

High temperature X-ray absorption analysis of transition metal complexes in magmatic fluids

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The synchrotron microprobe beam line (X26A) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, was used to collect X-ray absorption fine structure (XAFS) spectra from aqueous Fe, Cu and Zn complexes in fluid inclusions at temperatures ranging from 25°C to 500°C. A modified programmable heating stage was used to control the temperature of a fluid inclusion during spectrum acquisition. High salinity fluid inclusions, believed to contain magmatically generated brines, were selected from the Bingham Porphyry Cu deposit, Utah, and from a granite pegmatite in the Granulite Massif, Germany. Microthermometry, laser Raman, SEM/EDS, and *in situ* X-ray fluorescence analyses of the fluid inclusion indicate that they trapped metal-rich NaCl-KCl-H₂O brines with variable but small amounts of CO₂. In all inclusions the chloride concentrations are about 9 m. Analysis of the Zn K-edge XAFS spectra indicates that the tetrahedral chlorozinc

complex ($ZnCl_4^{2-}$) is dominant at high temperatures in the studied magmatic fluids. Furthermore, the Zn-Cl bond length decreases by nearly 0.01 Å for every 100°C increase in temperature.

The results show that the application of XAFS to fluid inclusions can provide direct information on metal speciation in hydrothermal solutions at ore-forming temperatures. These data are particularly useful for our understanding metal transport in hydrous-salt melts, where there are little experimental solubility data available. Unlike vibrational spectroscopic techniques (e.g., Raman, optical absorption), XAFS is element specific and can therefore be applied to structural analysis of aqueous species in a complex multicomponent system such as hydrothermal fluids. Minimum detection limit with the available X-ray microprobe is about 5000 ppm.