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A XANES study of Cu speciation in high-temperature brines using synthetic fluid inclusions

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Abstract

Cu *K*-edge X-ray absorption near edge structure (XANES) spectra were recorded from individual synthetic brine fluid inclusions as a function of temperature up to 500 °C. The inclusions serve as sample cells for high-temperature spectroscopic studies of aqueous Cu-Cl speciation. Cu^+ and Cu^{2+} can both be identified from characteristic pre-edge features. Mixed oxidation states can be deconvoluted using linear combinations of Cu^+ and Cu^{2+} spectra. This work illustrates how complex Cu XANES spectra can be interpreted successfully. Cu^{2+} is the stable oxidation state in solution at room temperature and Cu^+ at high temperatures. The change in oxidation state with temperature was completely reversible. Cu^+ was found to occur exclusively as the linear species $[CuCl_2]^-$ in solutions containing KCl with Cu:Cl ratios up to 1:6. In the absence of K^+, there is evidence for higher order coordination of Cu^+, in particular the tetrahedral complex $[CuCl_4]^{3-}$. The importance of such complexes in natural ore-forming fluids is yet to be determined, but may explain the vapor-phase partitioning of Cu as a Cl complex from a Cl-rich brine.

Keywords: XAS (XAFS, XANES), Cu in high-temperature brines, high-temperature studies, XANES of fluid inclusions, fluid phase, experimental petrology, synthetic fluid inclusions