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An experimental and computational study of sodium-aluminum complexing in crustal fluids

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Abstract—The stoichiometry and stability constants of Na-aluminate ($\text{NaAl}(\text{OH})_4^0$) ion pair were determined from both boehmite solubility and potentiometric measurements. Boehmite solubility was measured at temperatures from 125 to 350°C at pressures corresponding to equilibrium between liquid and vapor (P_{SAT}) in the system Na–NH₄–Cl–OH. Potentiometric measurements were performed at temperatures from 75 to 200°C in Na–Al–Cl–OH solutions, using a Na-selective glass electrode. $\text{NaAl}(\text{OH})_4^0$ stability constants derived independently from these two methods are in excellent agreement and increase markedly with increasing temperature from 0.8 at 25°C to 209 at 350°C.

Experimental results obtained in this study were combined with corresponding data reported by Castet et al. (1993) for boehmite solubility to generate, within the framework of the revised HKF model, the standard partial molal properties and equations of state parameters for $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_3^0$, and $\text{NaAl}(\text{OH})_4^0$. The solubilities of gibbsite, boehmite, and corundum calculated in Na-rich solutions using the thermodynamic data for Al aqueous species generated in this study are in close agreement with their experimental counterparts. Thermodynamic calculations carried out at temperatures up to 800°C and pressures up to 5 kbar indicate that the formation of $\text{NaAl}(\text{OH})_4^0$ ion pairs can markedly increase the solubility of Al-bearing minerals and thus, Al mobility, both in sedimentary basin and metamorphic fluids at pHs > 4.

1. INTRODUCTION

Knowledge of the thermodynamic properties of Al-bearing aqueous species facilitates calculation of aluminosilicate mineral solubility and Al mass transfer in geological systems. To better understand the role of Na–Al complexes in hydrothermal and metamorphic processes, the stability constant of $\text{NaAl}(\text{OH})_4^0$ was determined at temperatures between 75 and 350°C from both boehmite solubility and potentiometric measurements. Resulting thermodynamic data were used together with corresponding data for $\text{Al}(\text{OH})_4^-$ and Na^+ within the revised HKF (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1989, 1992) equations of state to derive association constants and thermodynamic properties of $\text{NaAl}(\text{OH})_4^0$ at temperatures from 25 to 800°C and pressures from 1 to 5000 bars. The purpose of this paper is to report the results of this research, and to evaluate the effect of Na-aluminate complexing on Al transport in natural processes.

A large number of studies have been devoted to characterizing Al complexing with hydroxide ion (Kittrick, 1966; May et al., 1979; Kuyunko et al., 1983; Couturier et al., 1984; Ragnarsdottir and Walther, 1985; Apps et al., 1989; Verdes, 1990; Verdes et al., 1992; Palmer and Wesolowski, 1992; Wesolowski, 1992; Bourcier et al., 1993; Castet et al., 1993; Wesolowski and Palmer, 1994; Pokrovskii and Helgeson, 1992, 1995), inorganic anions (Öhman and Forsling, 1981; Couturier, 1986; Korzhinsky, 1987; Sanjuan and Michard, 1987; Baumgartner and Eugster, 1988; Pokrovskii and Helgeson, 1992, 1994, 1995), and organic anions (Sjöberg and Öhman, 1985; Marklund et al., 1989; Marklund and Öhman, 1990; Thomas et al., 1990; Fein, 1991; Fein et al., 1995; Bénézeth et al., 1994; Palmer and Bell, 1994). One major recent result is the recognition that the anion complex $\text{Al}(\text{OH})_4^-$ is much more significant than the neutral $\text{Al}(\text{OH})_3^0$ at near neu-

tral pH conditions over a large range of temperatures and pressures (Anderson et al., 1991; Castet et al., 1993; Walther and Woodland, 1993). For example, from hydrolysis constants reported by Castet et al. (1993), it can be deduced that at 350°C and P_{SAT} the activity of $\text{Al}(\text{OH})_4^-$ should be greater than that of $\text{Al}(\text{OH})_3^0$ for all pH > 4.5.* Based on this observation, and on the fact that Na is the major cation present in most crustal fluids, several investigators have considered the possibility of alkali-aluminate complex formation and have attributed an important role to these complexes in Al transport during geological processes (Anderson and Burnham, 1967, 1983; Pascal and Anderson, 1989; Castet, 1991; Castet et al., 1992; Pokrovskii and Helgeson, 1992, 1995). Until now, however, no experimental investigation has been performed to establish the stability of these complexes over the wide range of temperatures and pressures typical of geochemical processes. The present study was initiated to provide these data. It is anticipated that they will enable a better description of Al behavior during sedimentary, hydrothermal, and metamorphic processes.

2. MATERIALS AND METHODS

2.1. Solubility Experiments

2.1.1. Boehmite synthesis

Boehmite (γAlOOH) was synthesized from pure synthetic gibbsite ($\alpha\text{Al}(\text{OH})_3$) (Riedel, De Haen AG SEELZE, Hannover 2504361). This gibbsite was ground, placed in an autoclave with 250 mL of deionized water, and heated at 300°C for two weeks. Then the solution and the solid phase were separated while maintaining temperature at 300°C to avoid precipitation of other aluminum hydrox-

* The term P_{SAT} is used in the present communication to denote pressures corresponding to equilibrium between liquid and vapor at any temperature.

Table 1. Values of the dissociation constants for H₂O, NaCl, NaOH, NH₃(aq), and NH₄Cl, and boehmite solubility constants (K_{s3} and K_{s4}) used in this study.

T°C	logK _{H₂O} (1)	logK _{NaCl} (2)	logK _{NaOH} (3)	logK _{NH₃(aq)} (1a)	logK _{NH₄Cl} (3)	logK _{s3} (3)	logK _{s4} (3)
25	-14.00	0.78	0.46	-4.75	0.67	-8.02	-15.19
50	-13.27	0.69	0.34	-4.73	0.79	-7.64	-14.32
60	-13.03	0.65	0.28	-4.74	0.85	-7.51	-14.00
70	-12.81	0.61	0.24	-4.76	0.88	-7.38	-13.37
75	-12.70	0.59	0.21	-4.77	0.90	-7.32	-13.56
80	-12.61	0.57	0.19	-4.79	0.91	-7.26	-13.42
90	-12.42	0.52	0.15	-4.82	0.95	-7.15	-13.17
100	-12.26	0.47	0.10	-4.85	0.95	-7.09	-12.96
125	-11.90	0.35	-0.03	-4.97	0.98	-6.96	-12.48
150	-11.63	0.21	-0.14	-5.12	0.96	-6.84	-12.06
170	-11.46	0.10	-0.24	-5.25	0.89	-6.76	-11.75
200	-11.28	-0.09	-0.38	-5.48	0.65	-6.65	-11.39
250	-11.17	-0.48	-0.78	-5.97	-0.06	-6.56	-10.99
300	-11.30	-1.01	-1.48	-6.62	-0.95	-6.35	-10.74
325	-11.49	-1.38	-1.98	-7.06	-1.65	-6.22	-10.76
350	-11.83	-1.93	-2.48	-7.64	-2.30	-6.10	-10.77

(1) SUPCRT92 (Johnson et al., 1992); (1a) logK for the reaction: NH₃+H₂O=NH₄⁺+OH⁻ (SUPCRT92, Johnson et al., 1992); (2) Shock et al. (1992); (3) Castet et al. (1993); Values of logK_{s3} and logK_{s4} in italics were calculated by linear interpolation of Castet et al. data as a function of reciprocal temperature.

ides (e.g., bayerite). The solid phase was rinsed repeatedly with deionized water and dried for 48 h at 150°C. X-ray diffraction analysis of the solid phase showed it to be well-crystallized pure boehmite. Depending on syntheses, the mineral contained between 15.5 and 16.2 wt% of H₂O as measured by thermogravimetric analysis. Such a H₂O excess, compared to the theoretical concentration (15 wt%), is often observed in natural and synthetic boehmites (Gout, 1978; Verdes, 1990; Castet et al., 1993). The specific surface area of boehmite, as measured by nitrogen adsorption (B.E.T. method), was found to range between 0.5 and 2 m²/g. Scanning electron microscopy observations showed the boehmite grains to be more than 1 µm in diameter, associated in aggregates of about 10 µm.

2.1.2. Solubility measurements

Boehmite solubility was measured as a function of Na concentration (0.1–1 mol/L) at temperatures from 125 to 350°C at P_{SAT} in the pH range 5–10. To avoid contamination of the solution resulting from reactor corrosion, experiments were performed in 400 mL pure Ti autoclaves. The autoclaves were placed in rocking furnaces to mix the solutions and avoid temperature gradients. Temperature was maintained constant ($\pm 1^\circ\text{C}$) and was measured with an externally calibrated thermocouple (Pt, type S, connected to RLC (APLTC 3988) reader). A 2 µm Ti filter was installed inside the autoclave to permit in situ solution filtration. During sampling, the valve and the sampling tube were water-cooled and the solution was filtered a second time at 25°C with a 0.01 µm filter (Sartorius 11318025N). Additional experiments were performed at 300, 325, and 350°C in a Hastelloy autoclave. This alloy exhibits better mechanical properties than pure Ti above 300°C. The sampling procedure was the same as in the other runs.

Three types of reactive solutions were used to cover a wide range of pH and Al concentrations: NH₃(aq)–NH₄Cl–NaCl, NaOH–NaCl, and NaOH. All solutions were prepared from Merck Suprapur (NaCl, NH₄Cl), Prolabo Normapur (NH₃(aq), 28 wt%) chemical products and Merck Titrisol solution for the NaOH stock solution (1 mol/L). The starting solutions were prepared just before each experiment and were never stored. pH was measured at 25°C with a combined glass electrode (Schott H62) standardized on activity scale using DIN 19266/NBS standards (pH 6.865, 4.008, and 9.180 at 25°C).

About 250 mL of solution and 0.5 g of boehmite were used in each experiment. Once the experiment reached the desired temperature, samples were taken periodically to monitor progress towards an equi-

librium Al concentration. The time necessary to achieve equilibrium was determined in previous studies for the temperatures and pHs used in this study (Verdes, 1990; Verdes et al., 1992; Castet et al., 1993). This time is always very short for the basic conditions prevailing in this study (for example, few hours at 170°C). For each run, solution sampling started a few days after attainment of thermal equilibrium and then proceeded periodically for up to 20 days. No systematic variations in Al concentration and pH were observed with time. Each sample was divided into six subsamples. Five subsamples were immediately diluted and acidified with 0.1 M HNO₃ (Merck Suprapur) or with 0.1 M HNO₃ + 0.1 M NaCl (Merck Suprapur) for Atomic Absorption Spectroscopy (AAS) dissolved Al analyses as described below. The last subsample (about 5 mL) was used to measure pH at 25°C. Several blank runs, conducted without boehmite at the same pH conditions and temperature as the experiments of interest were performed before experiments. Aluminum concentration never exceeded 10 ppb in the blank runs.

2.1.3. Calculation of chemical equilibria

Chemical equilibria were computed by solving a system of non-linear equations including dissociation equilibria of the components, and mass and charge balance equations. Equilibrium molalities, activity coefficients, and ionic strength were calculated using a Newton–Raphson algorithm. Consistency between activity coefficients and true ionic strength was obtained through an iterative method (Genthon, 1992). Only mononuclear Al species were considered in the calculations as Al concentrations were too low for polymeric Al complexes to form (the dimer Al₂(OH)₂O²⁻ was identified by Raman spectroscopy only for Al concentrations > 1.5 M, according to Moolenaar et al. (1970) and R. Gout (pers. commun.)). As a result, the boehmite solubility measurements were interpreted assuming that the following Al-bearing species were present in solution: Al(OH)₃⁰, Al(OH)₄⁻, and NaAl(OH)₄⁰ (see below the discussion on the Na-aluminate complex stoichiometry). The concentrations of positively charged Al species were too low to play a significant role in the calculations. Boehmite was the only solid phase considered in the calculations. Chemical equilibrium in NaOH solutions was computed from the following set of equations:

Boehmite solubility:

$$K_{s4} = m_{\text{Al(OH)}_4^-} \gamma_{\text{Al(OH)}_4^-} m_{\text{H}^+}^+ \gamma_{\text{H}^+}^+ \quad (1)$$

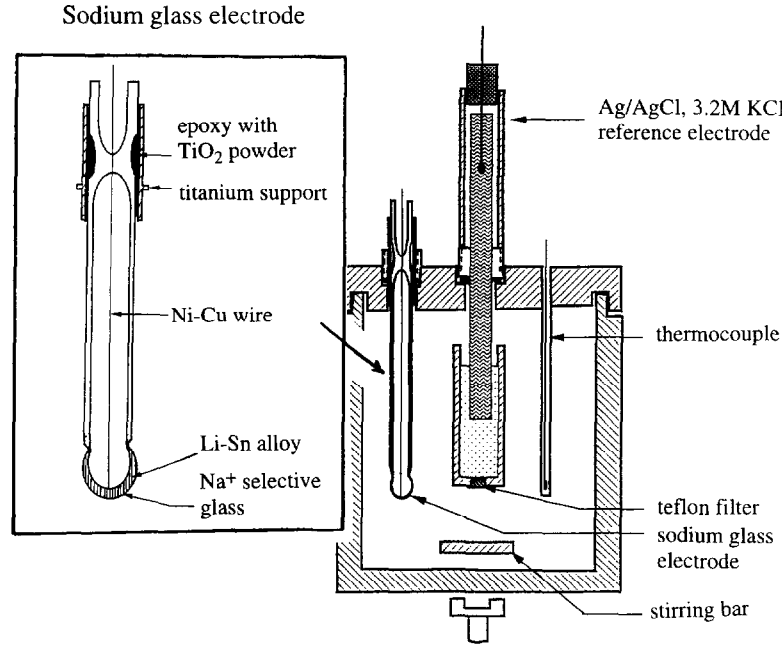


FIG. 1. Schematic illustration of the electrode and autoclave used for potentiometric study.

Dissociation of water and NaOH⁰:

$$K_{D,H_2O} = m_H \cdot \gamma_H \cdot m_{OH^-} \cdot \gamma_{OH^-}; \quad (2)$$

$$K_{D,NaOH} = m_{Na^+} \cdot \gamma_{Na^+} \cdot m_{OH^-} \cdot \gamma_{OH^-}. \quad (3)$$

Mass balance constraints on total Al and Na:

$$m_{Al} = m_{Al(OH)_4^-} + m_{NaAl(OH)_4^0} + m_{Al(OH)_3^0}, \quad (4)$$

where $m_{Al(OH)_3^0}$ is equal to K_{S3} , the third dissociation constant of boehmite (see Table 1),

$$m_{Na} = m_{Na^+} + m_{NaOH^0} + m_{NaAl(OH)_4^0}. \quad (5)$$

Charge balance equation:

$$m_{Na^+} + m_H^+ = m_{OH^-} + m_{Al(OH)_4^-}. \quad (6)$$

In these equations m_i and γ_i stand for the molal concentration and the activity coefficient of the i th species, respectively. For boehmite solubility in NaOH–NaCl and NH₄Cl–NH₃(aq)–NaCl solutions, NaCl⁰ and Cl[−], and NH₄⁺, Cl[−], NH₄Cl⁰, NH₃(aq), and NaCl⁰, respectively, have to be added in the input file together with the corresponding dissociation, mass, and charge balance equations.

The standard states adopted in this study for the solid phase and H₂O are unit activity for the pure mineral and fluid, respectively. For aqueous species, the standard state corresponds to unit activity coefficients for an hypothetical, one molal solution whose behavior is ideal. Molal activity coefficients of neutral species were assumed to be unity. Activity coefficients of charged species were calculated using the equation proposed by Helgeson et al. (1981) for concentrated salt solutions:

$$\log \gamma_i = -(A_\gamma \cdot Z_i^2 \cdot \sqrt{I}) / (1 + \beta \cdot B_\gamma \cdot \sqrt{I}) - \log(1 + 0.0180153 \cdot I) + (\omega_{abs,i} \cdot b_{NaCl} + b_{Na^+Cl^-} - 0.19(|Z_i| - 1)) \cdot I, \quad (7)$$

where I and Z_i denote the true ionic strength and the charge of the i th species, respectively. A_γ , B_γ , $\omega_{abs,i}$ (the Born coefficient of the i th species), b_{NaCl} , and $b_{Na^+Cl^-}$ (the short-range interaction parameters) were taken from Helgeson et al. (1981). A β parameter of $4 \cdot 10^{-8}$ cm was used for all the charged species.

The dissociation constants used in this study are compiled in Table 1 as a function of temperature. The dissociation constants for water and NH₃(aq) were taken from SUPCRT92 (Johnson et al., 1992),

those for NaCl⁰ from Shock et al. (1992). For NH₄Cl⁰ we used values reported by Castet et al. (1993) that were derived from the conductivity measurements reported by Read (1982) for temperatures from 25 to 250°C. NaOH⁰ values were taken from Castet et al. (1993), who used the conductivity measurements of Read (1982) up to 250°C and the high P - T data reported by Sverjensky et al. (1991) to calculate NaOH⁰ dissociation constant at P_{SAT} to 350°C. It should be noted that the NaOH⁰ dissociation constants in this work are in close agreement with those deduced from the conductivity measurements of Lukashov et al. (1975) for the temperature range 300–350°C and with the recent potentiometric measurements of Ho and Palmer (1994) in the range 100–250°C. At temperatures lower than 100°C, Ho and Palmer (1994) results yield a higher degree of dissociation for NaOH⁰. Boehmite dissociation constants used in this study (K_{S3} and K_{S4}) were taken from Castet et al. (1993) and are reported in Table 1.

2.2. Potentiometric Experiments

2.2.1. Experimental design

NaAl(OH)₄⁰ stability constant has been measured at temperatures from 75 to 200°C using a Na-selective electrode created by the St. Petersburg company “POTENTIAL” (Beliustin et al., 1992). Details on the electrode properties and potentiometric cell construction are given in Pokrovski et al. (1995). The main characteristic of the Na-selective glass electrode used in this study is that it has an electrochemically reversible solid contact with the glass ion-conducting membrane (Fig. 1). As a result, there is no internal solution in the electrode. The inner surface of the Li–Al–B-silicate glass is covered by a thin Li–Sn alloy that provides a reversible contact and remarkably stable potentials. At 25°C, the electrode resistance is too high to make precise measurements, however, this resistance decreases rapidly with increasing temperature. Thus, it allows electrical potential measurements in the 75–200°C temperature range using an ordinary potentiometer with a precision of 0.1 mV. In the present study a “Tacussel-2000” pH-meter with an input impedance $10^{13} \Omega$ was used. The upper temperature of the measurements was 200–210°C, because the melting point of the electrode alloy is approximately $215 \pm 10^\circ\text{C}$. Two electrodes were used simultaneously in each experiment. They were attached to Ti supports using an epoxy containing TiO₂ powder (Fig. 1).

The reference electrode is an external AgCl/Ag, 3.2 M KCl electrode with a construction analogous to that used by Krukov et al. (1966) and subsequently improved by Pokrovski et al. (1993) (see Fig. 1). The upper part of the electrode, located outside the reaction cell, is kept at 20°C to prevent the destruction of the Ag/AgCl element. The Teflon tube containing the 3.2 M KCl reference solution is filled with glass fibers to diminish possible thermal convection of the reference solution between the upper and the lower part of the electrode. A 0.1 μ m Teflon filter provides a liquid junction between the reference and the test solution.

Experiments were carried out in a Ti reaction cell placed in an oven and kept at constant temperature ($\pm 1^\circ\text{C}$). The solution was continuously stirred with a Teflon-coated magnetic stirring bar.

The following electrochemical cell was used:

Sn-Cu, Li-Sn alloy|Na-selective glass|test solution

containing $\text{Na}^+ || 3.2 \text{ M KCl, Ag/AgCl}$.

The e.m.f. of the cell is described by the equation:

$$E = E^\circ + 2.3026RT/F \log a_{\text{Na}^+} + E_j, \quad (8)$$

where R , T , and F stand for the gas constant, temperature in Kelvin, and the Faraday constant, respectively. E° , which depends only on temperature, represents the sum of the standard glass electrode potential and the total reference electrode potential ($E^\circ = E^\circ_{\text{glass}} + E_{\text{ref}}$), and E_j refers to the liquid junction potential. E_j was estimated from the limiting equivalent conductances of ions (Oelkers and Helgeson, 1989) using the Henderson equation (Bates, 1973). In solutions of constant Na concentration, E_j was found to be independent of anion identity (Cl^- , OH^- , or $\text{Al}(\text{OH})_4^-$) within $\pm 0.5 \text{ mV}$. E_j varied by less than $\pm 3 \text{ mV}$ as a function of Na concentration from 0.01 to 0.5 M.

2.2.2. Electrode calibration

Electrode calibration was performed in several NaCl solutions (0.01–0.5 M Na) over the 50–200°C temperature range at 25°C temperature intervals. The e.m.f. of the cell stabilized within 1–2 min after the attainment of the temperature of interest and remained constant for at least 0.5 h. To verify the reversibility of the electrode response, measurements were performed both on heating and cooling. All corresponding potentials were within $\pm 2 \text{ mV}$. Nevertheless, to increase the precision of measurements, particularly when comparing different solutions, only experimental potentials recorded on heating were used. Na^+ activity coefficients (γ_{Na^+}) were calculated using the extended Debye-Hückel equation, assuming $a = 4 \cdot 10^{-8} \text{ cm}$ and by adopting NaCl^0 association constants reported by Shock et al. (1992). It was assumed that $\gamma_i = 1$ for neutral aqueous species. The calibration parameters are given elsewhere (Pokrovski et al., 1994). The experimental slopes remain constant (within $\pm 5\%$) over the investigated Na^+ activity range (for details see Pokrovski et al., 1995). Additional measurements, performed in solutions of the same Na concentration but at pHs ranging from 7 to 12 and in the presence of different noncomplexing anions (NO_3^- , ClO_4^-), demonstrate that there was no influence of pH and anion composition on electrode response.

2.2.3. Preparation of aluminate solutions and experimental protocol

The principles of the measurements and data treatment have been described in the experimental study of NaSO_4^- and $\text{NaB}(\text{OH})_4^0$ association (Pokrovski et al., 1994, 1995). Briefly, the measurements consist of comparing, at the same temperature, the electrode cell potentials in two solutions of the same Na concentration: a 'reference' solution with known Na^+ activity, and an experimental aluminate solution. NaCl–NaOH mixtures were chosen as reference solutions because the NaCl^0 association constant is relatively well known (Shock et al., 1992) and Na^+ activity can be easily calculated using the extended Debye-Hückel equation. As a result, the difference in potentials can be directly attributed to the uptake of Na^+ by $\text{Al}(\text{OH})_4^-$ to form the $\text{NaAl}(\text{OH})_4^0$ ion pair.

The measurements were performed in two distinct solution pairs:

- 1) $0.077 \text{ M NaCl} + 0.078 \text{ M NaOH} \rightarrow 0.078 \text{ M NaAlO}_2 + 0.077 \text{ M NaOH}$;
- 2) $0.18 \text{ M NaCl} + 0.07 \text{ M NaOH} \rightarrow 0.18 \text{ M NaAlO}_2 + 0.07 \text{ M NaOH}$.

NaCl–NaOH solutions were prepared from the NaOH (1 mol/L) and HCl (1 mol/L) Merck Titrisol standard solutions. Aluminate solutions were obtained by dissolution of a synthetic $\text{Al}(\text{OH})_3$ gel in aqueous NaOH solutions. The $\text{Al}(\text{OH})_3$ gel was prepared by hydrolysis of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck Suprapur) with aqueous ammonia (28 wt%, Prolabo Normapur $\text{NH}_3(\text{aq})$). The gel was washed several times with deionized water (MilliQ) and separated from the supernatant by centrifugation. Then it was dissolved in 0.15 and 0.25 M NaOH and the resulting solution was twice filtered through a $0.45 \mu\text{m}$ Sartorius cellulose nitrate filter. The total aqueous Al concentration was measured by flame atomic absorption spectroscopy (see below) before, during, and after each experimental run. No change in Al concentration was detected during the course of $\sim 12 \text{ h}$ runs. Note that both Na and free NaOH concentrations measured after neutralization by HCl or $\text{Al}(\text{OH})_3$ were constant in each solution pair. This minimizes the difference between the diffusion potentials in the reference and test solutions ($\Delta E_j \sim 0.2\text{--}0.3 \text{ mV}$) and makes the effect of NaOH^0 formation negligible in the calculations. As a result NaOH^0 dissociation reaction does not have to be incorporated in the calculations.

2.3. Analytical Methods

Aqueous Al concentrations were measured by flame or flameless atomic absorption spectroscopy in a graphite furnace (Perkin Elmer Zeeman 5000). For the concentration range 5–40 ppm, an acetylene-nitrous oxide flame was used. Reproducibility of this method was better than 5% (as measured periodically with standard solutions). The Al detection limit, defined as three times the standard deviation on the blank, was 1 ppm. The Na concentration of the standard solutions and the diluted samples was 0.1 mol/L. A graphite furnace was used to measure Al concentrations over the range 5–40 ppb. Five stages of temperature rise were used to minimize interferences due to the matrix (110, 300, 600, 1350, and 2400°C). Reproducibility of these measurements was better than 5%; the detection limit was 2 ppb. The Na concentrations of the standard solutions and the samples were identical (0.01–0.001 mol/L). Aluminum standard solutions were prepared by weight dilution of a 1000 ppm Merck Al standard solution, using a 0.1 mol/L HNO_3 (Merck Suprapur) acid solution with an appropriate NaCl (Merck Suprapur) concentration. The analyses were conducted on five samples. The difference in Al concentration between five samples never exceeded 2–3%. Thus, the uncertainty of measured Al concentration was assumed to be that of the analytical method.

3. RESULTS AND DISCUSSION

3.1. Evidence for the Formation of $\text{NaAl}(\text{OH})_4^0$ from Solubility Measurements

The results of boehmite solubility measurements are listed in Table 2. The uncertainties in $p\text{Al}$ ($p\text{Al} = -\log m_{\text{Al, total}}$) values were always less than ± 0.02 . The uncertainties in calculated pHs are ± 0.15 and stem mainly from the corresponding uncertainties in NaOH^0 and $\text{NH}_3(\text{aq})$ dissociation constants.

A comparison between boehmite solubility measured in the present study in 1 mol/L sodium chloride solutions with corresponding values calculated in Na-free solutions for a similar ionic strength as a function of pH at 125 and 300°C can be made with the aid of Fig. 2. It can be seen in this figure that the presence of Na results in up to a sevenfold increase in solubility at 300°C. This cannot be accounted for by ionic strength differences, and suggests the presence of Na–Al complexes. Note also that the formation of Al-chloride complexes can be ruled out because no variation of boehmite solubility

Table 2a. Boehmite solubility in $\text{NH}_3(\text{aq})$ - NH_4Cl - NaCl solutions in the temperature range 125–350°C.

	$\text{NH}_3(\text{aq})$ (1)	NH_4Cl (1)	NaCl (1)	pH ₂₅ (2)	pH _T (3)	pAl (4)	T/°C
1	0.038	0.02483	0.03021	9.60	7.31	4.80	125
2	0.0055	0.009732	1.0257	9.23	6.21	4.86	170
3	0.0078	0.01013	0.1000	9.25	6.24	5.22	170
4	0.0055	0.009590	1.0175	9.24	5.82	4.73	200
5	0.0065	0.009778	0.5048	9.26	5.86	4.88	200
6	0.0055	0.009985	0.5058	9.18	5.77	5.07	200
7	0.0078	0.01013	0.1000	9.25	5.84	5.26	200
8	0.0055	0.009732	1.0257	9.23	5.81	4.83	200
9	0.0052	0.009638	1.0207	9.21	5.79	4.81	200
10	0.0045	0.009732	1.0257	9.14	5.22	4.91	250
11	0.0065	0.009939	0.5053	9.25	5.27	4.95	250
12	0.0058	0.009748	1.0224	9.25	5.33	4.86	250
13	0.043	0.02510	0.1001	9.60	5.31	4.84	300
15	0.047	0.02499	0.09997	9.64	5.35	4.78	300
16	0.043	0.02499	0.09997	9.60	5.31	4.80	300
17	0.035	0.02506	0.1001	9.51	5.22	4.86	300
18	0.037	0.02498	0.1000	9.54	5.18	4.88	325
19	0.019	0.02482	0.3023	9.30	5.08	5.01	325
20	0.017	0.02482	0.3023	9.25	5.03	4.99	325
21	0.040	0.02499	0.1003	9.57	5.27	4.92	350
22	0.033	0.02499	0.1003	9.49	5.18	4.95	350
23	0.030	0.02499	0.1003	9.48	5.14	4.94	350
24	0.041	0.02622	0.09007	9.56	5.24	4.74	350

(1) concentrations in mol/kg H_2O , those for $\text{NH}_3(\text{aq})$ were deduced from measured pH, and NH_4Cl , and NaCl concentrations; (2) pH measured at 25°C; (3) pH calculated at run temperature; (4) $\text{pAl} = -\log(m_{\text{Al}})$, $\Delta\text{pAl} < \pm 0.02$

is observed in $\text{NH}_3(\text{aq})$ - NH_4Cl solutions with increasing aqueous NH_4Cl concentration (up to 1 mol/L, Diakonov and Schott, 1995).

TABLE 2b. Boehmite solubility in NaOH - NaCl solutions in the temperature range 125–325°C

	NaOH (1)	NaCl (1)	pH _T (2)	pAl (3)	T/°C
1	0.02229	1.0426	9.79	2.22	125
2	0.02387	1.0393	9.82	2.21	125
3	0.02229	1.0426	9.41	2.10	150
4	0.02375	1.0514	9.44	2.07	150
5	0.009609	1.0198	8.79	2.38	170
6	0.009232	1.0190	8.79	2.42	170
7	0.009915	1.0189	8.79	2.35	170
8	0.009915	1.0189	8.47	2.26	200
9	0.009609	1.0198	8.47	2.28	200
10	0.009232	1.0190	8.47	2.31	200
11	0.009342	1.0191	7.97	2.17	250
12	0.009915	1.0189	7.97	2.14	250
13	0.009642	1.0191	7.39	2.07	300
14	0.009527	1.0217	7.36	2.07	300
15	0.007367	1.0242	7.37	2.20	300
16	0.01831	1.0193	7.91	1.83	300
17	0.009423	0.5048	7.77	2.12	300
18	0.009732	0.1021	8.11	2.11	300
19	0.02876	0.1001	8.50	1.62	300
20	0.04943	0.09997	8.67	1.39	325

(1) concentrations in mol/kg H_2O ; (2) calculated pH at run temperature; (3) $\text{pAl} = -\log(m_{\text{Al}})$, $\Delta\text{pAl} < \pm 0.02$

The identity of this Na-Al aqueous complex can be deduced by consideration of the speciation of Na-free solutions. A variety of evidence has led numerous investigators to conclude that $\text{Al}(\text{OH})_4^-$ is the dominant Al-bearing species in moderate to high pH Na-free solutions (Castet et al., 1993 and references therein). It thus seems reasonable to assume that the Na-Al complex that forms at moderate to high pH is created by an association reaction between Na^+ and $\text{Al}(\text{OH})_4^-$. To characterize the complex stoichiometry, a series of boehmite solubility measurements was performed at 300°C as a function of NaCl concentration (0.1–1 mol/L). The results are given in Fig. 3a,b which test the possible formation of 1:1 ($\text{NaAl}(\text{OH})_4^0$) and 2:1 ($\text{Na}_2\text{Al}(\text{OH})_4^+$) Na-Al complexes, respectively. For this comparison each complex was successively considered in the computation of chemical equilibria. The activity coefficient of $\text{Na}_2\text{Al}(\text{OH})_4^+$ was calculated

TABLE 2c. Boehmite solubility in NaOH solutions (300–325°C)

	NaOH (1)	pH _T (2)	pAl (3)	T/°C
1	0.02893	8.83	1.64	300
2	0.09619	9.19	1.12	300
3	0.03847	8.93	1.52	300
4	0.09619	9.10	1.09	325

(1) concentrations in mol/kg H_2O ; (2) calculated pH at run temperature; (3) $\text{pAl} = -\log(m_{\text{Al}})$, $\Delta\text{pAl} < \pm 0.02$

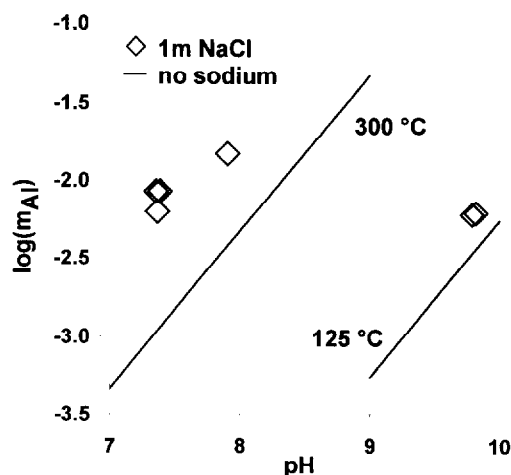


FIG. 2. Boehmite solubility at 125 and 300°C in 1 m NaCl solutions and in Na-free solutions of the same ionic strength. The solid curves represent calculated solubility in uncomplexing solutions using boehmite K_{S4} dissociation constants from Castet et al. (1993). Note the curves and symbols correspond to $I = 0.6$ at 300°C and to $I = 0.9$ at 125.

as described above. The linear increase of the ratio $a_{\text{NaAl}(\text{OH})_4^0}/a_{\text{Al}(\text{OH})_4^-}$ as a function of Na^+ activity observed in Fig. 3a is strong evidence for a 1:1 stoichiometry of the complex of the form $\text{NaAl}(\text{OH})_4^0$. In contrast, a linear increase of the ratio $a_{\text{Na}_2\text{Al}(\text{OH})_4^+}/a_{\text{Al}(\text{OH})_4^-}$ is not observed as a function of a_{Na^+} in Fig. 3b, which rules out the formation of 2:1 Na-Al complexes.

Values of the equilibrium constant (K_A) for the reaction



deduced from the solubility measurements reported in Table 2, using the Genthon (1992) chemical speciation code, are listed in Table 3. The uncertainties associated with these values stem mainly from the uncertainties in boehmite dissociation constants (± 0.1 in $\text{p}K_{S4}$, Castet et al., 1993) and calculated pH values (± 0.15 , see above). The uncertainties in measured Al concentrations are small (± 0.02). As a result, the uncertainties in $\log K_A$ values are estimated to be ± 0.2 .

3.2. Potentiometric Determination of $\text{NaAl}(\text{OH})_4^0$ Stability Constant

The results of the potentiometric study are given in Table 4. The potential differences between the solution pairs correspond to the average values obtained simultaneously using two different electrodes. Assuming that aqueous Na^+ activity is independent of anion identity, the difference ΔE in the e.m.f. between the NaCl and $\text{NaAl}(\text{OH})_4$ bearing solutions can be attributed to the formation of $\text{NaAl}(\text{OH})_4^0$. The greater the measured potential difference, the greater the degree of $\text{NaAl}(\text{OH})_4^0$ formation. Note also that for a given solution pair, the ratio $\Delta E/S$ (S = electrode experimental slope) increases with temperature indicating that Na-aluminate association increases. The $\Delta E/S$ ratios were used to calculate $\text{NaAl}(\text{OH})_4^0$ association constants by first computing the Na^+

activity in an aluminate solution of the same Na concentration as the reference solution, using:

$$\log a_{\text{Na}^+, \text{NaAl}} = \log a_{\text{Na}^+, \text{NaCl}} - \Delta E/S \quad (10)$$

and then combining this result with

$$\log K_A = \log a_{\text{NaAl}} - \log a_{\text{Na}^+, \text{NaAl}} - \log a_{\text{Al}(\text{OH})_4^-, \text{NaAl}}, \quad (11)$$

where a_{NaAl} and $a_{\text{Al}(\text{OH})_4^-, \text{NaAl}}$ represent the activities of the Na-Al complex and $\text{Al}(\text{OH})_4^-$, respectively. $\log a_{\text{Na}^+, \text{NaCl}}$ in NaCl-NaOH solutions was calculated using the computer code "BALANCE" (Akiniev, 1986), which is based on the Gibbs free energy minimization of the system. Stability constants for NaCl^0 were taken from Shock et al. (1992). Note also that $\text{Al}(\text{OH})_3^0$ was neglected in the calculation as its con-

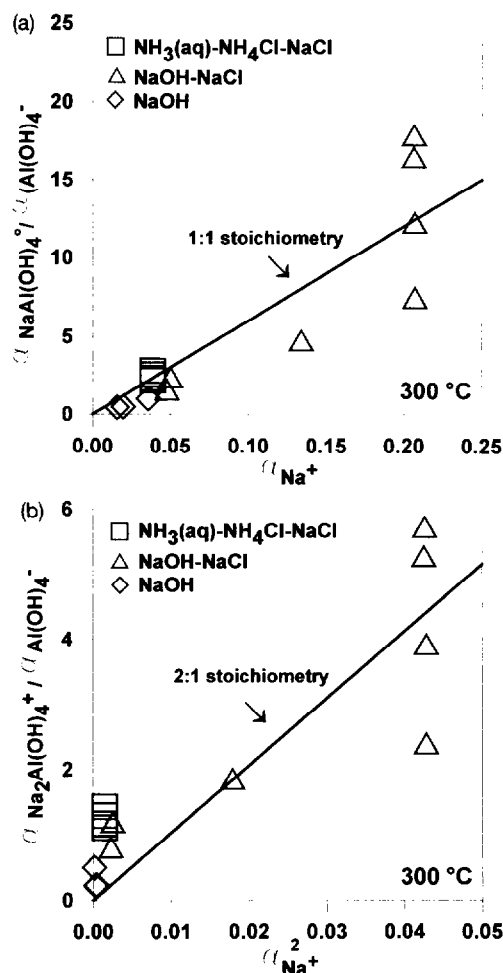


FIG. 3. (a) Plot of $a_{\text{NaAl}(\text{OH})_4^0}/a_{\text{Al}(\text{OH})_4^-}$ vs. a_{Na^+} deduced from boehmite solubility in NaCl alkaline solutions at 300°C. The symbols represent experimental results. The solid line represents a fit of the experimental data assuming the formation of a 1:1 Na-Al complex. The activity of the Na-Al complex corresponds to the difference between total Al measured in solution and the calculated $\text{Al}(\text{OH})_4^-$ concentration. (b) Plot of $a_{\text{Na}_2\text{Al}(\text{OH})_4^+}/a_{\text{Al}(\text{OH})_4^-}$ vs. a_{Na^+} deduced from boehmite solubility in NaCl alkaline solutions at 300°C. The symbols represent experimental results. The solid line represents a fit of the experimental data assuming the formation of a 2:1 Na-Al complex. The activity of the Na-Al complex was deduced from the difference between total Al measured in solution and the calculated $\text{Al}(\text{OH})_4^-$ concentration assuming the complex has the same activity coefficient as Na^+ .

Table 3. Values of the logarithm of $\text{NaAl}(\text{OH})_4^\circ$ association constant derived from solubility measurements.

T/°C	$\text{NH}_3(\text{aq})$ - NH_4Cl -NaCl	NaOH-NaCl	NaOH
125	0.63 (1)	0.37 (1)	
125		0.31 (2)	
150		0.52 (3)	
150		0.52 (4)	
170	0.77 (2)	0.61 (5)	
170	0.81 (3)	0.53 (6)	
170		0.67 (7)	
200	1.08 (4)	0.81 (8)	
200	1.04 (5)	0.77 (9)	
200	0.84 (6)	0.73 (10)	
200	0.81 (7)		
200	0.93 (8)		
200	0.99 (9)		
250	1.19 (10)	1.18 (11)	
250	1.29 (11)	1.24 (12)	
250	1.11 (12)		
300	1.66 (13)	1.90 (13)	1.44 (1)
300	1.69 (14)	1.94 (14)	1.44 (2)
300	1.74 (15)	1.77 (15)	1.37 (3)
300	1.78 (16)	1.56 (16)	
300		1.55 (17)	
300		1.52 (18)	
300		1.67 (19)	
325	1.92 (17)	1.83 (20)	1.87 (4)
325	1.44 (18)		
325	1.59 (19)		
350	1.80 (20)		
350	1.93 (21)		
350	2.02 (22)		
350	2.25 (23)		

Values in brackets correspond to run numbers in Tables 2a, b, c.

centration is $<10^{-6}$ M in these solutions. Combination of Eqn. 11 with Na mass balance constraints allows calculation of $\text{NaAl}(\text{OH})_4^\circ$ association constants using an iterative method for activity coefficients. Resulting association constants and uncertainties are given in Table 4. The uncertainties in log K originate from uncertainties in: (1) potential differences measured by two different electrodes, (2) uncertainty in the electrode slopes, (3) differences between liquid junction potentials in the NaCl–NaOH and NaAlO_2 –NaOH solutions (± 0.3 mV), and (4) NaCl° dissociation constants (± 0.5 log unit). It is interesting to note that roughly 50% of the uncertainties associated with the log K_A values generated in the present study stem from uncertainties in the NaCl° as-

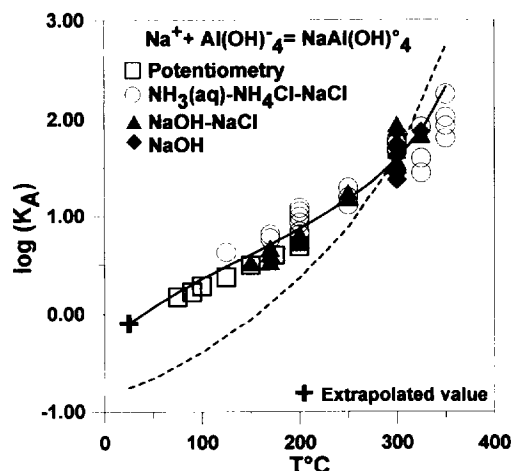


FIG. 4. Logarithm of $\text{NaAl}(\text{OH})_4^\circ$ association constant as a function of temperature at P_{SAT} . The symbols represent experimental data obtained in this study, but the solid line was generated using the revised HKF equation of state together with thermodynamic data and parameters given in Table 6. The dashed line represents the predictions of Pokrovskii and Helgeson (1992).

sociation constants used in the data regression. It can be seen in Table 4 that $\text{NaAl}(\text{OH})_4^\circ$ association constants determined in 0.15 and 0.25 M Na solution are the same within the limits of uncertainties. The ionic strength independence of association constants determined with the Na-selective electrodes has been also demonstrated for $\text{NaB}(\text{OH})_4^\circ$ and NaSO_4° ionic pairs (Pokrovski et al., 1995).

3.3. $\text{NaAl}(\text{OH})_4^\circ$ Association Constant as a Function of Temperature at Saturated Vapor Pressure

$\text{NaAl}(\text{OH})_4^\circ$ association constants deduced from both solubility and potentiometric measurements are depicted as a function of temperature in Fig. 4. A close agreement can be seen between the values deduced from solubility and potentiometric experiments. $\text{NaAl}(\text{OH})_4^\circ$ association constants measured in this study were extrapolated to 25°C from a plot of log K_A versus reciprocal temperature by assuming, in agreement with our data, that the heat capacity of reaction 9 ($\Delta_r C_p$) is equal to zero at $T \leq 125^\circ\text{C}$. This extrapolation yields a log K_A of -0.1 ± 0.2 at 25°C. It can be seen in Fig. 4 that the stability constant of $\text{NaAl}(\text{OH})_4^\circ$ increases markedly with temperature, from 0.8 at 25°C to ~ 209 at 350°C. Experimen-

Table 4. Measured cell potentials and $\text{NaAl}(\text{OH})_4^\circ$ association constants.

T/°C	0.15M Na			0.25M Na			average Log K_A
	ΔE (mV)	$\Delta E/S$	Log K_A	ΔE (mV)	$\Delta E/S$	Log K_A	
75	1.1 ± 0.1	0.015	0.12 ± 0.10	3.0 ± 0.2	0.040	0.20 ± 0.20	0.16 ± 0.13
90	1.2 ± 0.2	0.016	0.18 ± 0.15	3.0 ± 0.2	0.038	0.27 ± 0.20	0.23 ± 0.11
100	1.3 ± 0.1	0.030	0.17 ± 0.13	3.3 ± 0.2	0.041	0.32 ± 0.15	0.25 ± 0.10
125	2.6 ± 0.1	0.055	0.51 ± 0.20	3.7 ± 0.1	0.043	0.41 ± 0.15	0.46 ± 0.13
150	3.7 ± 0.1	0.040	0.69 ± 0.13	4.8 ± 0.2	0.052	0.54 ± 0.15	0.62 ± 0.14
175	5.2 ± 0.6	0.053	0.88 ± 0.15	5.2 ± 0.1	0.053	0.64 ± 0.15	0.76 ± 0.10
200	5.0 ± 0.8	0.048	0.90 ± 0.15	5.4 ± 0.6	0.052	0.72 ± 0.20	0.81 ± 0.13

Table 5. Thermodynamic data at 25°C and 1 bar and heat capacity power function coefficients for minerals used in this study.

	$\Delta_f G^\circ_{298}$ cal/mol	$\Delta_f H^\circ_{298}$ cal/mol	S°_{298} cal/mol K	$C^\circ_{p,298}$ cal/mol K	V°_{298} cm ³ /mol	a	b	c	d
Boehmite, $\gamma\text{AlO(OH)} (1)$	-219503	-238143	8.89	12.96	19.535	49.168	-8.3463e-3	-629.845	2.45378e5
Corundum, $\alpha\text{Al}_2\text{O}_3 (2)$	-378162	-400502	12.17	18.88	25.575	37.610	1.7184e-4	-236.147	4.53370e5

(1) Hemingway et al. (1991), (2) Robie et al. (1978), heat capacity equation: $C^\circ_p = a + bT + cT^{-0.5} + dT^{-2}$

tal values generated in this study are in fair agreement with those predicted by Pokrovskii and Helgeson (1992, 1995) at temperatures above 250°C (Fig. 4). However, this study yields stronger Al–Na association at low temperatures than that of Pokrovskii and Helgeson (1992, 1995), who reported a value of $\log K_A = -0.75$ at 25°C.

3.4. NaAl(OH)_4^0 Association Constant at High Temperatures and Pressures

The effect of the NaAl(OH)_4^0 aqueous species on mineral solubilities and the transport of aluminum can be predicted using thermodynamic properties for aqueous species in the system $\text{NaCl–Al}_2\text{O}_3\text{–H}_2\text{O}$ computed from the revised Helgeson–Kirkham–Flowers equations of state (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1989, 1992). Standard partial thermodynamic properties and equations of state parameters required for these calculations for the species in this system were obtained using the methods described below with the help of “HELGESON” (Akiniev, 1994) and “UT–HEL” (Shvarov, 1994) computer codes which are consistent with the revised HKF equations of state.

3.4.1. HKF equation of state coefficients

Na^+ , H_2O . The standard thermodynamic properties at 25°C and HKF parameters were taken from the SUPCRT92 database (Johnson et al., 1992).

Al(OH)_4^- . The standard molal thermodynamic properties and HKF equations of state parameters for Al(OH)_4^- were revised to better describe boehmite dissociation constants (pK_{s4}) measured by Castet et al. (1993) because the same solid phase and experimental technique were used both in this study and in that of Castet et al. (1993). This minimizes the uncertainties in NaAl(OH)_4^0 predicted properties. These data were retrieved by first calculating values of Al(OH)_4^- appar-

ent Gibbs free energies $\Delta G^\circ_{\text{Al(OH)}_4^-}$ from 25 to 350°C using pK_{s4} values reported by Castet et al. (1993) and boehmite thermodynamic data generated by Hemingway et al. (1991) (see Table 5). The data were subsequently regressed to generate the HKF equations of state parameters for Al(OH)_4^- . This regression was performed by specifying at 25°C the partial molal Gibbs free energy of formation ($\Delta_f G^\circ$), heat capacity (C°_p), volume (V°), and Born parameter (ω) as -312.156 kcal/mol (this study), 23.06 cal/mol K (Hovey et al., 1988), 46.3 cm³/mol (Hovey et al., 1988; Tremaine, 1988), and $1.0403 \cdot 10^5$ cal/mol (which corresponds to an effective radius of 3.31 Å for Al(OH)_4^- , Tremaine, 1988), respectively, and by choosing the best possible standard partial molal entropy at 25°C (S°), and c_1 , and c_2 HKF coefficients to describe the data. These calculations, performed with the “HELGESON” and “UT–HEL” software codes, led to the standard state properties and HKF equation of state parameters for Al(OH)_4^- shown in Table 6. The apparent Gibbs free energies of Al(OH)_4^- calculated from the resulting HKF parameters correspond to the experimental values within ± 90 cal/mol. The standard partial molal entropy of Al(OH)_4^- generated in this study ($S^\circ = 25.45$ cal/mol K) is in close agreement with that recently published by Wesolowski (1992) ($S^\circ = 26.62$ cal/mol K). In addition, the standard partial molal heat capacities and volumes of Al(OH)_4^- computed using these HKF equation of state parameters accurately reproduce the experimental measurements reported by Hovey et al. (1988), Caiani et al. (1989), and Chen et al. (1991) to 200°C.

Al(OH)_3^0 . Standard partial molal thermodynamic properties and HKF equations of state parameters for Al(OH)_3^0 were retrieved using the same procedure as that for Al(OH)_4^- . The $\Delta_f G^\circ$ at 25°C of Al(OH)_3^0 was deduced from pK_{s3} values reported by Castet et al. (1993) at 25°C and boehmite standard Gibbs free energy of formation at 25°C generated by Hemingway et al. (1991): $\Delta_f G^\circ = -265.250$ kcal/mol. Al(OH)_3^0 standard partial molal heat capacity and volume

Table 6. Standard partial molal thermodynamic properties at 25°C and 1 bar and HKF equation of state parameters for aqueous species used in this study.

	$\Delta_f G^\circ_{298}$ cal/mol	$\Delta_f H^\circ_{298}$ cal/mol	S°_{298} cal/mol K	$C^\circ_{p,298}$ cal/mol K	V°_{298} cm ³ /mol	c_1 cal/mol K	$c_2 \cdot 10^{-4}$ cal K/mol	$a_1 \cdot 10$ cal/mol bar	$a_2 \cdot 10^{-2}$ cal/mol	a_3 cal K/mol bar	$a_4 \cdot 10^{-4}$ cal K/mol	$\omega \cdot 10^{-5}$ cal/mol
$\text{Al(OH)}_4^- (1)$	-312156	-359107	25.45	23.06(2)	46.3(2)	49.0830	-8.0896	8.4190	12.9643	0.6535	-3.3149	1.0403(3)
$\text{Al(OH)}_3^0 (1)$	-265250	-300548	8.78	24.3	27.7	20.2216	1.9873	5.5507	5.7718	3.4809	-3.0176	0.0000
$\text{NaAl(OH)}_4^0 (1)$	-374611	-413601	48.8	32.2	53.6	60.7157	-14.0523	9.1267	14.3411	0.1121	-3.3719	0.0000

(1) This study, (2) Hovey et al. (1988), (3) Tremaine (1988)

Table 7. Calculated logarithm of $\text{NaAl}(\text{OH})_4^0$ association constant to 800°C and 5000 bar.

T°C	Pressure (bar)						
	PSAT	500	1000	2000	3000	4000	5000
25	-0.10	-0.17	-0.21	-0.27	-0.28	-0.28	-0.25
50	0.07	-0.01	-0.03	-0.08	-0.10	-0.10	-0.08
100	0.35	0.29	0.25	0.20	0.17	0.17	0.17
150	0.61	0.54	0.49	0.42	0.38	0.36	0.35
200	0.87	0.77	0.70	0.61	0.55	0.52	0.50
250	1.17	1.02	0.92	0.78	0.70	0.65	0.62
300	1.58	1.31	1.14	0.96	0.84	0.77	0.72
350	2.32	1.71	1.40	1.13	0.98	0.88	0.81
400			1.70	1.32	1.19	0.99	0.90
450			2.08	1.52	1.26	1.10	0.98
500			2.58	1.74	1.41	1.20	1.07
550			3.22	1.98	1.56	1.32	1.15
600			3.92	2.25	1.72	1.43	1.25
650				2.52	1.90	1.56	1.34
700				2.80	2.08	1.69	1.45
750				3.07	2.26	1.83	1.56
800				3.32	2.44	1.96	1.67

were calculated assuming a correlation between the thermodynamic properties of $\text{Al}(\text{OH})_n^{3-n}$ and the number of OH^- ligands in hydroxide complexes (Hovey, 1988; Tremaine, 1988). Linear plots of the standard partial molal non-solvation heat capacities and volumes against the number of OH^- groups in Al hydroxide complexes yield $C_p^\circ = 24.3 \text{ cal/mol} \cdot \text{K}$ and $V^\circ = 27.7 \text{ cm}^3/\text{mol}$. In the absence of direct measurements of $\text{Al}(\text{OH})_3^0$ heat capacity and molar volume, we chose not to attempt to estimate a value of the Born parameter from the correlations proposed by Shock et al. (1989) for neutral species. A value of zero was assigned to ω which is in agreement with the Born equation for neutral species. The HKF state parameters generated in this study are given in Table 6.

$\text{NaAl}(\text{OH})_4^0$. Equations of state parameters for this species were retrieved following the same procedure as for

$\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3^0$. The apparent Gibbs free energies of $\text{NaAl}(\text{OH})_4^0$ were deduced from the K_A values measured in this study (Table 3) and Na^+ and $\text{Al}(\text{OH})_4^-$ apparent Gibbs free energies. The value of the standard Gibbs free energy of formation of $\text{NaAl}(\text{OH})_4^0$ at 25°C is $\Delta_f G^\circ = -374.6 \text{ kcal/mol}$. The heat capacity of the complex at 25°C was derived by assuming $\Delta_f C_p^\circ = 0$ for reaction 9 (see explanation above) and the values of Na^+ and $\text{Al}(\text{OH})_4^-$ heat capacity at 25°C: $C_p^\circ = 32.2 \text{ cal/mol} \cdot \text{K}$. Values of $\text{NaAl}(\text{OH})_4^0$ association constant obtained in this study at P_{SAT} cannot be used to retrieve values of the a_1 – a_4 HKF parameters because of the small effect of pressure on equilibrium constants at these conditions. Following Pokrovskii and Helgeson (1992), these values were calculated assuming $\text{NaAl}(\text{OH})_4^0$ to be a chemical analog of $\text{NaB}(\text{OH})_4^0$ and the standard volume of reaction 9 to be the same as that of $\text{NaB}(\text{OH})_4^0$ reported by Rowe et al. (1989) ($\Delta_r V^\circ = 8.4 \text{ cm}^3/\text{mol}$). This leads to $V_{\text{NaAl}(\text{OH})_4^0}^\circ = 53.6 \text{ cm}^3/\text{mol}$. A value of zero was assigned to ω . Using the UT-HEL software code, the apparent Gibbs free energies of $\text{NaAl}(\text{OH})_4^0$ were regressed to generate the value of $\text{NaAl}(\text{OH})_4^0$ entropy at 25°C, and of c_1 and c_2 parameters. The standard thermodynamic properties and HKF equation of state parameters of $\text{NaAl}(\text{OH})_4^0$ retrieved by this regression are listed in Table 6.

3.4.2. $\text{NaAl}(\text{OH})_4^0$ association constant to 800°C and 5 kbar

$\text{NaAl}(\text{OH})_4^0$ association constants generated to 800°C and pressures to 5 kbar using the HKF equation of state parameters and standard thermodynamic properties listed in Table 6 are listed in Table 7 and depicted as curves in Figs. 4 and 5. It can be inferred from Fig. 5 that the stability of $\text{NaAl}(\text{OH})_4^0$ increases markedly with increasing temperature and decreasing pressure. This behavior is consistent with that of other weak neutral ion pairs (e.g., NaCl^0 (Shock et al., 1992); NaOH^0 (Ho and Palmer, 1994); KCl^0 and NaBr^0

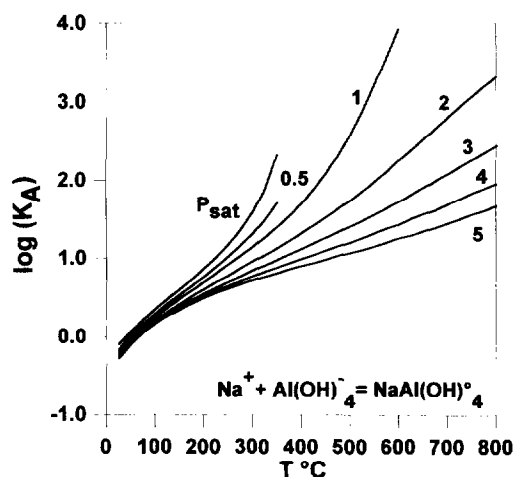


Fig. 5. Logarithm of $\text{NaAl}(\text{OH})_4^0$ association constant as a function of temperature at the indicated pressures (in kbar) calculated using the SUPCRT92 computer code (Johnson et al., 1992) and HKF parameters given in Table 6.

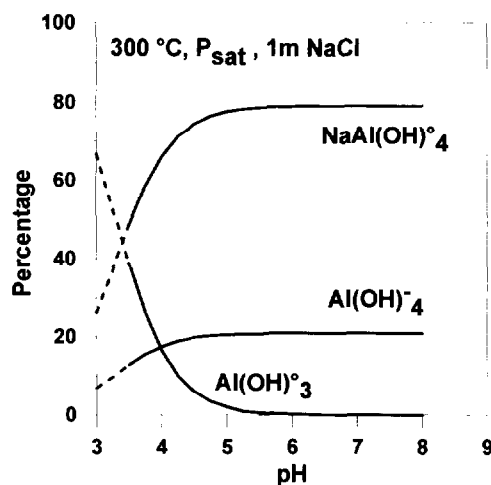


FIG. 6. Aqueous Al speciation as a function of pH in 1 m NaCl solution at 300°C and P_{SAT} . The distribution of Al species was calculated using thermodynamic parameters taken from Tables 1 and 6.

(Oelkers and Helgeson, 1988); $\text{NaB}(\text{OH})_4^0$ (Pokrovski et al., 1995)). The values derived in this study imply that the formation of $\text{NaAl}(\text{OH})_4^0$ can notably modify Al speciation in Na-rich solutions, even at moderate temperatures. For example, it can be seen in Fig. 6 that at 300°C, and P_{SAT} and in 1 m NaCl solution, conditions typical of many hydrothermal fluids, Na-aluminate complexes dominate Al speciation at pHs higher than 4 (about 80% of total Al is present as $\text{NaAl}(\text{OH})_4^0$). This result implies that Na-Al complexes can

Table 8. Calculated solubilities of gibbsite compared to literature experimental data.

T°C	NaOH mol/kg	NaCl mol/kg	pAl measured	pAl calculated	$\Delta\text{pAl}^{(1)}$
Wesolowski (1992)					
25	0.5143		1.45	1.37	0.08
25	1.019		1.14	1.02	0.12
25	3.045		0.60	0.42	0.18
25	0.01027		3.16	3.15	0.01
25	0.1002		2.17	2.14	0.03
25	0.00992	0.09038	3.17	3.14	0.03
25	0.1004	0.4001	2.15	2.05	0.10
25	0.01030	0.4901	3.13	3.04	0.09
25	0.01030	0.9851	3.12	2.96	0.16
25	0.1000	2.900	2.06	1.79	0.27
25	0.01000	2.991	3.04	2.79	0.25
25	0.1010	4.905	1.99	1.72	0.27
25	0.0108	4.987	2.97	2.67	0.30
50	0.5143		1.15	1.08	0.07
50	1.019		0.85	0.74	0.11
50	3.045		0.30	0.17	0.13
50	0.00993	0.09037	2.88	2.86	0.02
50	0.01030	0.4901	2.85	2.79	0.06
50	0.1004	0.4001	1.86	1.80	0.06
50	0.01030	0.9851	2.83	2.75	0.08
50	0.01000	2.991	2.76	2.66	0.10
50	0.1000	2.900	1.78	1.66	0.12
50	0.01100	4.987	2.70	2.58	0.12
50	0.10100	4.905	1.70	1.62	0.08
60	0.09972		1.76	1.68	0.08
60	0.09980	0.8976	1.74	1.69	0.05
(1) $\Delta\text{pAl} = \text{pAl}(\text{measured}) - \text{pAl}(\text{calculated})$, where $\text{pAl} = -\log(m_{\text{Al}})$.					

Table 8. Continued.

T°C	NaOH mol/kg	NaCl mol/kg	pAl measured	pAl calculated	$\Delta\text{pAl}^{(1)}$
Wesolowski (1992)					
70	0.1002		1.68	1.64	0.04
70	0.00992	0.09038	2.71	2.65	0.06
70	0.1004	0.4001	1.65	1.59	0.06
70	0.0103	0.4901	2.68	2.57	0.11
70	0.1002	0.8998	1.64	1.54	0.10
70	0.0103	0.9851	2.68	2.53	0.15
70	0.1000	2.900	1.58	1.44	0.14
70	0.0100	2.991	2.61	2.44	0.17
70	0.1010	4.905	1.53	1.40	0.13
70	0.0110	4.987	2.56	2.37	0.19
70	0.5143		0.95	0.88	0.06
70	1.019		0.65	0.54	0.11
70	3.045		0.10	-0.01	0.11
80	0.00982	0.09048	2.58	2.58	0.00
80	0.1004	0.4001	1.55	1.55	0.00
80	0.01030	0.4901	2.54	2.54	0.00
80	0.01030	0.9751	2.53	2.53	0.00
80	0.1000	2.900	1.48	1.51	-0.03
80	0.01000	2.991	2.48	2.51	-0.03
80	0.1006	4.9054	1.42	1.51	-0.03
80	0.01100	4.987	2.42	2.47	-0.05
Russell et al. (1955)					
50	0.4991		1.19	1.10	0.09
50	1.2505		0.78	0.63	0.15
60	0.5001		1.06	0.93	0.13
60	1.2358		0.66	0.48	0.18
60	2.2422		0.34	0.18	0.16
60	2.5145		0.28	0.12	0.16
60	2.9478		0.19	0.04	0.15
60	3.8545		0.03	0.09	0.12
90	0.5172		0.76	0.71	0.05
90	1.2252		0.36	0.29	0.07
90	2.2420		0.06	0.00	0.06
90	2.5050		0.00	-0.06	0.06
90	2.9160		-0.08	-0.13	0.05
90	3.8170		-0.23	-0.26	0.03
(1) $\Delta\text{pAl} = \text{pAl}(\text{measured}) - \text{pAl}(\text{calculated})$, where $\text{pAl} = -\log(m_{\text{Al}})$.					

control Al transport in sedimentary, hydrothermal, and metamorphic processes.

3.5. Analysis of Literature Solubility Data

The thermodynamic properties of $\text{NaAl}(\text{OH})_4^0$, $\text{Al}(\text{OH})_4^-$, and $\text{Al}(\text{OH})_3^0$ derived in this study can be used to predict mineral solubilities in alkaline solutions over a wide range of temperature and pressure. The comparison of calculated and experimental solubilities provides a test of the quality of the thermodynamic data retrieved in the present study and the speciation scheme selected for aqueous Al. In this section experimental solubilities of gibbsite, boehmite, and corundum in Na-bearing solutions are compared to the calculated solubilities.

3.5.1. Gibbsite

Gibbsite solubilities in NaOH–NaCl solutions at temperatures from 25 to 90°C were reported by Russell et al. (1955) and Wesolowski (1992). Most of these data are compared to calculated solubilities in Table 8. Calculated solubilities were generated with the aid of the Genthon (1992) computer code

Table 9. Calculated solubilities of boehmite compared to literature experimental data.

T°C	NaOH mol/kg	pAl measured	pAl calculated	ΔpAl (1)
Russell et al. (1955)				
100	2.24	0.27	0.26	0.01
100	2.53	0.21	0.20	0.01
100	2.94	0.14	0.12	0.02
100	3.93	0.00	-0.03	0.03
150	2.26	0.06	0.06	0.00
150	2.52	0.01	0.00	0.01
150	2.98	-0.07	-0.08	-0.01
150	2.94	-0.07	-0.07	0.00
150	3.91	-0.21	-0.21	0.00
150	5.24	-0.39	-0.35	0.04
170	2.27	-0.01	-0.02	-0.01
170	2.53	-0.06	-0.07	-0.01
170	2.96	-0.13	-0.15	-0.02
170	2.96	-0.14	-0.15	-0.01
170	3.78	-0.27	-0.26	0.01
170	5.11	-0.46	-0.41	0.05
Kuyunko et al. (1983)				
200	0.025	1.90	1.93	-0.03
200	0.50	0.60	0.57	0.03
200	2.41	-0.15	-0.15	0.00
200	5.08	-0.48	-0.49	0.01
250	0.025	1.79	1.80	-0.01
250	0.50	0.48	0.46	0.02
250	2.41	-0.24	-0.24	0.00
250	5.08	-0.58	-0.57	0.01

(1) $\Delta pAl = pAl(\text{measured}) - pAl(\text{calculated})$, where $pAl = -\log(m_{Al})$.

(see the section on the calculation of chemical equilibria) using gibbsite K_{S4} dissociation constants taken from Wesolowski and Palmer (1994) and thermodynamic properties of aqueous species reported in Table 6. The activity coefficients of charged aqueous species were computed using Eqn. 7 and parameters reported by Helgeson et al. (1981). Activity coefficients for neutral species were assumed to be unity. The activity of H_2O was assumed to be equal to one except for calculations performed to replicate the gibbsite solubility measurements of Russell et al. (1955) which were performed in concentrated NaOH solutions. For these latter calculations the H_2O activities reported by Russell et al. (1955) were adopted in the calculations. It can be seen in Table 8 that the solubilities calculated in this study reproduce within 0.1 log unit of Al concentration the large bulk of these solubility data. It should be noted, however, that the calculated solubilities are systematically slightly higher than their experimental counterparts and this difference increases with increasing sodium concentration and decreasing temperature. Typically, in ~ 1 m NaCl solutions, this difference increases from less than 0.02 log units at 80°C to approximately 0.15 at 25°C. The difference reaches 0.28 in 5 m NaCl solutions at 25°C. To perfectly fit all the solubility measurements performed by Wesolowski (1992) at 25°C, the $NaAl(OH)_4^0$ association constant needs to be ~ 0.5 log units lower than that obtained in the present study. Such a low association constant value would not, however, be consistent with the potentiometric determinations performed in this study at temperatures between 75 and 150°C. Because the calculated gibbsite solubilities depend heavily on pH, these differences may stem from uncer-

tainties in NaOH dissociation constants over the 25–100°C temperature interval. For example, values reported in the literature for NaOH dissociation constant at 25°C differ by more than one order of magnitude (see review in Pokrovskii and Helgeson, 1995). It should be emphasized in this regard that the potentiometric measurements of the $NaAl(OH)_4^0$ association constant performed in this study did not require knowledge of the $NaOH^0$ dissociation constant.

3.5.2. Boehmite

Boehmite solubilities measured by Russell et al. (1955) and Kuyunko et al. (1983) in NaOH solutions to 250°C are compared in Table 9 to those calculated in this study. For these calculations boehmite K_{S4} values were taken from Castet et al. (1993) and H_2O activities were taken from Russell et al. (1955). The thermodynamic properties of aqueous species were taken from the same sources listed above for the gibbsite solubility calculations. It can be seen from the values reported in Table 9 that there is an excellent agreement (better than 0.05 pAl units) between calculated and measured boehmite solubilities, even in solutions containing as much as 5 m NaOH. It should be noted that the $NaOH^0$ dissociation constant is better known over the 100–250°C temperature interval than at temperatures below 100°C. The results listed in Table 9 provide further support for the values of $NaAl(OH)_4^0$ association constant generated in this study.

3.5.3. Corundum

Corundum solubilities in NaOH solutions at temperatures from 400 to 700°C and pressures to 2.5 kbar have been reported by Barns et al. (1963) and Pascal and Anderson (1989). A number of these solubilities are represented as a

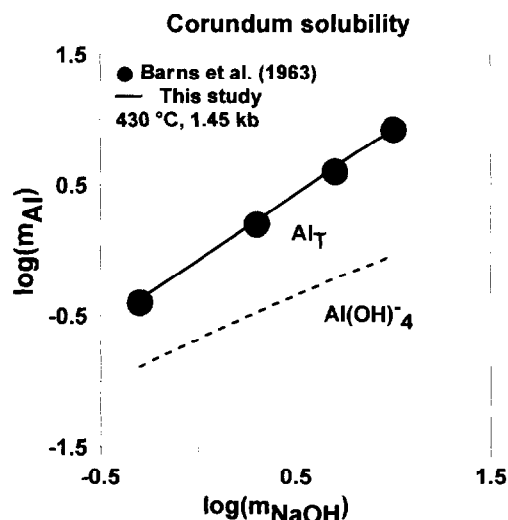


FIG. 7. Logarithm of corundum solubility in NaOH solutions at 450°C and 1.45 kbar. The symbols represent experimental measurements from Barns et al. (1963), but the curves were generated independently in the present study using data and parameters taken from Tables 5 and 6. NaOH dissociation constant for 450°C and 1.45 kbar was taken from Ho and Palmer (1994): $K_{D,NaOH} = 0.024$. Note that computed $Al(OH)_4^0$ concentration was too low ($\log m_{Al(OH)_4^0} = -6.4$) to be depicted in the figure.

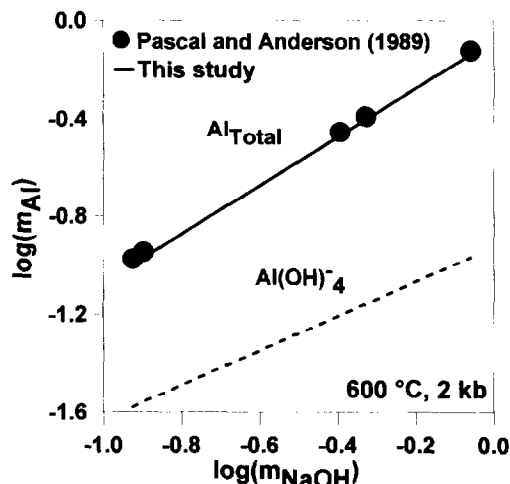


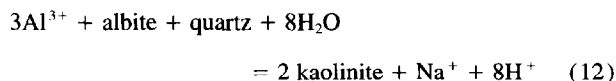
FIG. 8. Logarithm of the solubility of corundum in NaOH solutions at 600°C and 2 kbar. The symbols represent experimental measurements from Pascal and Anderson (1989) but the curves were generated independently in the present study using data and parameters taken from Tables 5 and 6. NaOH dissociation constant for run conditions (600°C, 2 kbar) was taken from Ho and Palmer (1994): $K_{D,NaOH} = 2.29 \cdot 10^{-3}$. Note that computed $Al(OH)_4^-$ concentration was too low ($\log m_{Al(OH)_4^-} = -6.7$) to be depicted in the figure.

function of NaOH concentration in Figs. 7 and 8. The solid curves in these figures correspond to the calculated total dissolved Al, but the dashed lines illustrate the molalities of individual aqueous aluminum species. For these calculations, the thermodynamic properties of corundum were taken from Robie et al. (1978) (see Table 5); those for H_2O from SUPCRT92 (Johnson et al., 1992) and NaOH dissociation constants were calculated from the equation proposed by Ho and Palmer (1994). The thermodynamic properties of aqueous Al species were calculated using the standard molal thermodynamic properties and HKF equation of state coefficients given in Table 6. It can be seen in Figs. 7 and 8 that the solubility curves, generated independently of the experimental data represented by the symbols, are in close agreement with their experimental counterparts (within ± 0.02 log units) at temperatures as high as 600°C and pressures to 2 kbar. Moreover, the Na-aluminate complex dominates Al speciation at all the temperatures and pressures depicted in these figures. As temperature increases, the proportion of sodium-aluminate complex increases (from 69% at 400°C, 1.45 kbar to 82% at 600°C, 2.14 kbar in 0.5 m NaOH solution), but the total Al concentration is essentially unaffected. Note that calculated corundum solubilities are relatively insensitive to the value of $NaAl(OH)_4^0$ association constant. For example, decreasing this value by one order of magnitude at 430°C and 2 kbar leads to a sharp decrease of $NaAl(OH)_4^0$ concentration but doesn't significantly change the calculated corundum solubility. As a result, corundum solubility measurements as a function of NaOH concentration cannot be used to generate accurate values of $NaAl(OH)_4^0$ association constant.

3.6. Effect of Na-aluminate Complexes on the Al Contents of Solutions in Equilibrium with Aluminosilicates

The mineral assemblages albite-quartz-kaolinite and Kfeldspar-muscovite-quartz were selected to illustrate the possible

role of Na-Al complexing on Al transport in crustal fluids. The effect of Na-Al complex formation on Al mobility in sedimentary basins was computed by calculating Al concentrations in a 1 m NaCl solution in equilibrium with the albite-quartz-kaolinite assemblage at 200°C and 1 kbar. This calculation was performed within the framework of the "Density model" (Anderson et al., 1991) using an equilibrium constant for the reaction:



generated from the data reported by Bowers et al. (1984), Al hydrolysis constants calculated from thermodynamic data reported by Castet et al. (1993), and the thermodynamic properties for $NaAl(OH)_4^0$ generated in this study. It can be seen in Fig. 9 that NaCl can significantly affect the solubility and transport of aluminum in sedimentary basin, as the addition of 1 m NaCl to this system increases the equilibrium Al concentration by a factor of 3–4 at $pH > 4$. Comparison of the relative importance of Na-Al and organic acid anions-Al complexes in sedimentary basins shows that the effects of acetate, which can be present at concentrations in excess of 3000 ppm in oil field waters, is roughly of the same magnitude as the presence of 1 m NaCl. For example, Bénézech et al. (1994) found that the addition of 10,000 ppm acetate to a solution in equilibrium with the mineral assemblage albite-kaolinite-quartz at 170°C increases the equilibrium Al activity by as much as a factor of 5–7 at $pH < 3.5$ –4 but has little or no effect in the solutions of higher pHs, typical of many sedimentary basin fluids. Dicarboxylic anions like oxalate or malonate form stronger complexes with Al than acetate. Fein (1994) calculated that the presence of 500 ppm oxalate may enhance gibbsite solubility at 80°C by ~ 2 –3 orders of magnitude over a wide pH range, from ~ 3.5 to ~ 6 . The presence of significant amounts (> 100 ppm) of dicarboxylic acid in

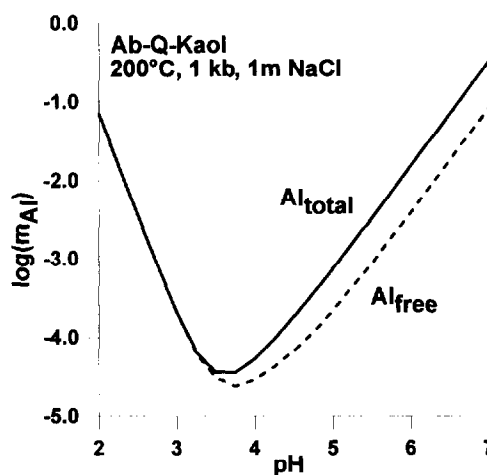


FIG. 9. Calculated Al concentration as a function of the pH in an aqueous solution containing 1 m NaCl in equilibrium with the mineral assemblage Albite-Quartz-Kaolinite at 200°C and 1 kbar. The amount of Al complexed with sodium is given by difference between calculated total Al (solid line) and free Al (dashed line). Free Al corresponds to the Al that is not complexed by Na ($m_{Al\text{ free}} = m_{Al^{3+}} + m_{Al(OH)^{2+}} + m_{Al(OH)_2^+} + m_{Al(OH)_3^0} + m_{Al(OH)_4^-}$).

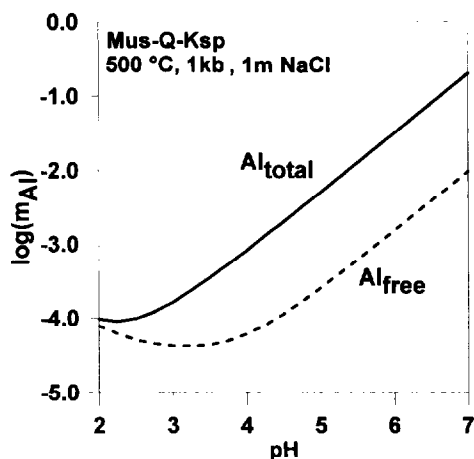
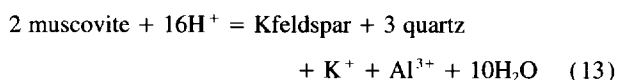


FIG. 10. Calculated Al concentration as a function of the pH in an aqueous solution containing 1 m NaCl in equilibrium with the mineral assemblage Muscovite-Quartz-Kfeldspar at 500°C and 1 kbar. The amount of Al complexed with sodium is given by difference between calculated total Al (solid line) and free Al (dashed line). Free Al corresponds to the Al that is not complexed by sodium ($m_{\text{Al free}} = m_{\text{Al}^{3+}} + m_{\text{Al(OH)}}^{2+} + m_{\text{Al(OH)}}^{+} + m_{\text{Al(OH)}}^0 + m_{\text{Al(OH)}}^{-}$).

oil field waters, however, has been recently questioned by several authors (Hanor et al., 1993; Kharaka et al., 1993; MacGowan and Surdam, 1993).

Na-Al complexing is also likely to considerably increase Al mobility in metamorphic fluids. An example of the role of Na-Al complexing in metamorphic fluids is illustrated in Fig. 10. Figure 10 depicts the computed Al concentration in a 1 m NaCl solution in equilibrium with the muscovite-quartz-Kfeldspar assemblage at 500°C and 1 kbar as a function of pH. The equilibrium constant for the reaction:



was calculated from the data of Bowers et al. (1984), Castet et al. (1993), and the present study as for reaction 12.[†] It can be seen that the addition of only one mole of NaCl rises the total Al in solution by a factor ~ 20 at all pH above 4. At these conditions, NaAl(OH)_4^0 accounts for 95% of the total Al concentration. The results depicted in Figs. 9 and 10 demonstrate that explicit account must be made for Na-Al complexation to accurately compute the fluid chemistry and transport properties of Al both in sedimentary basin and metamorphic fluids.

4. CONCLUDING REMARKS

1) Boehmite solubility measurements performed in Na-bearing solutions at temperatures from 125 to 350°C and potentiometric measurements performed at temperatures from 75 to 200°C with sodium selective glass electrodes were used to determine the stoichiometry and the stability constants of the Na-aluminate ion pair. Association constant values derived from potentiometric and solubility measurements were

found to be in close agreement. The complex has a 1:1 Na:Al stoichiometry and an association constant that increases markedly with temperature.

2) Experimental data obtained in this study were combined with boehmite solubility data (Castet et al., 1993) to generate, within the framework of the revised HKF model, standard partial molal properties and equations of state parameters for Al(OH)_4^- , Al(OH)_3^0 , and NaAl(OH)_4^0 .

3) The validity of the Al(OH)_4^- and NaAl(OH)_4^0 thermodynamic properties retrieved in the present study is supported by the close correspondence between calculated boehmite and gibbsite solubilities in Na-rich solutions and their experimental counterparts.

4) Species distribution calculations indicate that the formation of Na-Al complexes enhances Al concentration in sedimentary basin and metamorphic fluids. Thus, NaAl(OH)_4^0 likely controls Al transport in many crustal fluids.

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Update

Geochimica et Cosmochimica Acta

Volume 60, Issue 11, June 1996, Page 2061

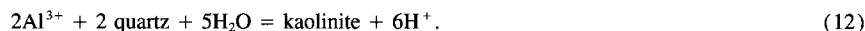
DOI: [https://doi.org/10.1016/0016-7037\(96\)88556-5](https://doi.org/10.1016/0016-7037(96)88556-5)



ERRATUM

Erratum to I. Diakonov, G. Pokrovski, J. Schott, S. Castet, and R. Gout (1996) "An experimental and computational study of sodium-aluminum complexing in crustal fluids." *Geochimica et Cosmochimica Acta* **60**, 197–211.

The first eleven lines of the first paragraph of section 3.6. should be replaced by: "The mineral assemblage quartz-kaolinite and corundum were selected to illustrate the possible role of Na-Al complexing on aluminum transport in crustal fluids. The effect of Na-Al complex formation on Al mobility in sedimentary basins was computed by calculating Al concentrations in a 1 m NaCl solution in equilibrium with the quartz-kaolinite assemblage at 200°C and 1 kbar. This calculation was performed within the framework of the "Density model" (Anderson et al., 1991) using an equilibrium constant for the reaction:



The third and fourth sentence of the second paragraph of section 3.6. should be replaced by: "Figure 10 depicts the computed Al concentration in a 1 m NaCl solution in equilibrium with corundum at 500°C and 1 kbar as a function of pH. The solubility of corundum was calculated from the data of Robie et al. (1978), Castet et al. (1993), and the present study as for reaction (12)."

Figures 9 and 10 should be replaced by the figures shown below.

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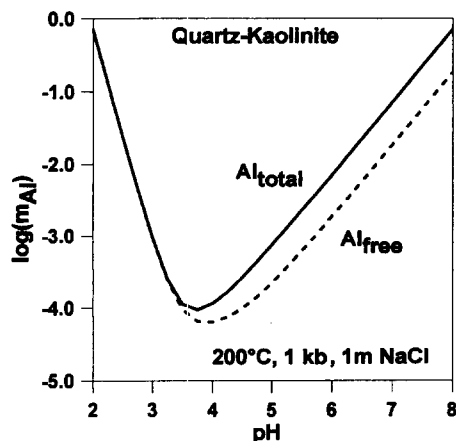


FIG. 9. Calculated Al concentration as a function of the pH in an aqueous solution containing 1 m NaCl in equilibrium with the mineral assemblage Quartz-Kaolinite at 200°C and 1 kbar. The amount of Al complexed with sodium is given by difference between calculated total Al (solid line) and free Al (dashed line). Free Al corresponds to the aluminum that is not complexed by sodium ($m_{\text{Al free}} = m_{\text{Al}^{3+}} + m_{\text{Al}(\text{OH})^{2+}} + m_{\text{Al}(\text{OH})_2^+} + m_{\text{Al}(\text{OH})_3^0} + m_{\text{Al}(\text{OH})_4^-}$).

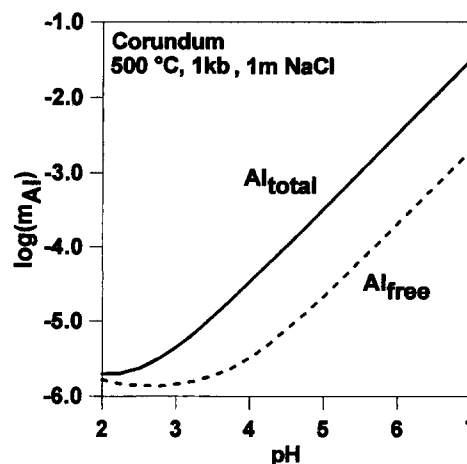


FIG. 10. Calculated Al concentration as a function of the pH in an aqueous solution containing 1 m NaCl in equilibrium with corundum at 500°C and 1 kbar. The amount of Al complexed with sodium is given by difference between calculated total Al (solid line) and free Al (dashed line). Free Al corresponds to the aluminum that is not complexed by sodium ($m_{\text{Al free}} = m_{\text{Al}^{3+}} + m_{\text{Al}(\text{OH})^{2+}} + m_{\text{Al}(\text{OH})_2^+} + m_{\text{Al}(\text{OH})_3^0} + m_{\text{Al}(\text{OH})_4^-}$).