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Minerals in hot water[1]

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> *We are at an embryonic stage in our study of metal complex equilibria at high temperatures and pressures.*
>
> Seward, 1981, p. 126

> *High-pressure/high-temperature solution chemistry . . . deserves far more experimental attention than it has so far received.*
>
> Helgeson, 1981, p. 172

ABSTRACT

Two centuries ago James Hall initiated the study of mineral-fluid interactions at elevated temperatures and pressures, and interest in hydrothermal synthesis has expanded ever since. The solubility of minerals in supercritical steam is dictated largely by the properties of the solvent. With increasing temperature, the dielectric constant of water decreases substantially, enhancing the degree of association of dissolved acids, bases, and salts. Pressure has the opposite effect through electrostriction, the collapse of the solvent around the hydrated ions. Metal complexing in supercritical chloride solutions depends on temperature, pressure, and chloride ion concentration. Dominant metal complexes can be identified from conductivity, spectroscopic, or solubility measurements. In the supercritical region, step-wise association reactions are endothermic and driven by the large entropy gain associated with the release of water from the structured environment to the bulk solvent. Because of decreased electrostatic shielding, metal-ligand interaction is largely electrostatic and ligand-field stabilization energies are low.

Solubility studies on Fe, Sn, and W minerals in HCl-NaCl solutions can be used to identify the dominant solute species. With increasing temperature, low-charge and neutral species become more abundant, but higher pressures favor dissociation and high ligand-ion concentrations favor anionic species. Modeling of metal transport in hydrothermal systems depends critically on speciation information, but reliable data in the supercritical region remain scarce.

INTRODUCTION

Are rocks and minerals made from fire or from water? Two hundred years ago this question was debated passionately by Hutton in Scotland, the proponent of volcanic action, and by Werner in Germany, who maintained that all rocks were precipitated from aqueous solutions. From today's perception it is easy to acknowledge that both views contain substantial truths. More interesting and more challenging is a search for common ground, a search that includes the interaction of minerals with aqueous fluids at elevated temperatures and pressures, a topic that has occupied much of my professional life. For a young student exposed to the traditions of Paul Niggli and Gerold Schwarzenbach in Zürich, this choice of topic was obvious. The path, however, has been neither short nor straight, and 35 years later I am just beginning to grasp the importance of the chemistry of hot aqueous solutions. If you feel that as president of MSA I should focus more on minerals and less on their environment, permit me to paraphrase the saying about famous men and their women: "behind every important mineral there once was a fluid."

In this discourse I will focus on the fluid and those properties that are important for our understanding of hydrothermal alteration, geothermal systems, ore deposits, metamorphic reactions, igneous processes, and even mantle degassing. After a brief historic review of hydrothermal experiments I will discuss speciation and metal transport in supercritical aqueous fluids, using data and insights gained recently with my students and associates, especially Glenn Wilson (1986). In the end, I hope to convince you that this frontier of geochemistry holds the key to our understanding of mineral-formation processes for a large portion of the earth.

150 YEARS OF HYDROTHERMAL SYNTHESIS: FROM HALL TO TUTTLE

Sir James Hall of Dunglass, Scotland, is generally acknowledged as the father of experimental geology. This is based on three sets of experiments which he carried out between 1790 and 1825 designed to test Hutton's theories: (1) crystallization of fused dolerites and basalts as well as

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[1] Adapted from the Presidential Address at the annual meeting of the Mineralogical Society of America, October 29, 1985, in Orlando, Florida.

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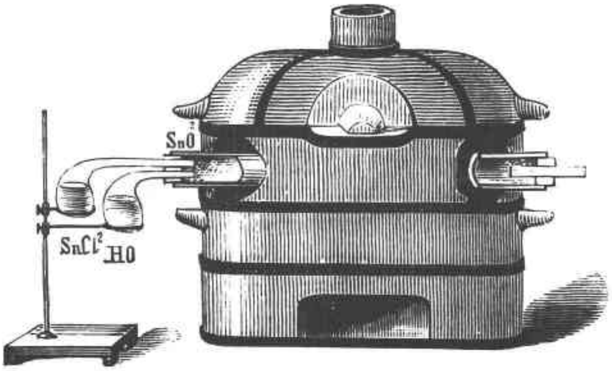

Fig. 1. Synthesis of cassiterite, achieved by passing $SnCl_2$ and H_2O vapors through a heated ceramic tube. From Daubrée (1849).

lavas from Etna and Vesuvius, (2) recrystallization of chalk to marble in heated, sealed gun barrels and (3) compression of layers of clay to imitate folding and faulting. My account of Hall's work is taken from Geikie's book *The Founders of Geology* (1905), in turn based on the first George Huntington Williams lectures delivered at Johns Hopkins University in 1896. For our present topic, Hall's second experiment is most significant. Hutton had concluded that basalts, dolerites, and other members of the "whinstone" family had formed by fusion, and yet many of them, especially their vesicles, contained calcite. How could calcite retain its CO_2 during fusion? Hutton proposed that pressure was the answer, and Hall, his friend and admirer, set out to test this suggestion. He enclosed chalk powder in gun barrels and exposed them to the highest temperatures obtainable in a glass factory. CO_2 was not released during the experiments, and a substance closely resembling marble was produced. The results vindicated Hutton's conjecture and were published in 1805 as an "Account of a Series of Experiments Showing the Effects of Compression in Modifying the Action of Heat" (Hall, 1805).

Hall had no disciples, but his methods and approaches inspired a group of French mining engineers and geochemists, especially Daubrée, Sénarmont, and Friedel who came to dominate experimental petrology until the end of the century. Daubrée, an outstanding experimentalist, covered as wide a range of topics as Hall did, including rock deformation and meteorites. His first paper (Daubrée, 1841) dealt with tin deposits he had visited in Saxony and Cornwall and the importance of the "mineralizers" B, F, PO_4, and Cl. His famous synthesis of cassiterite consisted of passing "$SnCl_2$" and water vapor through a heated ceramic tube at atmospheric pressure (Fig. 1): "If one passes through a ceramic tube heated to orange-white color two streams, one of tin chloride and the other of water, the mutual decomposition to stannic acid and hydrochloric acid is achieved with great ease" (Daubrée, 1849, p. 131–132).[2]

Quartz, TiO_2, and apatite were obtained in a similar manner. Sénarmont (1851) followed Hall's lead and synthesized a large number of minerals, including quartz, hematite, siderite, magnesite, stibnite, pyrite, sphalerite, chalcocite, and others by the "wet method" in sealed gun barrels, in other words, hydrothermal synthesis. He concluded that "ore veins are nothing else but immense canals, more or less obstructed, through which once passed waters capable of incrustation. These disgorging liquids and gases must be comparable to those of geysers and hot springs" (p. 132). Of his experiments he demanded that "a chemical synthesis which reproduces a single mineral species contemporaneous with a particular ore vein must be applicable at the same time to all other minerals present" (p. 130).

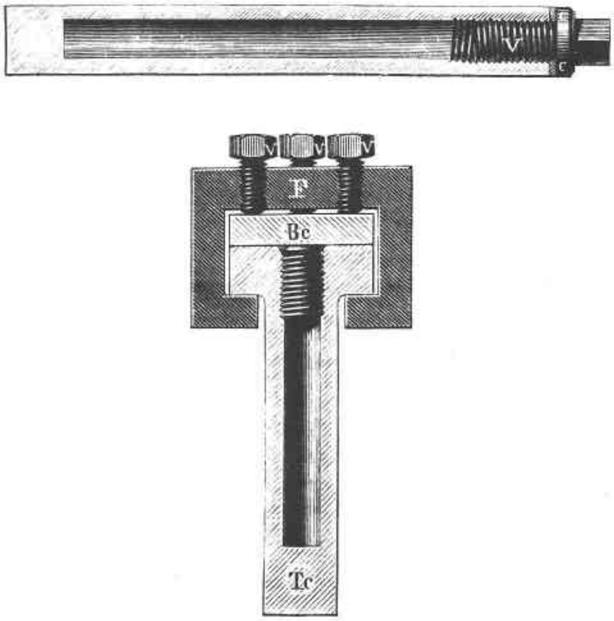

Fig. 2. Autoclaves used by Sénarmont (1851) and Daubrée (1857) in their hydrothermal experiments. From Daubrée (1879).

Starting materials were contained in sealed, evacuated glass ampules filled with water to 50% of their volume, which were placed in brass gun barrels also containing water. One end of the barrel was soldered shut with a steel plug, whereas the other was sealed with a threaded nut and an annealed copper disc. The barrels were placed at the top of the gas furnace at the foundry of Ivry and covered with coal dust and heated to 200–300°C. Sénarmont (1851) warned of the possible explosions "which are frequent and of great violence, in spite of the small quantity of liquid" (p. 136).

Daubrée (1857) followed similar procedures in his hydrothermal experiments, except that he used steel bombs. Figure 2 shows two of these bombs. Feldspar + quartz were produced by heating kaolin with water from the Plombières hot springs for 2 days.

Daubrée also mentions diopside, wollastonite, and pectolite. These and later experiments involving zeolites were summarized in his book (Daubrée, 1879). Friedel and

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[2] Translations by the author.

Sarasin (1879) initiated their extensive hydrothermal studies by synthesizing orthoclase from potassium silicate and $AlCl_3$. The early history of hydrothermal synthesis was summarized by Doelter (1890), Niggli and Morey (1913), and Morey and Ingerson (1937).

Toward the end of the century two other sets of famous geochemical experiments were carried out: those of Van't Hoff on marine evaporites and the studies by Vogt (1904) on magmatic differentiation. Although not concerned with hydrothermal conditions, Van't Hoff and his colleagues carried out the first systematic series of experiments designed to solve a petrologic problem (see Eugster, 1971, for a historical account). With the founding of the Geophysical Laboratory in Washington in 1905, the center of experimental petrology moved to the USA, where it has remained ever since. Between the two world wars, Morey and Goranson made the most notable contributions involving mineral equilibria in superheated steam, Morey with respect to mineral solubilities (Morey, 1942), and Goranson (1938) with respect to silicate melting at high water pressures. After World War II, hydrothermal experimentation grew rapidly to encompass all geochemical aspects, spurred by the technical innovations of O. F. Tuttle (1948). The Tuttle press consists of a hot cone-in-cone seal and was used for the classic papers on the system $MgO\text{-}SiO_2\text{-}H_2O$ (Bowen and Tuttle, 1949) and on feldspar equilibria (Bowen and Tuttle, 1950). Because of leaching problems, it has been replaced by the use of welded noble-metal tubes placed in cold-seal rod bombs, also a Tuttle invention. The study by Tuttle and Bowen (1958) on the system granite-H_2O remains a landmark in experimental petrology. I added procedures for controlling redox reactions in hydrothermal systems (Eugster, 1957), Hemley (1959) focused on acid-base reactions, whereas Franck (1956) measured dissociation equilibria at high P and T using conductivity methods. These techniques have remained essential for hydrothermal studies to this day. The explosive growth of experimental petrology during the fifties emanated largely from the Geophysical Laboratory, Harvard University, and Pennsylvania State University. With the successful synthesis of diamond by General Electric, the focus shifted to mantle mineralogy and ultra-high pressures, relegating hydrothermal research to a lesser role. Nevertheless, studies of mineral solubilities at several hundred to several thousand bars water pressure and temperatures from the subcritical to the supercritical range have remained the continuing concern of a small number of experimentalists. Examples are the classic investigations of Kennedy on quartz solubility (1950) and the exploratory work of Morey and Hesselgesser (1951) on the solubilities of a variety of silicates. Geochemists, economic geologists, and metamorphic petrologists interested in the transport of mineral matter and the growth and dissolution of minerals have relied heavily on these and subsequent contributions. The recent literature has been summarized by Holland and Malinin (1979) and Barnes (1979). Here I would like to point out that many of the fundamental problems of mineral-fluid interaction remain unsolved and must be dealt with if we ever hope to understand geothermal systems, hydrothermal ore deposits, and metamorphic processes. Most of the technical difficulties have been overcome, but we remain faced with an area of geochemistry in which correspondingly few data have been collected and in which predictions far outstrip facts.

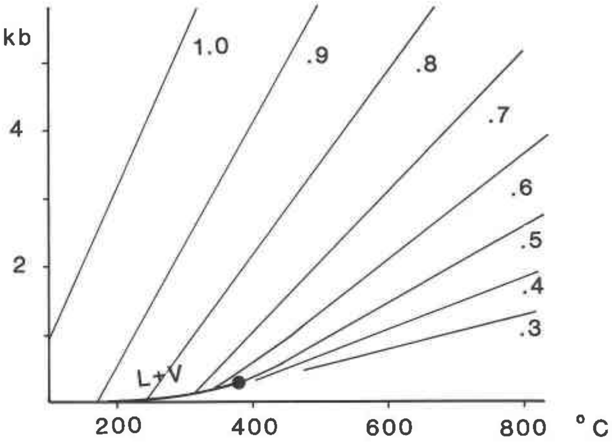

Fig. 3. Density, ρ (in g/cm³), of water vapor as a function of P (kbar) and T (°C). Also shown are the L + V curve and critical point. From the data of Burnham et al. (1969).

VERY HOT WATER

Minerals dissolve in aqueous fluids through the formation of one or more aqueous species in the form of simple ions or complexes. The nature of these species depends on pressure, temperature, and the composition of the fluid. Knowledge of the nature and concentration of the most abundant species is essential if we must know whether a fluid is supersaturated, saturated, or undersaturated with respect to a particular mineral, that is, whether the fluid is capable of precipitating or dissolving that mineral. Kinetic studies of mineral-fluid interaction also depend on speciation information. Speciation questions have been dealt with extensively with respect to surface waters, ground waters, and hot-spring waters. For those applications a large body of information is available (see, for instance, Stumm and Morgan, 1981; Truesdell and Jones, 1974; Henley et al., 1984). In contrast, no more than a few dozen publications contain data on near-critical and supercritical speciation, foremost among them the contributions of Franck (1981), Quist and Marshall (1968), Seward (1976, 1984), Frantz and Marshall (1984), and Crerar et al. (1978). Helgeson and coworkers (1981) have made significant progress in predicting solute species and their thermodynamic properties over a wide range of P and T, but experimental calibration is largely lacking. Metal-complex formation at elevated P and T was discussed recently by Seward (1981) and by Susak and Crerar (1985). Most data were obtained by spectroscopic methods at the pressure of the liquid + vapor equilibrium, and hence conclusions are applicable particularly to the *subcritical* low-pressure region. Here I would like to empha-

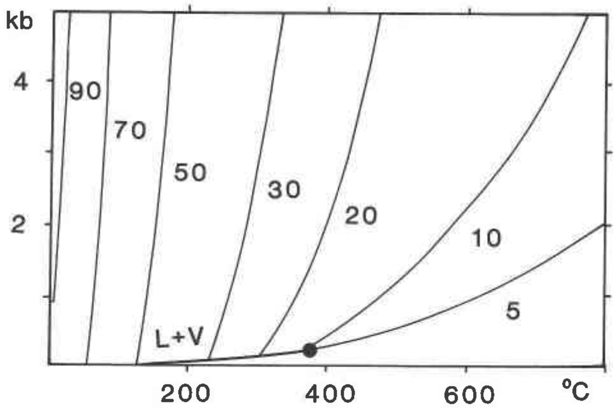

Fig. 4. Dielectric constant, ϵ, of water vapor as a function of P (kbar) and T (°C). Compiled from earlier data by Seward (1981). For more recent data, see Pitzer (1983) and McKenzie and Helgeson (1984).

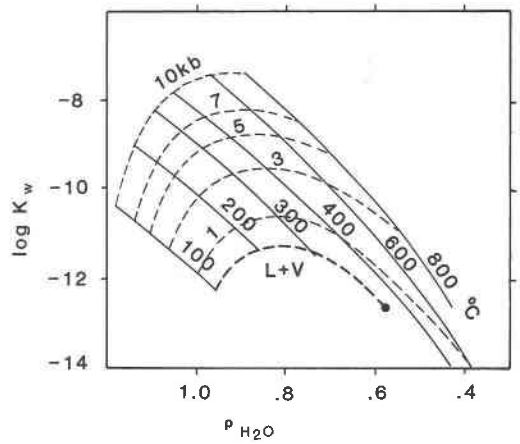

Fig. 5. Dissociation constant for water vapor, K_w, as a function of density, ρ_{H_2O}. Isotherms (°C, solid lines), isobars (kbar, lighter dashed lines), and the L + V curve (heavy dashed line) have been contoured. Calculated from various data (see Marshall and Franck, 1981) by Eugster (1981).

size the properties of *supercritical* fluids, where pressure plays a more dominant role. This is evident from the density of water vapor as a function of P and T (Fig. 3). Density changes with pressure can be substantial, particularly at the higher temperatures.

The remarkable ability of water to disassemble a tightly bonded ionic crystal such as NaCl (melting point, 800.5°C!) is based on its polar nature—its ability to insulate positive from negative charges by surrounding them with water dipoles. In the hydration shells surrounding the ions, water molecules are more ordered and more densely packed than in the bulk solvent. In general, anions are larger than cations and hence less hydrated because of the more diffuse localization of their charge. The solvating ability of water is reflected in its large dielectric constant, ϵ, which under ambient conditions exceeds 80, that is, the presence of water decreases an imposed electric field 80-fold.

Pressure and temperature profoundly affect the solvent properties of water as expressed by changes in ϵ (see Fig. 4). With increasing temperature, ϵ decreases substantially because of the greater kinetic energy of the dipoles. Conversely, ϵ increases with increasing pressure at constant temperature because of the decrease in volume associated with hydration. In the supercritical region of interest here, ϵ is 25 or less. For a recent summary see Pitzer (1983).

In the hydrothermal region, the dissociation constant of water, K_w, varies over four orders of magnitude, roughly from 10^{-13} to 10^{-9} (see, for instance, Marshall and Franck, 1981). These changes with P and T are due to changes in hydrogen bonding of the water molecule, the dielectric constant of water, and the partial molal volume of the solvated ions. Figure 5 shows K_w as a function of water density, ρ_{H_2O}, with isotherms and isobars contoured. Isobaric temperature increases initially lead to increased dissociation of the solvent, largely owing to a decrease in the hydrogen bonding. Eventually, however, the decrease in the dielectric constant becomes dominant, and the isotherms pass through a maximum, leading to increased association of the solvent. The temperatures at which the K_w isobars of Figure 5 pass through a maximum increase with increasing pressure, in agreement with the effect of pressure on ϵ illustrated in Figure 4. The behavior of the isotherms in Figure 5 are more straightforward. For every temperature considered, K_w increases monotonically with increasing pressure, because of electrostatic collapse of the solvent around the ions. As expressed by Ritzert and Franck (1968, p. 805), "at all temperatures ion dissociation is favored by compression. This is based on the denser packing of the water molecules in the hydration shells of the ions." The effect of a pressure increase is greatest at the higher temperatures, particularly above the critical temperature, a fact illustrated by the P-T dependence of ϵ illustrated in Figure 4. Above 400°C, a pressure change of as little as 1 kbar causes a dramatic shift in ϵ.

VERY HOT SOLUTES

The behavior of the solutes also is governed by changes in the dielectric constant and by electrostriction. For isobaric temperature increases, ϵ decreases, favoring association of the solutes. Conversely, an isothermal increase in pressure favors dissociation of the solutes caused by the rise in ϵ as a consequence of the improved hydrostatic shielding. The response of strong electrolytes is best illustrated by NaCl, for which data are available from Quist and Marshall (1968), illustrated in Figure 6. K_{NaCl} decreases with temperature and between 300 and 400°C, depending upon water pressure, reaches a value of one, that is, roughly half of the Na and Cl is present as uncharged $NaCl^0$ molecules:

$$NaCl^0 \rightleftharpoons Na^+ + Cl^- \qquad (1)$$

and

$$K_{NaCl} = \frac{[Na^+][Cl^-]}{[NaCl^0]} .$$

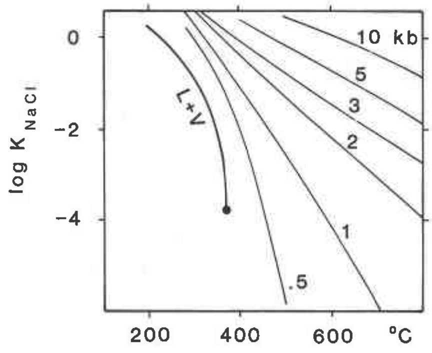

Fig. 6. Dissociation constant of NaCl in water vapor as a function of temperature (°C). Isobars have been contoured in kilobars. From the data of Quist and Marshall (1968).

Toward higher temperatures, K_{NaCl} continues to decrease dramatically, and above 500°C, NaCl is largely associated. As with the solvent, an increase in pressure favors dissociation owing to the tighter packing of the H_2O molecules around Na^+ and Cl^-, increasing the value of K_{NaCl}.

The data of Figure 6 were obtained from conductivity measurements in dilute solutions. At high salt concentrations, conductivities decrease to about one-third that in dilute solutions, and there is little temperature dependence between 300 and 600°C (Hwang et al., 1970; Klostermeier, 1973). Franck (1981, p. 73) concluded that "it is not yet possible to decide to what extent this diminution of charge carriers can be attributed to well defined associations of salt molecules, ion-pairs or triple ions."

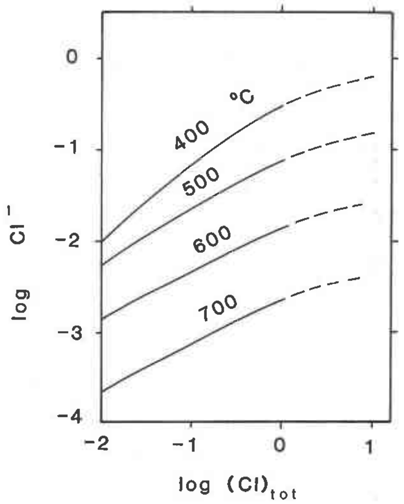

Fig. 7. Molality of free chloride ions as a function of total chloride concentration in NaCl-H_2O solutions at 1-kbar pressure. Isotherms are contoured in °C.

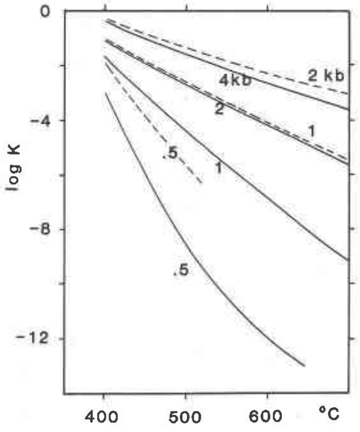

Fig. 8. Dissociation constant of HCl as a function of temperature (°C). Pressure is contoured in kilobars. From the data of Frantz and Marshall (1984). For comparison, the NaCl data of Figure 6 are shown as dashed curves.

Clearly, the molal K_{NaCl} values of Quist and Marshall (1968) cannot be used for concentrated solutions unless activity coefficient corrections are made. In dilute solutions, the concentration of free chloride ions can be calculated as a function of *P, T,* and total chloride molality, $(m_{Cl})_{tot}$, by combining Equation 1 with the electrical neutrality condition (Eq. 2). For a solution of NaCl, we have

$$[Na^+] + [H^+] = [Cl^-] + [OH^-], \qquad (2)$$

which simplifies to

$$[Na^+] \approx [Cl^-]$$

for a solution with a near-neutral pH and a total chloride molality of at least 10^{-4}. Results for a constant pressure of 1 kbar are shown in Figure 7. As the temperature increases, the concentration of chloride ions and with it the ionic strength, *I*, drop dramatically, reflecting increased association. On the other hand, the Cl^- concentration increases with increasing total chloride. An increase in pressure would raise the curves of Figure 7 toward higher Cl^- values. The difference between the molality of free chloride ions and the total chloride molality of the solution is largest in the supercritical region at moderate pressures. Here fluids rich in total chloride do not have many free

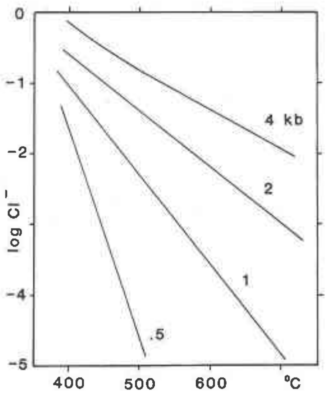

Fig. 9. Molality of free chloride ions for a 0.1-molar solution of HCl-H_2O as a function of temperature (°C). Pressure is contoured in kilobars.

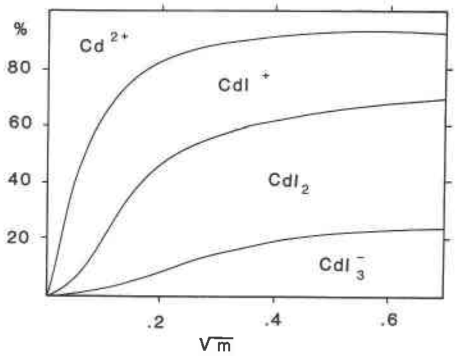

Fig. 10. Stepwise association of Cd ions at 25°C as a function of increasing cadmium iodide molality. From Robinson and Stokes (1959).

chloride ions. This distinction is crucial, because the formation of metal-chloride complexes depends on the activity of the chloride ions and not the total chlorinity of the solutions. In this region of dominant association, NaCl ceases to be the strong electrolyte it is at room temperature. Because it is based on changes in the solvent, this fate is shared by strong electrolytes in general: "as one moves into a low water-density and low dielectric-constant domain, a lot of solutes that we call strong electrolytes become weak electrolytes" (Pitzer, 1981, p. 175).

HCl behaves in a similar fashion. Figure 8 is based on the dissociation data of Frantz and Marshall (1984)

$$K_{HCl} = \frac{[H^+][Cl^-]}{[HCl]} . \quad (3)$$

A comparison with Figure 6 shows that HCl is somewhat more associated than NaCl at the same P and T. In the supercritical region, K_{HCl} is two to three orders of magnitude smaller than K_{NaCl}. In fact, the 2-kbar isobar for K_{HCl} coincides with the 1-kbar K_{NaCl} isobar. Figure 9 shows the molality of chloride ions for a solution of 0.1 mol ($HCl + Cl^-$) as a function of temperature. Isobars from 0.5- to 4-kbar water pressure are contoured. For similar P, T, and total chloride molality, supercritical HCl solutions contain even fewer free chloride ions than do NaCl solutions.

Dissociation data for other supercritical electrolytes are less complete, but the general trends with P and T are the same, since they are imposed by changes in the solvent. Strong acids, strong bases, and strong salts become weak acids, weak bases, and weak salts. Similarly, electrolytes that are weak at ambient temperatures become fully associated and are present dominantly as uncharged molecules. Consequently, ionic strengths of concentrated solutions are much lower than they are at room temperature. Because of the decreased electrostatic shielding in the low-density–low-dielectric-constant region, interactions between metal ions and ligands are largely electrostatic and hard in terms of Pearson's (1963) classification (see also Crerar et al., 1985). Ligand-field stabilization energies (LFSEs) in this region are greatly diminished.

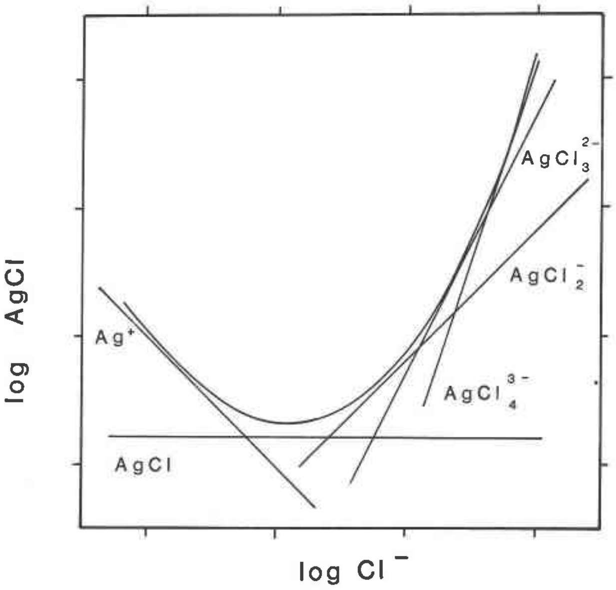

Fig. 11. Schematic drawing of the stepwise complexing of Ag ions as a function of chloride ion activity in equilibrium with cerargyrite. After Seward (1976).

Another important effect of the low ionic strengths of concentrated solutions at pressures and temperatures where association predominates is related to activity coefficients. In high-ionic-strength electrolyte solutions at room temperature, activity coefficients have been modeled successfully by adding two virial coefficients, the Pitzer coefficients, to the Debye-Hückel term (Harvie and Weare, 1980). We have used this method to predict the effects of evaporating seawater (Eugster et al., 1980) and to define the phase relations and brine compositions in the system $Na\text{-}K\text{-}Ca\text{-}Mg\text{-}Cl\text{-}SO_4\text{-}H_2O$ (Harvie et al., 1982). Harvie et al. (1984) have extended the approach to include carbonate and bicarbonate ions. At high temperatures, neutral complexes predominate, and such complexes can be assigned unit activity coefficients (Helgeson et al., 1981). For the charged complexes, a Debye-Hückel treatment may be adequate, because of the lesser importance of short-range order. Debye-Hückel constants as a function of P and T have been presented by Helgeson and Kirkham (1976). The definition of å, the radius of closest approach, remains to be clarified for each individual ion (see Helgeson et al., 1981). Nevertheless, activity-coefficient corrections in concentrated solutions at high P and T are not as difficult as they are at room temperature.

EFFECT OF LIGAND CONCENTRATION

Stepwise formation of metal complexing takes place at a given P and T in response to increasing ligand activity. This has been demonstrated at room temperature, for instance, for cadmium iodide, where the following sequence occurs as a function of iodide molality (see Fig. 10):

$$Cd^{2+} \rightarrow CdI^+ \rightarrow CdI_2 \rightarrow CdI_3^- .$$

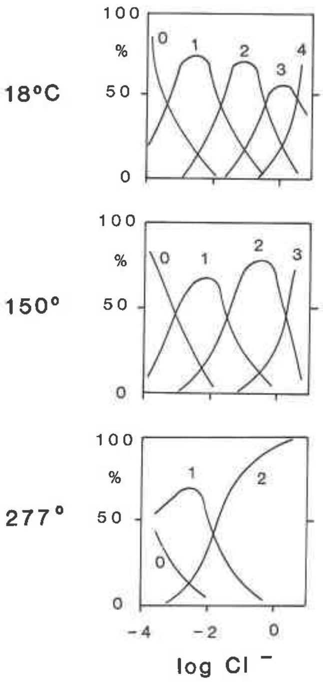

Fig. 12. Abundances of individual silver-chloro complexes as a function of total chloride concentration and temperature (°C). After Seward (1976).

In chloride solutions a similar situation has been reported by Seward (1976) for the case of silver chloride complexes, for temperatures from 18 to 353°C at pressures of the L + V equilibrium. With increasing a_{Cl^-}, achieved by adding NaCl, the following steps were observed:

$$Ag^+ \rightarrow AgCl \rightarrow AgCl_2^- \rightarrow AgCl_3^{2-} \rightarrow AgCl_4^{3-}.$$

These steps are illustrated schematically in Figure 11, with the silver concentration in solution controlled by the solubility of cerargyrite, AgCl. For a given temperature, the solubility curve can be interpreted as the sum of several chloride complexes which change in their abundance with changing NaCl concentrations. Seward's (1976) computer fit to his data is reproduced in Figure 12, with each complex identified by its ligand number. Figure 12 illustrates the simplification in speciation that takes place with rising temperature through increasing association. Below 100°C, all five species are found, whereas above 300°C, only AgCl and $AgCl_2^-$ are abundant. It should be remembered that at 350°C at the L + V curve, K_{NaCl} is 0.01—that is, for a total chloride molality of 0.1, the molality of the free chloride ion is only 0.026. At higher pressures, for the same temperature, larger values of $[Cl^-]$ can be reached by adding NaCl, presumably resulting in the formation of $AgCl_3^{2-}$ and $AgCl_4^{3-}$, even at 350°C and higher temperatures. Further experiments are necessary to check this conjecture.

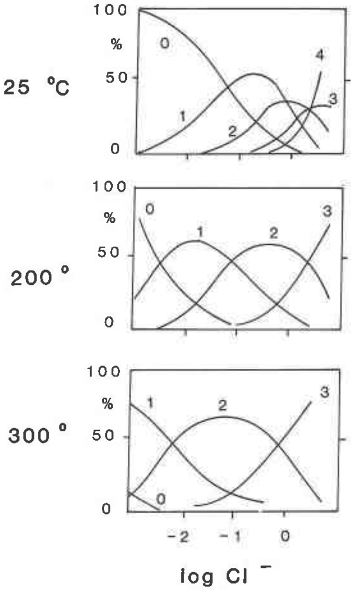

Fig. 13. Abundances of individual lead-chloro complexes as a function of total chloride concentration and temperature (°C). After Seward (1984).

Seward (1984) also investigated the stepwise formation of lead chloride complexes to 300°C, but using spectrophotometric methods. At 25°C, five species of the type $PbCl_n^{2-n}$ were found with n = 0, 1, 2, 3, and 4, whereas at 300°C only $PbCl^+$, $PbCl_2^0$ and $PbCl_3^-$ were abundant. The stepwise sequence in response to increasing Cl^- is typical for a bivalent cation:

$$Pb^{2+} \rightarrow PbCl^+ \rightarrow PbCl_2^0 \rightarrow PbCl_3^- \rightarrow PbCl_4^{2-} \rightarrow \ldots.$$

A comparison of the 25 and 300°C results is shown in

Table 1. Enthalpies (ΔH, in kJ/mol) of stepwise association for silver and lead-chloro complexes (from Seward, 1976, 1984)

T, °C	AgCl	$AgCl_2^-$	$AgCl_3^{2-}$	$PbCl^+$	$PbCl_2$	$PbCl_3^-$
25	-12.5	-17.6	-17.4	2.46	12.3	-17.5
150	0	3.8	-9.6	29.9	15.5	7.1
250	36.6	4.8		69.7	49.5	31.8
350	121	77.9				

Table 2. Entropies (ΔS, in J/(K·mol)) of stepwise association for silver and lead-chloro complexes (from Seward, 1976, 1984)

T, °C	AgCl	$AgCl_2^-$	$AgCl_3^{2-}$	$PbCl^+$	$PbCl_2$	$PbCl_3^-$
25	20	-22	-57	35	52	-65
150	55	38	-36	110	58	9.5
250	130	43		190	130	60
350	280	170				

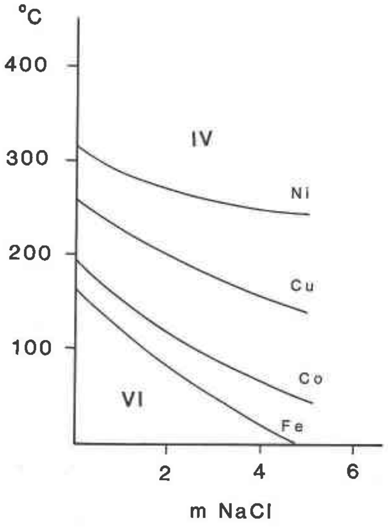

Fig. 14. Coordination change from sixfold to fourfold for Fe, Co, Cu, and Ni as a function of temperature and total chloride molality for pressures of the L + V curve. After Susak and Crerar (1985).

Figure 13, confirming the general trends exhibited by silver chloride complexing. Seward (1976, 1984) has extracted thermodynamic parameters from the equilibrium constants for the silver and lead complexes. He found that with rising temperatures, enthalpies (see Table 1) and entropies (see Table 2) become increasingly positive. At elevated temperatures, complexing reactions between these metals and chloride are all endothermic, that is, heat is required to replace the water molecules of the hydration shell with chloride ions. For instance, for an octahedral complex we have

$$(Pb(H_2O)_6)^{2+} + Cl^- \rightleftharpoons (PbCl(H_2O)_5)^- + H_2O. \quad (4)$$

Because the water is released from the structured environment of the complex into the highly disordered bulk solvent, a large entropy increase results, decreasing the free energy and stabilizing the complex. This situation is analogous to dehydration reactions during progressive metamorphism, which are driven largely by the entropy gain of the water liberated from the crystal structure. As Table 2 shows, for a given complex the entropy increases with increasing temperature because of the increasing disorder in the bulk solvent. Furthermore, "the large positive entropies also imply that inner sphere complex formation becomes more important at higher temperatures" (Seward, 1984, p. 129).

On the other hand, as the number of chloride ligands increases in the complex, both ΔH and ΔS decrease. This indicates a decrease in solvation linked to the decrease of positive charges (Seward, 1984, p. 129).

All of the data collected by Seward (1976, 1984) refer to the relatively low pressures of the L + V equilibrium, 200 bars or less. Increasing pressure, particularly in the supercritical region, will have a pronounced effect by stabilizing the more hydrated, lower-ligand species, increasing positive charges and degree of solvation. The effect of pressure is thus opposite to the effect of an increase in the chloride ion activity.

Pressure has a profound influence also on the coordination number of complexes, though data on this point are scarce in the supercritical region (see Seward, 1981). Increasing temperature and chloride ion concentration favor transition from octahedral to tetrahedal coordination. Figure 14 is taken from Susak and Crerar (1985) and shows data for the VI $\rightleftharpoons$ IV transition for Fe, Co, Cu, and Ni as a function of T and total chloride molality. Pressure is that of the L + V equilibrium. Lowering the coordination number decreases the charge on the inner-sphere complex which is favored in a low-dielectric-constant environment where coulombic attraction between metal ions and ligands is dominant. Pressure, however, stabilizes the higher coordination state, because it increases ϵ, favors dissociation and solvation, and by electrostriction leads to a volume decrease. This has been documented for Ni and Co at 500°C and 6 kbar by Lüdemann and Franck (1968). In the supercritical region, where water densities are comparatively low (see Figure 3), pressure will have a particularly pronounced effect in stabilizing 6-fold coordination. Although not yet reported, higher coordinations of 8 or 12 are possible.

SPECIATION AND SOLUBILITY DETERMINATIONS AT HIGH *P* AND *T*

In general, speciation information is derived from conductivity, solubility, or spectroscopic measurements. In this section, preliminary to discussing our data on Fe, Sn, and W and the solubilities of magnetite, cassiterite, and wolframite, the experimental procedures and data analysis methods used in those studies will be summarized briefly (see also Wilson, 1986; Eugster and Wilson, 1985; Eugster et al., 1986).

Mineral reactions involving HCl have been measured successfully using the Ag-AgCl buffer of Frantz and Eugster (1973). The assemblage Ag + AgCl in conjunction with an oxygen buffer controls f_{HCl} at P and T (Fig. 15c). This is necessary for reactions that consume or release significant amounts of HCl. However, because it restricts chloride ion molality to a single value for a given P and T, it is not a suitable method for speciation studies that depend on as large a range of Cl^- molality as possible. To overcome this limitation, Frantz and Popp (1979) used the "unbuffered" method, later termed the "modified Ag-AgCl buffer" (Boctor et al., 1980), shown in Figure 15b. The assemblage Ag + AgCl is placed with the charge, but no oxygen buffer is used. Instead, hydrogen sensors (Chou and Eugster, 1976) are placed inside, which monitor f_{H_2}. This, in conjunction with Ag + AgCl in the charge system, allows calculation of f_{HCl} at P and T. Because f_{O_2} is not controlled, the chloride ion molality can be varied independently. Using this method, Frantz and Popp (1979), Popp and Frantz (1979, 1980), and Boctor et al. (1980) determined speciation in chloride fluids for Mg, Ca, Na,

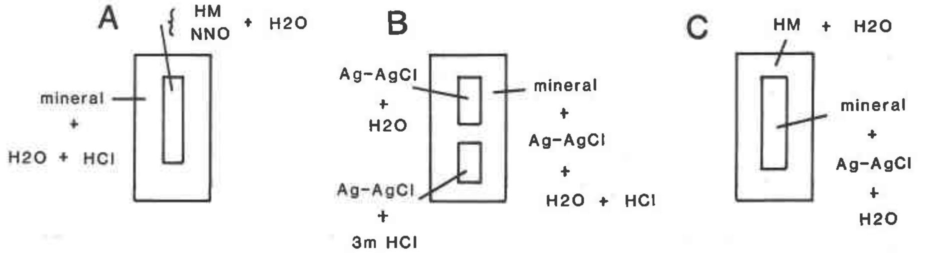

Fig. 15. Experimental arrangements for supercritical speciation determinations from mineral solubilities. (A) Method of Wilson (1986). See also Wilson and Eugster (1984, 1985), Eugster and Wilson (1985), Eugster et al. (1986). (B) "Unbuffered" or "modified buffer" method of Frantz and Popp (1979) and Boctor et al. (1980). (C) Ag-AgCl buffer method of Frantz and Eugster (1973). For details see text.

and Fe. The data for Mg and Ca were later retracted (Frantz and Marshall, 1982).

For metals that may have a valence in the fluid different from that in the solid, the "modified Ag-AgCl buffer" method cannot be used. In such cases, f_{O_2} must be strictly controlled. Chloride concentration must be fixed by the bulk composition of the fluid, and speciation is evaluated from the chemical analysis after quench by calculation of the relevant equilibria back to P and T (Wilson, 1986; Wilson and Eugster, 1984, 1985; Eugster et al., 1986). The experimental arrangement is depicted in Figure 15a. Total chloride molality and, through it, chloride ion molality at P and T are varied by adding different amounts of HCl, NaCl, or other soluble chlorides to the starting solution. To maximize solution volume, the oxygen buffer is placed in the smaller, inside tube, commonly 3.0-mm diameter Pt, whereas the charge is placed in the larger, 4.4-mm Au tube. After quench in a rapid-quench vessel (Rudert et al., 1976), the tube is opened in a glove box purged with water-saturated argon to prevent oxidation and evaporation. The pH is measured with a microelectrode, and aliquot solution samples are extracted for analysis. Chloride concentration is measured on the chloridometer or, preferably, the ion chromatograph. Metals are determined by AA, ion chromatograph, or other appropriate methods. For each experiment, P, T, and f_{O_2} are known. We also know the mass balances for chloride and for each of the metals, as well as the electrical neutrality condition for ambient P and T. For a single metal of valence x which is fully dissociated, we have

$$x[\mathrm{Me}^{x+}]^{1,25} + [\mathrm{H}^+]^{1,25} = [\mathrm{Cl}^-]^{1,25} + [\mathrm{OH}^-]^{1,25}. \quad (5)$$

Quench is very rapid, carried out at pressure, and oxidation is not possible. We have not observed evidence of mineral precipitation during or after quench. Consequently, the metal valence at P and T must also be x. Assuming the presence of a single dominant metal-chloride complex with the ligation number n, the electrical neutrality condition at P and T is

$$[\mathrm{H}^+]^{P,T} + (x - n)[\mathrm{MeCl}_n^{x-n}]^{P,T} = [\mathrm{Cl}^-]^{P,T} + [\mathrm{OH}^-]^{P,T}. \quad (6)$$

The chloride mass balance is given by

$$\mathrm{Cl}_{\mathrm{tot}} = [\mathrm{Cl}^-]^{P,T} + [\mathrm{HCl}]^{P,T} + n[\mathrm{MeCl}_n^{x-n}]^{P,T} \quad (7)$$

and the metal mass balance by

$$\mathrm{Me}_{\mathrm{tot}} = [\mathrm{MeCl}_n^{x-n}]^{P,T} \quad (8)$$

with $\mathrm{Cl}_{\mathrm{tot}}$ and $\mathrm{Me}_{\mathrm{tot}}$ obtained by chemical analysis after quench. The unknown quantities that must be calculated for each experiment, assuming a single dominant mononuclear metal-chloride complex, are $[\mathrm{H}^+]^{P,T}$, $[\mathrm{Cl}^-]^{P,T}$, $[\mathrm{HCl}^0]^{P,T}$, and $[\mathrm{MeCl}_n^{x-n}]^{P,T}$. At this point, x is known, but n is not. In addition to Equations 6, 7, and 8, the dissociation constant for HCl is also known for P and T (Frantz and Marshall, 1984)

$$K_{\mathrm{HCl}} = \frac{[\mathrm{H}^+][\mathrm{Cl}^-]}{[\mathrm{HCl}]}. \quad (9)$$

No additional independent relationship is available, and the five unknowns cannot be solved for directly. However, we know that n must be a small integer of value 0, 1, 2, 3, or 4, and following Wilson (1986), we solve Equations 6–9 *for each experiment,* assuming a value for n and comparing the results with the predicted slope. For instance, the oxide of a bivalent metal should dissolve in a chloride solution by a reaction such as

$$\mathrm{MeO} + 2\mathrm{H}^+ + n\mathrm{Cl}^- \rightleftharpoons \mathrm{MeCl}_n^{2-n} + \mathrm{H_2O} \quad (10)$$

with an equilibrium constant K_{10} of

$$\log K_{10} = \log [\mathrm{MeCl}_n^{2-n}] + 2\ \mathrm{pH} - n \log [\mathrm{Cl}^-] \quad (11)$$

for a standard state of pure solids and pure $\mathrm{H_2O}$ at P and T. If n was chosen correctly, plotting $\log [\mathrm{MeCl}_n^{2-n}] + 2$ pH vs. $\log [\mathrm{Cl}^-]$ for each experiment should produce a straight line of slope n and intercept of $\log K_{10}$. Comparison of the five or so plots will quickly reveal the proper choice for n, provided the scatter in the experimental data is not excessive.

The one-species assumption leads to less equivocal results than the "variation of slope" method traditionally used in speciation determinations (see, for instance, Seward, 1976; Crerar and Barnes, 1976; Frantz and Popp, 1979). Wilson (1986) has extended the calculations to include two or three dominant complexes, using least-squares procedures instead of the visual trial-and-error method described here. Wilson and Eugster (1985) successfully tested the method on their cassiterite-solubility data as well as on the talc data of Frantz and Popp (1979). If polynuclear species are present, however, solubility data alone cannot yield unequivocal speciation data.

The experimental procedures and data analysis described here are applicable to ligands other than chloride, such as (OH^-), (HS^-), (HCO_3^-). They do depend, however, on the availability of reliable data for the dissociation constants of the relevant acids, bases, and salts. For instance, if Reaction 10 proceeds in the presence of NaCl, Equations 6 and 7 must be modified as follows:

$$[H^+]^{P,T} + [Na^+]^{P,T} + (x - n)[MeCl_n^{x-n}]^{P,T} = [Cl^-]^{P,T} + [OH^-]^{P,T} \quad (6a)$$

and

$$Cl_{tot} = [Cl^-]^{P,T} + [HCl]^{P,T} + [NaCl]^{P,T} + n[MeCl_n^{x-n}]^{P,T}. \quad (7a)$$

The additional information obtained from

$$K_{NaCl} = \frac{[Na^+][Cl^-]}{[NaCl]} \quad (12)$$

allows the calculations to be carried out as before. If the pH is high enough for $NaOH^0$ to become a significant species, the constant

$$K_{NaOH} = \frac{[Na^+][OH^-]}{[NaOH]} \quad (13)$$

must be included. Unfortunately, K_{13} is not well known in the supercritical region.

MAGNETITE, CASSITERITE, AND WOLFRAMITE SOLUBILITY AND Fe, Sn, W SPECIATION

Magnetite solubility in supercritical chloride fluids was determined by Chou and Eugster (1977) using the Ag-AgCl buffer (Frantz and Eugster, 1973). Fe in solution was determined to be bivalent. $FeCl_2$ was thought to be the principal solute, but no definite proof was provided. Boctor et al. (1980) identified $FeCl_2$ as the main solute in equilibrium with hematite at 400–600°C, 1–2 kbar. Wang et al. (1984; see also Eugster and Wilson, 1985) have determined magnetite solubility in HCl and NaCl solutions at 600 and 650°C, 2 kbar, with f_{O_2} controlled by hematite–magnetite (HM) and nickel–nickel oxide (NNO) buffers. Fe-Cl complexes were identified using the procedures of Wilson (1986), described above. Assuming a single dominant Fe-Cl complex, abundances at P and T must be calculated for the following species: H^+, Na^+, $FeCl_n^{2-n}$, Cl^-, OH^-, HCl, and NaCl. Mass balances for Cl, Na, and Fe were determined after quench, dissociation constants for H_2O, HCl, and NaCl are available from the literature, and the electrical neutrality condition at P and T provides the seventh relation among the seven unknown species. Again, n is obtained by trial and error. At 600°C, 2 kbar, n was found to be 2, confirming $FeCl_2^0$ as the principal Fe-Cl complex. Figure 16 shows a plot of log $[FeCl_n^{2-n}]$ + $\frac{1}{6}$log f_{O_2} + 2 pH vs. log $[Cl^-]$ according to the reaction

$$\tfrac{1}{3}Fe_3O_4 + 2H^+ + nCl^- \rightleftharpoons FeCl_n^{2-n} + H_2O + \tfrac{1}{6}O_2 \quad (14)$$

for $n = 2$. The y intercept is 7.4, representing log K_{14}, and it is consistent with the results of Chou and Eugster (1977). Consequently, magnetite dissolution at this P and T can be written as

$$\tfrac{1}{3}Fe_3O_4 + 2H^+ + 2Cl^- \rightleftharpoons FeCl_{2(aq)} + H_2O + \tfrac{1}{6}O_2. \quad (14a)$$

At 650°C, both $n = 2$ and $n = 3$ produce plots compatible with the experiments available, making $FeCl_3^-$ another possible solute. Further work is necessary to clarify this point. Experiments performed in NaCl solutions at 650°C, 2 kbar, f_{O_2} controlled by NNO are shown in Figure 17 with $NaCl_{(tot)}$ molalities ranging from 0.5 to 2.8. Total Fe concentrations in solution range from 2×10^{-5} to 4×10^{-4} mol/L and are surprisingly low. Quench pH was between 8 and 9, and reversals were achieved by adding $FeCl_2$ to the starting solution. Magnetite solubility in NaCl solutions at 650°C, 2 kbar can be expressed by

$$\log [Fe] = -4.18 + 1.29 \log [NaCl]. \quad (15)$$

The increase in total Fe with NaCl could be due to the formation of $FeCl_3^-$ or perhaps a hydroxy-chloro complex. The low Fe contents of supercritical NaCl solutions in equilibrium with magnetite demonstrate that such fluids are not effective solvents even at high P and T. Similar conclusions were reached by Seyfried and Bischoff (1981) at lower temperatures from experiments of basalt alteration with NaCl brines. This can be interpreted by considering the reaction

$$Fe_3O_{4(s)} + 6NaCl_{(aq)} \rightleftharpoons 3FeCl_{2(aq)} + 3Na_2O_{(s)} + \tfrac{1}{2}O_2. \quad (16)$$

For Reaction 16 to proceed to the right, a solid or melt must be present with sufficient affinity to dissolve Na_2O and allow $FeCl_2$ to form. The amount of magnetite dissolved will be proportional to the amount of Na_2O consumed by that phase.

In acid solutions, we have found that total Fe molality in solution was, within experimental error, half the total chloride molality, suggesting a reaction such as

$$Fe_3O_{4(s)} + 6HCl \rightarrow 3FeCl_{2(aq)} + 3H_2O + \tfrac{1}{2}O_2. \quad (17)$$

During each experiment, essentially all of the initial HCl is consumed; that is, the amount of magnetite dissolved is directly proportional to the amount of HCl added. This, of course, is the case only when no other source of HCl is present such as the Ag-AgCl buffer. Reaction 17 will proceed to the right until all HCl is exhausted.

There is no difficulty in dissolving magnetite in basic NaCl solutions, because of the presence of NaOH:

$$Fe_3O_{4(s)} + 6NaCl_{(aq)} + 3H_2O \rightarrow 3FeCl_{2(aq)} + 6NaOH_{(aq)} + \tfrac{1}{2}O_2. \quad (18)$$

However, no relevant speciation studies have yet been reported, and other complexes, such as $Fe(OH)_3^-$ are sure to be present as well in such solutions.

At subcritical temperatures, $FeCl_2$ is replaced by $FeCl^+$ and Fe^{2+} as dominant Fe species. Dissociation constants

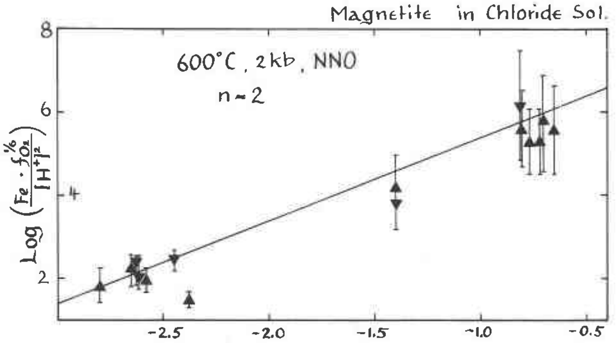

Fig. 16. Solubility of magnetite in HCl-NaCl-H_2O solutions as a function of free chloride ion molality at 600°C, 2 kbar, and f_{O_2} controlled by NNO. The solid line is drawn with a slope of 2, indicating that $FeCl_2$ is the dominant solute. From Wang and Eugster (in prep.).

for $FeCl_2$, according to

$$FeCl_2 \rightleftharpoons FeCl^+ + Cl^- \qquad (19)$$

and

$$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^-, \qquad (20)$$

have been reported by Crerar et al. (1978) at 300°C, but the data are not sufficiently complete to allow extrapolations (see also Wood and Crerar, 1985).

Cassiterite, SnO_2, is about 100 times less soluble than magnetite. Wilson (1986) studied its dissolution and speciation behavior between 400 and 700°C, at 1.5-kbar pressure, and his results are summarized briefly here (see also Eugster and Wilson, 1985). Dissolution can be represented by the reaction

$$SnO_{2(s)} + xH^+ + nCl^- \rightarrow SnCl_n^{x-n} + \frac{x}{2}H_2O + \frac{4-x}{4}O_2; \qquad (21)$$

x was found to be 2 or 4, depending on f_{O_2}, and n was found to be 1 or 2 for the stannous complexes ($SnCl^+$ and $SnCl_2$) and 3 for the stannic complex ($SnCl_3^+$). Figure 18 shows the results for 400 and 500°C with f_{O_2} fixed by NNO. A slope of 1 conforms to all experiments, indicating the reaction

$$SnO_{2(s)} + 2H^+ + Cl^- \rightarrow SnCl^+ + H_2O + ½O_2, \qquad (22)$$

and the intercept gives

$$\log K_{22} = 29.3 - (27\,500/T), \qquad (22a)$$

where T is in kelvins. Note that dissolution entails reduction of tin valence. Figure 19 gives the results for HM at 500 and 600°C. Here $SnCl_3^+$ is dominant, and we have

$$SnO_{2(s)} + 4H^+ + 3Cl^- \rightarrow SnCl_3^+ + 2H_2O \qquad (23)$$

and

$$\log K_{23} = 33.2 - (18\,100/T), \qquad (23a)$$

where T is in kelvins. $SnCl_2$ was found to be abundant at 600°C and dominant at 700°C with NNO. The stannous and stannic complexes are related by

$$SnCl^+ + 2Cl^- + 2H^+ \rightleftharpoons SnCl_3^+ + H_2, \qquad (24)$$

and this reaction has been plotted in Figure 20 for 500°C, 1.5 kbar as a function of pH and chloride molality at P and T, with f_{H_2} controlled by quartz-fayalite-magnetite (QFM) and HM. Obviously, higher Cl^- and lower pH favor the stannic complex. Equation 24 has also been plotted in Figure 21 as a function of f_{O_2} and T, with the pH controlled by the reaction

$$3KAlSi_3O_8 + 2H^+ \rightleftharpoons KAl_2AlSi_3O_{10}(OH)_2 + 6SiO_2 + 2K^+ \qquad (25)$$

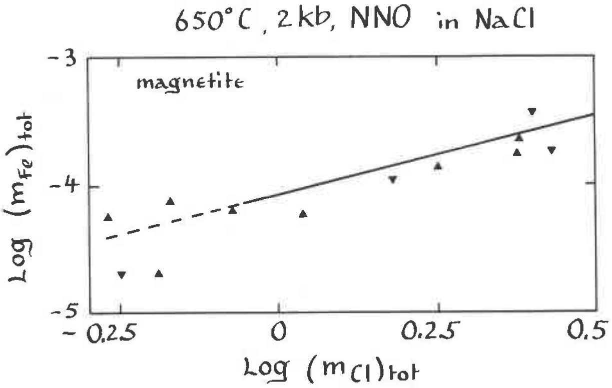

Fig. 17. Solubility of magnetite in NaCl-H_2O solutions at 650°C, 2 kbar, and f_{O_2} controlled by NNO, drawn as a function of total chloride molality. From Wang and Eugster (in prep.).

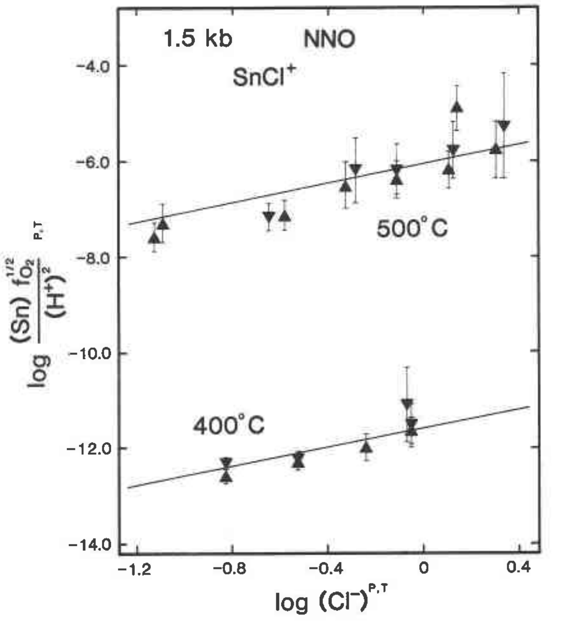

Fig. 18. Solubility of cassiterite in HCl-H_2O solutions, as a function of chloride ion molality at 400 and 500°C, 1.5 kbar, and f_{O_2} controlled by NNO. The solid lines have a slope of 1, indicating that $SnCl^+$ is the dominant solute. From Wilson (1986).

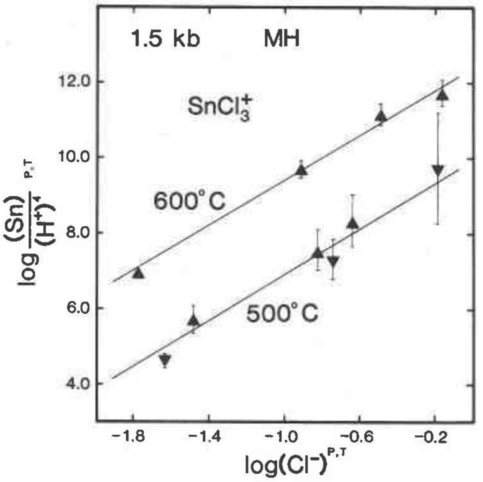

Fig. 19. Solubility of cassiterite in HCl-H_2O solutions as a function of chloride ion molality at 500 and 600°C, 1 kbar, and f_{O_2} controlled by MH. The electrical neutrality condition after quench indicated that Sn^{4+} was present in solution. The solid lines have a slope of 3, appropriate for $SnCl_3^+$ as dominant solute. From Wilson (1986).

proceeding in a solution with a total chloride molality of 2. The assemblage K-feldspar + muscovite is commonly observed in cassiterite deposits, and hence we may conclude that for such deposits $SnCl_3^+$ does not appear to be an important solute species. In order to evaluate Sn concentrations in solutions responsible for Sn-W deposits, Equation 22 has been plotted in Figure 22 for QFM, NNO, and HM and the pH defined by K-feldspar + albite + muscovite + 2 m (NaCl + KCl) at temperatures between

$$SnCl_3^+ + H_2O \rightleftharpoons SnCl^+ + 1/2O_2 + 2H^+ + 2Cl^-$$

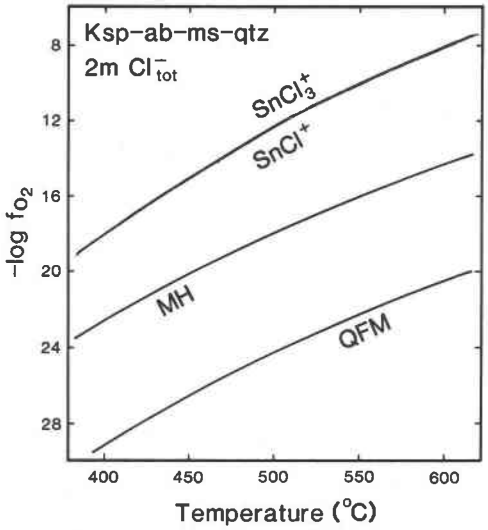

Fig. 21. Oxidation of $SnCl^+$ to $SnCl_3^+$ as a function of f_{O_2} and temperature with pH defined by the assemblage K-feldspar + albite + muscovite + quartz in a 2 *m* total chloride solution at 1.5-kbar pressure. The MH and QFM curves are shown for comparison. From Wilson (1986).

400 and 600°C. For these conditions, Sn concentration in solution increases with *T* and decreases with increasing f_{O_2}. For solutions to reach 1 ppm Sn, for NNO and feldspar-mica assemblages, a temperature of at last 450°C must be reached. This temperature is higher than the depositional temperature generally deduced from fluid-inclusion studies. Precipitation of cassiterite can be initiated by a drop in *T*, oxidation, an increase in pH and probably

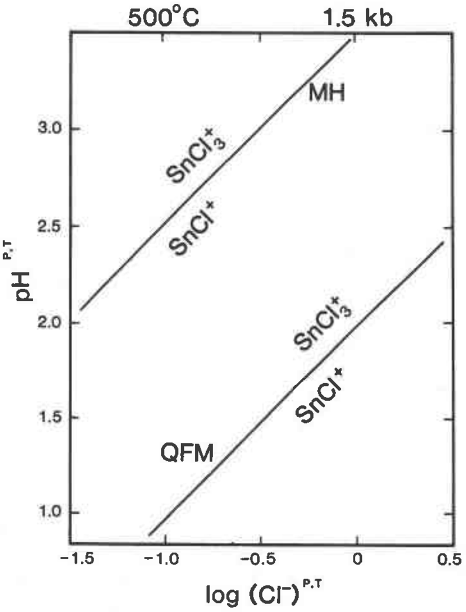

Fig. 20. Oxidation of $SnCl^+$ to $SnCl_3^+$ as a function of pH and Cl^- molalities at 500°C and 1.5-kbar pressure with f_{O_2} controlled by QFM and MH. From Wilson (1986).

$$SnO_2 + 2H^+ + Cl^- \rightleftharpoons SnCl^+ + H_2O + 1/2O_2$$

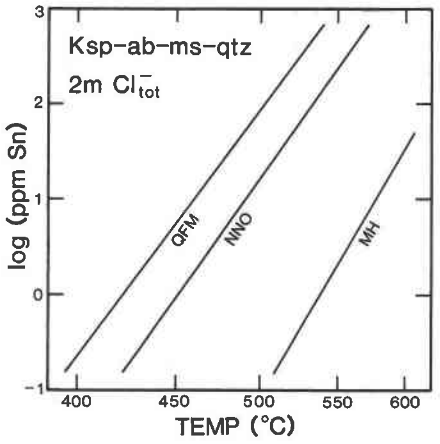

Fig. 22. Solubility of cassiterite in HCl-H_2O solutions as a function of temperature and f_{O_2} defined by QFM, NNO, or MH. The assemblage K-feldspar + albite + muscovite + quartz defines pH, and 2 *m* KCl defines the chloride molality. From Wilson (1986).

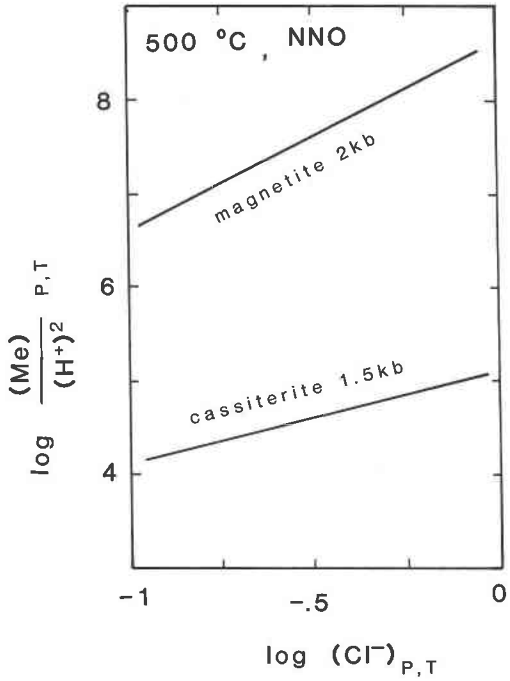

Fig. 23. Comparison of the solubility of magnetite and cassiterite in HCl-H_2O solutions, 500°C, 2 kbar (magnetite), 1.5 kbar (cassiterite) and f_{O_2} controlled by NNO. The slopes of the lines are 2 and 1, corresponding to $FeCl_2$ and $SnCl^+$, respectively. Data from Chou and Eugster (1977) and Wilson (1986).

also a drop in pressure. Precipitation can continue only if the H^+ or HCl produced during deposition is consumed, an aspect to be discussed shortly.

As mentioned earlier, cassiterite is much less soluble than magnetite, and a quantitative comparison is given in Figure 23. Because Fe is bivalent in solution, even at f_{O_2} values of HM (see also Boctor et al., 1980), magnetite precipitation also requires oxidation, but less so than cassiterite deposition.

The solubility of wolframite, $(Fe,Mn)WO_4$, was studied by Wang, Eugster, and Wilson (see Eugster and Wilson, 1985) by combining solubility experiments on tungstic oxide, WO_3, in HCl-H_2O solutions at 600°C, 2 kbar with data on $FeCl_2$. According to the 300°C spectroscopic measurements of Wesoloski et al. (1984) and the data of Ivanova and Khodakovskiy (1972), tungstic acid, H_2WO_4, is the only abundant species to be expected in the supercritical region, with bitungstate, HWO_4^-, and tungstate, WO_4^{2-}, significant possibly only at high pH. Our very preliminary data are compatible with the reaction

$$WO_{3(s)} + H_2O \rightleftharpoons H_2WO_4 \qquad (26)$$

using initial HCl molalities of 0–3. Calculated pH at P and T ranges from 2 to 6, and log K_{26} is -2.7 ± 0.5. When more complete and reliable information for K_{26} becomes available, free energies for HWO_4 can be combined with those for $FeCl_2$ (Chou and Eugster, 1977; Boctor et al., 1980) to calculate ferberite dissolution and precipitation according to

$$FeWO_{4(s)} + 2HCl \rightleftharpoons FeCl_2 + H_2WO_4. \qquad (27)$$

Ferberite can be precipitated through a decrease in chloride or HCl molality, a decrease in pH, an increase in $FeCl_2$ or H_2WO_4, and possibly also a decrease in P and T, but further work is necessary to clarify transport and deposition of wolframite.

LIGANDS OTHER THAN CHLORIDE

By far the largest amount of information available on supercritical complexes deals with chloride ligands. It is essential that more and better data be collected on (OH)-H_2O, carbonate-bicarbonate, and bisulfide complexes. Many other ligands may contribute to mass transport in specific settings, such as fluoride, borate, phosphate, arsenate, and others, but even less quantitative information is available on their role.

For (OH) complexes, the most extensive data set refers to $Si(OH)_4$ in equilibrium with quartz. Quartz solubility was used recently by McKenzie and Helgeson (1984) to estimate the dielectric constant of water, and an equation valid to 900°C and 10 kbar has been provided by Fournier and Potter (1982). According to Crerar and Anderson (1971) and Walther and Orville (1982), hydrated silicic acid is the dominant solute, and the dissolution reaction can be written as

$$SiO_{2(s)} + (n + 2)H_2O \rightleftharpoons H_4SiO_4 \cdot nH_2O. \qquad (28)$$

Crerar and Anderson (1971) suggest that $n = 2$. At subcritical temperatures and high pH, other species become important, such as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, as well as polynuclear species (see, for instance, Stumm and Morgan, 1981). Because of the high degree of association in supercritical fluids, it is unlikely that the activity of $(OH)^-$ can get high enough for reactions such as

$$H_4SiO_4 + (OH)^- \rightleftharpoons (H_3SiO_4)^- + H_2O \qquad (29)$$

to proceed sufficiently to the right to make $H_3SiO_4^-$ an important species, except perhaps in the high-pressure–low-temperature region. Data on K_{29} as a function of P and T are essential if we are to understand silica transport and deposition in supercritical fluids.

Judging from its role in subcritical fluids, $(OH)^-$ must also be an important ligand in neutral to basic supercritical fluids, although the high end of the pH scale is not accessible because of increased association. Speciation studies must be carried out in alkaline solutions for all major as well as the less abundant cations. Alteration of basaltic and ultrabasic crust by meteoric waters is the most likely environment for basic supercritical fluids to form. $(OH)^-$ complexes are particularly important for a number of ore-forming elements such as Mo, W, Nb, Ta, and As.

Our information on supercritical carbonate and bicarbonate complexes is equally scanty. Reliable solubility data for calcite above 350°C are not available. We can speculate that in situations of low solvent density, neutral carbonate or bicarbonate complexes, such as $NaHCO_3^0$,

$Na_2CO_3^0$, or $CaCO_3^0$, will be dominant, whereas charged bicarbonate complexes, such as $CaHCO_3^+$ should be restricted to high-density, high-pH conditions. The existence of neutral bicarbonate complexes can perhaps be inferred from the presence of nahcolite, $NaHCO_3$, crystals in some fluid inclusions (see Roedder, 1985).

Bisulfide complexing has been reviewed by Barnes (1979). Information is extremely scarce above 350°C, including the dissociation behavior of H_2S.

The question of fluoride complexing is raised often in connection with Sn-W deposits because of the abundance of topaz, lepidolite, and fluorite. Preliminary data (Wilson, 1986) show that cassiterite is at least 100 times less soluble in HF solutions than it is in HCl solutions, indicating that fluorine is extracted very efficiently by the solids and that fluorine complexes are not important for the transport of Sn in hydrothermal fluids. Ian Plimer (pers. comm.) has remarked recently that "just because the bridesmaid is at the wedding, this does not mean that she is getting married."

Redox, acid-base, and exchange reactions: How do metals move?

Supercritical fluids are involved in the formation of hydrothermal ore deposits such as those of the porphyry copper and tin-tungsten types. It is appropriate to ask how such fluids acquire the metals they transport and deposit as ore minerals, and how these processes are affected by the properties of the fluids. Somewhat arbitrarily we can divide the processes into redox, acid-base, and exchange reactions, even though a particular transport or deposition event may involve all three aspects. Studies of mineral solubilities in hydrothermal fluids have shown that for redox conditions of crust and mantle, transition and other metals often exhibit a lower valence in the aqueous fluids than they do in oxide or silicate minerals. For instance, Boctor et al. (1980) found ferrous chloride, $FeCl_2$, to be the principal solute in equilibrium with hematite, Fe_2O_3, at 400–600°C, 1–2-kbar pressure. Similarly, Wilson and Eugster (1984) reported stannous chloride, $SnCl^+$, as the dominant solute in equilibrium with cassiterite, SnO_2, at 400–500°C, 1.5 kbar, and f_{O_2} controlled by NNO. In oxygen-rich solids, such metals may have a higher valence because metal-oxygen bonds are dominant, whereas in the fluid, oxygen is bound largely to hydrogen. This difference implies that reduction is an important aspect of the dissolution of minerals containing these metals, just as deposition of the ore minerals requires oxidation. Noble metals, such as Au or Ag, on the other hand, are oxidized during dissolution. Their deposition is accompanied by reduction. No free oxygen is present in hydrothermal fluids, but electron transfer can be accomplished in a variety of ways, such as by changes in the H_2/H_2O, H_2S/H_2SO_4, CO_2/CH_4 ratios in the fluid or by changes in the oxidation states in the crystal lattices. Deposition may be triggered by the stability or instability of a particular mineral in response to changes in *P*, *T*, pH, or solution composition. Examples of oxidation and reduction reactions during ore deposition are

$$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2, \qquad (30)$$

$$SnCl^+ + 2H_2O \rightarrow SnO_2 + 2H^+ + Cl^- + H_2, \qquad (31)$$

$$2AuCl + H_2 \rightarrow 2Au + 2HCl, \qquad (32)$$

and

$$FeCl_2 + 2H_2SO_4 + 7H_2 \rightarrow FeS_2 + 2HCl + 8H_2O. \qquad (33)$$

Normally, the hydrogen produced (oxidation) or consumed (reduction) will be involved in a coupled reaction with ore or country-rock minerals, with solids providing most of the redox buffering. Differential loss or addition of hydrogen is possible also. Identification of the nature of the coupled processes requires detailed textural and compositional studies. An example of a coupled, oxygen-conserving redox reaction involving the simultaneous deposition of cassiterite and arsenopyrite was proposed by Heinrich and Eadington (1986):

$$3SnCl_2 + 2H_3AsO_3 + 2FeCl_2 + 2H_2S \rightarrow 3SnO_2 + 2FeAsS + 10HCl. \qquad (34)$$

During this reaction, Sn is oxidized from 2 to 4 and arsenic is reduced from 3 to 2.

The cassiterite deposits of Dachang, southeastern China, are associated with extensive sulfide mineralization, including pyrrhotite, pyrite, sphalerite, and sulfosalts. Sedimentologic evidence points to Devonian evaporites as the source for the sulfur (Eugster, 1983). Cassiterite and sulfide precipitation can be formulated as a combined redox reaction, using, for the sake of simplicity, $SnCl_2$ and $FeCl_2$ as the solutes and pyrite as the sulfide.

$$7SnCl_2 + FeCl_2 + 2H_2SO_4 + 6H_2O \rightarrow 7SnO_2 + FeS_2 + 16HCl. \qquad (35)$$

Acquisition of ore-forming elements by the evolving fluids is strongly dependent upon redox processes. Elsewhere, I have argued (Eugster, 1985a) that large, highly charged cations (LHCs) such as Sn, W, As, Sb, and Mo are mobilized early by fluids with a low f_{O_2} and low pH, whereas the bivalent octahedral cations (BOCs) such as Fe^{2+}, Mn^{2+} and Zn^{2+} are preferentially mobilized during later, more oxidizing conditions. However, the details of the acquisition process are more difficult to reconstruct than depositional processes.

The importance of acid-base reactions in metamorphic and ore-forming environments was pointed out by Hemley (1959), who studied reactions such as

$$KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2KCl \rightleftharpoons 3KAlSi_3O_8 + 2HCl, \qquad (36)$$

$$3Al_2Si_2O_5(OH)_4 + 2KCl \rightleftharpoons 2KAl_2AlSi_3O_{10}(OH)_2 + 2HCl + 3H_2O, \qquad (37)$$

and

$$NaAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2NaCl \rightleftharpoons 3NaAlSi_3O_8 + 2HCl. \qquad (38)$$

In each of these mineral-alteration reactions, Al is conserved in the solids, a metal chloride is consumed, and HCl is released. A similar effect was observed in the hydrothermal alteration of basalts by circulating sea water. Seyfried and Bischoff (1981) found that the precipitation of a magnesian chlorite was accompanied by the release of Ca^{2+} and H^+ to sea water. This acidity generated by the water-rock interaction is responsible for the solubilization of heavy metals. In contrast, near-neutral chloride solutions are not effective solvents for heavy metals (Eugster and Wilson, 1985). The key to forming effective ore fluids appears to be the production of acidity or alkalinity. Acidity can be produced in a variety of ways (see, for instance, Eugster 1985a, 1985b). In supercritical fluids the dominant processes will be (1) mineral precipitation, (2) mineral alteration, (3) boiling of melts, (4) fluid immiscibility, and (5) oxidation. It is clear from Reactions 30 to 35 that precipitation of ore minerals and release of ligands from the metal complexes produce acidity. Similarly, mineral alterations such as those of Reactions 36–38 are important sources of acidity as is the vesiculation of hydrous silicate melts. The latter process is induced by crystallization of anhydrous phases (see, for instance, Burnham, 1979). Separation of a vapor phase promotes the enrichment of acids such as HCl, HF, H_3BO_4 in the fluid. Judging from the widespread acid alteration associated with porphyry copper and tin-tungsten deposits, boiling of melts is a significant source for acid production. HCl dissolved in the melt is strongly fractionated into the aqueous fluid. Holland (1972) studied the distribution of Zn and Mn between NaCl-bearing granitic melt and fluid at 850°C, 2 kbar. Upon quench, he observed low pH values, and this I have interpreted (Eugster, 1985a) as due to hydrolyzation of NaCl dissolved in the melt by the reaction

$$2NaCl_{(melt)} + H_2O_{(fluid)} \rightarrow 2HCl_{(fluid)} + Na_2O_{(melt)}$$

being displaced to the right. At 700–750°C, Kilinc and Burnham (1972) found the ratio (m_{Cl}) solution/(m_{Cl}) melt to be between 13 and 83. Consequently, as long as NaCl is dissolved in the silicate melt, HCl production upon vesiculation continues, particularly if an immiscible NaCl liquid is present in the melt.

Fluid fractionation during *subcritical* boiling has been invoked as an important process responsible, for instance, for calcite precipitation in geothermal fields, with calcite supersaturation triggered by loss of CO_2 to the gas phase. Recently Gehrig (1980), Hendel and Hollister (1981), Sisson et al. (1981), Bowers and Helgeson (1983a, 1983b), and Skippen and Trommsdorff (1986) have pointed out that NaCl-rich H_2O-CO_2 fluids can remain immiscible to temperatures and pressures well above the critical point of H_2O (see also Takenouchi and Kennedy, 1965). In other words, subcritical boiling can occur over the whole range of conditions normally associated with supercritical fluids, provided substantial amounts of CO_2 and NaCl are present. The metamorphism of carbonate rocks is the most likely environment to provide these conditions. We may expect that during such boiling, volatile complexes such as HCl, HF, and some metal chlorides are preferentially fractionated into the CO_2-rich aqueous vapor.

Oxidation can be a powerful acid-producing mechanism, as, for instance, in the oxidation of pyrite responsible for acid mine drainage. Similar processes are possible under supercritical conditions provided an oxygen source exists:

$$2FeS_2 + 4H_2O + 7\tfrac{1}{2}O_2 \rightarrow Fe_2O_3 + 4H_2SO_4.$$

Metal transport is possible also in alkaline supercritical solutions, where hydroxy complexes are the dominant solutes. For a bivalent metal, Me^{2+}, we can expect $Me(OH)^+$, $Me(OH)_2^0$, $Me(OH)_3^-$, and $Me(OH)_4^{2-}$ to be present depending on pH, *P*, and *T*. Seward (1981) has summarized the relevant data for Fe^{2+}, Pb, Zn, Ni, UO_2, and Al, but few of the measurements extend much beyond 300°C, the limit for most spectrophotometric cells.

Exchange reactions between minerals and neutral or near-neutral supercritical fluids are effective mechanisms for metal acquisition and enrichment. Exchange constants for major elements in chloride solutions were discussed by Eugster and Ilton (1983). No data are available for the less abundant metals important to ore deposition. One would expect that metals such as Zn, Cu, and Pb could readily be picked up by chloride-rich hydrothermal fluids passing through wall rocks of appropriate composition, but the relevant experiments remain to be carried out.

More information is available on metal partitioning between silicate melts and hydrothermal fluids. Earlier work on this subject has been summarized by Candela and Holland (1984), who also measured the partitioning of Cu and Mo between silicate melts and aqueous chloride fluids at 750°C. Manning and Henderson (1984) studied the behavior of W in silicate melt–aqueous fluid systems at 800°C, and 1 kbar, using various ligands in the fluid. In general, speciation has not been fully defined in such fluids.

SUMMARY

Supercritical aqueous solutions are very different from electrolyte solutions near room temperature, and these differences have profound consequences on how water dissolves minerals and transports metals and ligands. Near room temperature, water is exceptionally effective in dissolving ionic crystals at any pH, whereas covalent structures, such as silicates, dissolve only at low or high pH. Dissolution rates vary widely from mineral to mineral. At high temperature, on the other hand, water is a good solvent for most minerals. Dissolution is influenced by acid and ligand concentrations and is dominated by the properties of the solvent through the formation of near-neutral complexes. Rates of dissolution of silicates appear to be independent of mineral constitution. According to Walther and Wood (1986, p. 208), "at 25°C silicate dissolution rates are pH-dependent and vary widely from one mineral to another. At high temperatures (300–700°C), however, the available data indicate that most minerals dissolve in aqueous and H_2O-CO_2 fluids with similar rate

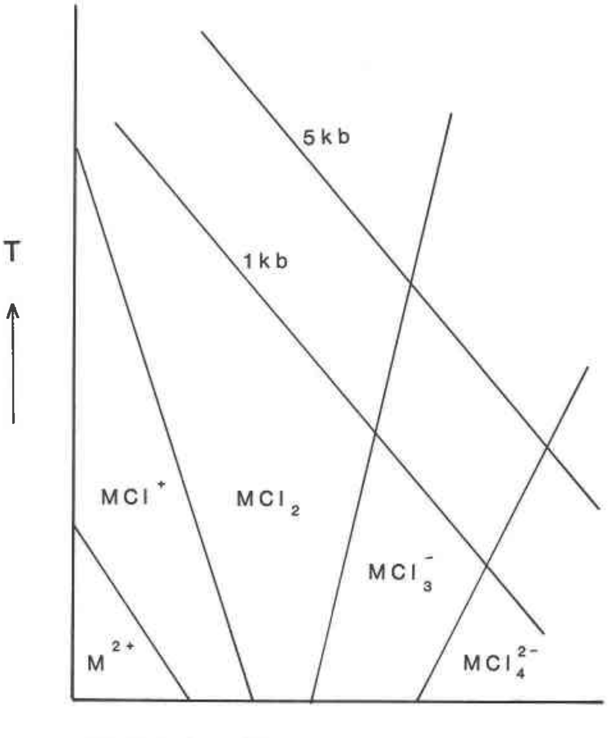

Fig. 24. Schematic drawing of the effect of *P, T,* and chloride ion molality on the stepwise complexing of a bivalent metal, M.

constants if their rates are normalized to a constant number of oxygen gram atoms." Above 300°C, dissolution rates can be expressed by the relation (Wood and Walther, 1983)

$$\log k = \frac{-2900}{\mathrm{T}} - 6.85 \text{ mol oxygen atoms/(cm}^2\cdot\text{s)}.$$

In supercritical fluids of low density, normally strong acids, bases, and salts become weak acids, bases, and salts, whereas otherwise weak acids, bases, and salts form neutral, associated complexes.

Because of the decrease in the dielectric constant, the degree of association of solutes increases with increasing temperature. Electrostriction causes pressure to have the opposite effect, enhancing dissociation of both solute and solvent. Pressure effects are particularly important in the low-density supercritical fluids to be expected in many metamorphic and igneous environments. The decrease in electric shielding in such fluids leads to dominantly electrostatic interaction between metal ions and ligands. Consequently, ligand-field effects are greatly diminished. Ionic strengths are low even in concentrated solutions, and activity coefficients can be approximated by a Debye-Hückel treatment. Minerals dissolve largely through the formation of inner-sphere complexes. Such complexes are tetrahedrally or octahedrally coordinated, depending upon pressure, although higher coordination numbers are possible. With increasing ligand-ion concentrations, stepwise complex formation takes place with ligands replacing H_2O molecules in the complex. Such association reactions diminish the number of positive charges and with it extent of solvation. They are endothermic and are driven by the entropy gain associated with dehydration. The formation of anionic complexes is restricted by the low abundance of ligand ions in these fluids. In Figure 24, the effects of *P, T,* and chloride-ion activity on complexing of a bivalent metal have been summarized schematically. Rising temperature restricts the abundance of cations and of free chloride ions, enhancing the dominance of near-neutral complexes. A rise of pressure counteracts the temperature effect.

At high temperatures, where minerals dissolve primarily through formation of complexes of no or low charge, information on such complexes has been obtained mainly from spectroscopic measurements in the low-pressure, subcritical L + V region. Data on supercritical complexes are much scarcer and confined largely to chloride ions as ligands. Mineral-solubility determinations can provide speciation information along with solubility products. The trial-and-error procedure developed by Glenn Wilson and illustrated here for cassiterite and magnetite solubility is capable of defining the abundances of one or more ligands. Spectroscopic data would be invaluable in confirming these conclusions. Metal transport can be accomplished also by carbonate-bicarbonate, bisulfide, and hydroxy complexes, but no supercritical data are available.

Redox, acid-base, and exchange reactions are the principal mechanisms by which metals are acquired by hydrothermal fluids. Redox reactions often seem to be coupled processes with no net oxygen transfer. Acids, whether dissociated or associated, are effective in releasing metals from minerals into the fluid. Such acids are produced by mineral precipitation, mineral alteration, boiling of melts, unmixing of fluids, and oxidation. Acid formed during precipitation of ore minerals is neutralized by wall-rock alteration. Metals are soluble also in alkaline fluids through the formation of hydroxy or carbonate complexes, but little is known of such fluids in the supercritical region.

Mineral dissolution and precipitation reactions occur on the molecular level, and yet their consequences are as far-reaching as some of the more glamorous global processes. Supercritical fluids are involved in ore deposition and metamorphic events, in igneous crystallization and mantle degassing, and yet we remain largely ignorant of their chemical properties and their interaction with minerals.

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