



## Contrasting regimes of Cu, Zn and Pb transport in ore-forming hydrothermal fluids



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### ABSTRACT

Sulfur and chlorine are the two most important ligands accounting for metal transport in the upper crust. In this study, four metal- and sulfur-saturated model fluids with varying salinities and redox states were simulated in the Fe-Cu-Pb-Zn-Au-S-C-H-O system, over a wide pressure-temperature (P-T) range (50–650 °C, 0.8–5.0 kbar), in order to compare the roles of chloride and bisulfide complexing for metal transport at the light of the latest available thermodynamic properties. The range in simulated Zn and Pb concentrations of the model fluids compares well with those of natural hydrothermal fluids, suggesting that the model can be used to evaluate hydrothermal ore-forming processes in Nature.

The modeling reveals two different modes of Cu, Pb and Zn complexing in sulfur-saturated hydrothermal solutions. At lower temperature, chloride complexes are the predominant Cu, Pb and Zn species in sulfide-saturated systems, as expected from previous studies. However, hydrosulfide Cu, Pb and Zn complexes predominate at higher temperature. The predominance of bisulfide complexing for base metals at high temperature in sulfur-saturated systems is related to the prograde dissolution of pyrite and/or pyrrhotite, which results in a rapid increase in sulfur solubility.

Metals transport as chloride or bisulfide complexes determines the modes of metal enrichment. In chloride-complexing dominated systems (e.g., Mississippi Valley Type deposits), low sulfide solubilities mean that the ore fluids cannot carry both reduced sulfur and metals, and ore precipitation is triggered when the ore fluid encounters reduced sulfur, e.g., via fluid mixing or via sulfate reduction. In contrast, in fluids where bisulfide complexing is predominant, cooling and desulfidation reactions are efficient mechanisms for base metal sulfide precipitation. Since both Au and base metals (Cu, Pb and Zn) are predicted to be transported as hydrosulfide complexes in high-temperature primary magmatic fluids in equilibrium with sulfide minerals, high-salinity is not a necessity for magmatic hydrothermal deposits such as porphyry- and skarn-style deposits.

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### 1. Introduction

The importance of hydrothermal solutions in forming various types of ore deposits is widely recognized. As revealed by fluid inclusion studies, fluids from deposits with varying ore-forming temperatures and geological characteristics can be described in the relatively simple H<sub>2</sub>O-NaCl-(CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>S) system. In such a simple system, chlorine and bisulfide (HS<sup>-</sup> and H<sub>2</sub>S(aq)) are regarded as the two most important ligands for metal (Au, Cu, Pb and Zn) transport (e.g., Mikucki,

1998; Mountain and Seward, 1999, 2003; Reed and Palandri, 2006; Etschmann et al., 2010; Seward et al., 2014).

The importance of chlorine in base metal (e.g., Cu, Pb and Zn) mineralization has been recognized for a long while (e.g., Sverjensky, 1987; Yardley, 2005; Lukanin et al., 2013). Reduced sulfur is thought to be most important in gold transport (Phillips and Evans, 2004; Williams-Jones et al., 2009; Phillips and Powell, 2010; Liu et al., 2014); however, recent experimental studies have revealed the potential of bisulfide complexing in transporting Cu, Pb, Zn, Ag, Pd and Pt in high-temperature fluids (Pokrovski et al., 2008, 2013; Etschmann et al., 2010; Barnes and Liu, 2012; Akinfiev and Tagirov, 2014; and references therein). Together with recent studies showing high concentrations of sulfur in fluids associated with magmatic hydrothermal copper-gold deposits (Seo et al., 2009; up to >0.5 m S), these studies suggest that the role of reduced sulfur in base metal transport may be more important than previously thought.

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In many previous thermodynamic studies, the temperature dependence of metal speciation was evaluated largely based on formation constants of chloride, hydrosulfide, and hydroxide complexes. Specifically, metal speciation and solubility was calculated under the conditions whereby the concentrations of  $\text{Cl}^-$  and reduced sulfur were fixed arbitrarily and independently of temperature (e.g., Stefánsson and Seward, 2003, 2004; Reed and Palandri, 2006). For example, calculations by Stefánsson and Seward (2003, 2004) show that Au(I) and Ag(I) hydrosulfides are important at low temperature, whereas chloride and hydroxide complexes become increasingly predominant at higher temperature, if the concentrations of  $\text{Cl}^-$  and total S are fixed in fluids. Similar conclusions were also drawn for Cu(I) and Pb(II) (Reed and Palandri, 2006).

However, the abundance of aqueous species is determined not only by their thermodynamic stability, but also by the availability of ligands. In general, fluid salinity is limited by the availability of chlorine in the source (e.g., sea water, sedimentary and metamorphic rocks, magma); large-scale halite saturation is reached mostly in cases whereby fluids interacted with halite-bearing evaporites. In contrast, the sulfur contents of crustal fluids at low temperature ( $\leq 300$  °C) are limited by the low solubility of sulfide minerals, in particular the ubiquitous Fe-sulfides pyrite and pyrrhotite. These minerals show extremely low solubility in reduced-sulfur containing fluids at low temperature. The solubility of pyrite and pyrrhotite increases with increasing temperature (i.e., prograde solubility; Seward et al., 2014), and aqueous fluids can dissolve more reduced sulfur at higher temperature. Consequently, prograde Fe sulfide dissolution and metal complexing are intimately coupled with each other in hydrothermal systems, and this will have a fundamental influence on metal speciation in nature.

The aim of this study is to review the potential significance of bisulfide complexing in ore fluids based on the existing thermodynamic properties. Simulations were conducted in the Fe-Cu-Pb-Zn-Au-S-C-H-O system for fluids with different salinities and redox states over a wide P-T range (50–650 °C, 0.8–5.0 kbar). The aqueous speciation and concentrations of metals and sulfur were calculated assuming equilibrium with native gold and sphalerite, galena, chalcopyrite (or bornite), and a Fe-S phase (pyrite or pyrrhotite). This simple system is of interest since these minerals host most of the World's Au, Cu, Pb and Zn resources, and Fe-sulfides are commonly associated with sulfide ores and are common accessory minerals in source rocks and along fluid flow paths. The calculated solubilities provide information on the maximum metal concentrations that can be carried by a particular fluid; they constrain the conditions under which a fluid may reach saturation with respect to particular metals (deposition mechanisms), and provide upper limits on the potential of a fluid to mobilize metals (mobilization from source rocks). To test the accuracy of the simulations, the predicted Cu, Pb, and Zn concentrations were compared with those of natural geothermal fluids.

## 2. Calculation methods and scopes

Thermodynamic modeling was carried out using the HCh package and an updated version of its Unitherm database (Shvarov and Bastrakov, 1999), which were designed to calculate fluid-rock chemical equilibrium over a P-T range of 0–1000 °C and 1–5000 bar. HCh can model chemical equilibrium at water density  $>0.35$  g/cm<sup>3</sup>, following the limitations of the Helgeson-Kirkham-Flowers (HKF) equation of state (Tanger and Helgeson, 1988); therefore only relatively high density fluids are taken into consideration, and any process involving liquid-vapor separation is beyond this contribution. The accuracy of the simulations is expected to be poor at fluid density  $\leq 0.5$  g/cm<sup>3</sup>, and this density contour is shown in Figs. 1–4.

During the modeling, the solid phases sphalerite, galena, chalcopyrite (or bornite), native gold and a Fe-S phase (pyrite or pyrrhotite) were kept in excess and in equilibrium with the  $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{H}_2\text{S}-\text{NaCl}$  solutions (the typical composition of crustal fluids; Table 1). The

calculations therefore represent the chemical compositions of metal- and sulfur-saturated solutions. The simulations were carried out over a P-T range of 50–650 °C and 0.8–5.0 kbar, which covers the ore-forming conditions of most hydrothermal deposit types.

Two different salinities were used in the simulation: (1) low-salinity fluids with 0.6 molal NaCl (~3.4 wt.%), which is similar to sea water, and to the typical salinity of metamorphic fluids (e.g., Goldfarb et al., 2005) and some primary magmatic fluids (e.g., Redmond et al., 2004; Klemm et al., 2008); and (2) high-salinity brine with 5 molal NaCl (~22.6 wt.%), which is a characteristic salinity of some magmatic fluids (e.g., ore fluids of porphyry deposits; Seedorff et al., 2005) and basinal brines (e.g., ore fluids of MVT deposits; Leach et al., 2005). To evaluate the influence of fluid redox state, calculations were conducted at different fugacity ratios of  $\text{CO}_2(\text{g})$  and  $\text{CH}_4(\text{g})$ . The  $\log[f\text{CO}_2(\text{g})/f\text{CH}_4(\text{g})]$  ratios were set at 8 and  $-2$  to simulate oxidized and reduced fluids, respectively. These values cover the redox states of most gold-forming fluids in metamorphic terranes (Mikucki, 1998), which are representative of regional-scale crustal fluids. Consequently four model fluids with different salinities and redox states are used in this study (Table 1): (1) an oxidized low-salinity fluid (Sol. #1); (2) an oxidized high-salinity fluid (Sol. #2); (3) a reduced low-salinity fluid (Sol. #3); and (4) a reduced high-salinity fluid (Sol. #4). Simulated mineral assemblage, fluid pH, total S, concentration ratios of  $\text{HS}^-$  to  $\text{Cl}^-$ , the speciation and concentrations of metals for these four solutions are plotted in P-T diagrams in Figs. 1–4.

Within the lower temperature regime ( $< \sim 400$  °C), the fluid pH is mainly buffered by the reactions  $\text{H}_2\text{S}(\text{aq}) = \text{HS}^- + \text{H}^+$  or  $\text{H}_2\text{CO}_3(\text{aq}) = \text{HCO}_3^- + \text{H}^+$ , depending on the fluid temperature and relative abundances of  $\text{H}_2\text{S}(\text{aq})$  and  $\text{H}_2\text{CO}_3(\text{aq})$ . As a result, the fluid pH remains near neutral (ca. neutral pH  $\pm 1$ ; Fig. 1A–E) through the whole P-T range. Due to the strong bonds between Fe(II) and  $\text{Cl}^-$  (Testemale et al., 2009), the solubility of Fe-S minerals increases with increasing fluid salinity, forming Fe(II) chlorides (mainly  $\text{FeCl}_2(\text{aq})$  and  $\text{FeCl}_4^{2-}$ ) and hydrosulfides ( $\text{H}_2\text{S}(\text{aq})$  and  $\text{HS}^-$ ) as major products. The formers are pH-neutral, however, the formation of aqueous hydrosulfides consumes  $\text{H}^+$  in the fluid. As a result, pH values of high-salinity fluids are about half a unit higher than the low-salinity fluids, especially at elevated temperatures ( $> \sim 300$  °C; cf. Fig. 1A and B; C and D). Sulfur in the fluids is derived mainly from the dissolution of the Fe-S minerals; the mineral assemblages are shown in Fig. 1.

## 3. Sources and selection of thermodynamic properties for metal complexes

All species included in the modeling, their equations of states, and the sources of the thermodynamic properties are listed in the Appendix Table A1. We took special care in selecting the properties of Pb, Zn, Cu, Fe and Au chloride, bisulfide and hydroxide complexes, which are likely to dominate the transport of these metals at high temperature. The selection criteria and general comments on data reliability for these complexes are discussed below.

The HKF parameters for Pb chloride complexes were taken from Sverjensky et al. (1997). Lukanin et al. (2013) recently demonstrated that the extrapolations from this model are consistent with experimental studies ranging from 25 to 500 °C and  $P_{\text{sat}}$  to 500 bar (e.g., Seward, 1984; Hemley and Cygan, 1992). Sverjensky et al. (1997) report HKF parameters for  $\text{Pb}(\text{HS})_2(\text{aq})$  and  $\text{Pb}(\text{HS})_3^-$ , based on the room-temperature study of Hemley (1953). We chose instead the properties of  $\text{Pb}(\text{HS})_2(\text{aq})$  that are incorporated in the Unitherm database of HCh, and were derived by using the modified Ryzhenko-Bryzgalin model (MRB) (Borisov and Shvarov, 1992) to fit Wood et al. (1987)'s solubility experiments (200–350 °C). The only other data on Pb hydrosulfide complexes are from the study of Giordano and Barnes (1979), which investigated the solubility of galena in NaHS solutions at varying pressures of  $\text{H}_2\text{S}(\text{g})$  (T to 300 °C,  $P_{\text{H}_2\text{S}(\text{g})}$  to 90 bar). Use of the Giordano and Barnes (1979) data resulted in Pb solubility

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