

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

Weihua Liu<sup>a,c,\*</sup>, D.C. McPhail<sup>b,c</sup>

<sup>a</sup>CSIRO Exploration and Mining and South Australia Museum, P.O. Box 312, Clayton South, Victoria 3169, Australia

<sup>b</sup>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

<sup>c</sup>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 ( $\text{CuCl}_{(\text{aq})}$ ,  $\text{CuCl}_2^-$ ,  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$ ) 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 seafloor hydrothermal systems. *Geochimica et Cosmochimica 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).

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.

© 2005 Elsevier B.V. All rights reserved.

**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 (Steeffel 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-

ties (e.g., Oelkers, 1996). Unfortunately, compared to minerals, the thermodynamic properties for aqueous species at high temperatures and pressures, especially for copper complexes, are still poorly understood.

Copper chloride complexes are likely to be the most important in transporting copper in porphyry environments. Numerous fluid inclusion studies reveal that chloride is the dominant potential ligand in hydrothermal fluids (Beane and Titley, 1981; Roeder, 1984; Haynes, 1986; Ulrich et al., 1999). There have been many experimental studies conducted to investigate copper speciation in chloride bearing solutions at elevated temperatures. The first experimental solubility study on copper(I)–chloride species at high temperatures was conducted at temperatures between 200 and 350 °C and vapour-saturated pressures by Crerar and Barnes (1976). They measured the solubility of chalcopyrite–pyrite–bornite and native copper–chalcocite assemblages in NaCl- and sulphide-bearing solutions and concluded that  $\text{CuCl}_{(\text{aq})}$  predominates in solutions with high chloride concentrations (greater than 0.1 m). Two other experimental studies suggest a similar result: Hemley et al. (1992) measured the solubility of Pb, Zn and Cu sulphide in 1 m chloride solutions between 300 and 500 °C; and Seyfried and Ding (1993, 1995) measured solubility of chalcopyrite at temperatures from 200 to 450 °C, pressures from 300 to 500 bars, and total chloride concentration from 0.3 to 1.97 m. In contrast, Var'yash and Rekharskiy (1982) and Var'yash (1992) indicated that  $\text{CuCl}_2^-$  predominated in their experiments (native copper solubility at 300 and 350 °C, 0.5 kbar, 0.01, 0.1 and 1 m chloride).

Recently several experimental studies investigated copper(I)–chloride complexing in hydrothermal brines using different techniques. Mineral solubility experiments (Xiao et al., 1998; Liu et al., 2001) determined that  $\text{CuCl}_2^-$  is the predominant complex at chloride concentration below 2 m and temperatures between 25 and 300 °C. This was also found in EXAFS studies (Fulton et al., 2000a,b) and a UV spectrophotometric study (Liu et al., 2002). At higher chloride concentrations, i.e., up to 9 m, Liu et al. (2002) found evidence for  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$ . In general these recent experimental studies agree well with each other and greatly enhanced our understanding of copper speciation in chloride brines below 350 °C and at vapour-saturated conditions.

In order to understand copper transport in magmatic-hydrothermal systems, such as porphyry copper deposits, we need reliable thermodynamic properties of copper chloride complexes at much higher temperatures and pressures than experimentally investigated. In this paper we: 1) estimate the thermodynamic properties of copper(I) chloride complexes up to 1000 °C and 5 kbar using the revised HKF equations-of-state (Tanger and Helgeson, 1988; Shock et al., 1992), based on experimentally derived log  $K$  values between 25 and 350 °C and vapour-saturated pressures; 2) assess the accuracy of predicted mineral solubility by comparing with experimental data at higher temperature and pressure; 3) predict solubility of chalcopyrite and speciation of copper chloride complexes in hydrothermal solutions based on the newly derived properties; and 4) use thermodynamic calculations to understand copper geochemistry and transport in the formation of hydrothermal copper deposits and discuss physico-chemical factors that control copper transport and depositions in magmatic-hydrothermal systems.

## 2. Extrapolation of thermodynamic properties for copper(I) chloride complexes to high temperatures and pressures

There have been a number of theoretical and empirical methods developed to extrapolate thermodynamic properties of aqueous metal complexes obtained under limited experimental conditions to wide ranges of temperature and pressure. These include isocoulombic models (Ruaya, 1988; Gu et al., 1994), density models (Mesmer et al., 1988; Anderson et al., 1991), and various models based on electrostatic theory (e.g., Helgeson, 1969; Helgeson and Kirkham, 1974; Helgeson et al., 1981; Schott et al., 1988; Shock and Helgeson, 1988; Tanger and Helgeson, 1988; Brady and Walther, 1990; Sverjensky et al., 1997). These studies have shown successful results, based on comparisons between predicted and measured thermodynamic properties; however, at high temperature (>300 °C) and pressure (> vapour-saturated) there are few reliable experimental data with which we can verify one model over another. Recently, a new equation-of-state for correlation and prediction of standard molal thermodynamic properties has

been developed based on Fluctuation Solution Theory (Plyasunov et al., 2000a,b; Sedlbauer et al., 2000). This approach successfully predicted thermodynamic properties of some non-electrolytes, such as  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , under both sub- and supercritical conditions.

Two of the above extrapolation methods have been used in previous studies to extrapolate the thermodynamic properties for copper(I) chloride complexes. Ruaya (1988) used the isocoulombic method, and Sverjensky et al. (1997) used the revised Helgeson–Kirkham–Flowers (HKF) equations-of-state (Tanger and Helgeson, 1988) to estimate  $\log K$  values for copper complexes beyond the range of experimental conditions. As shown in Liu et al. (2001, 2002), those estimated  $\log K$  values for copper(I) chloride complexes disagree with more recent experimentally derived values.

Sverjensky et al. (1997) predicted thermodynamic properties for 109 aqueous metal complexes, based on the HKF equations-of-state and correlations among equation-of-state parameters and standard partial molal properties at 25 °C and 1 bar (Shock and Helgeson, 1988, 1990; Shock et al., 1992). However, not all the predicted high T–P  $\log K$  values in Sverjensky et al. (1997) have the same degree of reliability. The metal complexes were divided into three groups with different levels of uncertainties in their estimated thermodynamic properties. For some complexes (Group I in Table 2 of Sverjensky et al., 1997), e.g.,  $\text{NaCl}_{(\text{aq})}$  and some chloride complexes of Li, K, Ag, Zn, Pb and Fe, standard partial properties and equation-of-state parameters were derived using experimental data over broad ranges of pressure and temperature and are likely to be more reliable than complexes for which there are few or no experimental data at high pressure and temperature. Estimates for copper(I) chloride complexes by Sverjensky et al. (1997) are in the least reliable Group III (Table 12 of Sverjensky et al., 1997) because of the absence of reliable experimental data at high pressure and temperature at that time. There is significant disagreement between their estimates and recent  $\log K$  values generated from solubility and spectrophotometric experiments. For example, there is up to one order of magnitude discrepancy in  $\log K$  values for  $\text{CuCl}_2^-$  (Liu et al., 2002). Recently, Akinfiev and Zotov (2001) also used the revised HKF model to estimate

thermodynamic properties of  $\text{CuCl}_{(\text{aq})}$  and  $\text{CuCl}_2^-$  complexes based on limited experimental data, but we still lack properties for  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$  that are likely important copper species in magmatic-hydrothermal solutions, as evidenced by experimental results up to 250 °C (Liu et al., 2001, 2002).

We choose to use the revised HKF equations-of-state in this study because they have been used successfully in several studies (Tanger and Helgeson, 1988; Shock et al., 1989; Sverjensky et al., 1997) and other methods have yet to be tested at the temperatures and pressures for which we need estimates of thermodynamic properties. Isocoulombic methods were not chosen because the extrapolations depend on the form of the isocoulombic reactions, which can be difficult to balance if model complexes, e.g., highly charged and/or high ligand to metal ratios, are unknown. The success of the isocoulombic extrapolation also depends on the reliability of thermodynamic properties for the model complexes in the reactions. In addition, the reliability of isocoulombic methods is yet to be demonstrated widely (Ruaya, 1988; Sverjensky et al., 1997). We also chose not to use methods based on density (e.g., Anderson et al., 1991), despite the ease of use, because the enthalpy and heat capacity of reaction for Cu(I) chloride complexes at reference conditions are not available. The new equation-of-state developed by Plyasunov et al. (2000a,b) and Sedlbauer et al. (2000) is promising but the estimation or correlation of the equation-of-state parameters still needs to be developed before it can be used for electrolytes and metal complexes (Sedlbauer et al., 2000).

### 2.1. Regression of HKF equation-of-state parameters and thermodynamic properties of copper(I) chloride complexes at 25 °C and 1 bar

Most of the HKF equation-of-state parameters were calculated using algorithms published in Tanger and Helgeson (1988), Shock et al. (1989, 1992) and Sverjensky et al. (1997). Three parameters were regressed from experimentally derived  $\log K$  values for the dissociation reactions of copper chloride complexes: i) the apparent standard free energy of formation ( $\Delta_f \bar{G}_{P_r, T_r}^0$ ) of each complex at the reference pressure (1 bar) and temperature (298.15 K); ii) the standard partial molal entropy ( $\bar{S}_{P_r, T_r}^0$ ) of each complex at the

reference P and T; and iii) the heat capacity of each complex at the reference P and T ( $\bar{C}_{P,T}^0$ ). The details of the thermodynamic equations and parameters are presented in the Appendix. The overall equation used to calculate log  $K$  for each complex as a function of pressure and temperature is (Sverjensky et al., 1997):

$$\log K = \frac{1}{2.303RT} \left\{ - \sum_i n_i \Delta_f \bar{G}_{i,T}^0 + \Delta_f \bar{G}_{P_r,T_r}^0 - \bar{S}_{P_r,T_r}^0 (T - T_r) - \left[ 0.6087 \bar{C}_{P_r,T_r}^0 - \omega_{P_r,T_r} X_{P_r,T_r} + 5.85 \right] f_1(T) - \left[ 2037 \bar{C}_{P_r,T_r}^0 - 30460 \right] f_2(T) + \omega_{P_r,T_r} f_3(P, T) + f_4(P, T) \right\} \quad (1)$$

where  $n_i$  and  $\Delta_f \bar{G}_{i,T}^0$  refer to the stoichiometric coefficients in the dissociation reactions and the free energies of formation for species (i.e.,  $\text{Cu}^+$  and  $\text{Cl}^-$ ) other than the copper chloride in each reaction.  $\Delta_f \bar{G}_{P_r,T_r}^0$ ,  $\bar{S}_{P_r,T_r}^0$ ,  $\bar{C}_{P_r,T_r}^0$  for each copper chloride complex were optimized simultaneously by minimizing the residuals between calculated and experimental log  $K$  (dissociation reactions) values using a simplex algorithm (Nelder and Mead, 1965). This was done conveniently using the Matlab® programming platform (Borse, 1997). The residual function is defined as the sum of the squares of the difference between

experimental and calculated log  $K$  values. The remaining variables and functions in Eq. (1) are defined in the Appendix.

Selected experimentally derived log  $K$  values were used in the fitting. For  $\text{CuCl}_{(\text{aq})}$ , there is a discrepancy of 0.5 log units between the two available experimental data sets of Xiao et al. (1998) and Liu et al. (2001). We did not include the values by Xiao et al. (1998) for  $\text{CuCl}_{(\text{aq})}$  because they rely on the accuracy of log  $K$  for Ag–Cl complexes, as mentioned in Liu et al. (2002). Four high temperature data sets for  $\text{CuCl}_2^-$  (Var'yash, 1992; Xiao et al., 1998; Liu et al., 2001; Liu et al., 2002) are in good agreement and are included, as well as the 25 °C properties from Fritz (1980) and Ciavatta and Iuliano (1998). We excluded the 250 °C datum of Liu et al. (2002) because it has a bigger experimental uncertainty than other data of that study. For  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$ , we used the high temperature properties of Liu et al. (2002) and the 25 °C data from Ciavatta and Iuliano (1998).

Regressed standard state thermodynamic properties and equation-of-state parameters are compiled in Table 1. The values for  $\text{CuCl}_{(\text{aq})}$  and  $\text{CuCl}_2^-$  from Akinfiev and Zotov (2001) are also listed for comparison. Our results for  $\text{CuCl}_{(\text{aq})}$  and  $\text{CuCl}_2^-$  are in good agreement with those reported by Akinfiev and Zotov (2001), despite differences in the experimental data fitted and calculation algorithms used between two studies. Using our parameters, the calculated formation constants for copper(I) chloride complexes for

Table 1

Equation-of-state parameters and standard partial molal properties at 25 °C for copper(I) chloride complexes regressed from experimentally derived formation constants (except for  $V_{P_r,T_r}^0$ , which is calculated based on regression equations of Sverjensky et al., 1997)

	$\text{CuCl}_{(\text{aq})}$	$\text{CuCl}_{(\text{aq})}$ (Akinfiev and Zotov, 2001)	$\text{CuCl}_2^-$	$\text{CuCl}_2^-$ (Akinfiev and Zotov, 2001)	$\text{CuCl}_3^{2-}$	$\text{CuCl}_4^{3-}$
$\Delta_f \bar{G}_{P_r,T_r}^0$ (Cal mol <sup>-1</sup> )	-25068	-24594	-58241	-57610	-88671	-117363
$\Delta_f \bar{H}_{P_r,T_r}^0$ (Cal mol <sup>-1</sup> )	-25506	-25824	-65648	-63330	-108868	-155689
$\bar{S}_{P_r,T_r}^0$ (Cal mol <sup>-1</sup> K <sup>-1</sup> )	33.098	30.455	51.978	57.669	51.330	32.778
$\bar{C}_{P_r,T_r}^0$ (Cal mol <sup>-1</sup> K <sup>-1</sup> )	1.755	-8.483	-27.456	-20.907	-46.119	18.092
$\bar{V}_{P_r,T_r}^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	17.22	19.285	45.43	34.754	76.86	112.37
$a_1$ (Cal mol <sup>-1</sup> bar <sup>-1</sup> ) × 10	4.108	4.404	8.266	6.8266	13.105	18.6
$a_2$ (Cal mol <sup>-1</sup> ) × 10 <sup>-2</sup>	2.2518	2.9716	12.4071	8.8868	24.2264	37.6459
$a_3$ (Cal K mol <sup>-1</sup> bar <sup>-1</sup> )	4.5698	4.5820	0.2096	2.2570	-4.8649	-10.626
$a_4$ (Cal K mol <sup>-1</sup> ) × 10 <sup>-4</sup>	-2.8721	-2.9018	-3.2919	-3.1464	-3.7806	-4.3353
$c_1$ (Cal mol <sup>-1</sup> )	6.5717	1.1950	-3.1775	1.2981	-0.0094	56.2186
$c_2$ (Cal K mol <sup>-1</sup> ) × 10 <sup>-4</sup>	-2.6885	-4.7626	-8.6389	-7.2932	-12.4404	0.6393
$\omega_{P_r,T_r}$ (Cal mol <sup>-1</sup> ) × 10 <sup>-5</sup>	-0.0380	0	0.8423	0.8094	2.4346	4.3136

The values for  $\text{CuCl}_{(\text{aq})}$  and  $\text{CuCl}_2^-$  from Akinfiev and Zotov (2001) are also listed for comparison.



100 to 1000 °C and 0.5 to 5 kbar are compiled in Tables 2–5 and plotted in Figs. 1–4.

Figs. 1 and 2 show comparisons between estimated and measured log  $K$  values between 25 and 350 °C and vapour-saturated pressure. Log  $K$  values estimated using two previous thermodynamic data sets for copper chloride complexes (Akinfiev and Zotov, 2001; Sverjensky et al., 1997) are shown for comparison. In most cases our values are in better agreement with the experimental data than those of Akinfiev and Zotov (2001) and much better than those of Sverjensky et al. (1997), a consequence of having more and more reliable experimental data available for our fits. In general, the P–T dependence of log  $K$  values for copper(I) chloride complexes at higher pressure and temperature, shown in Figs. 3 and 4, is similar to those for  $\text{NaCl}_{(\text{aq})}$ ,  $\text{LiCl}_{(\text{aq})}$  and  $\text{KCl}_{(\text{aq})}$  for which experimentally derived log  $K$  values are available (Oelkers and Helgeson, 1988). The P–T dependence is also similar to the predictions for many other metal chloride complexes where experimental data are available, such as  $\text{AgCl}_2^-$ ,  $\text{ZnCl}_{2(\text{aq})}$  and  $\text{MnCl}^+$  (e.g., Figs. 26 and 27 of Sverjensky et al., 1997).

## 2.2. Test of extrapolated log $K$ values at high temperatures and pressures

In order to test the accuracy of the extrapolated log  $K$  values at higher temperature and pressure than the experimental conditions used in our fitting, we com-

Table 2  
Predicted formation constants (log  $K$ ) for  $\text{CuCl}_{(\text{aq})}$

$T$ (°C)	$\text{Cu}^+ + \text{Cl}^- = \text{CuCl}_{(\text{aq})}$									
	0.5 kb	1 kb	1.5 kb	2 kb	2.5 kb	3 kb	3.5 kb	4 kb	4.5 kb	5 kb
100	3.75	3.70	3.66	3.63	3.61	3.59	3.58	3.57	3.57	3.57
200	3.68	3.58	3.51	3.45	3.40	3.36	3.33	3.30	3.28	3.26
300	3.96	3.74	3.60	3.48	3.40	3.32	3.26	3.21	3.17	3.13
400	4.72	4.16	3.88	3.68	3.52	3.40	3.30	3.22	3.15	3.09
500		5.00	4.37	4.02	3.77	3.58	3.43	3.31	3.20	3.12
600		6.36	5.09	4.50	4.13	3.85	3.64	3.47	3.33	3.21
700			5.86	5.08	4.57	4.20	3.92	3.70	3.52	3.37
800				5.63	5.04	4.59	4.25	3.98	3.77	3.59
900				6.11	5.48	4.99	4.60	4.29	4.06	3.87
1000					5.85	5.33	4.91	4.60	4.36	4.18

Values were calculated with Eq. (1), the parameters and properties listed in Table 1 and properties and parameters for  $\text{Cu}^+$  and  $\text{Cl}^-$  from Shock and Helgeson (1988).

Table 3  
Predicted formation constants (log  $K$ ) for  $\text{CuCl}_2^-$

$T$ (°C)	$\text{Cu}^+ + 2\text{Cl}^- = \text{CuCl}_2^-$									
	0.5 kb	1 kb	1.5 kb	2 kb	2.5 kb	3 kb	3.5 kb	4 kb	4.5 kb	5 kb
100	4.96	4.85	4.76	4.69	4.63	4.59	4.55	4.52	4.49	4.48
200	4.89	4.73	4.61	4.50	4.41	4.34	4.27	4.22	4.17	4.13
300	5.23	4.92	4.71	4.55	4.41	4.29	4.19	4.11	4.04	3.97
400	5.91	5.37	5.02	4.76	4.55	4.38	4.24	4.11	4.01	3.91
500		6.13	5.52	5.12	4.82	4.58	4.38	4.21	4.06	3.93
600		7.23	6.20	5.63	5.20	4.87	4.61	4.38	4.19	4.03
700			6.88	6.21	5.68	5.27	4.93	4.65	4.41	4.21
800				6.78	6.22	5.73	5.32	4.98	4.71	4.48
900				7.29	6.74	6.20	5.74	5.36	5.06	4.81
1000					7.20	6.62	6.13	5.73	5.42	5.19

Values were calculated with Eq. (1), the parameters and properties listed in Table 1 and properties and parameters for  $\text{Cu}^+$  and  $\text{Cl}^-$  from Shock and Helgeson (1988).

pare them with experimentally derived values and also compare predicted and measured copper concentrations from solubility experiments. For copper(I) chloride complexes, there are only two solubility experimental studies at temperature higher than 350 °C: Seyfried and Ding (1993) and Hemley et al. (1992).

### 2.2.1. Comparison with Seyfried and Ding (1993, 1995)

Seyfried and Ding (1993) measured the solubility of chalcopyrite mainly at 400 °C, 500 bars and 0.34–1.97 m total chloride. They used K-feldspar–musco-

Table 4  
Predicted formation constants (log  $K$ ) for  $\text{CuCl}_3^{2-}$

$T$ (°C)	$\text{Cu}^+ + 3\text{Cl}^- = \text{CuCl}_3^{2-}$									
	0.5 kb	1 kb	1.5 kb	2 kb	2.5 kb	3 kb	3.5 kb	4 kb	4.5 kb	5 kb
100	3.74	3.55	3.40	3.27	3.16	3.07	2.98	2.91	2.85	2.80
200	3.39	3.17	3.00	2.84	2.71	2.60	2.50	2.41	2.33	2.26
300	3.60	3.24	2.99	2.79	2.62	2.47	2.34	2.23	2.13	2.04
400	4.28	3.65	3.27	2.97	2.74	2.54	2.38	2.23	2.10	1.99
500		4.47	3.79	3.34	3.02	2.75	2.53	2.34	2.18	2.04
600		5.70	4.52	3.89	3.43	3.08	2.79	2.56	2.35	2.18
700			5.29	4.52	3.95	3.51	3.15	2.86	2.62	2.41
800				5.15	4.53	4.01	3.58	3.24	2.95	2.72
900				5.71	5.07	4.50	4.04	3.65	3.35	3.09
1000					5.55	4.96	4.47	4.06	3.75	3.51

Values were calculated with Eq. (1), the parameters and properties listed in Table 1 and properties and parameters for  $\text{Cu}^+$  and  $\text{Cl}^-$  from Shock and Helgeson (1988).

Table 5

Predicted formation constants (log  $K$ ) for  $\text{CuCl}_4^{3-}$ 

$T$ (°C)	$\text{Cu}^+ + 4\text{Cl}^- = \text{CuCl}_4^{3-}$									
	0.5 kb	1 kb	1.5 kb	2 kb	2.5 kb	3 kb	3.5 kb	4 kb	4.5 kb	5 kb
100	1.05	0.77	0.52	0.31	0.13	−0.04	−0.18	−0.31	−0.43	−0.54
200	0.92	0.63	0.39	0.18	−0.01	−0.18	−0.33	−0.47	−0.60	−0.72
300	1.71	1.32	1.04	0.79	0.59	0.40	0.24	0.09	−0.05	−0.17
400	3.15	2.48	2.08	1.77	1.52	1.30	1.11	0.94	0.78	0.65
500		4.11	3.40	2.95	2.62	2.35	2.12	1.92	1.75	1.59
600		6.20	4.94	4.30	3.85	3.50	3.22	2.98	2.77	2.60
700			6.51	5.71	5.14	4.71	4.37	4.09	3.85	3.65
800				7.08	6.45	5.95	5.55	5.23	4.96	4.73
900				8.34	7.68	7.13	6.70	6.35	6.07	5.83
1000					8.81	8.25	7.81	7.43	7.15	6.93

Values were calculated with Eq. (1), the parameters and properties listed in Table 1 and properties and parameters for  $\text{Cu}^+$  and  $\text{Cl}^-$  from Shock and Helgeson (1988).

vite-quartz to buffer acidity and either pyrite–pyrrhotite–magnetite (MPP) or hematite–magnetite–pyrite (HMP) to control  $f_{\text{S}_2}$  and  $f_{\text{O}_2}$ . They interpreted their experimental data assuming only one copper complex,  $\text{CuCl}_{(\text{aq})}$ , and derived a log  $K_{\text{CuCl}_{(\text{aq})}} = 5.75 \pm 0.16$  at 400 °C and 0.5 kbar for  $\text{Cu}^+ + \text{Cl}^- = \text{CuCl}_{(\text{aq})}$  (Seyfried and Ding, 1993, 1995). This value is higher than log  $K_{\text{CuCl}_{(\text{aq})}} = 4.72$  estimated in our study (Table 2); however, it is most likely because of their assumption of only  $\text{CuCl}_{(\text{aq})}$ . Recent experimental studies (solubility, Xiao et al., 1998; EXAFS, Fulton et al., 2000a; solubility and spectrophotometry, Liu et al., 2001, 2002) indicate that  $\text{CuCl}_2^-$  or other copper chloride complexes were probably the predominant copper complexes in the experiments by Seyfried and Ding (1993), rather than their assumption of  $\text{CuCl}_{(\text{aq})}$ . For instance, at 325 °C, the EXAFS study of Fulton et al. (2000a) showed that  $\text{CuCl}_2^-$  predominated at NaCl concentration greater than 0.5 m. Therefore the interpreted log  $K$  of association by Seyfried and Ding (1995) is too high, because the concentration of  $\text{CuCl}_{(\text{aq})}$  was lower than the measured total copper concentration in their experiments. In order to make a more direct comparison with their experiments, we calculated the solubility of chalcopyrite under their experimental conditions using our estimated properties for all copper chloride complexes. The calculation was carried out using the HCh program (Shvarov and Bastrakov, 1999), and the sources of thermodynamic properties for minerals and aqueous metal complexes are listed in Table 6. There are several sets of properties for  $\text{HCl}_{(\text{aq})}$ ; however, we used several published

sets of parameters for  $\text{HCl}_{(\text{aq})}$  (Sverjensky et al., 1991; Tagirov et al., 1997; Pokrovskii, 1999) and found they resulted in only small (<1%) differences in our calculations. Activity coefficients for neutral species were assumed to be one, and for charged aqueous species were calculated using the b-dot equation (Helgeson, 1969) with b-dot parameters for NaCl solutions from Oelkers and Helgeson (1990). The calculated activity coefficients, especially for  $\text{CuCl}_4^{3-}$ , are sensitive to the choice of the ion size parameter (Å), as shown by Liu et al. (2002), and this affects the calculated total copper concentrations, as we discuss next.

The predicted and measured copper concentrations and predicted distribution of copper(I) chloride complexes in experiments by Seyfried and Ding (1993) at 400 °C and 0.5 kbar are plotted in Fig. 5a for hematite–magnetite–pyrite (HMP) and Fig. 5b for magnetite–pyrite–pyrrhotite (MPP). In all cases the agreement between predicted and measured copper concentrations is within 0.2 log units and even better in some cases (Fig. 5). The differences could be a result of uncertainties in the experimental and analytical methods, the properties of the copper chloride complexes, chalcopyrite and the other minerals and/or estimates of activity coefficients. The uncertainty in the copper concentrations of the experiments by Seyfried and Ding (1993) is probably 5–10 mol%, based on the reproducibility of their experiments PPM-1-2 and PPM-2-2, 3, and they also mention that at high chloride concentrations equilibrium may not have been attained (p. 1912; Seyfried and Ding, 1993). Although it might be possible to refine the thermody-

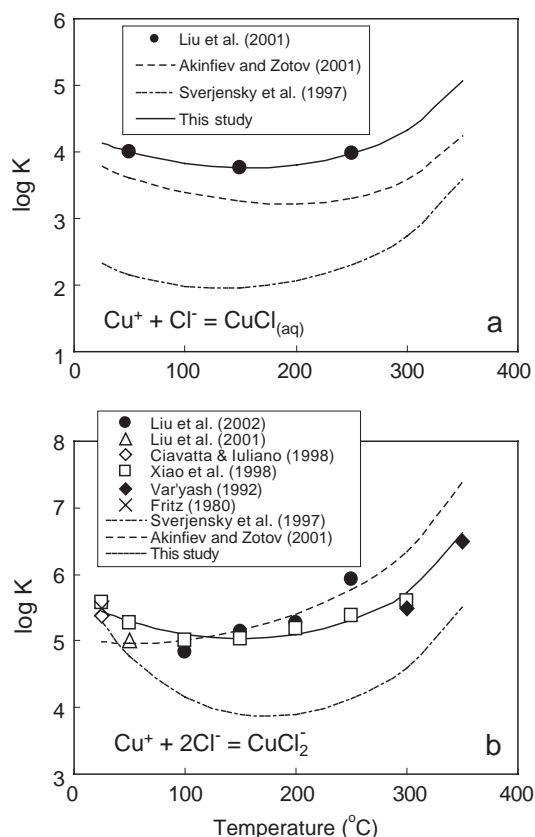


Fig. 1. Logarithm of formation constants ( $\log K$ ) for  $\text{CuCl}_{(\text{aq})}$  (a) and  $\text{CuCl}_2^-$  (b) complexes at temperatures from 25 to 350 °C. The solid curves are calculated using the revised HKF model with new equation-of-state parameters and properties regressed in this study. Comparisons are shown with Sverjensky et al. (1997) and Akinfiev and Zotov (2001).

namic properties of chalcopyrite and/or the copper complexes using the experimental data by Seyfried and Ding (1993), the discrepancies between measured and calculated copper concentrations are small. The speciation of copper can be sensitive to the choice of  $a$ -zero parameters in estimating activity coefficients (e.g., Liu et al., 2002) so we show the results of different choices below.

Fig. 6 shows the chalcopyrite solubility and copper speciation as a function of total chloride concentration in equilibrium with magnetite–pyrite–pyrrhotite and K–felspar–muscovite–quartz at 400 °C and 0.5 kbars, i.e., under similar conditions of the MPP-buffered experiments by Seyfried and Ding (1993), but we extended the chloride concentration up to 5 m. Liu

et al. (2002) showed that the biggest effects of different  $a$  values are for  $\text{CuCl}_4^{3-}$ , relative to  $\text{CuCl}_2^-$  and  $\text{CuCl}_3^{2-}$ , so we chose different values of  $a$  (4, 5, and 6) for  $\text{CuCl}_4^{3-}$  to show the effect on speciation and solubility. Note that  $\text{CuCl}_{(\text{aq})}$  is predicted to be only in minor concentrations regardless of  $a$ . At low chloride concentrations, e.g., less than 1 m, different values of  $a$  for  $\text{CuCl}_4^{3-}$  have a negligible effect on the speciation and total copper concentration, as  $\text{Cu}(\text{HS})_{(\text{aq})}$  and  $\text{CuCl}_2^-$  are predicted to be the predominant species. At higher chloride concentrations (>1.5 m),  $\text{CuCl}_2^-$ ,  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$  are predicted to become increasingly important and with increasing chloride concentrations, copper speciation and total

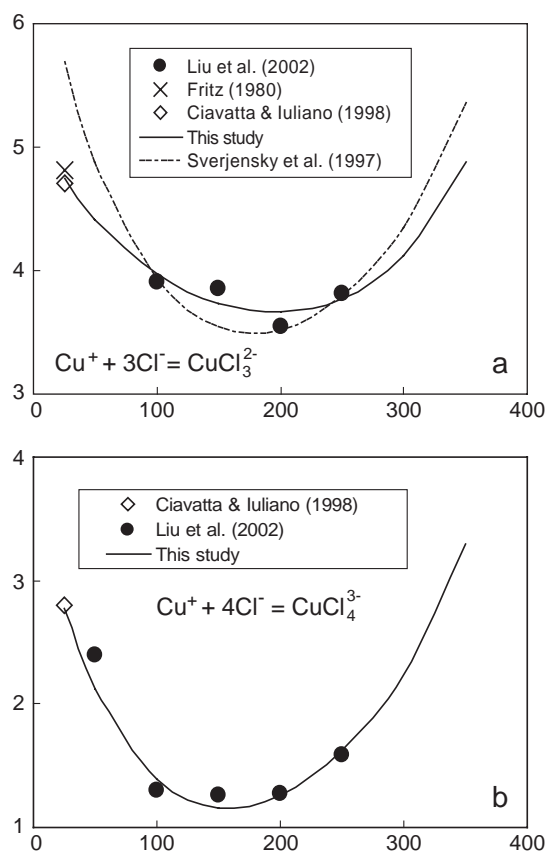


Fig. 2. Logarithm of formation constants for  $\text{CuCl}_3^{2-}$  (a) and  $\text{CuCl}_4^{3-}$  (b) complexes at temperatures from 25 to 350 °C and water vapour-saturated pressures. The solid curves are calculated using the revised HKF model with new equation-of-state parameters and properties regressed from the experimental data shown in the figures.  $\log K$  values calculated using the thermodynamic data for  $\text{CuCl}_3^{2-}$  from Sverjensky et al. (1997) are shown for comparison.



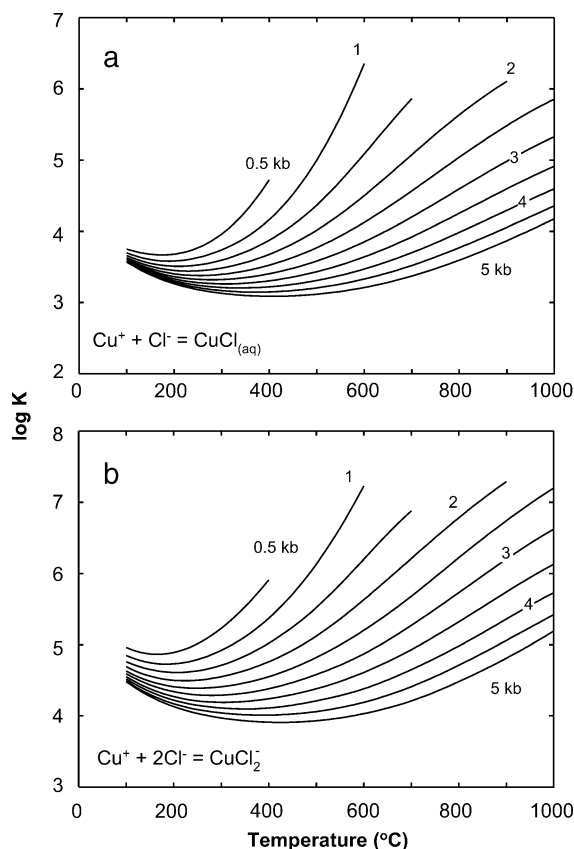


Fig. 3. Logarithm of formation constants for  $\text{CuCl}_{(\text{aq})}$  (a) and  $\text{CuCl}_2^-$  (b) complexes at 100–1000  $^{\circ}\text{C}$  and 0.5–5 kbar calculated based on the revised HKF model (Tanger and Helgeson, 1988) and the new equation-of-state parameters and thermodynamic properties derived in this study.

copper concentration are increasingly sensitive to the choice of  $\hat{a}$  for  $\text{CuCl}_4^{3-}$ . Decreasing  $\hat{a}$  from 6 to 4 greatly increases the contribution of  $\text{CuCl}_4^{3-}$  and the total predicted copper concentration by up to one order of magnitude in 5 m Cl solutions.  $\hat{a}=4$  for  $\text{CuCl}_4^{3-}$  results in predicted copper concentrations that are higher than measured in the experiments by Seyfried and Ding (1993) at 1.5–2.0 m total chloride,  $\hat{a}=6$  results in predictions lower than measured. We choose  $\hat{a}=5$  because we used it in fitting the lower temperature and pressure data and it results in the best agreement. Note, too, that the trends in measured and predicted copper concentrations are similar, which indicates that our estimates of activity coefficients for the copper complexes are reasonable at least under their experimental conditions.

The predicted iron concentrations are systematically less than measured, by a log unit or more (Fig. 5). Despite attempts to resolve the discrepancies, by using different published properties for the iron minerals and aqueous species, there is no obvious explanation. As with copper, the trends of measured and predicted iron concentrations are similar, indicating that calculated acidity, oxygen and sulfur fugacities and activity coefficients are unlikely to be the main reason. The systematic discrepancies probably indicate that the properties ( $\log K$ , free energy) of the iron minerals or aqueous complexes are off by a constant amount or the experimental data are in error but we do not follow this further here for the following reasons: i) in our calculations to compare with the experimental data by

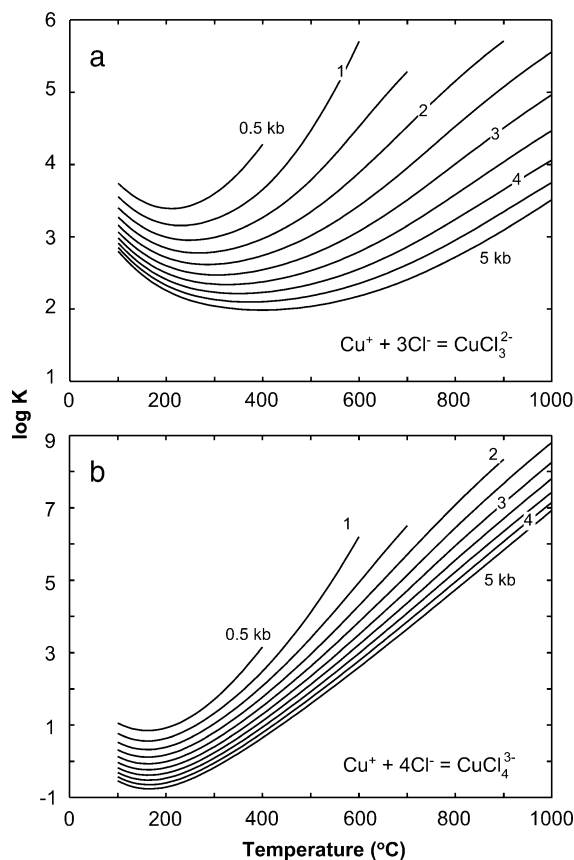


Fig. 4. Logarithm of formation constants for  $\text{CuCl}_3^{2-}$  (a) and  $\text{CuCl}_4^{3-}$  (b) complexes at 100–1000  $^{\circ}\text{C}$  and 0.5–5 kbar calculated based on the revised HKF model (Tanger and Helgeson, 1988) and the new equation-of-state parameters and thermodynamic properties derived in this study.

Table 6

Sources of thermodynamic properties used in this study

Cu chloride complexes	This study
$\text{Cu}(\text{HS})_{(\text{aq})}$ , $\text{Cu}(\text{HS})_2^-$	Akinfiev and Zotov (2001)
Fe complexes ( $\text{FeCl}^+$ , $\text{FeCl}_{2(\text{aq})}$ , Fe hydroxides)	Sverjensky et al. (1997)
Zn chloride complexes ( $\text{ZnCl}_n^{2-n}$ ; $n=1-3$ )	Sverjensky et al. (1997)
Pb chloride complexes: ( $\text{PbCl}_n^{2-n}$ ; $n=1-4$ )	Sverjensky et al. (1997)
Hematite and magnetite	Berman (1988)
Pyrrhotite	Robie and Hemingway (1995)
Pyrite	Helgeson et al. (1978)
K–Feldspar, muscovite and quartz	Berman (1988) <sup>a</sup>
Chalcopyrite	Helgeson et al. (1978)
Dissociation constant of water	Marshall and Franck (1981)
$\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$	Shock and Helgeson (1988)
$\text{HCl}_{(\text{aq})}$	Pokrovskii (1999)
$\text{NaCl}_{(\text{aq})}$ , $\text{KCl}_{(\text{aq})}$	Sverjensky et al. (1997)
$\text{HS}^-$	Shock and Helgeson (1988)
$\text{H}_2\text{S}_{(\text{aq})}$	Shock et al. (1989)

<sup>a</sup> Modified by Bastrakov (2000) to take into account the corrections for K and Na minerals suggested by Sverjensky et al. (1991).

Hemley et al. (1992), the agreement for iron, copper and other metals is good; and ii) the predicted iron concentrations do not affect our predicted copper concentrations — the mineral assemblage plus known concentrations of K, Na and Cl fix the copper concentrations independently of iron.

#### 2.2.2. Comparison with Hemley et al. (1992)

Hemley et al. (1992) measured the solubility of chalcopyrite + galena + sphalerite in 1 m KCl solutions at 300–500 °C and 0.5–2 kbar. The acidity of solutions was controlled by K–feldspar–muscovite–quartz (KMQ) and known K concentration, and  $f_{\text{S}_2}(\text{g})$  and  $f_{\text{O}_2}(\text{g})$  were controlled by pyrite–pyrrhotite–magnetite (MPP). They interpreted a formation constant for  $\text{CuCl}_{(\text{aq})}$  of  $\log K_{\text{CuCl}_{(\text{aq})}} = 6.22$  at 500 °C and 1 kbar, higher than our estimate of 5.0 (Table 2); however, as Seyfried and Ding (1993, 1995) did, they assumed  $\text{CuCl}_{(\text{aq})}$  was the only copper chloride complex. Their experimental results need to be reinterpreted to include more than one copper complex; however, the range of chloride concentrations in their experiments is not wide enough to discern changes in chloride complexes and the experiments are too complex to interpret readily.

We calculated the metal concentrations in 1 m total chloride solutions in equilibrium with K–feldspar–muscovite–quartz–pyrite–pyrrhotite–magnetite–sphalerite–galena–chalcopyrite and under the temperature and pressure conditions of Hemley et al. (1992). The sources of thermodynamic properties of minerals used are listed in Table 6. The thermodynamic properties and the HKF parameters for copper chloride complexes are from this study, those for iron chloride ( $\text{FeCl}^+$  and  $\text{FeCl}_{2(\text{aq})}$ ), zinc chloride ( $\text{ZnCl}^+$ ,  $\text{ZnCl}_{2(\text{aq})}$ , and  $\text{ZnCl}_3^-$ ) and lead chloride complexes ( $\text{PbCl}^+$ ,  $\text{PbCl}_{2(\text{aq})}$ ,  $\text{PbCl}_3^-$  and  $\text{PbCl}_4^{2-}$ ) are from Sverjensky et al. (1997) and for copper hydrosulphide complexes from Akinfiev and Zotov (2001). All calculations

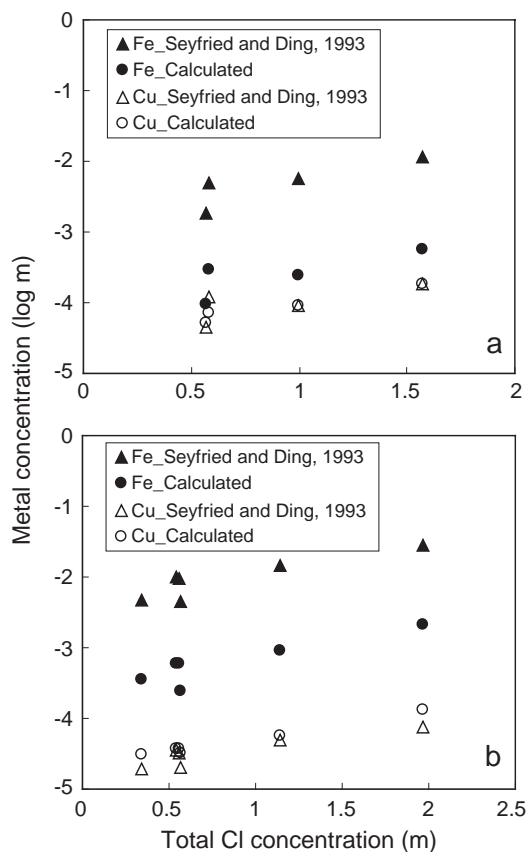


Fig. 5. (a) Calculated and measured solubility of chalcopyrite in NaCl–KCl solutions in equilibrium with K–feldspar–muscovite–quartz and hematite–magnetite–pyrite at 400 °C and 0.5 kbar. (b) Calculated and measured solubility of chalcopyrite in equilibrium with K–feldspar–muscovite–quartz and magnetite–pyrite–pyrrhotite at 400 °C and 0.5 kbar.

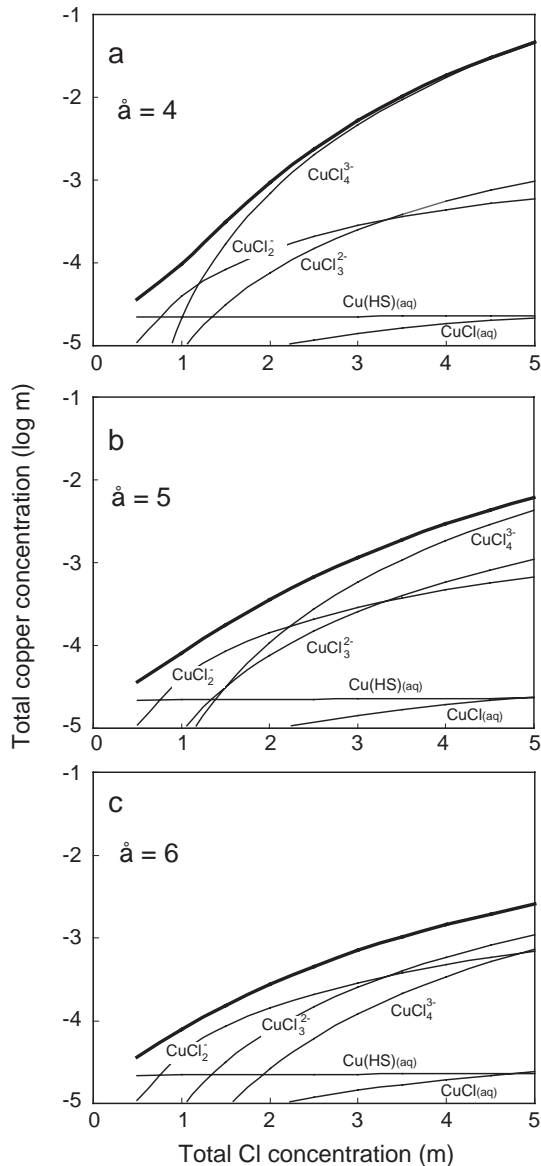


Fig. 6. The effect of  $a$ -zero on calculated copper concentration and copper speciation as a function of total chloride concentration in NaCl–KCl solutions in equilibrium with chalcopyrite, K–feldspar–muscovite–quartz and magnetite–pyrite–pyrrhotite at 400 °C and 0.5 kbar. The thick solid lines show total dissolved copper concentration and fine lines represent concentration of individual aqueous copper complexes.

were made using the HCh software (Shvarov and Bastrakov, 1999), using the same database and activity coefficient model as used in the previous section.

Calculated copper concentrations and the corresponding measured ranges from Hemley et al. (1992) are listed in Table 7. Two of the predicted copper concentrations are within the measured ranges, i.e., at 500 °C and 1 and 2 kbar, but lower for the other temperatures and pressures. At 300 °C, the predicted copper concentrations are lower than the measured ranges (0.9 versus 7–20 ppm at 1 kbar and 1.2 versus 9–21 ppm at 0.5 kbar). At 400 °C, the predicted copper concentrations are also lower than measured, although the trends with pressure are similar. In all cases, the predicted predominant copper complex is  $\text{CuCl}_2^-$ , typically more than 70 mol% and always more than 50 mol%. Note that this is the complex for which the properties are most reliable. The other copper complexes are predicted to be present at much lower concentrations, although at 500 °C, 1 kbar,  $\text{CuCl}_4^{3-}$  is predicted to be 21 mol% of total copper at 1 kbar and less at 2 kbar. The discrepancies could result from experimental uncertainty, e.g., Hemley et al. (1992) mention that for low copper concentrations, their results were susceptible to contamination and analytical difficulties, both of which would lead to higher than equilibrium measured copper concentrations and towards our predictions. However, they also mention that copper alloyed with gold in some of their experiments, especially at higher temperature. This might result in lower copper concentrations than equilibrium with chalcopyrite, but this depends on what phase was controlling the copper concentrations. Our activity coefficient estimates are also uncertain. We assumed  $a=5$  to be consistent with our fitting methodology and calculations at other temperatures and pressures; however, if  $a=4$  under the conditions of Hemley et al. (1992), the predicted concentrations at 500 °C are in closer agreement with measured ones, but there is little or no improvement at lower temperatures. There is too little information to know where the uncertainties lie, but the agreement between calculated and measured copper concentrations indicates solubility calculations are reliable to within a log unit, perhaps less, at P–T conditions up to 500 °C and 2 kbar.

Although not the focus of this study, we also calculated simultaneously the concentrations of iron, zinc and lead to compare with the experiments by Hemley et al. (1992). The predicted iron concentrations are higher than the measured ranges at 500 °C, 1 and 2 kbar, within the measured ranges at 400 °C, 1

Table 7

Calculated and measured metal concentrations in 1 m KCl solutions in equilibrium with K-feldspar–muscovite–quartz and pyrite–magnetite–pyrrhotite–sphalerite–galena–chalcopyrite

<i>T</i> (°C)	<i>P</i> (bar)	Cu (ppm)		Fe (ppm)		Pb (ppm)		Zn (ppm)	
		This study	Hemley et al. (1992)	This study	Hemley et al. (1992)	This study	Hemley et al. (1992)	This study	Hemley et al. (1992)
500	2000	66	66~105	3553	2313~2500	2079	945~1700	3110	928~1475
	1000	88	79~141	6968	5000~6110	3757	2372~3841	3766	2290~3092
400	2000	9	24~32	530	450~530	454	153~239	864	112~130
	1000	15	29~66	1262	1100~1467	1239	457~762	1320	333~537
	500	23	46~79	2071	2344~2884	2278	1050~1394	1617	905~1122
300	1000	0.87	7~20	125	166~349	103	43~62	210	23~51
	500	1.23	9~21	188	240~440	202	60~110	279	33~63

Measured values are the ranges quoted in Hemley et al. (1992).

and 2 kbar, and lower than the measured ranges at 300 °C, 0.5 and 1 kbar (Table 7). In general, however, the agreement between predicted and measured iron concentrations is good, i.e., within 14% at 1 kbar and 42% higher at 2 kbar at 500 °C, and within 25% at 300 °C. The agreement for Pb and Zn is not as good, but the discrepancies are within approximately 0.5 log units and the trends with pressure and temperature are the same (Table 7).

### 3. Copper transport in magmatic-hydrothermal solutions

In this section the results are presented for calculated solubility of chalcopyrite under conditions similar to magmatic-hydrothermal systems. The effects of temperature, pressure, salinity and pH on chalcopyrite solubility are calculated and shown in order to elucidate the physico-chemical factors controlling transport and deposition of copper in magmatic-hydrothermal systems. The examples used here are the Starra iron oxide–Au–Cu deposits, Australia, and the Bajo de la Alumbrera porphyry copper deposit, Argentina where metal concentrations in individual fluid inclusions have been reported, mineral paragenesis has been documented and fluid inclusion microthermometry data are available.

#### 3.1. Chalcopyrite solubility and copper content in ore-forming fluids

Williams et al. (2001) reported metal concentrations in fluid inclusions from the Starra iron oxide–

Au–Cu deposits, Australia. In that study metal concentrations were determined using proton-induced X-ray emission (PIXE) analysis of fluid inclusions from the earlier barren magnetite ironstone stage (400–550 °C, 34–52 wt.% NaCl equivalent) and later hematite mineralisation stage (220–360 °C, 29–42 wt.% NaCl equivalent). The estimated pressure for mineralisation stage is about 1 kbar (Rotherham et al., 1998). Measured copper concentrations are 190–1400 ppm, average of 615 ppm for the ironstone stage, and 197–2810 ppm, average of 1176 ppm for the hematite mineralisation stage.

We calculated chalcopyrite solubility using the same approach and data sources as used in the previous section, assuming that the solution pH is controlled by K–feldspar–muscovite–quartz for both stages, and redox by magnetite–pyrite–pyrrhotite in one case, and hematite–magnetite–pyrite in another. The total chloride concentration is assumed to be 10 m (arbitrarily 9 m NaCl and 1 m KCl), corresponding to 37 wt.% NaCl. Although there is uncertainty in the copper speciation and activity coefficient estimates (e.g., the  $\alpha$  parameter) under these conditions, the agreement between measured and predicted concentrations shown in previous sections suggests that we may be able to predict chalcopyrite solubilities to within an order of magnitude.

The calculated copper concentrations as a function of temperature are shown in Fig. 7. The ranges in homogenisation temperature and copper concentrations measured by PIXE from Williams et al. (2001) are shown for comparison. For the magnetite ironstone stage, the measured concentrations are clearly lower than the calculated copper concentration at the

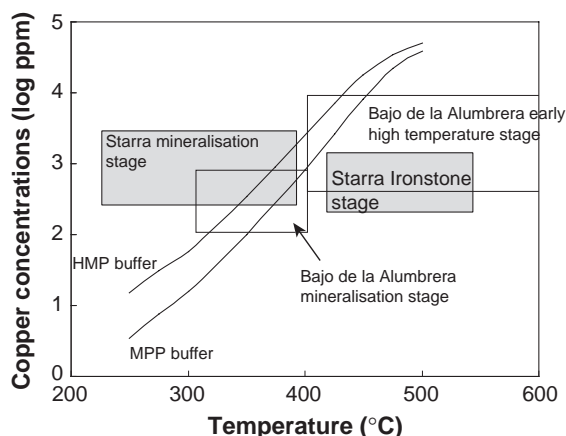


Fig. 7. Comparison between calculated chalcopyrite solubility and measured copper concentration in fluid inclusions from two copper deposits. The solid lines show calculated chalcopyrite solubility in 10 m chloride (9:1 NaCl:KCl) solutions at 1 kbar in equilibrium with hematite–magnetite–pyrite (HMP) and magnetite–pyrite–pyrrhotite (MPP), respectively. Both solutions are buffered with K–feldspar–muscovite–quartz. The two shaded boxes represent approximate ranges of homogenisation temperatures and copper concentrations in fluid inclusions (Williams et al., 2001). The two clear boxes show the range of homogenisation temperature and copper concentration in fluid inclusions from the porphyry copper deposit in Bajo de la Alumbrera, Argentina (Ulrich et al., 2001).

same temperature, indicating that the fluids were undersaturated with respect to chalcopyrite. This is consistent with the observed lack of mineralisation in this stage. For the hematite mineralisation stage, our calculated copper concentrations at 350–400 °C are in good agreement with the PIXE data. At lower temperatures, the calculated values are lower than the measured range (Fig. 7). As most fluid inclusions decrepitated on heating before total homogenisation (Williams et al., 2001), the ore-forming temperature should be higher than the measured homogenisation temperature range of 225–360 °C. Therefore, it is likely that copper mineralisation occurred when temperature dropped below 400 °C, where the fluid reached chalcopyrite saturation.

Ulrich et al. (2001) reported metal concentrations in fluid inclusions from the porphyry deposit of Bajo de la Alumbrera, Argentina where they measured the composition of individual inclusions using LA-ICP-MS techniques. The measured copper concentration remained approximately constant (0.05–1 wt.%, average 0.33 wt.%) in brine inclusions trapped at high

temperature (up to 750 °C) to temperatures of approximately 400 °C, then dramatically dropped to less than 0.07 wt.% at 305 °C (e.g., Fig. 7). Their highest pressure estimate is 1.3 kbar. The calculated chalcopyrite solubility at the mineralisation conditions (300–400 °C) and 1 kbar is in excellent agreement with the measured copper concentrations in the same temperature range, which support the evidence that chalcopyrite precipitation occurred over a narrow temperature range (Ulrich et al., 2001). At higher temperature (>450 °C), similar to Starra, the measured copper concentrations are much lower than our calculated chalcopyrite solubility at the corresponding temperature, indicating the fluids were undersaturated with respect to chalcopyrite until ~450 °C. Although the physico-chemical conditions responsible for metal transport and deposition in magmatic-hydrothermal ore-forming systems are difficult to define accurately, and the extremely high salinity of ore-forming fluids, and hence activity coefficients, make it difficult to predict metal speciation and mineral solubility accurately, these calculations indicate that the extrapolated thermodynamic properties for copper chloride complexes are sufficiently reliable to develop robust numerical models of copper transport and deposition over wide ranges of pressure and temperature.

### 3.2. Factors controlling copper transport and deposition

Based on the apparent success of the above calculation, the following paragraphs will detail the effects of varying salinity, pH, oxidation state, temperature and pressure on copper transport in magmatic-hydrothermal fluids.

Fig. 8 shows chalcopyrite solubility as a function of temperature and pressure in a 1 m NaCl solution in equilibrium with K–feldspar–muscovite–quartz and either hematite–magnetite–pyrite (HMP) or pyrite–pyrrhotite–magnetite (MPP) assemblages. It is clear that temperature is a major factor controlling chalcopyrite deposition, as found by Hezarkhani et al. (1999) and Ulrich et al. (2001). For example, at 1 kbar, a temperature decrease from 500 to 300 °C markedly decreases chalcopyrite solubility from 273 to 1 ppm copper in the HMP-buffered solution and 128 to 0.5 ppm in the MPP-buffered solutions.



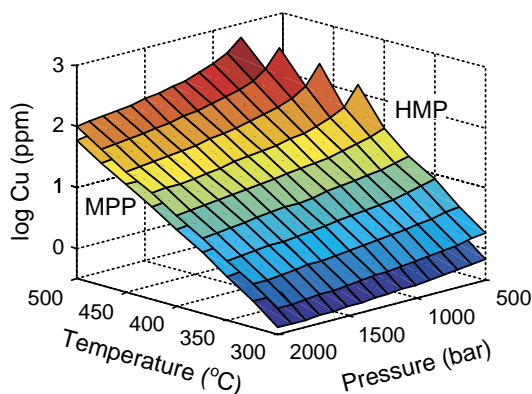
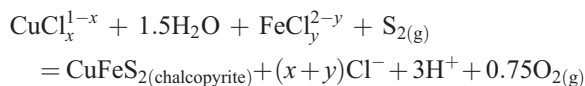


Fig. 8. Calculated chalcopyrite solubility as a function of temperature and pressure in 1 m NaCl solution in equilibrium with K-feldspar–muscovite–quartz, and hematite–magnetite–pyrite (HMP, upper surface) and magnetite–pyrite–pyrrhotite (MPP, lower surface) assemblages.

Change in pressure has an opposite effect, i.e., at a given temperature, decreasing pressure results in higher predicted chalcopyrite solubility. This is mainly due to the P–T dependence of the log  $K$  values of copper complexes shown in Figs. 3 and 4. It is clear from Fig. 8 that temperature has a stronger effect than pressure.

Fig. 9 shows chalcopyrite solubility as a function of pH and total NaCl concentration in solutions equilibrated with hematite–magnetite–pyrite (HMP) and magnetite–pyrite–pyrrhotite (MPP) assemblages at 400 °C and 500 bar. The calculations here were done using the speciation calculation software EQBRM (Anderson and Crerar, 1993). The thermodynamic data sources are the same as in previous sections. At a given temperature and pressure, chalcopyrite solubility decreases with decreasing chloride concentration and  $f_{O_2}$ , and increasing pH and  $f_{S_2}$ , as indicated by the following generalised reaction:



where  $x$  and  $y$  denote number of chloride ions in the copper and iron chloride complexes, respectively. For example, at pH=4, total dissolved copper concentration decreases from 16,843 ppm in 10 m NaCl solution to 70 ppm in 1 m NaCl solution, i.e., more than 99% of copper precipitated as chalcopyrite as

chloride concentration decreases from 10 m to 1 m. A decrease of chloride concentration in mineralising fluids can occur as a result of well-known fluid mixing of hypersaline magmatic fluids with meteoric and/or less-saline connate water. Numerous stable isotope studies (e.g., Sheppard et al., 1971; Taylor, 1979, 1997) indicate the evolution of mineralising fluids in porphyry copper systems from magmatic to non-magmatic brines. Acidity of the solutions also has significant effect on deposition of copper. In a 10 m NaCl solution at 400 °C, increasing pH from 4 to 6 would cause a decrease in dissolved copper concentration from 16,843 ppm to approximately 600 ppm.

The influence of the oxidation potential on solubility of chalcopyrite can be seen from the difference of chalcopyrite solubility between HMP-buffered solution and MPP-buffered solutions (Figs. 7–9). At a given temperature and chloride concentration, for example, decreasing log  $f_{O_2}$  from HPM buffer (–24.28 at 400 °C) to MPP buffer (–26.90 at 400 °C) is predicted to decrease chalcopyrite solubility by less than 1 log unit. Its effect is likely to have less marked than changes in chloride concentration, acidity and temperature, although the presence of reduced sulphur plays a vital role in the solubility of sulfide minerals.

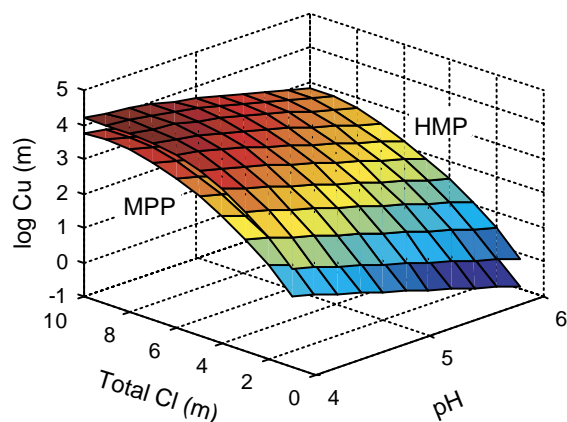


Fig. 9. Calculated chalcopyrite solubility in NaCl solutions at 400 °C and 0.5 kbar as a function of NaCl concentration and pH. The upper surface shows the copper concentration in solutions in equilibrium with hematite–pyrite–magnetite (HMP) and the lower surface shows the copper concentration in equilibrium with magnetite–pyrite–pyrrhotite (MPP).

Cooling, fluid mixing, boiling and fluid–rock interaction can all play important roles in the deposition of chalcopyrite from hydrothermal fluids. Previous modelling studies (e.g., Hemley and Hunt, 1992; Woitsekhowskaya and Hemley, 1995; Hezarkhani et al., 1999) have reached the same conclusion but the results of our recent experimental studies allow us to quantify more accurately the effects, especially those resulting from dilution of fluids. The calculations in this study show that in addition to cooling, dilution of saline mineralizing fluids can effectively cause the deposition of copper from the fluids. Detailed evaluation of each controlling factor requires more detailed geological and geochemical information related to the temporal and spatial relationships of alteration–mineralisation in specific deposits.

It is clear that chalcopyrite deposition in both the Starra and Bajo de la Alumbrera deposits occurs between 300–400 °C (Fig. 7). Fluid inclusion data of many porphyry copper deposits, such as in the South-western US (Beane and Titley, 1981) and the Sungan Porphyry copper deposit in Iran (Hezarkhani and Williams-Jones, 1998; Hezarkhani et al., 1999), also indicate that chalcopyrite mineralisation occurred within this temperature range. Our calculations show that most copper will effectively precipitate as chalcopyrite in this temperature range. These results all indicate that cooling is probably the major factor causing deposition of copper from these magmatic-hydrothermal fluids, especially for the Bajo de la Alumbrera and Starra deposits where no significant change of fluid salinity has been reported (Ulrich et al., 2001).

The calculations in this study show that at 400 °C and 0.5 kbar, in a 10 m chloride (9 m NaCl and 1 m KCl) solution in equilibrium with K–felspar–muscovite–quartz and hematite–magnetite–pyrite, about 4000 ppm copper can be dissolved in the solution. If this amount of copper precipitated as chalcopyrite to form a porphyry deposit containing 1 million tonnes of copper, a quantity of  $2.5 \times 10^8$  tonnes of brine is needed. Recent experimental studies showed that copper solubility in felsic melt is approximately 10–60 ppm (10–60 ppm at 800 °C and 1 kb, Williams et al., 1995; 22–30 ppm at 800 °C and 10 kbar, Jugo et al., 1999). Assuming that all the copper was from a magma containing 30 ppm of copper, 80% of which partitioned into the aqueous phase during the solidification of magma (Candela and Holland, 1986), one million tonnes of copper

could come from approximately  $4 \times 10^{10}$  tons of magma, or 14 km<sup>3</sup> in volume, assuming that average density of the magma is 3 g/cm<sup>3</sup> (Gammons and Williams-Jones, 1997). Thus we get approximately a brine/magma weight percentage of 0.6%. Petrological studies indicate that the initial water contents of the magmas with which extensive hydrothermal activity is associated generally range from 2.5 to 6.5 wt.% (Burnham, 1979), more than needed to generate the required brines. The high chloride concentration needed to form copper chloride complexes in magmatic brine comes from the strong partitioning of chlorine from magma to the aqueous phase (e.g., Burnham, 1979; Shinohara et al., 1989; Cline and Bodnar, 1991; Shinohara, 1994; Webster, 1997).

Although the above calculations were limited to the brine phase, the role of vapour phase in copper transport may also be important. In addition to its effect on acidity and sulfur content in the brines, the vapour itself may transport large amounts of copper, as recently indicated by high copper concentration in the vapour phase of fluid inclusions from the two porphyry copper deposits: Grasberg, Indonesia (Ulrich et al., 1999) and Bajo de la Alumbrera, Argentina (up to 4.5 wt.%, Harris et al., 2003). These values are similar to our estimates of copper concentration in brine, raising interesting questions about the interpretation and importance of liquid–vapour partitioning of copper. The first experimental study of copper transport in vapour phase (Archibald et al., 2002) has shown that 278 ppm copper could be transported as hydrated copper chloride complexes at 300 °C and water vapour pressure. This value is much lower than copper content observed in the vapour-rich inclusions of the above two deposits. More experimental work at temperatures higher than 300 °C is needed to understand quantitatively copper transport in vapours typical of porphyry systems.

#### 4. Conclusions

New equation-of-state parameters and the partial molal properties for copper(I) chloride complexes were successfully regressed from the experimental log *K* data collected between 25 and 350 °C. These new parameters and properties were used to calculate formation constants for copper(I) chloride complexes over wide ranges of temperature and pressure, which

in turn were tested by comparing calculated and measured chalcopyrite solubility. The good agreement between the predicted chalcopyrite solubility using extrapolated log  $K$  values and the measured values of Hemley et al. (1992) and Seyfried and Ding (1993) suggests that the extrapolated properties are reasonably good. More high T–P experimental studies at high chloride concentrations are, however, needed to improve the accuracy of the extrapolation, especially for  $\text{CuCl}_4^{3-}$ , a complex that is likely to be important in hypersaline brines. The formation constant of this complex could not be tested because it is likely to be important only at chloride concentration greater than 2 m, the limit of present experimental data for copper behaviour at high temperature and pressure.

Calculated chalcopyrite solubilities under similar conditions of two magmatic-hydrothermal copper deposits show that calculations using the newly derived properties are consistent with the measured copper concentrations in fluid inclusions from the Starra deposit, Australia and Bajo de la Alumbrera deposit, Argentina. For hydrothermal conditions typical of magmatic-hydrothermal copper deposits, calculated chalcopyrite solubility at different temperature, pressure, pH, chloride concentrations and oxidation potential indicates that hypersaline, neutral-weak acidic, and intermediate-reduced solution can transport thousands of ppm of copper at and above 400 °C. 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.

It is notable that solubility calculations rely heavily on the accuracy of the activity coefficient model used for high salinity and high temperature solutions. This is particularly the case for the triply charged complex  $\text{CuCl}_4^{3-}$ , the predominant copper chloride species in high salinity solutions. However, this study reveals that the stability of the  $\text{CuCl}_4^{3-}$  complex is vital to the understanding of copper transport and deposition in the hypersaline hydrothermal solutions ( $\text{NaCl} > 5$  m) typical of porphyry copper deposits. In addition, more research is necessary to understand the speciation and properties of iron chloride complexes at temperatures greater than 300 °C and pressure greater than vapour-saturated.

## Acknowledgments

Part of this paper is based on the WL's doctoral thesis, who thanks Monash University for providing his PhD scholarship. DCM acknowledges the support of an Australian Research Council Large Grant for this work. Comments from Brent McInnes on an early version of the manuscript helped to improve it. The authors also thank Dr. David Rickard and two anonymous Chemical Geology reviewers for their helpful reviews. [DR]

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2005.04.009](https://doi.org/10.1016/j.chemgeo.2005.04.009).

## References

- Akinfiev, N.N., Zotov, A.V., 2001. Thermodynamic description of chloride, hydrosulfide, and hydroxo complexes of Ag(I), Cu(I), and Au(I) at temperatures of 25–500 °C and pressures of 1–2000 bar. *Geochem. Int.* 39, 990–1006.
- Anderson, G.M., Crerar, D.A., 1993. *Thermodynamics in Geochemistry. The Equilibrium Model*. Oxford University Press.
- Anderson, G.M., Castet, S., Schott, J., Mesmer, R.E., 1991. The density model for estimation of thermodynamic parameters of reactions at high temperatures and pressures. *Geochim. Cosmochim. Acta* 55, 1769–1779.
- Archibald, S.M., Migdisov, A.A., Williams-Jones, A.E., 2002. An experimental study of the stability of copper chloride complexes in water vapor at elevated temperatures and pressures. *Geochim. Cosmochim. Acta* 66, 1611–1619.
- Barnes, H.L., 1979. Solubility of ore minerals. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*. John Wiley & Sons, pp. 404–460.
- Bastrakov, E.N., 2000. Gold metallogenesis at the Lake Cowal prospect NSW, PhD. The Australian National University.
- Beane, R.E., Titley, S.R., 1981. Porphyry copper deposits: Part II. Hydrothermal alteration and mineralization. *Econ. Geol.* 75, 214–269 (Anniversary Volume).
- Berman, R.G., 1988. Internally-consistent thermodynamic data for minerals in the system  $\text{Na}_2\text{O}$ – $\text{K}_2\text{O}$ – $\text{CaO}$ – $\text{MgO}$ – $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ – $\text{TiO}_2$ – $\text{H}_2\text{O}$ – $\text{CO}_2$ . *J. Petrol.* 29, 445–522.
- Borse, G.J., 1997. *Numerical Methods with MATLAB*. PWS Publishing Company.
- Brady, P.V., Walther, J.V., 1990. Algorithms for predicting ion association in supercritical  $\text{H}_2\text{O}$  fluids. *Geochim. Cosmochim. Acta* 54, 1555–1561.

- Burnham, C.W., 1979. Magmas and hydrothermal fluids. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*, pp. 71–136.
- Candela, P.A., Holland, H.D., 1984. The partitioning of copper and molybdenum between silicate melts and aqueous fluids. *Geochim. Cosmochim. Acta* 48, 373–380.
- Candela, P.A., Holland, H.D., 1986. A mass transfer model for copper and molybdenum in magmatic hydrothermal systems; the origin of porphyry-type ore deposits. *Econ. Geol.* 81, 1–19.
- Candela, P.A., Whitney, J.A.e., Naldrett, A.J.e., 1989. Magmatic ore-forming fluids; thermodynamic and mass transfer calculations of metal concentrations. *Rev. Econ. Geol.* 4, 203–221.
- Ciavatta, L., Iuliano, M., 1998. Copper(I) chloride complexes in aqueous solution. *Ann. Chim.* 88, 71–89.
- Cline, J.S., Bodnar, R.J., 1991. Can economic porphyry copper mineralization be generated by a typical calc-alkaline melt? *J. Geophys. Res. B, Solid Earth Planets* 96, 8113–8126.
- Crerar, D.A., Barnes, H.L., 1976. Ore solution chemistry V. Solubilities of chalcopryrite and chalcocite assemblages in hydrothermal solution at 200 to 300 °C. *Econ. Geol.* 71, 772–794.
- Fritz, J.J., 1980. Chloride complexes of CuCl in aqueous solution. *J. Phys. Chem.* 84, 2241–2246.
- Fulton, J.L., Hoffmann, M., Darab, J.G., 2000a. An X-ray absorption fine structure study of copper(I) chloride coordination structure in water up to 325 °C. *Chem. Phys. Lett.* 330, 300–308.
- Fulton, J.L., Hoffmann, M.M., Darab, J.G., Palmer, B.J., 2000b. Copper(I) and Copper(II) coordination structure under hydrothermal conditions at 325 °C: an X-ray absorption fine structure and molecular dynamics study. *J. Phys. Chem., A* 104, 11651–11663.
- Gammons, C.H., Williams-Jones, A.E., 1997. Chemical mobility of gold in the porphyry-epithermal environment. *Econ. Geol.* 92, 45–59.
- Gu, Y., Gammons, C.H., Bloom, M.S., 1994. One-term extrapolation method for estimating equilibrium constants of aqueous reactions at elevated temperatures. *Geochim. Cosmochim. Acta* 58, 3545–3560.
- Harris, A.C., Kamenetsky, V.S., White, N.C., van Achterbergh, E., Ryan, C.G., 2003. Melt inclusions in veins: linking magmas and porphyry Cu deposits. *Science* 302, 2109–2111.
- Haynes, D.W., 1986. Stratiform copper deposits hosted by low-energy sediments; II, nature of source rocks and composition of metal-transporting water. *Econ. Geol.* 81, 266–280.
- He, W., Bao, Z., Li, T., 1999. One-dimensional reactive transport models of alteration in the Tongchang porphyry copper deposit, Dexing district, Jiangxi Province, China. *Econ. Geol.* 94, 307–324.
- Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magmas in the formation of hydrothermal ore deposits. *Nature (Lond.)* 370, 519–527.
- Heinrich, C.A., Walshe, J.L., Harrold, B.P., 1996. Chemical mass transfer modelling of ore-forming hydrothermal systems; current practise and problems. *Ore Geol. Rev.* 10, 319–338.
- Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* 267, 729–804.
- Helgeson, H.C., Kirkham, D.H., 1974. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures; II, Debye–Huckel parameters for activity coefficients and relative partial molal properties. *Am. J. Sci.* 274, 1199–1261.
- Helgeson, H.C., Delany, J.M., Nesbitt, H.W., Bird, D.K., 1978. Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci.* 278A, 229.
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600 °C and 5 kb. *Am. J. Sci.* 281, 1249–1516.
- Hemley, J.J., Hunt, J.P., 1992. Hydrothermal ore-forming processes in the light of studies in rock-buffered systems. II, some general geologic applications. *Econ. Geol.* 87, 23–43.
- 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.
- Hezarkhani, A., Williams-Jones, A.E., 1998. Controls of alteration and mineralization in the Sungun porphyry copper deposit, Iran; evidence from fluid inclusions and stable isotopes. *Econ. Geol.* 93, 651–670.
- Hezarkhani, A., Williams-Jones, A.E., Gammons, C.H., 1999. Factors controlling copper solubility and chalcopryrite deposition in the Sungun porphyry copper deposit, Iran. *Miner. Depos.* 34, 770–783.
- Holzheid, A., Lodders, K., 2001. Solubility of copper in silicate melts as function of oxygen and sulfur fugacities, temperature, and silicate composition. *Geochim. Cosmochim. Acta* 65, 1933–1951.
- Jugo, P.J., Candela, P.A., Piccoli, P.M., 1999. Magmatic sulfides and Au:Cu ratios in porphyry deposits: an experimental study of copper and gold partitioning at 850 °C, 100 MPa in a haplogranitic melt pyrrhotite intermediate solid solution gold metal assemblage, at gas saturation. *Lithos* 46, 573–589.
- Liu, W., McPhail, D.C., Brugger, J., 2001. An experimental study of copper(I)–chloride and copper(I)–acetate complexing in hydrothermal solutions between 50 °C and 250 °C and vapor-saturated pressure. *Geochim. Cosmochim. Acta* 65, 2937–2948.
- Liu, W., Brugger, J., McPhail, D.C., Spiccia, L., 2002. A spectrophotometric study of aqueous copper(I)–chloride complexes in LiCl solutions between 100 °C and 250 °C. *Geochim. Cosmochim. Acta* 66, 3615–3633.
- Lowell, J.D., 1973. Porphyry copper deposits of the Southwest. *Econ. Geol.* 68, 139.
- Lowell, J.D., Guilbert, J.M., 1970. Lateral and vertical alteration–mineralization zoning in porphyry ore deposits. *Econ. Geol.* 65, 373–408.
- Marshall, W.L., Franck, E.U., 1981. Ion product of water substance, 0–1000 °C, 1–10,000 bars, new international formulation and its background. *J. Phys. Chem. Ref. Data* 10, 295–304.
- Mesmer, R.E., Marshall, W.L., Palmer, D.A., Simonson, J.M., Holmes, H.F., 1988. Thermodynamics of aqueous association and ionization reactions at high temperatures and pressures. *J. Solution Chem.* 17, 699–718.



- Nelder, J.A., Mead, R., 1965. A simplex method for function minimization. *Comput. J.* 7, 308–313.
- Oelkers, E.H., 1996. In: Lichtner Jr., P.C., Steefel, C.I., Oelkers, E.H. (Eds.), *Physical and Chemical Properties of Rocks and Fluids for Chemical Mass Transport Calculations*, Reactive Transport in Porous Media, vol. 34, pp. 131–191.
- Oelkers, E.H., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures. Dissociation constants for supercritical alkali metal halides at temperatures from 400 to 800 °C and pressures from 500 to 4000 bars. *J. Phys. Chem.* 92, 1631–1639.
- Oelkers, E.H., Helgeson, H.C., 1990. Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions. *Geochim. Cosmochim. Acta* 54, 727–738.
- Plyasunov, A.V., O'Connell, J.P., Wood, R.H., 2000a. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes; I, equations for partial molar volumes at infinite dilution and standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions. *Geochim. Cosmochim. Acta* 64, 495–512.
- Plyasunov, A.V., O'Connell, J.P., Wood, R.H., Shock, E.L., 2000b. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes; II, equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures. *Geochim. Cosmochim. Acta* 64, 2779–2795.
- Pokrovskii, V.A., 1999. Calculation of the standard partial molal thermodynamic properties and dissociation constants of aqueous  $\text{HCl}^\circ$  and  $\text{HBr}^\circ$  at temperatures to 1000 °C and pressures to 5 kbar. *Geochim. Cosmochim. Acta* 63, 1107–1115.
- Robie, R.A., Hemingway, B.S., 1995. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar ( $10^5$  Pascal) Pressure and at Higher Temperatures*. U.S. Geological Survey, pp. 461.
- Roedder, E., 1984. *Fluid Inclusions*. Mineral Society of America.
- Rotherham, J.F., Blake, K.L., Cartwright, I., Williams, P.J., 1998. Stable isotope evidence for the origin of the Mesoproterozoic Starra Au-Cu deposit, Cloncurry District, Northwest Queensland. *Econ. Geol.* 93, 1435–1449.
- Ruaya, J.R., 1988. Estimation of instability constants of metal chloride complexes in hydrothermal solutions up to 300 °C. *Geochim. Cosmochim. Acta* 52, 1983–1996.
- Schott, J., Walther, J.V., Dandurand, J.L., 1988. Solute thermodynamic properties at high-temperature and pressure modeled on solvent dielectric-properties. *Chem. Geol.* 70, 164.
- Sedlbauer, J., O'Connell, J.P., Wood, R.H., 2000. A new equation of state for correlation and prediction of standard molal thermodynamic properties of aqueous species at high temperatures and pressures. *Chem. Geol.* 163, 43–63.
- 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. *Geochim. Cosmochim. Acta* 57, 1905–1917.
- Seyfried, W.E., Ding, K., 1995. In: Humphris, R.A.Z.S.E., Mullineaux, L.S., Thomson, R.E. (Eds.), *Phase Equilibria in Subseafloor Hydrothermal Systems: a Review of the Role of Redox, Temperature, pH and Dissolved Cl on the Chemistry of Hot Spring Fluids at Mid-Ocean Ridges*, Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions, vol. 91. American Geophysical Union, pp. 248–272.
- Sheppard, S.M.F., Nielsen, R.L., Taylor Jr., H.P., 1971. Hydrogen and oxygen isotope ratios in minerals from porphyry copper deposits. *Economic Geol.* 66, 515–542.
- Shinohara, H., 1994. Exsolution of immiscible vapor and liquid phases from a crystallizing silicate melt; implications for chlorine and metal transport. *Geochim. Cosmochim. Acta* 58, 5215–5221.
- Shinohara, H., Iiyama, J.T., Matsuo, S., 1989. Partition of chlorine compounds between silicate melt and hydrothermal solutions; I, partition of NaCl–KCl. *Geochim. Cosmochim. Acta* 53, 2617–2630.
- Shock, E.L., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures; correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 °C. *Geochim. Cosmochim. Acta* 52, 2009–2036.
- Shock, E.L., Helgeson, H.C., 1990. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures; standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* 54, 915–945.
- Shock, E.L., Helgeson, H.C., Sverjensky, D., 1989. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures; standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* 53, 2157–2183.
- Shock, E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A., Helgeson, H.C., 1992. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: effective electrostatic radii to 1000 °C and 5 kb. *J. Chem. Soc. London. Faraday Trans.* 88, 803–826.
- Shvarov, Y.V., Bastrakov, E.N., 1999. HCh, a software Package for Geochemical Equilibrium Modeling: User's Guide. Record 1999/25. Australian Geological Survey Organisation.
- Sillitoe, R.H., 1972. A plate tectonic model for the origin of porphyry copper deposits. *Econ. Geol.* 67, 184–197.
- Sillitoe, R.H., 1973. The tops and bottoms of porphyry copper deposits. *Econ. Geol.* 68, 799–815.
- Steefel, C.I., Lasaga, A.C., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *Am. J. Sci.* 294, 529–592.
- Sverjensky, D.A., 1987. The role of migrating oil field brines in the formation of sediment-hosted Cu-rich deposits. *Econ. Geol.* 82, 1130–1141.
- Sverjensky, D.A., Hemley, J.J., D'Angelo, W.M., 1991. Thermodynamic assessment of hydrothermal alkali feldspar–mica–aluminosilicate equilibria. *Geochim. Cosmochim. Acta* 55, 989–1004.
- Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000 °C and 5 kb. *Geochim. Cosmochim. Acta* 61, 1359–1421.



- Tagirov, B.R., Zotov, A.V., Akinfiev, N.N., 1997. Experimental study of dissociation of HCl from 350 to 500 °C and 500 to 2500 bars; thermodynamic properties of  $\text{HCl}^\circ_{(\text{aq})}$ . *Geochim. Cosmochim. Acta* 61, 4267–4280.
- Tanger, J.C., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.* 288, 19–98.
- Taylor Jr., H.P., 1979. Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*, pp. 236–277.
- Taylor Jr., H.P., 1997. Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*, pp. 229–302.
- Titley, S.R., 1997. 1997 Jackling lecture; porphyry copper geology; a late century view. *Min. Eng.* 49, 57–63.
- Titley, S.R., Beane, R.E., 1981. Porphyry copper deposits: Part I. Geology settings, petrology, and tectogenesis. *Econ. Geol.*, 214–269 (75th Anniversary Volume).
- Ulrich, T., Guenther, D., Heinrich, C.A., 1999. Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. *Nature (Lond.)* 399, 676–679.
- Ulrich, T., Guenther, D., Heinrich, C.A., 2001. The evolution of a porphyry Cu–Au deposit, based on LA-ICP-MS analysis of fluid inclusions; Bajo de la Alumbrera, Argentina. *Econ. Geol.* 96, 1743–1774.
- Var'yash, L.N., 1992. Cu(I) complexing in NaCl solutions at 300 and 35 °C. *Geochem. Int.* 29, 84–92.
- Var'yash, L.N., Rekharskiy, V.I., 1982. Behavior of Cu(I) in chloride solutions. *Geochem. Int.* 18, 61–67.
- Webster, J.D., 1997. Exsolution of magmatic volatile phases from Cl-enriched mineralizing granitic magmas and implications for ore metal transport. *Geochim. Cosmochim. Acta* 61, 1017–1029.
- Williams, T.J., Candela, P.A., Piccoli, P.M., 1995. The partitioning of copper between silicate melts and two-phase aqueous fluids; an experimental investigation at 1 kbar, 800 °C and 0.5 kbar, 850 °C. *Contrib. Mineral. Petrol.* 121, 388–399.
- Williams, P.J., Dong, G., Ryan, C.G., Pollard, P.J., Rotherham, J.F., Memagh, T.P., et al., 2001. Geochemistry of hypersaline fluid inclusions from the Starra (Fe oxide)–Au–Cu deposit, Cloncurry District, Queensland. *Econ. Geol.* 96, 875–883.
- Woitsekhovskaya, M.B., Hemley, J.J., 1995. Modeling metal transport and deposition in butte-type hydrothermal systems. *Econ. Geol.* 90, 1329–1337.
- Xiao, Z., Gammons, C.H., Williams-Jones, A.E., 1998. Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300 °C and saturated water vapor pressure. *Geochim. Cosmochim. Acta* 62, 2949–2964.
- Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., Brimhall, G., Apps, J., 2001. Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 2. Applications to supergene copper enrichment and hydrothermal flows. *Am. J. Sci.* 301, 34–59.