

## Mineral solubilities in supercritical H<sub>2</sub>O solutions

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**Abstract:** Solubilities of minerals in supercritical H<sub>2</sub>O and H<sub>2</sub>O–CO<sub>2</sub> mixtures are of prime importance to our understanding of mineral transformations, fluid-flow and fluid-rock interactions in the earth's crust. This paper presents a review of available data on mineral solubility and speciation in aqueous fluids at elevated temperatures and pressures and with variable activities of Cl<sup>-</sup> and CO<sub>2</sub>.

As is to be expected from the decrease in the dielectric constant of the fluid, neutral or lower charged complexes become increasingly abundant as temperature and pressure are increased to supercritical conditions. Alkali and alkaline earth elements in aqueous solution exist primarily in chloride complexes because chloride is the most abundant complexing anion in crustal solutions. Neutral complexes that are unknown or significant only in alkaline solution at 25 °C become important in near neutral solutions at elevated temperatures and pressures. Of particular interest are sodium and potassium alumina and sodium and potassium silica complexes which are apparently quite stable at temperatures above 400 °C and 1 kbar.

Hydroxyls complex with cation species to an increasing degree in near neutral solutions as temperature is increased. The ability of a cation to complex hydroxyls is controlled to a large extent by its surface charge density. The higher the charge density the greater is the degree of hydrolyzation to form lower charged or neutral complexes. Surface charge density also affects the degree of chloride complexation of cations. It can be shown that the greater the surface charge density the greater the temperature dependence of the chloride electrolyte dissociation.

### INTRODUCTION

Excluding magmas, most mineral transformations from the earth's surface through the continental crust to the top of the mantle (~30-60 km depth) take place in the presence of a low viscosity fluid phase. The primary constituents of this fluid are H<sub>2</sub>O and CO<sub>2</sub> with CH<sub>4</sub> at times locally significant. Crustal fluids generally contain positively charged or neutral complexes of Na, K, Ca, Mg, Fe, Al, and Si with Cl<sup>-</sup>, OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> forming the dominant complexing anions. In general, these fluids are thought to be somewhat acidic to slightly alkaline. The acidity is buffered to some extent by the conjugate pair HCl<sub>(aq)</sub> and Cl<sup>-</sup> and the dissolution of carbonates and silicates. Additionally, ion pairing to form lower charged complexes with increasing temperature also helps limit pH to near neutral. Fig. 1 shows isopleths of the logarithm of the dissociation constant of H<sub>2</sub>O as a function of pressure and temperature. It can be deduced from Fig. 1 that neutral pH should be near 4.5 to 5.0 between 5 and 15 km depth (~1.5-4.5 kbar) in the crust.

Circulation of fluids through the crust may occur either pervasively by flow through interconnected pores or in a localized manner within discrete fractures. Within the upper 10 km of the earth's surface fluids can convect or circulate driven by gradients in density caused by local differences in temperature and salinity (ref. 1). As depth is increased below 6 to 10 km, however, the pressure differences between fluid and rock exceed the effective crushing strength of the rock, and the grain boundary pores collapse until fluid pressure equals rock pressure (ref. 2). At depths where the fluid pressure equals rock pressure the amount of fluid in the rocks at any one time is small (generally less than 0.1% by volume) but the amount that may have passed through a volume of rock and reacted with it may be 1000 times as great or greater (ref. 3-5). Because of increasing temperature with increasing depth (~10 ° to 40 °C/km) and the volumetric dominance of rock over fluid at any instant in time the fluid can be assumed to be in local equilibrium with the mineral surfaces it contacts. Thus ultimately it is the solubility of minerals in contact with the fluid that control the composition of the fluid (ref. 6, 7).

Both large scale dynamic physical processes (e.g., plate tectonics) and local heating (e.g., intrusion of magma) cause changes in temperature and/or pressure in crustal rocks (ref. 8,9). At depths greater than 10 km it is the release of H<sub>2</sub>O and CO<sub>2</sub> from unstable hydrous and carbonate minerals that is thought to be the major source of the fluid (ref. 2). Because this fluid has a much lower density than the surrounding rock, it fractures its way or percolates towards the earth's surface. Extensive mineral alteration

(metasomatism) commonly occurs due to reaction of migrating fluids as they equilibrate with mineral assemblages of widely different composition (e.g., siliceous carbonates or aluminum-rich pelites) at various temperatures and pressures.

Understanding the processes of fluid evolution, flow and metasomatism, therefore, requires knowledge of mineral solubilities in a wide range of supercritical solutions. This contribution is a brief review of our very limited knowledge of solubilities and solution equilibria with emphasis on work done recently at Northwestern University.

### STANDARD STATE AND ACTIVITY COEFFICIENT CONVENTIONS

The standard state for mineral phases is taken as the pure solid, and for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  the pure liquid, at any pressure and temperature. For aqueous species other than  $\text{H}_2\text{O}$  the standard state is defined as unit activity in a hypothetical one molal solution whose behavior is that of an infinitely dilute  $\text{H}_2\text{O}$  solution at any pressure and temperature.

Molal activity coefficients for uncharged aqueous species in supercritical  $\text{H}_2\text{O}$  solutions are generally regarded as unity based on this standard state if hydration is explicitly accounted for (see below) or in solutions where  $a_{\text{H}_2\text{O}}$ , the activity of  $\text{H}_2\text{O}$ , is near unity. Such an assumption is consistent with the thermodynamic behavior of the uncharged aqueous silica complex as a function of silica activity under supercritical conditions (ref. 10) and the approach to ideal mixing behavior of associated electrolytes in  $\text{H}_2\text{O}$  as temperature is increased (ref. 11, 12).

Molal activity coefficients of supercritical charged species will also be considered as unity throughout the following discussion. Because we will consider explicit speciation of complexes in solution and the degree of ion pairing is high, ionic strengths are often low. Therefore, electrostatic interactions are minimized. Additionally, in the computation of equilibrium constants, electrostatic effects often cancel to some extent across a reaction. Estimations of mean ionic molal activity coefficients for  $\text{NaCl}_{(\text{aq})}$ ,  $\gamma_{\pm}$ , by Helgeson, Kirkham, and Flowers (ref. 13) indicate  $\gamma_{\pm}$  varies between  $\sim 0.4$  and  $0.6$  for ionic strengths of  $0.1$  at temperatures between  $400^\circ$  and  $600^\circ\text{C}$  and  $2$  to  $3$  kbar. At ionic strengths of  $0.01$   $\gamma_{\pm}$  varies between  $\sim 0.6$  and  $0.8$ . In most cases provision for non-unit activity coefficients are not warranted by the uncertainty in the data.

### SINGLE OXIDE SYSTEMS

#### Quartz solubilities and silica speciation

It is reasonable to start with a review of quartz ( $\text{SiO}_2$ ) solubility because quartz is extremely widespread in the continental crust and its behavior is perhaps best understood. Fig. 2 shows isopleths of quartz solubility ( $\log$  molality  $\text{Si}$ ) in pure  $\text{H}_2\text{O}$  solvent as a function of pressure and temperature. As anticipated from its behavior at lower temperatures and pressures, quartz solubility increases both with increasing pressure and temperature. With decreasing pressure, as the steam phase region is approached, quartz solubility decreases dramatically with changes in pressure dominant over those of temperature.

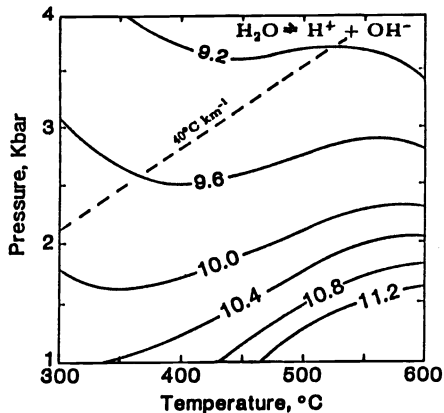


Fig. 1. Isopleths of  $\text{pK}$  for  $\text{H}_2\text{O}$  dissociation (ref. 13). Also shown is a  $40^\circ\text{C}$  per km geotherm for the crust.

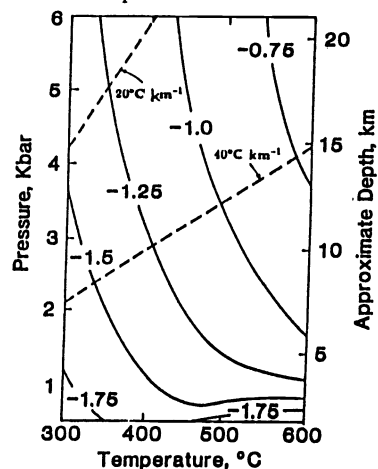


Fig. 2. Isopleths of  $\log$  molality of  $\text{SiO}_{2(\text{aq})}$  for quartz saturation. Also shown are  $20^\circ\text{C}$  and  $40^\circ\text{C}$  per km geotherms (ref. 10).

There is general agreement that silica exists as an uncharged hydrated monomer species in acidic to reasonably alkaline  $\text{H}_2\text{O}$  solutions (ref. 10, 14-16). No appreciable ionization of the hydrated monomer species takes place in subcritical solutions of  $\text{pH}$  less than  $\sim 9$  to temperatures of at least  $300^\circ\text{C}$  (ref. 17). For most fluids in the crust the quartz solubility reaction can therefore be written as:



The hydration number,  $n$ , of aqueous silica, becomes important in mixed H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> solutions where the activity of H<sub>2</sub>O relative to pure H<sub>2</sub>O departs significantly from unity as is clear from the equilibrium constant expression for reaction (1):

$$K_{(1)} = \frac{a_{\text{hydrated silica complex}}}{a_{\text{quartz}} a_{\text{H}_2\text{O}}^n} \quad (2)$$

$n$  has generally been regarded as 2 and the aqueous silica complex written, therefore, as Si(OH)<sub>4</sub> preserving the tetrahedral coordination of Si found in silicate minerals. Quartz solubility determinations where mixed volatile phases are used to vary  $a_{\text{H}_2\text{O}}$  indicate a value of  $n$  larger than 2, however. Fig. 3 shows quartz solubility at a number of supercritical pressures and temperatures in H<sub>2</sub>O-CO<sub>2</sub> mixtures as a function of mole fraction of H<sub>2</sub>O in the fluid (ref 18-20). Some uncertainty in  $a_{\text{H}_2\text{O}}$  exists as the mixing properties of CO<sub>2</sub> and H<sub>2</sub>O are not precisely known at these pressures and temperatures. The solubility behavior is, however, best accounted for by a value of  $n$  equal to 4 according to equation (2). A value of  $n$  equal to 4 is also obtained when Ar is used as the diluting fluid (ref. 21). Thus using a solvation model to account for the decreased solubilities in CO<sub>2</sub>-H<sub>2</sub>O mixtures suggests a species that is explicitly hydrated as SiO<sub>2</sub>(aq)·4H<sub>2</sub>O or considering tetrahedral coordination of hydroxyl, Si(OH)<sub>4</sub>·2H<sub>2</sub>O. Obviously in solutions where  $a_{\text{H}_2\text{O}}$  does not depart significantly from unity, explicit provision for hydration is not required. We will use the more familiar Si(OH)<sub>4</sub> formulation for the silica species when  $a_{\text{H}_2\text{O}} \approx 1$ . From a theoretical standpoint the thermodynamic properties of aqueous silica have been successfully modelled with the Helgeson-Kirkham equation of state (ref. 22) as a neutral hydrated polar molecule with a small effective charge (ref. 10).

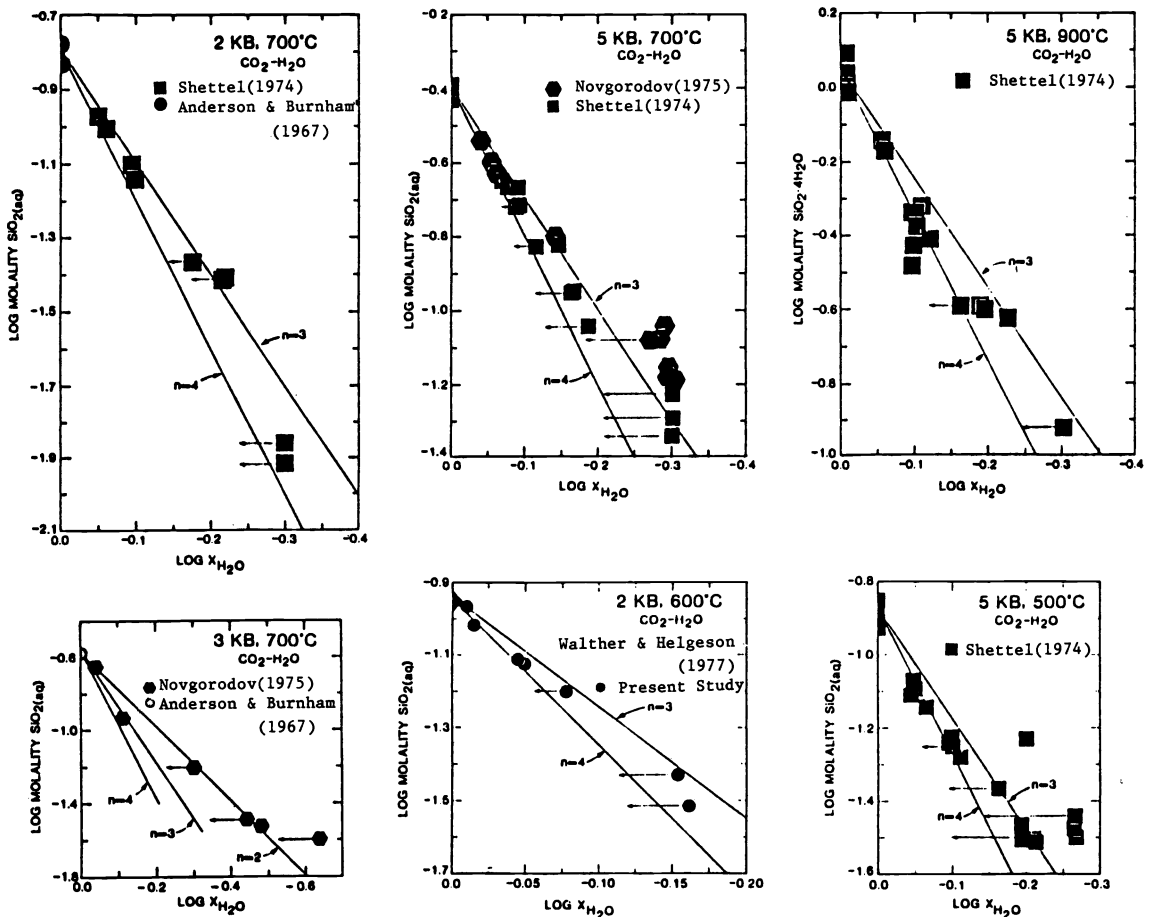


Fig. 3. Constant pressure and temperature plots for quartz solubility determinations in CO<sub>2</sub>-H<sub>2</sub>O mixtures. Endpoints of arrows show, for representative points, the shift in the connected point if the abscissa is changed to log activity of H<sub>2</sub>O. Lines marked  $n=2, 3$  or  $4$  give the predicted behavior for these hydration states of aqueous silica. Reprinted with permission from *Amer. Min.* (ref. 18).

Anderson and Burnham (ref. 23) have determined quartz solubilities in KOH, NaOH, HCl, KCl and NaCl solutions at 3 and 4 kbar and between 500° and 800°C. Within the uncertainty of their experimental data, addition of KOH and NaOH increases silica concentration on almost a mole for mole basis indicating

the importance of complex-forming reactions which may be written as:



respectively, with equilibrium constants that are large ( $>10^1$ ). From knowledge of the dissociation constant of  $\text{KOH}_{(\text{aq})}$  (see below), a rough distribution of species can be calculated for a given molality of  $\text{KOH}$ . At the highest  $\text{KOH}$  concentrations (0.113 molal) pH could be over 2.5 units more alkaline than neutral so that  $\text{Si}(\text{OH})_3\text{O}^-$  may become somewhat significant. Anderson and Burnham have shown, however, that ionization of  $\text{Si}(\text{OH})_4$  cannot be the dominant factor controlling silica increase with  $\text{KOH}$  addition. Although K-Si and Na-Si complexes have not been detected at 25 °C, Seward (ref. 17) has suggested that a Na-Si complex forms to a small but increasing extent as temperature is increased along the liquid-vapor saturation curve of  $\text{H}_2\text{O}$  to 300 °C.

No significant Si-Cl complex exists judging from quartz solubility behavior in  $\text{HCl}$  solutions. Anderson and Burnham (ref. 24) were able to calculate that the equilibrium constant for the reaction:



$K_{(5)}$  is roughly  $10^{-8}$  at 300 °C along the liquid-vapor saturation curve, rising to  $\sim 10^{-2}$  at 700 °C and 4 kbar. It is thought that a reaction analogous to (5) occurs in the potassium system as well although the data necessary to calculate its equilibrium constant are not available.

Significant ion pairing of silica with alkaline earths such as Ca and Mg appears not to occur in crustal solutions. Measured concentrations of Si for mineral solubilities in the  $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$  system are readily accounted for by the presence of the  $\text{Si}(\text{OH})_4$  complex only (ref. 10, 25, 26) with no contribution from Ca-Si or Mg-Si complexes. However, because of the relatively high concentrations of  $\text{Si}(\text{OH})_4$  in solution, small concentrations of a Ca-Si or Mg-Si complex important for transport of calcium and magnesium could go undetected.

#### Corundum solubility and Al speciation

Corundum ( $\text{Al}_2\text{O}_3$ ) solubilities in pure  $\text{H}_2\text{O}$  have been investigated recently by Becker, Cemic and Langer (ref. 27) and Ragnarsdottir and Walther (ref. 28) and are displayed in Fig. 4. Anderson, Pascal and Rao (ref. 29) have demonstrated that the dominant aluminum species in solution must be uncharged in the near neutral pH region under supercritical conditions. Therefore, the corundum solubility reaction can be written as:



In reaction (6) the alumina species is written as a monomer species because of the low concentration of aluminum and the high temperature involved. No information is available on the value of the hydration number,  $n$ .

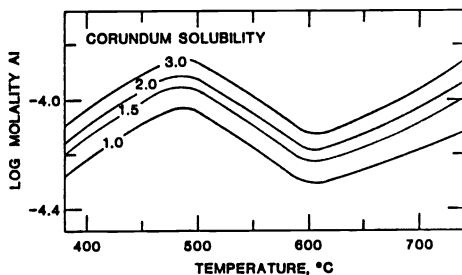


Fig. 4. The log molality of Al as a function of temperature labeled in kbar. Reprinted with permission from Pergamon Press (ref. 28).

In an analogous manner to alkali-silica complexing, increase in corundum solubilities with addition of  $\text{KOH}$  and  $\text{NaOH}$  indicates that K-Al and Na-Al complexes are reasonably stable in supercritical solutions. Their stoichiometry is apparently one alkali to one Al (ref. 23, 30) so that the complex forming reactions can be written as:



$K_{(7)}$  is on the order of  $10^1$  between 600 ° and 900 °C at pressures of 3 to 4 kbar.  $K_{(8)}$  is considered to be of similar magnitude to  $K_{(7)}$ .

Measured concentrations of Al for andalusite ( $\text{Al}_2\text{SiO}_5$ ) plus quartz solubilities in  $\text{H}_2\text{O}$  at 1 kbar are somewhat greater than those predicted with  $\text{Al}(\text{OH})_3(\text{aq})$  as the only Al species (ref. 31). Although the data are sparse some Al-Si complexing is suggested. Increases in the solubilities of corundum (ref. 32) and quartz + andalusite (ref. 33) in  $\text{HCl}$  under supercritical conditions indicate either that an Al-Cl complex or a positively charged species is stable under slightly acidic conditions.

**Portlandite and brucite solubilities and Ca and Mg speciation**

Supercritical portlandite (Ca(OH)<sub>2</sub>) solubilities in H<sub>2</sub>O are shown in Fig. 5 (ref. 34). The retrograde solubility behavior of portlandite at subcritical pressures and temperatures (ref. 35) is also apparent at higher pressures and temperatures. The solid lines in Fig. 5 were computed from the data of Helgeson and coworkers (ref. 22, 36, 37) assuming that Ca<sup>++</sup> is the dominant calcium species and that all activity coefficients are unity. The close agreement between the theoretically computed values and experimental determinations indicates that Ca<sup>++</sup> is not appreciably hydrolyzed in solution even though the solutions are alkaline. The solubility reaction can, therefore, be written as



Brucite (Mg(OH)<sub>2</sub>) solubilities are shown in Fig. 6 (ref. 34). Note that, relative to calcium in the portlandite experiments, the concentrations of magnesium in solution in equilibrium with brucite are significantly lower. Furthermore, there is a sigmoidal behavior at 2 kbar as a function of temperature not found in the portlandite experiments. In the case of brucite, calculations of brucite solubilities from the Helgeson and coworkers data for the reaction



are up to an order of magnitude lower than the measured values. This difference in concentration is best accounted for by the presence of a Mg(OH)<sup>+</sup> complex (ref. 34). Fig. 7 shows values of the dissociation constant of this complex computed by assuming that the difference between Mg concentration computed from equation (10) and the measured concentration of Mg in solution is due to Mg(OH)<sup>+</sup>. These values should be considered provisional until additional experimental data become available to validate the stoichiometry of the complex and nature of speciation.

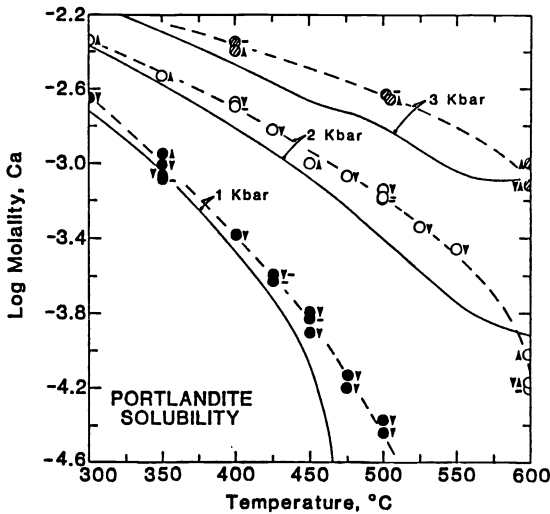


Fig. 5. Portlandite solubility in pure H<sub>2</sub>O as a function of temperature at 1, 2, and 3 kbar. Direction of approach to equilibrium: (▲) undersaturated, (▼) supersaturated, and (○) same. The solid lines are computed assuming Ca<sup>++</sup> is the dominant Ca species in solution. Reprinted with permission from Pergamon Press (ref. 34).

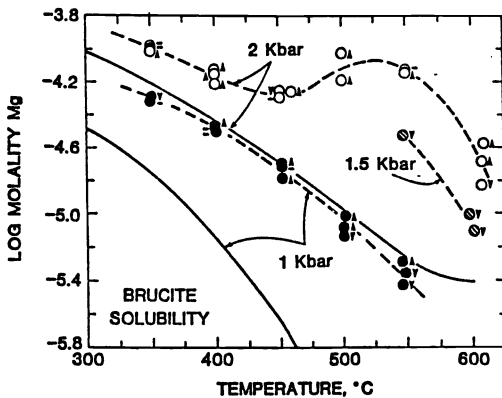


Fig. 6. Brucite solubility in pure H<sub>2</sub>O as a function of temperature at 1, 1.5 and 2 kbar. Direction of approach to equilibrium: (▲) undersaturated, (▼) supersaturated, and (○) same. The solid lines are computed assuming Mg<sup>++</sup> is the dominant Mg species in solution. Reprinted with permission from Pergamon Press (ref. 34).

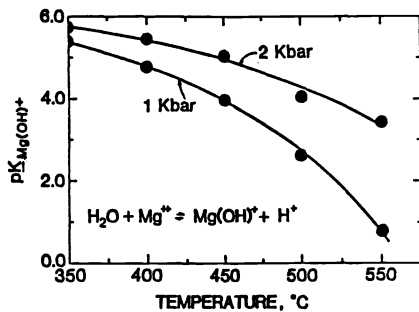


Fig. 7. Calculated negative logarithm of the equilibrium constant ( $pK_{Mg(OH)^+}$ ) for the reaction shown as a function of temperature at pressures of 1 and 2 kbar. Reprinted with permission from Pergamon Press (ref. 34).

### Magnetite and hematite solubilities and Fe speciation

No data exists on the supercritical solubility of Fe oxides in  $H_2O$ ; however, Sweeton and Baes (ref. 38) have determined the solubility of magnetite ( $Fe_3O_4$ ) in  $H_2O$  along the liquid-vapor curve to 300 °C and determined the first and second hydrolysis constants for  $Fe^{++}$ . Since oxygen fugacities in the crust are rarely greater than those buffered by magnetite plus hematite ( $Fe_2O_3$ ), most crustal fluids cannot contain significant amounts of  $Fe^{3+}$ . Extrapolating Sweeton and Baes' data along isopleths of the dielectric constant or density of  $H_2O$  to supercritical pressures and temperatures indicates that  $Fe(OH)^+$  should be dominant at 2 or 3 kbar and 400 ° to 500 °C with  $Fe(OH)_2(aq)$  dominant as temperature is increased at these pressures in near neutral solutions.

The solubility of magnetite in supercritical chloride solutions is known from the work of Chou and Eugster (ref. 39). At 2 kbar with the low fugacities of  $O_2$  appropriate for the crust, temperatures between 500 ° and 650 °C, and high total chloride concentrations (0.33 to 5.4 m),  $FeCl_2(aq)$  appears to be the dominant species. At the lowest temperature and chloride concentrations of Chou and Eugster there is some suggestion that  $FeCl^+$  is also significant along with  $FeCl_2(aq)$ . Similar investigations by Boctor, Popp, and Frantz (ref. 40) on hematite solubilities in supercritical chloride solutions confirm the interpretations of Chou and Eugster.

### Speciation of Na and K

No stable single oxides of Na or K are known to exist in crustal rocks. From the electrical conductance work of Franck (ref. 41) the dissociation constant of  $KOH_{(aq)}$  is known in supercritical solutions. At 2 kbar the dissociation constant varies from  $10^{-1.5}$  at 400 °C to  $10^{-2.2}$  at 600 °C. Therefore, even if solutions were 2 pH units more alkaline than neutral pH,  $K^+$  would dominate over the ion pair  $KOH_{(aq)}$  in the supercritical region. In addition, the dissociation of  $KOH_{(aq)}$  increases as pressure increases. One may conclude, therefore, that  $KOH_{(aq)}$  is not likely to be a significant complex of potassium in the earth's crust although it is important for determining equilibrium constants for reactions such as (3) above.

Because of the smaller ionic radius of Na,  $NaOH_{(aq)}$  is anticipated to have a smaller dissociation constant than  $KOH_{(aq)}$  at the same temperature and pressure. This is consistent with the limited conductivity data available (ref. 42). From the compilation of Gimblett and Monk (ref. 43) for  $NaOH_{(aq)}$  dissociation to 80 °C, we may estimate that  $NaOH_{(aq)}$  dissociation will be roughly an order of magnitude lower than  $KOH_{(aq)}$ . Though an order of magnitude more associated than  $KOH_{(aq)}$ ,  $NaOH_{(aq)}$  would not be an important species in the earth's crust except perhaps at high temperature ( $\geq 700$  °C) and low pressure ( $\leq 1$  kbar).

## MIXED OXIDE SYSTEMS

Most minerals in the earth's crust are complex silicates which show limited solid solution and dissolve incongruently. This is true, for example, of the most abundant crustal mineral, feldspar. Fig. 8 shows the extent of solid solution compositions of the major feldspar components found in the crust (ref. 44). Note the lack of significant solid solution along the anorthite-orthoclase join. This solid solution immiscibility often results in 2 feldspar phases in an equilibrium mineral assemblage of appropriate composition (e.g., granite). At 1 kbar and temperatures below 660 °C a solvus also exists between Na and K-feldspar (Fig. 9) and between Ca and Na-feldspar below  $\sim 1000$  °C (ref. 44,45).

Of hydrous minerals the micas play a central role in reactions in the continental crust. Mica minerals show a wide range of chemical composition and occur in most major rock types. Their general formula can be written as  $X_1Y_{2-3}Z_4O_{10}(A)_2$ . X is primarily some combination of K, Na or Ca; Y is mostly Al, Mg or Fe; Z is dominantly Si or Al; and A is mainly OH with (generally) minor F. Four of the major endmember mineral compositions are  $KAl_2(AlSi_3)O_{10}(OH)_2$  (muscovite),  $NaAl_2(AlSi_3)O_{10}(OH)_2$  (paragonite),  $KMg_3(AlSi_3)O_{10}(OH)_2$  (phlogopite) and  $KFe_3(AlSi_3)O_{10}(OH)_2$  (annite). Like the feldspars, micas show limited solid solution at low temperatures but become completely miscible at temperatures above  $\sim 850$  °C (Fig. 9; ref. 46).

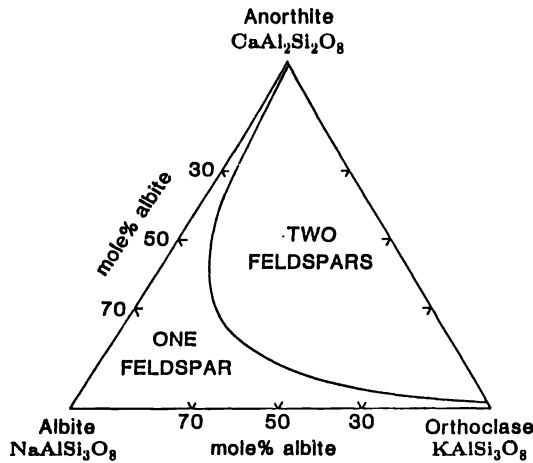


Fig. 8. Extent of ternary feldspar compositions in crustal rocks (one feldspar field) (ref. 44).

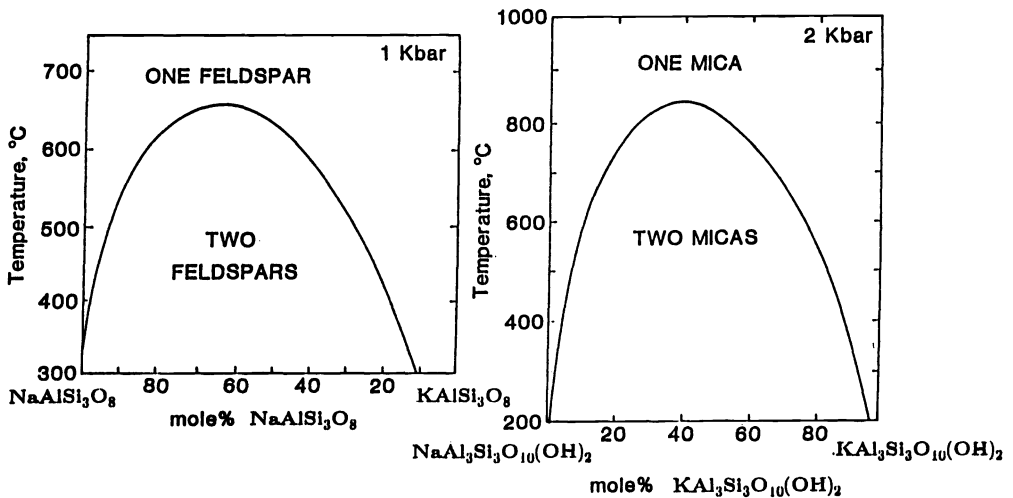
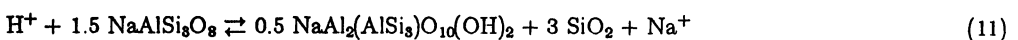


Fig. 9. The NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub> solvus at 1 kbar (ref. 45) and the paragonite-muscovite solvus at 2 kbar (ref. 46).

Because of the incongruent nature of dissolution of feldspars and micas in H<sub>2</sub>O solutions, it is convenient to unambiguously fix the chemical potential of all the components within experimental charges with solid phase assemblages plus H<sub>2</sub>O that are stable together at the pressure and temperature of interest. For instance, one of the most important three phase mineral assemblages stable over significant portions of the crust is albite + paragonite + quartz which at constant temperature and pressure buffers the chemical potential of Na, Al, and Si in solution at fixed  $a_{\text{H}_2\text{O}}$ . Experimentally determined concentrations of Si, Al and Na for this assemblage in H<sub>2</sub>O are shown in Fig. 10 at 1 and 2 kbar as a function of temperature (ref. 47). From the discussion above one can surmise that the important species to consider in solution are Si(OH)<sub>4</sub>, Al(OH)<sub>3(aq)</sub>, SiAl(OH)<sub>7(aq)</sub>, H<sup>+</sup>, OH<sup>-</sup>, Na<sup>+</sup>, NaAl(OH)<sub>4(aq)</sub> and NaSi(OH)<sub>5(aq)</sub>. Standard state partial molal free energies of Si(OH)<sub>4</sub> and Al(OH)<sub>3(aq)</sub> are known at these temperatures and pressures (ref. 10, 28) so that their concentration in solution in equilibrium with the albite + paragonite + quartz assemblage can be calculated from the available thermodynamic data for the solid phases (ref. 37). The minor contribution from SiAl(OH)<sub>7(aq)</sub> can be accounted for from the andalusite + quartz solubilities.

The total aluminum is assumed to be distributed between the species Al(OH)<sub>3(aq)</sub>, SiAl(OH)<sub>7(aq)</sub> and NaAl(OH)<sub>4(aq)</sub>. Thus the concentration of NaAl(OH)<sub>4(aq)</sub> can be determined by difference. Subtracting the contribution of NaAl(OH)<sub>4(aq)</sub> from total measured molality of Na we obtain the concentration of Na<sup>+</sup> + NaSi(OH)<sub>5(aq)</sub>. The ratio  $a_{\text{Na}^+}/a_{\text{H}^+}$  can be computed from the coefficients and equation of state of Helgeson and co-workers (ref. 22, 36, 37) by considering the reaction:



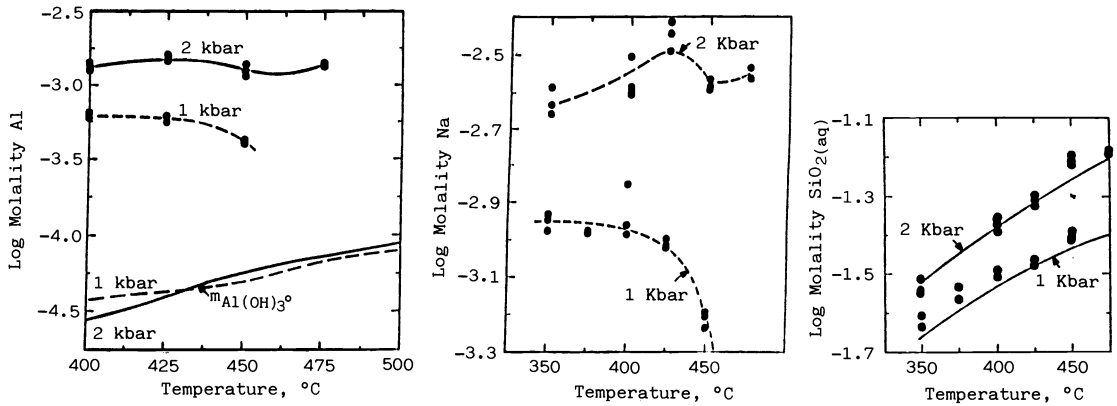
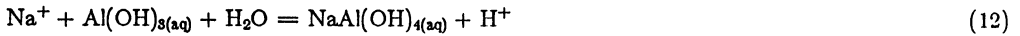


Fig. 10. Log molality of Al, Na, and Si in equilibrium with the assemblage albite + paragonite + quartz at 1 and 2 kbar as a function of temperature in pure H<sub>2</sub>O (ref 49). Lines marked  $m_{\text{Al(OH)}_3^0}$  indicate the predicted concentration of this species. Solid lines in SiO<sub>2</sub> diagram are for quartz solubility in pure H<sub>2</sub>O (ref. 10).

Because the solid mineral phases are pure,  $K_{(11)} = a_{\text{Na}^+}/a_{\text{H}^+}$ .  $K_{(11)}$  computed from the Helgeson data is probably quite accurate as the thermodynamic properties of Na<sup>+</sup> are well constrained from density, heat capacity, and other thermodynamic measurements of NaCl<sub>(aq)</sub> at high temperatures and pressures. This is shown in Fig. 11 where  $\log(a_{\text{Na}^+}/a_{\text{H}^+})$  for the fluid coexisting with solid phase assemblages at quartz saturation in the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O at 2 kbar are shown as a function of temperature calculated from the Helgeson data set. The pentagons were derived from the experimental charges as indicated above assuming no appreciable NaSi(OH)<sub>5(aq)</sub>. Because the experimentally derived values should lie along the albite-paragonite phase boundary there is some discrepancy between the experimentally derived values and the Helgeson data set. Any association of Na and Si would decrease the computed value of  $a_{\text{Na}^+}/a_{\text{H}^+}$  and increase the discrepancy shown in Fig. 11. It can be shown that if  $K_{(4)} \leq 10$  the amount of NaSi(OH)<sub>5</sub> will be small compared to Na<sup>+</sup> if one assumes the dissociation of NaOH<sub>(aq)</sub> is an order of magnitude lower than KOH<sub>(aq)</sub>. The computed equilibrium constant for the reaction:



is approximately  $K_{(12)} = 10^{-3}$  at 500 °C and 2 kbar (ref. 49).

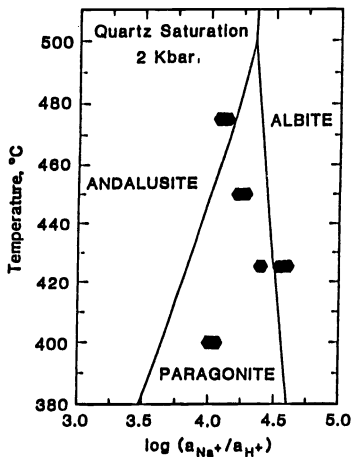


Fig. 11. Phase diagram for the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-HCl at 2 kbar and quartz saturation. Hexagons were calculated from measured solubilities of albite + paragonite + quartz (see text) (ref 47).

**Carbonate systems**

The solubility of calcite (CaCO<sub>3</sub>) in supercritical H<sub>2</sub>O solutions (ref. 48) is shown in Fig. 12. Calcite solubility is retrograde at 1 and 2 kbar to temperatures of at least 600 °C. At 3 kbar there is a minimum in solubility as a function of temperature near 500 °C. The solubility can be modelled assuming that Ca<sup>++</sup> and HCO<sub>3</sub><sup>-</sup> are the dominant calcium and carbonate species, respectively, from the data of Helgeson and co-workers (solid lines). It is apparent from the solubility results that another complex must become important above 400 °C. Besides the equilibrium





we must also consider the important reaction:



$K_{(14)}$  has been determined by Read (ref. 46) from electrical conductance studies at 1 and 2 kbar and temperatures from 25° to 250°C. Values for  $K_{(14)}$  at supercritical temperatures have been computed from solubility differences of calcite in pure and dilute CO<sub>2</sub> aqueous solutions assuming that total CO<sub>2</sub> can be distributed according to reaction (14) (ref. 50). These calculations give a value of  $K_{(14)} = 10^{-7.2}$  at 500°C and 2 kbar. If complexes such as CaCO<sub>3(aq)</sub>, CaHCO<sub>3</sub><sup>-</sup> or Ca(HCO<sub>3</sub>)<sub>2(aq)</sub> become important in these dilute CO<sub>2</sub> aqueous solutions, values of  $K_{(14)}$  will be overestimated by this computation.

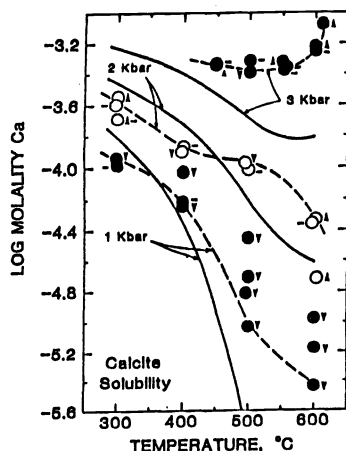


Fig. 12. Calcite solubility in pure H<sub>2</sub>O at 1, 2 and 3 kbar. Direction of approach to equilibrium: (A) undersaturated, (v) supersaturated, and (-) same. The solid lines are computed assuming Ca<sup>++</sup> is the dominant calcium species and HCO<sub>3</sub><sup>-</sup> the dominant carbon bearing species (ref 48).

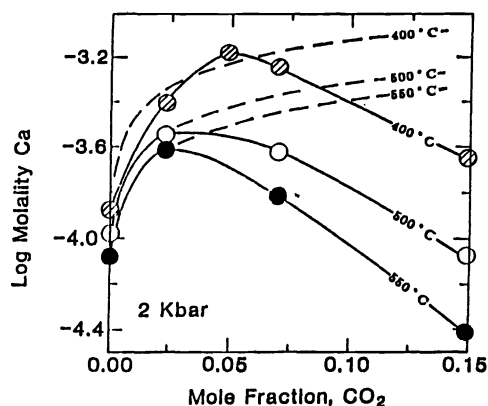


Fig. 13. Calcite solubility in H<sub>2</sub>O–CO<sub>2</sub> mixtures at 2 kbar. Solid lines connect points along isotherms. Dashed lines show predictions based on reactions (13) and (14) (ref. 50).

It can be seen from Fig. 13 that, as CO<sub>2</sub> is increased in solution, calcite solubility reaches a maximum and then decreases with additional CO<sub>2</sub>. This is presently being investigated and appears to reflect a hydration effect when the  $a_{\text{H}_2\text{O}}$  departs significantly from unity. Calcite solubilities have been determined by Malinin and Kanukov (ref. 51) in 1 molal NaCl as a function of CO<sub>2</sub> concentration at 500 bars between 200° and 600°C. A dramatic increase in solubility above 500°C suggests that a sodium bicarbonate or carbonate complex is stable in these solutions. Rubie and Gunter (ref. 52) have used data from the literatures to compute the equilibrium constant for



$K_{(15)}$  is reported to be 1.7 at 600°C and 1 kbar.

#### Chloride and fluoride complexes

Because of the ionic nature of the most abundant alkali and alkaline earth metals in H<sub>2</sub>O (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup>, as well as Fe<sup>++</sup>), they have the potential to form columbic complexes with the halogens F<sup>-</sup> and Cl<sup>-</sup>. For F<sup>-</sup>, these complexes are known to be reasonably strong at 25°C (ref. 53). Due in large part to the decreasing dielectric constant of the H<sub>2</sub>O solvent with increasing temperature, the columbic forces of attraction are enhanced. It is anticipated, therefore, that most of the fluorine should be complexed in supercritical H<sub>2</sub>O solutions as HF<sub>(aq)</sub> and neutral alkali and alkaline earth fluoride complexes. Fluoride, however, tends to be partitioned strongly into hydrous mineral phases such as micas and amphiboles so that its concentration in crustal fluids is low, diminishing its potential for mass transport of major solutes in the fluid phase (ref. 54-57). Chlorine, on the other hand, is both abundant and partitions strongly into the fluid phase (ref. 58, 59). Chloride complexes are therefore thought to be the dominant solute species in many H<sub>2</sub>O-rich crustal fluids at elevated temperatures and pressures.

Fig. 14 shows experimentally determined dissociation constants for some of the chloride complexes of geological interest, plus that for HF<sub>(aq)</sub>, as a function of temperature at 2 kbar pressure. Nearly all of the dissociation constants shown (ref. 41, 60-65) were determined from conductance measurements with most of those done by Franck and coworkers. Note that HF<sub>(aq)</sub> is significantly more associated than HCl<sub>(aq)</sub>. From corresponding state arguments we might suppose alkaline and alkali earth fluorides would be more associated than their chloride counterparts.

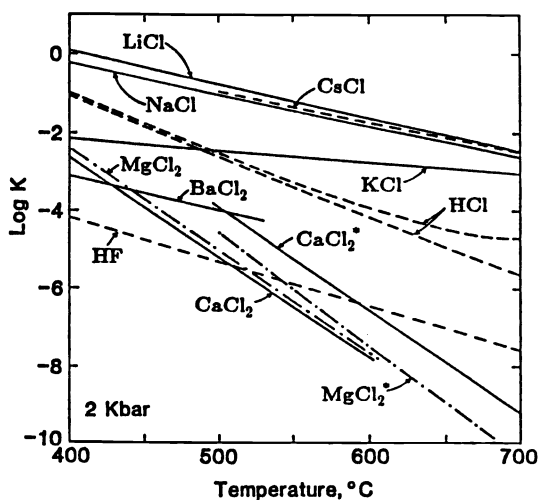


Fig. 14. Logarithm of the equilibrium constant for the dissociation of the electrolytes indicated at 2 kbar. "Starred" electrolytes are values obtained from solubility measurements; all others from electrical conductance studies.

The relative degree of dissociation at any one temperature among the electrolytes shown in Fig. 14 is apparently not predictable from electrostatic theory. In fact, at 2 kbar and temperatures below  $\sim 500^\circ\text{C}$   $\text{KCl}_{(\text{aq})}$  is more associated than  $\text{HCl}_{(\text{aq})}$  while the reverse is true above  $500^\circ\text{C}$ . However, the temperature dependence of the dissociation constants for the various electrolytes appear to follow their cationic potential,  $Z_1^+/r_1^+$ , where  $Z_1^+$  is the formal electrostatic charge of the cation and  $r_1^+$  the atomic radius of the cation  $i$ . As a proxy for  $r_1^+$  we can use the cation size determined from 6-coordination with oxygen in crystalline solids. This correlation is shown in Fig. 15 where the slope on the lines in Fig. 14 ( $d\log K/dT$ ) are plotted against the ionic potential of the cation species in the electrolyte. A reasonably good linear correlation exists, suggesting that a model based on charge density or Pearson hardness-softness of the cation would be fruitful (ref. 66-68).

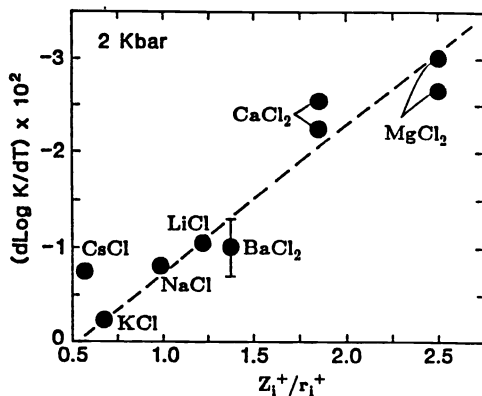


Fig. 15. Slope of lines shown in Fig. 14 ( $d\log K/dT$ ) versus the cation potential of the electrolyte in charge per angstrom at 2 kbar.

Shown in Fig. 16 is the pressure dependence of the dissociation constant at  $500^\circ\text{C}$ . Note also at  $500^\circ\text{C}$  and any pressure,  $d\log K/dP$  increases from  $\text{H} < \text{Na} < \text{Li}$  and  $\text{Ba} < \text{Ca} < \text{Mg}$  and may again be related to ionic potential. In any event such correlations afford a means of predicting the pressure and temperature dependence of the dissociation constant of unmeasured chloride electrolytes.

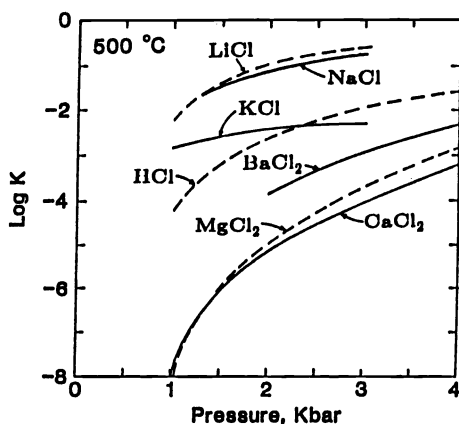
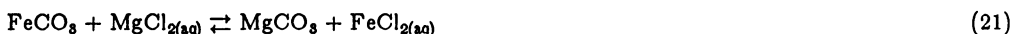
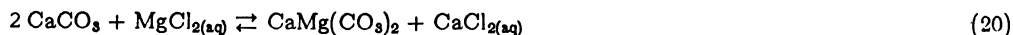
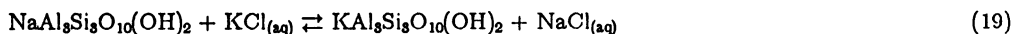
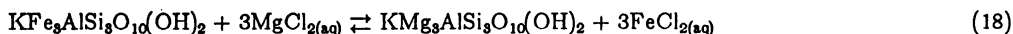
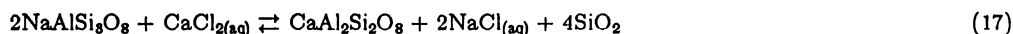


Fig. 16. Pressure dependence of the logarithm of the equilibrium constant for the dissociation constant of the indicated electrolyte at  $500^\circ\text{C}$ .

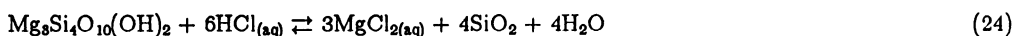
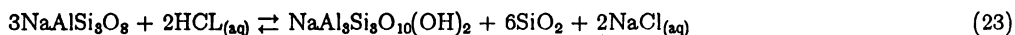
### Ion exchange experiments

Ion exchange experiments have been performed between feldspars, micas, and carbonates in chloride solutions. It is generally assumed that the dominant alkali or alkaline earth complexes in concentrated chloride solutions are neutral chloride complexes. Some of the important equilibria are



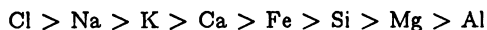
Reaction (16) has been studied by Orville (ref. 66), Fournier (ref. 67), Lagache and Weisbrod (ref. 68); reaction (17) by Orville (ref. 69); reaction (18) by Schlien (ref. 70, 71); reaction (19) by Iiyama (ref. 72); reaction (20) by Rosenberg and Holland (ref. 76), Rosenberg et al. (ref. 77); and reaction (21) by Johannes (ref. 78). Generally in these exchange reactions the solid phases show some degree of solid solution defined by the equilibrium composition across the solvus and can not be considered pure. Their activities are, therefore, significantly below unity relative to the pure phase with positive departure from ideality as anticipated by the solvus between the solids on opposite sides of the exchange reactions.

Besides exchange reactions fluid-mineral equilibria in chloride solutions with only one alkali or alkaline earth have been measured by unbuffered (ref. 79), Ag+AgCl buffered (ref. 80), and Ag + AgCl unbuffered techniques (ref. 81). The latter two techniques control the fugacity of HCl<sub>(aq)</sub>. Although the fugacity of HCl<sub>(aq)</sub> must be controlled or computed these reactions have the advantage in that the mineral phase can be considered to be pure and therefore standard state properties may be used:



Reaction (22) has been investigated by Hemley (ref. 79), Ivanov et al. (ref. 82), Shade (ref. 83), Montoya and Hemley (ref. 84), Gunter and Eugster (ref. 85); reaction (23) by Hemley and Jones (ref. 86), Montoya and Hemley (ref. 84); reaction (24) by Frantz and Popp (ref. 81); and reaction (25) by Gunter and Eugster (ref. 87), Popp and Frantz (ref. 88).

Many researchers have used the above data to determine the thermodynamic properties of solute complexes in chloride-rich supercritical aqueous solutions. Detailed discussion of the assumptions, techniques, and uncertainties can be found in recent synthesis papers (ref. 68, 89-97). Pelitic rocks, originating as clay-rich sediments, are the most abundant rock composition in the continental upper crust. In general it is to be expected that supercritical solute species abundances in fluid in contact with average metapelitic mineral assemblages follow



In calcium-rich pelitic rocks Ca may dominate over K. Depending on the abundance of chloride the order of Fe, Si, Mg and Al may also be affected. This order of solute species has been confirmed by experiments in multicomponent analog systems (ref. 98). The predominance of NaCl and KCl has also been confirmed by studies of fluid inclusions trapped in minerals undergoing metamorphism in the crust (ref. 99, 100). Examination of fluid inclusions indicate that chloride concentrations are highly variable in fluids in contact with pelitic rocks but are dominantly between 0.3 to 1.0 molal.

### CONCLUDING REMARKS

In recent years significant advances have been made in our understanding of the stability of aqueous species under supercritical conditions, but much work needs to be done. Particularly lacking is information on solute behavior in the important mixed solvent H<sub>2</sub>O-CO<sub>2</sub>. From what is known of complex formation a number of generalizations can, however, be made.

The degree of hydrolysis of cations to form lower charged or neutral complexes increases with increasing temperature, decreasing pressure and increasing charge density: K<sup>+</sup> < Na<sup>+</sup> < Ca<sup>++</sup> < Mg<sup>++</sup> < Al<sup>3+</sup> <

Si<sup>4+</sup>. Although unknown at earth surface conditions stable K-Al and Na-Al complexes have the potential to carry significant Al in supercritical solutions. It also appears that Al forms a positively charged species in acidic solution or it complexes to some extent with Cl but the nature of the species or stoichiometry of the complex is unclear at the present time. Na-Si and K-Si complexes are shown to exist and may be dominant relative to Na<sup>+</sup> and K<sup>+</sup> at high temperatures and low chloride concentrations with NaCl<sub>(aq)</sub> and KCl<sub>(aq)</sub> dominant at higher chloride concentrations. The dominant Si complex is apparently Si(OH)<sub>4</sub>·2H<sub>2</sub>O.

Hartman and Franck (ref. 101) have shown that the dissociation constant of KCl<sub>(aq)</sub> decreases with addition of Ar in supercritical H<sub>2</sub>O solutions. It would be anticipated that dilution of H<sub>2</sub>O with CO<sub>2</sub> would have similar effects. Thus speciation in supercritical CO<sub>2</sub>-rich solutions is probably dominated to an even greater extent by neutral complexes. The effects of CO<sub>2</sub> on solubility or species distribution cannot be evaluated at the present time.

Because of the large region of pressure-temperature space and the large number of significant components that need to be considered, direct experimental determination of all solution compositions of interest will not be possible. This is particularly true because of the technical difficulty of measurements in the supercritical region. Clearly experimental investigations must be designed to aid theoretical understanding and allow prediction and interpolation of unmeasured mineral solubilities and solution properties.

### Acknowledgements

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