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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 ± 0.10 and -10.59 ± 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 $NaAl(OH)^0_{4(aq)}$ or $NaAl(OH)_3Cl^0_{(aq)}$. The calculated constant for the reaction $Al(OH)_4^- + Na^+ = NaAl(OH)^0_{4(aq)}$ 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 $NaAl(OH)_3F^0_{(aq)}$ and $NaAl(OH)_2F^0_{2(aq)}$, according to $0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + HF^0_{(aq)} + H_2O = 0.5\ NaAlSi_3O_{8(cr)} + NaAl(OH)_3F^0_{(aq)} + H^+$, log K $= -5.17$ and -5.23 at 400°C and 450°C, 500 bars, respectively, and $0.5\ NaAl_3Si_3O_{12}H_{2(cr)} + Na^+ + 2\ HF^0_{(aq)} = 0.5\ NaAlSi_3O_{8(cr)} + NaAl(OH)_2F^0_{2(aq)} + H^+$, 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 $NaAl(OH)_2F^0_{2(aq)}$ in low-density fluids also increases relative to $NaAl(OH)_3F^0_{(aq)}$. These complexes, together with $Al(OH)_2F^0_{(aq)}$ and $AlOHF^0_{2(aq)}$, 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, $(Na,K)Al(OH)^0_{4(aq)}$, 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 (Gautier, 1999; Gautier et al., 2001). All minerals were ground and sieved to the 300- to 500-μm size fraction. Fine particles were removed by ultrasonic cleaning in deionized water.

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

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

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 ± 10% at a 95% confidence level. Several analyses of Al were performed using ICP-MS. The difference between these two methods was within ± 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 ± 0.01 unit for pH < 3.5 and up to ± 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 ± 5%. Fluoride concentrations were measured immediately after sampling with a Tacussel fluoride-selective electrode using TISAB-III (Orion) as an ionic strength and pH adjuster. This method yields fluoride concentrations with an accuracy of ± 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 ± 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-μm filter. An aliquot of 4 to 5 mL was