Standard Project

Experimental Report template

Proposal title: Solubility and speciation of As, Cu and Fe in high temperature gas mixtures: Implications for the transport and deposition of metals and metalloids in magmatic-hydrothermal systems.		**Proposal number:** 20131042
Beamline:BM30-B	**Date(s) of experiment:** from: 06/02/2014 to:11/02/2014	**Date of report:** 05/03/2014
Shifts:15	**Local contact(s):Denis Testemale**	*Date of submission:* *07/03/2014*

Objective & expected results (less than 10 lines):
The main aim of the experiments was to determine the ability of high temperature volcanic gas to mobilize and transport metals and semi-metals in shallow crustal environements (400 < T < 800 °C and P < 200 MPa). Especially, we wished to assess the effect of different ligands (Cl and S) on the speciation and solubility of As, Cu and Fe as the density of hydrothermal fluids decreases upon decompression en route to the surface (from $\rho > 0.5$ g.cm^{-3} to $\rho < 0.2$ g.cm^{-3}). Therefore, we conducted *in situ* X-ray absorption measurements in an autoclave developped on the BM30-B beamline for the study of supercritical fluids up to 800 °C and 200 MPa [1].

Results and the conclusions of the study (main part):

The experiments were conducted using vitreous carbon instead of Be for the high pressure windows of the autoclave [2]. The low absorption and high purity of vitreous C strongly decreases the detection limits to assess elements' solubility and speciation in transmission mode, which provided the opportunity to conduct our experiments at the Cu K-edge (8.988 keV). Aqueous solutions were loaded with a piece of metallic Cu in an internal high P-T vitrous carbon cell that is hermetically sealed by two vitreous C pistons and placed withing the high P-T autoclave [1]. The sample was first pressurized to 30 MPa before heating to the temperature of measurement. While heating, the pistons that enclose the sample moved freely within the internal cell to accommodate volume expansion. Solutions involving different ligands (Cl, S and Br) were hence analyzed from 325 to 600 °C at 30 MPa to assess the effect of temperature and fluid composition on Cu speciation and solubility in both aqueous fluids and low-density gas (0.7 to 0.1 g.cm^{-3}).
XAS spectra collected in transmission mode (Fig 1.) are used to determine the amount of Cu present in solution/gas mixture at given P-T-X conditions from the absorption edge height $\Delta\mu$ using the Beer-Lambert law [3]. We report a strong effect of fluid density and composition on the solubility of Cu. At 325 °C (ρ_{H2O} = 0.7 g.cm^{-3}), high concentrations of Cu are dissolved in HCl aqueous solutions. In 1.49 m HCl, all the Cu input is dissolved in the high T fluids, suggesting Cu solubility above 2 to 3 wt% , while for lower HCl contents (0.28 m), Cu solubility is about 4200 ±200 ppm. At 425 °C (ρ = 0.19 ± 0.05 g.cm^{-3}), there is still about 500 ppm Cu dissolved in the low-density gas mixture for 0.1 to 0.28 m HCl and Cu solubility increases up to 1000 ±200 ppm for 1.49m HCl. These results demonstrates the ability of high temperature HCl-bearing gas mixtures to carry significant amounts of Cu and are in good agreement with thermodynamic models of [4], who estimated that high temperature low-density HCl-bearing fluids could dissolve from several hundreds to thousands of ppm Cu depending on P-T-redox conditions.

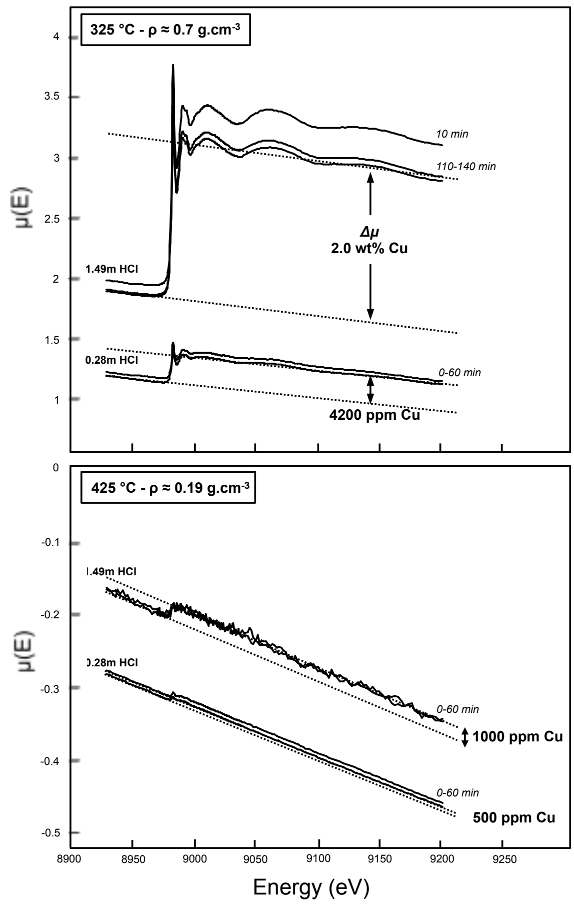

Fig.1. XAS spectra collected at the Cu K-edge in transmission mode to determine Cu solubility as a function of fluid composition and density.

Br and S appear to be less efficient ligands at the investigated conditions. In 0.125m HBr solution, Cu concentrations decrease continuously from about 3000 to 1000 ppm within 90 minutes at 325 °C and Cu concentrations are below detection at 425° C. In solutions containing 0.2m urea peroxide ($CH_6N_2O_3$) and native S, we observed systematic precipitation of CuS, suggesting that at such pH

and redox conditions, high temeprature gases cannot mobilize and transport of Cu.

XAS spectra collected in fluorescence mode provide further information about the effect of fluid composition and density on Cu speciation (Fig.2.). Changes in XANES spectra with composition and density are particularly useful in distinguishing different local environments around Cu atoms.

For Cl and Br solutions, all spectra display a sharp pre-edge located at 8.9820 ±0.0005 keV (A), regardless of composition and temperature (Fig. 2.). This characteristic feature is commonly attributed to linear Cu(I) complexes [3,5]. However, there are distinct changes in the shape of the post-edge oscillations (B) with increasing HCl content and increasing temperature. In the 0.28 m HCl solution (*solid black line on Fig.2.*), the after-edge is composed of a well-defined doublet, with the first feature slightly more intense that the second one at 325 °C. While previous solubility experiments [4] suggested that $CuCl(H_2O)$ could dominate Cu speciation in high density HCl-bearing fluids, this feature is characteristic of Cl-Cu(I)-Cl complexes [6]. With increasing HCl content (1.49 m) the XANEs spectra (*red solid line*) appears slightly flattened and displays a less intense pre-edge (A). However, the similar post-edge features suggest that $CuCl_2^-$ remains the dominant complex.

With increasing temperature, the XANES in the 0.28m HCl solution (black dashed line) remains quite similar, although the increase of the second feature of the post-edge (B), could correspond to the formation of Cl-Cu(I)-H_2O complexes [6]. On the contrary, the XANES collected in the 1.49m HCl gas mixture show significant differences. The whole spectrum is significantly flattened and the post-edge (B) feature is shifted to lower energy. These modifications point towards the addition of Cl around Cu as previously reported upon formation of trigonal $CuCl_3^{2-}$ complexes in high density brines [5]. In our low-density HCl-bearing gas, we attribute the modification of the XANES spectra to the formation of $CuCl(HCl)_2$ neutral complexes. While [4] favored the formation of CuCl(HCl) complexes at similar conditions, we note that in comparison to their study, our experimental XANES display a similar trend upon evolution from high to low-density fluids, *i.e.,* the addition of one Cl atom to the first coordination shell.

In the HBr solution (solid blue line), the strong intensity of the pre-edge (A) coupled to the significant broadening of the post-edge (B) points towards the formation of a linear complex involving both Br and H_2O.

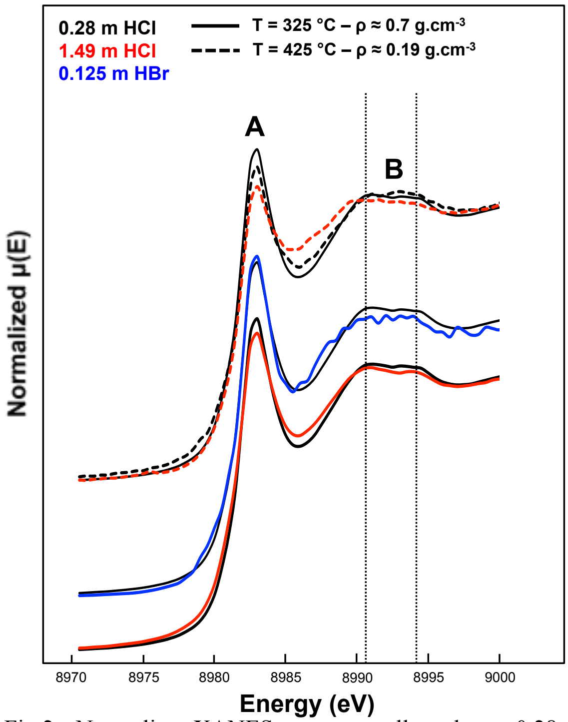

Fig.2. Normalize XANES spectra collected on 0.28-1.49m HCl and 0.125m HBr fluids at 325 and 425 °C at 30 MPa.

The experiments conducted on BM-30B beamline define, to the best of our knowledge, the first in situ constraints on Cu solubility and speciation in low-density gas mixtures. XAS spectra collected on different fluid compositions up to 600 °C at 30 MPa show the decrease of Cu solubility from several wt% to thousands of ppm with increasing temperature. Yet, the high Cu concentrations measured in low-density HCl gas mixtures (500 to 1000 ppm) provide evidence for the efficient mobilization of Cu by high temperature gases that are of critical importance to a better understanding of the processes leading to the formation of ore deposits. XANES analyses further enable distinction between the most likely complexes favoring Cu mobilization by high temeprature gases. EXAFS analyses are currently conducted using the Athena/Artemis packages to determine the structural parameters describing Cu local environement (number of neighbors and distances to nearest neighbors) in high density HCl fluids. Unfortunately, the concentrations of Cu dissolved in the low-density HCl and HBr solutions decrease the quality of the spectra and preclude accurate EXAFS analysis for these conditions.

Justification and comments about the use of beam time (5 lines max.):

The BM30-B beamline provides a unique environment for the *in situ* study of aqueous fluids and gases at P-T relevant for hydrothermal processes occuring in shallow crustal environments (400 < T < 800 °C and P < 200 MPa). The replacement of the classical high pressure optical windows (Be) of the HP/HT autoclave by C windows suggested by the beamline scientist enabled the quantification of Cu concentrations in solution as low as 250 ppm.

Publication(s):

- A manuscript describing the effect of fluid composition and density on the speciation and solubility of Cu in high temperature gas mixture is in preparation for submission to *Geochimica Et Cosmochimica Acta*.

- [1] Testemale et al., 2005. Rev. Sci. Inst. 76, 043905. [2] Testemale et al., *in prep.* [3] Liu et al., 2008. Geoch. Cosmo. Acta 72, 4094-4106. [4] Migdisov et al., 2014. 129, Geoch. Cosmo. Acta 33-53. [5] Brugger et al., 2007. Geoch. Cosmo. Acta 71, 4920-4941. [6] Fulton et al., 2000. Chem. Phys. Lett. 330, 300-308.