



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: ME-1137
Beamline: BM30B (FAME)	Date of experiment: from: 20 July 2005 to: 26 July 2005	Date of report: <i>Received at ESRF:</i>
Shifts: 24	Local contact(s): Jean-Louis Hazemann	

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Report:

Introduction: Magmatic-hydrothermal ore deposits contain most of the world's Cu, Au, Pb, Zn and Ag resources. The long-term goal of this project is to measure experimentally the speciation and solubility of metals in hydrothermal fluids and metal partitioning between solid, fluid and vapour at temperatures and pressures typical for the formation of natural ore deposits (350-550°C; 500-3000 bars) in H₂O-NaCl-H₂S-CO₂ fluids. In particular, we wish to address a major new paradigm in hydrothermal geochemistry: analyses of single fluid inclusions from magmatic-hydrothermal ore deposits (e.g., Porphyry Copper deposits) show that metals such as copper are actually enriched in a low-density "vapour" phase coexisting with a hypersaline brine. Traditional models –and available thermodynamic models- assume that metals strongly partition into the brine under these conditions. Understanding the role of vapour in these systems has the potential to revolutionise our understanding of the formation of some of the world's richest and biggest ore deposits. The present experiment aimed to:

- Determine the speciation of copper in hypersaline brines under magmatic hydrothermal conditions.
- Measure directly the partitioning of copper between liquid and vapour phases.
- Investigate the change in speciation of copper in HCl-NaCl-H₂O solutions as a function of density.
- Test the capability of the CNRS cell for in-situ solubility studies of copper minerals.

Results: Fluorescence and transmission Copper (8979 eV) *K*-edge XANES and EXAFS spectra of Cu(I) in acidic chloride solution were measured with the X-ray cell developed at the Laboratoire de Cristallographie. Despite the synchrotron working in 16 bunch mode with a maximum current of 90 mA, we were able to collect excellent XANES and EXAFS spectra at temperatures to 500°C and pressures to 700 bars for Cu concentrations ranging from 0.05 to 0.3 m.

Speciation experiments. A series of 6 solutions containing Cu(I) and varying salt concentrations were heated under isobaric conditions to 425-500°C: (i) 3.5 m NaCl, 700 b, 30-500 °C; (ii) 0.1 m NaCl, 350 b, 30-425 °C; (iii) 1.15 m NaCl, 450-360 b, 450 °C; (iv) 14 m NaCl, 600 b, 200-500 °C; (v) 6 m NaCl, 500 b, 30-450 °C; (vi) 15.6 m LiCl, 600 b, 25-400 °C. The most graphic experiment was without a doubt (vi), in which XANES

spectra show that the geometry of the Cu(I) complex changes from predominantly tetrahedral (CuCl_4^{3-}) at room temperature, to trigonal planar to linear at 400°C (Fig. 1). This set of spectra is very similar to the one obtained at SNBL (see experiment report ME-998) under isothermal conditions (150°C), varying the salt concentration from 17 m LiCl to 1.5 m LiCl.

Liquid-vapour partitioning experiments. Two experiments were conducted to measure directly the partitioning of Cu(I) between vapour and brine at 400°C. The solutions were pressurised, then heated to 400°C; the pressure was then released slowly until phase separation occurred. We were able to analyse the low density “vapour” phase, but due to the relatively large “dead” volume between the piston and the cell wall, the brine could not be analysed. EXAFS spectra were acquired at different pressures corresponding to increasing amount of vapour in the system.

Copper solubility in supercritical fluids of varying density. One experiment successfully measured CuCl(s) in a H_2O -HCl solution at 420°C, at pressures between 400 and 290°C (Fig. 2). Under these conditions the fluid remains one phase (supercritical); however, the density of the solution changes from 0.42 to 0.20 g/cm³. Results indicate a dramatic decrease in copper solubility, accompanied by subtle changes in speciation as recorded by EXAFS.

Figure 1: Cu Speciation: 15.6 m LiCl

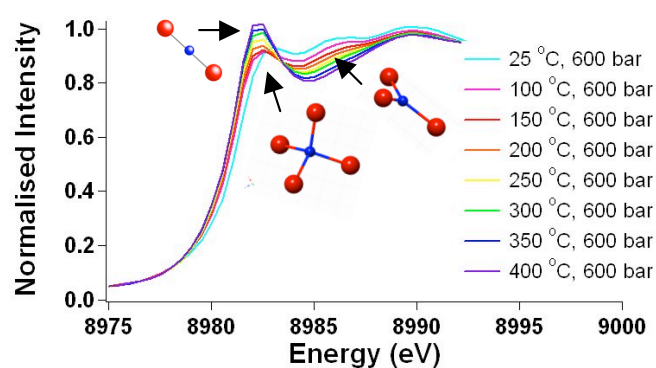
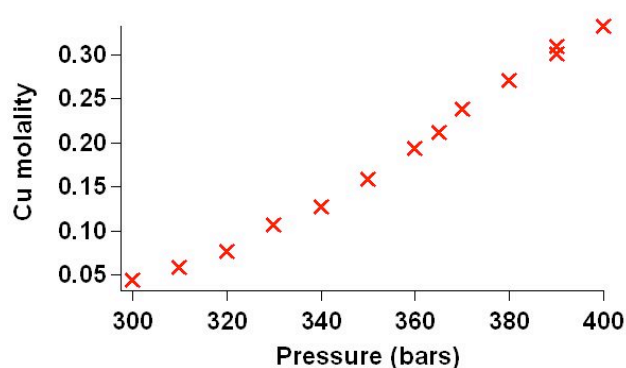


Figure 2: Cu Solubility, 420 °C



Conclusions and recommendations

We successfully obtained the first copper XANES and EXAFS data in supercritical fluids, and conducted the first in-situ copper solubility experiment in low density fluids.

1. We now have a complete, high quality XANES/EXAFS dataset on Cu(I) chloride solutions from 25°C to 500°C.
2. Detailed analysis of EXAFS data is made difficult by the complexity of the speciation in these solutions, which always contain a mixture of species, often with different geometries. Successful EXAFS analysis requires the integration of all available XANES, EXAFS, solubility and UV-Vis spectroscopic data. Preliminary results look good!
3. The solubility study shows that the amount of Cu in solution decreases significantly with decreasing pressure in the supercritical phase; under favourable conditions, a drop in pressure of 100 bars can result in the precipitation of 90% of the dissolved copper; the low density fluids can still carry a significant amount of copper. Hence, pressure may have a more significant role in the formation of ore deposits than previously assumed.
4. The present geometry of the piston prevented successful measurement of the partitioning of copper between brine and vapour. This can be overcome by current developments devoted to minimizing the dead-volume by high precision machining of the glassy carbon cell. However, the current dataset suggests that although low density “vapour” can carry significant amounts of copper, chloride complexes cannot explain the *preferential* partitioning of copper into the vapour phase. Therefore, the focus of the next study will be in studying additional ligands, such as bisulfide.