

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.

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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: Complexation and distribution of Cu between vapor phases (H₂O, S, Cl) and silicate melts: Implications for the formation of magmatic hydrothermal ore deposits.

Experiment number:
30-02 1027

Beamline:
BM-30B

Date of experiment:
from: 16/05/2012 to: 22/05/2012

Date of report:
30/08/2012

Shifts:18

Local contact(s): D. Testemale

Received at ESRF:

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Report:

Field observations and experimental studies provide strong evidences that the formation of porphyry ore deposits (Cu, Au, Mo) in subduction zone-related environments results from the exsolution of a Cl and/or S-rich volatile phase from crystallizing magmatic intrusions at $T < 1000$ °C and $P < 2$ kbar [1,2]. Depending on P-T conditions, two different volatile-rich phase are expected to contribute to the mobilization of Cu, Au and Mo in magmatic-hydrothermal environments: a low-density vapor phase (typical density $0.3\text{--}0.4$ g.cm⁻³) and a denser hypersaline aqueous phase (brine) [2].

The speciation of Cu in both low and high-density phases containing various amounts of Cl and S and ranging from basic to acidic conditions is over-all well-characterized [3,4,5,6,7]. However, as the strong effect of pressure, temperature and melt composition on the solubility of volatile species in arc magmas should in return affect the incorporation of Cu or Au in the exsolving volatile-rich phases [8], it appears critical to assess the nature of the metal species present 1) in arc magmas prior to volatiles exsolution and 2) in aqueous fluids that interact with silicate melts. Such data are of paramount importance if we want to improve our understanding of the processes controlling the transport and segregation of ore metals in subduction zones.

During the allocated beamtime at BM-30B, X-ray absorption (XAS) measurements were therefore conducted up to 700 °C and 1400 bars to determine the speciation of Cu in aqueous fluids equilibrated with haplogranite melts and Cu-bearing andesitic glasses whose compositions mimic that of magmatic-hydrothermal fluids and arc magmas.

The X-Ray Absorption Spectroscopy (XAS) measurements were conducted over the 8.7-9.9 keV energy range with an incident beam tuned by a Si(220) double crystal monochromator and focused down to $\sim 150 \times 300$ (VxH) μm . XAS spectra (EXAFS and/or XANES) were collected using a Canberra 30 elements detector set at 90 ° from the incoming beam.

Four different andesitic glasses synthesized under oxidizing conditions were analyzed to investigate the effect of Cl and S on Cu speciation in arc magmas. G1-03 and G1-05 are Cl and S-free compositions that

contain respectively 4000 and 1000 ppm Cu. GI- 183 contains 88 ppm Cu and 1.23 wt% Cl, and GI-165, 265 ppm Cu and 1850 ppm S (*courtesy of Z. Zajacz*). For XAS measurements, glass samples were mounted between kapton foils and positioned at 45 ° from the incoming beam and the X-ray detector. Spectra were also collected on well-characterized solid standards where Cu is found in different oxidation states, namely native Cu, copper oxides Cu(I)₂O and Cu(II)O, copper chloride Cu(I)Cl and Cu(II)Cl₂ and copper sulfide Cu(I)₂S and sulfate Cu(II)SO₄.

The high P-T experiments were conducted in an autoclave that was previously used to collect *in situ* XAS up to 600 °C and 0.6 kbar [3, 4, 5, 9]. To investigate the speciation of Cu in magmatic-hydrothermal fluids, the hydrothermal cell was loaded with a 2 or 4 m NaCl solution, a flake of native Cu and a piece of haplogranite glass. In order to constrain the effect of silicate melt on the speciation of Cu in the aqueous fluid, the speciation of Cu was also investigated in pure NaCl solution (2 m).

Completion of the experiments required to extend the available P-T range of the hydrothermal cell to conditions that prevail during the exsolution of magmatic-hydrothermal fluids from crystallizing magma bodies but also allow initiating hydrous melting of the experimental haplogranite glass, e.g., T > 600° C at pressure from 1 to 2 kbar. Simultaneous high temperature and high pressure (700 °C and 1.4 kbar) conditions were achieved thanks to modifications of the resistive heater to support higher power input than previously used [9]. The vitreous carbon internal cell was also equipped with longer pistons so that the viton O-rings ensuring hermetical sealing of the sample chamber at high P-T were as far away as possible from the hot spot of the assembly. After each heating step, the concentration of Cu in the aqueous fluid was monitored collecting X-Ray Fluorescence (SXRF) spectra with a monochromatic beam of 10.5 keV (Cu K₁-edge = 8.979 keV) to ensure that chemical equilibrium was achieved before XAS measurements. The preliminary results are summarized below.

1) Cu speciation in silicate glasses

The XANES spectra collected from 8970 to 9020 eV on the GI-03, GI-05 and GI-165 samples are reported in Fig. 1. The andesitic glasses share similar XANES features, with the white line located at 8984 eV that is characteristic of the 1s → 4p transition in Cu(I) compound [10]. The intensity of the absorption edge (A) decreases with decreasing Cu concentrations. The experimental XANES share more similarities with the spectrum of Cu₂O than the one of Cu₂S (e.g., quite similar white line and feature B around 8996 eV), suggesting that Cu is most probably present as Cu(I) oxides in arc magmas, in good agreement with the recent results of an experimental study that indicated that the similar solubility of Cu in S or Cl-bearing andesitic melts provides evidence that CuO_{0.5} is the dominant Cu specie in arc magmas[11]. While the small amount of GI-183 sample available (only few mg) combined with its low Cu concentrations (88 ppm) precluded to collect satisfying XANES spectra, this sample display similar pre-edge feature, suggesting that Cu(I) also occurs in Cl-bearing andesitic glass.

However, the XANES spectra present a small shoulder around 9004 keV (B), which is also present in the spectrum of native Cu and was attributed to the presence of nanoscale metallic Cu inclusions in oxidized silicate glasses [12]. The presence of copper nano -nuggets was not evidenced by time-resolved LA-ICPMS analyses of the glass samples [11] and could either suggest that quench of the silicate melt favor precipitation

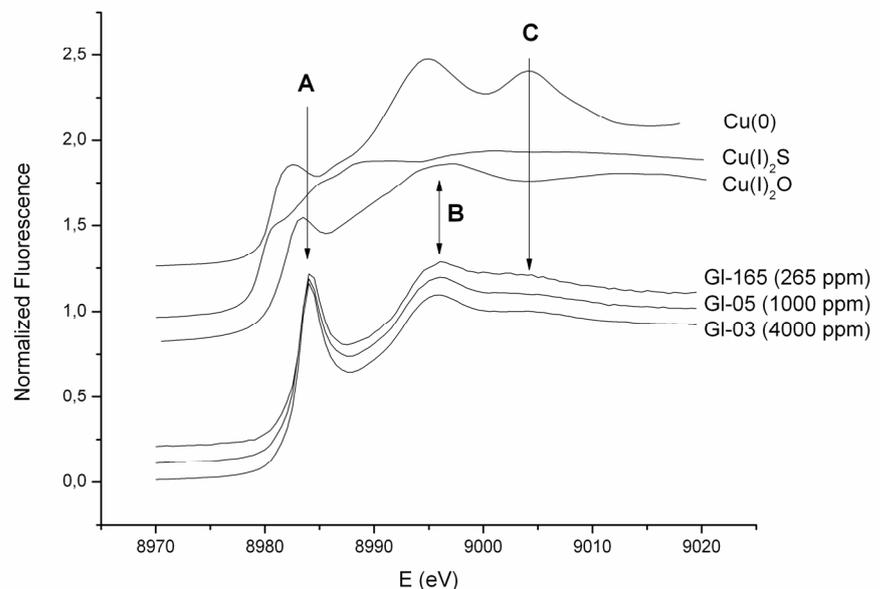


Figure 1 : Normalized Cu K-edge XANES spectra of the andesitic glasses GI-03, GI-05 and GI-165 in comparison to the one of standard compounds Cu(0) and Cu(I) oxide and sulfide.

of small amounts of the Cu originally dissolved in the high P-T andesitic melts or that the solubility of Cu in andesitic melts was slightly over-estimated in [11]. It hence appears necessary to conduct additional *in situ* XAS measurements to accurately address the speciation of Cu in high P-T andesitic melts.

2) Cu speciation in high P-T aqueous fluids

Unfortunately, systematic loss of the high P-T fluid was encountered at $T > 500$ °C, due to unexpected over-heating of the viton O-rings. Nevertheless, several XANES spectra collected in aqueous solutions from 200 to 500 °C and 1 to 1.4 kbar could be recovered. They are presented in Fig. 2, together with the XANES spectra of standard oxide and chloride Cu(I) compounds.

The XANES spectra collected in 2m NaCl solution at 500°C and 1.2 kbar do not resemble those of Cu_2O and CuCl but display a characteristic shape, with an intense pre-edge line around 8983. keV, that was attributed to the formation of linear CuCl_2^- complexes in low salinity LiCl solutions (< 2 m) up to 400 °C and 0.6 kbar [3]. The XANES spectra collected from 200 °C and 1 kbar to 500 °C and 1.4 kbar in aqueous fluid of experiments involving 2m NaCl solution + haplogranite glass are similar to the one of the 2m NaCl solution. This is consistent with the fact that only low amounts of Si, Na and Al dissolved in the aqueous fluid as the haplogranite glass did not experience hydrous melting at the investigated P-T conditions.

Further analyses are yet required to better quantify the effect of dissolved silicates on Cu speciation in high P-T magmatic-hydrothermal fluids, as well as Cu speciation in hydrous melts. The problematic sample loss encountered during the experiments was later solved by a modification of the internal cell design that ensures hermetical sealing of the sample chamber at high P-T (use of silicon O-rings instead of viton O-rings).

In an attempt to quantify the solubility of Cu in silicate melts, LA-ICPMS analyses of recovered quench haplogranite melt were also conducted at ETH Zurich. Measurements enabled detecting trace amounts of Cu (up to 5 ppm) that confirm the low solubility of Cu in the Cl and S-free granitic melts in comparison to andesite [11].

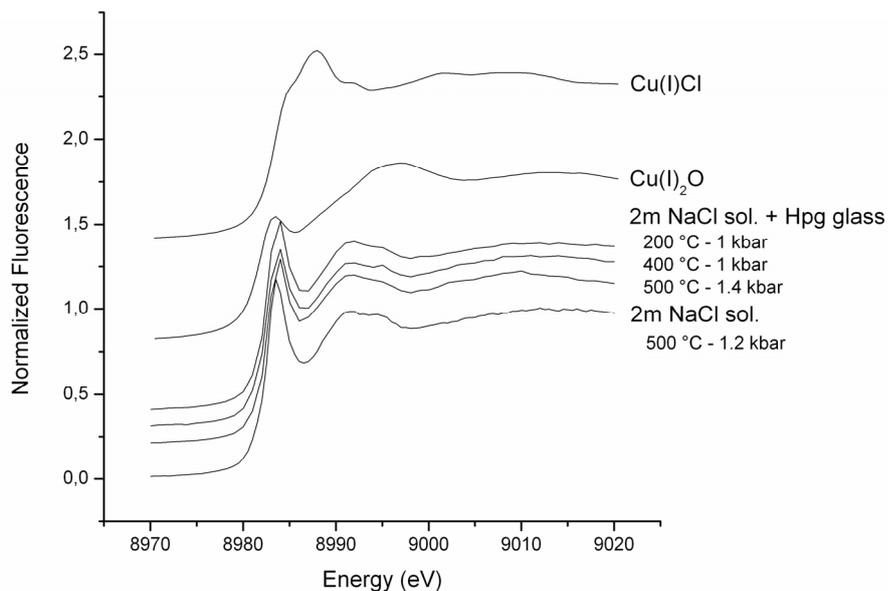


Figure 2: Normalized Cu K-edge XANES spectra collected at different P-T conditions in 2m NaCl aqueous solution in glass-free and glass-bearing experiments.

References: [1] H.L. Barnes, 1997. *Wiley, John & Sons, Incorporated*, 972 p. [2] Hedenquist, J.W., and Lowenstern, J.B., 1994. *Nature* **370**, 519-527. [3] Brugger, J. *et al.*, 2007. *Geochimica Et Cosmochimica Acta* **71**, 4920-4941. [4] Pokrovski, G.S. *et al.*, 2009. *Chemical Geology* **259**, 17-29. [5] Etschmann, B.E. *et al.*, 2010. *Geochimica Et Cosmochimica Acta* **74**, 4723-4739. [6] Cauzid, J. *et al.*, 2007. *Chemical Geology* **246**, 39-54. [7] Heinrich, C.A. *et al.*, 1999. *Geology* **27**, 755-758. [8] Zajacz, Z. *et al.*, 2010. *Earth and Planetary Science Letters* **297**, 50-56. [9] Testemale, D. *et al.*, 2005. *Review of Scientific Instruments* **76**. [10] Kau, L. *et al.*, 1987. *J. Am. Chem. Soc.* **109**, 6433-6443. [11] Zajacz, Z. *et al.*, 2012. *Geochimica et Cosmochimica Acta* **91**, 140-159. [12] Farges *et al.*, 2006. *Appl. Geoch.* **21**, 1715-1731.