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Experimental study of the stability of aluminate-borate complexes in hydrothermal solutions

Boris Tagirov,* Jacques Schott, Jean-Claude Harrichoury, and Jocelyne Escalier

Géochimie: Transferts et Mécanismes, CNRS-OMP-Université Paul-Sabatier, 38 rue des 36 Ponts, 31400 Toulouse, France

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Abstract—Formation of aqueous aluminate-borate complexes was characterized at 25°C using ^{27}Al NMR spectroscopy, and at 50–200°C via measurements of gibbsite and boehmite solubility in the presence of boric acid. ^{27}Al spectra performed at pH = 9 in Al-B solution with m(B) = 0.02 show the presence of two peaks at 80.5 and 74.5 ppm which correspond to $Al(OH)_4^-$ and a single Al-substituted Q^1_{Al} dimer, $Al(OH)_3OB(OH)_2^-$, respectively. In 0.08 m and 0.2 m borate solution, a third peak appears at 68.5 ppm which can be assigned to the Q^2_{Al} trimer $Al(OH)_2O_2(B(OH)_2)_2^-$. These chemical shifts are close to those measured for $Al(OH)_3OSi(OH)_3^-$ and $Al(OH)_2O_2(Si(OH)_3)_2^-$ (74 and 69.5 ppm, respectively; Pokrovski et al., *Min. Mag.***62a** (1998), 1194) which demonstrates the similar structure of Al-B and Al-Si complexes formed in alkaline solutions. Gibbsite and boehmite solubility were measured in weakly basic solutions as a function of boric acid concentration at 50°C and 78 to 200°C, respectively. Equilibrium was reached within several days at m(B) = 0.01–0.1, but more slowly at higher boron concentrations, and at 50°C and m(B) = 0.2, Al concentration increased continuously during at least 3 months as a result of the sluggish formation of Al-polyborates. The equilibrium constant of the reaction $Al(OH)_4^- + B(OH)_3{}^0{}_{(aq)} = Al(OH)_3OB(OH)_2^- + H_2O$ decreases very slowly with increasing temperature to 200°C. The log K values are 1.58 ± 0.10, 1.46 ± 0.10, 1.52 ± 0.15, and 1.25 ± 0.15 at 50, 78, 150 and 200°C, respectively, which result in the following values of the standard thermodynamic properties for this reaction: $\Delta_rG^0 = -9.22 \pm 3.25$ kJ/mol, $\Delta_rH^0 = -4.6 \pm 2.5$ kJ/mol, $\Delta_rS^0 = 15.5 \pm 6.9$ J/mol K. The thermodynamic data generated in this study indicate that Al-B complexes can dominate aqueous aluminum speciation in solutions containing ≥0.7 g/L of boron at temperature to at least 400°C. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

This work represents a part of a series of papers aimed at characterizing the structure and stability constants of the complexes formed between aluminum and geologically important ligands. Recently Pokrovski et al. (1998) and Salvi et al. (1998) have determined the stability of complexes formed by $Al(OH)_4^-$ and $Si(OH)_4^0$ and established that these species can dominate Al speciation in quartz-saturated neutral to alkaline natural fluids. Aqueous boric acid (H_3BO_3) exhibits chemical properties similar to those of silicic acid (H_4SiO_4). These weak acids exhibit close values of their first dissociation constant (log $K_d(H_3BO_3) = -9.24$ and log $K_d(H_4SiO_4) = -9.46$ at 25°C, Baes and Mesmer, 1976), and their dissociation products—borate ($H_2BO_3^-$) and silicate ($H_3SiO_4^-$) anions—are both hard (class "a") ligands according to Pearson's (1963) classification. Therefore, it is tantalizing to investigate the possibility of aluminate-boric acid complexing in aqueous solutions. Formation of these complexes can be favored by the abundance of boron in hydrothermal solutions and granite-derived fluids. Its concentration varies in the limits of 0.1–1.0 g/L (~0.01–0.1 m) in high temperature geothermal brines and orthomagmatic fluids (Yardley and Shmulovich, 1994). Besides, fluid inclusions with sassolite (H_3BO_3) crystals were recently discovered in tourmaline bearing miarolitic pegmatites sampled throughout the world (Peretyazhko et al., 2000). Calculated boric acid concentration in these fluids is 2.4–26 wt% (~0.4–4 m). The aim of the present study is to use ^{27}Al NMR spectroscopy and solubility measurements of gibbsite and boehmite in boric acid-bearing solutions to characterize the stoichiometry and stability of the aqueous complexes formed between aluminum and boric acid.

2. MATERIALS AND METHODS

2.1. ^{27}Al NMR Spectroscopy

^{27}Al NMR spectra were performed at pH = 8.95 ± 0.05 for three solutions with m(Al) = $4.6 \cdot 10^{-4}$m ± 0.4, and $m(B(OH)_3)$ = 0.02, 0.08, and 0.2. Alkaline Al stock solution (~0.05 mol/L) was prepared as follows (Gleb Pokrovski, private communication): 0.37 g of $AlCl_3 \cdot 6H_2O$ Riedel: pure, was dissolved in ~7–10 g of deionized H_2O. 1 mol/L $(CH_3)_4NOH$ solution (Aldrich A.S.C. reagent) was added under stirring to this $AlCl_3$ solution until the $Al(OH)_3$ precipitate, that first formed, completely redissolved (~7 g of $(CH_3)_4NOH$ are added). The obtained solution was completed with deionized H_2O to ~30 g. Finally, it was filtered through a 0.45 μm "Sartorius" cellulose nitrate filter. Measured pH value was ~12 which corresponds to 0.2–0.25 m of $(CH_3)_4NOH$. Boron 0.4 m stock solution was prepared from B_2O_3 Prolabo for analysis. Test solutions were prepared just before NMR analysis by the following method. Stock solutions were diluted to obtain concentrations of 2.5 times higher than those in the test solution. Then boric acid solution was slowly added to an equal volume of well stirred aluminate solution. During this operation pH was kept at ~9 by addition of ~15% NH_4OH solution. Finally,

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* Author to whom correspondence should be addressed, at Institut für Mineralogie und Petrographie, ETH-Zentrum, Sonneggstrasse 5, CH-8092 Zürich, Switzerland (boris.taguirov@erdw.ethz.ch).

H_2O was added to get the desired Al concentration. Al concentration and pH were measured before and after spectra acquisition and were always in the range $4.6 \cdot 10^{-4}$ m ± 0.4 and 8.95 ± 0.05, respectively, despite the fact that these solutions were supersaturated with respect to gibbsite.

^{27}Al NMR spectra were obtained using a Bruker AM 300 spectrometer equipped with a 10-mm multinuclear probe head. Samples were kept at ambient temperature (25 ± 2°C). To perform quantitative measurements, 3 mL of solution were placed in a 10-mm inner diameter glass tube. A 3-mm glass tube filled with D_2O and inserted in the 10-mm tube was used as field-frequency lock. ^{27}Al one-pulse experiments were performed at 78.206 MHz with a $\pi/6$ duration of 6 μs and a recycle time of 2 s. About $1 \cdot 10^5$ acquisitions were performed for each spectrum. NMR spectra were treated using DISR computer code supplied by Bruker Co. Exponential multiplication with line-broadening of 3 Hz was employed (Claridge, 1995), and the spectra were referenced to a 0.1 M aqueous solution of $Al(NO_3)_3$ ($Al(H_2O)_6^{3+}$).

2.2. pH Measurements

At ambient temperature and at 50°C and 78°C, pH was measured using a Schott H62 combination glass electrode standardized on the activity scale using DIN 19266/NBS standards (pH = 6.865 and 9.180 at 25°C). Accuracy of measurements was ±0.02 pH unit.

To check the validity of pH calculations carried out in this study, pH of several solutions with solute concentrations close to those used in the solubility experiments was measured at 100–175°C using a high-temperature potentiometric cell. Design of the cell is described elsewhere (Pokrovski et al., 1995; Zotov et al., 2002). The cell

Cu, Li-Sn alloy | H^+ selective glass S-121 | Test solution || 3.5M KCl | Ag, AgCl, Cu

20°C ⟵ 100-175°C ⟶ ⟵20°C⟶

consisted of 3 high-temperature solid-contact glass pH electrodes (Beliustin et al., 1992) together with the Ag/AgCl, 3.5 mol/L KCl external reference electrode thermostated at ambient temperature. Electrochemical cell calibrations were performed using 0.01 m HCl, 0.025 m NaAc + 0.025 m HAc, 0.08 m NaAc + 0.02 m HAc, 0.01 m $Na_2B_4O_7$, and 0.01 m NaOH (Ac stands for acetate). Calibration curves for one of the 3 electrodes are given in Figure 1. As the nonisothermal salt bridge contained a concentrated KCl solution flowing very slowly into the test solution, the liquid junction potential was taken to be zero for any test solution composition. Uncertainty on the measured e.m.f. values, confirmed by several measurements performed in the same solution was in the limits ±2 mV thus yielding uncertainty on calculated pH values of ±0.03 pH unit. Overall uncertainty on pH values measured at 100–175°C was ±0.05 pH unit.

2.3. Solubility Measurements

2.3.1. *Preparation of Solids and Experimental Solutions*

Gibbsite (α-$Al(OH)_{3(s)}$) was prepared following the method described in Wesolowski (1992). The raw material (~25 g) obtained from Riedel De Haen AG Seelze-Hannover (2504361) was grounded and washed several times with deionized water until the supernatant became clear within few minutes. It was then filtered through a Whatman phase separator, then placed in a Nalgene polypropylene bottle together with 1 L of 1 mol/L HCl and kept there for a period of ~10 d with periodical stirring. The obtained powder was again filtered, washed several times with deionized water on the filter and then many times by decantation until the pH of supernatant stabilized at ~6. Finally it was dried at 40°C during several days. XRD diffraction peaks of this product corresponded to synthetic gibbsite (JCPDS card 33–18). Gibbsite water content was 33.8 wt% as determined by thermogravimetric analysis (theoretical value is 36.4 wt%).

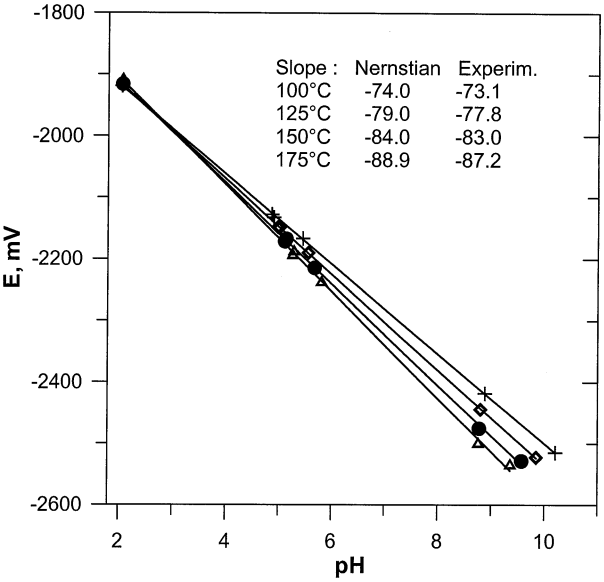

Fig. 1. Calibration curves at 100, 125, 150, and 175°C of the solid-contact glass electrode used in this study.

The method of boehmite (γ-AlOOH) synthesis is described elsewhere (Castet et al., 1993; Diakonov et al., 1996). Briefly, it consisted in reacting synthetic gibbsite with deionized water in titanium rocking autoclaves at 300°C and P_{sat}. Final product was washed with a large amount of deionized water and dried at 70°C during several days. XRD peaks of the obtained boehmite corresponded to JCPDS card 21–1307. The water content of this material was 15.7 wt% of H_2O (theoretical value is 15.0 wt%).

Experimental solutions were prepared using deionized water, Analytical Reagents Prolabo and Merck NaCl, $NaHCO_3$, $Na_2B_4O_7 \cdot 10\,H_2O$, $B(OH)_3$, NH_4Cl, Carlo Erba Reagento Puro 29% NH_3, and Merck Titrisol 1 M HCl and NaOH solutions. Doubly distilled HNO_3 was used to acidify sampled solutions and to prepare standard solutions for Al analyses.

2.3.2. *Solubility Measurements*

Experiments at 50°C and 78°C were performed in polypropylene flasks (gibbsite) and titanium reactors (boehmite), respectively. About 200 mL of the experimental solution was placed into the reactor (flask) together with 0.25 g of the solid phase. Reactors (flasks) were hermetically closed and immersed into a thermostated (within ±1°C) water bath. A hole in the cover allowed sampling of the solution by means of a 20 mL polyethylene syringe. The samples were immediately filtered at run temperature into 0.5 mol/L HNO_3 using a titanium filtration cell with a 0.22–0.45 μm Sartorius cellulose nitrate membrane.

Boehmite solubility measurements at 150 and 200°C were performed at P_{sat}. Experiments were carried out in pure titanium autoclaves placed in rocking furnaces which allow mixing of experimental solutions and thus minimization of temperature gradients (see description in Salvi et al., 1998). The autoclaves design enables injection of boehmite or a solution, as well as solution sampling, at run conditions. Temperature in the autoclaves was maintained constant (±1°C) and measured with externally calibrated thermocouples. About 250 mL of a NH_3/NH_4Cl boron-free solution was heated to the desired temperature and a first sample was taken and analyzed for a blank of Al. If measured concentration was <20 ppb, ~0.25 g of boehmite was injected into the autoclave. During sampling, solution was first filtered through a 5 μm in situ Ti filter, and then it was passed through a 0.22–0.45 μm Sartorius cellulose nitrate filter directly into 0.5 mol/L HNO_3 to obtain a ~0.1 mol/L HNO_3 sample solution. After equilibration of boehmite with the boron-free solution, a 1 M boric acid solution prepared by dissolution of H_3BO_3 in the starting NH_3/NH_4Cl solution was injected into the autoclave. Samples for boron analysis were taken into H_2O.

2.4. Analytical Methods

Aluminum concentration was determined by flame or flameless atomic absorption spectroscopy (Perkin Elmer Zeeman 5100 PC spectrophotometer). For the concentration range 5–50 ppm, in solutions prepared for ^{27}Al NMR spectroscopy, an acetylene-nitrous oxide flame was used. Accuracy of measurements was ±3%. A graphite furnace was used to measure Al concentration for solubility experiments over the range 5–55 ppb. A special program was developed to perform Al analyses in the presence of boron. This program includes the following steps: drying 1 at 100°C (30 s), drying 2 at 110°C (40 s), pyrolysis at 1800°C (30 s), atomization at 2500°C (3 s), and clean-out at 2600°C (6 s). Analyses were performed in 0.1 mol/L HNO_3. $Mg(NO_3)_2$ (1 wt% aqueous solution) was added to all samples as a matrix modifier. Detection limit calculated as 2 standard deviations of blank was 0.9 ppb, and reproducibility was ±3% at a 95% confidence level. A typical calibration curve obtained for the boron-free solutions is presented in Figure 2a. Figure 2b demonstrates that measured Al concentrations are independent on boron concentration to at least m(B) = 0.01. Before analysis, all samples were diluted to match this boron concentration limit.

Boron concentrations in solubility experiments at 150 and 200°C were determined over the concentration range 2–7.5 ppm with an Autoanalyser II Technicon colorimeter using the Azomethine H method. Reproducibility of boron concentrations monitored during experiments was ±1%.

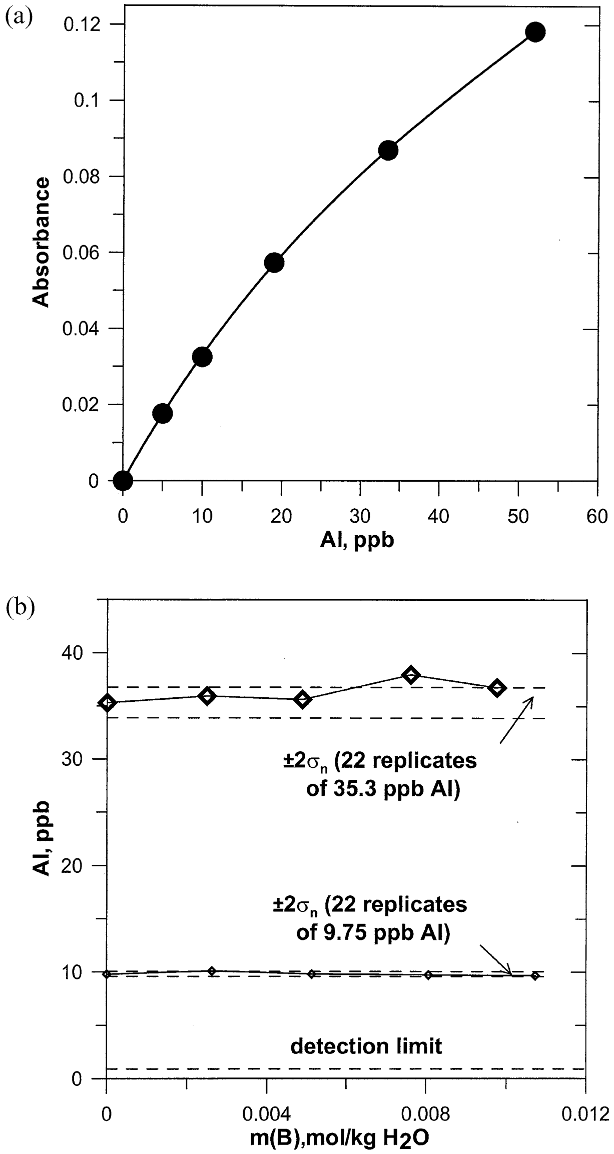

Fig. 2. Characterization of the AAS method of Al analysis. (a) Typical calibration curve. (b) Al concentration calculated using the calibration curve given in (a) for solutions containing 9.75 and 35.3 ppb of Al, but different concentrations of $Na_2B_4O_7$.

2.5. Speciation Calculations

Standard state adopted in the present study for the aqueous species was unit activity for a hypothetical, one molal ideal solution. For pure solid phase and H_2O, the standard state corresponds to a unit activity of the pure phase at given temperature and pressure. The activity coefficients of charged aqueous species were calculated according to Helgeson (1969)

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B\,\text{å}\,\sqrt{I}} + \Gamma_\gamma + B \cdot (T) \cdot I \qquad (1)$$

Γ_γ designates the mole fraction to molality conversion factor ($\Gamma_\gamma = -\log(1 + 0.0180153m^*)$ with m* standing for the sum of the concentrations of all solute species); $B\cdot$ corresponds to the deviation function at any given temperature; z_i denotes the charge of ith species; å, the ion size parameter, is taken equal to 4.5 Å for all species. For neutral species it was assumed

Table 1. Literature values of the logarithms of the dissociation constants of solution components used in the present study.

Species	25°C	50°C	78°C	100°C	125°C	150°C	175°C	200°C
H_2O[1]	−14.00	−13.27	−12.64	−12.26	−11.90	−11.63	−11.43	−11.28
$NaOH$[2]	0.21	0.19	0.15	0.12	0.07	0.01	−0.06	−0.15
$NaCl$[3]	0.78	0.69	0.57	0.47	0.35	0.21	0.06	−0.09
HCl[4]	0.71	0.83	0.85	0.81	0.70	0.54	0.34	0.10
H_2CO_3[5]	−6.35	−6.28	−6.31	−6.40	−6.54	−6.72	−6.94	−7.19
NH_3[6]	−4.74	−4.73	−4.77	−4.85	−4.97	−5.11	−5.28	−5.48
NH_4Cl[7]	0.67	0.78	0.90	0.98	1.00	0.96	0.84	0.64
$B(OH)_4^-$[8]	−4.76	−4.19	−3.63	−3.31	−2.98	−2.70	−2.46	−2.27
$NaB(OH)_4$[9]	−0.28	−0.29	−0.34	−0.40	−0.49	−0.59	−0.70	−0.81
$B_2O(OH)_5^-$[10§]	−4.70	−4.19	−3.74	−3.41	−3.11	−2.86	−2.64	−2.45
$B_3O_3(OH)_4^-$[11§]	−6.81	−5.99	−5.24	−4.70	−4.18	−3.72	−3.32	−2.96
$B_4O_5(OH)_4^{2-}$[12§]	−12.20	−10.32	−8.71	−7.60	−6.60	−5.78	−5.10	−4.54
CH_3COOH[13]	−4.76	−4.79	−4.86	−4.94	−5.05	−5.18	−5.33	−5.52
CH_3COONa[14]	0.10	0.07	−0.03	−0.14	−0.27	−0.43	−0.60	−0.78
$NaAl(OH)_4$[15]	0.10	−0.07	−0.23	−0.35	−0.48	−0.61	−0.74	−0.87

[1] $H_2O = H^+ + OH^-$ (SUPCRT92, Johnson et al., 1992).
[2] $NaOH = Na^+ + OH^-$ (Shock et al., 1997).
[3] $NaCl = Na^+ + Cl^-$ (SUPCRT92, Johnson et al., 1992).
[4] $HCl = H^+ + Cl^-$ (Tagirov et al., 1997).
[5] $H_2CO_3 = H^+ + HCO_3^-$ (Patterson et al., 1982).
[6] $NH_3 + H_2O = NH_4^+ + OH^-$ (SUPCRT92, Johnson et al., 1992).
[7] $NH_4Cl = NH_4^+ + Cl^-$ (interpolation of data given in Castet et al., 1993).
[8] $B(OH)_4^- = B(OH)_3 + OH^-$ (Mesmer et al., 1972).
[9] $Na^+ + B(OH)_4^- = NaB(OH)_4$ (Pokrovski et al., 1995).
[10] $B_2O(OH)_5^- + H_2O = 2\ B(OH)_3 + OH^-$ (Mesmer et al., 1972).
[11] $B_3O_3(OH)_4^- + 3\ H_2O = 3\ B(OH)_3 + OH^-$ (Mesmer et al., 1972).
[12] $B_4O_5(OH)_4^{2-} + 5\ H_2O = 4\ B(OH)_3 + 2\ OH^-$ (Mesmer et al., 1972).
[13] $CH_3COOH = CH_3COO^- + H^+$ (Mesmer et al., 1989).
[14] $CH_3COONa = CH_3COO^- + Na^+$ (SUPCRT92, 1998 update).
[15] $NaAl(OH)_4 = Na^+ + Al(OH)_4^-$ (Diakonov et al., 1996).
§ Original data obtained at I = 1.0 M were extrapolated to the standard state conditions using Eqns. 1 and 2.

$$\log \gamma_n = \Gamma_\gamma \qquad (2)$$

The dissociation constants of aqueous components used in the present study are listed in Table 1. Speciation calculations were performed with the help of GIBBS computer code within the framework of the HCh software package (Shvarov, 1999; Shvarov and Bastrakov, 1999). The pH values computed using dissociation constants listed in Table 1 always agree within ±0.01 unit with those calculated using H_2O dissociation constant determined potentiometrically by Sweeton et al. (1974), and NaCl and NaOH dissociation constants determined via electrical conductivity measurements by Ho et al. (1994) and Ho et al. (2000), respectively. Dissociation constant of NH_3 used in calculations (Table 1) lies between values determined by Hitch and Mesmer (1976) and Read (1982) via potentiometric and conductivity measurements, respectively. The difference of NH_3 dissociation constant determined in these two studies increases with the temperature and reaches 0.1 log unit at 200°C, P_s, that results in 0.1 unit difference of calculated pH for experimental solutions. However, stability constants of Al-B complexes calculated using listed above different sources of dissociation constants for H_2O, NaCl, NaOH, and $NH_{3(aq)}$ always agree within ±0.01 log unit.

2.6. Comparison of Calculated and Measured pH Values

The accurate computing of stability constants for Al-B complexes requires rigorous pH determinations. At 50 and 78°C measured in situ pH values were used in calculations of Al-B stability constants. These measured pH values and those calculated using stability constants listed in Table 1 agree within ±0.03 pH units (accuracy of pH measurements was ±0.02 pH units). At higher temperatures, pH values computed using the thermodynamic properties of aqueous species listed in Table 1 were used in calculation of Al-B complexes stability constants. To check the reliability of these pH calculations, pH values of several $m(B(OH)_3) = 0-0.172$ alkaline solutions measured at 100–175°C are compared in Table 2 with those calculated using the thermodynamic properties of aqueous species listed in Table 1. Measured and calculated pH values for solutions 1–5 (Table 2) are the same within the uncertainty of the measured values. However, pH values measured at 150 and 175°C in solution 6, which exhibits the highest boron concentration ($m(B(OH)_3) = 0.172$), are 0.08 unit lower than those calculated at the same temperatures (values in italic in Table 2). To get calculated pH match measured values, the fraction of boron incorporated into polyborates should be increased from 0.6 to 3% at 150°C and from 0.2 to 3% at 175°C. As a result, to compute the stability constant of Al-B complex in 0.172 m $B(OH)_3$ at 200°C we took a pH value 0.08 unit lower than that calculated using the constants listed Table 1.

3. RESULTS AND DISCUSSION

3.1. ^{27}Al NMR Spectroscopy

^{27}Al NMR spectra of three solutions with total boron concentration 0.02, 0.08 and 0.2 m at pH = 9 are shown in Figure

Table 2. Measured (meas) and calculated (calc) pH values for NH_3-NH_4Cl-$B(OH)_3$ solutions at temperatures 100–175°C. Uncertainty attached to the measured pH values is ±0.05 pH unit.

				100°C		125°C		150°C		175°C	
Solution	$m(NH_3)^1$	$m(NH_4Cl)^1$	$m(B(OH)_3)^1$	Meas	Calc	Meas	Calc	Meas	Calc	Meas	Calc
1	0.0193	0.020	0	7.49^2	7.45	7.07^2	6.99	6.59	6.58	6.23	6.21
2	0.0194	0.020	0.020	7.43	7.43	7.02	6.98	6.56	6.58	6.22	6.21
3	0.0194	0.020	0.0403	7.40	7.40	6.99	6.97	6.55	6.57	6.21	6.21
4	0.0194	0.020	0.0603	7.35	7.37	7.00	6.96	6.54	6.57	6.20	6.21
5	0.0194	0.020	0.101	7.31	7.31	6.93	6.93	6.51	6.55	6.18	6.20
6	0.0200	0.0217	0.172	7.16	7.18	6.85	6.86	*6.43*	*6.51*	*6.09*	*6.17*

[1] [mol/kg H_2O].

[2] Uncertainty of this value is ±0.10 pH unit.

3. The spectra parameters (chemical shift δ and linewidth LW) are given in Table 3. In the absence of boric acid a single peak corresponding to $Al(OH)_4^-$ was observed at 80.5 ppm. The absence of other peaks at 0 ppm $< \delta <$ 80.5 ppm demonstrates that concentration of other hydrolyzed and polymerized Al species was insignificant, which is in agreement with thermodynamic calculations based on available stability constants (cf. Baes and Mesmer, 1976). Al-B complexing in 0.02 m $B(OH)_3$ solution results in the appearance of an additional peak at 74.5 ppm. This chemical shift value is close to that observed for Al-substituted Q^1_{Al} silica dimer (74 ppm, Pokrovski et al., 1998). Therefore, Q^1_{Al} silica and boric acid dimers exhibit similar stoichiometry and structure. Accordingly, the formation reaction of the Al-substituted Q^1_{Al} boric acid dimer $[(OH)_3Al\text{-}O\text{-}B(OH)_2]^-$ can be written as

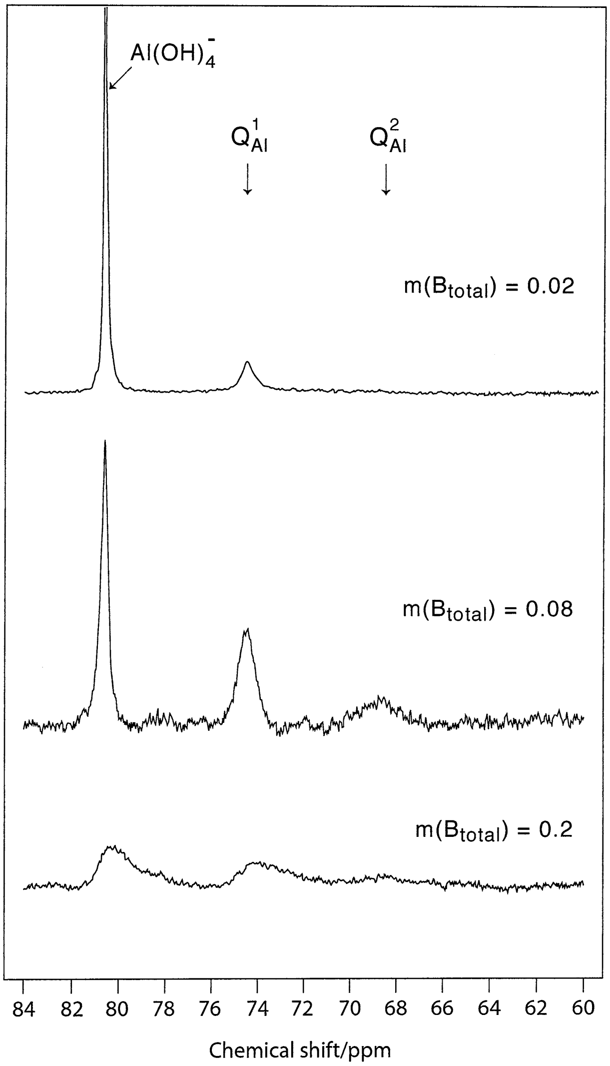

Fig. 3. ^{27}Al NMR spectra of solutions containing $4.6 \cdot 10^{-4}$m of Al and 0.02 m, 0.08 m and 0.2 m of $B(OH)_3$ at pH = 8.95.

$$Al(OH)_4^- + B(OH)^0_{3(aq)} = Al(OH)_3\,OB(OH)_2^- + H_2O \quad (3)$$

A third broader peak appears at 68.5 ppm in 0.08 and 0.2 m $B(OH)_3$ solutions. This chemical shift is almost identical to that observed for the Al-substituted Q^2_{Al} silica trimer $[Al(OH)_2O_2(Si(OH)_3)_2^-]$ (69.5 ppm, Pokrovski et al., 1998). Therefore, this peak can be attributed to Al-substituted Q^2_{Al} boric acid trimer $[(OH)_2B\text{-}O\text{-}Al(OH)_2\text{-}O\text{-}B(OH)_2]^-$

$$Al(OH)_4^- + 2\,B(OH)^0_{3(aq)} = Al(OH)_2O_2(B(OH)_2)_2^- + 2H_2O \quad (4)$$

It should be noted that the $Al(OH)_4^-$ peak at 80.5 ppm significantly broadens in 0.2 m $B(OH)_3$ (LW = 131 Hz vs. 14 Hz for 0.02m $B(OH)_3$ solutions) which may indicate that it assembles the contributions for $Al(OH)_4^-$ and Al-polyborate complexes. The formation of Al-substituted borate trimer and tetramer with ring structures is likely to occur because these polymers predominate in concentrated boric acid solutions (Mesmer et al., 1972).

Reaction 3 equilibrium constant can be approximated assuming $Al(OH)_4^-$ to $Al(OH)_3OB(OH)_2^-$ concentration ratio is equal to the ratio of 80.5 and 74.5 ppm NMR peak areas. For these calculations boric acid concentration was deduced from equilibrium constants given in Table 1. Resulting values listed in Table 3 should be considered as rough estimate of the formation constant of the Q^1_{Al} boric acid dimer.

3.2. Solubility Measurements

The results of gibbsite and boehmite solubility measurements are listed in Table 4 and illustrated in Figures 4 to 8. As shown in Figure 4 and 5, in $m(B(OH)_3) \leq 0.1$ solutions, equi-

Table 3. Parameters for ^{27}Al NMR spectra of $Al(OH)_4^- - B(OH)_3$ solutions. Al concentration is $4.6 \cdot 10^{-4}$ mol/kg H_2O, pH = 8.95.

$m(B_{total})$	0.02		0.08		0.20	
	δ, ppm	LW, Hz	δ, ppm	LW, Hz	δ, ppm	LW, Hz
$Al(OH)_4^-$	80.55	14	80.59	29	80.07	131
Q^1_{Al}[1]	74.50	51	74.42	70	73.86	211
Q^2_{Al}[2]	—	—	68.6		68.5	
$S(Q^1_{Al})/S(Al(OH)_4^-)$[3]	0.277		0.645		0.808	
$S(Q^2_{Al})/S(Al(OH)_4^-)$[3]	—		0.28		0.35	
log K_3	1.4		1.1		1.1	

[1] $Q^1_{Al} = Al(OH)_3OB(OH)_2^-$.
[2] $Q^2_{Al} = Al(OH)_2O_2(B(OH)_2)_2^-$.
[3] Peaks area ratio.

librium with gibbsite at 50°C and boehmite at 78°C is reached in a few days. However, the equilibration time is much longer in 0.2 m boron solution. At these conditions, only one solution (B_3) attained constant concentration at 78°C after ~50 d. Moreover, for solution S_7, Al concentration in solution in contact with gibbsite continuously increased even after 120 d (Fig. 6). A sluggish kinetics was also observed for the formation of aqueous silicate and aluminosilicate oligomers (Swaddle, 2001). It has been noted that ring and cage silicate structures are particularly unreactive and their formation takes place at the expense of the smaller oligomers and the monomer. Similar processes of polymerization with the successive formation of Al-B dimers, trimers and oligomers may take place in concentrated boric acid solutions.

Gibbsite and boehmite solubility in alkaline solutions can be described by

$$Al(OH)_{3(cr)} + OH^- = Al(OH)_4^- \quad (5)$$

$$AlOOH_{(cr)} + OH^- + H_2O = Al(OH)_4^- \quad (6)$$

The equilibrium constants for reactions 5 and 6 obtained in the present study in boron-free solutions are in close agreement with experimental data of Wesolowski (1992), Castet et al. (1993), Diakonov et al. (1996), Bénézeth et al. (2001) and Palmer et al. (2001), and thermodynamic data for the Na-Al-O-H system given in Tagirov and Schott (2001) (Table 5). However, in the presence of boric acid, aluminum concentrations measured in equilibrium with gibbsite at 50°C (Fig. 4) and boehmite at 78, 150 and 200°C (Figs. 5, 7, and 8) considerably exceeds gibbsite and boehmite solubility values calculated using reactions 5 and 6 equilibrium constants listed in Table 5. In accordance with ^{27}Al NMR spectroscopy data, the observed Al concentration increases stem from the formation of Al-B complexes

$$Al(OH)_{3(cr)} + B(OH)^0_{3(aq)} = Al(OH)_3OB(OH)_2^- + H^+ \quad (7)$$

$$AlOOH_{(cr)} + B(OH)^0_{3(aq)} + H_2O = Al(OH)_3OB(OH)_2^- + H^+ \quad (8)$$

$$Al(OH)_{3(cr)} + 2B(OH)^0_{3(aq)} = Al(OH)_2O_2(B(OH)_2)_2^- + H^+ + H_2O \quad (9)$$

$$AlOOH_{(cr)} + 2B(OH)^0_{3(aq)} = Al(OH)_2O_2(B(OH)_2)_2^- + H^+ \quad (10)$$

Values of Q^1_{Al} dimer ($Al(OH)_3OB(OH)_2^-$) and Q^2_{Al} trimer ($Al(OH)_2O_2(B(OH)_2)_2^-$) formation constants (Eqns. 3 and 4) can be calculated by subtraction of boehmite and gibbsite solubility products in the absence of boric acid (Eqns. 5 and 6) from those measured in boron-bearing solutions (Eqns. 7–10), and taking account of H_2O dissociation product (Table 1). These calculations were performed for each experimental series listed in Table 4. Equilibrium constants were calculated using the GIBBS computer code to match the observed change in aluminum concentrations. Computed values of Q^1_{Al} dimer ($Al(OH)_3OB(OH)_2^-$) stability constant (Eqn. 3) are listed in the last column of Table 4. The obtained log K_3 value appears to be independent of boric acid concentration within given experimental uncertainties when $m(B(OH)_3) \leq 0.1$ at 50°C and 78°C, and for all boric acid concentrations investigated in this study at 150°C and 200°C. This confirms the stoichiometry of reaction 3.

The values of log K_3 generated in this study are plotted against the reciprocal of temperature in Figure 9. In agreement with the isocoulombic approximation, the dependence of log K_3 on 1/T(K) is linear which implies $\Delta_r C_p^0 = 0$,

$$\log K_3 = 241.94(\pm 130.07)/T(K) + 0.81(\pm 0.36) \quad (11)$$

The value of log K_3 extrapolated to 25°C with the aid of Eqn. 11 (log $K_3 = 1.62 \pm 0.57$) is in reasonable agreement with the average log K_3 value deduced from ^{27}Al NMR peak areas, which is affected by much higher uncertainty (log K_3 = 1.2, Table 2).

The thermodynamic parameters of reaction 3 derived by differentiation of Eqn. 11 are compared in Table 6 with those for the reaction

$$Al(OH)_4^- + Si(OH)^0_{4(aq)} = Al(OH)_3OSi(OH)_3^- + H_2O \quad (12)$$

given in Pokrovski et al. (1998). In Figure 9 is compared the temperature dependence for reactions 3 and 12. It can be seen that the Al-B complex is less stable than its Al-Si counterpart at all investigated temperatures. For example, log K_3 = 1.62 and 1.32 (Eqn. 11) whereas log K_{12} = 3.78 and 2.66 at 25°C and 200°C, respectively. The stability of both Al-B and Al-Si

Table 4. Composition of experimental solutions (mol/kg H_2O), solubility of gibbsite and boehmite, and calculated values for reaction 3 equilibrium constant.

Solution	NaCl	$NaHCO_3$	$Na_2B_4O_7$	HCl	NaOH	pH[1]	m(Al)·10^6	log K_3
				50°C, gibbsite				
S0	0.0900	0.010	0	0	0.00065	8.54	3.85	
S2	0.0903	0	0.0050	0.0008	0	7.87	1.45	1.63
S3	0.0803	0	0.0100	0.0016	0	7.95	2.13	1.53
S4	0.0703	0	0.0151	0.0025	0	7.78	2.23	1.67
S5	0.0603	0	0.0201	0.0032	0	7.91	2.88	1.53
S6	0.0504	0	0.0252	0.0050	0.0080	7.75	2.39	1.54
S7	0	0	0.0504	0.0078	0	7.68		
								log $K_{3\ \mathrm{average}} = 1.58 \pm 0.10$
				78°C, boehmite				
S0	0.0900	0.010	0	0	0.00325	9.11	57.0	
S1	0.0954	0	0.0025	0	0	7.77	2.99	1.35
S2	0.0903	0	0.0050	0.00085	0	7.74	3.39	1.40
S3	0.0803	0	0.0100	0.0016	0	7.83	5.84	1.54
S4	0.0703	0	0.0151	0.0026	0	7.68	5.17	1.52
S5	0.0603	0	0.0201	0.0032	0	7.82	8.37	1.51
S7	0	0	0.0504	0.0081	0	7.68		
Solution	NH_4Cl	NH_3	$B(OH)_3$			pH	m(Al)·10^6	
				78°C, boehmite				
B0	0.0151	0.025	0			8.14	5.06	
B1	0.0201	0.028	0			8.10	4.48	
B2	0.0202	0.0305	0.101			7.80	7.74	1.45
B3	0.0204	0.0304	0.203			7.53	11.66	
								log $K_{3\ \mathrm{average}} = 1.46 \pm 0.10$
				150°C, boehmite				
B6	0.0217	0.02	0			6.56	3.19	
	0.0217	0.02	0.0524			6.55	8.06	1.49
	0.0217	0.02	0.128			6.53	15.8	1.54
								log $K_{3\ \mathrm{average}} = 1.52 \pm 0.15$
				200°C, boehmite				
B6	0.0217	0.02	0			5.86	3.49	
	0.0217	0.02	0.0746			5.86	7.95	1.25
B7	0.0217	0.02	0			5.86	4.06	
	0.0217	0.02	0.0448			5.86	6.31	1.11
	0.0217	0.02	0.172			5.77[2]	16.8	1.38
								log $K_{3\ \mathrm{average}} = 1.25 \pm 0.15$

[1] pH measured in situ at 50 and 78°C, and calculated at 150 and 200°C.
[2] Calculated as described in the text.

complexes decreases with increasing temperatures. However, the effect of temperature is much less pronounced for the Al-B complex ($\Delta_{r3}H = -4.6$ kJ/mol) than that for its Si counterpart ($\Delta_{r12}H = -17.2$ kJ/mol).

For $m(B(OH)_3) = 0.2$ and t = 78°C, only one experiment (solution B_3) reached equilibrium with boehmite. Aluminum concentration measured for this run was ~2 times higher than that calculated using reactions 3 and 6 equilibrium constants. Assuming that this increase in solubility stems from the formation of Al-substituted Q^2_{Al} boric acid trimer $[(OH)_2B\text{-}O\text{-}Al(OH)_2\text{-}O\text{-}B(OH)_2]^-$, we calculated log K_4 = 2.14 at 78°C. Note, however, that this value represent a higher limit of Q^2_{Al} formation constant as polyborates may form at these conditions. Formation of the Q^2_{Al} trimer was not observed in solubility experiments at $m(B) < 0.2$ and $50°C < t < 200°C$, whereas ^{27}Al NMR spectroscopy at 25°C indicated the presence of this complex at m(B) = 0.08 m. Therefore, this complex stability is also likely to decrease with increasing temperature.

3.3. Speciation in Boron-Rich Natural Fluids

Al speciation at 200°C in equilibrium with K-feldspar-muscovite-quartz and kaolinite-muscovite-quartz mineral assemblages is shown as a function of boric acid concentration in Figure 10. In near-neutral pH solutions (Fig. 10a), $Al(OH)_3OB(OH)_2^-$ becomes dominant at $m(B(OH)_3)$~0.1, whereas $Al(OH)_3OSi(OH)_3^-$ is predominant at lower B con-

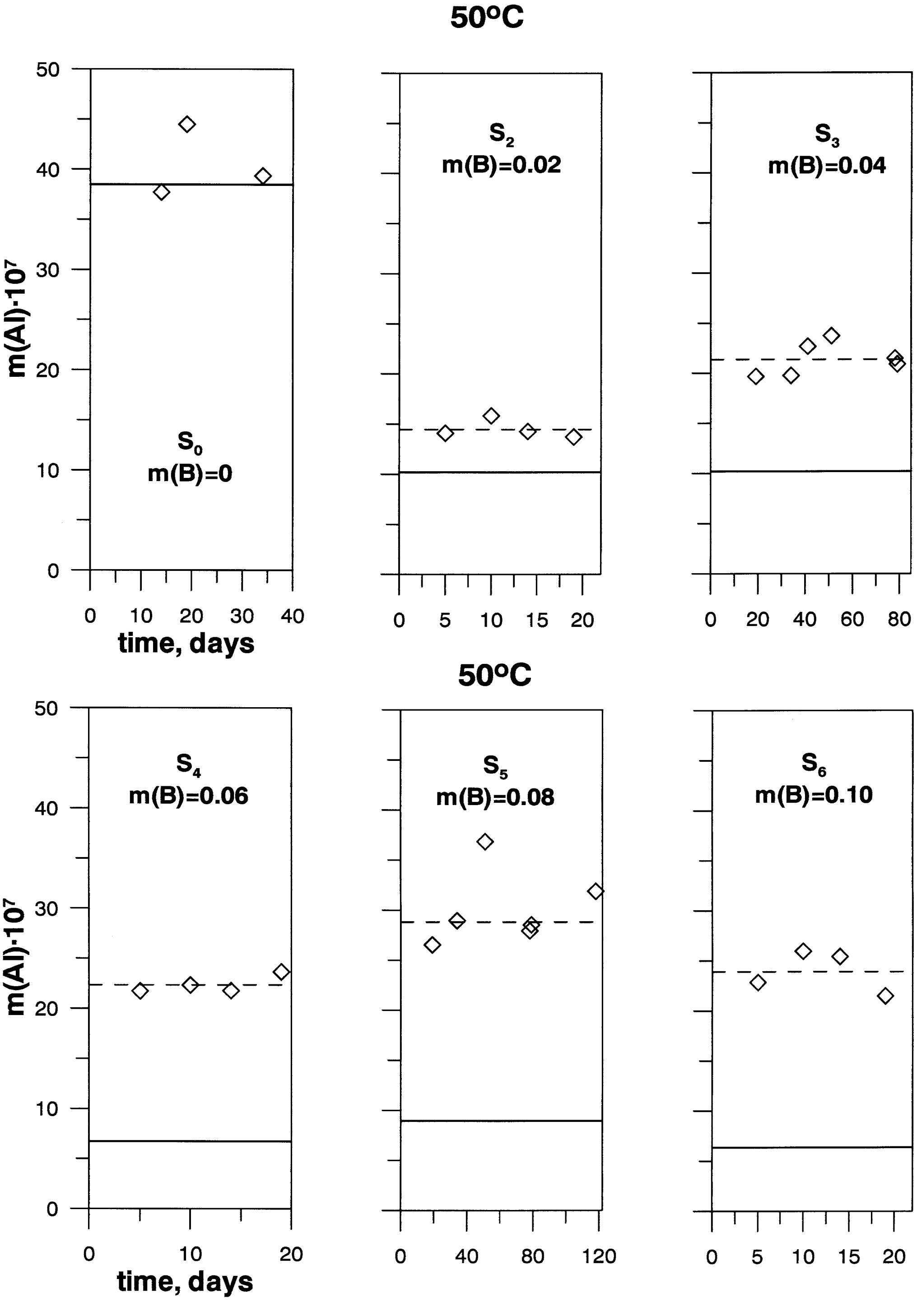

Fig. 4. Gibbsite solubility measured at 50°C in solutions containing ≤0.1 m of boric acid plotted vs. time. Diamonds represent experimental data, dashed lines show values taken for calculation of Al-B complex stability constant. Solid lines show $Al(OH)_4^-$ + $NaAl(OH)_4^0$ concentration. Solutions composition is given in Table 4.

centrations. With decreasing pH, the effect of boron on aluminum speciation becomes less pronounced and Al-B complexes dominate only at $m(B(OH)_3 > 0.3$ (Fig. 10b). Table 7 illustrates Al speciation in natural fluids from miarolitic pegmatites. Two contrasted fluid compositions, derived from fluid inclusion data reported in Peretyazhko et al. (2000), are presented. It can be seen that Al-B complexes dominate in both solutions whereas Al-Si and Na-Al complexes represent less than 10% of total aluminum. Note that these calculations provide an underestimate of the extent of Al-B complexing since the Q^2_{Al} trimer and, probably, polymeric borate complexes are likely to form in these B-rich fluids.

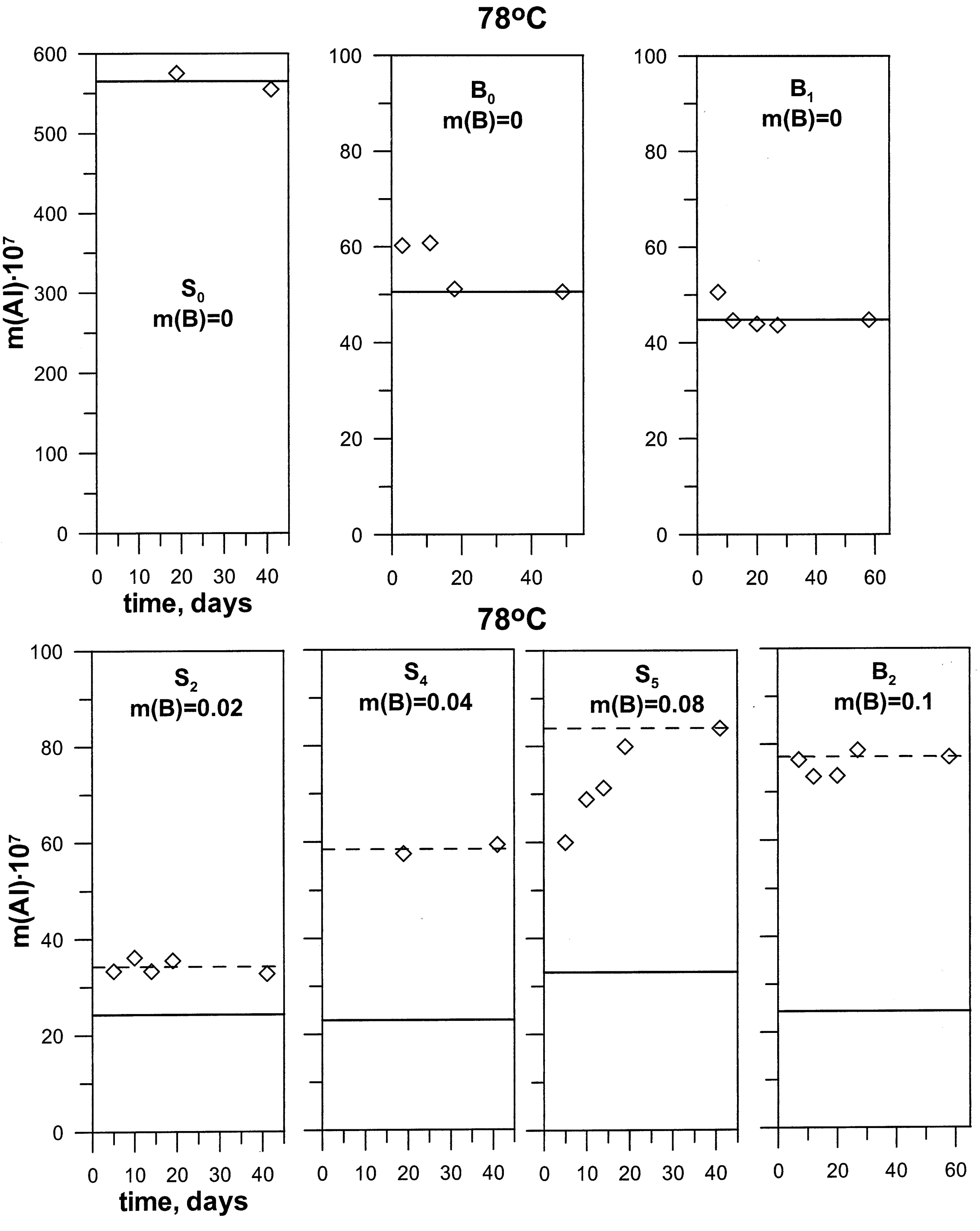

Fig. 5. Boehmite solubility measured at 78°C in solutions containing ≤0.1m of boric acid plotted vs. time (see Fig. 4 caption).

Extrapolation of $Al(OH)_3OB(OH)_2^-$ stability constant to supercritical temperatures using Eqn. 11 shows that this complex predominates in 1m NaCl weakly acid to alkaline solutions equilibrated with corundum at 400°C, 500 bars at boron concentration of 1.5 g/L. As boron concentrations found in the fluid inclusions from rare-metal pegmatites are usually 5–50 times higher (Peretyazhko et al., 2000), Al-B aqueous complexes are also likely to dominate Al speciation during the formation of tourmaline-bearing mineral assemblages.

4. CONCLUSIONS

The existence of aluminate-borate complexes was for the first time demonstrated from both ^{27}Al NMR spectroscopy and

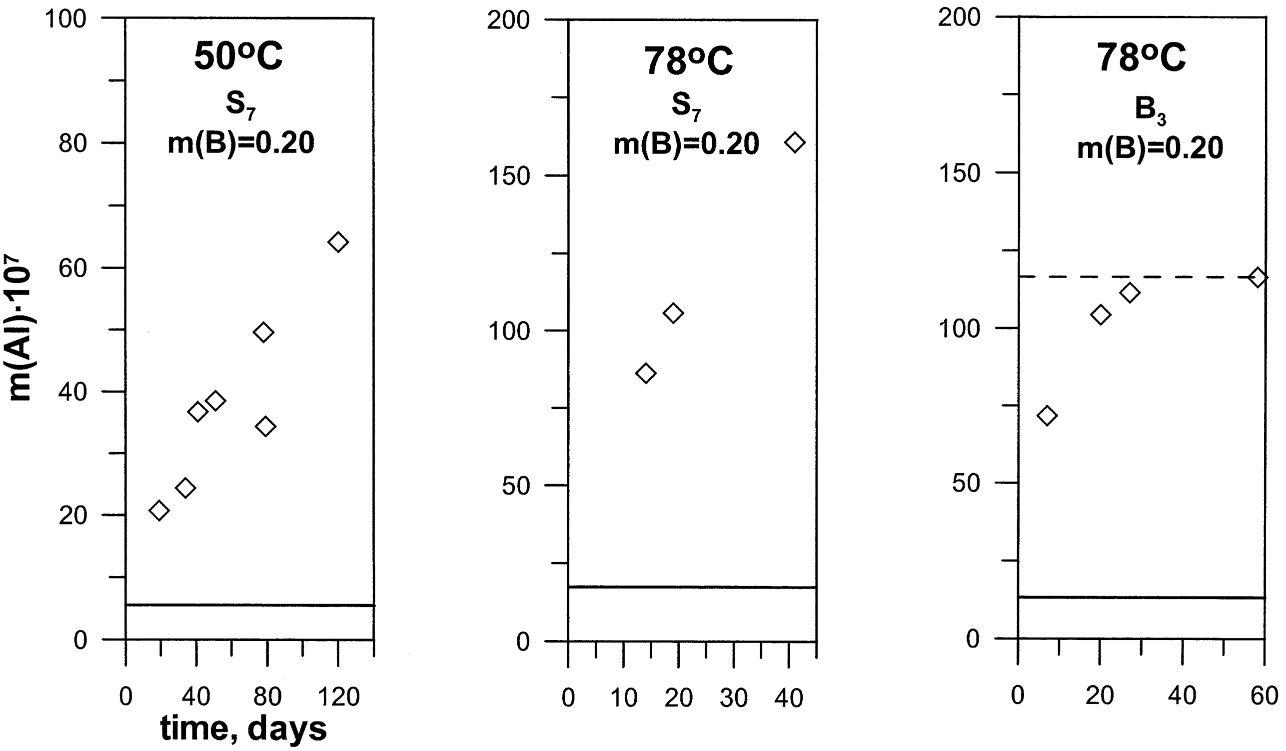

Fig. 6. Gibbsite and boehmite solubility measured respectively at 50°C and 78°C in solutions containing 0.2 m of boric acid as a function of time (see Fig. 4 caption).

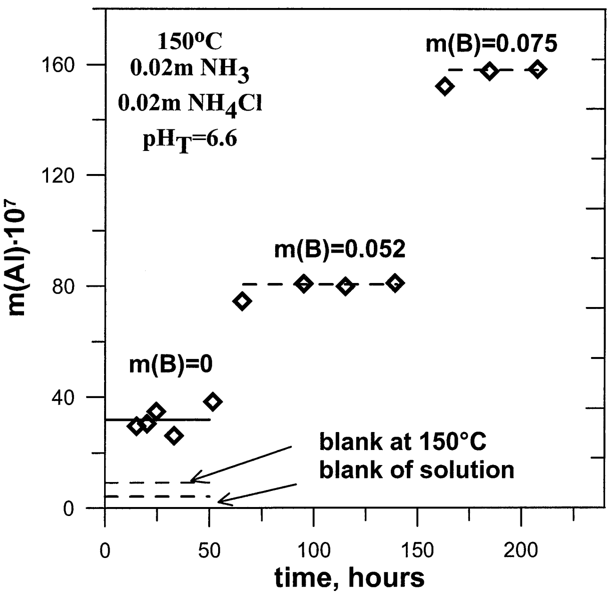

Fig. 7. Boehmite solubility measured at 150°C before and after boron injections plotted vs. time. Diamonds represent experimental data, but dashed lines show values taken for calculations of Al-B complex stability constant.

Table 5. Gibbsite and boehmite dissociation constants calculated from the experimental data given in Table 4, and using thermodynamic properties of Al aqueous species from Tagirov and Schott (2001) and thermodynamic properties of minerals from Hemingway and Robie (1977), Hemingway et al. (1977, 1991).

T, °C	log K_{exper}	log K_{calc}
50[1]	−0.83 ± 0.05	−0.83
78[2]	−0.88 ± 0.05	−0.92
150[2]	−0.45 ± 0.10	−0.52
200[2]	−0.11 ± 0.10	−0.11

[1] $Al(OH)_{3(cr)} + OH^- = Al(OH)_4^-$.

[2] $AlOOH_{(cr)} + OH^- + H_2O = Al(OH)_4^-$.

Table 6. Standard thermodynamic properties for reactions 3 and 12 at 25°C, 1 bar calculated from the weighted least-square fit shown in Fig. 9. Values of the formation constant of $Al(OH)_3OSi(OH)_3^-$ are taken from Pokrovski et al. (1998).

Complex	log K	$\Delta_r G$, kJ/mol	$\Delta_r H$, kJ/mol	$\Delta_r S$ (J/mol K)
$Al(OH)_3OB(OH)_2^-$	1.62 ± 0.57	−9.22 ± 3.25	−4.6 ± 2.5	15.5 ± 6.9
$Al(OH)_3OSi(OH)_3^-$	3.78 ± 0.05	−21.56 ± 0.29	−17.2 ± 0.2	14.7 ± 0.6

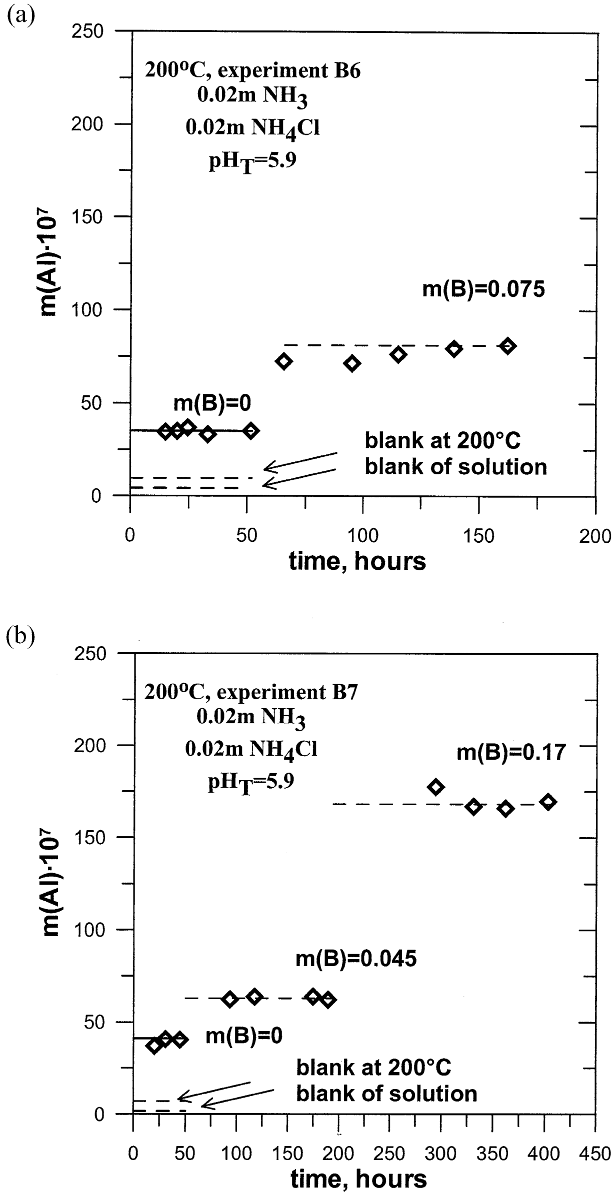

Fig. 8. Boehmite solubility measured during experiments B6 (a) and B7 (b) at 200°C before and after boron injections plotted vs. time (see Fig. 7 caption).

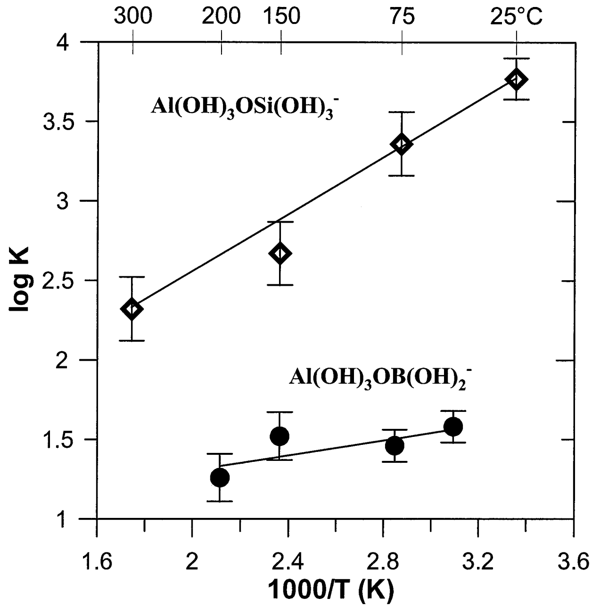

Fig. 9. Logarithm of the formation constants of Al-B (circles) and Al-Si (diamonds) complexes (Eqns. 3 and 12) as a function of the reciprocal of temperature. Lines show weighted least-square fit of the experimental data.

gibbsite/boehmite solubility measurements. ^{27}Al NMR spectra in the presence of boric acid are consistent with the formation of a single Al-substituted Q^1_{Al} dimer $Al(OH)_3OB(OH)_2^-$ and a Q^2_{Al} trimer $Al(OH)_2O_2(B(OH)_2)_2^-$. The thermodynamic parameters of the reaction $Al(OH)_4^- + B(OH)_3^0{}_{(aq)} = Al(OH)_3OB(OH)_2^- + H_2O$ were characterized using gibbsite and boehmite solubility measurements at 50–200°C. At 25°C $\log K = 1.62 \pm 0.57$, and this constant slightly decreases with increasing temperature ($\Delta_r H = -4.6 \pm 2.5$ kJ/mol). Thermodynamic calculations based on the results of the present study show that Al-B complexes are likely to dominate aluminum speciation in high temperature boron-rich natural fluids including those forming tourmaline-bearing mineral assemblages.

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Table 7. Al speciation in quartz-saturated aqueous fluids from miarolitic pegmatites ($m(Al_{total}) = 10^{-6}$). Fluid composition is taken from Peretyazhko et al. (2000), and thermodynamic properties of aqueous Al species from Tagirov and Schott (2001).

Type of pegmatite	Sub-rare-metal topaz-beryl	Rare-metal and muscovite beryl-tourmaline
t (°C)	284	264
P (bar)	500	500
m(NaCl)	1.11	0.82
$m(B(OH)_3)$	1.22	0.50
pH	4.21	4.44
	% of Al species	
$Al(OH)_3OB(OH)_2^-$	87	80
$Al(OH)_3OSi(OH)_3^-$	5	8
$NaAl(OH)_4^0$	5	7
$Al(OH)_4^-$	2.5	4
$Al(OH)_3^0$	0.5	1

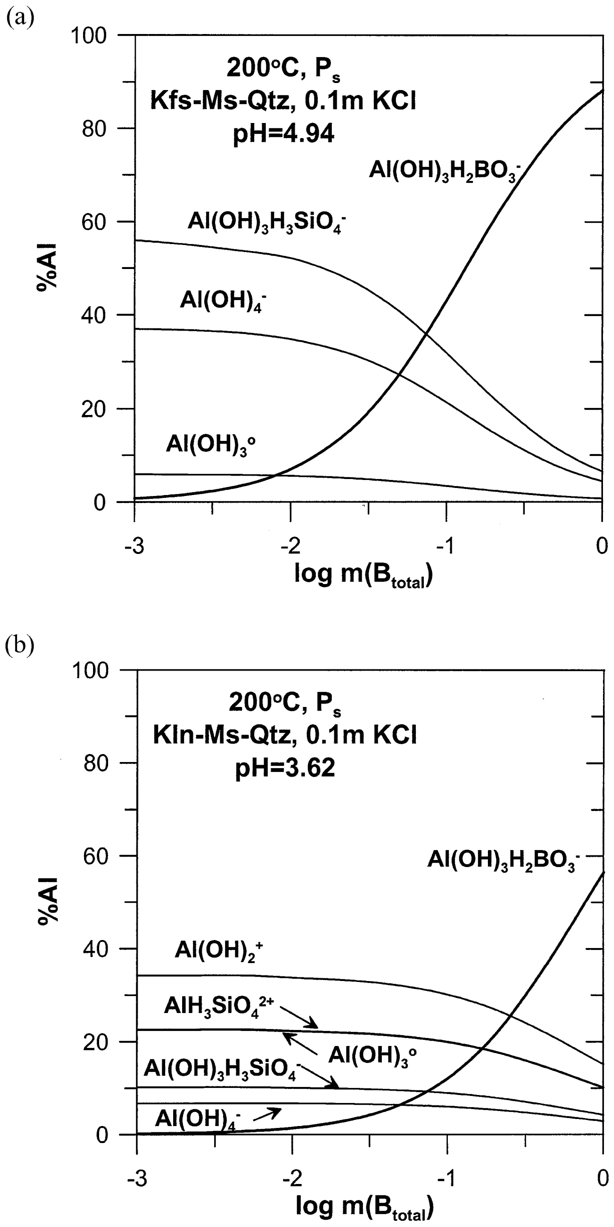

Fig. 10. Al speciation as a function of boric acid concentration in solutions in equilibrium with K-feldspar-muscovite-quartz (a) and kaolinite-muscovite-quartz (b) mineral assemblages at 200°C and P_s.

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