

Speciation and solubility of ore metal ions from studies of synthetic fluid inclusions at temperatures > 350°C

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Introduction

About half of all gold production and reserves outside South Africa and more than 60% of world copper deposits are of hydrothermal origin and are located in narrow volcano-plutonic belts along the Pacific and northeast Indian Ocean margins. These deposits, known as porphyry Cu(Au) and epithermal Au(Cu), are associated with magma bodies generated by subduction. Metal ions are extracted from the melt into an exsolving aqueous phase as water-soluble metal-ligand ion complexes. The aqueous phase may exist as brine (liquid), vapor, or supercritical fluid, depending on pressure, temperature, and phase composition. A deposit forms when the metal complexes are transported in this aqueous phase and undergo either cooling, decompression, or chemical reaction, causing precipitation and concentration. These processes often begin to occur at temperatures greater than 350°C and pressures in excess of 100 MPa.

In order to understand the formation of these hydrothermal ore deposits, it is necessary to determine both the solubility and speciation of ore-metal ions in supercritical solutions. Progress in this area has been limited by the difficulties of sampling fluids under hydrothermal conditions and designing spectroscopic sample cells capable of withstanding the vapor pressure of water. Our approach is to trap samples of a high-temperature fluid as inclusions (up to 100 μm) in optical grade quartz. These inclusions can be reheated along an isochore to the entrapment temperature allowing microbeam analysis of supercritical solutions [1].

Methods and Materials

The synthetic inclusions are prepared by sealing fractured quartz, water or brine, and various mineral assemblages in a capsule of the metal of interest, which is heated and pressurized in a cold-seal hydrothermal vessel. The pH is controlled by either the K-spar/muscovite/quartz or andalusite/muscovite/quartz reactions. The $f\text{O}_2$ can be defined by buffers such as Re-ReO₂ or Cu₂S-Cu₂O-Cu, and $f\text{S}_2$ can be determined by the presence of pyrrhotite/pyrite/magnetite. Solubility of the capsule at high temperature produces a metal-bearing solution that is trapped in the quartz as the fractures anneal [2]. Metal salts can also be added directly to the capsule resulting in artificially high metal concentrations at elevated temperature.

The GSECARS beamline 13-ID-C provides a scanning monochromatic microbeam suitable for the analysis of individual fluid inclusions. The beamline is equipped with a microscope viewing system that enables inclusions to be readily located. The samples are mounted within a commercial heating stage that is operable to 700°C. This

allows the *in situ* analysis of fluids at the entrapment temperature. Under these conditions, all precipitates dissolve and the metal content can be determined by synchrotron x-ray fluorescence analysis [3]. The metal speciation as a function of temperature, in conjunction with elemental mapping to ensure solubility, can be investigated by extended x-ray absorption fine structure (EXAFS).

Results

The GSECARS detection limit for most elements is two to three orders of magnitude lower than that available at a second-generation source [2]. The theoretical detection limit for Au in a 50 μm inclusion at a depth of 50 μm from the surface, based on results for silica capillaries and reasonable count times, was determined to be 0.3 ppm.

Preliminary EXAFS spectra were recorded at room temperature for a number of cobalt-chloride-bearing inclusions in good agreement with literature results for a mixture of octahedral and tetrahedral complexes. At elevated temperature, survey copper spectra were acquired for brine and vapor phase inclusions, with preliminary modeling suggesting predominantly oxygen coordination. An apparent change in bond length from 2.13 Å in the brine to 1.91 Å in the vapor was observed. EXAFS spectra for the vapor inclusions also exhibit variations with temperature.

Discussion

The capability to record EXAFS spectra from individual fluid inclusions as a function of temperature at GSECARS has been demonstrated. Using synthetic inclusions prepared under controlled chemical and physical conditions, the potential exists to rigorously explore aqueous geochemistry in the supercritical regime. The major constraint is the choice of fluid density, which limits the maximum accessible reheating temperature before decrepitation. Future work will investigate the complexation of Au, Ag, Cu, and Pb in both sulfide and chloride systems.

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