

**COPPER-CHLORIDE COMPLEXING IN HYDROTHERMAL BRINES.** D. C. "Bear" McPhail<sup>1</sup>, J. Brugger<sup>1</sup>, W. Liu<sup>1</sup>, L., Spiccia<sup>2</sup>, and J. Black<sup>1</sup>; <sup>1</sup>Department of Earth Sciences, Victorian Institute of Earth and Planetary Sciences, Monash University, Clayton, Victoria 3168, Australia ([bear@mail.earth.monash.edu.au](mailto:bear@mail.earth.monash.edu.au)), <sup>2</sup>Department of Chemistry, Monash University.

**Introduction:** The concentrations and transport of copper in ore-forming and other environments is controlled in part by how copper and chloride complex together in high-temperature brines. Despite the importance of copper in many types of hydrothermal ore deposits (e.g., porphyry, epithermal, SEDEX), little is known about the complexes of copper with chloride. Copper geochemistry is complicated because of the two important valence states of aqueous copper (Cu(I) and Cu(II)). We are studying the hydrothermal geochemistry of copper(I,II)-chloride complexes using a combination of mineral solubility and UV-Vis-NIR spectrophotometric experiments and thermodynamic modeling.

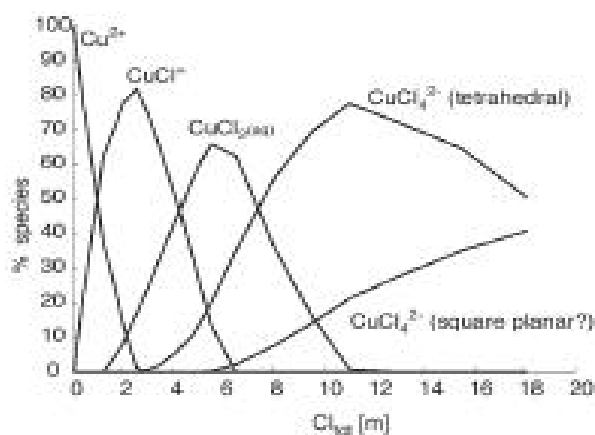
**Cuprite Solubility:** The solubility of cuprite (Cu(I)) was measured in preliminary experiments using water bath (under nitrogen atmosphere) and evacuated silica-glass tubes at temperatures between 25°C and 250°C, vapour-saturated pressure and in acetic-acid and phosphate pH buffered waters with variable NaCl concentrations (0m to 2m). Copper oxidized or disproportionated in all experiments with less than approximately 0.1m NaCl concentrations and in most water bath experiments, even when vessels were closed and under a constant flow of purified nitrogen. Successful experiments have been run at 50°C and 150°C using evacuated silica glass tubes, acetic-acid pH buffer (0.1m to 1.0 total acetate) and 0.01m to 2.0m NaCl. Aqueous copper is greater than 95% Cu(I) based on measured absorbance spectra and quantitative measurements using the neocuproine analytical method. At 150°C and measured  $\text{pH}_{25^\circ\text{C}} \sim 4.7$ , measured  $\log m_{\text{Cu, total}}$  increases linearly from -3 to -1 between  $\log m_{\text{Cl, total}}$  of -2 and 0, with a reproducibility of better than 6%. The slope of the curve is one, indicating that CuCl(aq) predominated at the conditions of the experiment. Total acetate concentration was varied at a constant 0.1m NaCl, resulting in a small increase in measured copper concentrations and indicating that some Cu(I)-acetate was present in the experiments.

**UV-Vis-NIR Spectrophotometry:** UV-Vis-NIR spectra of Cu(II)-chloride complexes have been measured successfully using conventional methods at 25°C, 60°C and 90°C for acidified 30ppm Cu (ultraviolet wavelengths) and 500ppm Cu (visible wavelengths) solutions between 0m and 18m LiCl. Cu(II)-chloride system was chosen for three reasons: i) to develop the necessary methodologies of running the experiments and interpreting the data; ii) extend the range of existing experimental data for Cu(II)-chloride species; iii) understand the positions and shapes of the important absorbance spectra for Cu(II) species so that we can identify potential interferences with the absorbances of

Cu(I) species. The UV spectra of Cu(II) complexes are easier to interpret than the visible spectra at all temperatures and indicate at least five species based on a principal component analysis. The most probable stoichiometries of species in these experiments were  $\text{Cu}^{2+}$ ,  $\text{CuCl}^+$ ,  $\text{CuCl}_2(\text{aq})$ ,  $\text{CuCl}_4^{2-}$  and an unknown species. There appears to be an octahedral-tetrahedral transition with increasing LiCl concentration, based on a comparison with solid-phase spectra. The transition is apparent between 2m and 5m LiCl at all three temperatures. A preliminary interpretation of the spectra indicates the change in predominance of species with LiCl concentration (Figure 1.). UV-Vis-NIR spectra of Cu(I)-chloride complexes in LiCl solutions was measured at 25°C but at higher temperature the copper oxidized too quickly to measure reliable spectra.

**High-temperature UV-Vis-NIR Spectrophotometry:** A newly designed titanium pressure cell with sapphire windows has been successfully tested to 300°C. The cell has four windows that allow both liquid and vapour spectra to be measured in the same experiment. We are currently using the cell to extend the temperature range for Cu(II)-chloride spectra, measure Cu(I)-chloride spectra, and detect liquid-vapour partitioning of Cu in chloride, bisulfide and ammine systems. Preliminary measurements of Cu(II)-chloride liquid-vapour up to 300°C do not show any copper vapour species.

**Thermodynamic Modeling:** Modeling suggests that disproportionation is important at low temperatures and low salinities. Comparisons of our data with recently published thermodynamic properties show good agreement for Cu(II)-chloride species at low salinity; however, there is less agreement for Cu(II)-chloride species at high salinities and Cu(I)-chloride species.



**Figure 1.** Estimated percentages of Cu(II)-chloride species derived from UV absorbance data at 25°C.