Copper speciation in vapor-phase fluid inclusions from the Mole Granite, Australia

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ABSTRACT

X-ray fluorescence elemental maps and Cu K-edge X-ray absorption near-edge structure (XANES) spectra were recorded for individual vapor and brine phase fluid inclusions from the Mole Granite, NSW, Australia. The maps indicate that Cu is concentrated in the vapor inclusions and, at room temperature, distributed uniformly in the condensed liquid. Opaque precipitates in these inclusions do not contain Cu. The absorption spectra identify the stable complexes as [Cu(H2O)6]2+ at 25 °C, [CuCl]∞ at 200 °C, and either [CuCl2]− or [CuCl(H2O)] at the homogenization temperature of around 400 °C. These changes in Cu coordination and oxidation state are fully reversible. We suggest that the vapor phase partitioning of Cu as a chloride complex from a high-density brine may occur under acidic conditions. Estimates of fluid acidity at the time of boiling may potentially predict the metal distribution between epithermal and porphyry-type environments in hydrothermal systems.

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 (Skinner 1979). Many of these hydrothermal deposits are associated with magma bodies generated by subduction and occur in two classes, known as porphyry and epithermal. In some cases, boiling hydrothermal fluids separate into a high density brine containing metal chloride complexes that form porphyry deposits and a low density, S-rich vapor that migrates toward the surface before precipitating a high sulfidation Au(Cu) epithermal deposit (e.g., Hedenquist et al. 1998). Clear field evidence of this relationship is provided by the coeval Far Southeast porphyry and Lepanto high-sulfidation epithermal Au deposits in the Philippines. In this system, high-salinity-brine fluid inclusions are abundant in the porphyry deposit (Mancano and Campbell 1995) but absent from inclusions associated with the enargite-hosted epithermal mineralization (Hedenquist et al. 1998). This difference suggests that phase separation simultaneously formed these deposits at different levels in the crust. If Cu partitions into the vapor phase during boiling, shallow high-sulfidation deposits may be enriched in Cu at the expense of deep-seated porphyry systems. Copper mineralization may occur in both settings, depending upon partition coefficients. In the absence of boiling or if Cu remains in the brine phase under different chemical conditions, a Cu-rich porphyry may occur, possibly associated with a Cu-poor, low-sulfidation epithermal deposit. To understand the formation of, and the relationship between, these various deposits it is necessary to determine the physical/chemical controls on metal partitioning between brine and vapor.

Experimental studies confirm that under most conditions, metals (Pb, Zn, and Cu) partition preferentially into brine relative to vapor (e.g., Hemley et al. 1992). However, high Cu concentrations in magmatic-related hydrothermal vapors have been reported (e.g., Ulrich et al. 1999; Audetat et al. 1998; Heinrich et al. 1992; Lowenstern et al. 1991). Heinrich et al. (1992) used Proton Induced X-ray Emission (PIXE) analyses of coexisting vapor (~1 wt% Cu and Cl) and brine (~0.1 wt% Cu and ~20 wt% Cl) fluid inclusions from the Mole Granite, NSW, Australia to show that Cu is strongly partitioned into the vapor. This preferential partitioning of Cu into the vapor (Dvapor/brine ~10) in contrast to Cl (DCl/brine ~0.05) is unexpected as Cu concentrations in the two phases might be expected to correlate with the total chloride concentration. Although there is evidence that Cu chlorides are volatile at high temperatures (Symonds et al. 1987), a volatile chloride complex was considered unlikely since chloride complexes dominate in the brine. Sulfur was also detected in the vapor (perhaps up to 1 wt%), suggesting that Cu may be transported as a volatile S species. Vapor inclusions occasionally contain a tetrahedral opaque precipitate, presumed to be chalcopyrite. This indicates low Cu solubility at room temperature and that dissolution of the sulfide at high temperature might produce a Cu-S complex, despite the limited solubility of sulfide compounds (Romberger and Barnes 1970; Crerar and Barnes 1976; Mountain and Seward 1999).

There is no spectroscopic evidence for vapor-phase Cu speciation. The main impediment to progress in this area is the difficulty of carrying out experiments above the critical point of water. X-ray absorption experiments of hydrothermal solutions generally have been limited to below 350 °C (e.g., Mosselmans et al. 1996; Seward et al. 1996). Fluid inclusions represent samples of hydrothermal fluids that can be re-heated...