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://wwws.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.

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: Complexation and distribution of Cu in hydrothermal fluids and silicate melts: Implication for Cu enrichment in magmatic hydrothermal ore deposits.**	**Experiment number**: EC-1090(IH-CH-752)
Beamline: BM-30B	**Date of experiment**: from: 10/04/2013 to: 16/04/2013 from: 19/07/2013 to: 22/07/13	**Date of report**: 30/08/2013
Shifts:30	**Local contact(s)**: D. Testemale	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M.Louvel, D.Testemale, J-L.Hazemann

Institut Neel - CNRS/UJF UPR2940 – Grenoble - France

Report:

High temperature aqueous fluids and magmatic vapors play a critical role in the formation of ore deposits in volcanic arcs [1]. Field observations and experimental studies indeed provide strong evidences that the formation of porphyry ore deposits (Cu, Au, Mo) results from the exsolution of a Cl and/or S-rich volatile phase from crystallizing magmatic intrusions at $T < 1000$ °C and $P < 200$ MPa [1]. 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 0.3–0.4 g.cm^{-3}) and a denser hypersaline aqueous phase (brine) [1]. Knowledge of the speciation, solubility and partition of metals (Cu, Au, Mo), but also of other elements constituting ore minerals (Fe, As, S), in these volatile-rich phases is fundamental to improve the modeling of porphyry ore deposits formation.
The speciation of As and Cu in both low and high-density Cl and S-bearing phases at basic to acidic conditions, as well as their vapor/brine partitioning behavior is over-all well-characterized [2,3,4,5,6]. However, most studies concentrated on relatively simple systems, *i.e.,* not taking into account the interaction between volatile-rich phases and arc magmas and were conducted at $P < 80$ MPa that only model the late-stage evolution of the hydrothermal system. The few studies investigating Cu partitioning between fluids and melts where either conducted at pressure where only a single phase fluid is present ($P > 1.5$kbar) or analyzed the coexisting brine and vapor as a single fluid phase [7,8].

During the allocated beamtime at BM-30B, we hence conducted experiments that aim to provide new constraints on the effect of pressure and temperature but also of fluid and melt composition on As and Cu behavior in magmatic-hydrothermal environments. Especially, we collected X-ray absorption (XAS) measurements up to 800 °C and 1500 bars to assess the speciation and fluid/melt or vapor/brine partition of these two elements. The first session conducted in April 2013 was dedicated to the investigation of Cu speciation and fluid/melt partition in systems involving H_2O, NaCl and haplogranite melts. A second session was conducted in July 2013 to study the effect of Cl and S on As speciation in aqueous solutions and vapors up to 700 °C and 1500 bars.

All experiments were conducted in an autoclave [9] that was optimized to collect *in situ* XAS up to 950 °C and 1.5 kbar. For experiments dedicated to Cu behaviour in magmatic-hydrothermal systems, the hydrothermal cell was loaded with a 2m 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, pure 2m NaCl solutions were also investigated. Additional experiments were also conducted with 1000 ppm Cu ±2m NaCl solutions to assess the effect of Cu saturation on Cu fluid/melt partition. Experiments investigating the effect of Cl and S on As behavior in high temperature aqueous fluids and vapors, were conducted using a 4000 ppm As – 2m NaCl solution and native S.

The X-Ray Absorption Spectroscopy (XAS) measurements were conducted around the Cu (8.7-9.9 keV range) and As K-edges (11.75-12.5 keV range) using an incident beam tuned by a Si(220) double crystal monochromator and focused down to ~ 150 x 300 (VxH) μm. XAS spectra were collected both in transmission and fluorescence mode using a Si diode and a Canberra 30 elements detector set at 90 ° from the incoming beam. After each heating step, the concentration of Cu or As in the different phases was monitored to ensure that chemical equilibrium was achieved before XAS measurements. Cu and As concentrations were then quantified to ±100 ppm from the absorption edge step of transmission spectra.

In the first set of experiments, we encountered complications during the transition from single phase fluid to two-phase fluid (brine+vapor). Especially, distinction between low-density vapor, high density brine, silicate melt and the C pistons was difficult as both pistons were moving freely to accommodate the volume expansion induced by increasing temperature. In order to facilitate data collection during the second set of experiments, the design of the internal cell was adapted with a fixed upper piston that ensured that all analyses were conducted solely in the vapor phase, without contamination of the signal by brine or melt.

The preliminary results are summarized below.

1) Cu speciation in hydrothermal fluids and haplogranite melts

XANES spectra were collected in aqueous fluids and high temperature vapors up to 800 °C and 150 MPa. In agreement with our previous experiments (Report 30-02 1027), we find that XANES spectra collected in Cu-bearing 2m NaCl solution up to 600°C and 150 MPa display an intense pre-edge line around 8982.5 keV that was attributed to the formation of linear $CuCl_2^-$ complexes [2] (Fig.1-B,C). However, there is a distinct change of speciation at 700 °C, *i.e,* after the separation of the fluid into a vapor and a brine phase, with a shift of the absorption edge of +0.5 eV and a broad flattening of the spectra (Fig.1-D). This spectrum strongly resembles those reported by [2] in low P-T highly saline solutions and suggests that Cu may be present as $CuCl_3^{2-}$ complex in high temperature vapors. The presence of haplogranite melt does not modify Cu speciation in single-phase fluid or high temperature vapor (Fig.1-E)

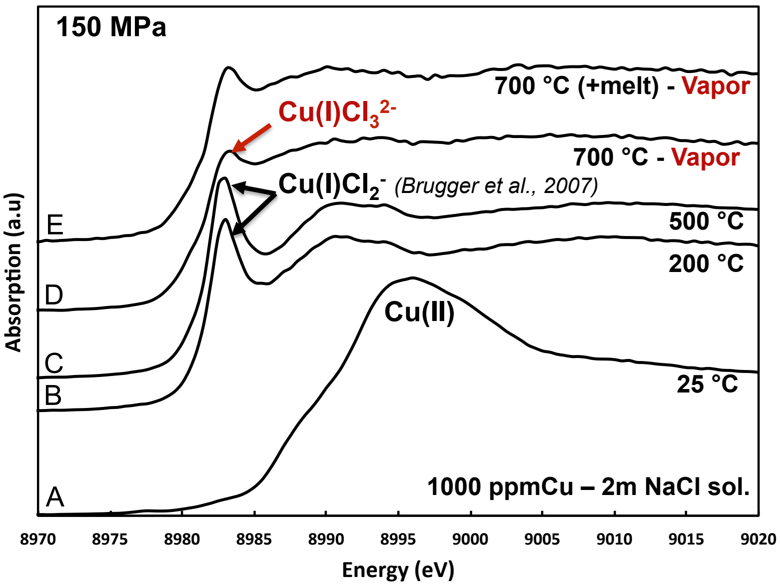

Fig. 1: Effect of temperature on the speciation of Cu in 2m NaCl (±melt) solutions at 150 MPa.

The low solubility of Cu in the haplogranite melt (20-50 ppm as determined by LA-ICPMS) precluded the investigation of Cu speciation at high P-T.

2) Cu partitioning in vapor-brine-melt system

The expansion of the sample volume with increasing temperature removed the melt globule outside of the optical windows, hence precluding *in situ* detemination of Cu concentrations in the haplogranite melt. However, pieces of quench melt were recovered after experiments and analyzed by LA-ICMPS at the ETH Zurich. At quench conditions (825 °C and 150 MPa), the haplogranite melt contains up to 20-50 ppm of Cu, which closely matches the concentrations reported by [8] in similar systems at 800 °C and 100 MPa. These low concentrations confirm the strong partitioning of Cu towards the fluid phases (vapor+brine).

In experiments conducted with 1000 ppm Cu – 2m NaCl solutions, Cu concentrations up to 2000 ppm were observed in the vapor phase at 600 °C and 100 MPa. These high concentrations suggest that Cu may strongly partition into the vapor phase. However, further experiments should be conducted at similar conditions using fixed lower piston to assess Cu concentrations in the coexisting brine.

3) As speciation in high temperature aqueous fluids, vapors and sulfosalt melts

XANES spectra were collected in 4000 ppm As – 2m NaCl solutions up to 700 °C at 50, 100 and 150 MPa. At all investigated P-T conditions, the XANES spectra exhibit a characteristic shape attributed to the formation of $As(OH)_3$ complexes [3]. The transition from single-phase fluid to vapor phase do not modify As speciation. Similarly, Fig. 2. shows that , in the presence of S, As remains as As(III) in the 2m NaCl aqueous fluid. At 400 °C and 100 MPa, we were also able to collect XAS spectra on a S melt globule equilibrated with the 2m NaCl solution. The edge position and the shape of the XANES spectra do not match those of As(III) but closely ressemble those of realgar (AsS) and orpiment (As_2S_3) presented in [4]. This suggest that As occurs as As(II) or As(III) sulfur complex in S melts.

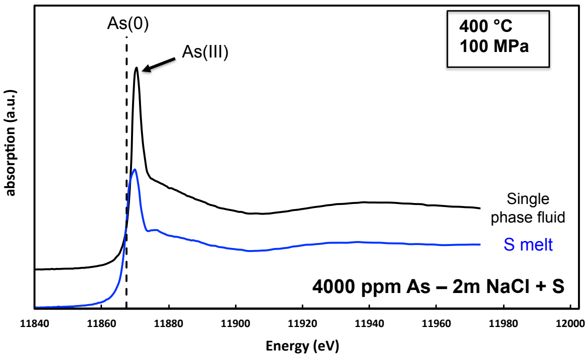

Fig.2: XANES spectra collected in 2m NaCl aqueous fluid (black) and coexisting S melt (blue) at 400 °C and 100 MPa. The dotted black line underlines the position of As(0) absorption edge.

4) Phase transition and densities in the H_2O-NaCl system

Following Beer-Lambert's law, the XAS data collected at the Cu and As K-edge also provide the opportunity to investigate the effect of temperature on the density of the analyzed fluids. In the investigated 2m NaCl solutions, the transition from a single phase fluid to a low density vapor phase that coexists with a denser hypersaline brine phase was monitored as a sudden decrease of the absorbption $\mu(E)$. For all loadings, the fluid density determined in the one phase domain closely match values predicted by [10] at 50, 100 and 150 MPa. However, the density data suggest that, with increasing pressure, the transition from the one phase to two-phase (vapor+brine) domain occurs at temperature significantly lower than expected from the Driesner and Heinrich's model (Fig.3). These observations have been further confirmed by visual observations conducted using sapphire internal cells at the Néel Institute.

This deviation from Driesner and Heinrich's model probably arise from the different experimental techniques used. However, we note that while the model of [10] was based on a significant number of experimental data at P < 50 MPa, this model only includes two datasets for extrapolation of fluid and vapor densities to 500 MPa. We hence plan to continue monitoring the density of NaCl solutions during our future measurements at the BM30-B beamline to ultimately built a new dataset on the effect of P-T-XNaCl on phase transition and brine and vapor densities in the H_2O-NaCl system.

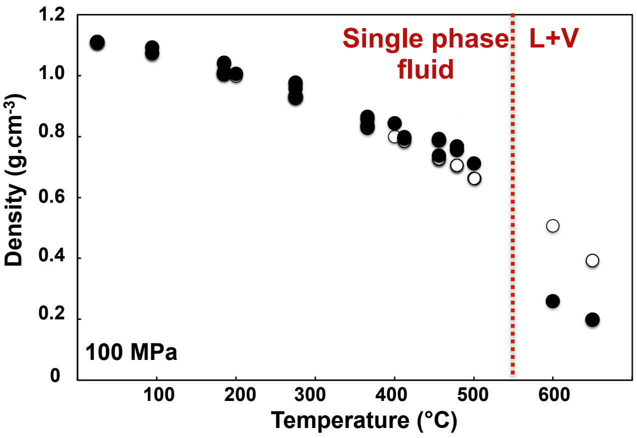

Fig.3: Comparison between experimental data (black circle) and theoretical values calculated from [10](white circle) for the density of 2m NaCl solution. The red dotted line underlines the transition to the brine+vapor domain. The model of [10] predicts that for the experimental conditions, this transitions should occur at 640 °C.

References: [1] Hedenquist, J.W., and Lowenstern, J.B., 1994. Nature 370, 519-527. [2] Brugger, J. et al., 2007. Geoch. Cosmo. Acta 71, 4920-4941. [3] Pokrovski, G.S. et al., 2002. Geochim. Cosmo. Acta 66, 2361-2378. [4] Etschmann, B.E. et al., 2010. Geoch. Cosmo. Acta 74, 4723-4739. [5] Cauzid, J. et al., 2007. Chem. Geol. 246, 39-54. [6] Rempel et al., 2012. Geoch. Cosmo. Acta 94, 199-216. [7] Zajacz et al., 2012. Geoch. Cosmo. Acta 91, 140-159. [8] Frank et al., 2011. Geoch. Cosmo. Acta 75, 2470-2482. [9] Testemale, D. et al., 2005. Rev. Scien. Instr. 76. [10] Driesner and Heinrich., 2007. Geoch. Cosmo. Acta 71, 4880-4901.