



## Corundum solubility and aluminum speciation in KOH aqueous solutions at 400°C from 0.5 to 2.0 kbar

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(Received May 24, 1995; accepted in revised form July 31, 1996)

**Abstract**—Corundum solubility has been measured in KOH aqueous solutions under supercritical conditions (400°C, from 0.5 to 2 kbar). The investigated concentration range ( $0.001 < m_{\text{KOH}} < 0.1 \text{ mol/kg H}_2\text{O}$ ) allowed to vary the species balance between diluted solutions dominated by aluminate ion,  $\text{Al}(\text{OH})_4^-$ , and more concentrated ones in which association of aluminate ion with  $\text{K}^+$  ion is appreciable. The dissociation constant of the complex  $\text{KAl}(\text{OH})_4^0$  and the equilibrium constant for hydrolysis of corundum have been simultaneously fitted to the measured solubilities through a speciation calculation.

The corundum hydrolysis ( $\frac{1}{2} \text{Al}_2\text{O}_3 + \frac{5}{2} \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$ ) equilibrium constant is in close agreement with the values calculated from thermodynamical data for corundum (Berman, 1988) and aqueous species (Johnson et al., 1992). Using the Density Model (Anderson et al., 1991) for extrapolating thermodynamical properties of aqueous species results in appreciably higher values for this equilibrium constant, not consistent with experimental data, due to the inadequacy of the Density Model for extrapolating water properties in the supercritical  $P$ - $T$  range.

For the  $\text{KAl}(\text{OH})_4^0$  dissociation reaction, the following values of  $\log K$ :  $-1.94 \pm 0.17$ ,  $-1.73 \pm 0.14$ , and  $-1.56 \pm 0.11$ , are obtained at 0.5, 1.0, and 2.0 kbar, respectively. These constants correspond to equal contributions of the aluminate ion and of the  $\text{KAl}(\text{OH})_4^0$  complex to the total dissolved Al in 0.1 m KOH solutions. At 600 and 700°C, 2 kbar, the same equilibrium constants calculated from literature experimental corundum solubilities are  $-2.43$  and  $-3.16$ , respectively.

From the calculated aluminate ion concentration in the system  $\text{Al}_2\text{O}_3$ - $\text{H}_2\text{O}$  and the literature values of corundum solubility in water, the neutral hydroxyde  $\text{Al}(\text{OH})_3$  is inferred to be probably the dominant Al aqueous species in the neutral pH range in this system.

### 1. INTRODUCTION

Understanding the mass transfer processes in geochemical systems requires the knowledge of the aqueous solubilities of minerals, including the Gibbs Free Energies of aqueous species at all pressures and temperatures of interest. Modeling of reaction paths describing fluid-rock interaction in a geochemical system relies critically on an accurate accounting of aqueous species. However, the thermodynamical data necessary for such calculations are often inadequate especially for aluminum above 25°C. For solid aluminum oxides and hydroxides the different thermodynamic compilations available (Helgeson et al., 1978; Robie et al., 1978; Berman, 1988; Apps et al., 1989) are in disagreement. At 25°C, the discrepancy is nearly an order of magnitude between various sources (May et al., 1979; Couturier et al., 1984; Palmer and Wesolowski, 1992; Hemingway et al., 1978; Helgeson et al., 1978) for the equilibrium constant of the following reaction:



The aluminum concentration for  $\text{Al}_2\text{O}_3$  solubility is very small at neutral pH even under supercritical conditions (Becker et al., 1983; Ragnarsdottir and Walther, 1985), and is too small to account for the observed relative mobility

of aluminum in geochemical systems at hydrothermal and supercritical conditions (Pascal, 1979; Moine et al., 1989). Although aluminum concentration is high at extreme conditions of pH (acidic and basic pH), the pH is often buffered in natural systems near neutrality. In natural geochemical systems, aqueous solutions are often dominated by electrolytes (e.g., NaCl, KCl, and HCl) which can be a source of ligands to form stable aluminum aqueous complexes. As proposed by many authors, aluminum transport at low temperatures is likely to involve aluminum-inorganic and organic aqueous complexes (Roberson and Hem, 1969; Pearson, 1969; Sillén and Martell, 1971; Sanjuan and Michard, 1987; Bourcier et al., 1987). At high temperature, experimental studies (Anderson and Burnham, 1967, 1983; Woodland and Walther, 1987; Pascal and Anderson, 1989; Castet et al., 1992; Diakonov et al., 1996) argue for alkali-alumina complexing at significant amounts to explain high concentrations of aluminum in solution (Pokrovskii and Helgeson, 1992, 1994, 1995). Other studies at low temperatures suggest the formation of chloride-aluminum complexes (Peryea and Kittrick, 1988; Hemingway et al., 1991). In contrast, at low temperature conditions ( $< 100^\circ\text{C}$ ), Wesolowski (1992) ruled out the possibility of chloride- $\text{Al}(\text{OH})_4^-$  complexing in significant amount and Palmer and Wesolowski (1992) ruled out  $\text{Al}^{3+}$ - $\text{Cl}^-$  interaction by a precise treatment of activity coefficients of ionic species using the specific ionic interaction approach (Pitzer, 1973). At high temperature, chloro-aluminum complexes have been called upon to ex-

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plain observed corundum (Korzhinskiy, 1987) and  $\text{Al}_2\text{SiO}_5$  polymorphs (Ostapenko et al., 1987) solubilities in HCl solutions. In the feldspar- $\text{H}_2\text{O}$  system (Davis, 1972) and three-aluminosilicate phases assemblages (such as feldspar-mica-quartz)- $\text{H}_2\text{O}$  systems (Anderson et al., 1987; Woodland and Walther, 1987; Pascal and Anderson, 1989; Walther and Woodland, 1993), high-temperature aluminum concentrations have been interpreted either by the aluminate ion (Walther and Woodland, 1993; Anderson, 1995) or by aluminum complexing with alkalis (Woodland and Walther, 1987) or alkalis and silica (Anderson and Burnham, 1983; Anderson et al., 1987; Pascal and Anderson, 1989).

These disagreements in interpretations of the experimental aluminum concentration are partly due to uncertainties in extrapolated thermodynamic equilibrium constants. With recent improvement (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992) of the electrostatic HKF model (Helgeson et al., 1981), measured aluminum concentrations over a wide temperature range can be reappraised as a whole. At lower temperatures ( $\leq 350^\circ\text{C}$ ), many experimental data are available (Kittrick, 1966; May et al., 1979; Couturier et al., 1984; Sanjuan and Michard, 1987; Bourcier et al., 1987; Peryea and Kittrick, 1988; Apps et al., 1989; Verdes, 1990; Palmer and Wesolowski, 1992, 1993; Wesolowski, 1992; Castet et al., 1993; Bourcier et al., 1993; Wesolowski and Palmer, 1994). As shown by the studies of Bloom and Weaver (1982), the problem of solid surface processes and buffer agents on the solubility measurement is perhaps the main origin of the inconsistencies between these data. The experiments by May et al. (1979) on the equilibrium between gibbsite crystals and oversaturated aqueous solutions of aluminum show a shift in the solubility curve at a pH of about 7 at  $25^\circ\text{C}$ . Sanjuan and Michard (1987, 1990) observed the same shift at the same pH at  $50^\circ\text{C}$  and concluded that aluminum concentration in high pH solutions is controlled by bayerite which supports the results from Verdes and Gout (1987). A complete experimental and modelling review of the gibbsite solubilities at  $50^\circ\text{C}$  in 0.1 m NaCl solutions with various pH buffers (acetate, bistris, and tris) has demonstrated that the discrepancy is mainly due to the organic buffer agents (Wesolowski and Palmer, 1994). This study permitted to establish an aluminum speciation model with an uncertainty of 0.2 log unit.

To avoid the problem of amorphous and/or microcrystalline phases encountered in experiments at low temperatures and also known in the case of silica polymorphs (Azaroual et al., 1996), we have investigated the solubility of corundum, at conditions close to diaspore-corundum equilibrium ( $400^\circ\text{C}$  and 0.5 to 2.0 kbar) in order to allow a simultaneous interpretation of both low-temperature and high-temperature experimental data. This work is focused on the speciation in neutral to alkaline pH conditions, where the most likely species are  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_4^-$ , along with a possible alkali-aluminate complex.

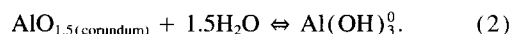
## 2. PREVIOUS STUDIES

Measurements of corundum solubility under supercritical conditions were performed by many authors (Morey, 1957;

Barns et al., 1963; Anderson and Burnham, 1967; Burnham et al., 1973; Ganeyev and Rummyantsev, 1974; Becker et al., 1983; Ragnarsdottir and Walther, 1985; Anderson et al., 1987; Pascal and Anderson, 1989). Detailed compilations of these experimental data, carried out by Pokrovskii and Helgeson (1991, 1995), show that aluminum concentration in pure water is very low under all temperature and pressure conditions while the respective contributions of  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_4^-$  are still under debate (Woodland and Walther, 1987; Walther and Woodland, 1993; Anderson, 1995). The solubility increases at increasing pH due to the effect of  $\text{OH}^-$  ions on  $\text{Al}(\text{OH})_4^-$  concentration.

### 2.1. Speciation in the System $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$

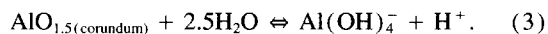
In pure water, the solubility of corundum has been measured by Becker et al. (1983) and Ragnarsdottir and Walther (1985) and interpreted by the authors as due to the neutral species,  $\text{Al}(\text{OH})_3^0$ . As in Anderson et al. (1987), the contribution of other aluminum species was neglected and only the following equilibrium reaction was considered:



On the other hand, Castet et al. (1993) showed that corundum solubility in pure water can be accounted for by only aluminate ion alone, using their thermodynamical constants and extrapolations at high temperatures with the Density Model (Anderson et al., 1991). These contrasting interpretations suggest that corundum solubility in pure water by itself is not sufficient to allow an accurate characterization of either  $\text{Al}(\text{OH})_4^-$  or  $\text{Al}(\text{OH})_3^0$  aqueous species.

### 2.2. Aluminum Speciation in Alkali Hydroxide Solutions

In alkaline solutions ( $\text{NaOH-}$  or  $\text{KOH-H}_2\text{O}$ ), the relatively high corundum solubility (Barns et al., 1963; Anderson and Burnham, 1967, 1983; Anderson et al., 1987; Pascal and Anderson, 1989) is interpreted by the authors as due to  $(\text{K,Na})\text{Al}(\text{OH})_4^0$  neutral complexes. However, in a recent reappraisal of these and other data on Al-silicates, Anderson (1995) selected a set of thermodynamic constants (Castet et al., 1993), extrapolated using the Density Model, which provides a self-consistent interpretation of the experimental data by the aluminate ion alone through reaction 3:



The contrast between the different interpretations of the same data, for both pure water and alkaline solutions, originates partly in the lack of precision of the values of free energies of formation obtained from the equations of state (where the uncertainty can be up to 6 kJ/mol for aqueous species, Shock and Helgeson, 1988). Furthermore, available experimental corundum solubilities in alkaline supercritical fluids (Barns et al., 1963; Anderson et al., 1987; Pascal and Anderson, 1989) are not suitable to interpret the interactions between alkali and aluminate ion because the solutions are too concentrated ( $>0.1$  mol/kg  $\text{H}_2\text{O}$ ) which has the following consequences: (1) the calculation of aqueous spe-

Table 1. Solubility of corundum in KOH solutions at 400°C. Speciation and activity coefficients are given in Appendices.

Sample N°	$m_{\text{KOH}}$ (mol/kg H <sub>2</sub> O)	$m_{\text{Al,anal}}$ (mol/kg H <sub>2</sub> O) weight-loss	$m_{\text{Al,anal}}$ (mol/kg H <sub>2</sub> O) ICP	$m_{\text{Al}}/m_{\text{K}}$ (mol. ratio)	Time (days)
P = 0.5 kbar					
C13A	0.001	(7.063±0.400)E-4		0.706	6
C17C	0.004	(2.718±0.080)E-3		0.679	7
C09A	0.008	(5.682±0.040)E-3		0.710	8
C14A	0.01	(6.906±0.070)E-3		0.691	6
C15C	0.04	(2.614±0.008)E-2		0.653	5
C15B	0.08	(5.602±0.010)E-2	5.84 E-2	0.700	5
C17A	0.1	(7.078±0.010)E-2	7.01 E-2	0.708	5
				$\bar{x} = 0.692$	
				$\sigma = 0.019$	
P = 1 kbar					
C10A	0.001	(7.018±0.250)E-4		0.702	6
C10B	0.004	(2.673±0.032)E-3		0.668	6
C11A	0.008	(5.314±0.037)E-3		0.664	6
C11B	0.01	(6.762±0.040)E-3	6.09 E-3	0.676	6
2C01B*	0.0101	(7.245±0.040)E-3		0.717	4
C16B	0.04	(2.704±0.008)E-2		0.676	6
C16A	0.08	(5.567±0.017)E-2	5.58 E-2	0.696	6
C17C	0.1	(7.080±0.170)E-2	6.82 E-2	0.708	6
				$\bar{x} = 0.688$	
				$\sigma = 0.019$	
P = 2 kbar					
C12A	0.001	(6.444±0.400)E-4		0.644	7
C18A	0.004	(2.805±0.100)E-3		0.701	7
C06A**	0.004	(2.689±0.100)E-3		0.672	3
C18B	0.008	(5.373±0.080)E-3		0.672	6
C17B	0.01	(6.443±0.080)E-3		0.644	6
C02B	0.0101	(7.141±0.080)E-3		0.707	3
C14C	0.04	(2.774±0.014)E-2		0.693	6
C15A	0.08	(5.656±0.010)E-2	5.44 E-2	0.707	6
C12C	0.1	(6.867±0.010)E-2	7.02 E-2	0.687	6
				$\bar{x} = 0.681$	
				$\sigma = 0.023$	

The pressure of samples with \* and \*\* are 1.1 and 2.1 kbar, respectively.

cies activity coefficients is not precise, and (2) if alkali-aluminate association actually takes place, the neutral species  $(\text{Na,K})\text{Al}(\text{OH})_4^0$  is likely to predominate over  $\text{Al}(\text{OH})_4^-$ , thus preventing any precise determination of the contribution of  $\text{Al}(\text{OH})_4^-$  ions to the measured solubility. Both difficulties have been avoided in the present study by using dilute KOH solutions (0.001–0.1 mol/kg H<sub>2</sub>O) for measuring the corundum solubility at 400°C and 0.5–2.0 kbar, in order to characterise precisely the aluminate ion and the possible complexation between  $\text{K}^+$  and  $\text{Al}(\text{OH})_4^-$ . These near critical experimental conditions are adequate to observe aqueous complexation because the lowered dielectric constant of water favours ion association, as predicted by the electrostatic approach (Fuoss and Kraus, 1933).

### 3. EXPERIMENTAL DATA

Natural corundum crystals from 4–40 mg were rinsed in dilute HCl, weighed on a Sartorius M500P balance (precision 2 µg), then sealed in gold capsules along with aliquots of freshly prepared KOH solution (0.5 to 2 mL). The capsules were brought to temperature and pressure in an internally heated pressure vessel fitted with a low-temperature-gradient furnace quoted in Roux and Lefèvre (1992) and described in detail in Roux et al. (1994). The temperature was measured by three thermocouples spaced about 2 cm apart. All experiments were performed at  $400 \pm 5^\circ\text{C}$  and under pressures of 0.5, 1.0, and  $2.0 \pm 0.05$  kbar, measured by means of a strain gauge calibrated against a Heise gauge. The run durations were 3 to 7 days (Table 1). After each run, the corundum solubility was

measured by the classical weight-loss method (Anderson and Burnham, 1965, 1967; Pascal, 1984). The uncertainty does not exceed 5% for solubilities in the most diluted solutions, and 0.5% for the more concentrated ones (Table 1). In order to check the weight-loss measurements, the more concentrated solutions were diluted in a 0.5 M HCl solution and analyzed by ICP (Table 1). Although less precise, the ICP results are consistent with the weight-loss ones.

The results at all three pressures, shown in Fig. 1, can be accounted for by a linear fit with a value of  $0.69 \pm 0.02$  for the ratio  $m_{\text{Al}}/m_{\text{K}}$  (Table 1). As noted by Pascal and Anderson (1989) at higher temperatures, the ratio  $m_{\text{Al}}/m_{\text{K}}$  (Fig. 2) is smaller than 1.0 at all investigated pressures and independent of KOH concentration and of pressure between 0.5 and 2.0 kbar. The value 0.69 for the ratio  $m_{\text{Al}}/m_{\text{K}}$  is consistent with the positive correlation of this ratio with

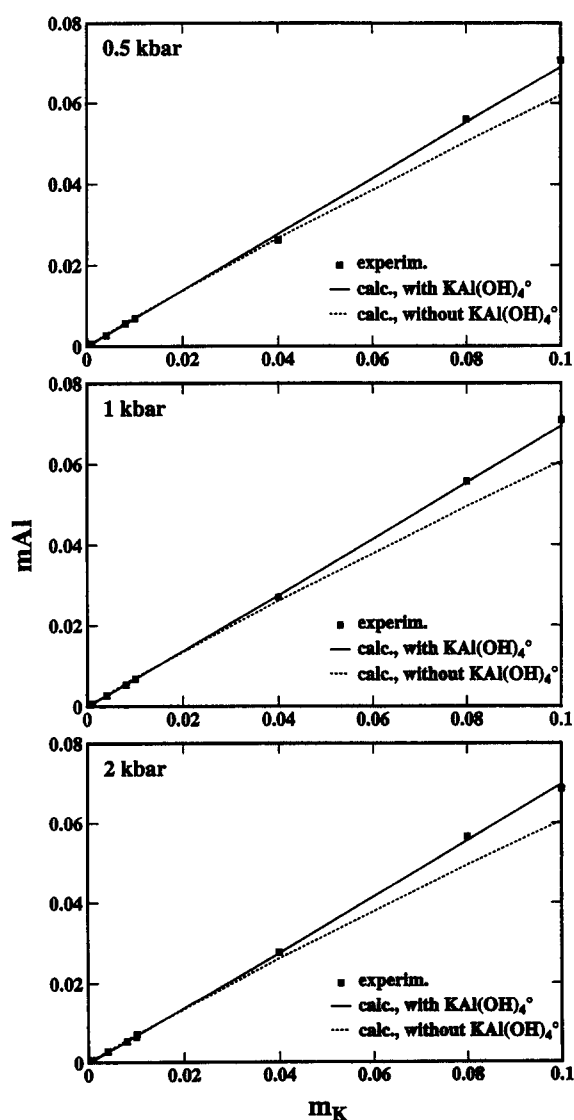


FIG. 1. Corundum solubility ( $m_{\text{Al}}$ , mol/kg H<sub>2</sub>O) vs. starting KOH molality of the solution ( $m_{\text{K}}$ ), at 400°C and 0.5, 1.0, and 2.0 kbar. Full squares represent measured values, solid lines represent  $\text{Al}(\text{OH})_4^- + \text{KAl}(\text{OH})_4^0$  concentrations calculated from the values of equilibrium constants  $K_3$  and  $K_6$  determined in this study (Table 2, columns (a)), and dotted lines represent  $\text{Al}(\text{OH})_4^-$  concentrations calculated assuming all dissolved Al is  $\text{Al}(\text{OH})_4^-$ , with equilibrium constant  $K_3$  from Table 2, columns (b).

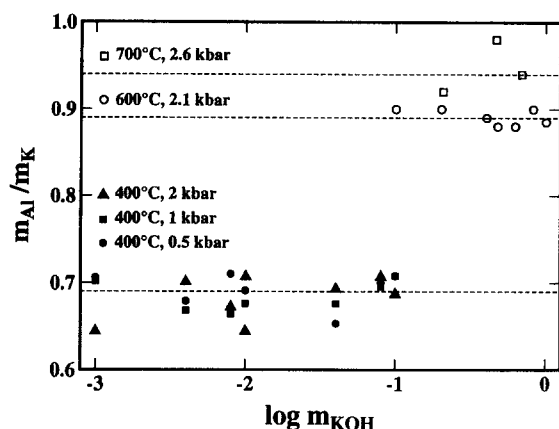


FIG. 2. Ratio  $m_{\text{Al}}/m_{\text{K}}$  vs.  $m_{\text{K}}$  in aqueous KOH solutions at equilibrium with corundum at different temperatures and pressures. Data from Pascal and Anderson (1989) (600° and 700°C), and from this study (400°C).

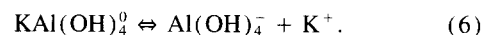
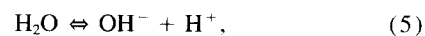
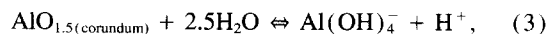
temperature, as observed from the results of Barns et al. (1963) and Pascal and Anderson (1989). The reported values are 0.72, 0.89, and 0.94 at 430, 600, and 700°C, respectively. The independence of solubility on pressure had also been observed by Barns et al. (1963) in NaOH solutions, at 430°C, from 1.45 to 3 kbar.

#### 4. INTERPRETATION

The linear relationship between Al and KOH molalities could be a response of  $\text{Al}(\text{OH})_4^-$  to pH according to reaction 3 if KOH were completely dissociated and if  $\gamma_{\text{Al}(\text{OH})_4^-} = \gamma_{\text{OH}^-}$ . However, Fig. 3 shows that in our experimental conditions, KOH is not completely dissociated and the percentage of association increases with decreasing pressure. Increasing KOH concentration should result in decreasing  $m_{\text{Al}}/m_{\text{K}}$  ratios, whereas the measured ratio does not show any dependence on concentration (Fig. 2), suggesting the presence of another Al-species such as produced by a partial association between  $\text{Al}(\text{OH})_4^-$  and  $\text{K}^+$  similar to the association between  $\text{OH}^-$  and  $\text{K}^+$ . The existence of a more charged ion such as  $\text{Al}(\text{OH})_5^{2-}$ , similar to  $\text{H}_2\text{SiO}_4^{2-}$  known at 25°C in high pH solutions (Seward, 1974), is unlikely because aqueous aluminium is tetracoordinated in basic solutions (Lippincott et al., 1952; Moolenaar et al., 1970). In order to check that  $\text{Al}(\text{OH})_4^-$ - $\text{K}^+$  association has a detectable influence on the ratio  $m_{\text{Al}}/m_{\text{K}}$  in the concentration range of the experimental data, two interpretations of the data are proposed, the first one assuming that K-Al complexing may exist, and the second one considering  $\text{Al}(\text{OH})_4^-$  as the only important Al-bearing species. The neutral hydroxyde  $\text{Al}(\text{OH})_3^0$  is not considered in these calculations, because its concentration, independent of pH, is smaller than or equal to the solubility of corundum in pure water,  $10^{-4}$  m at 400°C, 2 kbar (Ragnarsdottir and Walther, 1985), an order of magnitude below the Al concentrations measured in this study.

##### 4.1. Data Interpretation Assuming the Presence of Both $\text{Al}(\text{OH})_4^-$ and $\text{KAl}(\text{OH})_4^0$

The six aqueous species  $\text{Al}(\text{OH})_4^-$ ,  $\text{KAl}(\text{OH})_4^0$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ , and  $\text{KOH}^0$  are considered, and the solubility of corundum is controlled by the following equilibria:



At lower KOH concentrations (0.001 mol/kg  $\text{H}_2\text{O}$ ),  $\text{Al}(\text{OH})_4^-$  is likely to predominate because the concentrations are low enough to avoid association between  $\text{K}^+$  and  $\text{Al}(\text{OH})_4^-$ , and the pH is higher than the neutral values where the species  $\text{Al}(\text{OH})_3^0$  could contribute significantly to aluminium concentration. At higher KOH concentrations, high  $\text{K}^+$  activity should result in a larger association with  $\text{Al}(\text{OH})_4^-$  and a predominance of the complex  $\text{KAl}(\text{OH})_4^0$ . The expected contrast in speciation between low- and high-KOH concentration experiments permits determination of the equilibrium constants  $K_3$  and  $K_6$ , related to  $\text{Al}(\text{OH})_4^-$  and  $\text{KAl}(\text{OH})_4^0$ , respectively.

##### 4.1.1. Speciation calculation

Aluminum molalities are calculated by solving simultaneously appropriate mass and charge balance and mass action expressions. Equations of mass action of reactions 3–6 can be written as

$$K_3 = \frac{m_{\text{Al}(\text{OH})_4^-} \gamma_{\text{Al}(\text{OH})_4^-} m_{\text{H}^+} \gamma_{\text{H}^+}}{a_{\text{AlO}_{1.5}} (a_{\text{H}_2\text{O}})^{2.5}}, \quad (7)$$

$$K_4 = \frac{m_{\text{K}^+} \gamma_{\text{K}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-}}{m_{\text{KOH}^0} \gamma_{\text{KOH}^0}}, \quad (8)$$

$$K_5 = \frac{m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}, \quad (9)$$

$$K_6 = \frac{m_{\text{K}^+} \gamma_{\text{K}^+} m_{\text{Al}(\text{OH})_4^-} \gamma_{\text{Al}(\text{OH})_4^-}}{m_{\text{KAl}(\text{OH})_4^0} \gamma_{\text{KAl}(\text{OH})_4^0}}, \quad (10)$$

where  $K_r$  represents the equilibrium constant for the subscripted reaction  $r$ , and  $m_i$  and  $\gamma_i$  represent molality and activity coefficient for the subscripted aqueous species, respectively. Charge and mass balance equations are

$$m_{\text{K}^+} + m_{\text{H}^+} = m_{\text{OH}^-} + m_{\text{Al}(\text{OH})_4^-}, \quad (11)$$

$$m_{\text{Al, total}} = m_{\text{Al}(\text{OH})_4^-} + m_{\text{KAl}(\text{OH})_4^0}, \quad (12)$$

$$m_{\text{K, total}} = m_{\text{K}^+} + m_{\text{KOH}^0} + m_{\text{KAl}(\text{OH})_4^0}. \quad (13)$$

The values of  $K_3$  and  $K_6$  are obtained by a least-square refinement of the weighed Al molalities, i.e., by minimizing the function  $M = \sum \frac{(m_{\text{Al}}^{\text{measured}} - m_{\text{Al}}^{\text{calculated}})^2}{\sigma^2}$ , where  $\sigma^2 = \sigma_a^2 + \sigma_1^2 + \sigma_2^2$ . The symbol  $\sigma_a^2$  is the squared standard deviation of the weight loss determinations (Table 1), and  $\sigma_1$  and  $\sigma_2$ , assumed independent, are the squared standard deviations of the dissociation constants of  $\text{H}_2\text{O}$  and KOH, respectively,  $K_1$  and  $K_2$ , due to temperature fluctuations within and between experiments, taken as  $\pm 5^\circ\text{C}$  (pressure variations do not contribute significantly).

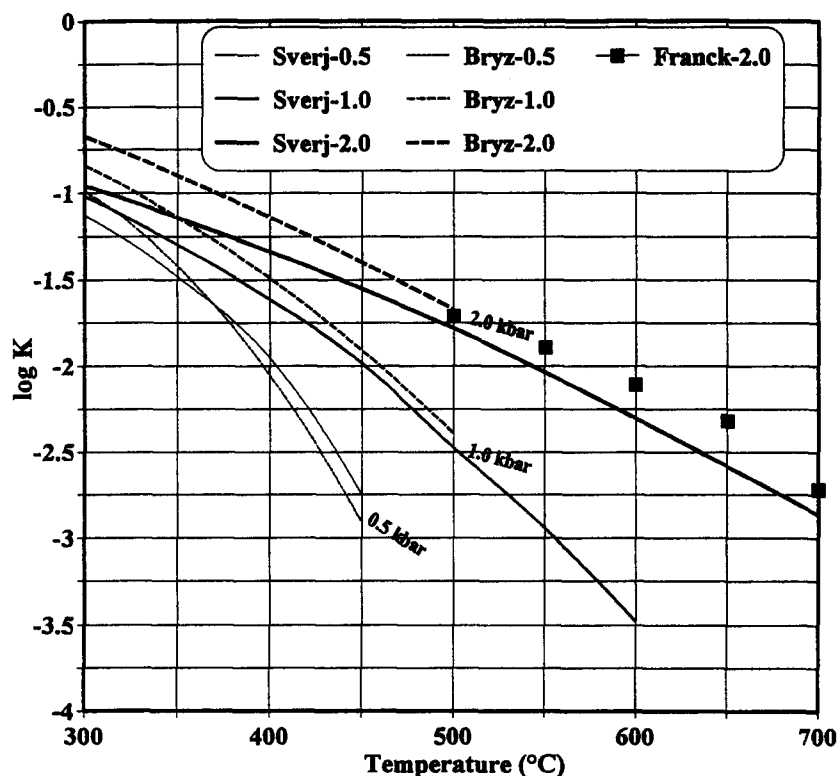


FIG. 3. Log  $K$  of the  $\text{KOH}^0$  association reaction vs. temperature at 0.5, 1.0, and 2.0 kbars. Solid curves are calculated using SUPCRT92 equations and parameters from Sverjensky et al. (1991). Dashed curves (a), (b), and (c) represent theoretical values as extrapolated by Bryzgalin (1986). The symbols correspond to the measurements of Franck (1956).

#### 4.1.2. Activity coefficients

Activity coefficients for aqueous species have been calculated using the extended Debye-Hückel equation with parameters given by Helgeson et al. (1981) combined with  $\text{H}_2\text{O}$  solvent functions in their revised forms (Tanger and Helgeson, 1988; Shock et al., 1992). Molal activity coefficients for neutral aqueous species subscripted (0) are taken to be unity in our experimental conditions where ionic strengths are small ( $[\text{KOH}] \leq 0.1$  molal), in accordance with experimental determinations of uncharged aqueous silica activity coefficients in NaCl solutions at 400°C (Xie and Walther, 1993); individual molal activity coefficients for ionic aqueous species are calculated using the HKF equation (Helgeson et al., 1981):

$$\log \gamma_i = \frac{-A_\gamma Z_i^2 \bar{I}^{1/2}}{1 + \bar{a} B_\gamma \bar{I}^{1/2}} - \log(1 + 0.018053 m^*) + [\omega_i^{\text{abs}} b_{\text{NaCl}} + b_{\text{Na}^+ \text{Cl}^-} - 0.19(|Z_i| - 1)] \bar{I}, \quad (14)$$

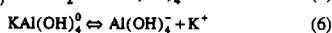
where  $A_\gamma$  and  $B_\gamma$  are Debye-Hückel solvent parameters which are evaluated from Shock et al. (1992) data;  $Z_i$  is the charge of species  $i$ ;  $\bar{I}$  stands for the true ionic strength of the solution in molality units of concentration. The term  $m^*$  is the sum of the molalities of all aqueous species in solution. The symbol  $\omega_i^{\text{abs}}$  is the pressure and temperature dependent absolute Born coefficient for the  $i^{\text{th}}$  aqueous species;  $b_{\text{NaCl}}$  is

a pressure and temperature dependent solvation parameter; and  $b_{\text{Na}^+ \text{Cl}^-}$  is a temperature and pressure dependent short-range interaction parameter for aqueous NaCl solutions. The effect of  $\text{KOH}^0$  on water properties (structural and dielectric properties) is assumed to be similar to those of  $\text{NaCl}^0$ , allowing the use of the HKF equations with parameters ( $g$ , etc. . . .) calibrated in NaCl solutions. The symbol  $\bar{a}$  refers to the ion size parameter, which is taken as 3.72 Å (Helgeson et al., 1981) in NaCl dominated fluids. Conventionally, a value of 3.65 Å constant for all ions is used in Pitzer equations (Pitzer, 1973). As pointed out by Oelkers and Helgeson (1988), the value given above introduces a negligible effect on the calculated values of  $\gamma_i$ . The value 3.72 Å can be considered as a good compromise for all ions at high temperature and pressure in the framework of the HKF equations. Thermodynamical data for water and aqueous species are those tabulated and extrapolated in SUPCRT92 (Johnson et al., 1992).

#### 4.1.3. KOH dissociation constant

The speciation calculation involves the dissociation constant of  $\text{KOH}^0$  (Eqns. 4 and 8). Figure 3 shows that measured values (Franck, 1956) of association constant of  $\text{KOH}^0$  are in good agreement with extrapolated ones (Sverjensky et al., 1991; Bryzgalin, 1986). Both extrapolation sets have

Table 2. Molal equilibrium constants of reactions fitted against experimental data at 400°C (this study):  $\text{AlO}_{1.5}(\text{corundum}) + 2.5 \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$  (3)



(a) assuming K-Al complexing, i.e. taking into account both reactions (3) and (6),

(b) assuming no K-Al complexing, i.e. taking into account only reaction (3)

Standard deviations  $\sigma$  and minimum value  $M$  are indicated for each fit (see text).

KOH dissociation constant from:		400°C, 0.5 kbar		400°C, 1 kbar		400°C, 2 kbar	
		(a)	(b)	(a)	(b)	(a)	(b)
Sverjensky et al (1991)	$\log K_3$	-11.00	-10.78	-10.51	-10.33	-9.95	-9.76
	$\sigma$	0.06	0.03	0.05	0.05	0.03	0.02
	$\log K_6$	-1.94		-1.73		-1.56	
	$\sigma$	0.17		0.14		0.11	
Bryzgalin (1986)	$M$	2.81	26.58	1.56	34.18	5.69	68.79
	$\log K_3$	-11.00	-10.74	-10.51	-10.36	-9.95	-9.80
	$\sigma$	0.07	0.02	0.06	0.05	0.03	0.02
	$\log K_6$	-2.04		-1.62		-1.41	
	$\sigma$	0.17		0.16		0.12	
	$M$	2.80	33.78	1.51	25.02	5.73	45.32

been considered in the fits presented in Table 2. At 400°C, 0.5, and 1.0 kbar, the difference between the two estimations is lower than 0.1 log unit. The maximum departure (observed at 400°C and 2.0 kbar), does not exceed 0.2 log unit, which may be considered as the uncertainty on KOH dissociation constant. This uncertainty has virtually no influence on the value of  $K_3$ , and results in the same uncertainty (0.2 log unit) on the value of  $K_6$ . The speciation calculation results at 400°C, presented in appendices and Table 3, are obtained using data from Sverjensky et al. (1991).

The equilibrium constants  $K_3$ – $K_6$  obtained from the least-square refinements, with the standard deviations  $\sigma$  and the corresponding values of the minimum function  $M$ , are summarised in Table 2 (columns a). The complete speciation calculation is given in Appendix A, and the calculated and measured Al concentrations vs. initial KOH molalities are shown in Fig. 1.

#### 4.2. Interpretation Assuming that All Dissolved Al is $\text{Al}(\text{OH})_4^-$

In this alternative interpretation, equilibrium 6 is not considered and only the value of  $K_3$  is fitted against the experi-

mental data, from similar calculations performed setting  $m_{\text{KAl}(\text{OH})_4^0}$  to 0 in the mass-balance relations 12 and 13. The values of  $K_3$ ,  $\sigma$  and  $M$  are indicated in Table 2 (columns b). The calculated Al concentrations are shown in Fig. 1 and the complete speciation calculation is given in Appendix B.

#### 4.3. Discussion

The minimum function value provides a measure of the quality of the least squares fit. If the model chosen for fitting the data is adequate and if the uncertainty of each data point is correctly evaluated, the minimum function should not be much larger than the difference between the number of data points and the number of fitted parameters, i.e., 5. This is indeed the case in the K-Al complexing interpretation, where the minimum function values are, respectively, 2.8, 1.6, and 5.7 at 0.5, 1.0, and 2.0 kbars (Table 2). When the same data are fitted by the speciation calculation assuming  $\text{Al}(\text{OH})_4^-$  is the only important Al-bearing species, the minimum function values are much larger: 27, 34, and 69. Before rejecting this model, we can apply the  $\chi^2$  test: the minimum function should be smaller than the critical value of  $\chi^2$  function corresponding to 5 degrees of freedom. For a level of significance of 1%, the value of  $\chi^2(5)$  is 15.09, indicating that the no-complex model does not suitably fit the data. The poorer adequacy of this model appears on the display of the relative discrepancies between calculated and measured  $m_{\text{Al}}$  against  $m_{\text{K}}$  (Fig. 4). In the former interpretation (assuming K-Al complexing), they are randomly distributed, whereas in the latter no-complex interpretation calculated Al concentrations are systematically smaller than measured ones at lower  $m_{\text{K}}$  and become larger at higher  $m_{\text{K}}$ . Although this comparison strongly favours the first two-species interpretation, the poorer adequacy of the no-complex model could be due to underestimated ionic activity coefficients for the most concentrated experiments (the highest ionic strength is 0.085 m and the corresponding activity coefficient for  $\text{Al}(\text{OH})_4^-$  is 0.60). A further discussion involves interpretation of solubility data at higher temperatures and higher KOH concentra-

Table 3. Molal equilibrium constants used in the present study. a, this study, assuming K-Al complexing; b, calculated from this study (400°C) and PASCAL and ANDERSON (1989) (600 and 700°C), assuming no K-Al complexing; c, calculated from SUPCRT92 for aqueous species and BERMAN (1988) for corundum; d, calculated by ANDERSON (1995) from Density Model; e, calculated from SYRJENSKY et al. (1991) at 400°C, and FRANCK (1956) at 600 and 700°C; f, POKROVSKII and HELGESON (1994); g, calculated in this study from data of RAGNARSDOTTIR and WALTHER (1985); h, WALTHER and WOODLAND (1993).

Reaction	logK					Ref.
	400°C, 0.5 kbar	400°C, 1 kbar	400°C, 2 kbar	600°C, 2 kbar	700°C, 2 kbar	
(3) $\text{AlO}_{1.5}^{\text{corundum}} + 2.5 \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$	-11.00	-10.51	-9.95			a
	-10.99	-10.51	-10.03	-10.26	-10.62	c
	-10.78	-10.33	-9.76	-9.16	-8.98	b
			-9.02	-8.90	-8.94	d
(4) $\text{KOH}^0 \rightleftharpoons \text{K}^+ + \text{OH}^-$	-1.95	-1.61	-1.34	-2.11	-2.72	e
(5) $\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$	-11.36	-10.81	-10.23	-10.93	-11.50	c
(6) $\text{KAl}(\text{OH})_4^0 \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{K}^+$	-1.94	-1.73	-1.56	-2.43	-3.16	a
	-2.54	-2.03	-1.53	-2.55	-3.11	f
(15) $\text{Al}(\text{OH})_3^0 + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$	-	-	-5.87			g
			-4.1			h

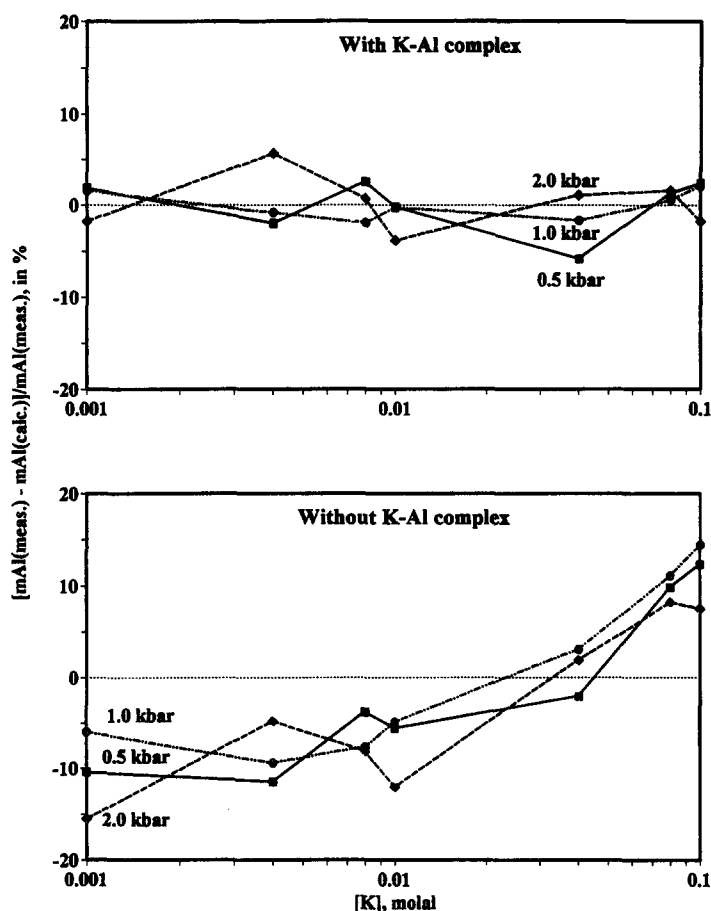


FIG. 4. Relative difference between calculated and measured corundum solubility, vs. starting KOH molality, at 400°C and 0.5, 1.0, and 2.0 kbar. (Top) calculation assuming K-Al complexation, with equilibrium constants from Table 2, columns (a). (Bottom) calculation assuming all dissolved Al is  $\text{Al}(\text{OH})_4^-$ , with equilibrium constants from Table 2, columns (b).

tions where K-Al complexing is expected to be more important (next section).

Log  $K_3$  values obtained from the two series of fits differ by less than 0.25 log unit (Table 2), which corresponds to 3.2 kJ on the free energy change of equilibrium (Eqn. 3), a difference no larger than the uncertainty on the determination of this free energy change from tabulated thermochemical parameters (Table 3). Apparent free energies of formation for aluminate ion and  $\text{H}_2\text{O}$  have been calculated from SUPCRT92 (Johnson et al., 1992), with parameters for  $\text{Al}(\text{OH})_4^-$  from Shock and Helgeson (1988). (As defined for example in Helgeson et al. (1978), the apparent free energy of formation of the species  $i$  at temperature  $T$  is the free energy change in the formation of this species at temperature  $T$  from the elements taken in their standard state). For corundum, we retained the thermodynamical parameters tabulated by Berman (1988).

The values of log  $K_3$  (Table 3) are remarkably consistent with those obtained from our first interpretation:  $-10.99$  (compared to experimental  $-11.00$ ) at 0.5 kbar,  $-10.51$  ( $-10.51$ ) at 1 kbar, and  $-10.03$  ( $-9.95$ ) at 2 kbars. Table 3 also shows the value  $-9.02$  for log  $K_3$  at 2 kbars determined

by Anderson (1995) from Density Model extrapolations (Anderson et al., 1991) of experimental data at subcritical conditions (Castet et al., 1993). In order to investigate where this difference of 1 log unit comes from, we have calculated the apparent free energies of formation of  $\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})_4^-$  according to the Density Model equations (Anderson, 1995) with parameters for water properties taken in Anderson et al. (1991) and for  $\text{Al}(\text{OH})_4^-$  from Castet et al. (1993) (Table 4). Table 4 also shows the apparent free energies of  $\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})_4^-$  calculated from SUPCRT92 (because this database uses the representation  $\text{AlO}_2^-$ , the apparent free energy of 2  $\text{H}_2\text{O}$  is added to that of  $\text{AlO}_2^-$  to

Table 4. Apparent free energies of formation of  $\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})_4^-$  at 400°C, 2 kbars, calculated from SUPCRT92 (JOHNSON et al., 1992), and from Density Model extrapolations of 25°C data from (1) CASTET et al. (1993) (2) JOHNSON et al. (1992).

	Density Model			SUPCRT92	
	$\Delta G_{25}^f$ kJ/mole	$\Delta H_{25}^f$ kJ/mole	$C_p^0(25^\circ)$ J/(mole.K)	$\Delta G_{400}^f$ kJ/mole	$\Delta G_{400}^f$ kJ/mole
$\text{Al}(\text{OH})_4^-$	(1) -1305.41	(1) -1495.78	(1) 96.48	-1357.50	-1356.22
$\text{H}_2\text{O}$	(2) -237.18	(2) -285.84	(2) 75.312	-266.97	-271.79

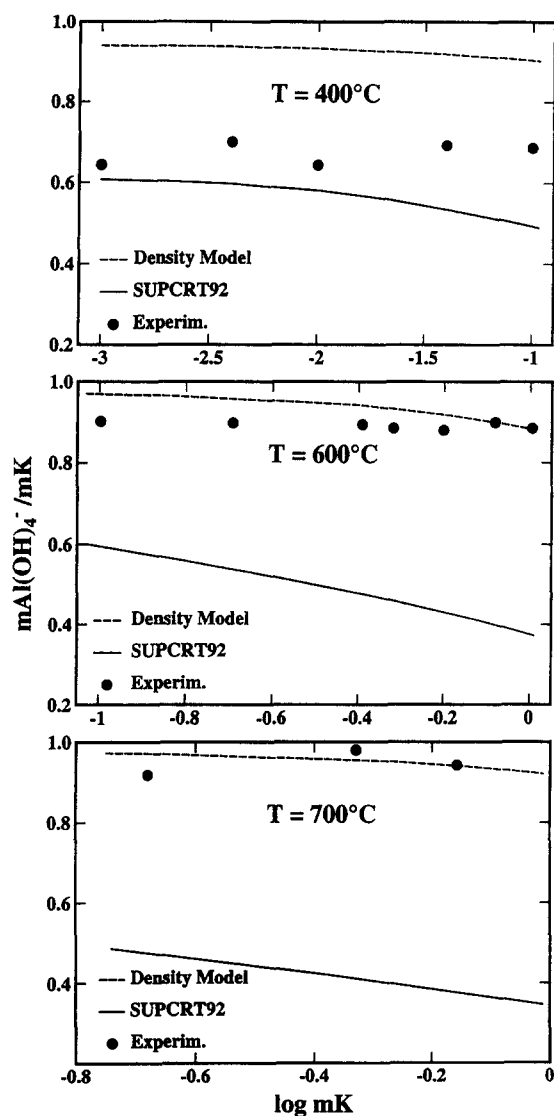


FIG. 5. Ratio  $m_{\text{Al}}/m_{\text{K}}$  vs. log of  $K$  molality, in KOH aqueous solutions at equilibrium with corundum at 2 kbars and 400°C, 600°C, and 700°C: experimental data (circles), and calculated ratio  $m_{\text{Al(OH)}_4^-}/m_{\text{K}}$ . Full lines are calculated from SUPCRT ( $\text{Al(OH)}_4^-$ ) and Berman (corundum), dashed lines from equilibrium constants given in Anderson (1995), calculated according to Density Model.

allow the comparison with the density model extrapolation of data from Castet et al., 1993). The value obtained for  $\text{H}_2\text{O}$  from the Density Model is 4.8 kJ larger than from SUPCRT92, whereas the values obtained for aluminate ion are within 1.3 kJ. The accuracy of SUPCRT92 parameters for water is attested by the close agreement of the ion product of water calculated from SUPCRT92 with recently published measurements and extrapolations (Chen et al., 1994). Using the Density Model for extrapolating water thermodynamical properties thus leads to overestimate  $\log K_3$  which results in overestimating the aluminate ion concentration at equilibrium with corundum in predictive calculations. At 400°, 2 kbars the resulting values of  $m_{\text{Al(OH)}_4^-}$  exceed the experimental concentrations (Fig. 5) by 46 to 31%, with  $m_{\text{Al}}/m_{\text{K}}$  ratios

ranging from 0.94 to 0.90, instead of the experimental value of 0.69, far beyond the experimental uncertainty.

In summary, the solubility data presented in this study could be approximately simulated by the aluminate ion only ( $\text{Al(OH)}_4^-$  does not contribute significantly in this pH range), using SUPCRT92 thermodynamical parameters for water, and for aluminate ion either SUPCRT92 or Density Model with data of Castet et al. (1993). However, the agreement between experimental data and calculations is much better when K-Al complexing is assumed. The same solubility data are not consistent with calculated aluminate ion concentrations, even without assuming K-Al complexing, when thermodynamical properties of  $\text{H}_2\text{O}$  are extrapolated according to the Density Model which is suitable for aqueous species, not for water. This result contrasts with the good agreement observed by Anderson (1995) between Density Model predictions for aluminate ion concentrations and experimental corundum solubilities in KOH aqueous solutions at 600°C, 2 kbars (Pascal and Anderson, 1989).

#### 4.4. Re-interpretation of Experimental Data at 600 and 700°C, 2 kbar

It is thus interesting to compare experimental corundum solubilities in KOH aqueous solutions at higher temperatures with predictive calculations of aluminate ion concentration from the two models. Table 3 shows the values of  $\log K_3$  at 600 and 700°C, 2 kbars, calculated from SUPCRT92 (aluminate ion,  $\text{H}_2\text{O}$ ) and Berman (1988) (corundum), and those extrapolated by Anderson (1995) using the Density Model (aluminate ion,  $\text{H}_2\text{O}$ ). As observed at 400°C, the latter are appreciably larger than the former, and the difference increases with increasing temperature (1.7 log unit at 700°). In Table 3 are also shown the values of  $\log K_3$  fitted against experimental data of Pascal and Anderson (1989), assuming no K-Al complexing. The speciation calculated for each data point is indicated in Appendix B. The values obtained for  $\log K_3$  are close to the Density Model extrapolations at both 600 and 700°C. This agreement appears in Fig. 5, where the aluminate ion concentrations at equilibrium with corundum, calculated from the two models, are presented vs. bulk potassium concentrations, along with the experimental solubilities. As noted by Anderson (1995) for the 600° data, the agreement between Density Model calculations and experimental data is satisfactory, and impressively good at 700°C. On the contrary, the SUPCRT + Berman calculation gives  $\text{Al(OH)}_4^-$  concentrations significantly smaller than the measurements. The reasons for considering the SUPCRT + Berman calculations as reliable at 600 and 700°C are that (1) they are perfectly consistent with experimental data at 400°C and all three investigated pressures and (2) the main difference with Density Model calculation is  $\text{H}_2\text{O}$  free energy of formation, for which there is experimental evidence that SUPCRT92 predictions are accurate. The discrepancies between calculated aluminate ion and measured Al concentrations observed at 600 and 700°C are interpreted by K-Al complexing, which is expected to be enhanced by higher temperatures and higher KOH concentrations. As compared to the SUPCRT + Berman calculations, the overestimation



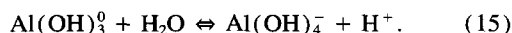
of  $\log K_3$  due to the Density Model leads to overestimate aluminate ion concentrations: at 600 and 700°C in rather concentrated KOH solutions ( $>0.1$  m), this overestimation is almost exactly compensated by K-Al complexation. This incidental compensation led Anderson (1995) to observe that experimental data were adequately consistent with any of the two speciation models considered here. On the contrary, at 400°C and lower KOH concentrations ( $<0.1$  m), K-Al complexation has too small an influence on corundum solubilities to compensate the overestimation of aluminate ion concentration due to the Density Model calculation.

Thus considering our first interpretation as most likely, to the determinations of  $KAl(OH)_4$  dissociation constant ( $K_6$ ) at 400°C were added values at 600 and 700°C, 2 kbars, fitted against experimental data from Pascal and Anderson (1989). Because the solutions involved in these experiments are too concentrated to allow a simultaneous determination of  $K_3$  and  $K_6$ ,  $K_3$  was calculated independently from SUPCRT + Berman data (Table 3). The values obtained for  $K_6$  are consistent with those given by Pokrovskii and Helgeson (1994) at 2.0 kbar at all three temperatures, but somewhat lower at 400°C, 1.0 and 0.5 kbar. The departure is important (0.60 in logarithmic units) at low water density (0.58 at 400°C, 0.5 kbar), in accordance with the loss in precision of equation of state at low water density.

The detailed speciation, given in the Appendix A, shows that at 400°C,  $Al(OH)_4^-$  is the dominant aluminum species in 0.001 m KOH solutions, as expected, which results in the good precision obtained on the value of  $K_3$ .  $KAl(OH)_4^0$  predominates for  $m_{KOH} > 0.1$  mol/kg  $H_2O$  (Fig. 6), representing 51%, 49%, and 47% of dissolved Al in 0.1 m KOH solutions at 0.5, 1.0, and 2.0 kbar, respectively. At 600 and 700°C,  $KAl(OH)_4^0$  becomes dominant at smaller KOH concentrations, representing 72% of dissolved Al in 0.1 m KOH solution and 87% in 1 m KOH solution at 600°C (Appendix A). This result is in agreement with the interpretation of corundum solubility in concentrated KOH solutions as mainly due to the neutral complex (Anderson and Burnham, 1967; Pascal and Anderson, 1989).

## 5. INTERPRETATION OF CORUNDUM SOLUBILITY IN PURE WATER

The values of  $K_3$  obtained in this study allow calculation of  $Al(OH)_4^-$  concentration in the system  $Al_2O_3-H_2O$ , to be compared with the published corundum solubilities in pure water at 400°C and 2 kbars:  $1.05 \times 10^{-4}$  and  $0.93 \times 10^{-4}$  m (Ragnarsdottir and Walther, 1985). The Al concentration in this system results from contributions of  $Al(OH)_4^-$  and  $Al(OH)_3^0$ , controlled by the equilibria (2), (3), and (5). The equilibrium constant  $K_2$  of reaction (2) ( $AlO_{1.5} + 1.5H_2O = Al(OH)_3^0$ ), or its equivalent with gibbsite or boehmite for lower temperatures, is hardly accessible experimentally, due in particular to the presence of polynuclear aqueous species and metastable solid phases in low temperature experiments, and to difficulties in pH buffering in high temperature experiments. The uncertainty on  $K_2$  directly affects the value of  $K_{15}$  which is thus poorly constrained:



The speciation in the system corundum- $H_2O$  has been calculated from  $K_3$  and  $K_5$  values (Table 2) and the charge and mass balance relations:

$$m_{H^+} = m_{OH^-} + m_{Al(OH)_4^-}, \quad (16)$$

$$m_{Al, total} = m_{Al(OH)_3^0} + m_{Al(OH)_4^-}. \quad (17)$$

The calculated pH is 4.88, slightly acidic (the neutral pH is 5.11), and the concentrations of  $Al(OH)_3^0$  and  $Al(OH)_4^-$ , respectively, account for 91% and 9% of the total dissolved Al.

The equilibrium constant of reaction (15),  $\log K_{15}$ , determined from this speciation calculation is  $-5.87$  (Table 3). Previously proposed values of  $\log K_{15}$  are  $-3.36$  (Anderson, 1995, from Density Model) and  $-4.1$  (Walther and Woodland, 1993), both implying that corundum solubility in pure water would be mainly due to aluminate ion, unless the pH were smaller than 3.36 or 4.1, respectively. On the contrary, according to the values of  $K_3$  determined above, the corundum solubilities of  $10^{-4}$  m measured by Ragnarsdottir and Walther (1985) would be mainly due to the aluminate ion only if the solution pH were higher than 5.87, whatever  $Al(OH)_3^0$  concentration. This is shown in Fig. 6 where corundum solubilities in the  $Al_2O_3-KOH-H_2O$  system, calculated from the equilibrium constants given in Table 3, are represented vs. in situ pH, along with experimental data from this study and Ragnarsdottir and Walther (1985). A pH of 5.87 is 0.76 units above neutral, and 1 unit above the pH calculated for the system  $Al_2O_3-H_2O$ . It must be noted that calculated  $Al(OH)_4^-$  concentration around the neutral pH (where the K-Al complex is unimportant) depends only on the value of  $K_3$  whose experimental determination is as accurate as 0.25 log unit, without any assumption on K-Al complexing. However, there is a large uncertainty on the actual pH in the pure water experiments, because small amounts of impurities may have a relatively large influence on pH in the neutral region. Therefore, it cannot be precluded that the pH could be higher than 5.87, although it more probably remains below, in the range where the dominant species is  $Al(OH)_3^0$ , as proposed by Ragnarsdottir and Walther (1985), and in accordance with calculations of Pokrovskii and Helgeson (1995).

## 6. CONCLUSION

The precise weight-loss method was used to measure corundum solubility in dilute KOH solutions under supercritical conditions. A speciation calculation fitted on experimental results enabled us to characterise  $Al(OH)_4^-$  ion and to evidence the  $KAl(OH)_4^0$  aqueous complex. The fitted equilibrium constant  $K_3$  (Table 3) is in excellent agreement with the value calculated from SUPCRT92 data for aluminate ion and water, and Berman (1988) for corundum, suggesting that these thermodynamical data are suitable for predictions at higher temperatures. This allowed us to re-interpret the previously published solubility data at 600° and 700°C, and to determine the  $KAl(OH)_4^0$  dissociation constant ( $K_6$ ). The values found at 2 kbars, 400 to 700°C, are in good agreement with those calculated by Pokrovskii and Helgeson (1994),

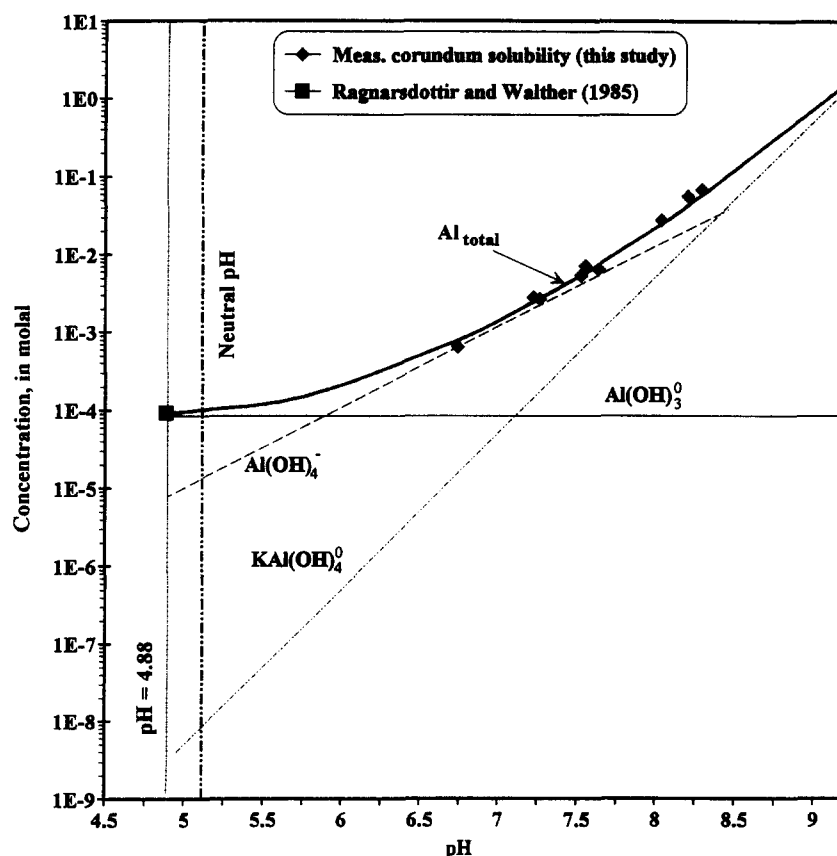


FIG. 6. Corundum solubility in pure water and KOH solutions (vs. pH) at 2.0 kbar and 400°C. The solid line represents total dissolved aluminum, the dotted and dashed lines refer to the molalities of individual species, calculated from equilibrium constants given in Table 3 (Ref. a for reactions (3) and (6), g for reaction (15)). The symbols represent measured corundum solubilities in pure water (Ragnarsdottir and Walther, 1985) and in KOH aqueous solutions (this work).

and show that K-Al complexing has to be taken into account in the interpretation of experimental data such as feldspar solubility in alkaline solutions. The characterization of aluminate ion allowed to interpret the solubility of corundum in pure water as mainly due to  $\text{Al}(\text{OH})_3^0$  (~91%), with a minor contribution of  $\text{Al}(\text{OH})_4^-$  (~9%) at 400°C and 2.0 kbars. If the existence of a pH range where the neutral species,  $\text{Al}(\text{OH})_3^0$ , predominates is questionable at low temperatures, <200°C (Michard, 1990; Bourcier et al., 1993) its importance seems likely in supercritical conditions. The field of predominance of the neutral species should increase with increasing temperature. The present characterisation of the neutral species using two measured values of corundum solubility (samples D45 and D72 in Ragnarsdottir and Walther, 1985) is not definitive. Other experimental measurements of aluminum solubility at 400°C and 2.0 kbar in the pH range between 5 and 7 (Fig. 6) are necessary to characterise more precisely this species.

**Acknowledgments**—This study was supported by a BRGM (Orléans) post-doc fellowship. Improvements to the first version of the manuscript benefitted from thoroughful reviews by G. M. Anderson, S. Castet, and J. V. Walther, and suggestions of D. J. Wesolowski. They are gratefully acknowledged.

Editorial handling: D. J. Wesolowski

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## APPENDIX A

**Speciation Calculation in the  $\text{Al}_2\text{O}_3$ –KOH– $\text{H}_2\text{O}$  System Assuming K–Al Complexing**

Speciation is calculated considering the following aqueous species:  $\text{Al}(\text{OH})_4^-$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{KAl}(\text{OH})_4^-$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ , and  $\text{KOH}^0$ . Dissociation constants for water and KOH as in Table 3. At 400°C, equilibrium constants  $K_3$  and  $K_6$  are obtained by least-square refinements of the data presented in this study. At 600 and 700°C,  $K_3$  is calculated from thermodynamical data of Berman (corundum) and SUPCRT92 (aqueous species) (table 3) and  $K_6$  fitted against the experimental data of Pascal and Anderson (1989).

[KOH]	[OH <sup>-</sup> ]	[K <sup>+</sup> ]	[KOH <sup>0</sup> ]	[Al(OH) <sub>3</sub> <sup>0</sup> ]	[KAl(OH) <sub>4</sub> <sup>-</sup> ]	$\gamma_{\text{OH}^-}$	$\gamma_{\text{K}^+}$	$\gamma_{\text{Al(OH)}_3^0}$	pH
<b>400°C, 0.5 kbar</b>									
0.001	2.88E-4	9.39E-4	1.89E-5	6.52E-4	4.16E-5	0.883	0.883	0.883	7.76
0.004	1.03E-3	3.37E-3	1.97E-4	2.34E-3	4.36E-4	0.797	0.797	0.797	8.27
0.008	1.89E-3	6.16E-3	5.73E-4	4.27E-3	1.26E-3	0.741	0.743	0.741	8.50
0.01	2.28E-3	7.45E-3	7.95E-4	5.17E-3	1.76E-3	0.722	0.723	0.722	8.57
0.04	7.15E-3	2.33E-2	5.19E-3	1.62E-2	1.15E-2	0.588	0.592	0.588	8.98
0.08	1.25E-2	4.08E-2	1.22E-2	2.83E-2	2.70E-2	0.515	0.521	0.515	9.16
0.1	1.49E-2	4.88E-2	1.59E-2	3.38E-2	3.52E-2	0.491	0.497	0.491	9.22
<b>400°C, 1.0 kbar</b>									
0.001	3.20E-4	9.62E-4	1.05E-5	6.42E-4	2.74E-5	0.912	0.912	0.912	7.27
0.004	1.18E-3	3.56E-3	1.23E-4	2.37E-3	3.20E-4	0.843	0.844	0.843	7.81
0.008	2.20E-3	6.63E-3	3.82E-4	4.42E-3	9.93E-4	0.797	0.798	0.797	8.05
0.01	2.68E-3	8.05E-3	5.41E-4	5.37E-3	1.41E-3	0.781	0.782	0.781	8.13
0.04	8.51E-3	2.56E-2	4.00E-3	1.71E-2	1.04E-2	0.666	0.670	0.666	8.56
0.08	1.48E-2	4.44E-2	9.88E-3	2.97E-2	2.57E-2	0.602	0.608	0.602	8.76
0.1	1.76E-2	5.29E-2	1.31E-2	3.53E-2	3.40E-2	0.580	0.588	0.580	8.82
<b>400°C, 2.0 kbar</b>									
0.001	3.38E-4	9.74E-4	6.23E-6	6.36E-4	1.96E-5	0.930	0.930	0.930	6.72
0.004	1.28E-3	3.67E-3	7.82E-5	2.40E-3	2.46E-4	0.873	0.873	0.873	7.27
0.008	2.41E-3	6.94E-3	2.55E-4	4.53E-3	8.03E-4	0.834	0.835	0.834	7.53
0.01	2.94E-3	8.47E-3	3.67E-4	5.53E-3	1.16E-3	0.820	0.821	0.820	7.61
0.04	9.56E-3	2.75E-2	3.01E-3	1.80E-2	9.47E-3	0.721	0.724	0.721	8.06
0.08	1.66E-2	4.78E-2	7.76E-3	3.12E-2	2.44E-2	0.666	0.672	0.666	8.27
0.1	1.97E-2	5.68E-2	1.04E-2	3.71E-2	3.28E-2	0.648	0.654	0.648	8.33
<b>600°C 2.0 kbar</b>									
0.1007	5.11E-3	2.90E-2	6.65E-3	2.39E-2	6.50E-2	0.589	0.590	0.589	8.41
0.2033	8.36E-3	4.74E-2	1.45E-2	3.91E-2	0.1414	0.531	0.533	0.531	8.58
0.4061	1.36E-2	7.70E-2	3.05E-2	6.34E-2	0.2986	0.475	0.477	0.475	8.74
0.4805	1.53E-2	8.66E-2	3.65E-2	7.13E-2	0.3574	0.462	0.465	0.462	8.78
0.6296	1.84E-2	0.1045	4.87E-2	8.61E-2	0.4764	0.442	0.445	0.442	8.84
0.8297	2.23E-2	0.1264	6.52E-2	0.1041	0.6381	0.422	0.426	0.422	8.90
1.011	2.55E-2	0.1447	8.04E-2	0.1192	0.7859	0.409	0.413	0.409	8.95
<b>700°C 2.0 kbar</b>									
0.2087	2.49E-3	2.14E-2	8.60E-3	1.89E-2	0.179	0.554	0.554	0.554	8.64
0.4679	4.33E-3	3.71E-2	1.98E-2	3.29E-2	0.411	0.482	0.484	0.482	8.82
0.6958	5.72E-3	4.91E-2	2.97E-2	4.34E-2	0.617	0.447	0.449	0.447	8.91

## APPENDIX B

**Speciation Calculation in the  $\text{Al}_2\text{O}_3$ – $\text{KOH}$ – $\text{H}_2\text{O}$  System Without K–Al Complexing**

Speciation is calculated considering the following aqueous species:  $\text{Al}(\text{OH})_4^-$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ , and  $\text{KOH}^0$ . Dissociation constants for water and  $\text{KOH}$  as in Table 3. Equilibrium constant  $K_3$  (Table 3) is obtained by least-square refinements of the data presented in this study (400°C), and from Pascal and Anderson (1989) (600 and 700°C).

[KOH]	[OH <sup>-</sup> ]	[K <sup>+</sup> ]	[KOH <sup>0</sup> ]	[Al(OH) <sub>3</sub> <sup>0</sup> ]	$\gamma_{\text{OH}^-}$	$\gamma_{\text{K}^+}$	$\gamma_{\text{Al(OH)}_3^0}$	pH
<b>400°C, 0.5 kbar</b>								
0.001	2.06E-4	9.86E-4	1.41E-5	7.80E-4	0.880	0.880	0.880	7.61
0.004	8.01E-3	3.83E-3	1.70E-4	3.03E-3	0.786	0.786	0.786	8.15
0.008	1.56E-3	7.46E-3	5.43E-4	5.90E-3	0.722	0.723	0.722	8.41
0.01	1.93E-3	9.22E-3	7.80E-4	7.29E-3	0.699	0.701	0.699	8.49
0.04	7.05E-3	3.37E-2	6.27E-3	2.67E-2	0.540	0.545	0.540	8.94
0.08	1.34E-2	6.39E-2	1.61E-2	5.05E-2	0.455	0.463	0.455	9.14
0.1	1.64E-2	7.84E-2	2.16E-2	6.20E-2	0.428	0.437	0.428	9.20
<b>400°C, 1.0 kbar</b>								
0.001	2.48E-4	9.92E-4	8.40E-6	7.43E-4	0.911	0.911	0.911	7.16
0.004	9.74E-4	3.89E-3	1.09E-4	2.92E-3	0.837	0.838	0.837	7.72
0.008	1.91E-3	7.63E-3	3.70E-4	5.72E-3	0.785	0.787	0.785	7.99
0.01	2.37E-3	9.46E-3	5.42E-4	7.09E-3	0.766	0.768	0.766	8.07
0.04	8.75E-3	3.50E-2	5.04E-3	2.62E-2	0.630	0.636	0.630	8.55
0.08	1.65E-2	6.60E-2	1.40E-2	4.95E-2	0.553	0.563	0.553	8.77
0.1	2.02E-2	8.08E-2	1.92E-2	6.06E-2	0.528	0.539	0.528	8.84
<b>400°C, 2.0 kbar</b>								
0.001	2.52E-4	9.94E-4	4.74E-6	7.43E-4	0.929	0.929	0.929	6.60
0.004	9.96E-4	3.94E-3	6.48E-5	2.94E-3	0.869	0.870	0.869	7.16
0.008	1.97E-3	7.77E-3	2.29E-4	5.80E-3	0.826	0.827	0.826	7.44
0.01	2.45E-3	9.66E-3	3.40E-4	7.21E-3	0.810	0.812	0.810	7.52
0.04	9.23E-3	3.64E-2	3.56E-3	2.72E-2	0.693	0.698	0.693	8.03
0.08	1.76E-2	6.94E-2	1.06E-2	5.18E-2	0.627	0.634	0.627	8.26
0.1	2.15E-2	8.51E-2	1.49E-2	6.36E-2	0.605	0.614	0.605	8.34
<b>600°C, 2.0 kbar</b>								
0.1007	1.62E-3	9.66E-2	4.12E-3	9.50E-2	0.450	0.453	0.450	7.79
0.2033	3.22E-3	0.1914	1.18E-2	0.1882	0.384	0.389	0.384	8.02
0.4061	6.24E-3	0.3710	3.51E-2	0.3647	0.339	0.348	0.339	8.25
0.4805	7.30E-3	0.4341	4.64E-2	0.4268	0.332	0.342	0.332	8.31
0.6296	9.35E-3	0.5560	7.35E-2	0.5467	0.325	0.338	0.325	8.44
0.8297	1.19E-2	0.7096	0.1201	0.6976	0.324	0.340	0.324	8.52
1.011	1.41E-2	0.8341	0.1725	0.8243	0.327	0.347	0.327	8.59
<b>700°C, 2.0 kbar</b>								
0.2087	6.08E-4	0.2029	5.80E-3	0.2023	0.297	0.301	0.297	7.76
0.4679	1.34E-3	0.4473	2.06E-2	0.4460	0.251	0.259	0.251	8.03
0.6958	1.96E-3	0.6535	4.22E-2	0.6516	0.245	0.256	0.245	8.18