Standard Project

Experimental Report template

Proposal title: High-resolution XAS investigation of Cu speciation in H2O-Cl-S supercritical fluids (SCF): Towards a better modelling of metal solubility in magmatic-hydrothermal systems		**Proposal number:** 16-01-801
Beamline: BM16	**Date(s) of experiment:** from: 03/02/2021 to: 09/02/2021	**Date of report:** 05/02/2023
Shifts: 15	**Local contact(s):** Denis Testemale	*Date of submission:* *05/02/2023*

Objective & expected results:
The objective of the experiments was to investigate the nature of Cu complexes in H_2O-Cl-S low-density high-temperature fluids, especially so as to assess whether neutral alkali complexes such as (Na,K)(Cl,S)Cu complexes can be detected with high-resolution technics. The thermodynamic properties of such complexes are well-known from molecular dynamics (MD) simulations but whether they are actually stable in natural fluids remains unknown. This in turn hinders our capacity to model Cu behavior in magmatic-hydrothermal systems and improve our understanding of the formation of porphyry/epithermal and VHMS ore deposits.

Results and conclusions of the study:
The speciation of Cu was investigated in four different solutions: 0.15-0.82mHCl, 0.5m LiCl, 1mKCl-0.15mHCl, 1mNaCl-0.2mHCl and 7.9m LiCl-0.2mHCl. Amongst those, the pure HCl and LiCl-bearing solutions were chosen to mimic compositions that were previously investigated to high-temperature by conventional XAS and sometimes compared to theoretical XANES spectra modeled with the ab initio FDMNES code (Brugger et al., 2007; Etschmann et al., 2010; Fulton et al., 2000; Louvel et al., 2017).
HERFD-XAS were collected up to 550°C at 60MPa at the BM16 beamline using the newly optimized autoclave of the FAME/FAME-UHD group. The high *P-T* HERFD-XAS measurements were conducted at the Cu K-edge (8979 eV) with a beam tuned down to 85x185 μm^2 (VxH at FWHM). HERFD-XAS were collected with 2x3 Si(444) crystal analyser spectrometer (CAS) placed under He_g atmosphere, coupled to a Vortex ® fluorescence detector for an energy resolution of 0.7-0.9 eV at 8046 eV (FWHM).
In comparison to previous measurements at the Cu K-edge with 'conventional' XAS (Experimental report A30-2-1064)[1], the use of HERFD-XAS enables the **identification of two features, previously unresolved under high P-T conditions**: 1) a pre-edge peak centered around 8981 eV that can be attributed to the 1s → 4d transition of Cu(I); and 2) the persistence of a two-crested post-edge feature in high-temperature low-density fluids (Figure 1). This later feature had previously been attributed to the formation of CuCl2- complexes referred to as the *'La structure'* in [2] in hydrothermal solutions. However, charged complexes are not expected to be stable in low-density 'gas like' fluids and we thus suggest that the *'La structure'* here underlines the formation of neutral complexes where Cu is indeed associated with two chlorine atoms but also alkalis. The formation of (Li,Na,K)CuCl2 complexes under high-temperature (T>450°C) is further supported by marked differences with spectra collected in 0.8m HCl, where the *'Lb*

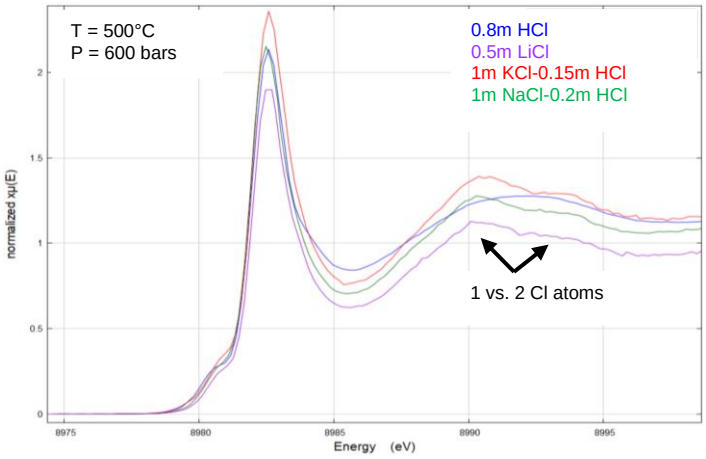

Fig. 1: XANES spectra of Cu in high-temperature low-density fluids. The arrows underline differences in the spectra that are suggested to correspond to the formation of $CuCl(H_2O)$ vs. $(Li,Na,K)CuCl_2$ neutral complexes.

structure' corresponding to $CuCl(H_2O)$ is clearly evidenced by a smooth and broad post-edge feature (Fig. 1). Further EXAFS analysis is currently under way.

Justification and comments about the use of beam time:
Our experimental results constitute the first direct evidence for the formation of neutral alkali complexes in high-temperature low-density fluids. Such complexes had previously been suggested from combined solubility experiments and MD simulations [3,4]. Our empirical confirmation will enable modelers to confidently choose such species when simulating Cu degassing and concentration in magmatic-hydrothermal settings, and hence improve the simulation of ore-forming processes for porphyry and epithermal ore deposits.
The success of this experiment results from efforts from the BM30/BM16 team to develop in-situ HERFD-XAS experiments. Our results demonstrate the capabilities of in-situ HERFD-XAS to probe metallic species that were previously undetectable through standard XAS measurements and pave the way towards new experiments investigating metal degassing as a function of magma composition as part of the ANR JCJC grant METGAS to Marion Louvel.

Publication(s):
[1] Louvel et al., 2017. Chem. Geol. 466, 500-511. [2] Fulton et al., 2000. Chem. Phys. Lett. 330, 300-308. [3] Mei et al., 2014. GCA 131, 196-212. [4] Zajacz et al., 2011. GCA 75, 2811-2827.