ELSEVIER

Chemical Geology 221 (2005) 21–39

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Thermodynamic properties of copper chloride complexes and copper transport in magmatic-hydrothermal solutions

Weihua Liu[a,c,*], D.C. McPhail[b,c]

[a]*CSIRO Exploration and Mining and South Australia Museum, P.O. Box 312, Clayton South, Victoria 3169, Australia*
[b]*Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME) and Department of Earth and Marine Sciences, The Australian National University, ACT 0200, Australia*
[c]*School of Geosciences, P.O. Box 28E, Monash University, Victoria, 3800, Australia*

Received 16 April 2004; received in revised form 2 April 2005; accepted 16 April 2005

Abstract

The behaviour of copper in hydrothermal waters and brines is poorly known at the pressure–temperature–salinity conditions typical of magmatic-hydrothermal systems, severely limiting our understanding of how much copper can be transported and deposited in such environments. We need to know the identity of relevant copper complexes and have reliable thermodynamic properties for them in order to understand and predict the solubilities of copper-bearing minerals, the partitioning of copper between liquid and vapour and which physico-chemical factors and processes control copper deposition in magmatic-hydrothermal systems. Under saline conditions, copper chloride complexes are likely to be the most important aqueous species of copper and recent experimental studies have shown good agreement for their derived properties up to approximately 300 °C, vapour-saturated pressure and up to approximately 9 m total chloride. There is still a need, however, to have reliable properties for higher temperature and pressure conditions.

In this paper we present new equation-of-state parameters and partial molal properties for aqueous Cu(I) chloride complexes ($CuCl_{(aq)}$, $CuCl_2^-$, $CuCl_3^{2-}$ and $CuCl_4^{3-}$) regressed from experimentally derived log K values derived between 25 and 350 °C and vapour-saturated pressure. The results are used to calculate formation constants for a wide range of temperature and pressure (0–1000 °C and 1–5000 bar). The extrapolation of the properties is tested by calculating chalcopyrite solubilities and comparing them with measured values from Seyfried and Ding (2003) [Seyfried, W.E., Ding, K., 1993. The effect of redox on the relative solubilities of copper and iron in Cl-bearing aqueous fluids at elevated temperatures and pressures: an experimental study with application to subseafloor hydrothermal systems. Geochimca et Cosmochimca Acta 57, 1905–1917]; 400 °C, 500 bars, 0.4–2 m chloride and Hemley et al. (1992) [Hemley, J.J., Cygan, G.L., Fein, J.B., Robinson, G.R., Jr., D'Angelo, W.M., 1992. Hydrothermal ore-forming processes in the light of studies in rock-buffered systems. I, Iron–copper–zinc–lead sulfide solubility relations. Econ. Geol. 87, 1–22]; 300–500 °C, 500–2000 bars, 1 m chloride. There is good agreement with these two experimental datasets, which indicates that our extrapolated thermodynamic properties are reliable at least over these ranges of pressure, temperature and chloride concentration.

---

* Corresponding author. CSIRO Exploration and Mining and South Australia Museum, P.O. Box 312, Clayton South, Victoria 3169, Australia. Fax: +61 3 9905 4903.

E-mail address: weihua.liu@csiro.au (W. Liu).

doi:10.1016/j.chemgeo.2005.04.009

The new properties are used to calculate chalcopyrite solubilities under similar conditions of two magmatic-hydrothermal copper deposits for which copper concentrations have been measured in individual fluid inclusions: the Starra iron oxide–Au–Cu deposit, Australia; and the Bajo de la Alumbrera porphyry copper deposit, Argentina. In both cases our calculated copper concentrations are consistent with the measured values in inclusions that trapped pre-mineralising and mineralising fluids. More generally, calculated chalcopyrite solubility at different temperature, pressure, pH, chloride concentrations and oxidation states indicates that hypersaline, neutral-weak acidic, and intermediate-reduced brines can transport thousands of ppm copper at 400 °C and above, raising interesting questions about the interpretation and importance of liquid-vapour partitioning of copper. Although cooling is probably the major factor responsible for copper deposition in magmatic-hydrothermal environments, fluid mixing, boiling and fluid–water interaction may be more important in other geological environments, e.g., iron–oxide–copper–gold and epithermal ore deposits.

Keywords: Thermodynamic properties; Copper; Chloride; Complexes; Magmatic-hydrothermal solutions; Porphyry deposits

---

1. Introduction

Metal transport in hydrothermal solutions is chemically controlled, at least in part, by the solubility of minerals and stability of aqueous metal complexes. It is well-known that metals transport in hydrothermal solutions mainly as aqueous complexes (Barnes, 1979), thus determining the nature and stability of aqueous metal complexes is essential in understanding the leaching, transport and deposition of metals. For the conditions found in magmatic-hydrothermal environments, e.g., porphyry ore deposits, we need to identify the important aqueous complexes and measure or estimate reliable thermodynamic properties for them. In addition, we need to understand the aqueous complexes at high temperature and pressure so that we can understand the importance of vapour transport of metals, such as recently indicated by high copper (up to 1.2 wt.%) and gold (up to 100 ppm) concentrations in vapour-rich fluid inclusion from two giant porphyry copper deposits (Ulrich et al., 1999).

For porphyry copper deposits, we now have an understanding of their tectonic setting, relationship to magmatism, geochronology, petrology and alteration, ore and gangue mineralogy and zoning (Lowell and Guilbert, 1970; Sillitoe, 1972, 1973; Lowell, 1973; Beane and Titley, 1981; Titley and Beane, 1981; Hedenquist and Lowenstern, 1994; Titley, 1997). The ore-forming temperatures and fluid salinities have been well documented (e.g., Beane and Titley, 1981; Roedder, 1984; Hezarkhani and Williams-Jones, 1998) and there are also many experimental and modelling studies dealing with the partitioning of ore-forming components (e.g., Cu, S, Cl) and water between silicate melt and fluids (Burnham, 1979; Candela and Holland, 1984, 1986; Candela et al., 1989; Shinohara et al., 1989; Cline and Bodnar, 1991; Shinohara, 1994; Williams et al., 1995; Webster, 1997; Holzheid and Lodders, 2001). Despite all of the above and related work, we still lack crucial information regarding the behaviour of copper in hydrothermal waters and brines at the conditions typical of porphyry systems. This severely limits our understanding of how much copper can be transported, the solubilities of copper-bearing minerals, the partitioning of copper between liquid and vapour and what physico-chemical factors and processes control copper deposition in porphyry deposits.

In the past two decades, with the enormous advances of computer technology and accumulation of physical and chemical properties of rocks and fluids, many geologists and geochemists have developed numerical modelling theories and software to simulate ore-forming and other geological processes. As well as improving our understanding of existing ore deposits, this gives us a powerful predictive tool useful in exploring for new deposits. The reliability of chemical mass transfer modelling, such as studies for copper deposits (Sverjensky, 1987; Cline and Bodnar, 1991), depends on the extent and quality of thermodynamic properties of mineral, aqueous and vapour species (Heinrich et al., 1996). Coupled fluid flow and reactive transport modelling (Steefel and Lasaga, 1994; He et al., 1999; Xu et al., 2001), a quickly expanding research area in geological modelling, also requires reliable thermodynamic and kinetic proper-