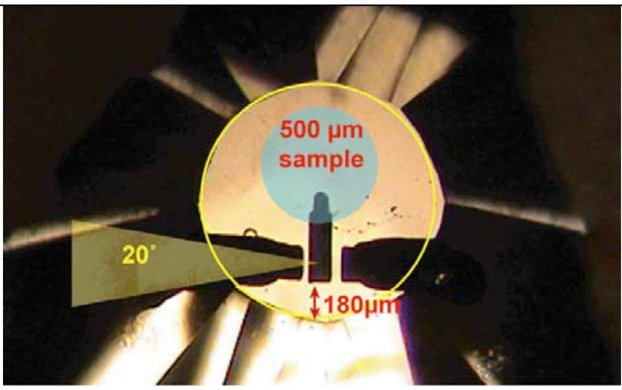
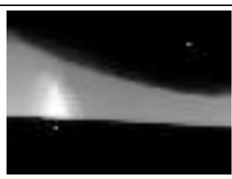


Figure 1. Photo of the face of the laser-drilled diamond cell. The face (yellow circle) is one mm in diameter. The 20˚ correspond to the solid angle to the detector in transmission mode; is fluorescence mode, photons travel through 180 μm of diamond.


(a)

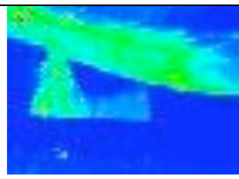

(b)

Figure 2. Imaging of Cu-bearing solution in the HyDAC. (a) Transmission signal, (b) Cu Kα; the triangle is the groove (low absorpion by diamond); the weak signal on the right is from the reservoir away from the groove (high absorption). The large copper signal on the top is due to contamination of the cement used to seal the diamond by copper solution (but it does not contribute to the background on the sample).