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Experimental determination and analysis of the solubility of corundum in 0.1 and 0.5 m NaCl solutions between 400 and 600°C from 0.5 to 2.0 kbar

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Abstract—Corundum, α -Al₂O₃, solubility was measured in 0.1 and 0.5 m NaCl solutions from 400 to 600°C between 0.5 and 2.0 kbar. The base-10 logarithm of Al molality at 2 kbar in 0.5 m NaCl increases from -2.45 at 400°C to -1.52 at 600°C. At 1 kbar, the solubility increases from -2.33 at 400°C to -1.03 at 600°C. These molalities are between 1 and 3 orders of magnitude greater than corundum solubility in pure H₂O (Walther, 1997). In 0.1 m NaCl, corundum solubility begins to decrease below that in pure water at 400°C as pressures are decreased below ~ 1.2 kbar. A distribution of species calculation considering the Al species NaAl(OH)₄⁰, Al(OH)₃⁰ and Al(OH)₄⁻ and using association constants reported in the literature demonstrate that Al(OH)₄⁻ is a significant species in equilibrium with corundum in pure H₂O. The calculations also indicate that another Al aqueous species containing Na or Cl besides NaAl(OH)₄⁰ must be present in NaCl solutions to give the observed increase in Al with increasing NaCl concentrations to 0.5 m. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Aqueous solutions at the elevated temperatures and pressures in the earth's crust reach solubility equilibrium with the minerals they contact relatively rapidly (Walther and Wood, 1984). Therefore, to understand mass transport, whether at the scale of a few cm between reactant and product minerals or at a km scale in the development of through-going veins, mineral solubilities in crustal fluids must be known. Because of the preponderance of Al-bearing minerals in the earth's crust, their solubility in crustal solutions is particularly important. Based on textural relations, a number of investigators have argued for a constant Al reference frame during metamorphic reactions (e.g., Carmichael, 1969), which assumes a low concentration of Al in solution. However, andalusite-, kyanite- and sillimanite-containing veins and segregations are relatively common in metamorphosed pelitic rocks (e.g., Foster, 1977; Rubenach and Bell, 1988) and indicate substantial transport of Al. To understand this differing mobility of Al, one needs to determine the solubility of Al-bearing minerals in crustal fluids.

In a previous study (Walther, 1997), the solubility of corundum in pure H₂O was determined and interpreted. The present investigation builds on the previous work by reporting and analyzing corundum solubilities in 0.1 and 0.5 m NaCl solutions from 400 to 600°C between 0.5 and 2.0 kbar.

2. DISCUSSION OF PREVIOUS WORK

Pokrovskii and Helgeson (1995) have reviewed reported mineral solubility determinations as well as measured aqueous solution thermodynamic properties in the system Al₂O₃-H₂O-NaCl. Based on these determinations, they built a thermodynamic model, which can be used to calculate the solubility of

corundum in supercritical aqueous NaCl solutions. However, their model underestimates the solubility of corundum in pure H₂O between 350 and 600°C for pressures between 0.5 and 2.2 kbar as measured by Walther (1997). At supercritical pressures and temperatures, their model parameters were constrained by the $670 \pm 5^\circ\text{C}$ corundum single-crystal weight loss solubility measurements of Becker et al. (1983) in pure H₂O. More recent single-crystal solubility measurements of corundum plus kyanite in pure H₂O at 700°C and 10 and 15 kbar made by Manning (2001) report higher solubility values consistent with the lower pressure extraction fluid-quench determinations of Walther (1997). As done widely in the literature where both charged and neutral aqueous species are abundant, Pokrovskii and Helgeson (1995) used an extended Debye-Hückel equation for the activity coefficient of charged species and a Setchénow-type equation for the activity coefficient of neutral species in solution. Using these two equations together in a model violates the Gibbs-Duhem constraint on activity coefficients as a function of composition. To understand this, consider a standard state for aqueous species based on unit activity of the aqueous species in a hypothetical 1-molal solution in which activity coefficients are taken as unity at infinite dilution at all pressures and temperatures. A Setchénow-type equation for the activity coefficient of a neutral species can then be written as

$$\log \gamma_n = \mathbf{b}_n I \quad (1)$$

where γ_n and \mathbf{b}_n denote the activity coefficient and Setchénow constant of the *n*th neutral species, respectively. *I* stands for the ionic strength of the solution computed from

$$I = 0.5 \sum_i m_i z_i^2 \quad (2)$$

where the summation is taken over all species in solution with *m_i* and *z_i* representing the molality and charge of the *i*th species, respectively. Eqn. 1 indicates the concentration of

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charged species through the ionic strength given in Eqn. 2 has an effect on neutral species activity coefficients. According to the Gibbs-Duhem constraint, this requires that neutral species have an effect on charged species activity coefficients in that

$$\left(\frac{\partial \log \gamma_n}{\partial m_i}\right)_{P,T,m_j} = \left(\frac{\partial \log \gamma_i}{\partial m_n}\right)_{P,T,m_j} \quad (3)$$

where m stands for the molality and γ the activity coefficient of the subscripted species. The subscript i denotes the mean ionic charged species and n the neutral species considered. The subscripts P, T , and m_j outside the brackets indicate pressure, temperature, and the molality of all the aqueous species except the i th or n th species are to be held constant during differentiation.

The traditional extended Debye-Hückel equation for charged species used by Pokrovskii and Helgeson (their Eqn. 6) does not include the effects of changes in the concentration of neutral species on γ_i . It needs to be modified when charged species-neutral species interactions (other than with H_2O molecules) become significant, as is the case in supercritical NaCl solutions. This can be handled in two different ways. When the concentration of neutral species is particularly large as in CO_2 -rich CO_2 - H_2O solutions, one can modify the A_γ and B_γ solvent parameters of the Debye-Hückel equation (e.g., Xie and Walther, 1993). In this approach one uses the dielectric constant and density of the mixture of neutral species with H_2O rather than the dielectric constant and density of pure H_2O in computing A_γ and B_γ . Another way to obtain Gibbs-Duhem consistency is to add a term to the extended Debye-Hückel equation to account for charged-neutral species interactions (e.g., Walther, 1997). In this case, one modifies the extended Debye-Hückel equation so that the mean ionic activity coefficients of charged aqueous species are computed from

$$\log \gamma_i = \frac{-A_\gamma z_i^2 I^{1/2}}{1 + B_\gamma \tilde{a} I^{1/2}} + b_\gamma I + 0.5 z_i^2 \sum_n \mathbf{b}_n m_n \quad (4)$$

where z_i stands for a species charge, b_γ denotes the Debye-Hückel extended term parameter, and \tilde{a} represents the ion size parameter. The summation in the last term is taken over all the n -neutral species in solution with m_n representing the molality of the n th neutral species. With the addition of the last term on the right to account for neutral species effects on charged species, the γ_i expression in Eqn. 4 satisfies the Gibbs-Duhem cross-differential constraint in Eqn. 3 as both derivatives equal $0.5 z_i^2 \mathbf{b}_n$. Using Eqn. 1 and 4, the energy of interaction between neutral and charged species in solution can be considered in a distribution of species calculation if values of \mathbf{b}_n as well as the speciation in the fluid can be determined.

The experiments used in Pokrovskii and Helgeson's analysis to obtain coefficients for the HKF (Helgeson, Kirkham, and Flowers) (Helgeson et al., 1981) equation of state were constrained dominantly by subcritical thermodynamic measurements where there are generally only small concentrations of neutral species. Therefore, the Gibbs-Duhem inconsistency should have only a minor effect on their fitting of HKF parameters. Their analysis led them to propose a significant stability

of a $NaAl(OH)_4^0$ aqueous complex in Na-rich solutions at subcritical conditions. This species was considered by Anderson and Burnham (1967) to be the dominant Al species in supercritical NaOH and NaCl solutions. Using Pokrovskii and Helgeson's derived values for the HKF equation of state, the molal equilibrium constant for the reaction, $Al(OH)_4^- + H^+ = Al(OH)_3^0 + H_2O$ of

$$K_{Al3/4} = \frac{\gamma_{Al(OH)_3^0} m_{Al(OH)_3^0} a_{H_2O}}{\gamma_{Al(OH)_4^-} m_{Al(OH)_4^-} \gamma_{H^+} m_{H^+}} \quad (5)$$

and for the reaction, $Na^+ + Al(OH)_4^- = NaAl(OH)_4^0$ of

$$K_{NaAl(OH)_4} = \frac{\gamma_{NaAl(OH)_4^0} m_{NaAl(OH)_4^0}}{\gamma_{Na^+} m_{Na^+} \gamma_{Al(OH)_4^-} m_{Al(OH)_4^-}} \quad (6)$$

can be computed as given in Table 3.

Diakonov et al. (1996) measured boehmite (γ - $AlOOH$) solubility in NaOH-NaCl aqueous solutions between 125 and 325°C at vapor saturation pressure. To account for the increased solubility of boehmite with increasing Na in solution, they also argued for a significant stability of $NaAl(OH)_4^0$ together with the species $Al(OH)_4^-$ in their solutions. Their distribution of species determinations, assuming no interactions between charged and uncharged species, were used to derive a different set of parameters for $NaAl(OH)_4^0$, $Al(OH)_3^0$ and $Al(OH)_4^-$ in the HKF equation. These parameters can also be used to calculate the equilibrium constant for Eqn. 5 and 6. Table 3 also gives their computed values of $K_{Al3/4}$ and $K_{NaAl(OH)_4}$.

There is significant disagreement between the two sets of equilibrium constants. Measurements of boehmite solubility in Na-free solutions from Castet et al. (1993) were used in the analysis of Diakonov et al. (1996) to determine $K_{Al3/4}$. At the highest temperature and pressure investigated, 350°C and vapor saturation, Castet et al. (1993) indicate that $Al(OH)_4^-$ dominates over $Al(OH)_3^0$ to 1.2 pH units more acid than neutral pH. Analyzing the available data, Pokrovskii and Helgeson argued for approximately equal concentrations of $Al(OH)_4^-$ and $Al(OH)_3^0$ at neutral pH and 350°C at vapor saturation pressure. The Apps et al. (1989) determinations of the equilibrium constant for Eqn. 5 indicate that $Al(OH)_3^0$ is dominant over $Al(OH)_4^-$ to 0.6 pH units more alkaline than neutral pH at 350°C.

Pascal and Anderson (1989), on the basis of measurements of corundum solubility in NaOH and KOH solutions between 400 and 700°C at 2 kbar, and analysis of the data of Anderson and Burnham (1967), concluded that it was likely that Al existed dominantly as $Al(OH)_3^0$ in supercritical pure H_2O solutions and increases in Al solubility with the addition of NaOH to the solution were due to the formation of $NaAl(OH)_4^0$ with little contribution of $Al(OH)_4^-$. Azaroual et al. (1996) determined corundum solubility at 400°C from 0.5 to 2.0 kbar in dilute (0.001–0.1 m) KOH solutions. Assuming no charged-neutral species interactions, they concluded that along with $Al(OH)_4^-$, $KAl(OH)_4^0$ likely became significant at their higher KOH concentrations. Walther (1997) demonstrated that their measured increases in solubility with increasing KOH could also be modeled without $KAl(OH)_4^0$ if \mathbf{b}_n for $Al(OH)_3^0$ is negative. The negative \mathbf{b}_n increases the

stability of $\text{Al}(\text{OH})_3^0$ as the ionic strength of the solution increases.

Corundum solubility measurements of Korzhinskii (1987) and Baumgartner and Eugster (1988), as well as the Al_2SiO_5 solubility investigation of Ostapenko et al. (1987) in supercritical aqueous HCl solutions, suggest Al-Cl complexes may become important in acid solutions although it is difficult to distinguish the extent of this as opposed to increased stability of Al^{+3} , $\text{Al}(\text{OH})^{2+}$, and/or $\text{Al}(\text{OH})_2^+$ with increasing concentrations of HCl in these solutions. Investigation of kaolinite, pyrophyllite, and andalusite solubility with quartz at 1.0 kbar between 150 and 500°C in $\text{AlCl}_3 + \text{HCl}$ aqueous solutions by Red'kin and Ivanov (1980) also indicate a higher concentration of Al in acidic Cl-containing solutions. More recent investigations at pressures and temperatures below the critical point of H_2O (Wesolowski, 1992; Palmer and Wesolowski, 1992) conclude that Al-Cl complexing does not occur.

From solubility measurements in pure H_2O of Walther (1997), the distribution of Al between $\text{Al}(\text{OH})_3^0$ and $\text{Al}(\text{OH})_4^-$ can be determined with a knowledge of the equilibrium constant given in Eqn. 5. The stability of $\text{NaAl}(\text{OH})_4^0$ can then be assessed by measuring the solubility of corundum in NaCl solutions, assuming no significant Al-Cl complexing in these solutions.

3. EXPERIMENTAL PROCEDURES

Experiments were performed using an extraction-quench technique with an apparatus described by Walther and Orville (1983). A quantity of 0.5 ± 0.02 g of high-purity (certified composition = 99.997 wt.%) $\alpha\text{-Al}_2\text{O}_3$ synthetic corundum from Alfa Aesar was used along with reagent-grade 0.1 m and 0.5 m NaCl solutions. Fines were removed from the corundum before loading in the charge volume by suspending the corundum in the NaCl solution, waiting 1 min for the larger corundum particles to settle, and decanting the solution of fines. This suspension procedure was repeated five times, after which the solution was clear to the eye within 1 min settling time. This corundum was loaded along with a solution of 0.1 m NaCl (C series) or 0.5 m NaCl (D and E series) into the charge volume. The Au-coated charge volume was contained in an autoclave of nickel/chromium/cobalt alloy. The autoclave was sealed with an unsupported stress seal and brought to elevated pressure and temperature by heating in a Nichrome wire furnace. Temperatures were measured with chromel/alumel thermocouples along the charge volume with gradients $< 1.2^\circ\text{C}$ with a computed accuracy of $\pm 2^\circ\text{C}$. The pressure was monitored with a Bourdon-tube Heise pressure gauge with $\pm 0.2\%$ accuracy. The system was allowed to equilibrate, at the pressure and temperature conditions of the 1st sample extraction, for 96 hr. While the ~ 35 cm^3 charge volume remained at the experimental pressure and temperature, approximately 1.6 g of solution was extracted through a fine capillary tube to a sample collector assembly. The extracted sample fluid was flushed from the sample collector volume with a 0.1M HCl solution to dissolve any Al that may have precipitated in the sample collector volume during decompression and cooling. Separating the fluid from the corundum before quenching the fluid eliminates back-reaction effects. If needed, new 0.1 m or 0.5 m NaCl solution was injected into the charge volume to replace the extracted fluid and/or increase the pressure to the desired value for the next extraction. The charge volume was allowed to equilibrate at pressure and temperature for at least 48 hr between sample extractions. Except for the minor dilution from the small amount of NaCl solution that was injected into the charge volume, the starting concentration of aqueous Al from which equilibrium was approached is given by the concentration measured in the previously extracted sample. Therefore, equilibrium was approached from both undersaturated and supersaturated conditions. The sample numbers in Tables 1 and 2 give the order in which fluids were extracted.

Table 1. Measured molality of Al in equilibrium with corundum in 0.1 molal NaCl at the indicated pressure and temperature.

Id No.	Temp °C	P bars	-log m (Al)
C-1	600	1000	2.990
C-2	600	980	3.033
C-3	600	748	3.303
C-4	600	755	3.328
C-5	600	752	3.322
C-6	600	751	3.249
C-7	600	1000	2.880
C-8	600	1000	2.913
C-9	600	1240	2.767
C-10	600	1252	2.710
C-11	600	1530	2.687
C-12	600	1502	2.715
C-13	550	980	2.780
C-14	550	1038	2.742
C-15	500	1001	2.860
C-16	500	996	2.874
C-17	500	1000	2.897
C-18	450	982	3.172
C-19	450	1060	3.112
C-20	400	1035	3.287
C-21	400	998	3.366
C-22	400	1100	3.210
C-23	400	1430	3.143
C-24	400	1505	3.098

Molalities reported as negative base-10 logarithms. Id numbers give the order of sampling. The starting Al molality indicating which direction equilibrium was approached is given by the concentration in the previous measurement.

The D samples represent one set of measurements in 0.5 m NaCl at the pressures and temperatures indicated. The E samples represent a repeated 0.5 m NaCl series, where the charge volume was opened, cleaned, and filled with new corundum and 0.5 m NaCl solution.

A direct-current plasma emission spectrometer (DCP) was used to analyze the Al in the flushing solution with analytical reproducibility of $\pm 5\%$ or better. Experimental reproducibility was determined by repeated measurements at the same pressure and temperature. For instance, the five measurements made in 0.5 m NaCl at 400°C and 2000 ± 10 bars from both the D and E series has a range of Al concentrations given by $3.55 \pm 0.21 \times 10^{-3}$ molal or a 6% uncertainty. Grain size and crystal defects did not seem to be important as results from undersaturation and oversaturation gave similar solubility values. Also, determinations made after the reaction vessel was at elevated pressure and temperature for 2 months gave similar results at similar pressures and temperatures as those made earlier.

There is a significant two-phase region in H_2O -NaCl solutions at supercritical temperatures and low pressures. Shown in Figure 1 is the boundary between the one-phase and two-phase region as a function of pressure and temperature for 0.1 and 0.5 m NaCl fluids. The boundaries at 500°C and below are from Bischoff and Pitzer (1989). The extrapolation to 600°C was done by considering their Figure 1 as well as pressure and temperatures where a single-phase and two-phases exist as reported by Sourirajan and Kennedy (1962). Examination of Figure 1 indicates the temperatures and pressures reported in Tables 1 and 2 are in the one-phase region.

4. RESULTS

Given in Table 1 are measured molalities of Al in equilibrium with corundum in 0.1 m NaCl solutions at the indicated pressure and temperature. In Table 2 are determinations in 0.5 m NaCl solutions. Log molalities of Al in 0.5 m NaCl at 400, 500, and 600°C as a function of pressure are plotted in Figure 2A, whereas determinations at 1 and 2 kbar as a function

Table 2. Measured molality of Al in equilibrium with corundum in 0.5 m NaCl at the indicated temperature and pressure.

Id No.	Temp °C	P bars	-log m (Al)
D-1	400	2000	2.432
D-2	400	2000	2.476
D-3	400	2000	2.447
D-4	450	2030	2.364
D-5	450	2000	2.263
D-6	500	2000	2.005
D-7	500	1500	1.999
D-8	500	1503	1.977
D-9	500	1505	1.977
D-10	500	1190	2.145
D-11	500	978	2.063
D-12	500	1000	2.069
D-13	500	850	1.824
D-14	550	1022	1.872
D-15	550	1000	1.860
D-16	550	1048	1.818
D-17	600	1395	1.704
D-18	600	1130	1.755
D-19	600	1002	1.901
D-20	600	999	1.834
D-21	600	1001	1.897
D-22	600	1428	1.654
D-23	600	1497	1.672
D-24	600	1502	1.651
E-1	249	1950	3.251
E-2	401	992	2.343
E-3	400	2010	2.469
E-4	400	1995	2.424
E-5	400	1502	2.381
E-6	400	1500	2.390
E-7	400	1015	2.326
E-8	400	1012	2.374
E-9	400	996	2.314
E-10	450	1050	2.178
E-11	500	1998	1.935
E-12	500	1930	1.924
E-13	500	1981	1.922
E-14	500	1502	1.973
E-15	500	1499	1.941
E-16	500	1146	1.943
E-17	500	1000	1.955
E-18	500	750	1.674
E-19	500	750	1.733
E-20	500	750	1.745
E-21	500	1005	1.920
E-22	600	1495	1.538
E-23	600	1970	1.444
E-24	600	1956	1.518
E-25	600	2010	1.500
E-26	600	2005	1.549
E-27	600	1606	1.595
E-28	600	1510	1.519
E-29	600	1501	1.656
E-30	600	1252	1.717
E-31	600	1065	1.595
E-32	600	998	1.783
E-33	600	1007	1.842
E-34	600	1002	1.831
E-35	600	868	1.960
E-45	550	990	1.859
E-46	550	1010	1.867
E-47	500	655	1.824
E-52	450	510	2.418
E-53	450	499	2.409
E-54	450	501	2.456
E-55	400	508	2.168
E-56	400	491	2.214
E-57	400	500	2.233
E-58	450	750	2.161
E-59	450	1000	2.089
E-60	450	1001	2.151
E-61	450	1001	2.156
E-62	450	1470	2.207
E-63	450	1501	2.271

Molalities reported as negative base-10 logarithms. Id numbers give the order of sampling. The starting Al molality, indicating which direction equilibrium was approached, is given by the concentration in the previous measurement.

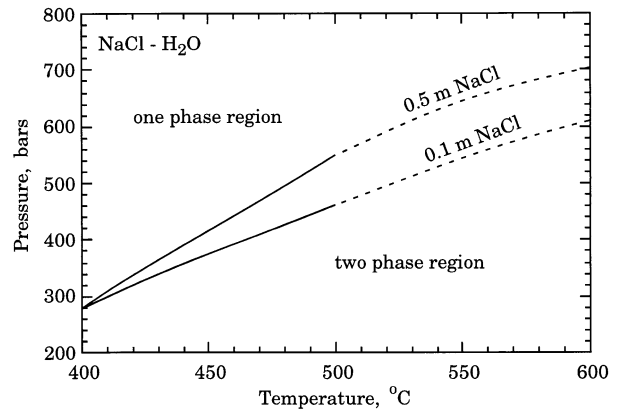


Fig. 1. Pressure-temperature phase diagram for the NaCl-H₂O system showing the regions where one- and two-phase fluids exist for 0.1 and 0.5 m NaCl solutions.

of temperature are shown in Figure 2B. Values from Table 2 were plotted if their pressures were within 20 bars of the indicated pressures. Figure 2 indicates that in 0.5 m NaCl solutions, corundum solubility at 2 kbar increases with temper-

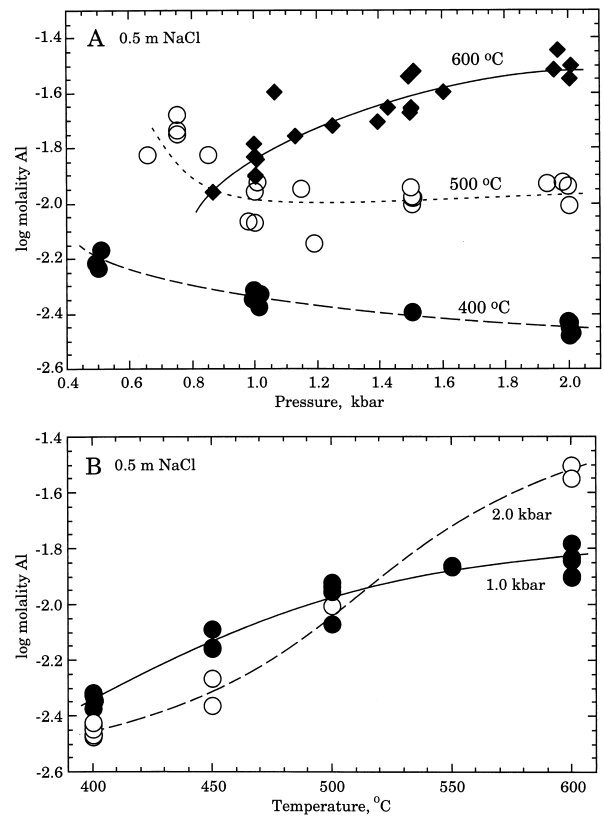


Fig. 2. (A) Base-10 logarithm of Al molality in 0.5 molal NaCl solutions in equilibrium with corundum at the indicated temperature as a function of pressure. Solid circles, open circles, and solid diamonds indicate measurements at 400, 500, and 600°C, respectively. (B) Base-10 logarithm of Al molality in 0.5 molal NaCl solutions at the indicated pressure as a function of temperature. Solid circles give measured values at 1.0 kbar and open circles at 2.0 kbar. The lines give visual fits to the data along the indicated isotherms and isobars.

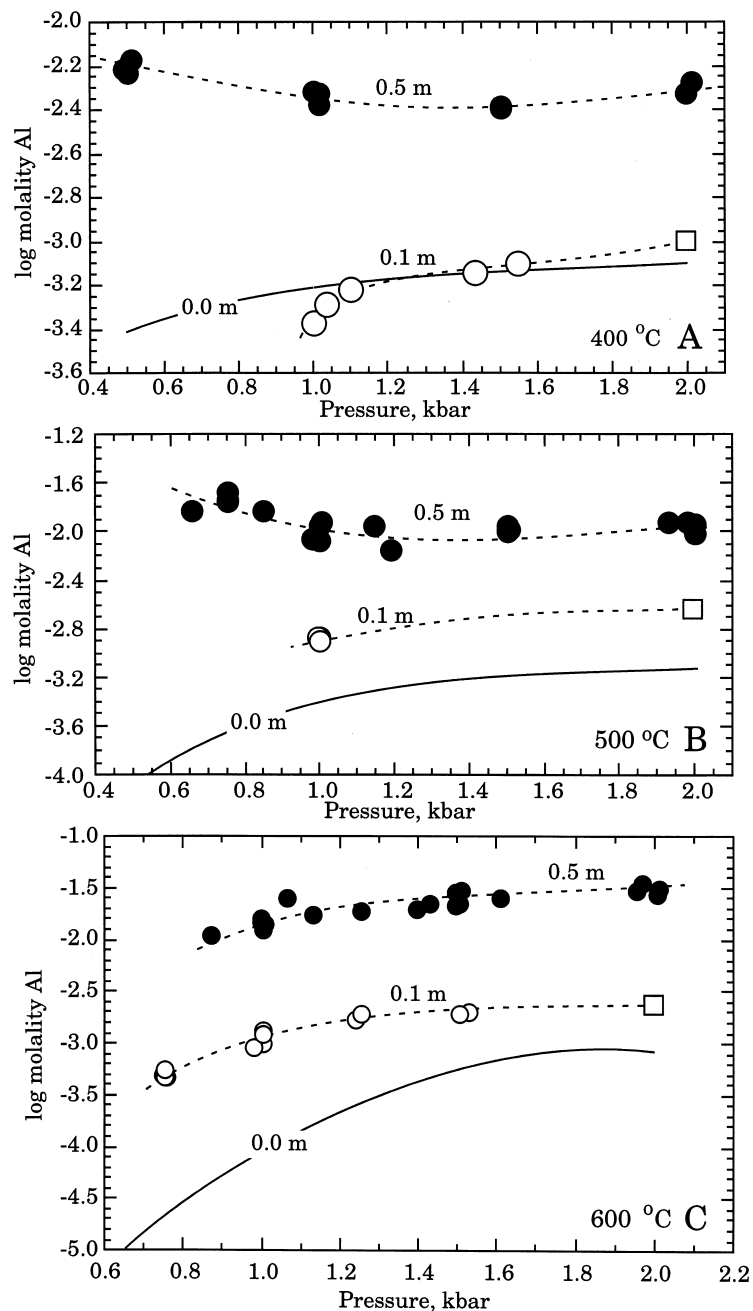


Fig. 3. Base-10 logarithm of Al molality in 0.1 (open circles) and 0.5 (solid circles) molal NaCl solutions in equilibrium with corundum as a function of pressure at (A) 400, (B) 500, and (C) 600°C. The dashed lines are visual fits to the data along the indicated isotherms. The solid lines give the solubility of corundum in pure H₂O from Walther (1997). The open squares are extrapolations of the data trends for 0.1 m NaCl to 2 kbar.

ature and at 600°C, corundum solubility increases with pressure. Decreasing pressure at 600°C decreases solubility, whereas at 400°C, decreased pressure increases solubility. This pressure dependency leads to the behavior illustrated in Figure 2B, where at temperatures of 500°C and below, increasing pressure from 1 to 2 kbar decreases corundum solubility in 0.5 m NaCl solutions.

Figure 3, panels A, B, and C, are plots of corundum solubility as a function of pressure at 400, 500, and 600°C,

respectively, for both 0.1 (open circles) and 0.5 m (filled circles) NaCl solutions. Also shown as a solid line are determinations in pure H₂O from Walther (1997). The open squares indicate values of corundum solubility in 0.1 m NaCl extrapolated to 2 kbar. These extrapolated values are used below to help constrain the speciation of 0.5 m NaCl solutions at 2 kbar and 400, 500 and 600°C.

Corundum solubility in 0.5 m NaCl is from 1.5 to ~3 orders

of magnitude greater than corundum solubility in pure H₂O, depending on the pressure and temperature considered. Note that corundum solubility in 0.1 m NaCl solutions at 400°C is less than that in pure H₂O at pressures below ~1.2 kbar. This indicates that corundum “salts out,” decreasing its solubility with increasing salt concentration to 0.1 m, but “salts in” as NaCl concentrations are increased to 0.5 m. Figure 3 indicates that corundum solubility salts in at both concentrations at higher pressures and temperatures. This behavior can be compared to quartz solubility in 0.49 and 0.83 molal NaCl solutions (Xie and Walther, 1993), which, relative to pure H₂O solutions at 1.0 kbar, changes from salting out for both concentrations at temperatures < 400°C to salting in at higher temperatures.

4.1. Speciation in the Fluid

What are the dominant aqueous Al species in solution that account for the observed solubility? To answer this question, one must build a model of aqueous species stability and interactions. It is only by building a model that the thermodynamic properties and, therefore, the solubilities of other Al bearing minerals can be predicted in NaCl-rich solutions where measurements have not been made. As discussed above, investigations at both subcritical and supercritical pressures and temperatures suggest that Al speciation in equilibrium with corundum in supercritical NaCl solutions comprises a combination of Al(OH)₃⁰, Al(OH)₄⁻ and NaAl(OH)₄⁰. The significantly higher solubilities in 0.5 m NaCl, relative to 0.1 m NaCl and pure water, imply strong interactions between NaCl and Al, further stabilizing Al in solution. This is consistent with formation of the species NaAl(OH)₄⁰. However, the salting out of corundum in 0.1 m NaCl at temperatures of 400°C and pressures below 1.2 kbar indicates that NaCl at concentrations of 0.1 m destabilizes Al in solution. This salting out behavior can be modeled with an activity coefficient of the neutral species, Al(OH)₃⁰, which is greater than unity implying a **b_n** in Eqn. 1 that is positive. As indicated above, Walther (1997) argued for a negative **b_n** for Al(OH)₃⁰ to stabilize that species in KOH solutions that did not include KAl(OH)₄⁰. The values reported here suggest that a better model is to include the species NaAl(OH)₄⁰ in supercritical NaCl solutions with a positive **b_n** for Al(OH)₃⁰ to account for decreased corundum solubility in 0.1 m NaCl relative to that in pure H₂O.

To understand the extent of interactions involved, a distribution of species model for the experimental solutions was constructed. Corundum solubility in pure H₂O was considered first. The Al species Al(OH)₃⁰ and Al(OH)₄⁻ were considered along with H⁺, OH⁻ in H₂O. These four aqueous species define the model system in equilibrium with corundum in pure H₂O. Activity coefficients were calculated using Eqn. 1 and 4 with all **b_γ** = 0.03 and **â** = 3.5 Å. **b_n** values were taken to be zero. The values of **b_n** are not significant, as with the low ionic strength of the solution, the activity coefficient of neutral Al(OH)₃⁰ will be near unity with any reasonable **b_n**.

With a standard state for corundum and H₂O of the pure phase at the temperature and pressure of interest, the activity of corundum and H₂O can be taken as unity. A standard state of

unit activity of the solute in a hypothetical 1 molal solution, where activity coefficients are taken as unity at infinite dilution at all pressures and temperatures, was used for aqueous species. Measurements by Walther (1997) give the total molality of Al in solution, Al_T, of

$$Al_T = m_{Al(OH)_3^0} + m_{Al(OH)_4^-}. \quad (7)$$

The equilibrium constant expressions for the disassociation of H₂O is

$$K_{H_2O} = \frac{\gamma_{H^+} m_{H^+} \gamma_{OH^-} m_{OH^-}}{a_{H_2O}}. \quad (8)$$

These two equations, together with the equilibrium constant expression given in Eqn. 5 and the equation of charge balance in solution, were used to obtain the distribution of species in solution by making use of the activity coefficient expressions in Eqn. 1 and 4. Using the Pokrovskii and Helgeson (1995) equilibrium constants for Eqn. 5, the dominate Al species in solution is computed to be Al(OH)₃⁰ with an order of magnitude less Al(OH)₄⁻ present for pressures to 2.0 kbar and temperatures to 600°C. The Diakonov et al. (1996) equilibrium constants produce nearly equal concentrations of Al(OH)₃⁰ and Al(OH)₄⁻ in solution at similar pressures and temperatures. One surmises in either case that both Al(OH)₃⁰ and Al(OH)₄⁻ are important species when considering the solubility of corundum in pure H₂O between 1.0 and 2.0 kbar and temperatures from 400 to 600°C.

From the computed distribution of species, the equilibrium constant for the reaction: 0.5 Al₂O₃ = Al(OH)₄⁻ + H⁺ of

$$K_{Cor} = \frac{\gamma_{Al(OH)_4^-} m_{Al(OH)_4^-} \gamma_{H^+} m_{H^+}}{a_{Cor} a_{H_2O}} \quad (9)$$

was determined. Values of K_{Cor} determined, using both the Pokrovskii and Helgeson (1995) and Diakonov et al. (1996) values of K_{Al3/4}, are given in Table 3.

Adding NaCl in the experiments reported here produces the additional charged species Na⁺ and Cl⁻ as well as the associated species HCl⁰, NaCl⁰, NaOH⁰, and NaAl(OH)₄⁰. The equilibrium constant expressions K_{NaAl(OH)₄} and K_{Cor} given in Eqn. 6 and 9, respectively, from either Pokrovskii and Helgeson (1995) or Diakonov et al. (1996) can be used together with the disassociation constants of HCl⁰, NaCl⁰, and NaOH⁰ of

$$K_{HCl} = \frac{\gamma_{H^+} m_{H^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{HCl^0} m_{HCl^0}} \quad (10)$$

$$K_{NaCl} = \frac{\gamma_{Na^+} m_{Na^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{NaCl^0} m_{NaCl^0}} \quad (11)$$

$$K_{NaOH} = \frac{\gamma_{Na^+} m_{Na^+} \gamma_{OH^-} m_{OH^-}}{\gamma_{NaOH^0} m_{NaOH^0}} \quad (12)$$

respectively, to do a distribution of species calculation. The required charge balance in solutions stipulates that

$$m_{H^+} + m_{Na^+} - m_{Cl^-} - m_{OH^-} - m_{Al(OH)_4^-} = 0.0 \quad (13)$$

The equations for total Na (Na_T) and total Cl (Cl_T) in solution necessitates that

Table 3. Molality of Al in equilibrium with corundum in pure H₂O times 10⁴ and the base-10 logarithm of the molal equilibrium disassociation constants of the indicated species at the indicated pressure and temperature.

Pres kbar	Temp °C	$m_{\text{Al}} \times 10^4$	log $K_{\text{H}_2\text{O}}$	log K_{NaCl}	log K_{HCl}	log K_{NaOH}	⁽¹⁾ log $K_{\text{Al}_3/4}$	^(1*) log K_{Cor}	⁽¹⁾ log $K_{\text{NaAl(OH)}_4}$	⁽²⁾ log $K_{\text{Al}_3/4}$	^(2*) log K_{Cor}	⁽²⁾ log $K_{\text{NaAl(OH)}_4}$
1.0	400	6.33	-10.72	-0.86	-1.88	-1.93	5.38	-8.62	1.97	3.74	-7.18	1.70
2.0	400	5.57	-9.74	(-0.25)	(-1.1)	-1.28	5.07	-8.38	1.46	3.38	-7.02	1.32
1.0	500	4.05	-11.86	-2.11	-4.26	-3.35	5.99	-9.40	3.13	3.99	-7.61	2.58
2.0	500	7.53	-10.29	-1.03	-2.64	-2.04	5.49	-8.65	2.15	3.16	-6.71	1.74
1.0	600	1.07	-13.51	-3.58	-6.90	-5.00	6.73	-10.72	4.61	4.84	-8.98	3.93
2.0	600	8.20	-10.88	-1.85	-4.19	-2.80	6.03	-9.13	2.93	3.13	-6.65	2.25

Solubility of corundum in molality, m_{Al} , from Walther (1997). The disassociation constants of the indicated subscripted species of $K_{\text{H}_2\text{O}}$, K_{NaCl} , K_{HCl} , K_{NaOH} are from Quist (1970), Quist and Marshall (1984), Frantz and Marshall (1984), and Pokrovskii and Helgeson (1995), respectively. The equilibrium constants in Eqn. 5 and 6, $K_{\text{Al}_3/4}$ and $K_{\text{NaAl(OH)}_4}$, labeled (1) and (2), are from Pokrovskii and Helgeson (1995) and Diakonov et al., (1996), respectively. The equilibrium constant in Eqn. 9, K_{Cor} , calculated from Walther (1997) and Pokrovskii and Helgeson (1995) is labeled (1*), whereas that derived from Walther (1997) and Diakonov et al. (1996) is labeled (2*). Values in parentheses are extrapolated.

$$\text{Na}_T = m_{\text{Na}^+} + m_{\text{NaCl}} + m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4^0} \quad (14)$$

and

$$\text{Cl}_T = m_{\text{Cl}^-} + m_{\text{NaCl}} + m_{\text{HCl}}. \quad (15)$$

Values of Na_T and Cl_T are known and one can assume the activity of corundum and H₂O in these solutions is unity. The b_n of all neutral species were taken as zero. $K_{\text{H}_2\text{O}}$, K_{HCl} , K_{NaCl} , and K_{NaOH} values are taken from Quist (1970), Frantz and Marshall (1984), Quist and Marshall (1968), and Pokrovskii and Helgeson (1995), respectively. These can be used together with the values of K_{Cor} calculated above. The equilibrium constants used are given in Table 3. A distribution of species calculation was done using these constraints and the total Al in solution calculated.

Figure 4 shows measured corundum solubility in 0.1 (open circles) and 0.5 m (filled circles) NaCl solutions at 1 kbar (A) and 2 kbar (B) as a function of temperature. The open squares are the extrapolated values in 0.1 m NaCl from Figure 3. Also shown as short dashed lines are values of corundum solubility in pure H₂O reported by Walther (1997). Displayed as long dashed and solid lines are the calculated solubilities at 0.1 and 0.5 m NaCl using the Pokrovskii and Helgeson (1995) and Diakonov et al. (1996) values of K_{Cor} and $K_{\text{NaAl(OH)}_4}$, respectively, together with the parameters outlined above. Note that the Diakonov et al. (1996) values predict a somewhat greater solubility than the Pokrovskii and Helgeson (1986) values. In general, calculations using either set of K_{Cor} and $K_{\text{NaAl(OH)}_4}$ does not give the order of magnitude difference of solubility observed at 1.0 kbar nor the half an order of magnitude of difference at 2.0 kbar between 0.1 m and 0.5 m NaCl solutions.

An attempt was made to fit the corundum solubilities in 0.0, 0.1, and 0.5 m NaCl solutions to obtain new values of K_{Cor} and $K_{\text{NaAl(OH)}_4}$ at a particular pressure and temperature. This was unsuccessful as no K_{Cor} that reproduced corundum solubility in pure H₂O could be combined with a value of $K_{\text{NaAl(OH)}_4}$ to obtain the solubility in both 0.1 and 0.5 m NaCl solutions with any set of values of b_n for the neutral species. Addition of a Al(OH)_2^+ species did not help as the extent of the difference in solubility between 0.1 and 0.5 m NaCl solutions found experimentally

could not be reproduced. This implies another species besides NaAl(OH)_4^0 is required to increase solubilities in NaCl-rich solutions. This could be any additional Al species that also contains Na and/or Cl. The work of Wesolowski (1992) and Palmer

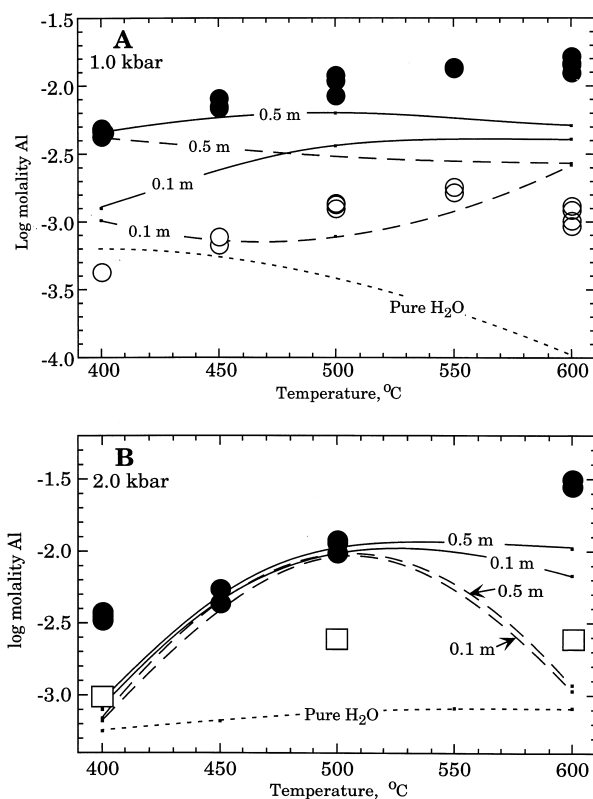


Fig. 4. Base-10 logarithm of Al molality in 0.1 (open circles) and 0.5 (solid circles) molal NaCl solutions in equilibrium with corundum as a function of temperature at (A) 1.0 and (B) 2.0 kbar. The solid lines labeled 0.1 m and 0.5 m are the calculated corundum solubilities in 0.1 and 0.5 m NaCl solutions using the Diakonov, et al. (1996) equilibrium constants in Eqn. 5 and 6. The long dashed lines are the calculated solubilities with the Pokrovskii and Helgeson (1995) equilibrium constants in Eqn. 5 and 6. The short dashed lines give the solubility of corundum in pure H₂O from Walther (1997). The open squares are extrapolated solubilities from this study for 0.1 m NaCl at 2 kbar.

and Wesolowski (1992) indicate Al-Cl complexing does not occur at subcritical conditions. If this is also true in supercritical solutions, then another Cl-absent Al-Na complex must exist in these solutions. The dielectric constant of H₂O at supercritical temperatures and pressures of 2.0 kb and below investigated here is reasonably low. Because of this, another neutral species like Na₂Al(OH)₅⁰ may become stable. Alternatively, because of the significant computed stability of the negatively charged species Al(OH)₄⁻ in equilibrium with corundum in pure H₂O, perhaps a negatively charged Na-Al species becomes stable in the solutions. Such a species could be NaAl(OH)₅⁻. A variety of polynuclear complexes, in alkali chloride solutions at the pressures and temperatures investigated here, have been argued for by Oelkers and Helgeson (1990). Only more investigations in the Al₂O₃-NaCl-H₂O system at supercritical temperatures and pressures will reveal the stoichiometry of the dominate Al species in NaCl-rich solutions at depth in the earth's crust.

5. CONCLUDING REMARKS

The solubility of corundum is significantly higher in 0.5 m NaCl solutions relative to that in pure H₂O. At 2.0 kbar and 600°C, solubility in 0.5 m NaCl is ~3 orders of magnitude greater. Therefore, unlike in pure H₂O, Al will be significantly mobile in 0.5 m NaCl solutions as nearly millimolar concentrations are present at corundum saturation. Interestingly, at 400°C in 0.5 m NaCl, as pressure is decreased from 2.0 to 0.5 kbar, corundum solubility increases somewhat. However, at 600°C, as pressure is decreased from 2.0 to 0.8 kbar, corundum solubility in 0.5 m NaCl decreases.

A distribution of species calculation, which includes the relative stability of the Al species Al(OH)₃⁰, Al(OH)₄⁻ and NaAl(OH)₄⁰ proposed by Pokrovskii and Helgeson (1995), as well as that proposed by Diakonov et al. (1996), indicate that NaAl(OH)₄⁰ is the dominate Al species in the computed near-neutral to slightly alkaline 0.1 and 0.5 m NaCl solutions. However, these calculations failed to reproduce the measured corundum solubilities within the accuracy of the measurements even when activity coefficients of neutral species were allowed to depart from unity. In particular, the increase in solubility between 0.1 and 0.5 m NaCl solutions was underestimated, implying another Al aqueous complex is becoming important.

It is also evident that activity coefficients of neutral species, based on a standard state of unit activity of the aqueous species in a hypothetical 1 molal solution, where activity coefficients are taken as unity at infinite dilution at all pressures and temperatures, are not likely to be unity in 0.1 to 0.5 molal supercritical electrolyte solution. These interactions require a modification of the commonly used extended Debye-Hückel equation for charged species in these solutions.

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