

# Copper(I) in brines up to supercritical conditions

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Accurate modeling of the transport and deposition of metals in brines and vapors relies on the availability of accurate thermodynamic properties for all major minerals, aqueous, and vapor species of interest. The nature and stability of metal complexes depends upon the coordination chemistry of the metal. Over the years, we have used a combination of experimental techniques (i.e. cuprite solubility experiments; UV-Vis spectrophotometry, XANES & EXAFS spectroscopy) to achieve a quantitative understanding of the speciation of Cu(I) in acidic aqueous chloride solutions over a broad range of conditions (salinity between 0-40 wt% Equiv. NaCl; T 25-450°C; P<sub>sat</sub> to 500 bars; solution density down to 0.2 g/cm<sup>3</sup>).

At room temperature, with increasing chloride concentration, the speciation of Cu(I) changes from the linear complexes [H<sub>2</sub>O-Cu-Cl](aq) and [Cl-Cu-Cl]<sup>-</sup>, to a probably trigonal planar complex [CuCl<sub>3</sub>]<sup>2-</sup>, to the tetrahedral [CuCl<sub>4</sub>]<sup>3-</sup> complex at very high salinity. The stability of the high-order complexes decreases with increasing temperature; for example, Cu(I) exists predominantly as a linear complex in a 14 m LiCl solution at 400°C, 400 bars.

The affinity of copper(I) chloride complexes for the vapor phase was investigated by measuring the solubility of nantokite (CuCl<sub>(s)</sub>) *in-situ* by XANES spectroscopy at the FAME beam-line at the ESRF, Grenoble. The experiment was conducted in H<sub>2</sub>O acidified to pH 2 with HCl. The temperature was kept constant at 420°C, and the pressure was varied from 400 to 300 bars. Under these conditions the solvent remains under supercritical conditions, but its density decreases from ~0.4 g/cm<sup>3</sup> to ~0.2 g/cm<sup>3</sup>. The solubility of copper decreases from ~0.3 m to 0.05 m as pressure decreases from 400 to 300 bars, suggesting that copper is more efficiently transported as chloride complexes in high-density brines than in low density fluids. The P-T conditions of the experiment are similar to those found in mid-oceanic hydrothermal vents ("black smokers"), and these results suggest that most of the copper in mid-oceanic fluids may precipitate near the seafloor during decompression from lithostatic to hydrostatic pressures.