Cassiterite solubility and tin speciation in supercritical chloride solutions

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Abstract—In order to model the evolution of hydrothermal cassiterite deposits, a quantitative understanding of the chemistry of cassiterite-fluid reactions under supercritical conditions is needed. To obtain this information, the solubility of cassiterite in HCl solutions was measured in closed-system experiments from 400 to 700°C, 1.5 kb, with the oxygen fugacity controlled by nickel-nickel oxide (NNO) and hematite-magnetite (HM). From the measured total chloride and tin concentrations, and the conditions of electrical neutrality at $P$ and $T$, a set of equations was established for each run. By solving the equations simultaneously and finding the best-fit solution for all runs at the same set of $P$ and $T$ conditions, data were obtained on the identity of the dominant aqueous tin-chloride species and the equilibrium constants for the cassiterite dissolution reaction,

$$SnO_2 + XH^+ + nCl^- \rightleftharpoons SnCl_{X-n}^+ + \frac{X}{2} H_2O + \frac{4 - X}{4} O_2,$$

where $X$ is the oxidation state of aqueous tin and $n$ is the ligation number of the tin-chloride species.

With the $f_{O_2}$ of NNO at 400 to 600°C, it was found that $SnCl^+$ and $SnCl_2^+$ are dominant in solution, and at 700°C only $SnCl_3^+$ was detected. With the $f_{O_2}$ of HM at 500 and 600°C, $SnCl_2^+$ was found to be dominant. The equilibrium constants for the cassiterite dissolution reaction are given by

$$\log K = -3.217 + \frac{2.640 \times 10^4}{T} - \frac{2.143 \times 10^7}{T^2},$$

for $X = 2$ and $n = 1$ ($T$ in Kelvin);

$$\log K = 70.080 - \frac{8.246 \times 10^4}{T} + \frac{1.891 \times 10^7}{T^2},$$

for $X = 2$ and $n = 2$; and

$$\log K = 59.064 - \frac{3.511 \times 10^4}{T},$$

for $X = 4$ and $n = 3$.

The bivalent species dominate under natural ore-forming conditions. The solubility of cassiterite is a strong function of temperature, $f_{O_2}$, and pH. In order to obtain significant concentrations of tin in solution it is necessary to have temperatures above about 400°C, $f_{O_2}$’s at or below those defined by NNO, and pH’s at or below those defined by the K-feldspar + muscovite + quartz assemblage. Appropriate changes in any of these conditions can cause cassiterite precipitation. The experimental results are in general agreement with studies of natural systems where the high temperature, low pH, and low $f_{O_2}$ environment is indicated by phase relations and fluid inclusion data.

INTRODUCTION

CASSITERITE, $SnO_2$, is the principle ore mineral of tin, and its primary deposits are usually found to be associated with granitic intrusions. The ore may be found within altered portions of the granite, the so-called greisens, or in hydrothermal veins within the granite or the country rock. Some of the best-known deposits are those of Cornwall (southeast England), Erzgebirge (Czechoslovakia), the Iberian Peninsula, Bolivia, Malaysia, Korea, and southeast China. The extensive literature on tin deposits is summarized in books by TAYLOR (1979), ISHIHARA and TAKENOUCHI (1980), EVANS (1982), HALLS (1985), and KWAK (1987). Many individual deposits have been studied in detail with contributions by KELLY and TURNEAURE (1970, Bolivia), BAUMANN et al. (1974, Czechoslovakia), SILITOE et al. (1975, Bolivia), KELLY and RYE (1979, Portugal), COLLINS (1981, Tasmania), PATTERSON et al. (1981, Tasmania), ZHANG and LI (1981, China), JACKSON et al. (1982, England), CLARK et al. (1983, Peru), EADINGTON (1983, Australia), BRAY and SPOONER (1983, England), KWAK (1983, Tasmania), VON GRUENEWALDT and STRYDOM (1985, S. Africa), JACKSON and HELGE-
son (1985b, Malaysia), Peterson (1986, Canada), Puchner (1986, Alaska), Sun and Eadington (1987, Australia), and many others. Although an extensive set of data is available now on mineral associations, fluid inclusions, and stable isotopes, little is known with respect to the hydrothermal transport of tin and the factors which initiate and sustain the precipitation of cassiterite and the associated sulfides. This information, which is a crucial ingredient of any genetic model, may be obtained from solubility measurements carried out under carefully controlled conditions. We report here the results of such experiments between 400°C and 700°C at 1.5 kb pressure in the presence of chloride-bearing fluids.

Previous cassiterite solubility determinations at temperatures up to 400°C were carried out in solutions of sodium hydroxide (Klintsova and Barsukov, 1973), silicic chloride (Nekrasov and Ladze, 1973), acidic and alkaline fluoride (Klintsova et al., 1975), and chloride and nitrate (Dadze et al., 1982). Unfortunately, oxygen fugacity was not controlled in these studies, and hence the nature of the tin solutes cannot be established. Kovalenko et al. (1986) measured cassiterite solubility in HCl solutions at 500°C, 1.0 kb with the NNO oxygen fugacity buffer. They interpreted their results in terms of the species, SnCl₄²⁻, for solutions of 0.01–0.50 m HCl. Recently, Pabalan (1986) has measured cassiterite solubility in subcritical solutions.

Cassiterite solubility has been predicted from theoretical considerations. Patterson et al. (1981) concluded that SnCl₃ is the most abundant species between 30 and 350°C with minor amounts of SnCl₂⁺ and SnCl₄²⁻. Eadington (1982) suggested that between 250 and 400°C under acid conditions SnCl₄²⁻ and SnF⁺ are dominant, whereas hydroxide species dominate under basic conditions. Jackson and Helgeson (1985a) found that between 250 and 350°C under slightly acid to alkaline conditions hydroxide complexes of tin predominate, whereas under very acid conditions, SnCl₂⁰ and SnCl₃ are abundant. Obviously, these predictions must be checked by direct experiment before they can be used with any degree of confidence.

**EXPERIMENTAL PROCEDURES AND RESULTS**

General procedures used in solubility and speciation studies have been discussed by Wilson (1986), Wilson and Eugster (1984), and Eugster et al. (1987). To permit speciation calculations, the total metal concentration must be measured as a function of free ligand concentration at pressure and temperature. Multiple regression analysis is used to account for the metal concentration in terms of several metal-ligand species. Alternatively, if only one species is present, a graphical analysis suffices. In order to define solubility with respect to several species, the free ligand concentration must be varied as widely as possible between measurements. Applications of these procedures in room temperature to subcritical hydrothermal solutions have been discussed by Rossotti and Rossotti (1961), Johansson (1970), Seward (1973, 1976), Crerar et al. (1978), Hartley et al. (1980), Wood and Crerar (1985), and others.

Experiments carried out under supercritical conditions require special care. Small-volume, sealed noble metal capsules are used, providing usually no more than 80 µl solution. The control of the chemical conditions, such as pH, is difficult, and in situ conditions cannot be monitored directly. The only measurements that can be made are those done after the system is quenched to room temperature. The in situ conditions must then be back-calculated from those measurements. In addition to pressure and temperature, the oxygen fugacity, fO₂, must be controlled, using the appropriate oxygen buffer assemblage. This is particularly important for multivalent metals. In order to minimize back reactions during quench, rapid-quench techniques are used (Eugster et al., 1987).

Chloride solutions were chosen for the present study due to their known dominance in ore-forming environments (Haapala and Kinnunen, 1982; Collins, 1981; and many others). To keep the solution composition as simple as possible, the experiments were performed in HCl solutions. From these experiments, the dominant tin-chloride speciation and the equilibrium constants for the cassiterite dissolution reactions can be determined. Since tin exists in either the bivalent or quadravalent state, the reactions that govern the solubility of cassiterite in HCl solutions are

\[
\text{SnO}_2 + 2\text{H}^+ + n\text{Cl}^- \leftrightarrow \text{SnCl}_{n}^{2-n} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (1, n)
\]

and

\[
\text{SnO}_2 + 4\text{H}^+ + n\text{Cl}^- \leftrightarrow \text{SnCl}_{n}^{2-n} + 2\text{H}_2\text{O} \quad (2, n)
\]

where n is the ligand number of an individual mononuclear tin-chloride species and is a small integer. For different ligand concentrations, different species (hence, different values of n) can exist. Also, since there are likely to be more than one species in solution at a given set of conditions, a number
of reactions of this form will represent the system. The equilibrium constants for these reactions are expressed as

\[ K_{1,n} = \frac{(\text{SnCl}_2^{2-n})f_{\text{Sn}}^2}{(\text{H}^+)^2(\text{Cl}^-)^n} \quad (3,n) \]

and

\[ K_{2,n} = \frac{(\text{SnCl}_4^{6-n})}{(\text{H}^+)^4(\text{Cl}^-)^n} \quad (4,n) \]

where brackets indicate molality at pressure and temperature, and H\textsubscript{2}O and SnO\textsubscript{2} are in their standard states of pure liquid and solid, respectively, at \( P \) and \( T \). Activity coefficients for the aqueous species are assumed to be unity, which implies a standard state of unit activity at 1 molal concentration of the species in a solution of ionic strength equal to that of the experiments. For this reason, application of the results should be limited to solutions which have total chloride concentrations in the range represented by the experiments. The goal of the experiments described here was to determine the values of \( n \) for the most dominant tin-chloride species and the values of the corresponding equilibrium constants, \( K_{1,n} \) and \( K_{2,n} \).

The experimental setup, shown in Fig. 1, consists of 45 mg reagent grade SnO\textsubscript{2} with 60–80 µl HCl solution, between 0.18 and 3.3 molal, in a sealed gold metal tube (4.0 mm I.D., 4.2 mm O.D, 25 mm long). The oxygen buffer, either hematite-magnetite (HM) or nickel-nickel oxide (NNO), is contained within an inner, sealed platinum metal tube (2.8 mm I.D., 3.0 mm O.D., 15 mm long) together with 25 µl distilled water. This variation of the standard double-tube arrangement (see Eugster and Wones, 1962) provides a larger solution volume for analysis and a quicker extraction. Each run was held at temperature and 1.5 kb pressure for between 14 and 90 days in a 30 cm long cold-seal pressure vessel with a 30 cm long rapid-quench extension (see Eugster et al., 1987). To effect reversals, run temperature was approached from below in some runs, and from above in the others. For approach from above, the runs were first held at 100°C higher than the final run temperature for 1 day before being brought down to the run temperature.

After a run was quenched, the capsule was cleaned, weighed, and centrifuged at 14,000 G for 40 seconds. It was placed in a glovebox purged with water-saturated argon to prevent oxidation and evaporation. The fluid was extracted and collected on a teflon watchglass. Aliquots of 10 or 20 µl were diluted in volumetric flasks to 5 or 10 ml with 1.2 N HCl for the Sn analysis, and with 10 to 50 ml distilled water for the chloride analysis. The remaining fluid was used to measure pH with a combination microelectrode while still in the glovebox. Chloride concentrations were measured with a Buchler chloridometer and tin with an AA spectrophotometer and graphite furnace. Excellent precision was achieved in the tin analysis by using a stabilized temperature platform, adding 500 ppm Ni(NO\textsubscript{3})\textsubscript{3} to the solution, and adding 10% H\textsubscript{2} to the purge gas (Slavin et al., 1981; Rayson and Holcombe, 1982). The estimated uncertainty in the tin and chloride determinations is estimated to be ±5% based on the number of dilutions and the precision of the measurements. A check on gold concentrations revealed no detectable gold in solution. Results of the successful experiments are listed in Table 1.

**INTERPRETATION OF DATA: REGRESSION PROCEDURES**

From the measurements of total chloride, total tin, and \( pH \) at 25°C, the oxidation state of aqueous tin can be calculated. In these acid solutions, the contribution of OH\textsuperscript{−} can be neglected, thus, the room-temperature charge balance equation becomes

\[ X_{\text{Sn}}^{n} + (10)^{-pH} = C_{\text{t}} \quad (5) \]

where \( X \) is the oxidation state of aqueous tin, \( X_{\text{Sn}}^{n} \) and \( C_{\text{t}} \) are the tin and chloride concentrations measured after quench, and \( pH \) is the pH of the quenched solution. The largest uncertainty in calculating \( X \) from Equation (5) arises from the \( pH \) measurement (see Table 1), because of the extremely small fluid volume and possible poisoning of the microelectrode by tin ions. Nevertheless, the average value of \( X \) at all temperatures is 2.18 ± 0.24 for runs buffered by NNO, and 3.63 ± 0.77 for runs buffered by HM. Due to the uncertainty associated
with this determination, and the lack of a clear relationship between the calculated values of \(X\) and \(C_{\text{total}}\), we assume that only one oxidation state of aqueous tin is present in significant quantities. Note that a mixture of oxidation states is impossible in both the HM and NNO runs due to the many orders of magnitude difference in \(f_{O_2}\) between these two buffers. Thus, it appears that aqueous tin is bivalent and quadravalent under the conditions of NNO and HM, respectively.

Because of the use of rapid-quench techniques and the extraction of the fluid under an inert atmosphere, we assume that \(X\) is also the oxidation state of tin in solution at \(P\) and \(T\). Consequently, once \(X\) is known, the electrical neutrality equation at \(P\) and \(T\) can be expressed as

\[
(H^+)_{P,T} + \sum \left[ X - n \right] \left( \text{SnCl}^{X-n}_{\text{aq}} \right)_{P,T} = (\text{Cl}^-)_{P,T},
\]

(6)

where the summation is over all species, \(\text{SnCl}^{X-n}_{\text{aq}}\), that exist in solution at significant concentrations. The tin and chloride mass balance at \(P\) and \(T\) are given by

\[
\text{Sn}_{\text{total}} = \sum \left( \text{SnCl}^{X-n}_{\text{aq}} \right)_{P,T},
\]

(7)

and

\[
\text{Cl}_{\text{total}} = (\text{Cl}^-)_{P,T} + (\text{HCl}^0)_{P,T}
\]

\[+ \sum n \left( \text{SnCl}^{X-n}_{\text{aq}} \right)_{P,T}.
\]

(8)

In addition, the dissociation of HCl\(^0\) at \(P\) and \(T\) yields the following expression:

\[
K_{\text{HCl}} = \frac{(H^+)_{P,T}(\text{Cl}^-)_{P,T}}{(\text{HCl}^0)_{P,T}},
\]

(9)

(assuming unit activity coefficients) where the values for \(K_{\text{HCl}}\) are from FRANTZ and MARSHALL (1984). Finally, the dissociation reaction for the \(n\)th tin chloride species,

\[
\text{SnCl}^{X-n}_{\text{aq}} \rightarrow \text{SnCl}^{X-n+1}_{\text{aq}} + \text{Cl}^-,
\]

(10,n)

provides the relation,

\[
K_{10,n} = \frac{(\text{SnCl}^{X-n+1}_{\text{aq}})_{P,T}(\text{Cl}^-)_{P,T}}{(\text{SnCl}^{X-n}_{\text{aq}})_{P,T}}.
\]

(11,n)

One equation of this form can be written for each two consecutive tin-chloride species that are proposed to exist in solution. In other words, if a total of \(m\) consecutive species are proposed, there will be \(m - 1\) independent equations of the form of Equation (11,n). Together with Equations (6), (7), (8), and (9), there will be a total of \(m + 3\) equations describing the conditions of each individual run.

In this set of equations, however, there are \(2m + 2\) unknowns for each run: \((\text{Cl}^-)_{P,T}\), \((H^+)_{P,T}\), \((\text{HCl}^0)_{P,T}\), \((\text{SnCl}^{X-n}_{\text{aq}})_{P,T}\), \(\ldots\), \((\text{SnCl}^{X-n}_{\text{aq}})_{P,T}\), and \(K_{10,n+1}, \ldots, K_{10,n_m}\). A set of runs at the same pressure and temperature must then be considered as a whole, and the equations solved by nonlinear least squares regression. Since the unknown \(K_{10,n}\)'s are constant for a set of runs at a given \(P\) and \(T\), the regression is expressed by \(m - 1\) equations of the form

\[
\frac{d\sigma^2}{d(\log K_{10,n})} = 0
\]

(12)
which expresses the condition of least squares best fit (Bevington, 1969; Draper and Smith, 1981).

Using the case where \(X = 2\) as an example, the standard deviation, \(\sigma\), is defined by

\[
\sigma^2 = \frac{1}{R} \sum_{i=1}^{R} [\log K_{1,n}^i - \log K_{1,n}]^2,
\]

where \(K_{1,n}^i\) is the value of the equilibrium constant for Reaction (1) as determined by run \(i\), \(K_{1,n}\) is the mean value for all runs at the same pressure and temperature, and \(R\) is the total number of runs under that set of conditions. The standard deviation is the same if it is defined in terms of \(\log K_{1,n}\) (as in Equation 13), \(\log K_{1,n-1}\) or \(\log S_{\text{total}}\). Thus, the standard deviation is independent of \(m\) and can be compared between trials of the calculation where different species, and different numbers of species, are considered. With equations of the form of (11,n) and (12), and Equations (6), (7), (8), and (9), there are \(2m + 2\) equations, and the system is fully defined.

This regression analysis can be expressed as

\[
\log K_{1,n} = f(K_{10,n}, S_{\text{total}}, C_{\text{total}}),
\]

with \(\log K_{1,n}\) (or \(\log K_{2,n}\) if \(X = 4\)) as the response variable, \(K_{10,n}\) as the regression parameter, and \(S_{\text{total}}\) and \(C_{\text{total}}\) as the predictor variables from each individual run \(i\). The function, \(f\), represents the combination of Equations (3) or (4), (6), (7), (8), (9), and (11,n), but due to the nature of this set of equations, it cannot be expressed explicitly as a simple regression equation. The analysis can be performed, however, by repeatedly solving the equations (function \(f\)) for different values of \(K_{10,n}\) until a minimum is found in \(\sigma\). The solution where \(\sigma\) is at a minimum will yield the best-fit values for the unknowns.

**INTERPRETATION OF DATA: INITIAL SPECIES SELECTION**

In order to minimize computational difficulty and to avoid over-fitting the data, it is helpful to initially identify the most important species in this system under the temperature and pressure conditions of interest. To do this, Equations (6) through (12) are simplified by assuming that only a single species is present (i.e., \(m = 1\)) in a set of runs. The equations are solved for the set of runs considering each possible species, one at a time, and the fits of the results are compared.

With only one species, Reaction (10) is undefined as are Equations (11,n) and (12). Equations (6), (7), (8), and (9) define the system completely for the unknowns \((H^+)^{P,T}\), \((Cl^-)^{P,T}\), \((HC1O)^{P,T}\), and the concentration of the single tin-chloride species, \((SnCl^{2-n})^{P,T}\). The best value of \(n\) is found by minimizing the standard deviation as a function of the species chosen, or \(n\). This will be illustrated graphically here. Equations (3) and (4) can be rearranged to the following form:

\[
\log \left( \frac{(SnCl^{2-n})^{1/2}}{(H^+)^2} \right) = n \log (Cl^-) + \log K_{1,n},
\]

and

\[
\log \left( \frac{(SnCl^{4-n})}{(H^+)^4} \right) = n \log (Cl^-) + \log K_{2,n},
\]

where all terms are at \(P\) and \(T\). Equations (15) and (16) describe straight lines of slope \(n\). Figure 2 shows the run data for 400°C, buffered by NNO (where \(X = 2\)) where Equations (6) through (9) are solved assuming the presence of \(Sn^{2+}\) (a), \(SnCl^+\) (b), and \(SnCl_2^2\) (c). A line of slope \(n\) is positioned by using \(\log K_{1,n}\) as the y-intercept. Figure 2(a) shows that the data do not fit the model of \(Sn^{2+}\) (\(n = 0\)) as the dominant tin-chloride species. In Fig. 2(b), the trend of the points is slightly steeper than the reference line, and in Fig. 2(c), it is slightly shallower. Thus, the mean value of \(n\) is between 1 and 2 and it is concluded that significant amounts of \(SnCl^+\) and \(SnCl_2^2\) are present in solution at 400°C. This is also indicated by the standard deviations which are approximately equal for \(n = 1\) and \(n = 2\), and lower than for \(n = 0\).

The same conclusions can be drawn for the data at 500°C, NNO (Fig. 3) and 600°C, NNO (Fig. 4), although the standard deviations show a slight preference for \(n = 1\) at 500°C and \(n = 2\) at 600°C. Thus, a final model must include both \(SnCl^+\) and \(SnCl_2^2\) at these temperatures as well. At 700°C, NNO (Fig. 5), the only reasonable fit of the two data points is for \(n = 2\). The ratio of \(Cl_{\text{total}}\) to \(Sn_{\text{total}}\) for most of these runs does not permit \(n = 3\).

Under the conditions of HM (where \(X = 4\)) at 500 and 600°C, Figs. 6 and 7 indicate that \(SnCl_2^2\) is dominant.

**INTERPRETATION OF DATA: FINAL SPECIATION CALCULATIONS**

Knowing that \(SnCl^+\) and \(SnCl_2^2\) are the species of interest at 400 to 700°C and NNO, both can be considered simultaneously. The results will yield

\[
SnO_2 + 2H^+ + Cl^- \leftrightarrow SnCl^+ + H_2O + \frac{1}{2}O_2
\]

(1,1)
and \( K_{1,2} \) for the reaction
\[
\text{SnO}_2 + 2\text{H}^+ + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_2^+ + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2. \tag{1,2}
\]

Equations (6), (7), (8), and (9) are written with \( \text{SnCl}_2^+ \) and \( \text{SnCl}_2 \) as the aqueous tin species and Equation (11,n) takes the form of
\[
K_{10,2} = \frac{(\text{SnCl}_2^+)^{P,T}(\text{Cl}^-)^{P,T}}{(\text{SnCl}_2)^{P,T}}. \tag{11,2}
\]

Combined, these 5 equations can be solved for the unknowns of an individual run at \( P \) and \( T \), \( (\text{SnCl}_2^+)^{P,T}, (\text{SnCl}_2)^{P,T}, (\text{H}^+)^{P,T}, (\text{Cl}^-)^{P,T}, (\text{HClO})^0{P,T}, \) provided that a value is assumed for \( \log K_{10,2} \).

For a set of runs, the procedure is to assume a value of \( \log K_{10,2} \), solve the set of equations for each run, and calculate \( \sigma \) by Equation (13). This is done repeatedly using different values of \( \log K_{10,2} \) until a minimum is found in \( \sigma \), and Equation (12) is satisfied. The minimum indicates the best fit of the data to the two-species model.

The regression analysis is illustrated in Fig. 8 where \( \sigma \) is plotted against different assumed values of \( \log K_{10,2} \). At 400, 500, and 600°C, the calculations yield a distinct minimum in \( \sigma \) at \( \log K_{10,2} = -0.45, 0.16, \) and \(-1.35\), respectively. This confirms that, statistically, the best fit of these experimental data is for a model where a combination of both \( \text{SnCl}_2^+ \) and \( \text{SnCl}_2 \) is present. As the assumed value of \( \log K_{10,2} \) is made larger or smaller, \( \sigma \) increases rapidly before finally leveling off at the value obtained when only one species is assumed to be present (\( \text{SnCl}_2^+ \) or \( \text{SnCl}_2 \), respectively). For the 700°C data, \( \sigma \) decreases rapidly as the assumed value of \( \log K_{10,2} \) is decreased to about \(-3.75\). At that point, \( \sigma \) nearly reaches its lowest value; approximately that obtained when only \( \text{SnCl}_2 \) was assumed to be present. As the assumed value of \( \log K_{10,2} \) is made smaller, \( \sigma \) continues to decrease, but only very slightly, while the resulting \( \log K_{1,2} \) remains constant. Thus, at 700°C, it can be concluded that \( \text{SnCl}_2 \) is dominant in this concentration range and that the maximum amount of \( \text{SnCl}_2^+ \) compatible with the data is determined by \( \log K_{1,1} \leq \log K_{1,2} + (-3.75) \).
FIG. 3. Experimental cassiterite solubility results at 500°C, 1.5 kb, and NNO (oxidation state of tin is 2). See Fig. 2 caption.

FIG. 4. Experimental cassiterite solubility results at 600°C, 1.5 kb, and NNO (oxidation state of tin is 2). See Fig. 2 caption.
The best-fit results are listed in Table 2. These are illustrated in Fig. 9 for 400°C (a), 500°C (b), 600°C (c), and 700°C (d), at 1.5 kb and NNO. Again, as in Figs. 2 through 7, the solubility diagram as defined by Equation (15) is used where the data points represent the total solubility of cassiterite calculated for each run. The bold curve is the best-fit curve through the points and is determined by both \( \log K_{1,1} \) and \( \log K_{1,2} \). It is the sum of the two lighter lines shown for the individual species, SnCl\(^+\) and SnCl\(_2\)^+. Figure 9(a, b, and d) shows that there is no strong systematic deviation of the points from the mean at 400, 500, and 700°C. This is an indication that no tin-chloride species other than the two considered are present in detectable amounts. At 600°C (Fig. 9c), however, the two points to the far right (open triangles) which lie above the mean suggest that a third species, SnCl\(_3\), may be present at the highest chloride concentrations. These two runs were not included in the regression analysis. Addition of this third species would probably not significantly change the values obtained for \( \log K_{1,1} \) and \( \log K_{1,2} \). The best-fit values of \( \log K_{10,2} \) and the mean values determined for \( \log K_{1,1} \) and \( \log K_{1,2} \) are listed in Table 3. The uncertainties shown are based on the estimated errors in the \( C_{\text{total}} \) and \( S_{\text{total}} \) measurements which are carried through the entire calculation by the standard method of error propagation (Rees, 1984; Bevington, 1969).

For the experimental data from runs buffered by HM where \( X = 4 \) at 500 and 600°C, the fit to the one-species model (SnCl\(_3\)^+) is as good as can be expected. No attempt was made to improve the fit by the addition of other species to the calculations. The mean values for \( \log K_{2,3} \) as determined in the previous section are also given in Table 3.
THERMODYNAMIC PARAMETERS

The equilibrium constants determined in this study can be represented as a function of temperature by an equation of the form

$$\log K = a + \frac{b}{T} + \frac{c}{T^2}$$  \hspace{1cm} (17)

where the coefficients $a$, $b$, and $c$ are determined by least-squares regression of the data in Table 3 and $T$ is in Kelvin. The coefficients for Reactions 1,1; 1,2; 2,3; and 10,2 are given in Table 4.

In Fig. 10, log $K$ is plotted against $1/T(K)$ for Reactions 1,1; 1,2; 2,3; and 10,2. The uncertainties in log $K$ are less than or equal to the size of the symbols. The regression curve as defined by Equation (17) is also shown. The non-unique solutions for log $K_{1,1}$ and log $K_{10,2}$ at 700°C are the maximum possible values. These were not used in determining the regression curves but are included in Fig. 10 to show that they are compatible with the extrapolations of the lower temperature data.

For comparison, the data of Patterson et al. (1981) and Jackson and Helgeson (1985a) at 350°C and pressure equal to the saturated vapor pressure of water ($P_{sat}$) are also plotted in Fig. 10. Although the difference in pressure makes this comparison only approximate, there is reasonable agreement in the value for log $K_{10,2}$. Shown also is the value for log $K_{1,2}$ at 500°C, 1.0 kb from Kovalenko et al. (1986) which shows reasonable agreement as well.

The results for log $K_{10,2}$ as a function of temperature can be used to derive information on the thermodynamics of complex dissociation. The slope of the lower curve in Fig. 10 is related to the standard enthalpy of reaction, $\Delta H_{10,2}^0$, by the equation

$$\frac{d}{dT} \log K_{10,2} = -\frac{\Delta H_{10,2}^0}{R} \frac{d(1/T)}{dT}$$  \hspace{1cm} (18)

where $R$ is the gas constant and $T$ is in Kelvin. The entropy of reaction, $\Delta S_{10,2}^0$, is given by

$$\Delta S_{10,2}^0 = \frac{\Delta H_{10,2}^0}{T} + 2.303 R \log K_{10,2}$$  \hspace{1cm} (19)

The resulting values of $\Delta H_{10,2}^0$ and $\Delta S_{10,2}^0$ are listed in Table 5. It can be seen that $\Delta H_{10,2}^0$ and $\Delta S_{10,2}^0$ are both positive at 400°C and negative at temperatures of 500°C and above. There is a systematic decrease in both $\Delta H_{10,2}^0$ and $\Delta S_{10,2}^0$ with increasing temperature from 400 to 700°C. As discussed by Seward (1981), this reflects the changing nature of the solvent, the hydration of the charged species, and the chemical bonding between the metal ion and the ligand. The positive enthalpy at 400°C is indicative of predominantly covalent bonding. The charged species are not strongly solvated under these conditions and relatively little water is involved in the reaction. Thus, a small positive entropy is caused by an increase in the number of particles and an increased vibrational and rotational energy in the system. At 500°C and above, the increasingly negative entropy values are indicative of an increase in the electrostatic (ionic) character of the bonding with temperature. The negative $\Delta S_{10,2}^0$ values indicate that what solvation water is involved in the reaction is derived from an increasingly disordered solvent.

GEOLOGIC APPLICATIONS

Data presented here can be used to predict the oxidation state of aqueous tin, the nature of the aqueous tin-chloride complexes in natural environments, the solubility of cassiterite in ore fluids, and mechanisms likely to cause cassiterite precipitation. The physical and chemical conditions existing at the time of cassiterite deposition, such as $f_{O_2}$, $T$, $pH$, and salinity, can be estimated from mineralogical, fluid inclusion, and isotopic studies.
Acidic conditions are indicated by the common occurrence of acid-alteration assemblages in cassiterite deposits, such as greisenization of granitic host-rock, alteration of feldspars to muscovite, alteration of biotite to muscovite or chloride in schists, and the formation of skarns in carbonate rock. These alterations set an upper limit on the pH of the ore-forming fluids at below neutral near the site of deposition, although the fluids could be more acidic at their source. Individual studies of fluid inclusions and phase relations indicate that mineralizing fluids had pH values in the range of 3.9 to 5.4 at the site of ore deposition (PATTERSON et al., 1981; JACKSON and HELGESON, 1985b).

Oxygen fugacities of the ore-forming fluids at Renison Bell, Tasmania were estimated by PATTERSON et al. (1981) using CO$_2$/CH$_4$ ratios in fluid inclusions, and at Mt. Lindsay, Tasmania by KWAK (1983) using a rare occurrence of iron-titanium oxides. They found values between those defined by the NNO and QFM buffers. Topaz rhyolites associated with small cassiterite deposits in the western United States have $f_{O_2}$ values approximately equal to those defined by the QFM buffer (CHRISTIANSEN

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**Fig. 8.** The standard deviation as defined by Equation (13) plotted against assumed values for log $K_{10.2}$. A minimum in the curve is where Equation (12) is satisfied and indicates the value of log $K_{10.2}$ which best fits the experimental data. No minimum is found at 700°C, but the largest permissible value of log $K_{10.2}$ is indicated (see text).
### Table 2. Best-fit results of cassiterite solubility data

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{SnCl}_2^2)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{1,1}$</th>
<th>$\log K'_{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-0.858</td>
<td>-1.146</td>
<td>-0.738</td>
<td>-1.355</td>
<td>-11.196</td>
<td>-10.746</td>
</tr>
<tr>
<td>41</td>
<td>-0.618</td>
<td>-0.713</td>
<td>-0.545</td>
<td>-1.356</td>
<td>-11.147</td>
<td>-10.697</td>
</tr>
<tr>
<td>44</td>
<td>-0.424</td>
<td>-0.358</td>
<td>-0.383</td>
<td>-1.429</td>
<td>-10.970</td>
<td>-10.520</td>
</tr>
<tr>
<td>45</td>
<td>-0.855</td>
<td>-1.146</td>
<td>-0.741</td>
<td>-1.379</td>
<td>-11.141</td>
<td>-10.691</td>
</tr>
<tr>
<td>46</td>
<td>-0.436</td>
<td>-0.370</td>
<td>-0.384</td>
<td>-1.336</td>
<td>-11.165</td>
<td>-10.715</td>
</tr>
<tr>
<td>47</td>
<td>-1.210</td>
<td>-1.761</td>
<td>-1.001</td>
<td>-1.418</td>
<td>-11.160</td>
<td>-10.710</td>
</tr>
<tr>
<td>48</td>
<td>-1.151</td>
<td>-1.690</td>
<td>-0.989</td>
<td>-1.496</td>
<td>-10.957</td>
<td>-10.507</td>
</tr>
</tbody>
</table>

400°C, NNO ($\log f_O = -27.572$)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{SnCl}_2^2)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{1,1}$</th>
<th>$\log K'_{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>-0.255</td>
<td>-0.669</td>
<td>-0.254</td>
<td>-3.323</td>
<td>-4.752</td>
<td>-4.912</td>
</tr>
<tr>
<td>24</td>
<td>-0.254</td>
<td>-0.667</td>
<td>-0.253</td>
<td>-3.452</td>
<td>-4.949</td>
<td>-4.654</td>
</tr>
<tr>
<td>28</td>
<td>-0.709</td>
<td>-1.577</td>
<td>-0.708</td>
<td>-3.267</td>
<td>-4.865</td>
<td>-5.025</td>
</tr>
<tr>
<td>29</td>
<td>-0.435</td>
<td>-1.030</td>
<td>-0.435</td>
<td>-3.429</td>
<td>-4.540</td>
<td>-4.700</td>
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<tr>
<td>49</td>
<td>-0.652</td>
<td>-1.464</td>
<td>-0.651</td>
<td>-3.283</td>
<td>-4.832</td>
<td>-4.992</td>
</tr>
<tr>
<td>50</td>
<td>-0.398</td>
<td>-0.955</td>
<td>-0.397</td>
<td>-3.569</td>
<td>-4.260</td>
<td>-4.420</td>
</tr>
<tr>
<td>51</td>
<td>-1.122</td>
<td>-2.403</td>
<td>-1.120</td>
<td>-3.462</td>
<td>-4.476</td>
<td>-4.636</td>
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<tr>
<td>62</td>
<td>0.053</td>
<td>-0.055</td>
<td>0.053</td>
<td>-3.343</td>
<td>-4.711</td>
<td>-4.871</td>
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<tr>
<td>76</td>
<td>-0.090</td>
<td>-0.340</td>
<td>-0.090</td>
<td>-3.265</td>
<td>-4.868</td>
<td>-5.028</td>
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<tr>
<td>77</td>
<td>-0.075</td>
<td>-0.310</td>
<td>-0.075</td>
<td>-3.447</td>
<td>-4.505</td>
<td>-4.665</td>
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</table>

500°C, NNO ($\log f_O = -22.796$)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{SnCl}_2^2)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{1,1}$</th>
<th>$\log K'_{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>-1.475</td>
<td>-1.600</td>
<td>-1.475</td>
<td>-4.315</td>
<td>-0.928</td>
<td>0.422</td>
</tr>
<tr>
<td>72</td>
<td>-1.005</td>
<td>-0.659</td>
<td>-1.005</td>
<td>-4.270</td>
<td>-1.016</td>
<td>0.334</td>
</tr>
<tr>
<td>73</td>
<td>-0.996</td>
<td>-0.642</td>
<td>-0.996</td>
<td>-4.325</td>
<td>-0.906</td>
<td>0.444</td>
</tr>
<tr>
<td>84</td>
<td>-1.469</td>
<td>-1.587</td>
<td>-1.468</td>
<td>-4.334</td>
<td>-0.890</td>
<td>0.460</td>
</tr>
<tr>
<td>85</td>
<td>-1.017</td>
<td>-0.684</td>
<td>-1.017</td>
<td>-4.346</td>
<td>-0.864</td>
<td>0.486</td>
</tr>
<tr>
<td>100</td>
<td>-1.221</td>
<td>-1.092</td>
<td>-1.221</td>
<td>-4.321</td>
<td>-0.915</td>
<td>0.435</td>
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<tr>
<td>101</td>
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<td>-0.199</td>
<td>-0.775</td>
<td>-4.340</td>
<td>-0.877</td>
<td>0.473</td>
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</table>

600°C, NNO ($\log f_O = -19.113$)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{2,3}$</th>
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</thead>
<tbody>
<tr>
<td>90</td>
<td>(-2.173)</td>
<td>-0.595</td>
<td>-2.172</td>
<td>-4.825</td>
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<tr>
<td>91</td>
<td>(-1.791)</td>
<td>0.169</td>
<td>-1.790</td>
<td>-4.878</td>
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</table>

600°C, NNO ($\log f_O = -16.187$)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{2,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>-0.648</td>
<td>-0.646</td>
<td>-3.151</td>
<td>13.892</td>
</tr>
<tr>
<td>64</td>
<td>-1.710</td>
<td>-1.653</td>
<td>-2.567</td>
<td>13.516</td>
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<tr>
<td>66</td>
<td>-0.848</td>
<td>-0.845</td>
<td>-2.993</td>
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<tr>
<td>67</td>
<td>-0.764</td>
<td>-0.761</td>
<td>-2.912</td>
<td>13.165</td>
</tr>
<tr>
<td>69</td>
<td>-0.186</td>
<td>-0.185</td>
<td>-3.398</td>
<td>13.959</td>
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</tbody>
</table>

500°C, HM

<table>
<thead>
<tr>
<th>Run</th>
<th>$\log (\text{SnCl}_4)$</th>
<th>$\log (\text{Cl}^-)$</th>
<th>$\log (\text{H}^+)$</th>
<th>$\log K'_{2,3}$</th>
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</thead>
<tbody>
<tr>
<td>82</td>
<td>-0.495</td>
<td>-0.495</td>
<td>-4.520</td>
<td>19.069</td>
</tr>
<tr>
<td>86</td>
<td>-1.971</td>
<td>-1.962</td>
<td>-3.688</td>
<td>18.666</td>
</tr>
<tr>
<td>87</td>
<td>-0.921</td>
<td>-0.921</td>
<td>-4.283</td>
<td>18.973</td>
</tr>
<tr>
<td>88</td>
<td>-0.166</td>
<td>-0.166</td>
<td>-4.613</td>
<td>18.782</td>
</tr>
</tbody>
</table>

600°C, HM

All concentrations are for the species at 1.5 kb and $T$. Parentheses indicate maximum permitted values at 700°C (see text).

et al., 1986). HAAPALA and KINNUNEN (1982) summarized published data on fluid inclusions in cassiterite from tin deposits around the world. They found that the most common values for homoge-
tures could be 100°C or more higher than the homogenization temperatures.

Salinities of ore-forming fluids as determined by fluid inclusion studies of cassiterite deposits are variable, ranging from about 1 m NaCl equivalent to as high as 8 m (HAAPALA and KINNUNEN, 1982; ROEDDER, 1984). Most commonly, however, during the stage of cassiterite formation, salinities were in the range of 1 to 2 m (KELLY and RYE, 1979; COLLINS, 1981; PATTERSON et al., 1981; ZAW and DAW, 1983; JACKSON and HELGESON, 1985b; JACKSON et al., 1982; NORMAN and TRANGCOT-Chasan, 1982). Estimates of fluid pressures range from 100 to 1800 bars (HAAPALA and KINNUNEN, 1982).

To obtain the relationship between stannous and stannic chloride complexes in hydrothermal fluids, Reactions (1,1) and (1,2) can be combined with Reaction (2,3) to yield the following:

\[
\text{SnCl}^+ + 2\text{Cl}^- + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SnCl}_2^+ + \text{H}_2\text{O} \tag{20}
\]

and

\[
\text{SnCl}_2^0 + \text{Cl}^- + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SnCl}_2^+ + \text{H}_2\text{O}. \tag{21}
\]

The equilibrium constants for these reactions can be obtained by combining the data listed in Table 4:

### Table 3. Best-fit equilibrium constants for Reactions (1,1), (1,2), (10,2), and (2,3)

<table>
<thead>
<tr>
<th>(T (°C))</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log K_{1,1})</td>
<td>-11.14</td>
<td>-4.76</td>
<td>-0.93</td>
<td>(1.58)</td>
</tr>
<tr>
<td></td>
<td>±0.15</td>
<td>±0.21</td>
<td>±0.06</td>
<td>±0.09</td>
</tr>
<tr>
<td>(\log K_{1,2})</td>
<td>-10.69</td>
<td>-4.92</td>
<td>0.42</td>
<td>5.33</td>
</tr>
<tr>
<td></td>
<td>±0.16</td>
<td>±0.22</td>
<td>±0.07</td>
<td>±0.10</td>
</tr>
<tr>
<td>(\log K_{10,2})</td>
<td>-0.45</td>
<td>0.16</td>
<td>-1.35</td>
<td>(-3.75)</td>
</tr>
<tr>
<td>(\log K_{2,3})</td>
<td>—</td>
<td>13.64</td>
<td>18.87</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>±0.25</td>
<td>±0.16</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Fig. 9.** Experimental cassiterite solubility at 400 (a), 500 (b), 600 (c), and 700°C (d), all at 1.5 kb and NNO (oxidation state of tin is 2). Each point represents the best-fit solution of Equations (6), (7), (8), (9), (11,2), and (12) as discussed in the text and Fig. (8). The standard deviation, \(\sigma\), is defined by Equation (13). The average estimated error bar is shown on the right-hand side of each diagram and is based on the estimated 5% uncertainty in the tin and chloride measurements (uncertainty in the horizontal direction is smaller than the size of the symbols). See text for explanation of the two runs at 600°C represented by open symbols.
Table 4. Coefficients for Equation (17) for Reactions (1,1), (1,2), (10,2), and (2,3)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1)</td>
<td>(1,2)</td>
<td>(10,2)</td>
<td>(2,3)</td>
</tr>
<tr>
<td>( a )</td>
<td>( b )</td>
<td>( c )</td>
<td>( d )</td>
</tr>
<tr>
<td>(-3.217 \times 10^4)</td>
<td>(-8.246 \times 10^4)</td>
<td>(1.054 \times 10^5)</td>
<td>(-3.511 \times 10^4)</td>
</tr>
<tr>
<td>(-70.080)</td>
<td>(-8.246 \times 10^4)</td>
<td>(1.054 \times 10^5)</td>
<td>(-3.904 \times 10^4)</td>
</tr>
<tr>
<td>(-70.812)</td>
<td>(59.064)</td>
<td>(-3.511 \times 10^4)</td>
<td>(-3.217 \times 10^7)</td>
</tr>
</tbody>
</table>

\[
\log K_{20} = 62.28 - \frac{6.15 \times 10^4}{T} + \frac{2.14 \times 10^7}{T^2} \tag{22}
\]

and

\[
\log K_{21} = -11.02 + \frac{4.74 \times 10^4}{T} - \frac{1.89 \times 10^7}{T^2} \tag{23}
\]

Equations (22) and (23) are only valid at 500 and 600°C because Reaction (2,3) was only determined at these temperatures. The relation between stannous and stannic chloride species depends on chloride ion concentration, \( p\bar{H} \), and \( f_{O_2} \). To evaluate the relative importance of these two oxidation states of aqueous tin in natural fluids, Equations (22) and (23) were used to plot the boundary between stannous chloride dominance and stannic chloride dominance. This is shown in Fig. 11 as a function of \( f_{O_2} \) and \( T \) for a 2 m \( Cl_{\text{total}} \) fluid in equilibrium with the assemblage K-feldspar + muscovite + quartz. This assemblage is commonly associated with cassiterite deposits, and at a given KCl concentration, it fixes the \( p\bar{H} \) of the fluid. For reference, the oxygen buffer curves for HM and QFM are also shown. The boundary between stannous and stannic dominance lies well above the region of \( f_{O_2} \) typical of cassiterite-bearing fossil hydrothermal systems. Thus, only the stannous species are expected to be found in such systems. This conclusion holds even if the \( p\bar{H} \) is as much as 1.5 units lower. The species \( SnCl^+ \) and \( SnCl_2^2\) then, are the tin-chloride species of importance under most natural hydrothermal conditions.

The total solubility of cassiterite as a function of temperature is plotted in Fig. 12 at the oxygen buffers QFM, NNO, HM. Again, it was assumed that a fluid of 2 m \( Cl_{\text{total}} \) is in equilibrium with the acid buffer assemblage K-feldspar-muscovite-quartz. The two species, \( SnCl^+ \) and \( SnCl_2^2\), make up the total tin concentration in the fluid. Figure 12 shows that low \( f_{O_2} \) and high temperature are required for significant concentrations of tin in solution. For instance, at 500°C and QFM, the tin concentration is only 1 ppm. If the \( p\bar{H} \) is decreased by 1 unit, that concentration is obtained at 400°C, QFM. That, however, is probably the lowest \( p\bar{H} \) obtainable in this temperature range. Therefore, for the transport

Table 5. Enthalpy and entropy of Reaction (10,2)

<table>
<thead>
<tr>
<th>( T (°C) )</th>
<th>( \Delta H^0 (kJ) )</th>
<th>( \Delta S^0 (kJ/K) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>203.7</td>
<td>0.294</td>
</tr>
<tr>
<td>500</td>
<td>-83.56</td>
<td>-0.105</td>
</tr>
<tr>
<td>600</td>
<td>-305.0</td>
<td>-0.375</td>
</tr>
<tr>
<td>700</td>
<td>(-481.0)</td>
<td>(-0.566)</td>
</tr>
</tbody>
</table>
of 1 ppm Sn or more in solution, it is necessary to have temperatures in excess of 400°C, pH at or below that of the K-feldspar-muscovite-quartz assemblage, and oxygen fugacity in the area of QFM-NNO. A decrease in temperature, increase in pH, or increase in oxygen fugacity can cause the deposition of cassiterite.

The solubilities of cassiterite and magnetite are compared in Fig. 13 where the data for magnetite are from CHOU and EUGSTER (1977). Although the solubilities of these two minerals are dependent on the same parameters, Fig. 13 shows that cassiterite solubility has a stronger dependence on oxygen fugacity and temperature than does magnetite solubility. At QFM, for instance, iron concentration decreases by about 4 orders of magnitude from 700 to 400°C whereas the tin concentration decreases by about 8 orders of magnitude at the same pH and chloride ion concentration. Consequently, at 500°C or lower, fO₂ near NNO, and free chloride ion concentration of 0.1 molar or more, Fe solutes greatly dominate Sn solutes in a fluid in equilibrium with magnetite + cassiterite.

Using the data presented here, the mechanisms responsible for cassiterite deposition can be quantitatively evaluated. Accepting SnCl⁺ and SnCl₂⁻ as the dominant species, precipitation is given by the reverse of Reaction (1),

\[
\text{SnCl}_n^{2-} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SnO}_2 + 2\text{H}^+ + n\text{Cl}^-
\]  

(24)

Reaction (24) can be driven to the right by a drop in temperature, an increase in fO₂ and/or pH, and probably also a change in pressure, although the pressure dependency was not evaluated. For the conditions depicted in Fig. 12, for instance, a drop of 50°C can decrease the tin concentration in solution by as much as an order of magnitude. Similarly, a one unit increase in pH, all other parameters held constant, forces cassiterite to become supersaturated by two orders of magnitude. An increase in pH is most likely caused by interaction of the acidic ore fluids with the country rock, such as carbonates at Dachang (S.E. China) and Renison Bell (Tasmania) or schists at Panasqueira (Portugal). Acid neutralization by carbonates occurs through the reaction

\[
\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]  

(25)

and can be monitored by the increased Ca²⁺ contents of fluid inclusions (KWAK and TAN, 1981a,b). In schists and granites, H⁺ can be consumed
Solubility experiments in supercritical HCl solutions can provide the information necessary to identify the dominant aqueous species and to for-
mulate and quantify mineral dissolution-precipitation reactions. This leads to a better understanding of the processes responsible for mineral transport and deposition. From cassiterite solubility experiments we found that the dominant tin-chloride species in supercritical HCl solutions are SnCl$_4^-$ and SnCl$_2^2-$ under geologically reasonable $p$H and $f_O_2$ conditions from 400 to 700°C, 1.5 kb. The species, SnCl$_4^-$, has also been identified at a lower $p$H and higher $f_O_2$ from 500 to 600°C. For the transport of significant quantities of tin in hydrothermal solutions, high temperature, low $p$H and $f_O_2$, and low $p$H are required. These conditions are reflected in many natural tin deposits. Deposition of cassiterite can be initiated by a drop in temperature, a rise in pH through reaction with wallrock, a redox reaction with coupled precipitation, or mixing with dilute meteoric waters. Although these mechanisms have been suggested previously, solubility data presented in this paper permit quantitative evaluation of individual processes.

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REFERENCES


Cassiterite solubility-tin speciation, supercritical chloride solutions


