

Cu solubility and complexation in high-temperature aqueous fluids

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Understanding of the genesis of hydrothermal copper ore deposits requires robust knowledge of the transport properties of Cu in aqueous fluids over a wide range of pressure and temperature. The aim of this study is to combine experimental and computational techniques to investigate the Cu solubility and complexation in sulfur-bearing fluids at high temperatures and pressures.

Synthetic CuS crystals were equilibrated in aqueous NaCl \pm HCl solutions at 500 and 600 °C and pressures up to 650 MPa using modified hydrothermal diamond-anvil cells [2]. Dissolved Cu concentrations, determined from confocal synchrotron-radiation X-ray fluorescence (XRF) spectrometry at equilibrium conditions, ranged between 25 ppm at 500 °C, 320 MPa and 338 ppm at 600 °C, 445 MPa. Cu solubility increased with temperature along an isochore and decreased with pressure at constant temperature. Chlorine-rich fluids yielded higher dissolved Cu contents.

Cu complexation was studied by *in-situ* X-ray near-edge absorption structure (XANES) and Raman spectroscopy at comparable conditions to the XRF experiments. The XANES spectra are in good agreement with CuCl₂⁻ complexes in solution [3], whereas the Raman spectra clearly show a different shape than expected for purely Cu–Cl bands [4]. We tentatively interpret those as mixed Cu–Cl–HS/H₂S complexes, which will be verified by *ab-initio* molecular dynamics simulations with subsequent quasi-normal mode analysis.

[1] Hedenquist & Lowenstern (1994) *Nature* **370**, 519-527.

[2] Schmidt & Rickers (2003) *Am. Mineral.* **88**, 288-292.

[3] Fulton *et al* (2000) *Chem. Phys. Lett.* **330**, 300-308.

[4] Applegarth *et al* (2014) *J. Phys. Chem. B* **118**, 204-214.