Copper Speciation in Vapor-phase Fluid Inclusions from the Mole Granite, Australia

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Introduction

Most of the world's Cu and Au ore deposits result from the transport of metals by aqueous solutions at high temperatures and pressures. Many of these hydrothermal deposits are associated with magma bodies generated by subduction. In some cases, boiling hydrothermal fluids separate into a high-density brine containing metal chloride complexes that form a porphyry deposit and a low-density S-rich vapor that migrates toward the surface before precipitating a high-sulfidation Au(Cu) epithermal deposit. The factors that control metal partitioning between coexisting brine and vapor are the key to understanding the metal distribution in this system.

Experimental studies indicate that under most conditions, metals such as Pb, Zn, and Cu partition preferentially into brine relative to vapor. However, high Cu concentrations in magmatic-related hydrothermal vapors are found in nature. For example, proton-induced x-ray emission (PIXE) analyses of coexisting vapor and brine fluid inclusions from the Mole Granite, New South Wales, Australia, found preferential partitioning of copper into the vapor in a ratio of approximately 10:1 [1].

The factors that control Cu partitioning during boiling are unknown. Integral to understanding the process is Cu coordination. The main impediment to determining Cu speciation under hydrothermal conditions is the difficulty of undertaking experiments above the critical point of water. Fluid inclusions represent samples of a hydrothermal fluid, trapped in a mineral such as quartz, which can be reheated to the entrapment temperature. This allows their use as sample cells (natural pressure vessels) for high-temperature spectroscopy.

In this study, x-ray fluorescence elemental maps and Cu K-edge x-ray absorption near-edge structure (XANES) spectra were recorded at temperatures up to 400˚C for individual vapor and brine phase inclusions from the Mole Granite [2].

Methods and Materials

The fluid inclusions studied ranged in size from 20 to 50 μm. The condensed liquid in vapor-phase inclusions homogenized to vapor at ~400˚C. Experiments were undertaken at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) beamline 13-ID-C. The x-ray beam was focused by using Kirkpatrick-Baez mirrors to a spot size of less than 3 μm for mapping experiments. A slightly larger, more diffuse beam was used for XANES measurements to avoid beam-induced sample decomposition and to minimize the effect of any thermal motion.

Results

Figure 1 shows a room temperature optical image and Cu and Fe x-ray fluorescence maps of a vapor-phase fluid inclusion. A brine inclusion at a different depth can also be seen in the bottom right of the image. At room temperature, the low-density vapor-phase inclusion contains a large bubble and a small amount of condensed liquid. The Cu partitioning of interest is between the coexisting phases of the boiling fluid trapped as vapor and brine inclusions, not between the bubble and condensed liquid of the vapor inclusion (the result of cooling). The relative positions of features in the x-ray map differ from those observed optically because of the projection onto a horizontal plane of fluorescence intensity arising from different depths. Figure 1b indicates that Cu is concentrated in the vapor-phase inclusion relative to the brine inclusion, in agreement with the results of PIXE analyses. It is also apparent that Cu is homogeneously distributed in the condensed liquid phase of the vapor inclusion and not concentrated in the opaque precipitate, which appears as a cold spot. Figure 1c shows that this opaque precipitate is an Fe-rich phase. The size of the opaque precipitate is exaggerated in the x-ray map because of the fluorescence excitation from the scattered incident beam. Iron in solution is concentrated in the coexisting brine inclusion.

Cu K-edge XANES and extended x-ray absorption fine structure (EXAFS) spectra identify $[Cu(H_2O)_6]^{2+}$ at 25˚C, $[CuCl_2]^-$ at 200˚C, and either $[CuCl_2]^-$ or $[CuCl(H_2O)]$ at the homogenization temperature of around 400˚C.

Discussion

The presence of Cu in the solution phase is contradictory to conventional thinking, which has assumed concentration in the opaque precipitate. The opaque is Cu-free and Fe-rich and probably corresponds to magnetite partially oxidized to hematite. The room temperature Mole Granite XANES spectrum is consistent with numerous literature results for Cu^{2+} coordinated by
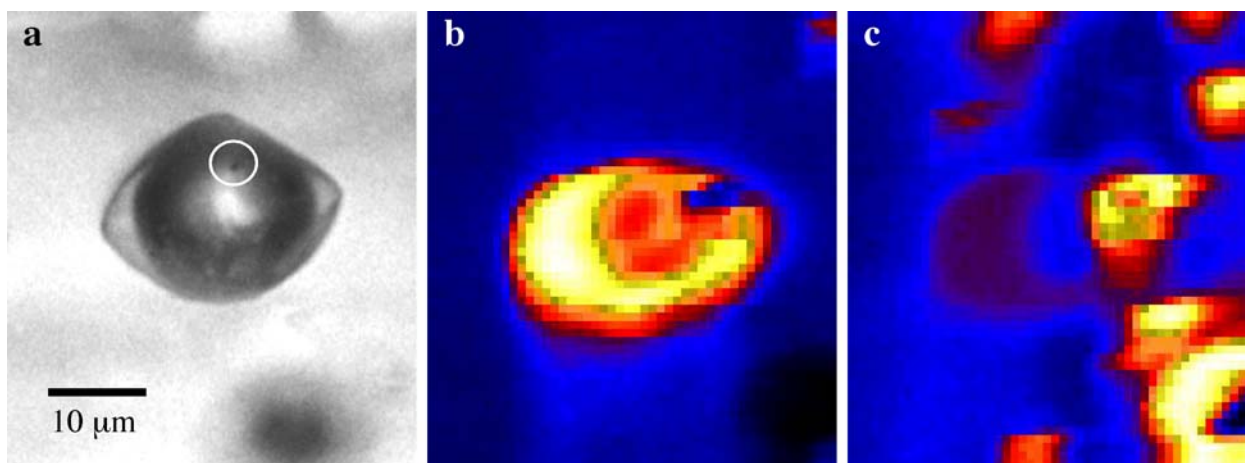
FIG. 1. (a) Optical, (b) Cu K_α, and (c) Fe K_α room temperature images of vapor-phase (center) and brine-phase (lower right) fluid inclusions in quartz. The precipitate is circled in (a). The pixel size in the x-ray maps is 2×2 μm.

six oxygens. No Cu^{2+} chloride complexing is expected for the salt contents determined by PIXE. The presence of an aquated Cu^{2+} ion is also consistent with the uniform distribution of Cu in solution seen in the x-ray map.

At 250°C, a strong feature near 8985 eV characteristic of the 1s $\rightarrow$ 4p transition of Cu^+ is observed. The intensity of this transition suggests that Cu is linearly coordinated and that all the Cu is Cu^+. The reduction of Cu^{2+} to Cu^+ is strongly favored at high temperatures. The similarity of the XANES spectra to previous results on high-temperature Cu/Na/Cl solutions [3], together with preliminary EXAFS data, suggest that Cu exists as the linear $[CuCl_2]^-$ complex. The molar ratio of Cu to Cl in these vapor inclusions is also approximately 1:2. At 400°C, a slightly different spectrum is observed, similar to that reported for Cu:Cl ratios of around 1; it was previously tentatively assigned as $[CuCl(H_2O)]$ [3]. This Cu:Cl ratio is inappropriate for the Mole Granite, but it is possible that at temperatures above the critical point, the charge neutral $[CuCl(H_2O)]$ complex is favoured because of the decrease in the dielectric constant of water. It is also possible that the high-temperature spectrum corresponds to $[CuCl_2]^-$ above the critical point. The Cu speciation appears to change from $[Cu(H_2O)_6]^{2+}$ at room temperature to $[CuCl_2]^-$ in a high-temperature solution, with either $[CuCl_2]^-$ or $[CuCl(H_2O)]$ occurring in the vapor.

The changes in oxidation state and speciation are fully reversible with temperature cycling, and rapid sequential scans were identical. In preliminary experiments, some spectra did exhibit a systematic change with beam exposure, identified as the reduction of Cu ions to Cu metal. Decomposition depends strongly on the photon flux and was eliminated by using a defocused beam. The stability and reversibility of the system suggest that the temperature-dependent change in the Cu oxidation state is a real chemical effect.

It is not clear under what conditions Cu should partition as a chloride complex into a vapor phase from a chloride-rich brine. A possible controlling variable is pH. Under basic conditions, $[CuCl_2]^-$ would be solvated by water and unlikely to be volatile, whereas $[CuCl_2]H$ might readily partition into the vapor phase (analogous to the behaviour of Cl^- and HCl). If this is correct, estimates of fluid acidity at the time of boiling may be an important indicator of the type of mineralization (porphyry, epithermal, or both) that might be expected.

References

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