Pergamon

PII S0016-7037(01)00867-5

An experimental study of the stability of copper chloride complexes in water vapor at elevated temperatures and pressures

S. M. ARCHIBALD,* A. A. MIGDISOV, and A. E. WILLIAMS-JONES

Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Quebec, H3A 2A7, Canada

Abstract—The solubility of copper chloride in liquid-undersaturated HCl-bearing water vapor was investigated experimentally at temperatures of 280 to 320°C and pressures up to 103 bars. Results of these experiments show that the solubility of copper in the vapor phase is significant and increases with increasing f_{H_2O}, but is retrograde with respect to temperature. This solubility is attributed to the formation of hydrated copper-chloride gas species, interpreted to have a copper-chlorine ratio of 1:1 (e.g., $CuCl$, Cu_3Cl_3, etc.) and a hydration number varying from 7.6 at 320°C, to 6.0 at 300°C, and 6.1 at 280°C. Complex formation is proposed to have occurred through the reaction:

$$3 \; CuCl^{solid} + nH_2O^{gas} \rightleftharpoons Cu_3Cl_3 \cdot (H_2O)_n^{gas} \tag{A1}$$

Log K values determined for this reaction are -21.46 ± 0.05 at 280°C (n = 7.6), -19.03 ± 0.10 at 300°C (n = 6.0), and -19.45 ± 0.12 at 320°C (n = 6.1), if it is assumed that the vapor species is the trimer, $Cu_3Cl_3(H_2O)_{6-8}$. Calculations based on the above data indicate that at 300°C and HCl fluxes encountered in passively degassing volcanic systems, the vapor phase could transport copper in concentrations as high as 280 ppm. Theoretically, this vapor could form an economic copper deposit (e.g., 50 million tonnes of 0.5% Cu) in as little as ~20,500 yr. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The process of boiling, which separates a homogeneous aqueous fluid into vapor and liquid components, is a common feature of several types of ore forming hydrothermal systems, e.g., those forming porphyry copper deposits, high- and low-sulfidation Au-Ag deposits, and Sn-W veins (Henley and Mc-Nabb, 1978; Eastoe, 1982; Hedenquist and Lowenstern, 1994). Most studies that have investigated boiling in such systems have focused on the role it plays in the precipitation of ore and gangue minerals (Drummond and Ohmoto, 1985; Spycher and Reed, 1989), but few have considered the possibility that metals could be transported in the vapor phase (Henley and Mc-Nabb, 1978; Hedenquist and Lowenstern, 1994; Heinrich et al., 1992; Migdisov et al., 1999; Archibald et al., 2001).

In natural systems, the most convincing evidence that the vapor phase could play an important role in metal transport has come from active volcanoes where metals, including copper, have been detected in significant concentrations in gas condensates and fumarolic encrustations. In the case of copper, the concentrations measured in gas condensates range from 0.1 to 1.0 ppm at Cerro Negro, San Cristobal (both Nicaragua), Colima (Mexico) and Merapi (Indonesia), and from 0.2 to 8.4 ppm at Momotombo, Nicaragua (Gemmell, 1987; Symonds et al., 1987; Taran, 2000). The highest concentrations reported are those where the magma is basaltic to intermediate in composition. The occurrence of copper minerals such as paratacamite ($Cu_2(OH_3)Cl$), chalcocyanite ($CuSO_4$), chalcanthite ($CuSO_4 \cdot 5(H_2O)$), nantokite ($CuCl_2$), eriochalcite ($CuCl_2 \cdot 2H_2O$), chalcocite (Cu_2S) and covellite (CuS) in sublimates around fuma-

roles of Central American and Italian volcanoes (Stoiber and Rose, 1974) is further evidence for the vapor transport of copper.

In ore-forming environments, direct evidence for vapor transport of copper is based on analyses of fluid inclusions. Lowenstern et al., (1991) using a X-ray microprobe, determined that copper was several hundred times more concentrated in magmatic vapor than a coexisting pantellerite (peralkaline) melt. A proton-induced X-ray emission fluid inclusion study of a tin deposit in the Mole Granite (NSW, Australia) showed copper concentrations to be two orders of magnitude higher in vapor-rich than in co-existing brine-rich inclusions (Heinrich et al., 1992). Finally, recent LAM-ICPMS analyses by Ulrich et al. (1999) and Heinrich et al. (1999) have yielded copper concentrations as high as 3.3 wt.% in vapor-rich fluid inclusions from Bajo de la Alumbrera, a gold-rich porphyry Cu deposit in Argentina; significantly, co-existing brine inclusions contain <0.76 wt.% Cu.

Thermodynamic calculations using metal volatility data and fluid compositions can be used to estimate the solubility of metals in hydrothermal vapors (e.g., Symonds et al., 1987; Spycher and Reed, 1989; Symonds and Reed, 1993; Getahun et al., 1996; Taran et al., 2000). However, such estimates do not take into account interaction between the metal and the gas (solvent), which in the case of active volcanoes is largely water (Symonds et al., 1994). In one of the few studies to investigate the role of hydration in the solubility of an economic metal in vapor, Migdisov et al. (1999) showed that the presence of water vapor increases the concentration of AgCl in vapor by 1.5 to 2 orders of magnitude, and that silver dissolves as the species $AgCl(H_2O)_3$. Archibald et al. (2001) noted that water has a dramatic effect on the solubility of gold in the vapor, enhancing

---

* Author to whom correspondence should be addressed (sandy@eps.mcgill.ca).

Table 1. Fugacities and mole fractions of gas species at 280°C. The values of log fCu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$ were subjected to a "Poynting correction" that was typically about 0.25, 0.29 and 0.34 bars at temperatures of 280, 300 and 320°C, respectively.

Temp. (°C)	H$_2$O (ml)	log f H$_2$O (/bar)	log X Cu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$	log fCu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$ (/bar)
280	2.03	1.64	−7.78	−5.92
280	2.22	1.67	−7.77	−5.87
280	2.41	1.69	−7.54	−5.61
280	2.49	1.70	−7.48	−5.53
280	2.58	1.71	−7.49	−5.52
280	3.67	1.72	−7.31	−5.33
300	2.13	1.69	−7.94	−6.02
300	2.31	1.71	−7.49	−5.53
300	2.70	1.75	−7.71	−5.68
300	3.10	1.79	−7.48	−5.39
300	3.26	1.80	−7.20	−5.09
300	3.40	1.81	−7.51	−5.39
300	3.46	1.81	−7.10	−4.97
320	3.16	1.79	−7.51	−5.35
320	2.96	1.81	−7.61	−5.42
320	3.13	1.82	−7.64	−5.42
320	3.33	1.84	−7.17	−4.92
320	3.52	1.85	−7.41	−5.12
320	3.72	1.86	−7.30	−5.00
320	3.88	1.87	−7.11	−4.78
320	4.07	1.89	−7.18	−4.83
320	4.26	1.89	−7.22	−4.85
320	4.55	1.90	−7.15	−4.75

it by at least 15 orders of magnitude at 300°C through the formation of hydrated chloride species.

Considering that copper is transported principally as a chloride complex in high temperature aqueous liquids (Crerar et al., 1985; Var'yash, 1992; Xiao et al., 1998; Liu et al., 2001; Brugger et al., 2001), and that HCl is an important component of volcanic gases (Symonds et al., 1994), it seems likely that copper will partition into the vapor phase as a gaseous copper chloride complex. Several experimental studies have investigated the vapor transport of copper as chloride complexes (e.g., Martynova, 1964; Tskhvirashvili et al., 1970; Krabbes and Oppermann, 1977; Williams et al., 1995; Vercher et al. 1995; Xiao, 1999). However, only the studies of Williams et al. (1995) and Xiao (1999) involved water vapor, and only that of Xiao (1999) was for temperatures typically encountered in ore forming hydrothermal systems. This study complements the liquid-vapor experiments of Xiao (1999) by investigating copper solubility in the vapor-only field.

2. EXPERIMENTAL METHODS

The experimental method used was similar to that employed by Migdisov et al. (1999), and involved interacting a H$_2$O ± HCl vapor with CuCl (solid). Experiments were conducted at temperatures between 280 and 320°C and pressures low enough for the aqueous vapor to be undersaturated with respect to liquid (Tables 1 and 2). Experiments were conducted in a Fisher Isotemp® forced-draft oven (Model 838F). To reduce thermal gradients, the oven was modified by adding an aluminum box with 1.5-cm thick walls to hold the autoclaves. As a result of this modification, gradients were less than 0.5°C per meter. A chrome-alumel thermocouple placed inside the aluminum box was used to obtain accurate readings of internal temperatures.

Experiments were performed in autoclaves constructed from grade II titanium alloy (ASTM B348) (Fig. 1). The internal surfaces of each autoclave were preconditioned with nitric acid to produce a protective layer of TiO$_2$. The volumes of the autoclaves (~100 cm^3) were determined by filling them with 25°C distilled water from a Teflon® beaker and weighing this beaker before and after filling. The weighing was performed to an accuracy of ±0.1 g.

Before each run, dry nitrogen gas was passed through the autoclaves for 10 to 20 min to remove any atmospheric gases. During experiments,

Table 2. Fugacities and mole fractions of gas species at 320°C and a constant f_{H_2O} of 80.0 bars. The values of log fCu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$ were subjected to a "Poynting correction" that was typically about 0.38 bars.

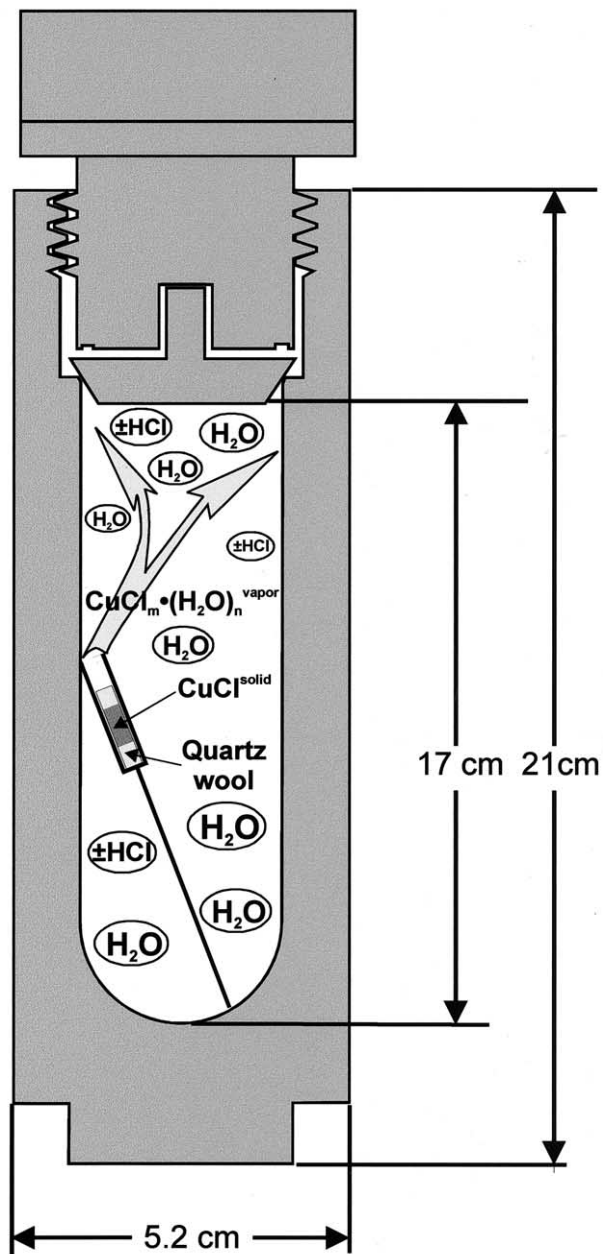| Temp. (°C)	H$_2$O (ml)	pH	log fHCl (/bar)	log X Cu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$	log fCu$_{3-4}$Cl$_{3-4} \cdot$ (H$_2$O)$_n$ (/bar)
320	5.17	3.73	−3.30	−7.25	−6.87
320	4.53	3.61	−3.18	−7.29	−6.91
320	4.47	3.29	−2.86	−7.26	−6.88
320	4.67	3.00	−2.57	−7.15	−6.77
320	4.51	2.66	−2.23	−7.37	−6.99
320	4.52	2.35	−1.92	−7.26	−6.88
320	4.45	2.26	−1.83	−7.28	−6.90
320	4.54	1.97	−1.54	−7.26	−6.88
320	4.56	1.84	−1.41	−7.28	−6.90
320	4.48	1.67	−1.24	−7.33	−6.96

Fig. 1. Section through a titanium autoclave of the type used in this study. The autoclaves were constructed from titanium alloy (grade 2 ASTM B348). The ampoule contains the solid CuCl reagent packed between two layers of quartz wool.

autoclaves were loaded with an open quartz-glass ampoule which contained copper (I) chloride powder (Alfa Aesar, 99% purity) in a narrow quartz-glass tube, packed with porous quartz-glass wool at either end. Cu(I)Cl was chosen as a reagent, as copper is dominantly univalent in ore-forming solutions (Wood and Samson, 1998), and the nitrogen purge would remove potential oxidants. A known volume of nanopure water was placed in the bottom of the autoclave using a pipette to prevent contact of the solution with the solid CuCl. The volume of water placed in the autoclave corresponded to an amount that would ensure that the system was liquid-undersaturated at the experimental conditions, and that copper dissolution was entirely in the dry vapor phase. It was assumed that copper chloride would have a much lower vapor pressure than water. Therefore, the total pressure in

a run was assumed to be equal to that of pure water vapor. This pressure was calculated by using the autoclave volume and the equation of state for water of Kestin et al. (1984).

In experiments conducted to investigate the effect of P_{HCl} on the solubility of CuCl in vapor HCl was added to the nanopure water in quantities that yielded solutions with pH values from 1.7 to 3.7, and ensured the vapor was liquid-undersaturated. The P_{HCl} of the vapor was calculated from the pH of the solution at 25°C and an assumption that 1 mol of $[H]^+$ would produce one mole of HCl in the gaseous phase at the temperature of investigation (Ruaya and Seward, 1987; Tagirov et al., 1997).

After each run, the autoclave was quenched rapidly by placing it in a cold-water bath, and passing over a stream of compressed air over it, until room temperature was attained. The quartz-glass capsules containing the copper chloride charge were then removed from the vessel and 1 mL of nitric acid (Fisher Scientific Optima®-grade HNO_3) plus 1 to 3 mL of nanopure water were added to dissolve any copper on the wall of the autoclave. The quartz-glass holders were not washed (see below), but the titanium covers were washed several times to remove any condensate. Concentrations of copper dissolved in condensates and washing solutions were determined by instrumental neutron activation analysis (INAA) with a detection limit of 0.2 ppm.

The final step of the experimental procedure was to analyse the spent copper chloride charges using X-ray diffraction. These analyses showed that the charges consisted of nantokite (CuCl) and traces of atacamite ($Cu_2Cl(OH)_3$). The atacamite is interpreted to have formed during quenching and/or exposure to atmospheric moisture before analysis.

Two potential, but important, sources of experimental error are condensation on the colder parts of the autoclave during runs, and partitioning of Cu from vapor into liquid. Condensation during an experiment may produce an irreversible transfer of copper from the sample to the autoclave wall during cooling or heating, and this could lead to considerable overestimation of metal solubility in the vapor phase. To minimize this effect, the holder for the copper chloride reagent was not washed with nitric acid when recovering the condensate. The second potential source of error is partitioning of copper from vapor into liquid (water) during heating or quenching. The much higher solubility of Cu in the liquid (several orders of magnitude) could result in appreciable overestimation of the solubility of Cu in the vapor. However, neither of these processes seems to have been significant in the experiments, as the kinetic runs (see below) do not show evidence of increasing concentration with time (i.e., a transport reaction), or a scattering of concentrations (i.e., condensation).

3. RESULTS

To determine the duration necessary to reach equilibrium, and investigate problems associated with experimental errors, a series of experiments of variable duration (kinetic runs) were performed. These experiments were conducted for run times of 1 to 15 days, at 320°C and for a bulk density close to that of liquid-saturated vapor. At this temperature, equilibrium was attained after 6 days (Fig. 2). In experiments at 320°C, autoclaves were left in the furnace for at least 12 days, while at 280°C this time was extended to 21 days. Figure 2 shows that once equilibrium was attained, Cu solubilities were reproducible to approximately ±12%. If condensation had occurred on the inner surface of the autoclave at the run temperature, the concentrations measured should not have been reproducible.

Three isotherms (280, 300, 320°C) were chosen to evaluate the solubility of copper chloride in the vapor phase. Twenty-three HCl-free experiments were conducted to investigate the effect of f_{H_2O} on copper solubility (Table 1), while an additional 10 experiments, all at 320°C, were performed to investigate the effect of f_{HCl} at constant pressure (Fig. 3, Table 2). The vapor pressure in the CuCl-H_2O system varied from 53 to 100 bars, and was close to that of the liquid-vapor boundary.
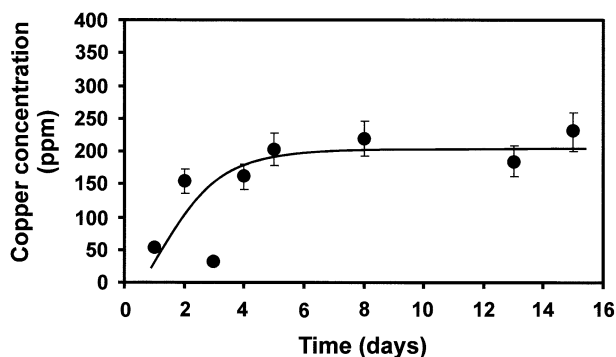
Fig. 2. Solubility of copper, at $P_{HCl} = 0$ and $P_{H_2O} = 103.5$ bars, as a function of time. Data suggest that equilibrium was attained after 6 days at 320°C.

The results of our experiments show that copper concentrations correlate positively with P_{H_2O} at 280, 300 and 320°C (at constant P_{HCl}), indicating that the solubility of copper in the vapor phase depends on the fugacity of H_2O (Fig. 4). By contrast, experiments performed at 320°C and constant P_{H_2O} indicate that CuCl concentration is independent of P_{HCl} (Fig. 3). Our experiments also show that copper solubility is retrograde over the temperature interval 280 to 320°C and P_{H_2O} from 53 to ~100 bars (Fig. 5).

4. DISCUSSION

As the concentration of copper in the vapor increases with increasing f_{H_2O}, it can be assumed that the dominant species has the stoichiometry $CuCl_{m+1}(H_2O)_n^{gas}$. The formation of this species can be described by the reaction:

$$CuCl^{gas} + m \cdot HCl^{gas} + n \cdot H_2O^{gas} \rightleftharpoons CuCl_{m+1} \cdot (H_2O)_n^{gas}$$

$$+ \frac{m}{2} \cdot H_2^{gas} \qquad (1)$$
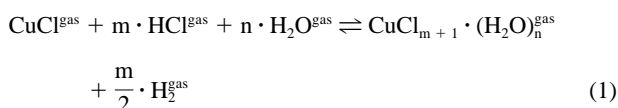
where n is the hydration number of the copper species in vapor, and $CuCl^{gas}$ represents the vapor pressure of $CuCl^{gas}$ over
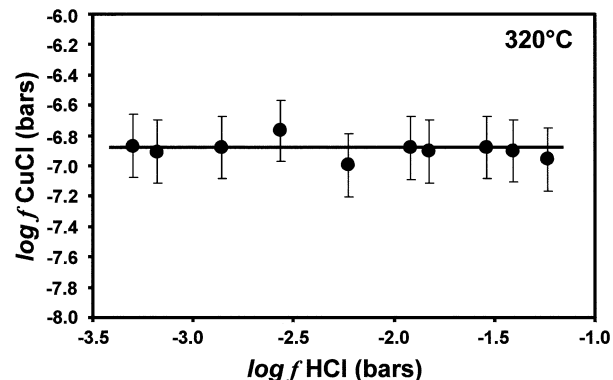

Fig. 3. Plot of log fCuCl versus log fHCl (constant fH$_2$O) at 320°C. The zero slope of the data distribution indicates that CuCl solubility was independent of log fHCl, and that the copper-bearing species has the stoichiometry $CuCl(H_2O)_n$.
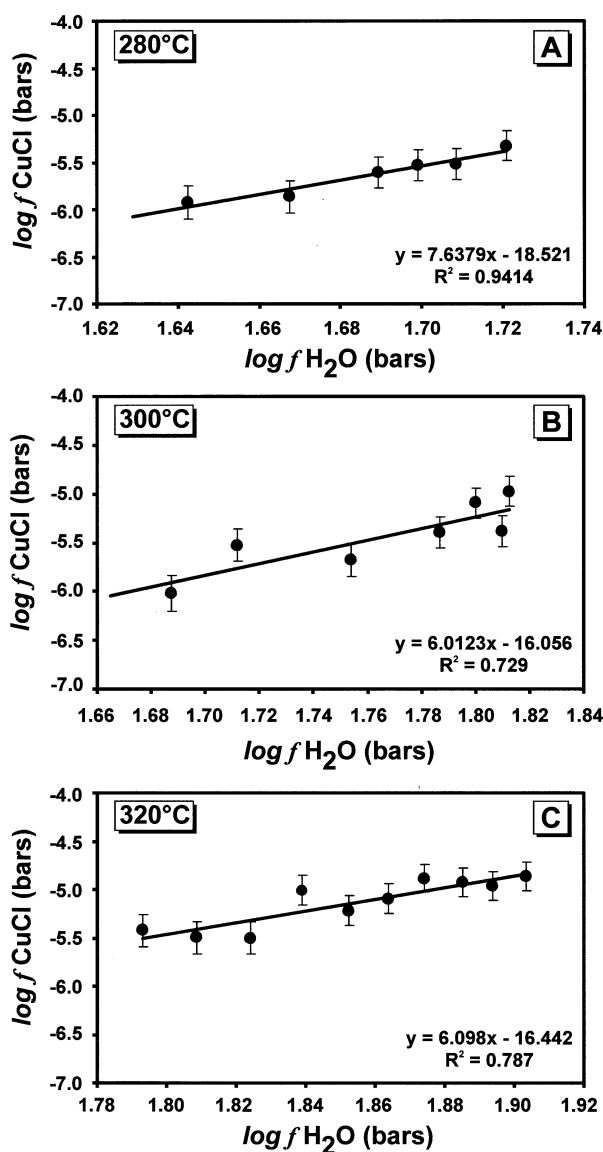

Fig. 4. Plots of log fCuCl versus log fH$_2$O (at constant fHCl) at three isotherms (a, 280°C; b, 300°C; c, 320°C). The slopes are 7.6, 6.0 and 6.1 at temperatures of 280, 300 and 320°C, respectively. This suggests that the stoichiometry of the Cu-bearing species is $CuCl(H_2O)_{8-6}$ assuming a momomer form, or $Cu_3Cl_3(H_2O)_{8-6}$ for the trimer.

$CuCl^{solid}$. This equation can also be used for non-hydrated species such as $CuCl_2$ and $CuCl_3$.

In our study, the experimental method was designed to investigate the dependence of copper concentration on the fugacity of H_2O, and does not allow differentiation among species with the same metal-ligand ratio (i.e., CuCl is indistinguishable from Cu_3Cl_3). We are therefore able to determine the ratio of Cu:Cl, but not the absolute number of Cu and Cl atoms in the molecule.

4.1. Thermodynamic Approach

Data from our experiments were interpreted assuming that the vapor was an ideal mixture of non-ideal gases (cf., Marshall
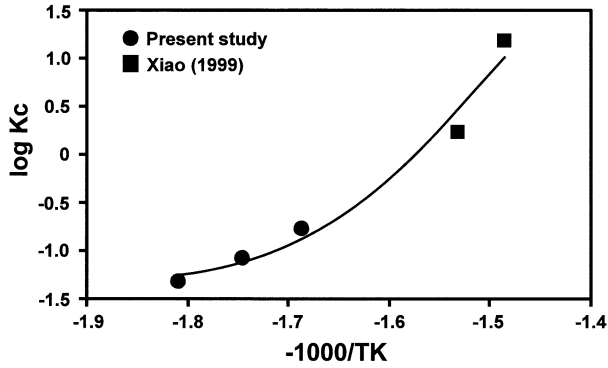
Fig. 5. A plot of temperature (expressed as $-1000/T$ in Kelvin) versus log Kc comparing the results from the present study with those of Xiao; 1999 (see text for further details). The solid line represents a second order polynomial fit to the data.

1972, Armellini and Tester 1993, Migdisov et al. 1999, Archibald et al. 2001). The equilibrium constant for reaction 1 is given by:

$$\log K_f = \log f_{CuCl_{m+1} \cdot (H_2O)_n} + \frac{m}{2} \cdot \log f_{H_2} - n \cdot \log f_{H_2O}$$

$$- m \cdot \log f_{HCl} - \log f_{CuCl} \quad (2)$$

Differentiating log K with respect to $\log f_{HCl}$, while holding temperature, f_{O_2} and f_{H_2O} constant, and considering that the equilibrium constant of a homogeneous gaseous reaction is independent of total pressure, Eqn. 2 becomes

$$\left(\frac{\partial \log f_{CuCl_{m+1}(H_2O)_n}}{\partial \log f_{HCl}} \right)_{T, f_{O_2}, f_{H_2O}} = m \quad (3)$$

where m, the chlorine ligation number, is the slope of a trend describing the experimental data by the orthogonal co-ordinates, $\log f_{CuCl_{m+1}(H_2O)_n}$ and $\log f_{HCl}$.

The hydration number of the vapor species was calculated in a similar manner. Differentiating Eqn. 2 with respect to $\log f_{H_2O}$ (using the approach outlined in Archibald et al. (2001) we obtain:

$$\left(\frac{\partial \log f_{CuCl_{m+1}(H_2O)_n}}{\partial \log f_{H_2O}} \right)_{T, f_{O_2}, f_{HCl}} = n + \left(\frac{\partial \log f_{CuCl^{gas}}}{\partial \log f_{H_2O}} \right)_{T \dots} \quad (4)$$

As the system investigated was not homogeneous (i.e., it contained both solid and vapor), we applied a "Poynting correction" to make it effectively homogeneous for the purpose of thermodynamic description (Sandler, 1989; p. 225). This involved correcting the change in pressure of CuCl^{gas} over the crystalline phase from that for a total pressure of $P_1 = 1$ bar (standard state) to that for P_2, the pressure of the run:

$$\ln \frac{f_2^0}{f_1^0} = \int_{P_1}^{P_2} \frac{V^0}{R \cdot T} dP \quad (5)$$

As changes in the molar volume of the copper chloride (solid) with temperature are negligible at the experimental

temperatures (280, 300, 320°C), we assumed that V° is constant and that Eqn. 5 can therefore be expressed as:

$$\ln \frac{f_2^0}{f_1^0} = \frac{V^\circ \cdot (P_2 - P_1)}{R \cdot T} \quad (6)$$

where V° is the molar volume, CuCl = 23.91 cm mol^{-1}, and f_1° and f_2° are the fugacities of this component in states 1 and 2.

Substituting Eqn. 6 into Eqn. 4 we now obtain

$$\left(\frac{\partial \log f_{CuCl_{m+1}(H_2O)_n}}{\partial \log f_{H_2O}} \right)_{T, f_{O_2}, f_{HCl}} = n + \left(\frac{V^{\rightleftharpoons} \cdot (P_2 - P_1)}{R \cdot T} \right) \quad (7)$$

4.2. Data Analysis

In our calculations, we assumed that f_{HCl} was negligible (when HCl was present in the experiments) compared to f_{H_2O}. Values of f_{H_2O} were calculated from the equation of Kestin et al. (1984), and the fugacity of $CuCl_{m+1}(H_2O)_n$ in vapor was calculated from the concentration of copper in quenched condensate (Tables 1 and 2). The mole fraction of copper is therefore given by the equation:

$$X_{CuCl_{m+1} \cdot (H_2O)_n} \cong \left(\frac{M_{CuCl_{m+1} \cdot (H_2O)n}}{M_{H_2O}} \right) \quad (8)$$

where M is the number of moles of the corresponding compound in 1000g of H_2O.

It was further assumed that

$$\log f_{CuCl_{m+1} \cdot (H_2O)_n} = \log X_{CuCl_{m+1} \cdot (H_2O)_n} + \log f_{H_2O} \quad (9)$$

i.e., the gas phase was an ideal mixture, and therefore obeyed Raoult's Law.

The results of our thermodynamic interpretations of the data are presented in Tables 1 and 2, and express the concentrations of copper chloride species as mole fractions and fugacities. Values of $\log f_{CuCl}$ are shown as a function of f_{HCl} at 320°C in Figure 3, and indicate that CuCl solubility is independent of f_{HCl} at constant f_{H_2O}. This relationship further suggests that there is one dominant copper species in the vapor, and that it has a ratio of Cu:Cl = 1:1 (e.g., $CuCl(H_2O)_n$, $Cu_3Cl_3(H_2O)_n$, etc.). An early transpiration investigation of the Cu-HCl system by Brewer and Lofgren (1950) discovered that copper could form several vapor species including the monomer (CuCl), dimer (Cu_2Cl_2), trimer (Cu_3Cl_3) and tetramer (Cu_4Cl_4). Later, Peterson (1973) and Shiller (1976), using transpiration mass spectroscopy, showed that Cu_3Cl_3 and Cu_4Cl_4 were the dominant copper chloride species in vapor, and this was confirmed by Krabbes and Opperman (1977). It therefore seems likely that the Cu:Cl ratio of 1:1 interpreted from our experiments reflects dominance of either $Cu_3Cl_3(H_2O)_n$ or $Cu_4Cl_4(H_2O)_n$.

Further evidence for the above conclusion comes from the calculated hydration numbers. The hydration number of the proposed vapor species $Cu_{3-4}Cl_{3-4} \cdot (H_2O)_n$ was interpreted from the variation of $\log f_{Cu_{3-4}Cl_{3-4} \cdot (H_2O)_n}$ with $\log f_{H_2O}$ at constant $\log f_{HCl}$ (as in Eqn. 7). From Figure 4, it is apparent that f_{CuCl} correlates positively with f_{H_2O}. The data at 280°C, which were collected from HCl-free experiments, yielded a slope of 7.6, while those at 300 and 320°C yielded slopes of 6.0 and 6.1, respectively. These results indicate statistical hydration

Table 3. A summary of equilibrium constants derived in this study for the inferred trimer (Cu_3Cl_3) species, x = 3, and teramer (Cu_4Cl_4), x = 4.

Temperature (°C)	Reaction	Log K (± 1 σ error) x=3	Log K (± 1 σ error) x=4
280	$XCuCl + 7.6H_2O = Cu_xCl_x \cdot (H_2O)_{7.6}$	−21.46 ± 0.05	−22.46 ± 0.05
300	$XCuCl + 6.0H_2O = Cu_xCl_x \cdot (H_2O)_{6.0}$	−19.03 ± 0.10	−20.03 ± 0.18
320	$XCuCl + 6.1H_2O = Cu_xCl_x \cdot (H_2O)_{6.1}$	−19.45 ± 0.12	−20.45 ± 0.12

(solvation) numbers of ~7.6 at 280°C, ~6.0 at 300°C, and ~6.1 at 320°C for the above species. However, the possibility of a vapor species with a monomer nucleus, $CuCl(H_2O)_{6-7.6}$, can not be dismissed without further work.

To calculate the value of log K for the overall reaction (Eqn. 1), a slight modification is needed so that copper chloride is in its standard state (i.e., solid). The equation becomes:

$$3\,CuCl^{solid} + n \cdot H_2O^{gas} = Cu_3Cl_3 \cdot (H_2O)_n^{gas} \qquad (10)$$
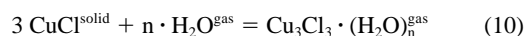
Log $K_{(10)}$ values were calculated for each of the isotherms investigated (Table 3). The equilibrium constants and errors for reaction (10), when the vapor species is the trimer (Cu_3Cl_3), are −21.46 ± 0.05 (n = 7.6), −19.03 ± 0.10 (n = 6.0), −19.45 ± 0.12 (n = 6.1), at temperatures of 280, 300 and 320°C, respectively. When calculated as the tetramer (Cu_4Cl_4), the corresponding log K values become −22.46 ± 0.05 (n = 7.6), −20.03 ± 0.18 (n = 6.0), and −20.45 ± 0.12 (n = 6.1). The errors are expressed as one sigma deviations and refer only to experimental uncertainties.

The partition coefficient for Cu between the vapor ($Cu_{3-4}Cl_{3-4}$) and Σ liquid ($CuCl$, $CuCl_2^-$, $CuCl_3^{2-}$, etc.) was calculated from the concentration of the $Cu_{3-4}Cl_{3-4} \cdot (H_2O)_6$ vapor species, determined using the log K's derived above, and the concentration of the Cu species in the liquid determined using log K's from Xiao et al. (1998). The vapor/liquid partition coefficients calculated at a pH of 4 and a Cl^- concentration of 1M are 0.00152, 0.00014 and 0.00003 at temperatures of 280, 300 and 320°C, respectively. These coefficients suggest that copper chloride prefers the liquid phase at these temperatures and vapor-saturated pressures, and that this preference is greatest at 320°C. As the hydration number was not constant for the isotherms investigated, it is not possible to extract values of fundamental thermodynamic parameters such as entropy, enthalpy and heat capacity from the data.

4.3. Comparison with Other Studies

There have been relatively few experimental studies of the solubility of metals or metal chlorides in water vapor at elevated temperatures and pressures, and most of them have dealt with sodium chloride (Armellini and Tester, 1993; Bischoff et al., 1986). Recently, however Barnes and Seward (1997), Xiao (1999), Migdisov et al. (1999) and Archibald et al. (2001) have investigated the solubility of mercury, copper, silver and gold, respectively. These studies, except that of Barnes and Seward (1997) on mercury, were conducted to obtain the hydration number (stoichiometry) of the cation. Armellini and Tester (1993) concluded that $NaCl^{gas}$ has a hydration number of four between 450 and 550°C and 100 to 250 bars, Migdisov et al. (1999) concluded that $AgCl^{gas}$ has a hydration number of three,

and Archibald et al. (2001) reported a variable hydration number for $AuCl^{gas}$, from 4 at 300°C to 2 at 360°C.

Xiao (1999) estimated the partitioning of copper between liquid and vapor by measuring the solubility of CuCl(s) in the two-phase (liquid and vapor) system $NaCl-HCl-H_2O$ at temperatures from 360 to 400°C and NaCl molalities up to 7 M. Native copper was added to control the redox state of the system. The important conclusions of this study (summarized in Williams-Jones et al., in press) were that 1) copper is relatively soluble in the vapor phase; 2) the solubility is prograde; 3) copper and sodium have very similar partition coefficients; and 4) CuCl(s) dissolves congruently in the vapor as the species $CuCl \cdot (H_2O)_n$. The hydration number of the copper species varies from unity at 360°C, to four at 380 and 400°C. These conclusions are very similar to those of the present study except that the hydration number of the copper species in the vapor was lower, and the solubility of Cu in the vapor was retrograde.

To compare our equilibrium constants with the concentration constants (Kc) of Xiao (1999) we recalculated them for liquid saturated conditions using the relationship employed by Xiao (1999):

$$\log K_c = \log m_{CuCl \cdot (H_2O)_n} - n \cdot \log \rho_{H_2O} \qquad (11)$$

where Kc is the equilibrium relationship and ρH_2O is the density of water. The two sets of data are compared in Figure 5 and agree well. They also indicate that the non-thermodynamic concentration constant increases with increasing temperature.

The high hydration numbers obtained in our study (≥ 6) would seem to support the idea that we are dealing with trimer and/or tetramer copper species, which contrasts with the findings for gold and silver that the vapor species have monomeric nuclei (Archibald et al., 2001 and Migdisov et al., 1999, respectively). Based on our experimental data, it is evident that the hydration number decreases slightly with increasing temperature (i.e., 7.6 at 280°C, to 6.0 at 320°C). A similar decrease was noted in the $Au-HCl-H_2O$ system (Archibald et al., 2001), and was attributed to a decrease in stability of the solvation shell with increased temperature. This decrease was also noted by Seward et al. (1996) for aquated Ag^+ in liquid AgCl solutions up to 350°C, while Fulton et al. (2000) noted a similar trend for Cu in aqueous $CuBr_2$ solutions up to 325°C.

Using the thermodynamic data of Pankratz (1984), it was possible to calculate the theoretical vapor pressure of $CuCl^{gas}$ and $Cu_3Cl_3^{gas}$ at temperatures similar to those of the present study. Considering the monomer first, values of log f_{CuCl} are calculated to be −17.10, −16.44, −15.81 at temperatures of 280, 300 and 320°C, respectively. These values increase by
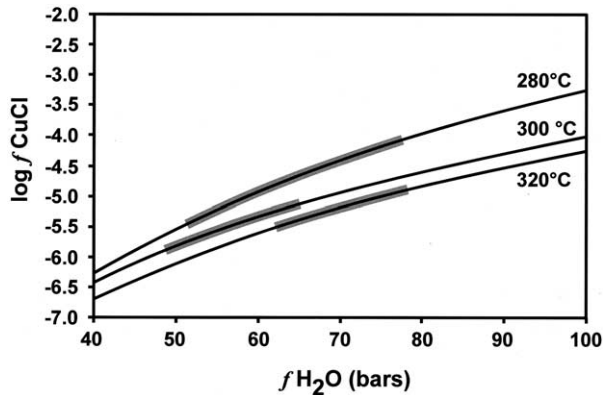
Fig. 6. Plot of log fCuCl versus log f_{H_2O} (at constant f_{HCl}) at three isotherms (280°C, 300°C and 320°C) using the regression equations calculated in Figure 4, and illustrating the retrograde nature of Cu solubility at these conditions. The shaded area represents the f_{H_2O} range for each experiment.

three orders of magnitude when partial pressures are calculated as Cu_3Cl_3, i.e., the log fugacities of Cu_3Cl_3 are -13.87, -13.31 and -12.79, respectively. In our experiments, log $f_{Cu_xCl_xnH_2O}$ varied from -6.0 to -5.3 at 280°C, -6.0 to -5.0 at 300°C, and -5.5 to -4.8 at 360°C (at variable f_{H_2O}). When comparing the fugacities of the non-hydrated species with the hydrated species determined in this study, it is evident that hydration significantly enhances copper solubility; by as much as seven orders of magnitude for trimer species and thirteen orders of magnitude for monomer species.

Although the fugacities of the hydrated species in our study appear superficially to indicate that solubility increases with temperature, in fact they document retrograde solubility. This is because f_{H_2O} was higher in experiments performed at higher temperature (Fig. 6). As proposed by Archibald et al. (2001) for gold, we attribute this behaviour to the reduction in hydration of the copper species with increasing temperature.

4.4. Geological Implications

It has long been known that the crystallization of magma in porphyry systems causes volatiles (e.g., H_2O, HCl, HF and CO_2) in the melt to exsolve, and that the exsolved orthomagmatic phase is typically dominated by vapor, rather than liquid (Henley and McNabb, 1978; Burnham, 1997). Despite this latter observation and the persuasive arguments of Henley and McNabb (1978) to the contrary, most researchers believe that the bulk of copper transport is by the brine (Christiansen et al., 1983; Candela and Holland, 1986; Manning and Pichavant, 1988; Candela, 1989; Cline and Bodnar, 1991). However, recent micro-analytical studies of porphyry mineralization utilizing LAM-ICP-MS have shown that the vapor is enriched in Cu, Au and As relative to the corresponding liquid (Ulrich et al., 1999; Heinrich et al. 1999). For example, as noted earlier they showed that vapor-rich fluid inclusions at Bajo de la Alumbrera (a large porphyry copper deposit in Argentina) contain up to 3.3 wt.% Cu, while co-existing liquid-rich inclusions only contain < 0.76 wt.% Cu.

Clearly the possibility that the vapor phase may play an important role in the transport of Cu in the porphyry environ-

ment must now be given more serious consideration. We have therefore used the results of our experiments to estimate the minimum time required to form a hypothetical 50 million tonne porphyry copper deposit with a grade of 0.5% Cu from a CuCl-bearing vapor.

As HCl is an important component of volcanic gas discharge (Symonds et al., 1994), we have used HCl flux rates to constrain the amount of copper that can be carried by the vapor. Two rates were selected, namely those for White Island (110 tonnes of HCl per day; Le Cloarec et al., 1992) and Mount Etna (300 tonnes per day; Buat-Ménard and Arnold, 1978). Note however, that HCl fluxes up to 500 tonnes per day have been reported for some volcanoes, e.g., Galeras in Columbia (Goff et al., 1994). At 300°C and a water vapor pressure of 100 bars, we would expect 278 ppm of copper to be present in the vapor as a hydrated copper chloride complex. Using this value and a HCl flux of 110 tonnes per day, it would take 22,400 yr to form the hypothetical ore deposit specified above, assuming the system is 100% efficient. Even with an efficiency of 40% it would only take ~56,000 yr to deposit the same amount of copper. If we use a flux of 300 tonnes per day and an efficiency of 40%, the same deposit can form in 20,500 yr. These durations are well within the 300 ka time-frame predicted by Cathles et al. (1997) for a near-surface felsic intrusion to cool to a temperature of 300°C.

Obvious limitations of the above calculations are that they ignore the possibility that other gases, notably H_2S, and SO_2 may be more important in the transport of copper than HCl and that phases like covellite and chalcocite may saturate at much lower concentrations of copper than nantokite (CuCl). However, they do show that vapor transport can be appreciable and could therefore play a more significant role in the formation of economic copper deposits than was previously thought possible.

5. CONCLUSIONS

We have shown experimentally that appreciable concentrations of Cu can be transported in chloride-bearing water vapor, and that these concentrations are 10 orders of magnitude greater than those of the water-free system. However, the solubility is retrograde over the temperatures investigated (280 to 320°C). The reason for the high solubility is the formation of a hydrated copper-chloride species via a reaction of the type:

$$xCuCl^{gas} + n \cdot H_2O^{gas} = Cu_xCl_x \cdot (H_2O)_n^{gas} \qquad (12)$$
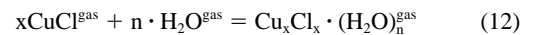
The copper-chlorine ratio for the nucleus of the species is 1:1 and the overall stoichiometry is interpreted to be $Cu_{3-4}Cl_{3-4} \cdot (H_2O)_{7.6}$, $Cu_{3-4}Cl_{3-4} \cdot (H_2O)_6$ and $Cu_{3-4}Cl_{3-4} \cdot (H_2O)_6$ at temperatures of 280, 300 and 320°C, respectively. This reduction in the hydration number of the copper complex with increasing temperature may explain why there is a corresponding reduction in copper concentration (retrograde solubility).

At a geologically realistic temperature and HCl gas flux, our data indicate that water vapor with chlorinities typical of orthomagmatic vapors has the potential to transport significant concentrations (~280 ppm) of Cu. This vapor or its condensed derivatives could theoretically form an economic copper deposit (50 million tonnes of 0.5% Cu) in <20,500 yr.

REFERENCES

Archibald S. M., Migdisov A. A. and Williams-Jones A. E. (2001). The stability of Au-chloride complexes in water vapor at elevated temperatures and pressures. *Geochim. Cosmochim. Acta.* **65,** 4413–4423.

Armellini F. J. and Tester J. W. (1993) Solubility of sodium chloride and sulfate in sub- and supercritical water vapor from 450–550°C and 100–250 bars. *Fluid Phase Equilib.* **84,** 123–142.

Barnes H. L. and Seward T. M. (1997) Geothermal Systems and Mercury Deposits. In *Geochemistry of Hydrothermal Ore Deposits*, Third Edition. (eds. H. L. Barnes, John Wiley and Sons) pp. 699–736, New York.

Bischoff J. L., Rosenbaure R. J. and Pitzer K. S. (1986) The system NaCl-H$_2$O: relations of vapor-liquid near the critical temperature of water and of vapor-liquid-halite from 300 to 500°C. *Geochim. Cosmochim. Acta.* **50,** 1437–1444.

Brewer L. and Lofgren N. (1950) The thermodynamics of gaseous cuprous chloride, monomer and trimer. *J. Am. Chem. Soc.* **72,** 3038–3045.

Brugger J., Black J., McPhail D. C. and Spiccia L. (2001). Complexation of metal ions in brines: Application of spectroscopy in the study of the Cu(II)-LiCl-H2O system between 25 and 90°C. *Geochim. Cosmochim. Acta.* **65,** 2691–2708.

Buat-Ménard P. and Arnold M. (1978) The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. *Geophys. Res. Lett.* **5,** 245–248.

Burnham W. (1997) Magmas and Hydrothermal Fluids. In *Geochemistry of Hydrothermal Ore Deposits*, Third Edition. (eds. H. L. Barnes, John Wiley and Sons) pp. 63–123, New York.

Candela P. A. (1989) Calculation of magmatic fluid contributions to porphyry-type ore systems: predicting fluid inclusion chemistries. *Geochem. J.* **23,** 295–305.

Candela P. A. and Holland H. D. (1986) A mass transport model for copper and molybdenum in magmatic hydrothermal systems: the origin of porphyry-type ore deposits. *Econ. Geol.* **81,** 1–19.

Cathles L. M., Erendi A. H. J. and Barrie T. (1997) How long can a hydrothermal system be sustained by a single intrusive event? *Econ. Geol.* **92,** 766–771.

Christiansen E. H., Burt D. M., Sheridan M. F. and Wilson R.T. (1983) The petrogenesis of topaz rhyolites from the western United States. *Contrib. Mineral. Petrol.* **83,** 16–30.

Cline J. S. and Bodnar R. J. (1991) Can economic porphyry copper mineralization be generated by a typical calc-alkaline melt? *J. Geophys. Res.* **96,** 8113–8126.

Crerar D. A., Wood S. A., Brantley S. and Bocarsly A. (1985) Chemical controls on the solubility of ore-forming minerals in hydrothermal solutions. *Can. Mineral.* **23,** 333–352.

Drummond S. E. and Ohmoto H. (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems. *Econ. Geol.* **80,** 126–147.

Eastoe C. J. (1982) Physics and chemistry of the hydrothermal system at the Pangua porphyry copper deposit, Bougainville, Papua New Guinea. *Econ. Geol.* **77,** 127–153.

Fulton J. L., Darab J. G. and Hoffmann M. M. (2000). A transition from a six- to a four-coordinate Ni^{2+} complex in high-temperature aqueous solutions from X-Ray absorption spectroscopy. In *Steam, Water, and Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry* (eds. P. R. Tremaine, P. G. Hill, D. E. Irish, and P. V. Balakrishnan), pp. 593–598. NRC Research Press, Ottawa, Canada.

Gemmell J. B. (1987) Geochemistry of metallic trace elements in fumarole condensates from Nicaraguan and Costa Rican volcanoes. *J. Volcanol. Geotherm. Res.* **33,** 161–181.

Getahun A., Reed M. H. and Symonds R. B. (1996) Mount St. Augustine Volcano fumarole wall rock alteration: mineralogy, zoning, composition and numerical models of its formation process. *J. Vol. Geotherm. Res.* **71,** 73–107.

Goff F., Stimac J. A., Larocque A. C. L., Hulen J. B., McMurtry G. M., Adams A. I., Roldan M. A., Trujillo P. E. Jr, Counce D., Chipera S. J., Mann D. and Heizler M. (1994) Gold degassing and deposition at Galeras Volcano, Colombia. *GSA Today.* **4,** 241, 244–247.

Hedenquist J. W. and Lowenstern J. B. (1994) The role of magmas in the formation of hydrothermal ore deposits. *Nature* **370,** 519–526.

Heinrich C. A., Ryan C. G., Mernagh T. P. and Eadington P. J. (1992) Segregation of ore metals between magmatic brine and vapor: A fluid inclusion study using PIXE microanalysis. *Econ. Geol.* **87,** 1566–1583.

Heinrich C. A., Gunther D., Audétat A., Ulrich T and Frischknecht R. (1999) Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology* **27,** 755–758.

Henley R. W. and McNabb A. (1978) Magmatic vapor plumes and ground-water interaction in porphyry copper emplacement. *Econ. Geol.* **73,** 1–20.

Kestin J., Sengers J. V., Kamgar-Parsi B. and Levelt Sengers J. M. H. (1984) Thermophysical Properties of Fluid H$_2$O. *J. Phys. Chem. Ref. Data.* **13,** 175–183.

Krabbes G. and Oppermann H. (1977) Die Thermodynamik der Verdampfung der Kuper(I)-Halogenide. *Z. anorg. allg. Chem.* **435,** 33–44.

Le Cloarec M. F., Allard P., Ardouin B., Giggenbach W F. and Shappard D. S. (1992) Radioactive isotopes and trace elements in gaseous emissions from White Island, New Zealand. *Earth Planet. Sci. Lett.* **108,** 19–28.

Lowenstern J. B., Mahood G. A., Rivers M. L. and Sutton S. R. (1991) Evidence for extreme partitioning of copper into a magmatic vapor phase. *Science.* **252,** 1405–1409.

Liu W., McPhail D. C. and Brugger J. (2001). An experimental study of copper (I)-chloride and copper(I)-acetate complexing in hydrothermal solutions between 50 and 250°C and vapor-saturated pressure. *Geochim. Cosmochim. Acta.* **65,** 2937–2948.

Manning D. A. C. and Pichavant M. (1988) Volatiles and their bearing on the behaviour of metals in granitic systems. In *Recent Advances in the Geology of Granite-related Mineral Deposits* (eds. R. P. Taylor and D. F. Strong), Special Volume 39, 12–24. The Canadian Institute of Mining and Metallurgy.

Marshall W. L. (1972) A further description of complete equilibrium constants. *J. Phys. Chem.* **76,** 720–731.

Martynova O. I. (1964) Some problems of the solubility of involatile inorganic compounds in water vapour at high temperatures and pressures. *Russ. J. Phys. Chem.* **38,** 587–592.

Migdisov A. A., Williams-Jones, A. E. and Suleimenov O. M. (1999) The solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures. *Geochim. Cosmochim. Acta.* **63,** 3817–3827.

Pankratz L. B. (1984) Thermodynamic Properties of Halides. United States Dept. of the Interior, Bureau of Mines, 826pp.

Peterson D. E. (1973) Sublimation thermodynamics and kinetics of cuprous-chloride. Part I: vacuum balance-torsion experiments. Part II: mass-spectrometer experiments. Ph.D. dissertation, University of Kansas, 484pp.

Ruaya J. R. and Seward T. M. (1987) The ion-pair constant and other thermodynamic properties of HCl up to 350°C. *Geochim. Cosmochim. Acta.* **51,** 121–130.

Sandler S. I. (1989) Chemical and Engineering Thermodynamics. John Wiley and Sons, New York, New York, 622 pp.

Seward T. M., Henderson C. M. B., Charnock J. M. and Dobson B. R (1996) An X-ray absorption (EXAFS) spectroscopic study of aquated Ag$^+$ in hydrothermal solutions to 350°C. *Geochim. Cosmochim. Acta.* **60,** 2273–2282.

Shiller B. (1976) A transpiration-mass spectrometric technique for the determination of the thermodynamic properties of chloride vapor transport reactions. Ph.D. dissertation, Colorado School of Mines, Golden, Colorado, 197 pp.

Spycher N. F., and Reed M. H. (1989) Evolution of a Broadlands-type

epithermal ore fluid along alternative P-T paths; implications for the transport and deposition of base, precious, and volatile metals. *Econ. Geol.* **84,** 328–359.

Stoiber R. E. and Rose W. I. (1974) Fumarole incrustations at active Central American volcanoes. *Geochim. Cosmochim. Acta.* **38,** 495–516.

Symonds R. B. and Reed M. H. (1993) Calculation of multicomponent chemical equilibria in gas-solid-liquid systems; calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens. *Am. J. Sci.* **293,** 8, 758–864

Symonds R. B., Rose W. I., Reed M. H., Lichte F. E. and Finnegan D. L. (1987) Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. *Geochim. Cosmochim. Acta.* **51,** 2083–2101.

Symonds R. B., Rose W. I., Bluth G. J. S., and Gerlach T. M. (1994) Volcanic-gas studies: Methods, results and applications. In *Volatiles in Magmas* (eds. M. R. Carroll and J. R. Holloway), pp. 1–66. Washington D.C., Mineralogical Society of America.

Tagirov B. R., Zotov A. V. and Akinfiev N. N. (1997) Experimental study of dissociation of HCl from 350 to 500°C and 500 to 2500 bars; thermodynamic properties of $HCl^{\circ}_{(aq)}$. *Geochim. Cosmochim. Acta.* **61,** 4267–4280.

Taran Y. A. Bernard A., Gavilanes J-C. and Africano F. (2000). Native gold in mineral precipitates from high-temperature volcanic gases of Colima volcano, Mexico. *Appl. Geochem.* **15,** 337–346.

Tskhvirashvili P. G., Vasadze L. E. and Antidze T. T. (1970) Generalisation of data on the distribution between water and its vapour by methods of comparative calculation. *Russ. J. Phys. Chem.* **44,** 1587–1589.

Ulrich T., Günther D. and Heinrich C. A. (1999) Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. *Nature.* **399,** 676–678.

Var'yash L. N. (1992) Cu(I) complexing in NaCl solutions at 300°C and 350°C. *Geochem. Int.* **29,** 84–92.

Vercher E., Pena M. P. and Martinez-Andreu A. (1995) Isobaric Vapor-Liquid Equilibrium for ethanol + water + copper(II) Chloride. *J. Chem. Eng. Data.* **40,** 657–661.

Williams T. J., Candela P. A. and 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-Jones A. E., Migdisov A. A., Archibald S. M., and Xiao Z. (2002) Vapor-transport of ore metals. In *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar* (eds. R. Hellman and S. A. Wood), pp. 279–305. Special Publication No. ●●. The Geochemical Society.

Wood S. A. and Samson I. M. (1998) Solubility of ore minerals and complexation of ore metals in hydrothermal solutions. In *Techniques in Hydrothermal Ore Deposit Geology* (eds. J. P. Richards and P. B. Larson). Reviews in Economic Geology, v. 10, 33–80.

Xiao Z. (1999) Experimental and theoretical studies of the solubility of copper in liquid and vapor in the system NaCl-HCl-H₂O. Ph.D. dissertation, McGill University, Canada, 251pp.

Xiao Z. and Williams-Jones A. E. (1999) An experimental study of copper(I) chloride solubility in water vapor at 360°C. Program with Abstracts—Geological Association of Canada; Mineralogical Association of Canada, Joint Ann. Meeting. **24,** 137.

Xiao Z., Gammons C. H. and Williams-Jones A. E. (1998) An experimental study of copper chloride complexing at temperatures from 40°C to 300°C and saturated vapor pressure. *Geochim. Cosmochim. Acta.* **62,** 2949–2964.