



PII S0016-7037(01)00631-7

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

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(Received December 12, 2000; accepted in revised form March 6, 2001)

Abstract—The transport of copper is affected by complexing with ligands such as chloride, bisulphide and acetate. Many copper deposits are formed from hydrothermal waters and brines and in order to understand their formation we need thermodynamic properties of aqueous copper species. The solubility of cuprite experiments in pH-buffered acetate and chloride solutions was determined at 50°C, 150°C and 250°C and water vapor saturated pressures. Chloride and acetate concentrations were varied using NaCl (0.001m to 2 m) and NaAc (0.1m to 2 m, where Ac refers to acetate). Measured copper concentrations varied between 0.0001 m and 0.2 m and show systematic increases with increasing temperature and acetate or chloride concentration. Logarithms of the formation constants (log K) of copper complexes were fitted by a simplex function minimization method, then speciation models and uncertainties of fitted log K values were examined by residual maps and speciation plots of experimental solutions. Interpretation of our experimental data shows that $\text{CuCl}_{(\text{aq})}$, CuCl_2^- , $\text{CuAc}_{(\text{aq})}$ and CuAc_2^- were present in our experiments at all temperatures. CuCl_3^{2-} is an important complex at 50°C, but cannot be detected unequivocally at 150°C and 250°C. This study presents the first experimentally-derived log K values for copper(I) acetate complexes ($\text{CuAc}_{(\text{aq})}$ and CuAc_2^-). The derived log K values of copper(I) chloride complexes ($\text{CuCl}_{(\text{aq})}$ and CuCl_2^-) are similar to recently published experimentally derived values (Xiao et al., 1998). Based on new log K values generated from this study, our calculations indicate that copper transport as acetate complexes is important in acetate-bearing fluids lacking competition of other ligands such as Cl^- and HS^- . Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

The geochemistry of copper in hydrothermal solutions is poorly known, despite its importance in controlling the transport and deposition of copper in the Earth's crust and hydrothermal ore processing. Identifying the important copper aqueous species and measuring reliable thermodynamic properties of those species over wide ranges of temperature and solution composition provide a basis for numerical modeling of ore-forming geochemical conditions, mechanisms and processes, which in turn will be helpful in improving exploration strategies and techniques.

Numerous studies of fluid inclusions from copper deposits and fluid composition of modern hydrothermal systems indicate that chloride is one of the most important components in ore-forming fluids (e.g., Barnes, 1979; Heinrich et al., 1989). For sediment-hosted copper deposits, usually formed at low temperature (<200°C), copper chloride complexes are thought to be important for copper transport (e.g., Rose, 1976; Haynes and Bloom, 1987; Sverjensky, 1987). However, mainly due to the lack of reliable copper(I)-chloride complexing data at elevated temperature, the mechanisms of copper transport and deposition in hydrothermal systems are still not well understood.

Compared to other metals found in economic concentrations in hydrothermal deposits (e.g., Fe, Au and Ag), fewer studies of copper-chloride complexing at high temperatures are available in the literature. These include the experimental studies of Crerar and Barnes (1976), Hemley et al. (1992), Var'yash

(1992), Seyfried and Ding (1993, 1995) and Xiao et al. (1998), and the theoretical studies of Helgeson (1969), Ruaya (1988) and Sverjensky et al. (1997). There are still discrepancies in the nature of the predominant copper chloride complexes and their equilibrium constants (see review in Xiao et al., 1998).

Copper-acetate complexes may also be important in transporting copper in low-temperature geological environments. Acetate is considered to be the predominant organic species in basin brines and oil field water (e.g., Carothers and Kharaka, 1978; Surdam et al., 1984; Hanor and Workman, 1986; Kharaka et al., 1986; Fisher, 1987). Kinetic experiments indicate that acetate may survive for a considerable time at temperatures up to 300°C (Kharaka et al., 1983; Drummond and Palmer, 1986; Palmer and Drummond, 1986) and the aqueous complexation of carboxylic acid anions with metal ions may further enhance their thermal stability (Fein et al., 1994).

Shock and Koresky (1993) estimated dissociation constants of many possible metal-acetate complexes over wide ranges of temperature and pressure using the equations of state for aqueous species (Helgeson et al., 1981; Tanger and Helgeson, 1988). However, there are only a few experimental studies on metal-acetate complexing at high temperatures, such as Pb (Hennet et al., 1988; Giordano, 1989; Yang et al., 1989), Zn (Hennet et al., 1988; Yang et al., 1989), Al (Fein, 1991; Palmer and Bell, 1994), Fe (Palmer and Drummond, 1988; Palmer and Hyde, 1993), Nd (Wood et al., 2000) and Cd (Benezeth and Palmer, 2000). The available experimentally determined log K values for copper-acetate complexes are only for copper(II) at 25°C (Lloyd et al., 1952; Archer and Monk, 1964). There are no data available for Cu(I)-acetate complexes, which are potentially important in geological environments.

The aims of this study were to identify the important aqueous

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copper(I) chloride and acetate complexes, measure their thermodynamic properties at temperatures between 50°C and 250°C, the range of temperature important for sedimentary basin brines, and resolve the discrepancies in the results from previous studies of copper(I) chloride complexes.

2. EXPERIMENTAL METHODS

Cuprite (cuprous oxide, -200 mesh, 99% purity, purchased from CERAC, Wisconsin) was chosen to avoid redox reactions in the experiments. The purity of the cuprite was confirmed by X-ray diffraction, gravimetrically by heating a sample in air and oxidizing to Cu_2O and by dissolving an accurately weighed amount of sample and analyzing the copper concentration. The cuprite powder was pressed into small pellets of 0.1 to 0.2 g and then sintered in evacuated silica tubes at 600°C overnight. Analytical-grade sodium chloride and acetic acid were purchased from BDH Chemicals and trisodium acetate from Ajax Chemicals and used without further preparation. All stock and standard solutions were prepared using freshly boiled double-deionised water.

The silica tube technique used in this study is similar to that described in other studies (e.g., Seward, 1976; Gammons, 1996; Xiao et al., 1998). The experiments were conducted in silica tubes (inner diameter = 7 mm, length 20–22 cm) that were sealed under a slight vacuum created with a mechanical vacuum pump. The tubes were prepared with a narrow constriction approximately 5 cm from one end of the tube. This allowed separation of solid and liquid during quenching of the experiments. The tubes were placed in a continuously stirred water bath for 50°C experiments, where the temperature was maintained within $\pm 0.2^\circ\text{C}$. For experiments at 150°C and 250°C, the tubes were placed in a forced-air convection laboratory oven and the temperature was maintained within 1.0°C. The 150°C experiments were unsupported and the 250°C experiments were supported in stainless pressure vessels containing 15 to 20 mL of water to minimize the pressure difference inside and outside the silica tubes.

At the end of each experiment, the silica tube (or pressure vessel containing tubes at 250°C) was inverted immediately to separate the solid and liquid phases and minimize solid-liquid reactions during quench. For the 250°C experiments, the pressure vessels were cooled with a fan for 10 min then immersed in water for another 10 min before retrieving the silica tubes. For experiments at lower temperatures the silica tubes were immediately immersed into water for approximately 5 min. The cuprite pellets were examined under binocular microscope after experiments and there was no change in their initial red colour. Most of the quenched solutions were clear, although white copper(I) chloride precipitate formed after quench in experiments with the highest copper concentration. Occasionally the experimental solutions were light blue, indicating oxidation of copper, and those experiments were discarded.

For the solutions with no precipitates, an accurately weighed small portion (0.3–1 g) of the quenched solution was filtered with a syringe filter (0.45 μm) and analyzed for copper. The pH of the remaining solution was measured using an Orion ROSS Semimicro electrode and an Orion 290A pH meter. The uncertainty in the measured pH is estimated as ± 0.02 U, based on repeated measurements and reproducibility of samples and standards. For those experiments with precipitate, pH was measured first and then several drops of concentrated nitric acid were added to the solution to dissolve the precipitate thoroughly. Copper concentrations were measured using the neocuproine method (Gahler, 1954) with a CARY 100 spectrometer. Analytical uncertainties are less than approximately 3%, based on duplicate measurements of samples and reproducibility of standards. Cu (II) concentrations in the successful experiments were negligible based on the lack of color in experimental solutions and lack of absorbance in UV-Vis light range that would indicate Cu(II) (e.g., Brugger et al., 2001). We estimate the detection limit for Cu(II) from UV-Vis absorbance to be approximately 5 ppm in chloride-free solutions and less than 1 ppm in 2 m NaCl solutions.

2.1. pH Control

Acetic acid/sodium acetate (HAc/NaAc, Ac refers to acetate throughout this paper) mixtures were chosen to buffer pH because

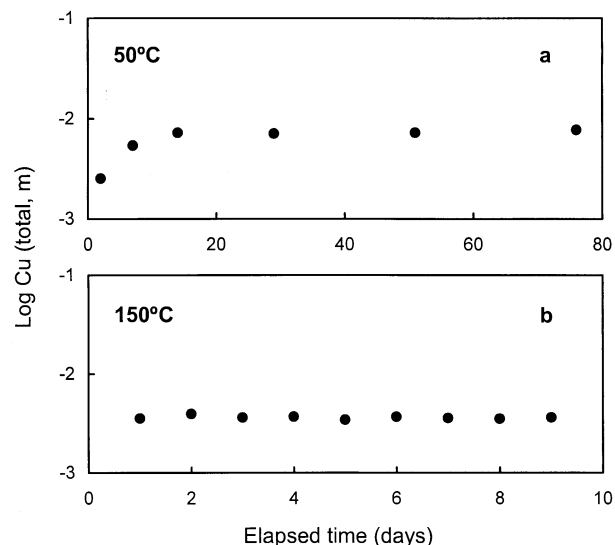


Fig. 1. Cuprite solubility as a function of experimental time in sodium chloride and acetate solutions at 50°C (a) NaCl = 0.1 m, NaAc = Hac = 0.2 m and 150°C (b) NaCl = 0.1 m, NaAc = 0.07 m, Hac = 0.03 m).

ionization constants of acetic acid at elevated temperatures have been precisely determined by potentiometric methods (Mesmer et al., 1989) and the decarboxylation of acetate at temperatures up to 300°C has also been determined (Kharaka et al., 1983; Drummond and Palmer, 1986; Palmer and Drummond, 1986). A 1:1 concentration ratio of sodium acetate and acetic acid was used to optimize the buffer capacity. The pH values of initial and quenched solutions were measured to check the effectiveness of the pH buffer. In experiments to determine copper(I)-acetate complexing (0.1 m NaCl, relatively low copper concentrations), initial and final pH values were all within 0.1 and typically within 0.02 U (Appendix 1). In experiments with the highest NaCl (2.0 m) and copper concentrations (approximately 10000 ppm) the final pH values were up to 1.2 U higher than the initial pH values. The capacity of the pH buffer was probably exceeded because of the dissolution of cuprite; however, this was accounted for in the interpretation below.

2.2. Determination of the Time for Equilibrium

Equilibration times were determined by running identical experiments for different durations and measuring the resulting copper concentrations. The results show that constant copper concentrations are reached in less than two weeks for 50°C experiments and 48 h for 150°C (Fig. 1). To ensure experiments had time to reach equilibrium, we ran 50°C experiments for one month, 150°C experiments for 10 d, and 250°C experiments for 3 d.

Copper concentrations were reproducible within 8% ($\pm 2\sigma$), based on the multiple identical experiments used to determine equilibration times and therefore includes both analytical uncertainty and experimental error.

Three series of experiments were run to vary temperature, NaCl concentration and total acetate concentration. Temperatures were 50°C, 150°C and 250°C and NaCl concentration was varied between 0.001 m and 2 m at each temperature. Experiments at low NaCl concentrations (<0.001m) were not conducted because Cu(I) would disproportionate to Cu(II) and native copper. At high NaCl concentrations (>2 m) high cuprite solubility (e.g., approximately 10000 ppm total copper) exceeded the pH-buffer capacity and prevented accurate measurements of copper concentration. For all copper(I)-chloride complexing experiments the concentration of total acetate was 0.4 m (1:1 ratio of NaAc and HAc). Preliminary experiments indicated complexing of copper(I) with acetate so the concentration of total acetate was varied to identify the important copper(I) acetate species and measure their thermodynamic properties. Two series of copper(I)-acetate complexing experi-

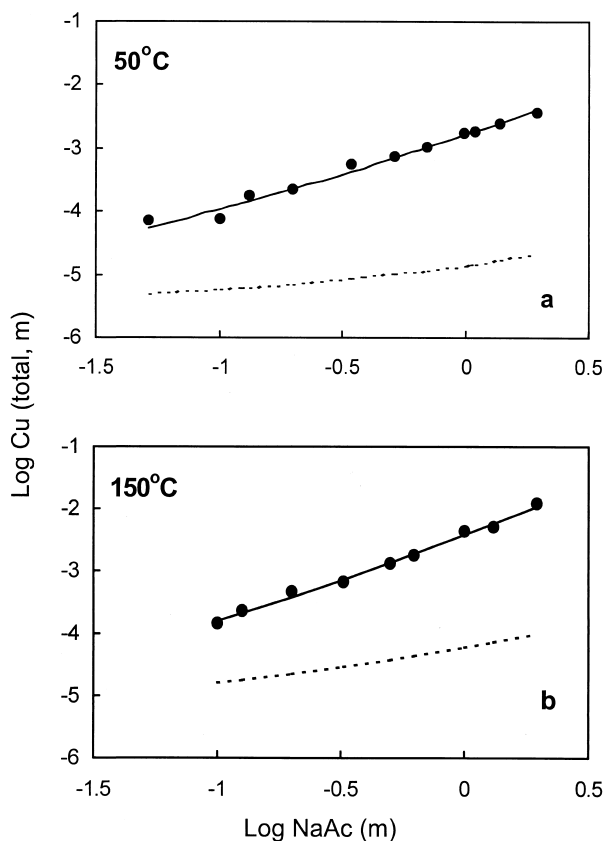
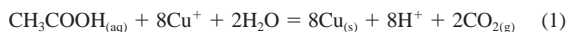


Fig. 2. Cuprite solubility as a function of NaAc concentration in NaAc solutions (Series I) at 50°C (a) and 150°C (b). The solid circles represent experimental data. The solid lines show calculated solubility based on log K values from this study and the dashed lines indicate calculated solubility using log K values for CuAc_(aq) of Shock and Koresky (1993).

ments were run at 50°C and 150°C: Series I without NaCl and Series II with 0.1 m NaCl. Sodium acetate and acetic acid concentrations were varied between 0.01 m and 2 m (i.e., total acetate concentration between 0.02 m and 4 m). Copper(I)-acetate complexing experiments at 250°C were unsuccessful as many tubes exploded in experiments containing sodium acetate concentrations greater than approximately 1 m total acetate. The explosions probably resulted from gases generated from the minor decarboxylation of acetate (e.g., Palmer and Drummond, 1986). Another possibility is the thermochemical reduction of copper(I) to native copper by acetate:



This is unlikely because measured quench pH was the same or greater than the initial pH and no native copper was observed in experiments where pressure was noted but the tubes remained intact.

3. RESULTS

The solubility measurements of cuprite in chloride- and acetate-bearing solutions are tabulated in Appendices I and II, and shown in Figures 2, 3 and 4. In general, copper concentrations increase with increasing temperature and acetate and chloride concentrations. Note that the pH of the HAC-NaAc buffer increases with increasing temperature because of the change of ionization constants for acetic acid (Mesmer et al., 1989), resulting in smaller increases in copper concentration

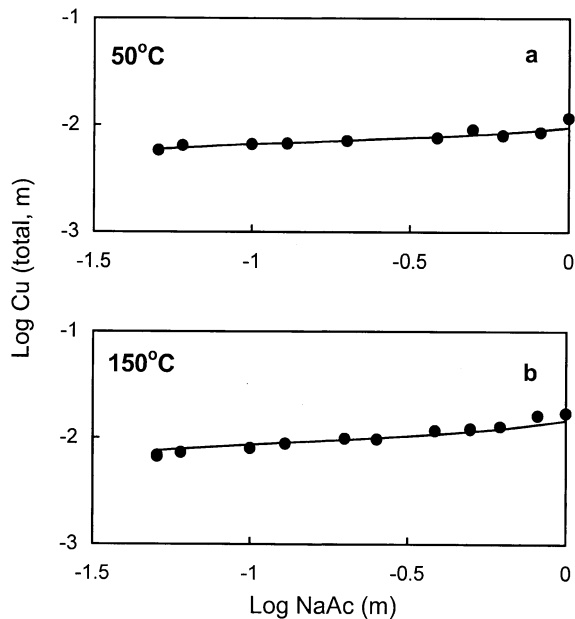


Fig. 3. Cuprite solubility as a function of NaAc concentration in NaAc and 0.1 m NaCl solutions (Series II) at 50°C (a) and 150°C (b). The solid circles represent experimental data. The solid lines show calculated solubility based on log K values from this study.

with temperature than would be expected if the pH remained constant. The details of the results from each set of experiments are presented below.

In the acetate-complexing experiments, copper concentrations increased with increasing acetate concentration and increasing temperature (Fig. 2 and 3). Note that the total acetate in solution is twice the amount shown in the tables because the ratio of HAC to NaAc is one. In the acetate-complexing experiments without NaCl the copper concentrations increase from 4.3 ppm to 226 ppm between 0.05 m NaAc and 1.97 m NaAc at 50°C and 9 ppm to 472 ppm between 0.1 m NaAc and 1.96 m NaAc at 150°C (Appendix 1). In the acetate-complexing experiments with 0.1 m NaCl added, the copper concentrations are higher (359 ppm to 612 ppm at 50°C and 424 ppm to 896 ppm at 150°C, Appendix 1 and Fig. 3), indicating the presence of copper(I)-chloride complexing. The slopes of copper versus NaAc are shallower than in the NaCl-absent experiments, indicating that Cu-chloride complexing predominated at all acetate concentrations but Cu-acetate complexing became more important at higher acetate concentrations.

Figure 4 shows the results of cuprite solubility measurements at 50°C, 150°C and 250°C as a function of chloride concentration. The measured copper concentrations range from 18 ppm to 9740 ppm and increase with increasing chloride concentration but the slopes of the curves are shallow at low and high chloride concentrations. This reflects a change in copper complexing at low chloride concentration (e.g., Cu-acetate to Cu-chloride) and increasing pH at high chloride concentration (Appendix 2). The pH increases at high chloride concentrations at all temperatures because the amount of cuprite dissolving increases and the hydrogen ion activity decreases and the capacity of the pH buffer was exceeded. Note that the copper concentrations approach the concentration of the buffer chem-

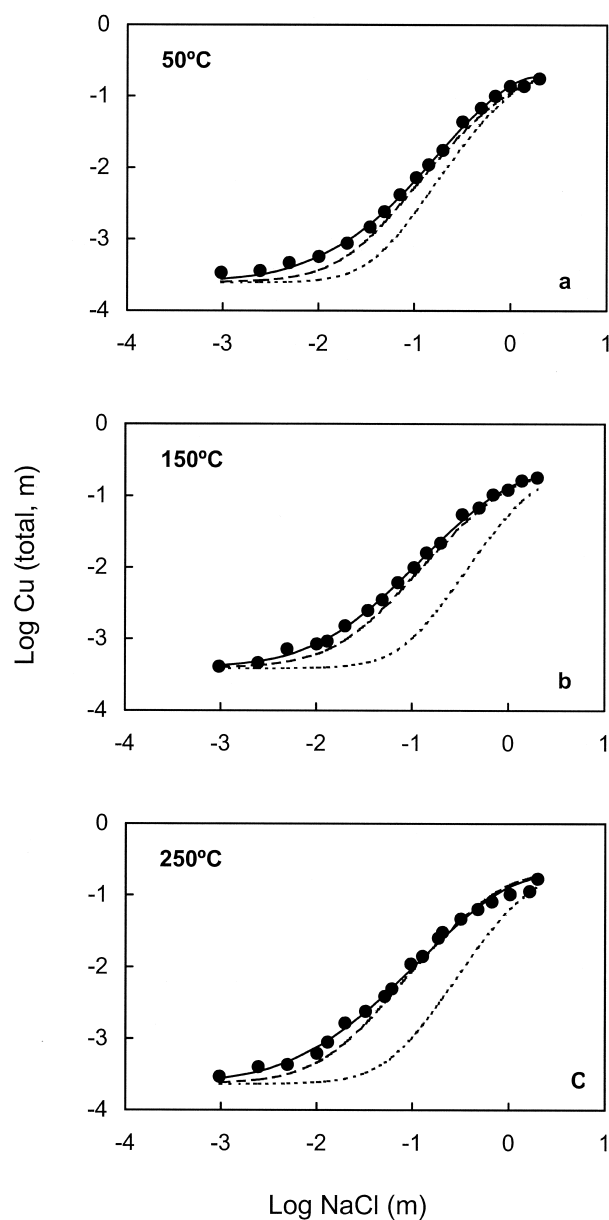


Fig. 4. Cuprite solubility as a function of NaCl concentration in NaCl solutions (Series III) at 50°C (a), 150°C (b) and 250°C (c). The solid circles represent experimental data. The solid lines show calculated solubility based on log K values from this study, the dashed and dotted lines indicate calculated solubility using log K values of Xiao et al. (1998) and Sverjensky et al. (1997), respectively.

icals at the highest copper concentrations for all temperatures (Fig. 4). At all temperatures the slopes of the curves at intermediate NaCl concentrations are greater than one, indicating a mixture of $\text{CuCl}_{(\text{aq})}$, CuCl_2^- and possibly CuCl_3^{2-} . Copper concentrations increase slightly with increasing temperature between 50°C and 150°C at the same chloride concentrations and then decrease between 150°C and 250°C. This is a result of the pH of the HAc/NaAc buffer increasing with temperature as mentioned above.

There were competing effects on the solubility of cuprite in our experiments, i.e., increased solubility with increasing tem-

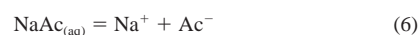
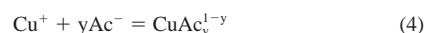
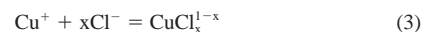
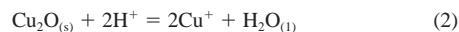
perature and acetate and chloride concentrations, and decreased solubility with increasing pH as a result of increasing temperature and the pH buffer capacity being exceeded in the high solubility experiments. We account for all these effects in the quantitative interpretation of the experimental data.

4. DATA INTERPRETATION

The aims of this section are to identify the copper(I) complexes in our cuprite solubility experiments and derive accurate log K values of their formation reactions. Formation constants of copper(I) chloride and acetate complexes were fitted to the solubility data using non-linear least squares regression according to the following procedure. First, a thermodynamic model was developed to include the likely copper complexes and relevant mass action, mass balance, charge balance and activity coefficient equations. Second, the solubility of cuprite was predicted, using the equilibrium constants of previous studies, and compared with our measured results. Third, log K values were optimized by minimizing residuals between calculated and observed cuprite solubility for each series of experiments at each temperature. Finally the uncertainties of the optimized log K values were estimated by mapping residual contours around optimized log K values. This also helped in evaluating the accuracy of the thermodynamic model, i.e., the number and identity of the copper complexes.

4.1. Thermodynamic Model and Calculation of Cuprite Solubility

Equilibria that control cuprite solubility in NaCl and NaAc solution can be described by the following mass action equations:



where subscripts x and y represent the number of chloride and acetate ligands, respectively. The presence of hydroxide complexes of Cu and Na was probably insignificant in our experiments, based on the pH ranges in our experiments (approximately 4.6–4.8 at 50°C and 5.5–6.1 at 250°C) and published values of hydrolysis constants for Cu(I) (e.g., $\log K_{\text{CuOH}} = -11.36$ at 25°C and -6.39 at 250°C; calculated from results of Var'yash, 1990), Ag(I) ($\log K_{\text{AgOH}} = -12.0$ at 25°C) and Na^+ ($\log K_{\text{NaOH}} = -14.18$ at 25°C; Baes and Mesmer, 1976; -10.6 at 250°C; Pokrovskii and Helgeson, 1995)

The standard states used in this study are defined as the pure mineral and liquid at the temperature and pressure of interest for solid phases and H_2O , and a hypothetically ideal one molal solution referenced to infinite dilution at the temperature and pressure of interest. The activity of H_2O was assumed to be unity and molal activity coefficients of neutral species were also assumed to be unity. For the charged species, the individual molal activity coefficients were calculated using the following extended Debye-Hückel expression (Helgeson, 1969):

$$\log \gamma_i = -\frac{AZ_i^2 I^{1/2}}{1 + \tilde{a}BI^{1/2}} + B^*I \quad (9)$$

Where γ_i and Z_i are the activity coefficient and the charge of the *i*th ion, *I* is true ionic strength, **A** and **B** are Debye-Hückel coefficients, \tilde{a} refers to the "distance of closest approach" of the *i*th ion and B^* is deviation function taken from Table 26 of Helgeson et al. (1981). For NaAc solutions, there are no B^* parameters available, so those for NaCl were used, as in the Giordano (1989) study of anglesite solubility in acetate solutions. We tested alternative B^* parameters for acetate solutions and

Table 1. Equilibrium constants used in the calculations of this study.

Equation	Log K 50°C	150°C	250°C	Source
$\text{Cu}_2\text{O}_{(s)} + 2\text{H}^+ = 2\text{Cu}^+ + \text{H}_2\text{O}$	-1.498	-0.086	1.017	SUPCRT92 (Johnson et al., 1992)
$\text{NaCl}_{(\text{aq})} = \text{Na}^+ + \text{Cl}^-$	0.691	0.214	-0.478	SUPCRT92 (Johnson et al., 1992)
$\text{NaAc}_{(\text{aq})} = \text{Na}^+ + \text{Ac}^-$	0.06	-0.44	-1.25	Shock & Koresky (1993)
$\text{HCl}_{(\text{aq})} = \text{H}^+ + \text{Cl}^-$	0.792	0.517	-0.389	SUPCRT92 (Johnson et al., 1992)
$\text{HAc}_{(\text{aq})} = \text{H}^+ + \text{Ac}^-$	-4.786	-5.180	-5.978	Mesmer et al. (1989)

the results showed that calculated copper concentrations are not sensitive to our choice, i.e., the difference between predicted copper concentrations using B^* parameters for either NaCl or LiCl at 150°C is only 0.2%.

The mass balance equations for chloride, acetate, sodium and charge are:

$$m_{\text{Cl}_{(\text{total})}} = m_{\text{Cl}^-} + \sum x m_{\text{CuCl}_x^{1-x}} + m_{\text{NaCl}_{(\text{aq})}} + m_{\text{HCl}_{(\text{aq})}} \quad (10)$$

$$m_{\text{Ac}_{(\text{total})}} = m_{\text{Ac}^-} + \sum y m_{\text{CuAc}_y^{1-y}} + m_{\text{NaAc}_{(\text{aq})}} + m_{\text{HAc}_{(\text{aq})}} \quad (11)$$

$$m_{\text{Na}_{(\text{total})}} = m_{\text{Na}^+} + m_{\text{NaCl}_{(\text{aq})}} + m_{\text{NaAc}_{(\text{aq})}} \quad (12)$$

$$2m_{\text{H}^+} + 2m_{\text{Cu}^+} + m_{\text{Na}^+} = \sum [(1-x)m_{\text{CuCl}_x^{1-x}}] + \sum [(1-y)m_{\text{CuAc}_y^{1-y}}] + m_{\text{Cl}^-} + m_{\text{Ac}^-} \quad (13)$$

Where m refers to the molal concentrations of the subscripted components (i.e., $\text{Cl}_{(\text{total})}$, $\text{Ac}_{(\text{total})}$ and $\text{Na}_{(\text{total})}$) and aqueous species. Equations 10 to 13 can be solved simultaneously to obtain the concentrations and activities of all the species in the solution, provided that all the equilibrium constants are known and activity coefficients are estimated. The total dissolved copper concentration can be calculated by summing up the concentrations of all copper-bearing species:

$$m_{\text{Cu}_{(\text{total})}} = m_{\text{Cu}^+} + \sum m_{\text{CuCl}_x^{1-x}} + \sum m_{\text{CuAc}_y^{1-y}} \quad (14)$$

The equilibrium constants for the relevant reactions, except for those involving Cu complexes, are listed in Table 1. The dissociation constants of $\text{HCl}_{(\text{aq})}$ and $\text{NaCl}_{(\text{aq})}$ were calculated with SUPCRT using the original database (Johnson et al., 1992). The dissociation constants for $\text{HAc}_{(\text{aq})}$ are experimentally determined values (Mesmer et al., 1989), whereas those for $\text{NaAc}_{(\text{aq})}$ are from theoretical estimates (Shock and Koresky, 1993) that are based on room-temperature experimental data and are in good agreement with the potentiometric experimental data between 20°C and 240°C of Fournier et al. (1998). The dissolution constants for cuprite (i.e., log K for Eqn. 2) were also calculated using SUPCRT92 with the original 1992 database (Johnson et al., 1992). The formation constants for copper(I) acetate and chloride complexes were fitted to our experimental data (i.e., Eqn. 2 and 3).

4.2. Regression Method

Equilibrium constants could not be derived from our experimental data using conventional regression methods (e.g., multiple linear regression). For example, assuming two copper(I) acetate complexes were present in our copper(I)-acetate experiments (no copper chloride complexes), the solubility of cuprite can be calculated by combining the mass balance for copper (Eqn. 14) and equilibrium constant expressions for cuprite solubility (K_1 ; Eqn. 2) and the formation of acetate complexes ($K_{\text{CuAc}_{(\text{aq})}}$, $K_{\text{CuAc}_2^-}$; Eqn. 4):

$$m_{\text{Cu}_{(\text{total})}} = K_1^{1/2} a_{\text{H}^+} \left(\frac{1}{\gamma_{\text{Cu}^+}} + \frac{K_{\text{CuAc}_{(\text{aq})}} a_{\text{Ac}^-}}{\gamma_{\text{CuAc}_{(\text{aq})}}} + \frac{K_{\text{CuAc}_2^-} a_{\text{Ac}^-}^2}{\gamma_{\text{CuAc}_2^-}} \right) \quad (15)$$

γ and a represent the individual molal activity coefficient and activity of the subscripted species. The formation constants of copper(I) species were regressed to our experimental data using a linear least squares regression method; however, negative values of K resulted. In an attempt to circumvent this problem, a modified least squares method

was used (ridge regression; Wood and Crerar, 1985). This was also unsuccessful because the standard error of estimation increased continuously with an increasing ridge regression coefficient/factor.

We therefore developed a non-linear least square method to derive log K values for copper(I) acetate and chloride complexes by minimizing the difference between calculated and measured solubility data. The residual function to be minimized is defined as:

$$S = \sum [\log(m_{\text{Cu}_{(\text{total, measured})}}) - \log(m_{\text{Cu}_{(\text{total, calculated})}})]^2 \quad (16)$$

where the $m_{\text{Cu}_{(\text{total, measured})}}$ values are the measured copper concentrations and the $m_{\text{Cu}_{(\text{total, calculated})}}$ values are calculated using a distribution of species calculation for each experiment. Each series of experiments at each temperature is treated separately. The calculated solubility depends on the values of the equilibrium constants for reactions shown in the thermodynamic model section above. The residual S is minimized by a nonlinear iterative simplex method for function minimization (Nelder and Mead, 1965), which was implemented using the MatLab programming environment (Borse, 1997). Published log K values (i.e., Sverjensky et al., 1997; Xiao et al., 1998) were used as initial guesses and multiple parameters (i.e., log K values) were optimized simultaneously.

4.3. Copper(I)-Acetate Complexing

The log K values for copper(I)-acetate cumulative formation reactions (Eqn. 4) were fitted to experimental data (Series I; Appendix 1) at 50°C and 150°C. The slopes of measured log Cu versus log NaAc concentrations for both temperatures are higher than 1, suggesting the presence of two complexes (Fig. 2); therefore, one complex is unlikely to be sufficient to describe the experimental data at both temperatures. We tested the possibility of only one complex by fitting with only one fit parameter (log K for the formation of $\text{CuAc}_{(\text{aq})}$ in one case and CuAc_2^- in another) but the resulting calculated slopes of log Cu versus log NaAc concentrations were either too shallow or too steep and the residuals were large (e.g., at 50°C, $S = 0.13$ for $\text{CuAc}_{(\text{aq})}$ and $S = 1.2$ for CuAc_2^- , compared to $S = 0.057$ with both complexes).

To assess the accuracy of the model (i.e., number and type of complexes) and fitted log K values, we calculated maps of the residual function (S) as a function of log K values (Fig. 5). We calculated residuals using three copper(I) acetate complexes to address the possibility that more than two complexes were present in our experiments. This results in a 3-dimensional object, but for clarity we show 2-dimensional cross sections of residual contours in Figure 5. Two example residual plots are shown for the 150°C copper-acetate (Series I) experiments, one for log $K_{\text{CuAc}_{(\text{aq})}}$ versus log $K_{\text{CuAc}_2^-}$ (Fig. 5a) and another for log $K_{\text{CuAc}_{(\text{aq})}}$ versus log $K_{\text{CuAc}_3^{2-}}$ (Fig. 5b). There are several important aspects to note. First, there is a single minimum with respect to log $K_{\text{CuAc}_{(\text{aq})}}$ and log $K_{\text{CuAc}_2^-}$ at a given value of log $K_{\text{CuAc}_3^{2-}}$ (e.g., Fig. 5a). This indicates that both complexes were present in significant concentrations in the experimental solutions. Second, there is no single minimum for log $K_{\text{CuAc}_3^{2-}}$ (e.g., Fig. 5b). Statistically, this means the model is "ill-conditioned" and has more parameters than are needed (Draper and Smith, 1998; p. 512). While CuAc_3^{2-} may have been present in the experiments it was not in concentrations high enough to be detected unequivocally. We calculated speciation plots to see what the possible concentrations of CuAc_3^{2-} might have been in our experiments (Fig. 6). Using an estimate of log $K_{\text{CuAc}_3^{2-}} = 1.5$, the calculated concentration of CuAc_3^{2-} is approximately 10 mol.% of the total dissolved copper at 150°C (Fig. 6b). Higher values of log $K_{\text{CuAc}_3^{2-}}$ result in higher predicted

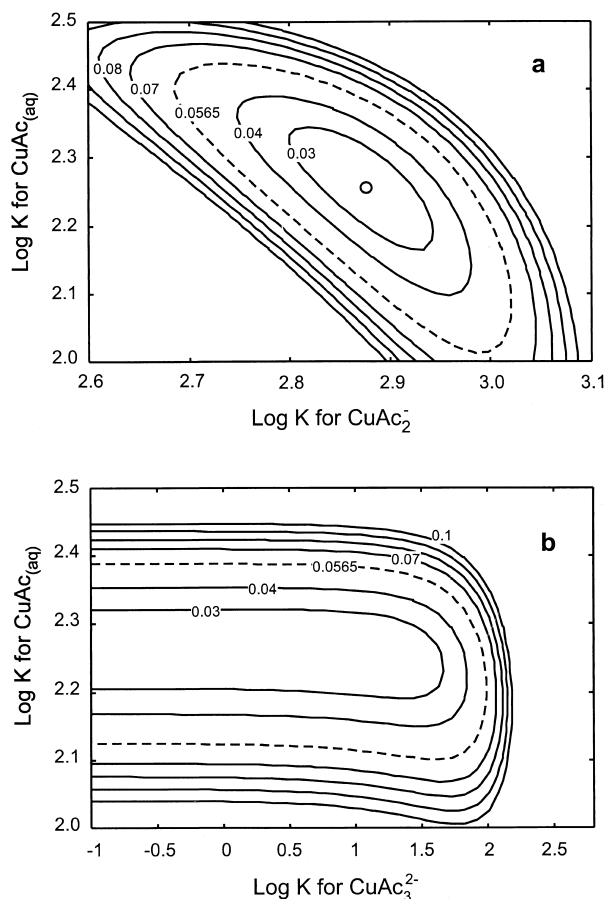


Fig. 5. Residual contours of copper-acetate complexing experiments (Series I, without NaCl) at 150°C. The circle shows the value of fitted log K for $\text{CuAc}_{(\text{aq})}$ and CuAc_2^- . The lines and values represent the residuals between measured and calculated solubility as a function of the log K values for copper(I) acetate complexes (a) $\text{CuAc}_{(\text{aq})}$ vs CuAc_2^- ; (b) $\text{CuAc}_{(\text{aq})}$ vs CuAc_3^{2-} , see text).

concentrations of CuAc_3^{2-} , up to 30 mol.% at a log $K_{\text{CuAc}_3^{2-}} = 2$ (the maximum approximate value at the 95% confidence interval—see discussion below), but the residuals double. In any case, if the complex exists, we could estimate an upper limit on the log $K_{\text{CuAc}_3^{2-}}$, e.g., <1.5 to 2 at 150°C, and <1 to 1.5 at 50°C based on a similar residual map.

The fitted log K values at 50°C and 150°C for our preferred model ($\text{CuAc}_{(\text{aq})}$ and CuAc_2^-) are presented in Table 2. The calculated and measured solubilities of cuprite in acetate solutions are in excellent agreement (Fig. 2). The log $K_{\text{CuAc}_{(\text{aq})}}$ decreases with increasing temperature; however, the log $K_{\text{CuAc}_2^-}$ increases with increasing temperature (Table 2). This indicates CuAc_2^- complex is more important at higher temperature, reflected in the calculated speciation of copper-acetate complexes (Fig. 6b).

4.4. Evaluation of Uncertainties

The residual contours also provide a convenient way to estimate uncertainties in estimated log K values. A statistical method was used to calculate approximate confidence regions for non-linear regression (Draper and Smith, 1998). As an example, the approximate confidence region at the 95% confidence level for the 150°C copper(I)-acetate experiments is within the residual contour of 0.0565 (Fig. 5). At 150°C the maximum estimated uncertainty in log $K_{\text{CuAc}_{(\text{aq})}}$ is approximately ± 0.21 and for log $K_{\text{CuAc}_2^-}$ it is approximately ± 0.16 . The actual uncertainties in both values are likely to be smaller because we did not account for the covariance that is evident in Figure 5. The uncertainties

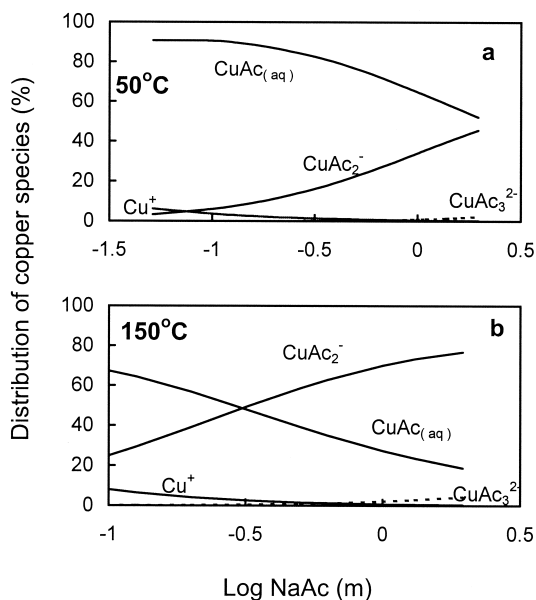


Fig. 6. Speciation of copper(I) acetate complexes as a function of NaAc concentration for copper-acetate complexing experimental solutions (Series I, without NaCl) at 50°C (a) and 150°C (b).

are slightly larger for the 50°C experiments (Table 2) because there is slightly more scatter in the lower temperature data (Fig. 2).

4.5. Copper(I)-Chloride Complexing

The copper(I)-chloride experimental data were interpreted using the same methodology as for the copper-acetate data. At low chloride concentrations (<0.01 m), the slopes of copper versus chloride are shallow, reflecting little copper-chloride complexing and copper-acetate complexes predominating (based on our results above). We used the log K values for the copper-acetate complexes derived above in fitting log K values for copper chloride complexes for experiments at 50°C and 150°C. For the copper(I)-chloride experiments at 250°C, log K values of both copper(I) chloride and acetate complexes were fitted simultaneously to the experimental data. For the copper(I)-chloride complexing experiments at all temperatures, the data suggest at least two copper chloride complexes in the solutions; however, we tested several alternatives. A single copper(I) chloride complex (either $\text{CuCl}_{(\text{aq})}$ or CuCl_2^-) is insufficient to describe the experimental data, based on analogous calculations and fits in the acetate section above. To test for the possible existence of the third copper(I) chloride complex (CuCl_3^{2-}), we included three complexes (i.e., $\text{CuCl}_{(\text{aq})}$, CuCl_2^- and CuCl_3^{2-}) in our calculations.

Figure 7a shows residual contours as a function of log $K_{\text{CuCl}_{(\text{aq})}}$ versus log $K_{\text{CuCl}_2^-}$ and Figure 7b shows contours for log $K_{\text{CuCl}_3^{2-}}$ versus log $K_{\text{CuCl}_2^-}$ for copper(I)-chloride complexing experiments at 150°C. Similar to the situation of Cu-Ac complexing experiments discussed

Table 2. Equilibrium constants derived from cuprite solubility experiments.

Reaction	log K		
	50°C	150°C	250°C
$\text{Cu}^+ + \text{Ac}^- = \text{CuAc}_{(\text{aq})}$	2.55 ± 0.15	2.26 ± 0.21	
$\text{Cu}^+ + 2\text{Ac}^- = \text{CuAc}_2^-$	2.49 ± 0.3	2.88 ± 0.16	
$\text{Cu}^+ + \text{Cl}^- = \text{CuCl}_{(\text{aq})}$	$3.99 (-0.2/+0.1)$	3.76 ± 0.1	3.97 ± 0.1
$\text{Cu}^+ + 2\text{Cl}^- = \text{CuCl}_2^-$	$5.01 (-0.9/+0.4)$	5.12 ± 0.1	5.20 ± 0.2
$\text{Cu}^+ + 3\text{Cl}^- = \text{CuCl}_3^{2-}$	$5.51 (-0.8/+0.5)$		

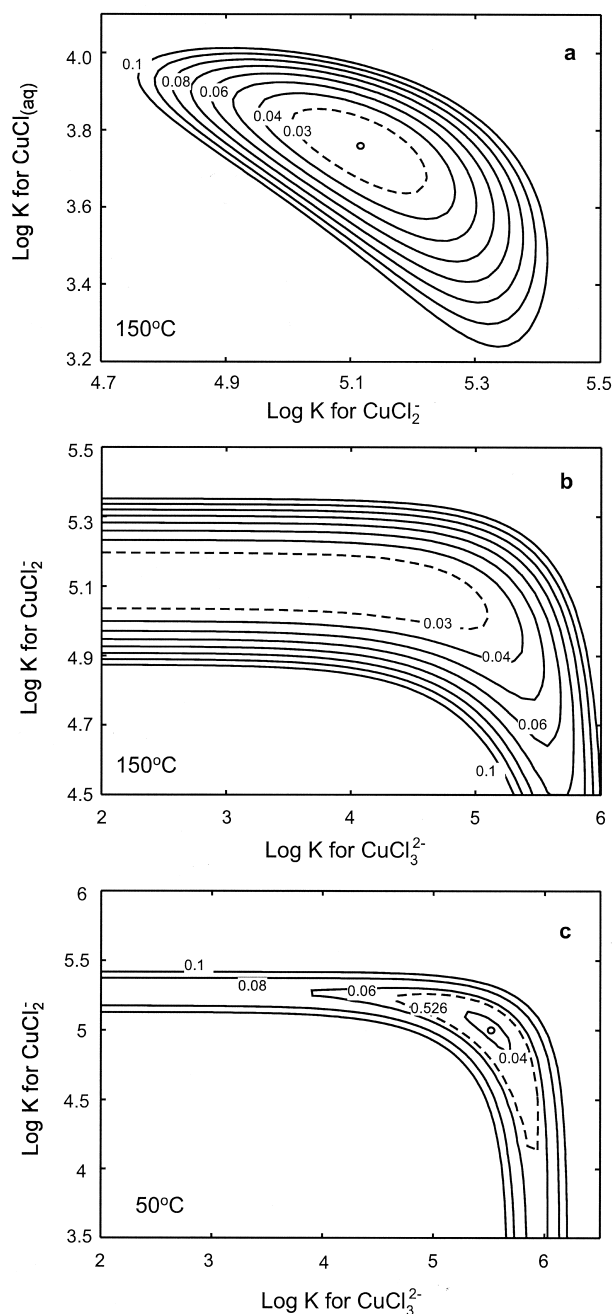


Fig. 7. Residual contours of copper-chloride complexing experiments at 150°C (a and b) and 250°C (c). The circles show the values of fitted log K for $\text{CuCl}_{(\text{aq})}$ and CuCl_2^- . The lines and values represent the residuals between measured and calculated solubility as a function of log values of copper(I) chloride complexes and dot lines show a approximate 95% confidence region (see text for details).

above, there is a single minimum in the residuals for $\log K_{\text{CuCl}_{(\text{aq})}}$ versus $\log K_{\text{CuCl}_2^-}$ (Fig. 7a), indicating the presence of the two complexes. In contrast, and again similarly to the Cu-acetate complexing, there is no single minimum for log K values for CuCl_3^{2-} at 150°C (Fig. 7b) and similarly at 250°C; however, there is at 50°C (Fig. 7c). This indicates that CuCl_3^{2-} existed in our 50°C experiments but we cannot say unequivocally that it existed in our experiments at higher temperatures. Figure 8 shows the calculated percentages of copper species in experimental solutions including three copper(I) chloride complexes

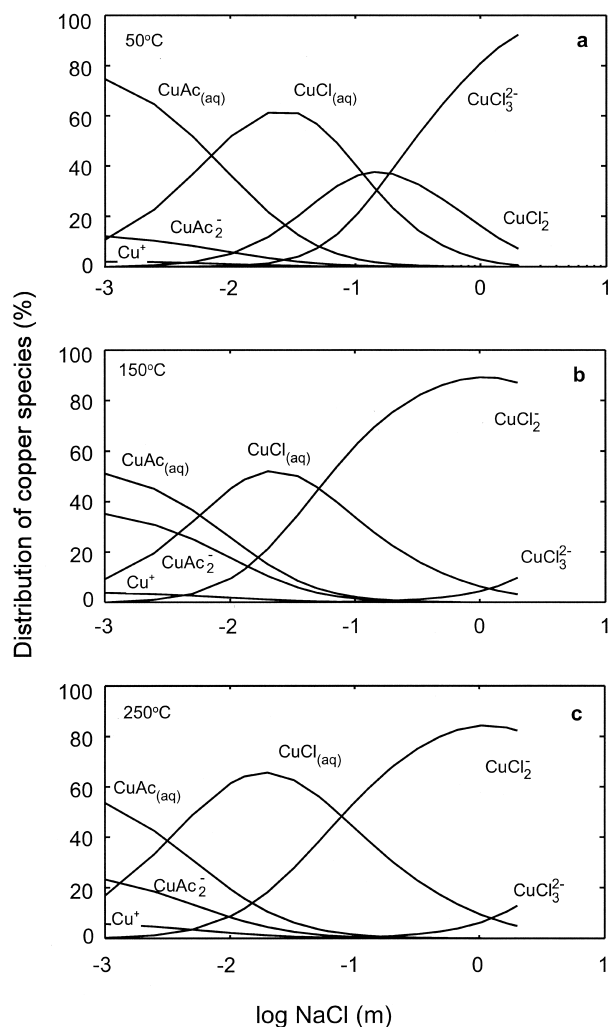


Fig. 8. Speciation of copper(I) complexes as a function of NaCl concentration for copper-chloride complexing experimental solutions with 0.2 m NaAc and HAc (Series III) at 50°C (a), 150°C (b) and 250°C (c). See Text for details.

($\text{CuCl}_{(\text{aq})}$, CuCl_2^- and CuCl_3^{2-}) and the fitted log K values listed in Table 2. The log K values for CuCl_3^{2-} (3.54 and 3.78 at 150°C and 250°C, respectively) used to estimate how much of the complex might have existed in our experiments are from Sverjensky et al. (1997). The speciation plots at all temperatures show that $\text{CuAc}_{(\text{aq})}$ and CuAc_2^- complexes are important at lower chloride concentration (<0.01 m), $\text{CuCl}_{(\text{aq})}$ predominates at chloride concentrations between approximately 0.01–0.1 m, and CuCl_2^- (and CuCl_3^{2-} at 50°C) predominates at higher chloride concentration. The concentrations of CuCl_3^{2-} are predicted to be small in most experimental solutions (<10 mol% of total copper at the highest chloride concentrations) at 150°C and 250°C. If the $\log K_{\text{CuCl}_3^{2-}}$ values of Xiao et al. (1998) are correct, then the percentage of CuCl_3^{2-} would be even smaller. This, combined with the information from residual map, indicates that we cannot derive an accurate log K for this complex from the experiments at temperatures of 150°C and 250°C of this study, although we can still estimate an upper limit for $\log K_{\text{CuCl}_3^{2-}}$ based on the 95% confidence contour on the residual maps, i.e., <5 at 150°C (e.g., Fig. 7b) and 250°C. However, at 50°C CuCl_3^{2-} was an important complex in our experiments, based on the residual plot (Fig. 7c) and the speciation plot (Fig. 8a), which shows that CuCl_3^{2-} predominated at NaCl concentration greater than 0.5 m.

The experimental data for chloride concentrations greater than 0.1 molal were regressed separately to include the possibility of poly-

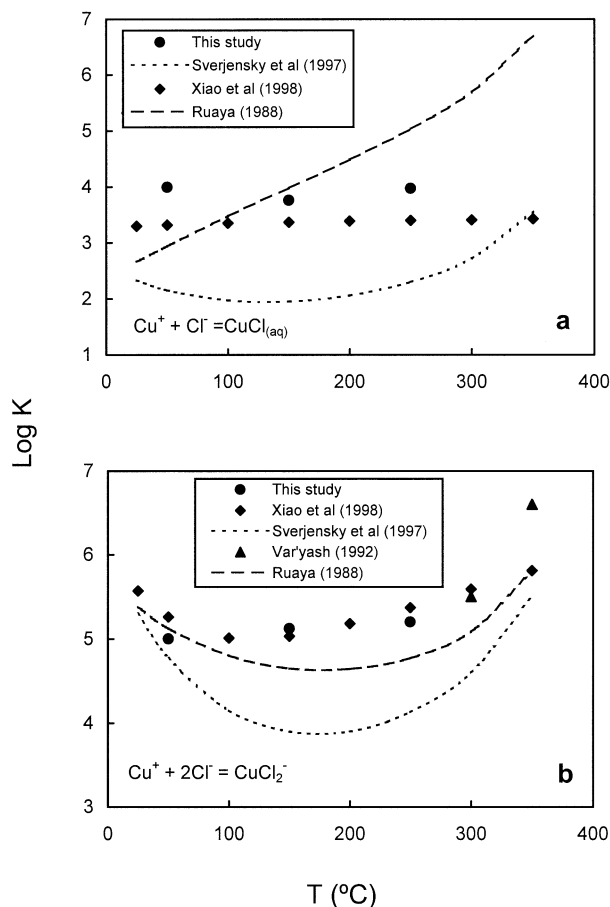


Fig. 9. Formation constants for $\text{CuCl}_{(\text{aq})}$ (a) and CuCl_2^- (b) complexes at temperatures from 25°C to 350°C. Results from this study and several previous studies (Ruaya, 1988; Var'yash, 1992; Sverjensky et al., 1997 and Xiao et al., 1998) are shown for comparison.

nuclear copper(I) chloride complexes such as $\text{Cu}_2\text{Cl}_{2(\text{aq})}$. The residuals increased markedly (e.g., $S > 1$), indicating that poly-nuclear complexes do not exist under the conditions of our experiments.

The fitted log K values for $\text{CuCl}_{(\text{aq})}$ and CuCl_2^- at 50°C, 150°C and 250°C, and CuCl_3^{2-} at 50°C are listed in the Table 2 and plotted on the residual map in Figure 7a for the 150°C experiments. The calculated cuprite solubility based on the fitted log K values is plotted in Figure 4, showing good agreement between calculated and measured solubility, except for several low solubility data points for 50°C experiments. The fitted log K values for the formation of $\text{CuCl}_{(\text{aq})}$ change little or within estimated uncertainty with increasing temperature, although the value 150°C is slightly lower (Table 2; Fig. 9a). The log K values for CuCl_2^- increase from 5.01 at 50°C to 5.20 at 250°C.

The uncertainties in the fitted log K values for copper(I) chloride complexes were estimated using the same approach as for copper(I)-acetate. For example, the approximate 95% confidence region is within the 0.0314 contour for 150°C experiments (Fig. 7a), indicating an uncertainty of ± 0.1 in the log K values for both $\text{CuCl}_{(\text{aq})}$ and CuCl_2^- . The uncertainties of log K values for 50°C and 250°C experiments shown in the Table 2 were estimated in the same way. The uncertainties of log K values at 50°C are larger than other temperatures because the fit was more complicated because of the additional complex (CuCl_3^{2-}). As mentioned above, covariance was not accounted for so the fitted log K values are likely to be even more accurate.

As a test of the fitted properties, the solubility of cuprite was calculated for the Series II copper(I)-acetate experiments (total acetate concentration varied between 0.1 m and 2 m, NaCl concentration constant at 0.1 m) and compared with the experimental data. Figure 3

shows excellent agreement between calculated and measured solubility. Copper(I) chloride complexes predominated in the experimental solutions although copper(I) acetate complexes contributed in a minor way to the solubility of cuprite as seen by the slight increase in slope of cuprite solubility with increasing acetate concentration (Fig. 3).

Finally, to test the accuracy of cuprite dissolution constants (i.e., log K for Eqn. 2) calculated with SUPCRT from properties of Helgeson et al. (1978) for cuprite and Shock and Helgeson (1988) for Cu^+ —on which our regression of log K for copper chloride and acetate complexes were based—we fitted simultaneously log K for cuprite dissolution and log $K_{\text{CuCl}_{(\text{aq})}}$ and $K_{\text{CuCl}_2^-}$ to our copper-chloride complexing experiments. Our fitted log K values for cuprite dissolution are -0.0857 ± 0.15 at 150°C and 1.02 ± 0.3 at 250°C, in excellent agreement with those calculated with SUPCRT (-0.086 and 1.017; Table 1). Fitted values of log $K_{\text{CuCl}_{(\text{aq})}}$ and $K_{\text{CuCl}_2^-}$ are also within the error range of our corresponding values listed in Table 2. Our fitted log K value for cuprite dissolution at 50°C is -1.20 ± 0.2 , 0.3 log units higher than the value calculated with SUPCRT (-1.498 ; Table 1), and the association constants for $\text{CuCl}_{(\text{aq})}$ and CuCl_2^- decreased by 0.4 and 1 log units, respectively. We prefer the log K values for cuprite dissolution calculated with SUPCRT and the log K values for copper complexes fitted above (Table 2), because of the greater amount of scatter in our low-salinity experimental data at 50°C (Fig. 4a).

5. DISCUSSION

5.1. Comparison with Previous Work

5.1.1. Copper(I) acetate complexes

The only log K values for copper(I) acetate complexes available in the literature are for $\text{CuAc}_{(\text{aq})}$ (0.32 at 50°C and 0.74 at 150°C, Shock and Koretsky, 1993). Our data suggest not only much higher log K value for $\text{CuAc}_{(\text{aq})}$, but also the existence of a new copper(I) acetate complex CuAc_2^- . For comparison, the measured and calculated solubility of cuprite in acetate solutions is shown in Figure 2. The results show that the solubility calculated using properties from Shock and Koretsky (1993) underestimates the measured solubility by approximately an order of magnitude at low acetate concentration and the difference increases with increasing acetate concentration. The discrepancy is probably because of a lack of experimental and thermodynamic data for copper(I) acetate complexes in their calculations, which were based on a correlation with other monovalent element-acetate complexes such as Na^+ , K^+ , Li^+ and Ag^+ , where there was poor agreement (see Fig. 7a in Shock and Koretsky, 1993). More importantly, chemical reactivity and trends of IB group elements (Cu, Ag and Au) are much different from that of monovalent alkali metal ions due to the $d^{10}s^1$ electronic configurations in group IB elements. Cu^+ is expected to form much stronger coordination bonds with ligands compared with Li^+ , K^+ and Na^+ (Greenwood and Earnshaw, 1997). Similarly, the stability constants of Nd^{3+} -acetate complexes from a recent potentiometric study (Wood et al., 2000) are also higher than the theoretical estimates of Shock and Koretsky (1993) by several log units. Furthermore, experimental studies of the acetate complexing with Cu^{2+} (Archer and Monk, 1964) and other metals such as Pb (Giordano, 1989; Yang et al., 1989) and Zn (Yang et al., 1989) suggest two or even three metal-acetate complexes.

5.1.2. Cu-chloride complexes

The derived log K values for copper(I) chloride complexes from this study are plotted in Figure 9 as a function of temperature. Several sets of log K values from previous studies are shown for comparison. Xiao et al. (1998) investigated copper(I)-chloride complexing in 0.01 to 1 m NaCl solutions at temperatures between 40°C and 300°C and suggested a three complex model ($\text{CuCl}_{(\text{aq})}$, CuCl_2^- , CuCl_3^{2-}). Our results for log $K_{\text{CuCl}_{(\text{aq})}}$ are in fair agreement with those of Xiao et al. (1998), although our values are up to 0.5 log units higher (Fig. 9a). The log $K_{\text{CuCl}_2^-}$ values from this study are in excellent agreement with those of Xiao et al. (1998; Fig. 9b), confirming the results of both studies. Xiao et al. (1998) also considered the possibility of CuCl_3^{2-} and provided formation constants for that complex at 25–350°C. Our derived log $K_{\text{CuCl}_3^{2-}} = 5.0 (-0.9/+0.4)$ at 50°C is higher than Xiao et al.'s (1998) value of 3.61 but similar to Sverjensky et al.'s (1997) value of 4.88. Further experimental studies need to be done to refine the log K value for

CuCl_3^{2-} . We refitted the 150°C experimental data of Xiao et al. (1998) using the same methodology as in interpreting our experiments. We found that there is no single minimum in the residuals plotted as a function of log K values ($\log K_{\text{CuCl}_2^-}$ versus $\log K_{\text{CuCl}_3^{2-}}$) and the calculated concentration of CuCl_3^{2-} has a maximum of 5.1% of total copper concentration in their experiments using their log K value of CuCl_3^{2-} . We conclude that in solutions with a chloride concentration less than 2 m between 150°C and 250°C, CuCl_3^{2-} cannot be detected by the methods used in this study and Xiao et al. (1998).

The trend of $\log K_{\text{CuCl}_2^-}$ with temperature also appears to be consistent with the results of Var'yash (1992) at 300°C and 350°C, although there is a discrepancy in the two available values at 350°C (Fig. 9b). Var'yash (1992) used the data of that study and re-interpreted the data of Var'yash and Rekharskiy (1982) and argued that CuCl_2^- was the predominant complex in both studies. They reported log K values at 300°C and 350°C; however, the values may not be accurate because they only used three chloride concentrations, 0.01, 0.1 and 1 m, and could not identify other copper(I) chloride complexes (e.g., $\text{CuCl}_{(\text{aq})}$).

Two other sets of formation constants of copper(I) chloride complexes are shown in Figure 9, based on the empirical and theoretical studies of Ruaya (1988) and Sverjensky et al. (1997). The Ruaya (1988) values were estimated using an isocoulombic method and the Sverjensky et al. (1997) estimation using the equations of state of Tanger and Helgeson (1988). The results of both these studies are in disagreement with the experimental results of our study and those of Xiao et al. (1998), although there is some agreement between Ruaya (1988), Xiao et al. (1998) and our study for CuCl_2^- (Fig. 9b). As Xiao et al. (1998) discussed, Sverjensky et al. (1997) probably underestimated the strength of Cu(I) chloride complexes because of a lack of experimental data.

5.2. Copper Speciation in Hydrothermal Solutions

Equilibrium constants of copper(I) acetate and chloride complexes generated in this study can be used to understand better the transport of copper in hydrothermal fluids. As a simplified example, Figure 10 illustrates the predominance areas of aqueous copper-chloride, -acetate and -hydrosulphide complexes as a function of the activities of $\text{H}_2\text{S}_{(\text{aq})}$ and chloride at 50°C and 150°C. To draw the diagrams we chose a copper concentration known for reduced oil field brines (0.067 ppm, Sverjensky, 1987) and a typical acetate concentration in sedimentary basin fluids (1000 ppm, Kharaka et al., 1986). The pH is fixed at 5 and $\log f\text{O}_2$ (atm scale) is fixed at -60 at 50°C and -50 at 150°C, as reduced sulfur species are stable under these conditions. The formation constants of the copper(I) hydrosulphide complexes are from Mountain and Seward (1999). Copper(I) acetate complexes ($\text{CuAc}_{(\text{aq})}$) predominate in solutions with chloride activity less than 0.001 and $\text{H}_2\text{S}_{(\text{aq})}$ activity less than 10^{-8} . Copper(I) chloride complexes predominate at chloride activities greater than 0.001 and at the acetate concentration used in drawing the diagrams, depending on the activity of $\text{H}_2\text{S}_{(\text{aq})}$ (Fig. 10). At the $\text{H}_2\text{S}_{(\text{aq})}$ activity and Cl⁻ concentration (assumed to be activity in this simplified example) for oil field water defined by Sverjensky (1987) the predominant chloride complex is CuCl_3^{2-} at 50°C and CuCl_2^- at 150°C, although at the lower temperature of 50°C $\text{CuHS}_{(\text{aq})}$ becomes more important (Fig. 10).

6. CONCLUSIONS

The solubility of cuprite has been measured successfully in pH-buffered acetate and chloride solutions between 50°C and 250°C. A new method of interpreting solubility data has been developed to evaluate the accuracy of thermodynamic models used to derive thermodynamic properties from solubility data. The following conclusions can be drawn from this study:

1. The cumulative formation constants for $\text{CuCl}_{(\text{aq})}$ and CuCl_2^- derived in this study are in agreement with the study of Xiao et al. (1998), indicating that previous discrepancies are now resolved. Based on our experimental data, CuCl_3^{2-} is an important complex at 50°C and chloride concentrations greater than approximately 0.5 m, and it may become important at chloride concentrations greater than approximately 2 m at higher temperatures, although new experiments at higher chloride concentration are necessary to confirm its exis-

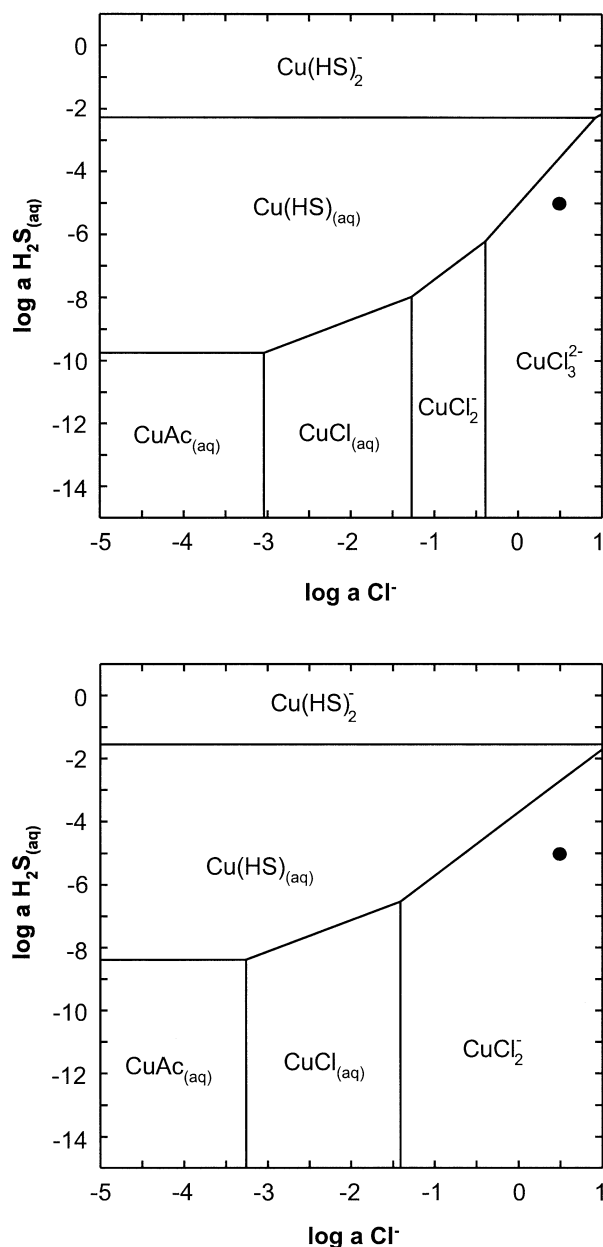


Fig. 10. $\text{H}_2\text{S}_{(\text{aq})}$ -Cl Activity diagrams for copper speciation in brines with 0.067 ppm Copper and 1000 ppm acetate, pH = 5, and $\log f\text{O}_2 = -60$ for 50°C (a) and -50 for 150°C (b). Log K values for copper(I) acetate and chloride complexes from this study, for copper(I) hydrosulphide complexes from Mountain and Seward (1999). The dots represent the H_2S activity and Cl concentration of oil field water defined by Sverjensky (1987).

tence at temperatures greater than 100°C. A higher temperature (up to 350–500°C) experimental study is also needed to better understand copper transport in porphyry and other high temperature hydrothermal copper deposits.

2. The cumulative formation constants for $\text{CuAc}_{(\text{aq})}$ and CuAc_2^- at 50°C and 150°C have been derived from the experiments of this study. The results show that the complexes are more stable than suggested by values estimated theoretically by Shock and Koresky (1993). Copper(I) acetate complexes may be important in transporting copper in low chloride and low sulphide (either low total sulphur or oxidised) waters.

3. The data interpretation method developed in this study is effective and has advantages over conventional interpretation methods, where different speciation models were often discriminated solely on the magnitude of total residuals calculated for the alternate models. The new method uses calculated residual contours and speciation plots to evaluate the speciation models used to interpret solubility data and to estimate uncertainties.
4. The copper(I) chloride complex, CuCl_2^- , is likely to be the most important species for transporting copper in sedimentary basin and oil field brines, although at lower chlorinities CuCl_3^{2-} is likely to become important.

Acknowledgments—This paper is part of the first author's doctoral thesis. WL thanks Monash University for funding his Ph.D. scholarship. The research was funded by an Australia Research Council Large Grant to DCM. JB acknowledges a grant from the Swiss National Science Foundation. We thank C. Gammons, A. Williams-Jones and S. Wood for their constructive and beneficial reviews.

Associate editor: S. A. Wood

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APPENDIX 1. Cuprite solubility in acetate solutions.

Series I at 50°C, without NaCl					Series II at 50°C, with 0.1 m NaCl				
Sample No	NaAc(m)	pH_initial 25°C	pH_final 25°C	Cu(ppm)	Sample No	NaAc(m)	pH_initial 25°C	pH_final 25°C	Cu(ppm)
Fa-1	0.051	4.64	4.63	4.3	AC-1	0.051	4.57	4.59	359
Fa-2	0.101	4.62	4.62	4.8	AC-2A	0.060	4.54	4.55	399
Fa-3	0.133	4.62	4.62	11	AC-2	0.100	4.58	4.57	404
Fa-4	0.199	4.62	4.61	14	AC-3A	0.129	4.55	4.60	408
Fa-5	0.344	4.63	4.62	35	AC-3	0.200	4.61	4.55	427
Fa-6	0.519	4.62	4.61	46	AC-4A	0.386	4.59	4.59	440
Fa-7	0.705	4.63	4.62	64	AC-4	0.500	4.64	4.51	514
Fa-8	0.997	4.65	4.61	105	AC-5A	0.621	4.65	4.64	446
Fa-9	1.101	4.65	4.70	115	AC-5B	0.815	4.69	4.66	464
Fa-10A	1.383	4.87	4.72	148	AC-5	0.999	4.72	4.63	612
Fa-10	1.969	4.74	4.77	226					

Series I at 150°C, without NaCl					Series II at 150°C, with 0.1m NaCl				
Sample No	NaAc(m)	pH_initial 25°C	pH_final 25°C	Cu(ppm)	Sample No	NaAc(m)	pH_initial 25°C	pH_final 25°C	Cu(ppm)
Ac-7	0.100	4.65	4.64	9	AC-1	0.051	4.57	4.70	424
Ac-8A	0.126	4.56	4.61	14	X-1	0.051	4.57	4.77	414
Ac-8	0.200	4.65	4.65	28	AC-2A	0.060	4.54	4.65	453
Ac-9A	0.324	4.58	4.63	39	AC-2	0.100	4.58	4.65	491
Ac-9	0.501	4.67	4.65	75	AC-3A	0.129	4.55	4.63	536
Ac-10A	0.627	4.55	4.56	98	AC-3	0.20	4.61	4.64	594
Ac-10	1.003	4.66	4.65	221	Y-1	0.253	4.58	4.65	579
Ac-11A	1.313	4.65	4.65	239	AC-4A	0.386	4.59	4.63	681
Ac-11	1.960	4.73	4.74	472	AC-4	0.500	4.64	4.66	685
					Z-1	0.500	4.61	4.68	693
					AC-5A	0.621	4.65	4.68	715
					AC-5B	0.815	4.64	4.67	875
					AC-5	0.999	4.72	4.71	896

APPENDIX 2. Cuprite solubility measurements in NaCl solutions buffered by 0.2m NaAc-HAc (Series III).

	50°C				150°C				
	PH_initial 25°C	PH_final 25°C	NaCl(m)	Cu(ppm)	pH_initial 25°C	pH_final 25°C	NaCl(m)	Cu(ppm)	
F-0C	4.63	4.64	0.0010	21	R-0c	4.63	4.63	0.0010	25
F-0b	4.63	4.64	0.0025	22	R-0b	4.63	4.64	0.0025	28
F-0A	4.63	4.64	0.005	28	R-0a	4.63	4.64	0.005	44
F-1	4.62	4.63	0.010	35	R1-1	4.66	4.66	0.010	51
F-2	4.63	4.63	0.020	53	R1-2a	4.65	4.66	0.013	56
F-3A	4.63	4.62	0.035	90	R1-2	4.66	4.65	0.020	92
F-3	4.63	4.63	0.049	147	R1-3A	4.60	4.62	0.035	151
F-4A	4.61	4.63	0.071	254	R1-3	4.65	4.64	0.049	213
F-4	4.60	4.62	0.105	437	R1-4A	4.59	4.62	0.071	370
F-5A	4.59	4.64	0.142	659	R1-4	4.64	4.64	0.105	601
F-5	4.57	4.64	0.199	1052	R1-5A	4.57	4.70	0.142	963
F-6A	4.55	4.70	0.320	2606	R1-5	4.53	4.70	0.199	1323
F-6	4.52	4.84	0.500	4011	R1-6A	4.53	4.77	0.335	3261
F-7A	4.52	4.88	0.699	5874	R1-6	4.58	4.88	0.500	4021
F-7	4.49	5.12	0.997	7955	R1-7A	4.48	5.05	0.699	6059
F-8A	4.43	5.22	1.388	7820	R1-7	4.53	5.10	0.997	6954
F-8	4.41	5.63	2.002	9656	R1-8A	4.42	5.38	1.388	9181
					R1-8	4.47	5.71	2.002	9740

	250°C			
	pH_initial 25°C	pH-final 25°C	NaCl(m)	Cu(ppm)
T-0c	4.63	4.72	0.0010	18
T-0b	4.63	4.73	0.0025	25
T-0a	4.63	4.69	0.0050	26
T-1	4.63	4.73	0.010	38
T-2	4.63	4.75	0.013	55
T-3	4.63	4.76	0.020	100
T-4	4.61	4.78	0.033	146
T-5	4.61	4.83	0.052	237
T-6	4.59	4.84	0.061	302
T-7	4.59	4.89	0.096	669
T-8	4.58	4.92	0.128	848
T-9	4.55	4.99	0.186	1520
T-10A	4.55	5.00	0.206	1827
T-10	4.53	5.11	0.320	2779
T-11	4.50	5.22	0.480	3758
T-12	4.46	5.31	0.672	4733
T-13	4.43	5.65	1.035	5915
T-14	4.40	5.23	1.654	6279
T-15	4.37	5.31	2.006	9206