



PII S0016-7037(01)00876-6

Experimental determination and analysis of the solubility of corundum in 0.1-molal CaCl₂ solutions between 400 and 600°C at 0.6 to 2.0 kbar

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(Received May 16, 2001; accepted in revised form November 2, 2001)

Abstract—Corundum (α -Al₂O₃) solubility was measured in 0.1-molal CaCl₂ solutions from 400 to 600°C between 0.6 and 2.0 kbar. The Al molality at 2 kbar increases from 3.1×10^{-4} at 400°C to 12.7×10^{-4} at 600°C. At 1 kbar, the solubility increases from 1.5×10^{-4} m at 400°C to 3.4×10^{-4} m at 600°C. These molalities are somewhat less than corundum solubility in pure H₂O (Walther, 1997) at 400°C but somewhat greater at 600°C. The distribution of species was computed considering the Al species Al(OH)₃⁰ and Al(OH)₄⁻, consistent with the solubility of corundum in pure H₂O of Walther (1997) and association constants reported in the literature. The calculated solubility was greater than that measured except at 600°C and 2.0 kbar, indicating that neutral-charged species interactions are probably important.

A Setchénow model for neutral species resulted in poor fitting of the measured values at 1.0 kbar. This suggests that Al(OH)₃⁰ has a greater stability relative to Al(OH)₄⁻ than given by the models of Pokrovskii and Helgeson (1995) or Diakonov et al. (1996). The significantly lower Al molalities in CaCl₂ relative to those in NaCl solutions at the same concentration confirm the suggestions of Walther (2001) and others that NaAl(OH)₄⁰ rather than an Al-Cl complex must be significant in supercritical NaCl solutions to give the observed increase in corundum solubility with increasing NaCl concentrations. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The previous literature on supercritical corundum solubility was reviewed recently in Walther (2001). It is generally considered that the dominant species in equilibrium with corundum in pure H₂O at supercritical conditions is a neutrally or negatively charged monomer species, which can be written as Al(OH)₃⁰ and Al(OH)₄⁻, respectively. In NaCl aqueous solutions, NaAl(OH)₄⁰ also appears to be important. Corundum solubility in supercritical pure H₂O (Walther, 1997) and in 0.1- and 0.5-*m* NaCl solutions (Walther, 2001) to 600°C and 2 kbar have been reported previously. No definitive work has been reported for Al speciation in supercritical CaCl₂-rich solutions despite the fact that CaCl₂ can be a substantial component in many midcrustal fluids (cf. Crawford and Hollister, 1986). The present investigation builds on the previous work by reporting and analyzing corundum solubilities in 0.1-*m* CaCl₂ from 400 to 600°C between 0.6 and 2.0 kbar.

2. 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.%) α -Al₂O₃ synthetic corundum from Alfa Aesar was used along with reagent-grade 0.1-*m* CaCl₂ solutions. X-ray diffraction analysis of the corundum both before and after the experiments produced no peaks that were not attributed to corundum. In particular, no peak was found near $d = 11.5$ (see Ragnarsdóttir and Walther, 1985). Fines were removed from the corundum before loading in the charge volume by suspending the corundum in the CaCl₂ solution, waiting a minute 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 after 1 min of settling time. This corundum was

loaded along with the 0.1-*m* CaCl₂ solution 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 less than 1.2°C and 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 first sample extraction for 96 h. While the ~ 35 cm³ charge volume remained at the experimental pressure and temperature, approximately 1.6 g of solution was extracted through a fine 316 stainless steel capillary tube to a sample collector assembly. The fluid was withdrawn slowly over a 1/2-min interval to ensure that no boiling occurred in the charge volume near the end of the capillary tube. The extracted sample fluid was flushed from the sample collector volume with a 0.1-mol/L HCl solution to dissolve any Al that may have precipitated in the sample collector volume during decompression and cooling. Blank tests were performed to confirm that no detectable Al was contributed by reaction between the 0.1-mol/L HCl flushing solution and the sample collector volume. Separating the fluid from the corundum before quenching the fluid eliminates back-reaction effects. If needed, new 0.1-*m* CaCl₂ solution was injected into the charge volume through a fine capillary tube to replace the extracted fluid and/or increase the pressure to that desired for the next extraction. The charge volume was allowed to equilibrate at pressure and temperature for at least 48 h between sample extractions. Except for the minor dilution from the small amount of CaCl₂ solution that was injected into the charge volume between samplings, 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 Table 1 give the order in which fluids were extracted. As with H₂O-NaCl, there is likely a significant two-phase region in H₂O-CaCl₂ fluids at supercritical temperatures and low pressures. Judging from parallels with the H₂O-NaCl system (see Fig. 1 in Walther, 2001), the measurements reported here are in the one-phase region.

A direct-current plasma emission spectrometer was used to analyze the Al in the flushing solution with analytical reproducibility of $\pm 5\%$ or better. Experimental reproducibility was determined by repeated

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Table 1. Corundum solubility in 0.1-*m* CaCl₂ at the indicated pressure and temperature.

ID No.	<i>T</i> (°C)	<i>P</i> (bars)	−log <i>m</i> (Al)	ID No.	<i>T</i> (°C)	<i>P</i> (bars)	−log <i>m</i> (Al)
F-1	198	2000	3.580	F-25	600	1378	3.173
F-2	290	2000	3.682	F-26	600	1262	3.254
F-3	329	2000	3.777	F-27	600	1165	3.303
F-4	373	2000	3.849	F-28	600	1075	3.396
F-5	400	2000	3.499	F-29	600	998	3.523
F-6	400	2000	3.614	F-30	600	1002	3.492
F-7	400	2000	3.445	F-31	600	1001	3.397
F-8	425	2000	3.453	F-32	550	1000	3.486
F-9	450	2000	3.356	F-33	550	1002	3.513
F-10	450	2000	3.346	F-34	500	1002	3.460
F-11	475	2000	3.284	F-35	500	1002	3.518
F-12	400	2000	3.450	F-36	500	1001	3.552
F-13	400	2000	3.503	F-37	450	1002	3.619
F-14	500	2100	3.142	F-38	450	992	3.590
F-15	500	2000	3.068	F-39	400	996	3.782
F-16	500	1985	3.071	F-40	400	1003	3.831
F-17	500	2010	3.019	F-41	400	999	3.856
F-18	600	2090	2.882	F-42	400	1502	3.774
F-19	600	2003	2.859	F-43	400	1505	3.772
F-20	600	1992	2.834	F-44	400	1261	3.793
F-21	600	1998	2.896	F-45	400	1052	3.775
F-22	600	1810	3.125	F-46	400	828	3.789
F-23	600	1640	3.061	F-47	400	735	3.739
F-24	600	1500	3.170	F-48	400	625	3.992

Solubility of corundum given as the negative of the base-10 logarithm of molality. The ID number gives the order of sampling.

measurements at the same pressure and temperature. For temperatures and pressures at which three different measurements were made, agreement with the reported concentration varied from 4 to 20%. Grain size and crystal defects did not seem to be important, as results from under- and oversaturation gave similar solubility values. Also, determinations made after the reaction vessel was at elevated pressure and temperature for 6 weeks gave similar results at similar pressures and temperatures as those made earlier.

3. RESULTS

Given in Table 1 are measured molalities of Al in equilibrium with corundum in 0.1-*m* CaCl₂ solutions at the indicated pressures and temperatures. The measured solubilities are plotted in Figure 1 at 1.0 and 2.0 kbar as a function of temperature. Also shown as a solid line in the figure are values for corundum solubility in pure H₂O reported by Walther (1997). For comparison, corundum solubilities in 0.1- and 0.5-*m* NaCl from Walther (2001) are also plotted. Note that corundum solubility in 0.1-*m* CaCl₂ plots significantly below that of 0.1- and 0.5-*m* NaCl solutions, although the temperature dependence at both 1.0 and 2.0 kbar is similar. At both 1.0 and 2.0 kbar relative to corundum solubility in pure H₂O, the solubility in 0.1-*m* CaCl₂ is lower at 400°C but increases with increasing temperature, becoming somewhat greater than pure H₂O solubility as the temperature approaches 600°C.

Figure 2 shows corundum solubility measurements in 0.1-*m* CaCl₂ at 400 and 600°C as a function of pressure. Again, for comparison, solubility in pure H₂O from Walther (1997) and in 0.1-*m* NaCl from Walther (2001) are also shown. Note that the pressure dependence at 400°C is of similar magnitude as that of pure H₂O, but the solubilities are offset by ~0.6 log units. At 600°C, corundum solubility in 0.1-*m* CaCl₂ is ~0.4 log units less than in 0.1-*m* NaCl. Corundum solubility in 0.1-*m* CaCl₂ is

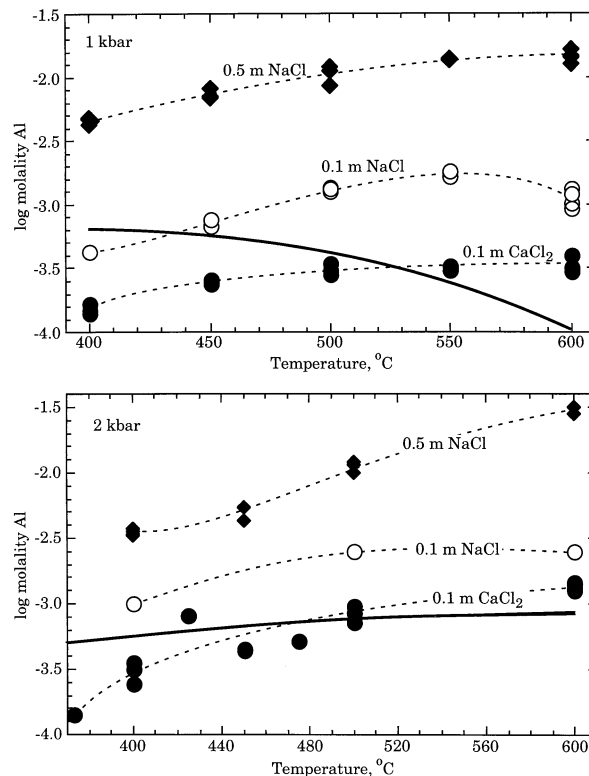


Fig. 1. Base-10 logarithm of Al molality in 0.1-molal CaCl₂ (solid circles) from this study and in 0.1-molal (open circles) and 0.5-molal (solid diamonds) NaCl from Walther (2001) in equilibrium with corundum at 1.0 and 2.0 kbar as a function of temperature. The solid line gives values of corundum solubility in pure H₂O from Walther (1997). The dashed lines give visual fits to the data in the indicated solution.

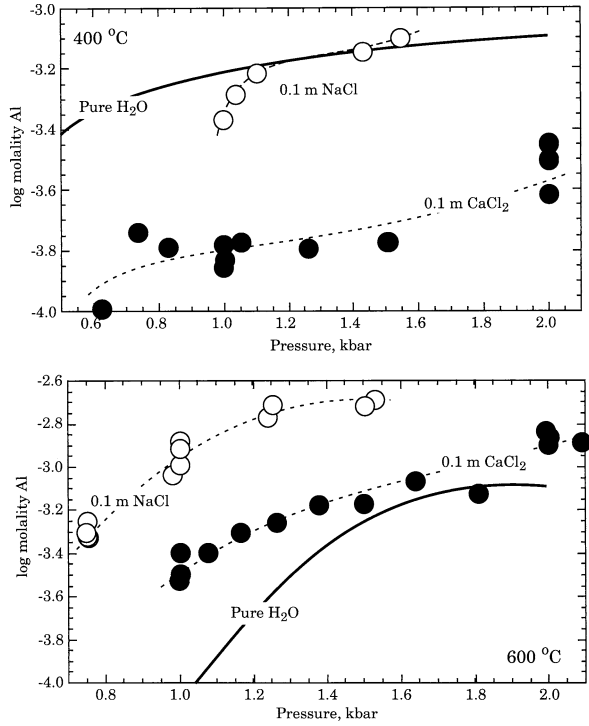


Fig. 2. Base-10 logarithm of Al molality in 0.1-molal CaCl₂ (solid circles) from this study and in 0.1-molal NaCl (open circles) from Walther (2001) in equilibrium with corundum at 400 and 600°C as a function of pressure. The solid lines give values of corundum solubility in pure H₂O from Walther (1997). The dashed lines give visual fits to the data in the indicated solution.

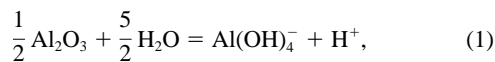
significantly greater than in pure H₂O at 1 kbar, but as pressure increases to 2 kbar, solubilities are nearly equal.

4. DISCUSSION

4.1. Speciation in the Fluid

To understand the extent of interactions involved, a distribution-of-species model for the experimental solutions can be constructed. A standard state for corundum and H₂O of the pure phase at the temperature and pressure of interest was used. Unit activity of the solute in a hypothetical 1 molal solution, for which activity coefficients are taken as unity at infinite dilution at all pressures and temperatures, was used as the standard state for aqueous species. Al(OH)₃⁰ and Al(OH)₄⁻ were considered to be the only significant Al species in the CaCl₂ aqueous solutions.

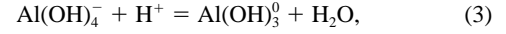
To obtain the constraints for the calculation of the distribution of species, an equilibrium between corundum and Al(OH)₄⁻ can be written as



with an equilibrium constant expression given by

$$K_{\text{Cor}} = \frac{\gamma_{\text{Al(OH)}_4^-} m_{\text{Al(OH)}_4^-} \gamma_{\text{H}^+} m_{\text{H}^+}}{a_{\text{Cor}}^{1/2} a_{\text{H}_2\text{O}}^{5/2}}. \quad (2)$$

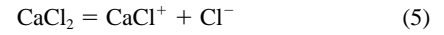
In this equation and those that follow, γ_i , m_i , and a_i stand for the activity coefficient, molality, and activity of the i th sub-scripted species. The relationship between the two Al species in solution can be expressed as



with an equilibrium constant expression of

$$K_{\text{Al}3/4} = \frac{\gamma_{\text{Al(OH)}_3^0} m_{\text{Al(OH)}_3^0} a_{\text{H}_2\text{O}}}{\gamma_{\text{Al(OH)}_4^-} m_{\text{Al(OH)}_4^-} a_{\text{H}^+}}. \quad (4)$$

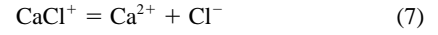
The Ca speciation in solution is assumed to be some combination of CaCl₂, CaCl⁺ and Ca²⁺. The species CaOH⁺ and CaOH₂⁰ were not considered to be important on the basis of the portlandite (Ca(OH)₂) solubility measurements of Walther (1986) and Fein and Walther (1989). The three calcium species considered can be related by the following two reactions and their mass action expressions:



with

$$K_{\text{CaCl}_2} = \frac{\gamma_{\text{CaCl}^+} m_{\text{CaCl}^+} \gamma_{\text{Cl}^-} m_{\text{Cl}^-}}{\gamma_{\text{CaCl}_2} m_{\text{CaCl}_2}} \quad (6)$$

and



with

$$K_{\text{CaCl}^+} = \frac{\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{Cl}^-} m_{\text{Cl}^-}}{\gamma_{\text{CaCl}^+} m_{\text{CaCl}^+}}. \quad (8)$$

The distribution-of-species calculation also used the mass action expression for the disassociation of H₂O of

$$K_{\text{H}_2\text{O}} = \frac{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{OH}^-} m_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \quad (9)$$

and that for HCl disassociation of

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

Charge balance in solution requires that

$$m_{\text{H}^+} + 2m_{\text{Ca}^{2+}} + m_{\text{CaCl}^+} - m_{\text{Cl}^-} - m_{\text{OH}^-} - m_{\text{Al(OH)}_4^-} = 0.0. \quad (11)$$

The total Ca (Ca_T) and total Cl (Cl_T) in solution are constrained by

$$\text{Ca}_T = m_{\text{Ca}^{2+}} + m_{\text{CaCl}^+} + m_{\text{CaCl}_2} \quad (12)$$

and

$$\text{Cl}_T = m_{\text{Cl}^-} + m_{\text{CaCl}^+} + 2m_{\text{CaCl}_2} + m_{\text{HCl}}. \quad (13)$$

Assuming the activities of corundum and H₂O in these solutions are unity, the molalities of the nine aqueous species considered to exist in the 0.1-*m* CaCl₂ solution—Al(OH)₃⁰, Al(OH)₄⁻, H⁺, OH⁻, HCl, Cl⁻, CaCl₂, CaCl⁺, and Ca²⁺—can be related with the nine relationships given in Eqn. 2, 4, 6, and

Table 2. Molality of Al in equilibrium with corundum in pure H₂O and in 0.1-*m* CaCl₂ times 10⁴ and the base-10 logarithm of the molal equilibrium disassociation constants of the indicated species at the indicated pressure and temperature.

<i>P</i> (kbar)	<i>T</i> (°C)	Pure H ₂ O (<i>m</i> _{Al} × 10 ⁴)	0.1- <i>m</i> CaCl ₂ (<i>m</i> _{Al} × 10 ⁴)	log <i>K</i> _{H₂O}	log <i>K</i> _{HCl}	log <i>K</i> _{CaCl₂}	log <i>K</i> _{CaCl⁺}	log <i>K</i> _{Al_{3/4}}	Setchénow <i>b</i> _γ	log <i>K</i> _{Cor}
1.0	400	6.33	1.51	-10.72	-1.8 8	-1.17	-2.92	5.38	8.8	-8.62
2.0	400	5.57	3.06	-9.74	(-1.1)	-0.61	-2.01	5.07	2.4	-8.38
1.0	500	4.05	3.10	-11.86	-4.26	-2.75	-5.33	5.99	(10.65)	-9.40
2.0	500	7.53	8.87	-10.29	-2.64	-1.64	-3.53	5.49	0.6	-8.65
1.0	600	1.07	3.41	-13.51	-6.90	-4.54	-8.10	6.73	12.5	-10.72
2.0	600	8.20	12.73	-10.88	-4.19	-2.67	-5.08	6.03	-1.4	-9.13

Solubility of corundum in molality, *m*_{Al}, in pure H₂O from Walther (1997) and in CaCl₂ from this study. The disassociation constants of the indicated subscripted species of *K*_{H₂O} are from Quist (1970), *K*_{HCl} from Frantz and Marshall (1984), *K*_{CaCl₂} and *K*_{CaCl⁺} from Frantz and Marshall (1982), and *K*_{Al_{3/4}} from Pokrovskii and Helgeson (1995). *K*_{Cor} is calculated from Walther (1997) and Pokrovskii and Helgeson (1995), as given in Walther (2001). Values in parentheses are extrapolated.

8 to 13. *K*_{H₂O} values are taken from Quist (1970), *K*_{HCl} from Frantz and Marshall (1984), and *K*_{CaCl₂} and *K*_{CaCl⁺} from Frantz and Marshall (1982), as given in Table 2. Also given in Table 2 are values of *K*_{Al_{3/4}} determined by Pokrovskii and Helgeson (1995) along with the value of *K*_{Cor} derived from it that reproduced the corundum solubility in pure H₂O given in Walther (1997). This *K*_{Al_{3/4}} was used rather than the lower values of *K*_{Al_{3/4}} determined by Diakonov et al. (1996). Diakonov et al.'s (1996) *K*_{Al_{3/4}} values are based on extrapolation of measurements of Castet et al. (1993) to higher temperatures with the aid of SUPCRT92 (Johnson et al., 1992). Palmer et al. (2001) called into question the results of Castet et al.'s (1993) determinations at their highest temperatures. It should be noted that even Pokrovskii and Helgeson's (1995) values of *K*_{Al_{3/4}} appear too small, at least at 1 kbar (see below).

The activity coefficients of the *i*th charged species, *γ*_{*i*}, can be modeled with an extended Debye-Hückel equation given by

$$\log \gamma_i = \frac{-A_\gamma z_i^2 I^{1/2}}{1 + B_\gamma \tilde{a} I^{1/2}} + b_\gamma I, \quad (14)$$

where *A*_γ and *B*_γ are Debye-Hückel parameters that depend on the density and dielectric constant of H₂O and can be calculated from equations given in Helgeson and Kirkham (1974). *z*_{*i*} stands for the charge of a species, *b*_γ denotes the Debye-Hückel extended-term parameter, and *ā* represents the ion size parameter. For calculations reported in this contribution, all *b*_γ = 0.03 and *ā* = 3.5 Å. *I*, the ionic strength, is computed from

$$I = 0.5 \sum_i m_i z_i^2, \quad (15)$$

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. Initially, no interactions between neutral species or between neutral and charged species were considered, so that neutral species activity coefficients are taken as unity. Using these constraints, a distribution-of-species calculation can be performed and the total Al in solution calculated. Results of these calculations are indicated with dashed lines in Figure 3. Note that the measured solubilities of corundum are significantly lower than the calculated solubilities, except near 2 kbar and 600°C. This implies that the stability of at least one of the aqueous species at infinite dilution must be in error, and/or the interactions between neutral and charged species in solution are

lowering Al species stability. The behavior of corundum solubility in CaCl₂ solutions relative to pure H₂O argues for significant neutral-charged species interactions. At temperatures below ~500°C, adding CaCl₂ to solution decreases solubility. Given the small changes in pH for these solutions and therefore the small change in relative abundance of Al(OH)₄⁻ and Al(OH)₃⁰ (see below), this implies that CaCl₂ is lowering Al species stability.

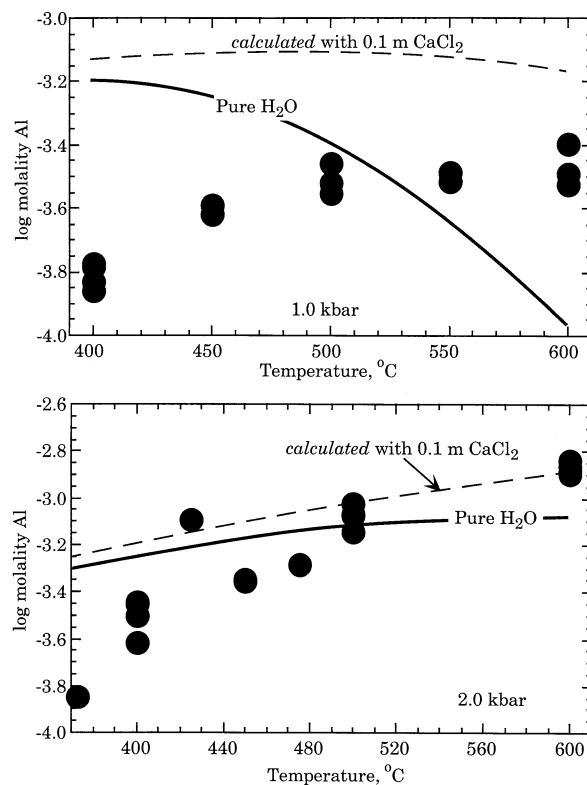


Fig. 3. Base-10 logarithm of Al molality in equilibrium with corundum in 0.1-molal CaCl₂ (solid circles) from this study at 1.0 and 2.0 kbar as a function of temperature. The solid lines give values of corundum solubility in pure H₂O from Walther (1997). The dashed lines give calculated values in 0.1-molal CaCl₂, assuming no interactions between charged and neutral aqueous species (see text).

4.2. Consideration of Charged and Neutral Species Interactions

It has been shown from changes in quartz solubility with changing concentrations of electrolyte in aqueous solutions that charged species affect the stability and therefore the activity coefficients of the neutral SiO₂(aq) species at the pressures and temperatures considered here (Xie and Walther, 1993). These interactions are typically modeled with a Setchénow-type equation. It seems reasonable, therefore, to consider nonunity activity coefficients of neutral species in the CaCl₂ solutions in equilibrium with corundum. A Setchénow equation for neutral species activity coefficients can be written as

$$\log \gamma_n = \mathbf{b}_n I, \quad (16)$$

where γ_n and \mathbf{b}_n denote the activity coefficient and Setchénow constant of the n th neutral species, respectively. As pointed out in Walther (2001), if neutral species activity coefficients are modeled with a Setchénow-type equation, then a term needs to be added to the traditional extended Debye-Hückel equation for the activity coefficient of charged species given in Eqn. 14 to retain Gibbs-Duhem consistency. One, therefore, has

$$\log \gamma_i = \frac{-A_\gamma z_i^2 I^{1/2}}{1 + B_\gamma \tilde{a} I^{1/2}} + b_\gamma I + 0.5 z_i^2 \sum_n \mathbf{b}_n m_n. \quad (17)$$

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.

Values of \mathbf{b}_n for the neutral species CaCl₂, HCl, and Al(OH)₃⁰ can be input into the distribution-of-species calculation by making use of Eqn. 16 and 17 to obtain consistency between calculated and measured Al in solution. For this calculation, \mathbf{b}_n values were considered to be the same for the three neutral species considered. Judging from values of \mathbf{b}_n determined in subcritical H₂O solutions and those calculated for supercritical conditions (Walther, 1997), this assumption is only a first approximation. The \mathbf{b}_n values obtained by matching the reported corundum solubility are given in Table 2. As to be expected, the positive values of \mathbf{b}_n lower the calculated solubility in solution. This procedure, however, failed at temperatures near 500°C when the pressure was 1 kbar. The failure to fit at 500°C and 1.0 kbar stems from the fact that the measured Al in solution is below that calculated for Al(OH)₄⁻ of 4.0×10^{-4} *m* when interactions between charged and neutral species were not considered. Therefore, measured Al in solution can not be fit by lowering the stability of the species Al(OH)₃⁰ with a large positive \mathbf{b}_n . This implies that $K_{\text{Al3/4}}$ must be greater than the value calculated from the equations of Pokrovskii and Helgeson (1995) to decrease the stability of Al(OH)₄⁻ relative to Al(OH)₃⁰. The calculated Al species distribution and pH are tabulated in Table 3. Because no values of \mathbf{b}_n can be used to decrease the solubility of corundum to the measured values, the values calculated at 500°C and 1 kbar are only approximate. It is clear that these solutions have significant concentrations of both Al(OH)₄⁻ and Al(OH)₃⁰ when using Pokrovskii and Helgeson's (1995) $K_{\text{Al3/4}}$. Note that the solutions are calculated to be slightly acidic to slightly alkaline, as the pH is within ~1 pH unit of neutral.

The last term in Eqn. 17 can be significant in the calcula-

Table 3. Calculated molality of Al species and pH in 0.1-*m* CaCl₂ using the parameters in Table 2.

<i>P</i> (kbar)	<i>T</i> (°C)	Al(OH) ₄ ⁻ (<i>m</i> _{Al} × 10 ⁴)	Al(OH) ₃ ⁰ (<i>m</i> _{Al} × 10 ⁴)	pH
1.0	400	1.06	0.45	4.3
2.0	400	1.29	1.72	4.2
1.0	500	(1.9)	(3.3)	(6.0)
2.0	500	2.43	6.47	4.8
1.0	600	2.40	1.01	7.6
2.0	600	5.24	8.53	5.6

Values in parentheses have greater uncertainty.

tions. For instance, at 600°C and 1.0 kbar, a value of $\mathbf{b}_n = 12.5$ was needed to fit the measured Al concentration in solution. Using this value of \mathbf{b}_n , the value of γ of single-charged aqueous species in solution is calculated to be 2.8 rather a value near 0.6 if $\mathbf{b}_n = 0.0$. γ_n for this solution is calculated to be 0.0009. This occurs because the computed ionic strength of the solutions at 600°C and 1.0 kbar is only 1.6×10^{-5} . These large effects due to \mathbf{b}_n are needed to fit the solubility unless the value of $K_{\text{Al3/4}}$ is increased. Only further investigations will determine the relative significance of interactions of charged and uncharged species as opposed to errors in reported standard state properties of aqueous species that determine $K_{\text{Al3/4}}$.

5. CONCLUDING REMARKS

Examination of Figures 1 to 3 indicates that corundum is significantly less soluble in pure H₂O and 0.1-*m* CaCl₂ than in 0.1-*m* NaCl. This implies that a Na-Al species such as NaAl(OH)₄⁰ must be stable, increasing the solubility, while a Al-Cl species does not have a significant stability. Because solutions in pelitic rocks in the earth's crust are in contact with alkali-rich aluminosilicates, they tend to react to maintain their pH near neutral. It would, therefore, appear that the difference in Al concentration in solution implied by textural arguments for Al immobility as opposed to those that precipitate veins that contain Al-silicates could be due to differences in the concentration of alkalis such as Na in solution rather than in changes in pH.

Corundum solubility in CaCl₂ is less than in pure H₂O at temperatures below ~500°C but greater above 500°C. Therefore, this electrolyte changes from "salting out" of corundum to "salting in" near 500°C at both 1.0 and 2.0 kbar. This can be compared to quartz, which changes from "salting out" to "salting in" in NaCl solutions at ~400°C at 1.0 kbar (Xie and Walther, 1993). According to Debye-Hückel theory, if the dominant Al species were charged, the added electrolyte should increase corundum stability somewhat (see Fig. 8 in Palmer et al., 2001). The lower measured solubility in CaCl₂ solutions implies that the neutral Al species predominates in these solutions. Therefore, the values of the equilibrium constant of reaction (Eqn. 3), $K_{\text{Al3/4}}$, between Al(OH)₃⁰ and Al(OH)₄⁻ proposed in the literature must be modified to increase the stability of Al(OH)₃⁰. At 600°C and 1.0 kbar, using the relative stability of Al(OH)₃⁰ and Al(OH)₄⁻ proposed by Pokrovskii and Helgeson (1995), the calculated ratio of the molality of Al(OH)₃⁰/Al(OH)₄⁻ = 0.18, and the calculated solubilities are too large if no interactions between neutral and charged species are con-

sidered. If Setchénow coefficients are used to obtain consistency between measured and calculated solubilities, the ratio becomes 0.42. Under these conditions, the activity coefficients of single-charged aqueous species are calculated to be 3.5.

On the basis of a standard state of unit activity of the aqueous species in a hypothetical 1-molal solution for which activity coefficients are taken as one at infinite dilution at all pressures and temperatures, assuming that activity coefficients are unity for neutral species in supercritical electrolyte solutions will lead to significant errors in species distribution calculations. Judging from measured corundum solubility reported here, as well as those reported for quartz (e.g., Xie and Walther, 1993) in electrolyte solutions, it seems clear that activity coefficients of neutral species should not be considered as unity. The interactions present require a Setchénow-type model for neutral species and significant modification of the commonly used extended Debye-Hückel equation for charged species in these solutions.

Acknowledgments—I would like to thank A. Zotov, K. Shmulovich, K. V. Ragnarsdóttir, and an anonymous reviewer for their helpful comments on an earlier version. This work was supported by National Science Foundation grant EAR-9802100.

Associate editor: K. Ragnarsdóttir

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