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# Experimental study of aluminum speciation in fluoride-rich supercritical fluids

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**Abstract**—The solubility of the albite-paragonite-quartz mineral assemblage was measured as a function of NaCl and fluorine concentration at 400°C, 500 bars and at 450°C, 500 and 1000 bars. Decreasing Al concentrations with increasing NaCl molality in F-free fluids of low salinity (mNaCl < 0.01) demonstrates that $Al(OH)_4^-$ dominates Al speciation and is formed according to the reaction $0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + 2\ H_2O = 0.5\ NaAlSi_3O_{8(cr)} + Al(OH)_4^- + H^+$. Log K results for this reaction are $-11.28 \pm 0.10$ and $-10.59 \pm 0.10$ at 400°C, 500 bars and 450°C, 1000 bars, respectively. Upon further salinity increase, Al concentration becomes constant (at 400°C, 500 bars) or even rises (at 450°C, 1000 bars). The observed Al behavior can be explained by the formation of $NaAl(OH)_{4(aq)}^0$ or $NaAl(OH)_3Cl_{(aq)}^0$. The calculated constant for the reaction $Al(OH)_4^- + Na^+ = NaAl(OH)_{4(aq)}^0$ expressed in log units is equal to 2.46 and 2.04 at 400°C, 500 bars and 450°C, 1000 bars, respectively. These values are in good agreement with the predictions given in Diakonov et al. (1996). Addition of fluoride at m(NaCl) = const = 0.5 caused a sharp increase in Al concentration in equilibrium with the albite-paragonite-quartz mineral assemblage. As fluid pH was also constant, this solubility increase indicates strong aluminum-fluoride complexation with the formation of $NaAl(OH)_3F_{(aq)}^0$ and $NaAl(OH)_2F_{2(aq)}^0$, according to $0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + HF_{(aq)}^0 + H_2O = 0.5\ NaAlSi_3O_{8(cr)} + NaAl(OH)_3F_{(aq)}^0 + H^+$, log K $= -5.17$ and $-5.23$ at 400°C and 450°C, 500 bars, respectively, and $0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + 2\ HF_{(aq)}^0 = 0.5\ NaAlSi_3O_{8(cr)} + NaAl(OH)_2F_{2(aq)}^0 + H^+$, log K $= -2.19$ and $-1.64$ at the same P-T conditions. It was found that temperature increase and pressure decrease promote the formation of Na-Al-OH-F species. Stability of $NaAl(OH)_2F_{2(aq)}^0$ in low-density fluids also increases relative to $NaAl(OH)_3F_{(aq)}^0$. These complexes, together with $Al(OH)_2F_{(aq)}^0$ and $AlOHF_{2(aq)}^0$, whose stability constants were calculated from the corundum solubility measured by Soboleva and Zaraisky (1990) and Zaraisky (1994), are likely to dominate Al speciation in metamorphic fluids containing several ppm of fluorine. *Copyright © 2002 Elsevier Science Ltd*

## 1. INTRODUCTION

Despite numerous studies devoted to the thermodynamics of aqueous aluminum, little is known about speciation of this metal at metamorphic conditions. The stability of $Al^{3+}$ and its hydrolyzed species has been rigorously characterized to 350°C at saturated water vapor pressure via gibbsite and boehmite solubility measurements (e.g., Castet et al., 1993; Pokrovskii and Helgeson, 1995; Tagirov and Schott, 2001, and references therein). Thermodynamic calculations based on these data suggest that in noncomplexing solutions, $Al(OH)_4^-$ dominates aqueous Al speciation in moderately acidic to alkaline supercritical fluids. At higher temperatures, however, density and dielectric constant of water decrease causes a contraction of Al hydration shell together with a reduction of the hydration number due to strong ion association (Seward et al., 1996, 1999; Driesner et al., 1998). As a result, ligand-rich supercritical fluids may contain clusters analogous to those predicted by Oelkers and Helgeson (1993) and Driesner et al. (1998). Strong complexation of aluminum with the fluid components is consistent with recent petrographic and mineralogic studies (Moine et al., 1989, 1998; Zaraisky, 1994), which show high aluminum mobility documented by extensive aluminum silicate minerals alteration in supercritical Na-, Cl-, and/or F-rich fluids.

Experimental studies aimed at characterizing Al speciation in supercritical conditions include (1) the solubility of corundum in pure water (Ragnarsdottir and Walther, 1985; Walther, 1997), in HCl- and HF-rich fluids (Korzhinsky, 1987; Baumgartner and Eugster, 1988; Zaraisky, 1994), alkaline NaOH and KOH solutions (Barns et al., 1963; Anderson and Burnham, 1967; Pascal and Anderson, 1989; Azaroual et al., 1996) and (2) the solubility of silicate mineral assemblages in pure water and solutions of alkali chlorides (Anderson et al., 1987; Woodland and Walther, 1987; Haselton et al. 1988; Pascal and Anderson, 1989; Walther and Woodland, 1993). Alkali-aluminum complexes, $(Na,K)Al(OH)_{4(aq)}^0$, have been shown to form in high-temperature alkaline solutions (Anderson and Burnham, 1967; Anderson et al., 1987; Pascal and Anderson, 1989; Azaroual et al., 1996; Diakonov et al., 1996).

Very few studies were directed at characterizing the influence of ligands other than $OH^-$ and $Na^+/K^+$ on Al behavior at metamorphic conditions. However, fluid inclusion analyses demonstrate that HF is an abundant component of high-temperature crustal fluids (Bottrel and Yardley, 1988; Yardley and Shmulovich, 1994) and can affect aluminum speciation and transport. The purpose of this paper is to determine the stoichiometry and stability of the Al species that form in fluoride-bearing NaCl-rich metamorphic fluids.

Because Al speciation is very sensitive to pH, this parameter should be reliably fixed or determined in experiments aimed at extracting thermodynamic information on aqueous Al. In this study, to insure independence of solution pH on acids and bases dissociation, as well as to mimic conditions prevailing in natural systems, all experiments were performed in the presence of a

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Table 1. X-ray powder pattern for paragonite.

| d (nm) | Integral intensity |
|--------|--------------------|
| 9.859 | 8 |
| 9.600 | 98 |
| 7.056 | 1 |
| 4.947 | 2 |
| 4.796 | 54 |
| 4.787 | 6 |
| 3.529 | <1 |
| 3.301 | 4 |
| 3.205 | 100 |
| 3.024 | <1 |
| 2.804 | 2 |
| 2.420 | <1 |
| 1.986 | <1 |
| 1.927 | 6 |
| 1.609 | 4 |
| 1.477 | 10 |
| 1.308 | 8 |
| 1.137 | <1 |
| 1.130 | <1 |
| 1.030 | <1 |
| 1.028 | <1 |

mineral buffer: the albite-paragonite-quartz assemblage. This assemblage controls the $Na^+/H^+$ activity ratio, consequently fixing the activities of all charged Al hydroxide complexes for a given NaCl concentration. As a first step, Al speciation was determined as a function of NaCl concentration. Subsequently, the effect of fluorine on total Al concentration was investigated at constant NaCl concentration — pH, $m(Al(OH)_n^{3-n})$, and m(Na-Al complexes) are fixed. Aluminum speciation in a fluorine-bearing system was computed using the results of the present study together with data of Soboleva and Zaraisky (1990) and Zaraisky (1994) on Al complexation in aqueous HF solutions.

## 2. MATERIAL AND METHODS

### 2.1. Preparation and Characterization of Solid Phases

Solid phases used were low-albite from Amelia Courthouse (sample 49-58-51) and natural paragonite separated from albitite (sample 82964 from Fersman Mineralogical Museum of the Russian Academy of Science). Results of XRD and chemical analyses of paragonite are given in Tables 1 and 2, respectively. Position and intensity of major peaks correspond to ASTM file 24-1047 of synthetic paragonite 1M. Note that this paragonite contains small amounts of K. In most experiments, we used synthetic quartz characterized in Gautier (1999). Few experiments with a fluid/minerals mass ratio < 10 were performed with natural quartz (Gau-

Table 2. Chemical composition of paragonite (at. %), determined by ion-microprobe analysis.

| | |
|---|---|
| O | $61.13 \pm 0.035$ |
| Na | $4.94 \pm 0.17$ |
| Mg | $0.092 \pm 0.03$ |
| Al | $16.25 \pm 0.15$ |
| Si | $16.85 \pm 0.10$ |
| Cl | $0.01 \pm 0.01$ |
| K | $0.40 \pm 0.11$ |
| Ca | $0.11 \pm 0.05$ |
| Ti | $0.02 \pm 0.01$ |
| Fe | $0.09 \pm 0.03$ |
| Ni | $0.01 \pm 0.01$ |
| Total | 99.6 |

tier, 1999; Gautier et al., 2001). All minerals were ground and sieved to the 300- to 500-$\mu$m size fraction. Fine particles were removed by ultrasonic cleaning in deionized water.

### 2.2. Preparation and Analysis of Experimental Solutions

Solutions were prepared from doubly deionized water provided by a MilliQplus system. Merck Titrisol hydrochloric acid, sodium hydroxide, and standard solutions of aluminum, silica, sodium, and potassium were used. Experimental solutions and pH standards were prepared using Pro Analysi Merck reagents. Doubly distilled $HNO_3$ was used to acidify solutions extracted after experiments and to prepare analytical standards.

Silica concentrations were determined with an Autoanalyser II Technicon colorimeter using the molybdate blue method (Koroleff, 1966). Aluminum was analyzed by flameless Atomic Absorption Spectroscopy (AASF, Perkin Elmer 5100 PC) in a graphite furnace. Al concentrations in diluted samples ranged between 2 and 50 ppb. To avoid matrix effects, Al standards were prepared with an Si concentration matching that of the samples (15 ppm, in general, and up to 35 ppm in several samples). The analytical method is described in detail in Salvi et al. (1998). Accuracy of this method was within $\pm$ 10% at a 95% confidence level. Several analyses of Al were performed using ICP-MS. The difference between these two methods was within $\pm$ 15%.

Total HCl concentration at experimental conditions ($m(HCl)_{total} = [HCl^0] + [H^+]$) was assumed to correspond to the solution acidity at 25°C. pH of experimental solutions was measured immediately after sampling using a Mettler Toledo (U 402-mol/L3-S7/60) microelectrode. When experimental solutions contained < 0.1m NaCl, 0.01m HCl and DIN 19266/NBS pH 6.865 and 4.008 standards were used. For more concentrated solutions, $10^{-3}$ and $10^{-2}$ m HCl standards with NaCl concentration equal to experimental value were used. Accuracy of measurements was $\pm$ 0.01 unit for pH < 3.5 and up to $\pm$ 0.05 unit for pH = 3.5 to 5. Higher pH values are not reported because of the influence of $CO_2$ and other solution components.

Sodium and potassium were analyzed by Atomic Emission Spectroscopy (Perkin Elmer 5100 PC). Reproducibility of these measurements was $\pm$ 5%. Fluoride concentrations were measured immediately after sampling with a Tacussel fluoride-selective electrode using TI-SAB-III (Orion) as an ionic strength and pH adjuster. This method yields fluoride concentrations with an accuracy of $\pm$ 2%.

Total uncertainty of the experimental data presented in Table 3 is 30% (0.12 log unit) for Al concentration, 20% (0.10 log unit) for Si, 5% (0.02 log unit) for Na, and 40% (0.15 log unit) for total concentration of HCl. These values account for analytical uncertainties and concentration differences for experiments performed at the same P-T conditions.

### 2.3. Solubility Measurements

Solubility of the albite-paragonite-quartz assemblage was measured in 20-mL titanium autoclaves. Before the experiments, the inner surfaces of the autoclaves were passivated with 15% $HNO_3$ at 400°C and 1 kbar for 3 d. Mixtures of the solid phases (albite + paragonite + quartz) were loaded into the autoclaves together with dilute NaCl solutions (m(NaCl) < 1.0) or with water and $NaCl_{(cr)}$ at higher salt concentrations. The mass of each mineral in the mixture was 0.45 to 0.50 g except for a few experiments in concentrated NaCl solutions that were performed with up to 1.5 g of quartz. Therefore, the liquid/solid ratio ranged from 7 to 20, depending on solution volume and minerals mass. After loading, autoclaves were hermetically closed and placed into a preheated furnace. The temperature was controlled within $\pm$ 5°C and pressure was determined by the degree of filling of the autoclave according to the PVT properties of the $NaCl-H_2O$ system (Potter and Brown, 1977). Several identical runs were performed to monitor attainment of equilibrium. No systematic variations in Al concentration were observed with time from a few days after attainment of thermal equilibrium up to 3 weeks. Duration of experiments listed in Table 3 varied from 11 to 22 d. Quenching was carried out with compressed air (for 5–7 min) or water (quenching time was several seconds). After quenching, the experimental solution was extracted from the autoclave and filtered through a Sartorius 0.45-$\mu$m filter. An aliquot of 4 to 5 mL was

Table 3. Composition of experimental solutions in equilibrium with the albite-paragonite-quartz assemblage.

| m(Na), initial | m(NaF), initial | log m(F), final | duration. days | log m(Na), final[a] | log m(Al), final | log m(HCl)[b] | log m(Si) |
|---|---|---|---|---|---|---|---|
| | | | | **400°C, 500 bar** | | | |
| 0 | 0 | 0 | 18 | −3.547 | −3.82 | <−5 | −1.86 |
| 0.002 | 0 | 0 | 18 | −2.716 | −4.52 | <−5 | −1.82 |
| 0.01 | 0 | 0 | 18 | −2.027 | −4.94 | <−5 | −1.78 |
| 0.1 | 0 | 0 | 18 | −1.035 | −4.84 | <−5 | −1.49 |
| 0.505 | 0 | 0 | 18 | −0.341 | −4.87 | −3.54 | −1.53 |
| 0.505 | 0 | 0 | 18 | −0.341 | −4.95 | −3.71 | −1.64 |
| 1.02 | 0 | 0 | 18 | −0.039 | −4.83 | −2.73 | −1.48 |
| | | | | **450°C, 1000 bar** | | | |
| 0 | 0 | 0 | 15 | −3.222 | −3.37 | <−5 | −1.68 |
| 0.002 | 0 | 0 | 15 | −2.708 | −3.98 | −4.92 | −1.67 |
| 0.01 | 0 | 0 | 15 | −2.025 | −4.40 | −4.61 | −1.54 |
| 0.1 | 0 | 0 | 15 | −1.059 | −5.04 | −3.27 | −1.41 |
| 0.505 | 0 | 0 | 15 | −0.366 | −4.87 | −2.84 | −1.32 |
| 1.02 | 0 | 0 | 15 | −0.051 | −4.62 | −2.52 | −1.34 |
| 3.0 | 0 | 0 | 11 | 0.450 | −3.93 | −1.84 | −1.39 |
| 3.5 | 0 | 0 | 19 | 0.544 | −4.31 | −2.28 | −1.30 |
| | | | | **400°C, 500 bar** | | | |
| 0.505 | 0 | — | 17 | | −4.95 | −3.71 | −1.95 |
| 0.505 | 0.000505 | −3.26 | 22 | | −4.25 | −3.33 | −1.96 |
| 0.505 | 0.00101 | −3.08 | 22 | | −4.00 | −3.21 | −1.95 |
| 0.505 | 0.00202 | −2.81 | 17 | | −3.85 | −3.21 | −1.81 |
| 0.505 | 0.00505 | −2.57 | 22 | | −3.21 | −3.33 | −2.04 |
| 0.505 | 0.0101 | −2.14 | 17 | | −2.91 | −3.25 | −1.80 |
| | | | | **400°C, 500 bar** | | | |
| 0.505 | 0 | — | 13 | | −5.15 | −2.89 | −1.71 |
| 0.505 | 0 | −4.03 | 15.5 | | −4.95 | −2.60 | −1.69 |
| 0.505 | 0.000505 | −3.26 | 15.5 | | −4.57 | −2.65 | −1.67 |
| 0.505 | 0.000505 | −3.33 | 13 | | −4.67 | −2.93 | −1.74 |
| 0.505 | 0.00101 | −3.00 | 15.5 | | −4.46 | −2.63 | −1.68 |
| 0.505 | 0.00202 | −2.75 | 13 | | −4.16 | −2.83 | −1.71 |
| 0.505 | 0.00505 | −2.41 | 15.5 | | −3.69 | −2.54 | −1.63 |
| 0.505 | 0.00505 | −2.39 | 13 | | −3.63 | −2.39 | −1.50 |
| 0.505 | 0.0101 | −2.21 | 13 | | −3.25 | −2.40 | −1.45 |

[a] In experiments with added fluorine, final sodium concentration was calculated according to m(Na), final = m(NaCl), total + m(NaF), total.
[b] Measured at 25°C in quenched solutions.

taken for pH and pF measurements and ~0.3 mL were diluted with deionized water for silica analyses. The remaining solution was acidified to obtain a 0.1M $HNO_3$ solution and used for Al, Na, and K analyses. To check for the possible precipitation of an Al-bearing solid during quenching, after several runs the autoclave walls and mineral mixture were rinsed with 0.5-m $HNO_3$, and this solution was added to the solution sampled before rinsing. Difference in Al concentration between non-treated and acid-rinsed samples was within 5%. Presence of each mineral after experiments was controlled optically, and in several cases, verified by XRD analysis.

### 2.4. Speciation Calculations

Speciation calculations were carried out using the GIBBS computer code (Shvarov and Bastrakov, 1999). Standard state adopted for the aqueous species is unit activity for a hypothetical one-molal solution, which exhibits ideal behavior. For minerals and $H_2O$, the standard state corresponds to unit activity of the pure phase at given temperature and pressure. The activity coefficients of charged aqueous species were calculated according to Helgeson (1969):

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

where $\Gamma_\gamma$ designates the mol-fraction-to-molality conversion factor ($\Gamma_\gamma = -\log(1 + 0.0180153 m^*)$) and $m^*$ corresponds to the sum of the concentrations of all solute species. $B\bullet$ stands for the deviation function at any given temperature; $z_i$ denotes the charge of $i^{th}$ species; $å$, the ion size parameter, is taken equal to 4.5 Å for all species. For neutral species it was assumed
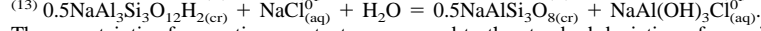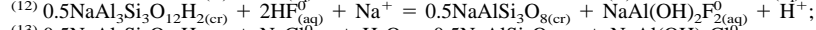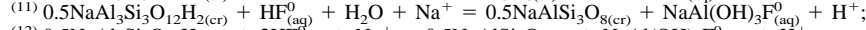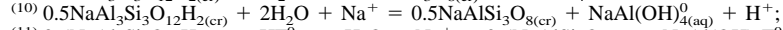
$$\log \gamma_n = \Gamma_\gamma. \qquad (2)$$

Thermodynamic properties of minerals were taken from Berman (1988) corrected by Sverjensky et al. (1991). Thermodynamic properties of water and aqueous species (except Al complexes) were calculated using the SUPCRT92 computer code (Johnson et al., 1992), whereas thermodynamic data for $NaOH^0_{(aq)}$ and $HCl^0_{(aq)}$ were taken from Shock et al. (1997) and Tagirov et al. (1997), respectively. Note that $HCl^0_{(aq)}$ does not participate in the formation reactions of Al species (Eqn. 5, 10, 12, 15, 16) and is present in experimental solutions at low concentrations compared to other chloride-bearing species. Therefore its Gibbs

Table 4. Reaction constants and Gibbs free energies (kJ/ mol) for aqueous aluminum and silica complexes.

| Complex I | 400°C, 500 bar | | 450°C, 500 bar | | 450°C, 1000 bar | | Source II |
|---|---|---|---|---|---|---|---|
| | log K | $\Delta g°$ | log K | $\Delta g°$ | log K | $\Delta g°$ | |
| $Si(OH)_2F_2^{0(1)}$ | 1.20 | −1584.8 | 3.19 | −1632.4 | 0.17 | −1588.0 | {a} |
| $AlF^{2+(2)}$ | −0.72 | −730.3 | 0.41 | −745.3 | −1.63 | −718.3 | (b) |
| $AlF_2^{+(3)}$ | 0.47 | −1090.3 | 0.76 | −1102.2 | −0.47 | −1085.5 | (b) |
| $AlF_3^{0(4)}$ | −0.16 | −1426.9 | −1.02 | −1429.6 | −1.13 | −1427.7 | (b) |
| $Al(OH)_2F_2^{-(5)}$ | −4.83 | −1573.2 | −6.61 | −1565.4 | −5.19 | −1582.0 | (b) |
| $Al(OH)_2F^{0(6)}$ | −1.89 | −1270.8 | −2.01 | −1279.5 | −1.99 | −1278.3 | (b) |
| $AlOHF_2^{0(7)}$ | 0.06 | −1365.1 | 0.02 | −1376.6 | 0.03 | −1375.6 | (b) |
| $Al(OH)_3^{0(8)}$ | −6.50 | −1137.8 | −6.58 | −1144.4 | −6.46 | −1142.9 | (b) |
| $Al(OH)_4^{-(9)}$ | −11.28 ± 0.10 | −1356.2 | — | — | −10.59 ± 0.10 | −1369.8 | (c) |
| $NaAl(OH)_4^{0(10)}$ | −8.82 ± 0.15 | −1680.1 | −8.94 | −1694.6 | −8.55 ± 0.50 | −1695.5 | (c) |
| $NaAl(OH)_3F^{0(11)}$ | −5.17 | −1796.5 | −5.23 | −1815.3 | — | — | (c) |
| $NaAl(OH)_2F_2^{0(12)}$ | −2.19 | −1903.8 | −1.64 | −1934.5 | — | — | (c) |
| $NaAl(OH)_3Cl^{0(13)}$ | −4.44 ± 0.52 | −1608.1 | — | — | −4.43 ± 0.10 | −1619.8 | (c) |

**I** Constants are given for the reactions:
(1) $SiO_{2(cr)} + 2HF^0_{(aq)} = Si(OH)_2F^0_{2(aq)}$;
(2) $0.5Al_2O_{3(cr)} + HF^0_{(aq)} + 2H^+ = AlF^{2+} + 1.5H_2O$;
(3) $0.5\,Al_2O_{3(cr)} + 2HF^0_{(aq)} + H^+ = AlF_2^+ + 1.5H_2O$;
(4) $0.5Al_2O_{3(cr)} + 3HF^0_{(aq)} = AlF^0_{3(aq)} + 1.5H_2O$;
(5) $0.5Al_2O_{3(cr)} + 2HF^0_{(aq)} + 0.5H_2O = Al(OH)_2F_2^- + H^+$;
(6) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + HF^0_{(aq)} = 0.5\,NaAlSi_3O_{8(cr)} + Al(OH)_2F^0_{(aq)}$;
(7) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + 2HF^0_{(aq)} = 0.5NaAlSi_3O_{8(cr)} + AlOHF^0_{2(aq)} + H_2O$;
(8) $0.5Al_2O_{3(cr)} + 1.5H_2O = Al(OH)^0_{3(aq)}$;
(9) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + 2H_2O = 0.5NaAlSi_3O_{8(cr)} + Al(OH)_4^- + H^+$;
(10) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + 2H_2O + Na^+ = 0.5NaAlSi_3O_{8(cr)} + NaAl(OH)^0_{4(aq)} + H^+$;
(11) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + HF^0_{(aq)} + H_2O + Na^+ = 0.5NaAlSi_3O_{8(cr)} + NaAl(OH)_3F^0_{(aq)} + H^+$;
(12) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + 2HF^0_{(aq)} + Na^+ = 0.5NaAlSi_3O_{8(cr)} + NaAl(OH)_2F^0_{2(aq)} + H^+$;
(13) $0.5NaAl_3Si_3O_{12}H_{2(cr)} + NaCl^0_{(aq)} + H_2O = 0.5NaAlSi_3O_{8(cr)} + NaAl(OH)_3Cl^0_{(aq)}$.
The uncertainties for reaction constants correspond to the standard deviation of experimental data ($\sigma_n$).
**II** Source of thermodynamic data for listed complexes: [a]UNITHERM (Shvarov and Bastrakov, 1999); [b]Tagirov and Schott (2001); [c]this study; source of the thermodynamic properties of other aqueous species and minerals is given in section 3.3.
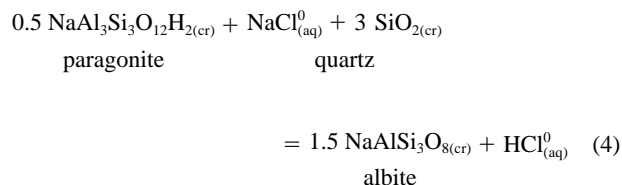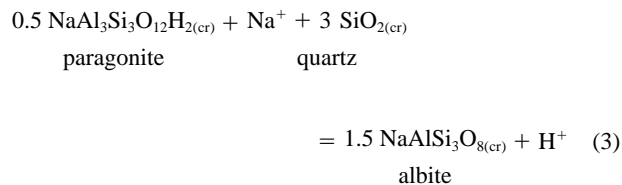
free energy does not affect calculated thermodynamic properties of Al complexes. Gibbs free energies and formation constants for aqueous Al and Si complexes adopted from the literature and used in the speciation calculations are listed in Table 4.

## 3. RESULTS AND DISCUSSION

### 3.1. Al Speciation in NaCl Solutions

Solubility experiments in Cl-bearing solutions were performed at 400°C, 500 bars and 450°C, 1000 bars. The initial NaCl concentration varied from 0 to 3.5 m. Experimental results are listed in Table 3 and depicted in Figure 1a,b. Figure 1b shows that results of the present study carried out in NaCl-free solutions are in excellent agreement with the solubility of the albite-paragonite-quartz assemblage measured in pure water by Woodland and Walther (1987) despite the different experimental techniques, i.e., Morey-type reaction vessel allowing sampling of the experimental solution in Woodland and Walther (1987) and batch autoclaves in this work, and different analytical methods, i.e., directly coupled plasma spectroscopy (DCP) used in Woodland and Walther (1987) and AASF used in the present study.

Reaction of paragonite plus quartz to form albite tooks place in experiments with high NaCl concentrations according to the reactions controlling chemical equilibrium between the albite-paragonite-quartz assemblage and an aqueous solution (Hemley, 1959; Montoya and Hemley, 1975; Sverjensky et al., 1991):

$$0.5\,NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + 3\,SiO_{2(cr)}$$
$$\text{paragonite} \qquad \text{quartz}$$

$$= 1.5\,NaAlSi_3O_{8(cr)} + H^+ \quad (3)$$
$$\text{albite}$$

$$0.5\,NaAl_3Si_3O_{12}H_{2(cr)} + NaCl^0_{(aq)} + 3\,SiO_{2(cr)}$$
$$\text{paragonite} \qquad \text{quartz}$$

$$= 1.5\,NaAlSi_3O_{8(cr)} + HCl^0_{(aq)} \quad (4)$$
$$\text{albite}$$

In a few high-NaCl runs, quartz or paragonite were completely consumed as shown by their absence in the residual solid after experiment. These experiments were therefore discarded. To verify the reliability of experimental results for concentrated NaCl solutions, several runs were performed with a greater amount of quartz (1–1.5 g instead of 0.45–0.50 g). Results of these experiments are consistent with those performed with a smaller mass of quartz.

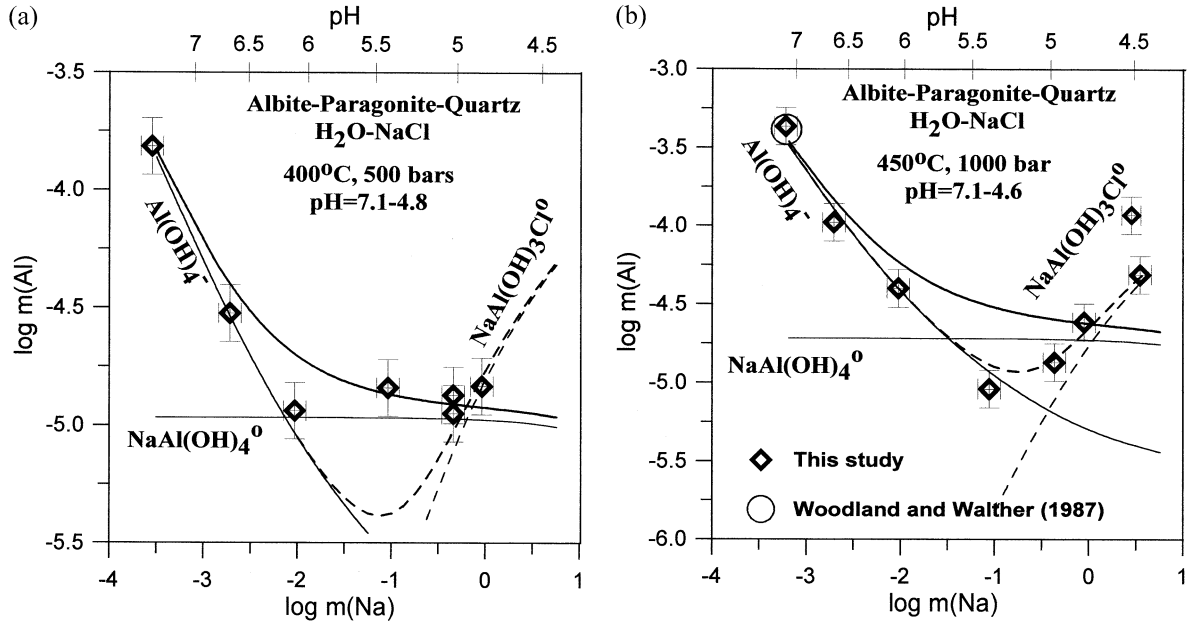Equilibria involved in the formation of Al-hydroxide complexes can be described by the following general equation:
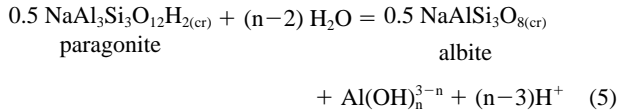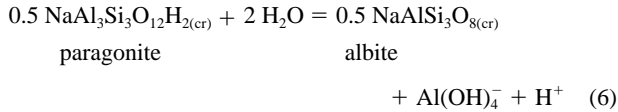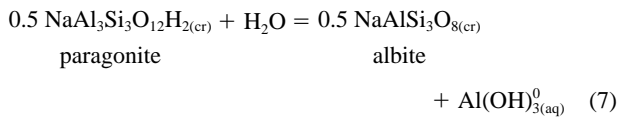
Fig. 1. Logarithm of Al concentration in equilibrium with the albite-paragonite-quartz assemblage at 400°C, 500 bars (a) and 450°C, 1000 bars (b) as a function of the logarithm of the total Na concentration. Symbols represent experimental data, but the curves were calculated using the thermodynamic properties for Al complexes taken from Table 4. The thick line corresponds to total Al concentration for the $Al(OH)_4^- + NaAl(OH)_{4(aq)}^0$ speciation model, and thin solid lines show concentrations of these species. The thick dashed line gives total Al concentration for the $Al(OH)_4^- + NaAl(OH)_3Cl_0^{(aq)}$ speciation model, and the thin dashed line shows the concentration of $NaAl(OH)_3Cl_{(aq)}^0$.

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + (n-2)\ H_2O = 0.5\ NaAlSi_3O_{8(cr)}$$

paragonite                         albite

$$+ Al(OH)_n^{3-n} + (n-3)H^+ \quad (5)$$

For the pH range of interest (from near neutral to slightly acid, depending on NaCl concentration) only two hydroxide species ($Al(OH)_4^-$ and $Al(OH)_3^0$; Pokrovskii and Helgeson, 1995; Shock et al., 1997; Tagirov and Schott, 2001) can form in significant amounts according to:

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + 2\ H_2O = 0.5\ NaAlSi_3O_{8(cr)}$$

paragonite                         albite

$$+ Al(OH)_4^- + H^+ \quad (6)$$

and

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + H_2O = 0.5\ NaAlSi_3O_{8(cr)}$$

paragonite                         albite

$$+ Al(OH)_{3(aq)}^0 \quad (7)$$

with

$$K_6 = (H^+) \cdot (Al(OH)_4^-) \quad (8)$$

and
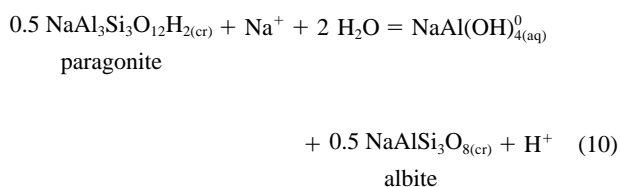
$$K_7 = (Al(OH)_{3(aq)}^0) = [Al(OH)_{3(aq)}^0] \quad (9)$$

where (i) and [i] denote the activity and concentration of the *i*th species, respectively. Examining Eqn. 3, 6, and 8, one can conclude that if $Al(OH)_4^-$ dominates aqueous Al speciation, the concentration of Al in solution is proportional to the pH and thus pNa of the fluid ($\log(Al(OH)_4^-) = \log K_6 + pH = \log K_6 - \log K_3 + pNa$).

Experimental data plotted in Figure 1a,b show that in dilute NaCl solutions, Al concentration decreases by ~1.5 log units on addition of NaCl. It follows that $Al(OH)_4^-$ is the dominant aluminum species for log m(NaCl) < −2 at 400°C and 500 bars, and for log m(NaCl) < −1.5 at 450°C and 1000 bars. It should be noted that aqueous Al concentration in dilute NaCl solutions may also be affected by the formation of $Al(OH)_3H_3SiO_4^-$ (aq), whose stability constant has been determined by Pokrovski et al. (1998) and Salvi et al. (1998), or by feldspar-like Na-Al-Si-(OH) complex as suggested by Anderson and Burnham (1983), Anderson et al. (1987), and Pascal and Anderson (1989). Formation of these complexes may lead to total aluminum concentration increase in basic and neutral solutions. Calculations of Al speciation in natural fluids given in Salvi et al. (1998), Arnòrsson (1999), Stefànsson and Arnòrsson (2000), and Tagirov and Schott (2001) indicate that aluminum-silicate complexes can be dominant in alkaline solutions saturated with respect to quartz at subcritical temperatures. Experimental data reported in Pokrovski et al. (1998) and Salvi et al. (1998) demonstrate that the stability of Al-Si complexes decreases with increasing temperature. However, as quartz solubility increases with temperature, Al-Si complexes may form in appreciable amounts even in supercritical crustal fluids. For example, extrapolation of the stability constants

reported in Pokrovski et al. (1998) and Salvi et al. (1998) shows that $Al(OH)_3H_3SiO_4^-{}_{(aq)}$ may account for ~80% of total Al at 400°C, 500 bars in chloride-free fluids buffered by the albite-paragonite-quartz assemblage. Such estimates, however, can be affected by substantial uncertainties at supercritical temperatures. Conversely, as shown above, the dependence of aqueous Al concentration on NaCl concentration at the experimental conditions of the present study can be precisely described without these species. Moreover, Al concentration measured in NaCl-free solutions is in good agreement with predictions based on the thermodynamic properties of $Al(OH)_4^-$ given in Diakonov et al. (1996) and Tagirov and Schott (2001). Therefore we did not try to approximate the possible effect of Al-Si complexes on Al speciation. More experimental data are necessary to characterize the stability of these species at supercritical temperatures.

Contrary to dilute solutions, experiments with m(NaCl) > 0.1 show no dependence of aqueous Al on NaCl at 400°C and 500 bars (Fig. 1a), whereas in experiments at 450°C and 1000 bars (Fig. 1b), Al concentration increases proportionally to the NaCl content of the solution. This behavior demonstrates that $Al(OH)_4^-$ is not the dominant Al species at these conditions. The presence of $Al(OH)_3^0{}_{(aq)}$ should be considered because as shown by Eqn. 7, its formation does not depend on pH. However, speciation calculations based on the thermodynamic properties of Al hydroxide complexes derived from solubility measurements at subcritical temperatures (Castet et al., 1993; Bénézeth et al., 1997, 2001) show that $Al(OH)_3^0$ should account for < 1% of total aqueous aluminum at the conditions prevailing in our experiments. For example, at 400°C and 500 bars, the calculated $Al(OH)_3^0{}_{(aq)}$ molality is $3.7 \cdot 10^{-7}$ (Diakonov et al., 1996), $1.4 \cdot 10^{-7}$ (Tagirov and Schott, 2001) or $3.4 \cdot 10^{-8}$ mol/kg $H_2O$ (Shock et al., 1997). Such a difference between measured (~$2 \cdot 10^{-5}$ m) and calculated Al concentration cannot be explained by the uncertainties attached to the thermodynamic properties of aqueous species and minerals. Aluminum chloride and hydroxide chloride species also can be ruled out because they can only form in concentrated HCl solutions (Korzhinsky, 1987; Baumgartner and Eugster, 1988). For example, at 400 to 700°C and 2 kbar pressure, $Al(OH)_2Cl^0{}_{(aq)}$ dominates Al speciation at m(HCl) from 0.1 to 0.5 mol/kg $H_2O$ and $AlOHCl_2^0{}_{(aq)}$ at higher concentrations of HCl. These conditions were never met in our experiments.
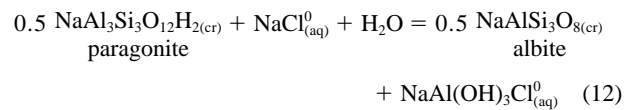
As shown by Anderson and Burnham (1967, 1983), Pascal and Anderson (1989), Azaroual et al. (1996), and Diakonov et al. (1996), a sodium- or potassium-aluminate complex, $(Na,K)Al(OH)_4^0{}_{(aq)}$, can form in high-temperature Na- or K-bearing solutions. If this species prevails, the Al concentration is also independent of fluid composition, as shown by Eqn. 3 and

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + 2\ H_2O = NaAl(OH)_4^0{}_{(aq)}$$
$$\text{paragonite}$$

$$+ 0.5\ NaAlSi_3O_{8(cr)} + H^+ \quad (10)$$
$$\text{albite}$$

with

$$K_{10} = (H^+) \cdot (NaAl(OH)_4^0{}_{(aq)})/(Na^+) \quad (11)$$

Aqueous Al concentrations calculated, using $Al(OH)_4^-$ and $NaAl(OH)_4^0{}_{(aq)}$ formation constants from Table 4, are plotted as a function of NaCl molality in Figure 1a,b (thick solid line). A good agreement is observed between calculated and experimental data at 400°C, 500 bars which demonstrates that $NaAl(OH)_4^0{}_{(aq)}$ dominates Al speciation at high NaCl concentrations (Fig. 1a), but at 450°C, 1000 bars the calculated curve does not match the observed aqueous Al increase with NaCl concentration. This deviation may be because the activity coefficient model used (Eqn. 1, 2) is inadequate for supercritical concentrated solutions. An alternative explanation is the possible formation of Na-Al-OH-Cl complexes at high NaCl concentrations. $NaAl(OH)_3Cl^0{}_{(aq)}$ is the simplest species that could cause the measured Al concentration increase according to:

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + NaCl^0{}_{(aq)} + H_2O = 0.5\ NaAlSi_3O_{8(cr)}$$
$$\text{paragonite} \qquad\qquad\qquad \text{albite}$$

$$+ NaAl(OH)_3Cl^0{}_{(aq)} \quad (12)$$

with

$$\text{with } K_{12} = (NaAl(OH)_3Cl^0{}_{(aq)})/(NaCl^0{}_{(aq)}) \quad (13)$$

As shown by Eqn. 12, the Al concentration should be proportional to $[NaCl^0]$ (or to total sodium concentration at a first approximation) if $NaAl(OH)_3Cl^0{}_{(aq)}$ dominated Al speciation. The thick dashed line in Figure 1a,b shows the calculated $[Al_{tot}]$, assuming that $Al(OH)_4^-$ and $NaAl(OH)_3Cl^0{}_{(aq)}$ dominate Al speciation in diluted and concentrated NaCl solutions, respectively. This curve agrees markedly better with experimental data than that assuming the formation of $NaAl(OH)_4^0{}_{(aq)}$ except for one point obtained at 400°C, 500 bars and 0.1 m (NaCl). At this solubility minimum, however, the Al concentration may be affected by impurities in the minerals (i.e., traces of fluorine were detected in several grains of paragonite by microprobe analyses). It is thus possible that formation of an F-bearing equivalent to $NaAl(OH)_3Cl^0{}_{(aq)}$ (e.g., $NaAl(OH)_{4-n}F_n^0{}_{(aq)}$; see below), albeit in small amounts, contributed to bias-measured Al concentrations at this solubility minimum. Nonetheless, more experimental data are necessary to confirm the formation of $NaAl(OH)_3Cl^0{}_{(aq)}$ and determine its stability. Therefore, for the purpose of this study, we preferred to describe the Al speciation in concentrated NaCl solutions with $NaAl(OH)_4^0{}_{(aq)}$, for which well-defined thermodynamic data are available (Pokrovskii and Helgeson, 1995; Diakonov et al., 1996).

Gibbs free energies for $Al(OH)_4^-$ and $NaAl(OH)_4^0{}_{(aq)}$ are listed in Table 4. These values were obtained from speciation calculations using the GIBBS computer code to best fit the experimental data. Thermodynamic properties of $NaAl(OH)_4^0{}_{(aq)}$ and formation constants for these species calculated in this manner and those reported in Diakonov et al. (1996) are in good agreement. For example, from Table 4 one can calculate a log K for the reaction

$$Na^+ + Al(OH)_4^- = NaAl(OH)_4^0{}_{(aq)} \quad (14)$$
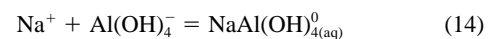
equal to 2.46 and 2.04 at 400°C, 500 bars and 450°C, 1000 bars, respectively, which are consistent with the values given in Diakonov et al. (1996) for the same P-T conditions, i.e., 2.19 and 2.08. Similarly, the Gibbs free energy of $NaAl(OH)_4^0{}_{(aq)}$
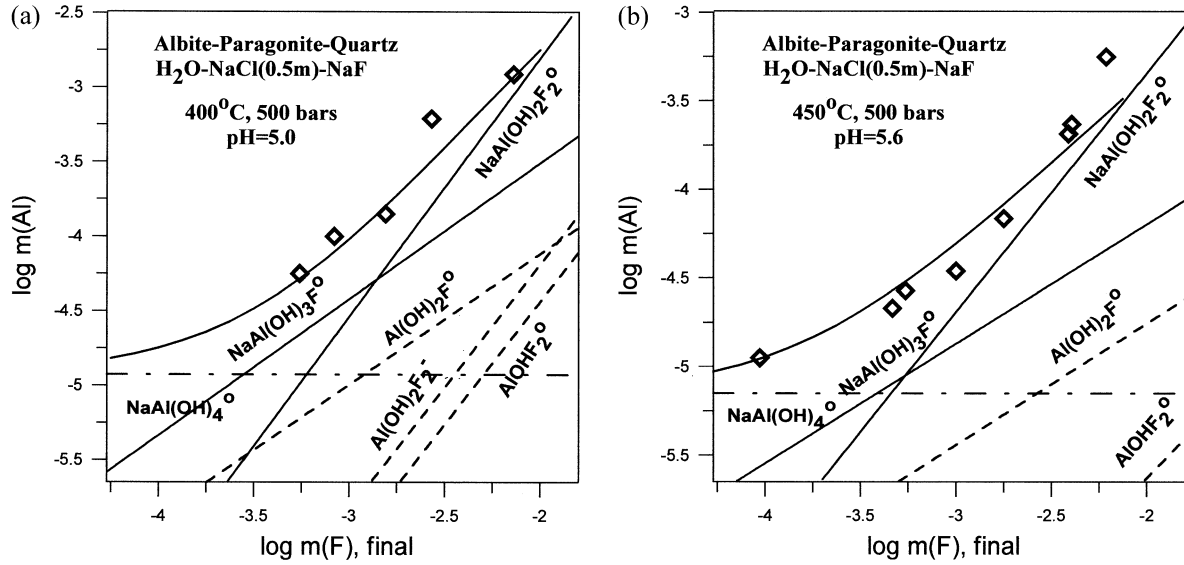
Fig. 2. Logarithm of Al concentration in equilibrium with the albite-paragonite-quartz assemblage at 400°C, 500 bars (a) and 450°C, 500 bars (b) as a function of the logarithm of total fluorine concentration. Symbols represent experimental data. The thick solid curve corresponds to the calculated total Al concentration, whereas the thin solid curves represent the concentration of complexes whose Gibbs free energies were fitted in this study. Dashed lines correspond to concentrations of other Al species (their thermodynamic properties are listed in Table 4).
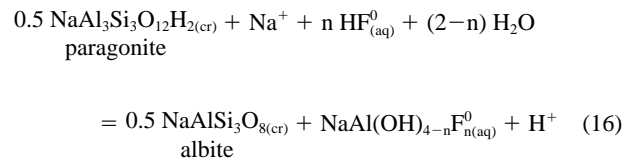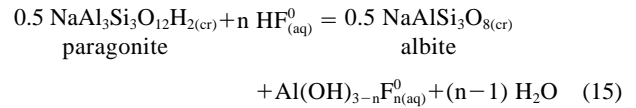
calculated in the present study for both experimental P-T conditions agree within 1 kJ/mol ($<$ 0.1 log unit of the reaction constant) with the values recommended by Diakonov et al. (1996). In contrast, at 450°C, 500 bars, Diakonov et al. (1996) give the Gibbs free energy for $NaAl(OH)_{4(aq)}^0$, which is 4.6 kJ/mol more negative than that calculated in the present study. This discrepancy leads to an uncertainty of 0.33 log unit on the reaction constant and may arise from poor performance of the HKF model in describing the thermodynamic properties of low-density fluid components. However, this uncertainty is close to those in the experimental data listed in Table 4, and, therefore, Al speciation at metamorphic conditions should be properly described using the formation constants for $NaAl(OH)_{4(aq)}^0$ given in Diakonov et al. (1996).

### 3.2. Al Speciation in Fluoride-Bearing Systems

To quantify fluorine impact on aluminum speciation in near-neutral supercritical fluids, the Al concentration in equilibrium with the albite-paragonite-quartz assemblage was measured at 400 and 450°C at 500 bars as a function of NaF concentration. NaCl concentration was kept constant in all experiments and equal to 0.505 m. As the NaF concentration did not exceed 10% of total Na, pNa and pH were assumed to be constant to a first approximation of fluid speciation. This assumption implies that, according to Eqn. 6 and 10, concentrations of $Al(OH)_4^-$ and $NaAl(OH)_4^0$ are also constant (note that, as discussed above, for m(NaCl) = 0.505, the latter species dominates Al speciation in fluoride-free solutions). Measured Al concentrations are listed in Table 3 and depicted in Figure 2a,b as a function of total fluorine concentration. An increase in Al concentration of up to two orders of magnitude obtained from fluoride-bearing experiments indicates strong aluminum-fluoride complexing at near-neutral pH (calculated pH values are

5.6 and 5.0 at 450 and 400°C, respectively). Formation of topaz was observed in runs performed with m(NaF) $>$ 0.1; paragonite was not found in the reaction products after these runs, whereas aqueous fluorine and aluminum concentrations were below the detection limit.

The observed increase of Al concentration in F-bearing solutions can be explained by the formation of $Al(OH)_{3-n}F_{n(aq)}^0$ and $NaAl(OH)_{4-n}F_{n(aq)}^0$ according to the reactions

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + n\ HF_{(aq)}^0 = 0.5\ NaAlSi_3O_{8(cr)}$$
paragonite $\qquad\qquad$ albite

$$+ Al(OH)_{3-n}F_{n(aq)}^0 + (n-1)\ H_2O \quad (15)$$

$$0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + n\ HF_{(aq)}^0 + (2-n)\ H_2O$$
paragonite

$$= 0.5\ NaAlSi_3O_{8(cr)} + NaAl(OH)_{4-n}F_{n(aq)}^0 + H^+ \quad (16)$$
albite

with

$$K_{15} = (Al(OH)_{3-n}F_{n(aq)}^0)/(HF_{(aq)}^0)^n \quad (17)$$

$$K_{16} = (NaAl(OH)_{4-n}F_{n(aq)}^0) \cdot (H^+)/(Na^+) \cdot (HF_{(aq)}^0)^n \quad (18)$$

Mixed Al-OH-F complexes form in mildly acid hydrothermal and metamorphic fluids, as proven by measurement of corundum solubility in HF solutions (Soboleva and Zaraisky, 1990; Zaraisky, 1994). The formation of different $Al(OH)_{3-n}F_n^0$ complexes was checked by fitting Soboleva and Zaraisky (1990) and Zaraisky (1994) corundum solubility data with the FITEQL 3.1 computer code (Herbelin and Westall,

Table 5. Reaction constants and Gibbs free energy values of aluminum hydroxide fluoride complexes at 1000 bars pressure calculated from corundum solubility data of Soboleva and Zaraisky (1990) and Zaraisky (1994).

| | 300°C | | 400°C | | 500°C | | 600°C | |
|---|---|---|---|---|---|---|---|---|
| | log K | $\Delta g°$ | log K | $\Delta g°$ | log K | $\Delta g°$ | log K | $\Delta g°$ |
| $Al(OH)_2F$ [a] | $-0.71 \pm 0.10$ | $-1254.6$ | $-1.23 \pm 0.10$ | $-1272.8$ | $-2.02 \pm 0.20$ | $-1287.3$ | — | — |
| $AlOHF_2$ [b] | $0.97 \pm 0.20$ | $-1335.9$ | $0.51 \pm 0.10$ | $-1361.0$ | $-0.07 \pm 0.10$ | $-1387.6$ | $-0.47 \pm 0.10$ | $-1416.8$ |

[a] $0.5Al_2O_{3(cr)} + HF^0_{(aq)} + 0.5H_2O = Al(OH)_2F^0_{(aq)}$;
[b] $0.5Al_2O_{3(cr)} + 2HF^0_{(aq)} = AlOHF^0_{2(aq)} + 0.5H_2O$.
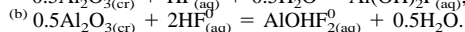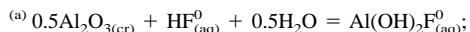
1994). Results of these calculations presented in Table 5 and depicted in Figure 3a–d demonstrate that $Al(OH)_2F^0_{(aq)}$ and $AlOHF^0_{2(aq)}$ provide the best fit of experimental data. Standard thermodynamic properties and HKF equation of state parame-

ters (Tanger and Helgeson, 1988) for $Al(OH)_2F^0_{(aq)}$ and $AlOHF^0_{2(aq)}$ calculated using the formation constants of these species from Table 5 are given in Tagirov and Schott (2001). These data were used in the present study to calculate solute
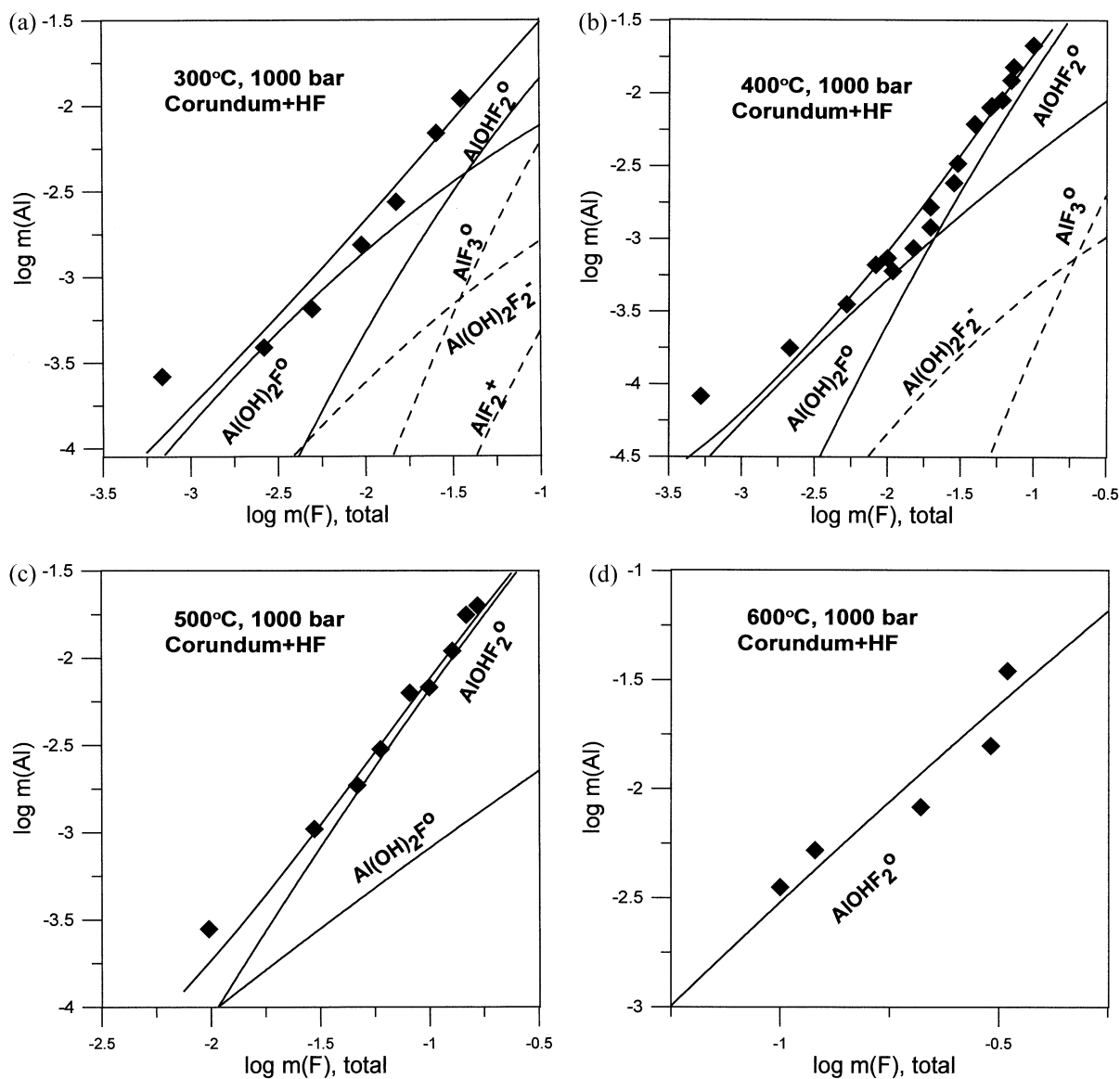


Fig. 3. Logarithm of Al concentration in equilibrium with corundum at 300°C (a), 400°C (b), 500°C (c), and 600°C (d) and 1000 bars as a function of the logarithm of total HF concentration. The symbols represent experimental data of Zaraisky (1994), but the curves were calculated as in Figure 2.

Table 6. Speciation (mol/kg $H_2O$) of an aqueous fluid (m(NaCl) = 0.5) in equilibrium with the albite-paragonite-quartz mineral assemblage at 400°C, 500 bars and 450°C, 1000 bars. Fluorine concentrations are m(F) = $8.31 \cdot 10^{-4}$ and $10^{-3}$, respectively. Thermodynamic properties of aqueous Al species are from Table 4.

| Species | 400°C, 500 bars | 450°C, 500 bars |
|---|---|---|
| $H^+$ | 2.5E-5 | 1.5E-5 |
| $OH^-$ | 1.2E-6 | 1.5E-6 |
| $H_4SiO_4^0$ | 2.0E-2 | 1.8E-2 |
| $Si(OH)_2F_2^0$ | 7.5E-6 | 2.5E-4 |
| $F^-$ | 1.8E-5 | 7.5E-6 |
| $HF^0$ | 6.9E-4 | 4.1E-4 |
| $HF_2^-$ | 9.2E-7 | 9.5E-6 |
| $Cl^-$ | 2.1E-1 | 9.4E-2 |
| $HCl^0$ | 2.3E-4 | 5.6E-4 |
| $Na^+$ | 2.1E-1 | 9.4E-2 |
| $NaOH^0$ | 4.6E-7 | 4.5E-7 |
| $NaF^0$ | 1.5E-5 | 5.2E-6 |
| $NaCl^0$ | 2.9E-1 | 3.0E-1 |
| $Al(OH)_3^0$ | 1.4E-7 | 1.7E-7 |
| $Al(OH)_4^-$ | 3.2E-6 | 3.2E-6 |
| $Al(OH)_2F^0$ | 9.0E-6 | 3.8E-6 |
| $AlOHF_2^0$ | 5.5E-7 | 1.6E-7 |
| $Al(OH)_2F_2^-$ | 8.9E-7 | 5.9E-8 |
| $NaAl(OH)_4^0$ | 8.6E-6 | 1.5E-5 |
| $NaAl(OH)_3F^0$ | 3.3E-5 | 1.5E-5 |
| $NaAl(OH)_2F_2^0$ | 2.2E-5 | 2.4E-5 |
| Total Al | 7.7E-5 | 6.1E-5 |
| pH | 5.0 | 5.6 |



Fig. 4. Logarithm of calculated Al concentration in equilibrium with corundum at 400°C, 500 bars as a function of pH in pure water (solid line) and in a 0.5-m NaCl solution (dashed line). Curves were generated using thermodynamic data for Al complexes taken from Table 4. The symbols correspond to calculated corundum solubilities in pure water (filled rhomb) or in a 0.5-m NaCl solution (open rhomb).

speciation in equilibrium with the albite-paragonite-quartz assemblage. Note that these complexes alone cannot account for the effect of fluorine on Al concentration in sodium-bearing near-neutral solutions. Calculated thermodynamic properties of $NaAl(OH)_3F^0_{(aq)}$ and $NaAl(OH)_2F^0_{2(aq)}$ complexes are listed in Table 4. These values were determined using the GIBBS computer code to obtain the best description of experimental data.

Several sources of errors can affect the calculated formation constants for Na-Al-OH-F complexes. First, knowledge of the stability constants for the other fluoride-bearing aqueous complexes is necessary to calculate the thermodynamic properties of F-bearing Al complexes. The formation of $Si(OH)_2F^0_{2(aq)}$ may markedly change fluorine speciation, especially in high-temperature solutions. No experimental determinations of its stability are available at these conditions. Therefore, we used for $Si(OH)_2F^0_{2(aq)}$ stability the value listed in the UNITHERM database (Shvarov and Bastrakov, 1999), which was estimated using the low-temperature measurements of Kuyunko (1984). Solute speciation calculations reported in Table 6 for two solutions in equilibrium with the albite-paragonite-quartz assemblage show that 1 and 50% of total fluorine can be present as $Si(OH)_2F^0_{2(aq)}$ at 400°C and 450°C, 500 bars, respectively. Therefore, it follows that uncertainties in the calculated formation constants for Na-Al-OH-F species should increase in high-temperature, low-density solutions.

Another source of error arises from the fact that the Gibbs free energy of paragonite can be affected by the formation of fluor-paragonite, due to the incorporation of fluorine. However, available experimental data reviewed in Zhu and Sverjensky (1991) suggest that at the conditions of our experiments, the mol fraction ($X_F$) of fluor-paragonite should not exceed 0.1. The activity coefficient for the $X_{OH}$ = 0.9 hydroxyl-paragonite
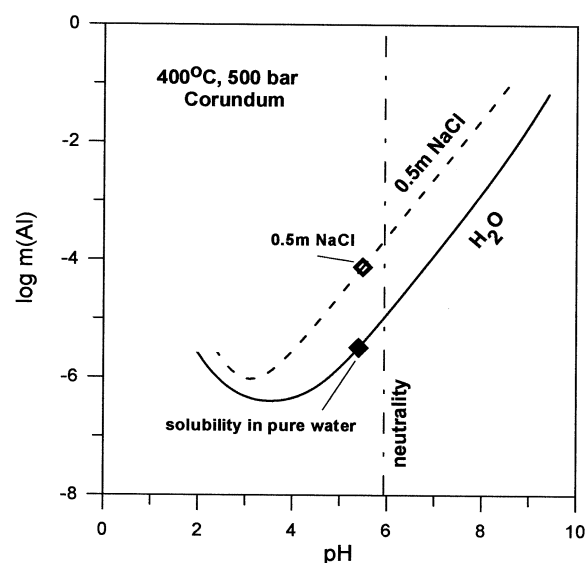
endmember in the solid solution can range from 1 (ideal solution) to 0.9 or 1.1 (regular solution; Garrels and Christ, 1965). This corresponds to a change of the hydroxyl-paragonite Gibbs free energy of ~1 kJ/mol at 400 to 450°C (< 0.1 log unit for the reaction constant), which has only a minor effect on the calculated formation constants values for Na-Al-OH-F complexes. To resume the above discussion, total uncertainties associated with the formation constants for mixed Na-Al-OH-F complexes calculated in this study should not exceed 1 log unit.

## 4. EFFECT OF pH, NaCl, AND F ON THE SOLUBILITY OF AL-BEARING MINERALS

The thermodynamic data generated in the present study show that Al mobility in a supercritical fluid is mostly governed by the activity of NaCl and HF as well as by the pH. Figure 4 shows corundum solubility calculated as a function of pH in pure water and in a 0.5-m NaCl fluid at 400°C, 500 bars. The slopes of the curves indicate that above a pH of ~4, $Al(OH)_4^-$ dominates Al speciation. The figure also shows that a solution in equilibrium with corundum is ~0.6 pH units more acid than neutrality due to the reaction

$$0.5\ Al_2O_{3(cr)} + 2.5\ H_2O = Al(OH)_4^- + H^+ \qquad (19)$$
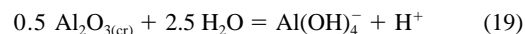
Addition of acid to a solution of neutral pH in equilibrium with corundum yields a significant solubility decrease as illustrated in Figure 4. Moreover, the pH of a pure aqueous fluid equilibrated with the albite-paragonite-quartz assemblage is alkaline (pH > 7; Fig. 5). Therefore, although $Al_2O_3$ activity is lower in aluminosilicate minerals than in corundum, aqueous Al concentration in equilibrium with the albite-paragonite-quartz assemblage in pure water (Fig. 5) is several times higher than that in equilibrium with corundum in pure water (Fig. 4). This behavior was indeed observed in measurements of corun-
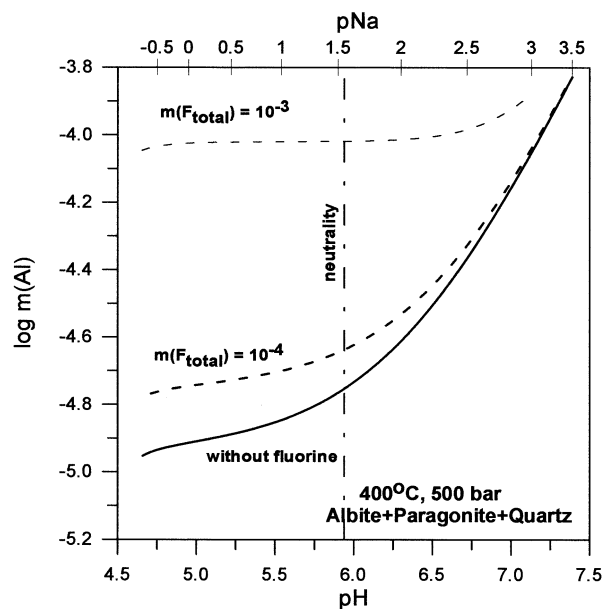
Fig. 5. Logarithm of calculated Al concentration in equilibrium with the albite-paragonite-quartz assemblage at 400°C, 500 bars as a function of pH. Thermodynamic data for Al complexes are from Table 4. The solid line corresponds to Al concentration in a fluorine-free solution but thin- and thick-dashed lines show Al concentration in a $10^{-3}$ m and $10^{-4}$ m total F solution, respectively.
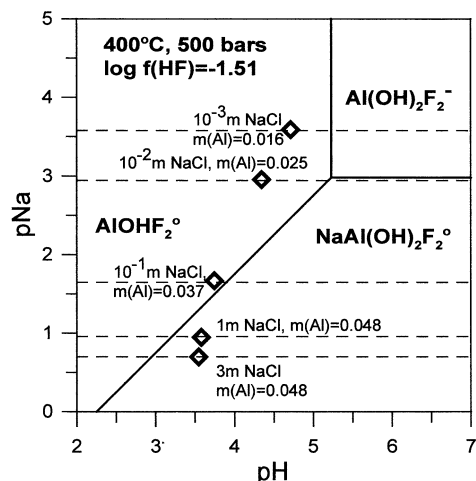


Fig. 6. pNa-pH predominance diagram showing Al speciation in the Henderson molybdenite deposit ore-forming fluid (Gunow et al., 1980) at 400°C, 500 bars and for log f(HF) $= -1.51$. Horizontal dashed lines show pNa for different NaCl concentrations, and symbols correspond to pH values calculated for fluids of given m(NaCl) in equilibrium with muscovite. Thermodynamic properties of Al aqueous species are from this study, whereas those for other aqueous species are from SUPCRT92 and Shock et al. (1997). Muscovite and fluormuscovite thermodynamic properties were taken from Sverjensky et al. (1991) and Zhu and Sverjensky (1991), respectively.

dum solubility (Ragnarsdottir and Walther, 1985) and of Al concentrations in equilibrium with the albite-paragonite-quartz and the potassium feldspar-muscovite-quartz mineral assemblages (Woodland and Walther, 1987; Walther and Woodland, 1993). In the presence of NaCl, formation of $NaAl(OH)_{4(aq)}^0$ and the decrease in the activity coefficients of charged species yield an increase in equilibrium Al concentration of about one order of magnitude (m(NaCl) = 0.5) compared to that in pure water at similar pH values (dashed and solid lines, respectively, in Fig. 4).

An outcome of this study is that the solubility of aluminum silicate minerals is more affected by the presence of fluorine in NaCl-bearing (acid) solutions than in sodium-free (more alkaline) solutions (Fig. 5). Al concentration increases ~1.5 times at 400°C, 500 bars when fluorine concentration reaches $10^{-4}$ m (~2 ppm, thick dashed lines in Fig. 5). With further addition of fluorine, the aluminum concentration dramatically increases and reaches $10^{-4}$ m when m(F, total) $= 10^{-3}$. Results of the present study suggest that the temperature increase and pressure decrease promote the formation of Na-Al-OH-F complexes with an increase of $NaAl(OH)_2F_{2(aq)}^0$ stability relative to that of $NaAl(OH)_3F_{(aq)}^0$. It follows that Al mobility will be more important in fluorine-bearing, high-temperature, low-density fluids.

Fluorine concentrations in fluids associated to hydrothermal ore deposits vary widely and can reach $10^{-1}$ m. HF concentration from $10^{-3}$ to $10^{-1}$ m was estimated in Aksyuk (2000) for different types of skarn deposits. Greisens are also characterized by high fluorine concentrations of $10^{-2}$–$10^{-1}$ m (Bottrel and Yardley, 1988; Zaraisky, 1994). For example, extremely high fluorine concentrations have been found in micas from the Henderson molybdenite greizen deposit (Gunow et al.,

1980). Log $f(H_2O)/f(HF)$ in this ore body derived from micas fluorine contents averages ~3.9 at 350 to 400°C. Using a value of log $f(H_2O)/f(HF) = 3.82$ at 400°C (Fig. 8 in Gunow et al., 1980), we obtain log f(HF) $= -1.51$ (m($HF_{(aq)}^0$ = 0.041) at 400°C, 500 bars. A diagram showing aqueous aluminum speciation corresponding to these P-T-f(HF) conditions is shown in Figure 6. High HF concentration leads to predominance of the aluminum hydroxide fluoride complexes at all pNa-pH conditions. Dashed horizontal lines show pNa for different NaCl concentrations. $AlOHF_{2(aq)}^0$ predominates at m(NaCl) < 0.1 m, but $NaAl(OH)_2F_{2(aq)}^0$ dominates Al speciation at higher NaCl concentrations. Al concentrations are extremely high (n·0.01 m) due to Al-F interaction and increase toward the predominance field of $NaAl(OH)_2F_{2(aq)}^0$. These results show that in supercritical fluoride-bearing fluids, aluminum is transported as Al-OH-F and Na-Al-OH-F complexes, depending on pH and NaCl concentration.

## 5. CONCLUDING REMARKS

Solubility of the albite-paragonite-quartz mineral assemblage was measured at 400 and 450°C, 500 and 1000 bars as a function of NaCl and NaF concentrations. In NaCl-bearing, NaF-free systems, Al concentration decreases by ~1.5 log units when the NaCl molality increases to m(NaCl)≈0.01. This demonstrates that $Al(OH)_4^-$ dominates Al speciation at these conditions. On further increase in NaCl molality, Al concentration becomes constant at 400°C, 500 bars, and increases at 450°C, 1 kb. This can be explained by the formation of $NaAl(OH)_{4(aq)}^0$ and/or $NaAl(OH)_3Cl_{(aq)}^0$. Calculated constants of the reaction $Na^+ + Al(OH)_4^- = NaAl(OH)_{4(aq)}^0$ are $10^{-2.46}$ and $10^{-2.04}$ at 400°C, 0.5 kb and 450°C, 1 kb, respectively, and are in good agreement with the data of Diakonov et al. (1996).

In the fluoride-bearing system, $NaAl(OH)_3F^0_{(aq)}$ and $NaAl(OH)_2F^0_{2(aq)}$ dominate Al speciation in near-neutral NaCl-rich metamorphic fluids. Formation of these complexes yields up to a $\sim$100-fold increase of aqueous Al concentration in equilibrium with the albite-paragonite-quartz mineral assemblage. These complexes, together with $NaAl(OH)^0_{4(aq)}$, can explain aluminum high mobility in sodium- and fluoride-rich environments that are typical for the formation of greisens (Burt, 1981) and sapphire deposits (Moine et al., 1998).

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