

Report for the Experiment EC-324,

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Effect of sulphur on copper transport in hydrothermal vapour and supercritical fluid

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Aims and background

Hydrothermal ore deposits contain most of the world's Cu, Au, Pb, Zn, Ag and U resources. But a major controversy has arisen concerning the formation of World-class porphyry-copper deposits. Current models and all available experimental data suggest that copper should partition strongly into the high-density hypersaline brines. This view has been challenged in the last decade by analyses of natural fluid inclusions showing that Cu, and Au, may partition preferentially in the low-density vapours coexisting with the brines (Heinrich et al., 1992; Ulrich et al. 1999; Cauzid et al., accepted). If confirmed, this would have major implications for our understanding of the formation of many important ore deposits, but also for ore processing and metal recycling technologies.

In vapour phase all existing experimental studies and thermodynamical calculations suggest that those Cu(I) chloride complexes are not sufficient to explain the high copper concentrations (up to weight percents). And since S partitions preferentially in the vapour phases ($\text{H}_2\text{S}(\text{g})$, $\text{S}_2(\text{g})$, $\text{SO}_2(\text{g})$), the existence of copper-sulphide vapour species has been implied (Mountain and Seward, 1999; Archibald et al., 2002; Pokrovski et al. 2005a; William-Jones and Heinrich, 2005). But the current lack of spectroscopic data prevents from concluding on the speciation of those copper-sulphide species. This is the missing piece of information to interpret further XAS data on natural inclusions.

The aim of this experiment is thus to collect high quality XAS data on these copper- sulphide complexes in low density Cu-S-NaOH-H₂O and Cu-S-NaCl-H₂O vapour systems. This is a crucial step in the understanding of Cu mobility in the Earth crust and resolving of this highly debated issue in economic geology and mining engineering.

Experiments

A series of XAS measurements were conducted for the sample solutions listed in Table 1. For each solution the cell was pressurized to 600 bars, then XAS data were collected during heating from 30°C to 381-600°C, and phase separation was attempted either by isobaric heating or isothermal decompression.

The evolution of the XANES spectra for the 2 m NaHS solution coexisting with a piece of $\text{Cu}_2\text{S}_{(\text{s})}$ (Solution 2, Table1) are plotted in Fig. 1a. This pre-edge peak is characteristic of copper(I) in aqueous solution and has been observed in previous XAS studies of Cu(I)-chloride solutions (e.g., Fulton et al., 2000; Brugger et al. 2007; Liu et al., 2008). There was no significant change in the spectra with further heating from 240 °C to 428 °C, and decompressing from 600 to 220 bars at 428 °C. The most noticeable difference between Cu-Cl and Cu-S XANES spectra is in the second peak – which is relatively symmetric in the [O-Cu-Cl] spectrum, but skewed towards the right in the Cu-S spectrum (Fig. 1b).

Table 1 Solution samples used in XAS measurements. The pH at 400C , 600 bar were calculated using HCh (Shvarov and Bastrokov, 1999) and only provide a qualitative indication. The density is pure water density calculated using NIST database.

Sample #	Composition	Estimated pH at 400C, 600b	T (°C)	P (bar)	density (g/cm ³)
Sol#1	9 M NaHS + 5.8 mg Cu ₂ S + 4.1 mg Cu	9.0	550	600	
Sol#2	2m NaHS + 0.4 mg Cu ₂ S	8.61	30-428	600-220	1.08-0.56
Sol#3	1.56 m thioacetamide (CH ₃ CSNH ₂) + 0.4 mg Cu ₂ S	5.33	30-500	600	1.09-0.26
Sol#4	2 m NaHS + 0.6 mg Cu ₂ S	8.61	30-592	600	1.07-0.16
Sol#5	1.4 m thioacetamide + 1.2 mg Cu ₂ S	5.35	30-475	600	0.96-0.24
Sol#6	H ₂ O calibration				
Sol#7	9 m S + 1.9 mg Cu ₂ S	2.31	30-600	600-360	1.07-0.42
Sol#8	2m NaCl + 2.5 m S + 0.5 m anthracene + 0.4 mg Cu ₂ S	4.68	30-600	600	
Sol#9	1.5 m NaCl + 3.6 m S + 1.7 mg Cu ₂ S	3.63	30-522	600-350	1.08-0.14

The effect of pH on the Cu-S complex was investigated in near-neutral (Sols. 3 and 5, pH_{400°C} ~ 5) and acidic (Sol. 7, pH_{400°C} ~ 2) conditions. Under acidic conditions (Sol. 7), the copper concentrations are below the detection limits, and the most XANES spectra are very noisy and resemble the mixture of copper in the window and Cu₂S solids. Under near neutral conditions (Sols. 3 and 5) the XANES spectra at the room temperature 600 bars resembles the spectrum of Cu₂S_(s), and again the solubility is close to the detection limit. With heating the pre-edge peak at 8992.3 eV emerged and increased until at 287°C the XANES spectrum is similar to those of the basic solutions (Sols. 2 and 4, Fig. 3).

The solutions with both S and Cl show subtle variations in the XANES spectra with heating. At lower temperatures the second peak is more symmetrical while at higher temperatures it resembles [Fulton et al. \(2000\)](#)'s Cl-Cu-Cl structure, indicating that the predominant species is CuCl₂⁻ (Fig. 2), which is in agreement with estimations based on available data, calculated using HCh. This observation is also in good agreement with the previous XANES studies suggesting that CuCl₂⁻ predominates in natural fluid inclusions from porphyry copper deposits (e.g., [Cauzid et al., 2007](#)) where the ore-fluids are expected to be a mixture of Cl and S, as evident by the presence of chalcopyrite daughter crystals in some of the inclusions.

Results

1. This study has provided the first in-situ evidence of the solubility of copper sulfides and the structure of the predominant copper species in sulfuric fluids at high temperature. We find that linear Cu(HS)₂⁻ predominates in alkaline solutions (Fig. 3), which indicates that aqueous Cu-S complexing at high temperature and pressure is simpler than under ambient conditions where various types of multi-nuclear species have been identified ([Helz et al, 1993](#)).
2. The Cu₂S solubility we observed in this study shows a remarkably good agreement with the solubility calculations using available thermodynamic data for copper hydrosulfide complexes (mainly Cu(HS)₂⁻) from [Mountain and Seward \(1999, 2003\)](#) and [Akinfiyev and Zotov \(2001\)](#),

suggesting that these data are reasonable and can be used for modeling of copper transport in hydrothermal sulfuric fluids (Fig. 4).

- The phase separation data from this study shows that significant amounts of copper can be partitioned into vapor phase (Fig. 5), with apparent partitioning coefficients around 0.3-0.8, in good agreement with the results of Pokrovski et al. (2008) and Simon et al. (2008). The predominant species in the vapor phase is likely to be $\text{Cu}(\text{HS})(\text{H}_2\text{S})$. However, most available experimental data still are not able to explain the preferential partition of copper into the vapor phase observed in many natural fluid inclusions from porphyry deposits.
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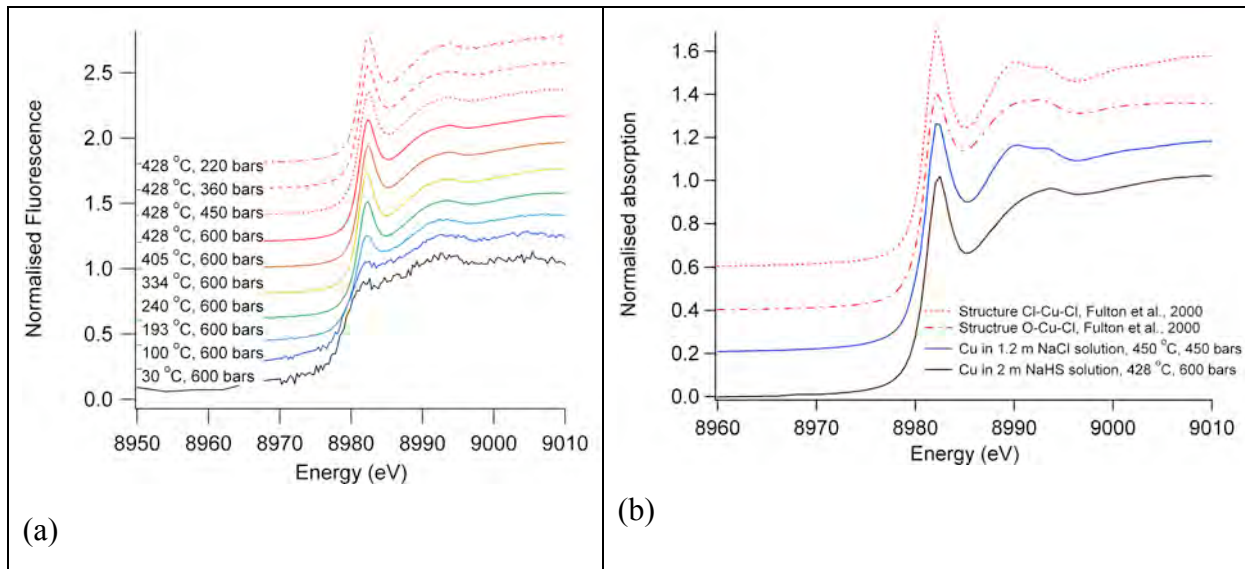


Figure 1 XANES spectra of 2 m NaHS solution (Sol. 2). (a) Evolution of Copper K-edge XANES with increasing temperature from 30 °C to 428 °C at 600 bars, then decreasing pressure to 220 bars at 428 °C. (b) Comparison XANES spectrum at 428 °C, 600 bars with the [O-Cu-Cl] and [Cl-Cu-Cl] spectra from Fulton et al. (2000). A spectrum of Cu in 1.2 m NaCl solution at 450 °C and 450 bars (Brugger et al., 2007) is also shown.

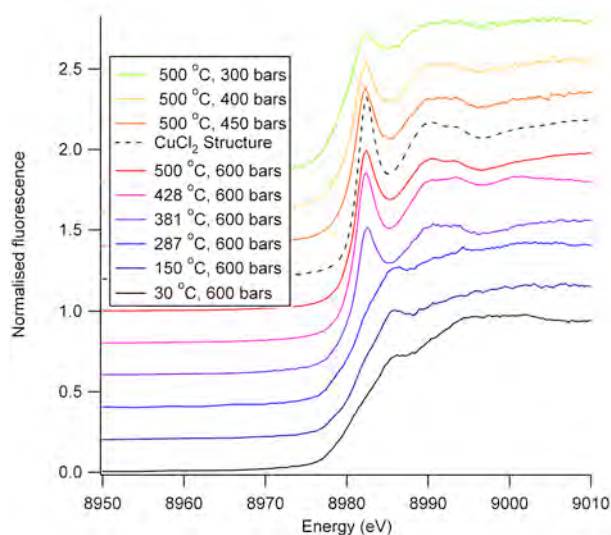


Figure 2 Evolution of Cu K-edge XANES spectra for solution 9 (mixed S-Cl) as a function of temperature from 30 to 500 °C at 600 bars, and 450 to 300 bar at 500 °C. The spectrum of Cl-Cu-Cl from Fulton et al. (2000) is also shown for comparison.

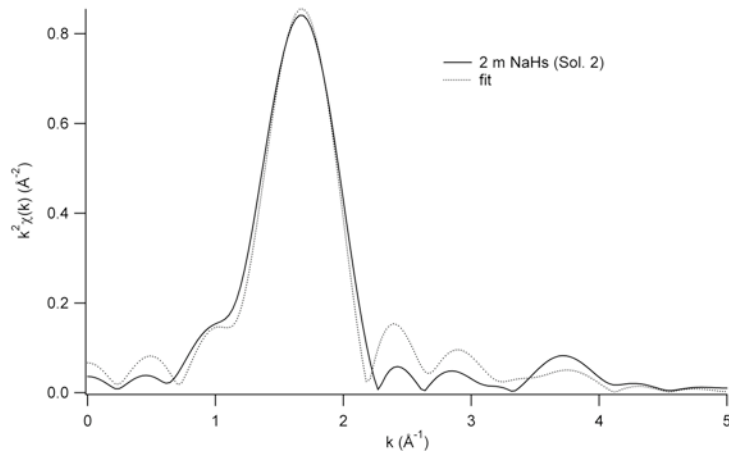


Figure 3 EXAFS fit of Sol. 2 at 428 °C and 600 bars. Refinement details: $n = 1.7(2)$ S atoms bonded to Cu at a distance of $2.149(9)$ Å. The linear molecule is bent slightly at an angle of $\sim 23^\circ$ (as determined from fitting multiple scattering peak).

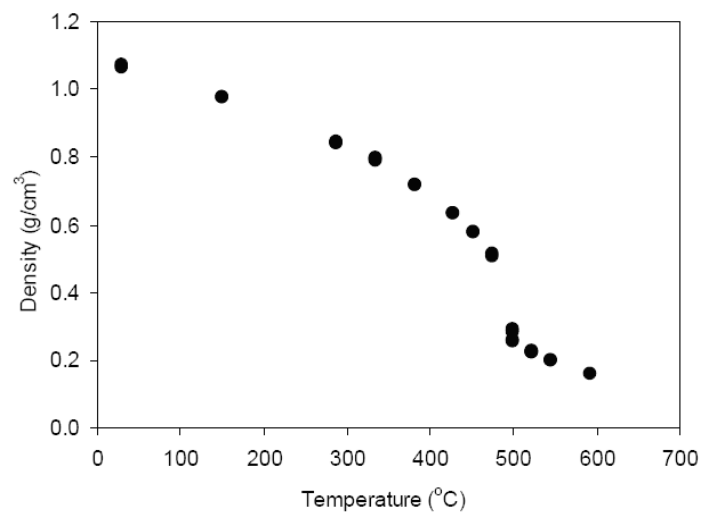


Figure 4 Measured density of solution #4 (2 m NaHS + Cu₂S solids) as a function of temperature when heating from 30 to 546 °C at 600 bars. The fluid density drops sharply above 475 °C, indicating the transition from liquid to vapor phase.

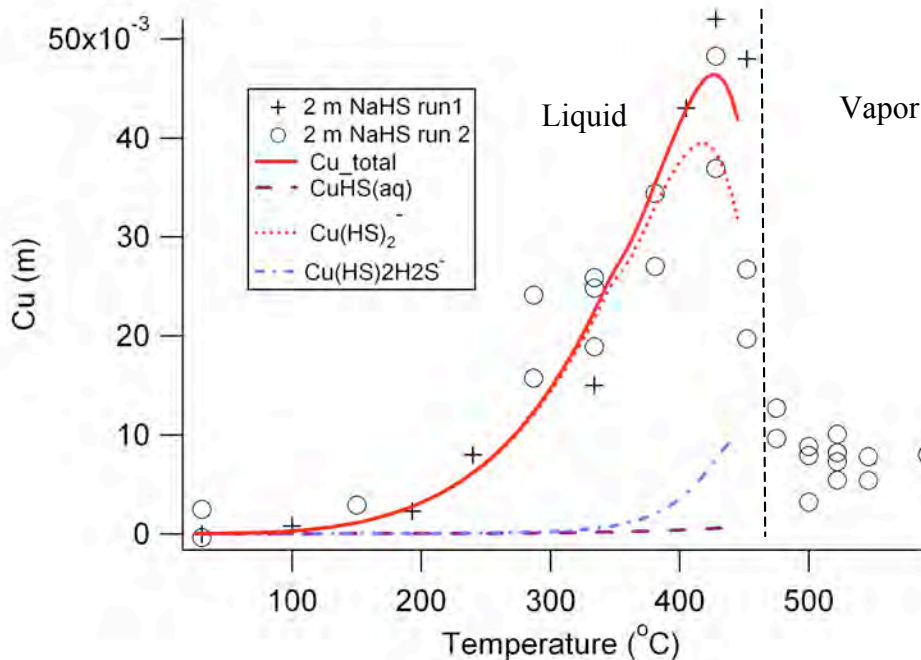


Figure 5 Chalcocite (Cu_2S) solubility in a 2 m NaHS solution at 600 bars and as a function of temperature from 25 to 592 °C. The crosses and circles represent two runs of the same sample composition (Sol2. 2 and 4), and the curve is the calculated solubility using HCh (Shvarov and Bastrokov, 1999), see text for details. The dashed line represents the boundary between liquid and vapor phases estimated from density measurements.

PUBLICATIONS ISSUE FROM THIS EXPERIMENT:

1. **Brugger, J., Etschmann, B., Testemale, D., Liu, W., Hazemann, J.-L., Proux, O. and Müller, H.** (to be submitted in 2009) An XAS study of the structure of Cu(I) sulfide complexes in hydrothermal brines and vapours (25°C to 600°C, 600 to 180 bars). *Geochimica et Cosmochimica Acta*.
2. **Schmidt Mumm, A., Brugger, J., Chongbin Zhao and Schacht, U.** (submitted 5/6/2009) Fluids in geological processes – the present state and future outlook. GEXPLO-S-09-00149. *Journal of Geochemical Exploration*.
3. **Brugger, J., Pring, A., Ryan, C., Reith, F., Etschmann, B., Liu, W., O'Neill, B. and Ngothai, Y.** (Accepted 26/3/2009) Probing ore deposits formation: new insights and challenges from synchrotron and neutron studies. *Radiation Physics and Chemistry*. <http://dx.doi.org/10.1016/j.radphyschem.2009.03.071>.
4. **Etschmann, B., Liu, W., Brugger, J., Testemale, D., Hazemann, J.-L., Müller, H. and Proux, O.** (2009) Copper speciation and partitioning between vapor and liquid phases in hydrothermal sulfuric solution. Goldschmidt conference, June 21 - 26 in Davos, Switzerland. *Geochimica et Cosmochimica Acta*, 73, A341-A341.
5. **Liu, W., Brugger, J., Etschmann, B., Testemale, D., Hazemann, J.-L.** (2009) A synchrotron X-ray absorption spectroscopic study of copper solubility and speciation in supercritical water. GEOFLUID 2009 Conference, April 15-18 2009, Adelaide, South Australia. *J. Geochemical Exploration*.
6. **Brugger, J., Pring, A., Reith, F., Etschmann, B. and Liu, W.** (2009) Towards Molecular-level Understanding of Geochemical Processes in Mineral Exploration. GEOFLUID 2009 Conference, April 15-18 2009, Adelaide, South Australia. *J. Geochemical Exploration*. DOI:10.1016/j.gexplo.2008.11.050.

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