

X-ray photoelectron spectroscopic measurement of the temperature dependence of leaching of cations from the albite surface

Yang Chen ^a, Susan L. Brantley ^{a,*}, Eugene S. Ilton ^b

^a Department of Geosciences, Pennsylvania State University, University Park, PA 16802 USA

^b Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, PA 18015 USA

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Abstract

Polished albite single crystals were dissolved in flow or semi-batch reactors containing solutions at pH 2.9 ± 0.1 at 5°, 50°, and 90°C until steady state dissolution was achieved. At steady state, all effluent solutions contained $\leq 1.4 \times 10^{-4}$, 5.1×10^{-5} , and 3.6×10^{-5} mol l⁻¹ of Si, Al and Na, respectively. Solution chemistry data was consistent with preferential Na and Al leaching during the early dissolution for experiments at 5 and 50°C, while stoichiometric dissolution dominated reaction at 90°C. Depth profiles of Si, Al, and Na were measured on the crystal surfaces after dissolution using angle-resolved X-ray photoelectron spectroscopy (ARXPS). The extent of Na and Al leaching in the near-surface layer of albite, as measured by ARXPS under the experimental conditions, was observed to decrease with increasing temperature. The decreased leaching of Al and Na at higher temperature is interpreted as the result of competition between dissolution of the surface layer and diffusion of Al and Na from the leached layer into the solution. Higher dissolution rates relative to diffusion rates at elevated temperatures are inferred to have decreased the thickness of the leached layer. These results indicate that the activation energy for albite dissolution (65 kJ mol⁻¹) is higher than that for cation diffusion in the surface layer by about 10 kJ mol⁻¹. Such an estimated activation energy is almost identical to that measured for diffusion of Na through albite glass, as reported in the literature. XPS measurements of crystal surfaces dissolved at pH 2.9 at 90°C as a function of time also show that the Al concentration of the albite surface did change measurably during dissolution from 0 to 1 week, but did not change measurably during dissolution from ~1 to 6 weeks. The Na concentration of the surface decreased rapidly from bulk values within the first week of leaching, and then increased slightly at 6 weeks of leaching. Relatively rapid attainment of a steady state surface chemistry may imply that the long periods needed for attainment of steady state dissolution in rate experiments is related more to slow reactions such as (1) repolymerization and structural re-equilibration, or (2) development of etch pits and porosity, as opposed to fast reactions such as cationic diffusion. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although feldspar dissolution has been extensively studied over the past 25 years, the mechanism

* Corresponding author. Tel.: +1-814-863-1739; fax: +1-814-865-3191; e-mail: brantly@geosc.psu.edu

and surface chemistry of feldspar dissolution is still poorly understood and is a matter of controversy (e.g., Blum and Stillings, 1995 (and references therein); Brantley and Stillings, 1996; Walther, 1997; Brantley and Stillings, 1997). Early studies using X-ray photoelectron spectroscopy (XPS) suggested that dissolution of feldspar and other minerals in natural environments and in the laboratory was stoichiometric (Wilson, 1975; Petrovic et al., 1976; Berner and Holdren, 1977, 1979). For example, the examination of naturally weathered plagioclase grains by Berner and Holdren (1979) revealed no evidence for leached layers thicker than 20 Å with a composition different from that of the bulk. However, indirect evidence obtained from solution chemistry data (e.g., Chou and Wollast, 1984, 1985) showed that albite dissolution in acid solution at 25°C formed a cation-leached, silica-enriched surface layer on the order of several tens of angstroms thick at the surface of feldspar. With the further advances in surface analytical techniques (e.g., angle-resolved XPS, secondary ion mass spectrometry (SIMS), Rutherford back-scattering, resonance nuclear reaction analysis, etc.), numerous experiments have now verified the presence and some of the characteristics of the leached layer (e.g., Casey et al., 1988; Nesbitt and Muir, 1988; Petit et al., 1989, 1990; Muir et al., 1989, 1990; Casey and Bunker, 1990; Schweda, 1990; Hellmann et al., 1990; Muir and Nesbitt, 1991; Hellmann, 1994, 1995). With these surface analytical techniques, one is able to measure the concentration profiles of species on the surface of feldspar to a depth of several tens to thousands of angstroms.

The discrepancy between the earlier XPS work on laboratory-dissolved feldspars and the evidence of the leached layers suggested by solution chemical analysis was explained by Schweda (1990), who argued that the earlier dissolution experiments were run in the presence of buffer solutions. As noted by several workers, use of buffer and salt solutions can modify the surface chemistry behavior (e.g., Stillings and Brantley, 1995). The direct evidence collected by Petit et al. (1989) showed that very thin leached layers developed when crystals were reacted in solution with initially high Na concentrations. To explain discrepancies reported for naturally weathered samples, Hellmann (1995) also suggested that the samples examined by Berner and Holdren (1979) were

probably weathered at close to neutral pH conditions where chemical affinity differences may have been important, and where leached layers are generally negligible. Most recently, Nugent et al. (1998a; b) suggested that most naturally weathered feldspars from acidic soils may be coated with aluminosilicate coatings that are difficult to image (i.e., investigators have not known the coatings were present). These coatings have surface composition different from the “true” weathered feldspar surface.

Despite the remaining inconsistencies, the accumulation of data on surface analysis of feldspar and other minerals has greatly influenced the understanding of the mechanisms of silicate dissolution. It is now generally accepted that, during dissolution at acidic conditions over a range of temperatures, a cation-leached, silicon-enriched layer develops on the surface of feldspar (e.g., Blum and Stillings, 1995; Brantley and Stillings, 1996). Thickness of the layer generally increases as pH decreases from neutral to acid conditions and as An component increases (e.g., Hellmann, 1995; Brantley and Stillings, 1996). Leached layers are especially deep for certain high An content compositions such as labradorite (Schweda et al., 1997). Documentation using energy dispersive spectroscopic analysis (EDS) and Raman spectroscopy for albite dissolved briefly at 200°C has also suggested that Na and Al surface leaching is spatially heterogeneous on some altered alkali feldspar surfaces (Gout et al., 1997). Similar results documenting heterogeneous leaching have also been reported by other workers (e.g., Hellmann, 1995).

Cation leaching from the surface layer of feldspar was explained by Petit et al. (1989; 1990) as the result of ion exchange between the alkalis and hydrogen species. However, these authors also observed that there is not a simple 1:1 correspondence between hydrogen uptake and cation release in leached albite (see also Hellmann et al., 1990). Similar results were reported by Casey et al. (1988; 1989) who observed that the amount of cations that were leached out of labradorite was much greater than the amount of hydrogen added to the surface. Casey et al. (1989) also observed that surface H-inventories on feldspar increase with an increase in temperature. Some of the deficiency in H in the surface has been attributed to repolymerization of the feldspar network, with release of H₂O (Casey et al., 1989). The

most extensive research into the formation of leached layers on albite for dissolution at temperatures $> 100^{\circ}\text{C}$ are described in a series of papers by Hellmann et al. (Hellmann et al., 1990, 1997; Hellmann, 1994, 1995, 1997). In contrast to the previous citations for work at lower temperatures, these workers have documented that under some conditions, the H incorporation into the leached layer is greater than the loss of cations from that layer (Hellmann et al., 1997). Under acid conditions, these workers argue that the leached layer is formed by interdiffusion of Na and H along with structural rearrangements in the silicate network (including preferential Al hydrolysis and polymerization reactions). Although Hellmann (1995) calculates from solution chemistry that the depth of leaching of Na at 100°C and pH 2 decreases with increasing temperature to 300°C , his results are ambiguous at other temperatures because of precipitation of Al-containing phases and he suggests that more data is needed to thoroughly corroborate a temperature dependence.

In this paper we investigate whether the extent of leaching increases or decreases with temperature on albite dissolved in acid solution from 5 to 90°C , and we investigate the rate of cation leaching at 90°C . We compare samples dissolved under steady state conditions in dilute, buffer-free solution at pH 2.9.

Angle-resolved XPS was used for chemical analysis of the surface of albite. XPS yields compositional and chemical-state information for the near-surface region of solids (see Hochella, 1988 for review). Variation of the angle of the sample surface with respect to the photoelectron detector changes the information depth, d (the depth over which 95% of the signal originates), for XPS analyses by $d = 3\lambda \sin \phi$, where λ is the attenuation length for the photoelectrons of interest, and ϕ is the angle between the detector and the sample surface (or the take-off angle for photoelectrons). Using Eq. 5.21 in Seah (1990) to calculate λ for Al 2p, Na 2s, and Si 2p in feldspar, d ranges from about 15 Å to 90 Å as ϕ varies from 10 to 90° , assuming a clean and flat surface, and Al K α X-rays. The presence of adventitious carbon would decrease the information depth at all take-off angles, but to a greater extent at lower take-off angles. Another problem in interpreting exact depth from the take-off angle is that, as surface roughness increases, depth sensitivity is increasingly

lost. Therefore, for the experiments reported here and for ARXPS data reported in the literature for leached albite (e.g., Hellmann et al., 1990), actual conversion from take-off angle to depth for all angles is imprecise (roughness may be a particular problem for samples leached at 90°C). Note that potential artefacts related to adventitious carbon and roughness complicates interpretation of published XPS results, as well as this work: we mention these problems not because they are more severe in our experiments, but rather to emphasize why we did not calculate information depths from take-off angles used during ARXPS. In addition, relative comparisons among samples treated similarly, such as those described here, should yield robust conclusions.

2. Experiments

2.1. Samples and experimental conditions

Albite samples obtained from Harvard Mineralogical Museum (Cat. No. 102576) originated from Lac Pied des Monts mica mine, Charlevoix, Quebec, Canada. Using SEM analysis, we observed that these crystals contain infrequent micron-sized inclusions of potassium feldspar, mica, and apatite (in decreasing frequency of occurrence). Crystals of Quebec albite (see Table 1 for bulk composition as measured by electron microprobe (EM)) were cut into cylinders 1–2 mm in thickness and 6 mm in diameter. One side of the crystal was then polished sequentially using corundum, carbide, and diamond paste to 0.25 microns. To minimize leaching during polishing, mineral oil was used instead of water. The polished crystals of albite were ultrasonically cleaned in ultra-pure acetone, dried at 105°C , and stored in a desiccator before experiments. Albite powder, also used in the dissolution experiments, was prepared by grinding Amelia albite crystals (see Stillings and

Table 1
Electron microprobe analysis of Quebec albite

Wt.%					Total	Mole ratio	
SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	(%)	Al/Si	Na/Si
65.75	21.46	10.69	1.69	0.29	99.89	0.38	0.32

Brantley, 1995 for composition) to a size fraction of 100–200 mesh. This size-fractionated powder was then ultrasonically cleaned using ultrapure acetone to remove fine particles attached to the surface of large grains. This material was further treated with heavy liquid (bromoform) to remove any impurities with different specific gravities. Prior to the experiments, the albite grains were thoroughly washed ultrasonically with acetone and heated in an oven at 105°C for over a month (Chen and Brantley, 1997). Powder was used in the flow-through experiments so as to observe measurable changes in solution chemistry during the experiment while the polished planchets were dissolving.

Five experiments, divided into two groups, were conducted (Table 2). Group 1 was run at the same pH (pH = 2.9 measured at 25°C) but different temperatures, and group 2 was run at the same pH (pH = 2.9) and temperature (90°C), but for different reaction durations. Group 1 experiments reveal the effect of temperature on leaching, and group 2 experiments reveal the rate of leaching at 90°C and pH 2.9.

The experiments at temperatures of 5° and 50°C were conducted in continuously stirred flow-through 81-ml reactors made of polycarbonate (Fig. 1, Table 2). These experiments are the identical experiments described by Chen and Brantley (1997). Reactors were submerged in water baths which maintained temperature to $\pm 1^\circ\text{C}$. Polished single crystals (four samples in each reactor) were mounted in the reactors while fluid was pumped through at rates of 0.077 ml h⁻¹ (5°C) and 0.16 ml h⁻¹ (50°C). Albite

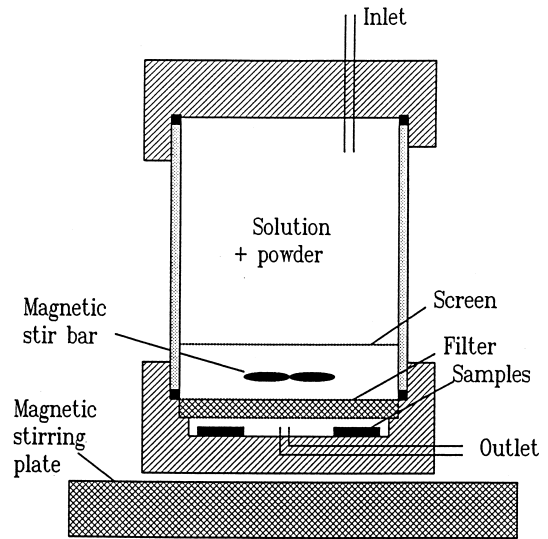


Fig. 1. Reactor used for 5° and 50°C leaching experiments. Both polished crystals and albite powder were included in each reactor so that changes in surface chemistry and solution chemistry could be monitored. These experiments are identical to those described by Chen and Brantley (1997).

powder was also present in each reactor, separated from the stirring bar by a mesh screen (Fig. 1). Flow rates were different so as to maintain low concentrations of Na, Al, and Si in reactors in an effort to preclude precipitation reactions of such phases as kaolinite, gibbsite, and halloysite. Outlet fluid passed through a 0.45 μm filter while leaving the reactor. Chemistry of output solutions was continuously monitored (Chen and Brantley, 1997), and experi-

Table 2
Experimental conditions

Run	T (°C)	pH ^a	Solution concentration (mol/l) ^b			Duration (h)
			Si	Al	Na	
AB5-2	5	2.9	1.2×10^{-5}	4.4×10^{-6}	2.2×10^{-6}	4300
AB50-1	50	2.9	1.4×10^{-4}	5.1×10^{-5}	3.6×10^{-5}	4600
AB90-1W	90	2.9	2.8×10^{-6}	1.1×10^{-6}	8.7×10^{-6}	192
AB90-2W	90	2.9	2.8×10^{-6}	1.1×10^{-6}	8.7×10^{-6}	355
AB90-6W	90	2.9	2.8×10^{-6}	1.1×10^{-6}	8.7×10^{-6}	1005

^a Measured at 25°C.

^b Concentrations of Si, Al, and Na at 5° and 50°C were measured steady state concentrations. However, concentrations at 90°C were the maximum concentrations calculated using the rate equation (Chen and Brantley, 1997): $\log r = -2.71 - 3410/T - 0.5\text{pH}$, where r is the dissolution rate in mol albite (NaAlSi₃O₈) cm⁻² s⁻¹, T is temperature in K. Other parameters used in calculating the concentrations were: volume of solution = 30 ml, reaction time before solution was replaced with fresh solution = 48 h, maximum surface area = 5.9 cm² (initially there were seven disks 6 mm in diameter and 1.5 mm thick on average in each reactor).

ments were terminated when the system reached steady state (see Table 2). Steady state was defined as that point where the concentrations of Na, Al, and Si were constant over time within experimental error. In most cases, dissolution at steady state was stoichiometric, although measurement of (generally) low concentrations of Na by inductively coupled plasma atomic emission spectroscopy precluded extremely accurate estimation of Na release rates. Low levels of element concentrations for some conditions in flow-through dissolution experiments with feldspars commonly precludes accurate estimation of stoichiometry of dissolution.

For experiments at 90°C, we could not use samples from the experiments described by Chen and Brantley (1997) due to breakage of the samples during the runs, and we therefore used a non-stirred polyethylene batch reactor to reproduce similar experiments and samples. In contrast to the lower temperature experiments, seven polished crystals were placed in 30 ml of solution with no powder present. The solution in the batch reactor was replaced with fresh solution every other day so that solution pH did not change significantly (± 0.05). Albite crystal samples were removed from the reactor after ~ 1 (192 h), ~ 2 (355 h), and 6 (1005 h) weeks.

All solutions in this study were made to pH 2.9 using ultra-pure HCl and distilled, deionized water. Based on the results of our previous experiments at 90°C (Chen and Brantley, 1997), approximately 6 weeks were required for albite dissolution to reach steady state at 90°C under similar pH conditions. Based upon our earlier calculations (Chen and Brantley, 1997), it is estimated that pH under all run conditions was equal to 2.9 ± 0.1 (where variability relates to observed variability in measurements).

2.2. Angle-resolved XPS analysis

After reaction, the single crystals of albite were removed, rinsed in distilled water, and ultrasonically cleaned in ultrapure acetone, and then were analyzed using angle-resolved XPS. XPS analyses were performed with a Scienta ESCA-300 spectrophotometer (Lehigh University). All measurements used monochromatic Al K_{α} X-rays. The analyzer operating parameters of 300 eV pass energy and a 1.1 mm slit

yielded a Fermi level width of 0.66 eV. The total power applied to the rotating anode for X-ray generation was 3.0 kW. Angle-resolved data were acquired at 90, 45, 30, 20, 15 and 10° take-off angles and consisted of high-resolution regional scans over line positions of the elements of interest (Na 2s, Al 2p, and Si 2p). Total analysis times were 2.5 minutes for Si, and ranged from 5 to 9 minutes for Na and Al. The analytical reproducibility was 5%. Al K_{α} photoionization cross sections were used as first-order sensitivity factors for semi-quantification (Scofield, 1976). This was deemed adequate because the experimental information of most interest was contained in the relative compositional changes from sample to sample, and from angle to angle. Backgrounds were subtracted with a linear fit.

3. Results

Chen and Brantley (1997) reported that the dissolution experiments at 5 and 50°C (the identical experiments reported here) were initially nonstoichiometric, and release rates decreased with time over thousands of hours until steady state was achieved at 4300 h (5°C) or 4600 h (50°C). Experiments at 90°C were also nonstoichiometric initially (but for only several tens of hours), and did not attain steady state until about 600 h. Nonstoichiometric dissolution was consistently observed as molar Na release rate and Al release rate > Si release rate (Fig. 2). Such nonstoichiometric dissolution could be related to precipitation reactions; however, saturation indices of three of the most likely secondary phases were calculated using PHREEQC, v. 1.6 (Parkhurst, 1995) as indicating undersaturated solutions: $SI_{\text{kaolinite}} = -9.03$ (90°C), -4.7 (50°C), -10.9 (5°C); $SI_{\text{gibbsite}} = -2.7$ (90°C), -2.6 (50°C), -4.9 (5°C); $SI_{\text{halloysite}} = -13.5$ (90°C), -9.5 (50°C), -16.0 (5°C). Thus, no precipitates were expected. In addition, precipitation of these phases (even if it occurred) could not explain the *enhanced* release of Na and Al observed with respect to Si. Finally, no pure silica phases were oversaturated in the experiments.

Na- and Al-depletion of surfaces was generally documented using XPS, especially at lower temperatures (Table 3). The at.% Na, Al, and Si in the near-surface of albite leached at 5°, 50° and 90°C at

pH 2.9 are tabulated in Table 3 and mole ratios of samples measured at 6 weeks are plotted in Fig. 3 as a function of take-off angle. For comparison, mole ratios calculated from an electron microprobe (bulk) analysis of an unleached sample are also plotted on the same graphs.

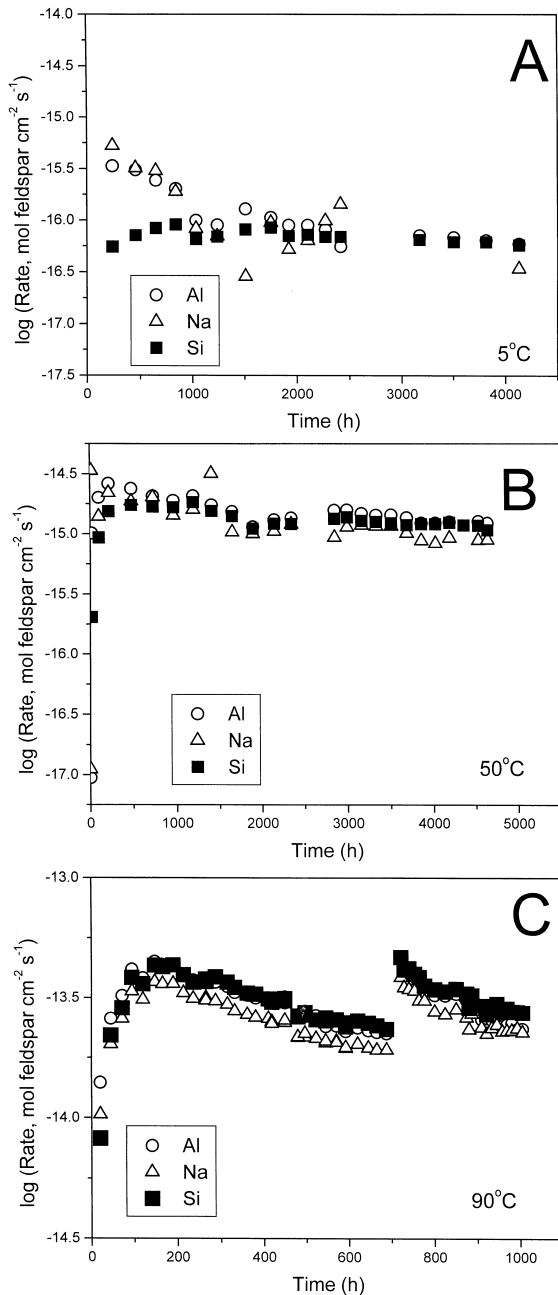


Fig. 3 clearly shows that a Na- and Al-depleted, Si-enriched layer forms on the surface of albite samples leached at 5° and 50°C. Leaching at 90°C (6 week sample as plotted in Fig. 3), if present, is much less developed. For these experimental conditions, the extent of leaching (total loss of cation integrated over the outer 90 Å of albite surface) of Na and Al relative to Si decreases with increasing temperature.

A reference range bar is also plotted on both Fig. 3A and B, centered at the average EM composition to indicate an estimate of the range in Al/Si or Na/Si due to chemical heterogeneities among crystal blanks. These ranges were measured by Nugent et al. (1998a; b) using XPS on ten blank samples of Quebec albite prepared and polished similarly to our samples. Data from the sample measured here was also incorporated into the range. Measurements by Nugent et al. (1998a; b) were completed using a different instrument and slightly different analytical conditions (Al 2p, Si 2p and Na peaks from a Kratos XSAM 800 spectrometer utilizing different sensitivity factors; 90° take-off angle). The samples reported by Nugent et al. (1998a; b) were polished in the presence of distilled water and were cleaned by ultra-violet ozone cleaning (UVOC) for a minimum of 20 min before analysis to remove adventitious carbon. In contrast, samples reported here were polished without water and were not treated by UVOC. In tests, we observed that the same sample run between the two instruments yielded at.% ratio data that was reproducible to within 4%, but that at.% ratios measured on samples run on the Kratos XSAM 800 with and without UVOC treatment could vary by as much as 20%. Variability in Na/Si ratios were much larger than variations in Al/Si ratios. Therefore, presumably because of polishing and UVOC

Fig. 2. (A) The log (dissolution rate, mol feldspar $\text{cm}^{-2} \text{s}^{-1}$) based upon Na, Al, or Si as measured by Chen and Brantley (1997) at 5°C. (B) The log (dissolution rate, mol feldspar $\text{cm}^{-2} \text{s}^{-1}$) based upon Na, Al, or Si as measured by Chen and Brantley (1997) at 50°C. These experiments are the identical experiments reported here (see text). (C) The log (dissolution rate, mol feldspar $\text{cm}^{-2} \text{s}^{-1}$) based upon Na, Al, or Si as measured by Chen and Brantley (1997) at 90°C for experiment 6-90a. This experiment was repeated as a batch experiment for the leaching work reported in this paper (see text). Break in data at approximately 700 h is due to a change in flow rate.

Table 3
Results of leaching experiments

Sample	Angle (°)	Atomic concentration (%) ^a		
		Si	Al	Na
Unleached	10	66.2	13.7	18.5
	15	59.4	15.8	22.6
	20	57.1	16.7	23.7
	30	55.3	18.6	23.5
	45	55.2	19.7	22.2
	90	56.1	20.1	20.9
AB5-2	10	91.9	4.6	3.4
	15	91.9	4.9	4.0
	20	90.1	5.4	4.5
	30	88.1	6.4	5.5
	45	85.3	8.3	6.5
	90	82.8	9.7	7.5
AB50-1	10	70.6	15.6	13.8
	15	69.8	16.2	14.0
	20	70.0	16.7	13.3
	30	69.4	16.9	13.7
	45	67.9	17.2	14.9
	90	68.2	17.4	14.4
AB90-1W	10	66.1	20.1	13.8
	15	66.4	19.6	14.1
	20	66.5	20.1	13.4
	30	64.4	20.2	15.4
	45	65.1	19.8	15.1
	90	65.7	19.4	14.9
AB90-2W	10	68.5	18.2	13.3
	15	67.1	18.6	14.2
	20	67.2	18.3	14.4
	30	66.3	19.2	14.6
	45	64.6	18.9	16.4
	90	66.1	18.9	14.9
AB90-6W	10	62.3	19.5	17.2
	15	62.7	19.0	17.5
	20	61.6	19.8	17.8
	30	62.0	20.3	16.8
	45	61.5	20.2	17.5
	90	61.1	20.1	17.7

^a Atom $X/(Na + Si + Al)$, integrated over the analysis depth.

differences, Na/Si ratios of the surfaces were observed to differ greatly between the untreated sample here (Na/Si = 0.37) and the average of 10 blanks reported by Nugent et al. (1998a; b) (Na/Si = 0.23). Differences in the Al/Si ratio were much smaller (0.36 compared to 0.37 respectively).

We argue, however, that although differences in protocol and instrumentation caused differences in *magnitudes* of ratios, the *ranges* measured in the previous study are undoubtedly representative of

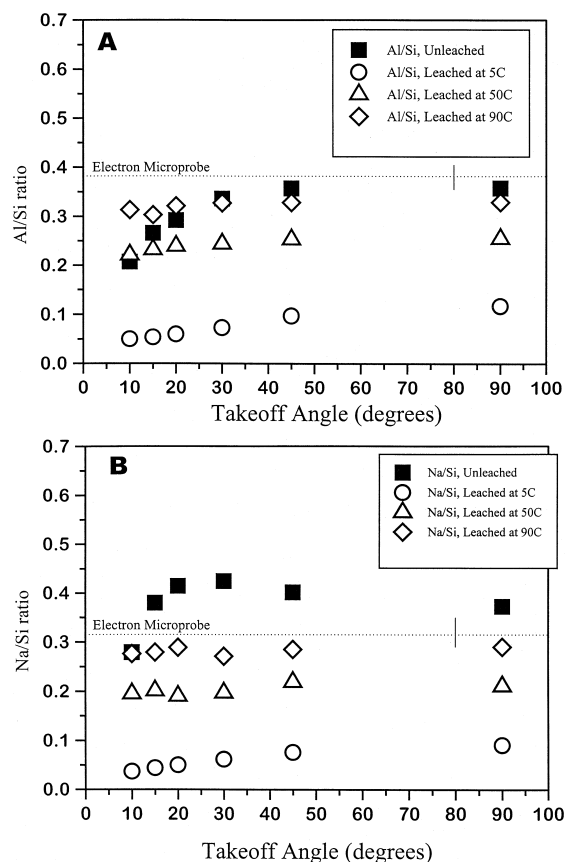


Fig. 3. (A) Change of Al/Si mole ratio with take-off angle for unleached albite and albite leached under conditions in Table 2. All samples leached 6 weeks. Depth of analysis increases with take-off angle up to approximately 90 Å at 90° (see text). Line labeled electron microprobe represents an electron microprobe (bulk) analysis of unleached, polished Quebec albite sample. The range bar plotted at 80° take-off angle is an estimate of the range in Al/Si due to heterogeneity of different blank plinets, as measured by Nugent et al. (1998a; b). This range in composition should be plotted at 90 Å for comparison to XPS data, but it has been shifted slightly for clarity of presentation. Samples used for range estimate were prepared and measured by XPS using a slightly different protocol, and a different instrument (see text). The range bar has been centered over the EM value because the blank samples were prepared with water during polishing and absolute ratios differed slightly from blanks in this study. (B) Change of Na/Si mole ratio with take-off angle for unleached albite and albite leached under conditions as in (A). Depth of analysis increases with take-off angle up to approximately 90 Å at 90° (see text). Line labeled electron microprobe represents an electron microprobe (bulk) analysis of unleached, polished Quebec Albite sample. The bar plotted at an 80° take-off angle is an estimate of the range in Na/Si due to heterogeneity of different blank plinets, as measured by Nugent et al. (1998a; b) and by the authors. (See (A) and text).

variability in the natural Quebec albite material because reproducibility of XPS measurements for the same analysis area on one blank were well within 5%. Such inter-sample heterogeneity, also observed by Hellmann et al. (1990) is most likely due to the variable concentration of secondary phases in the albite. For these reasons, ranges from Nugent et al. (1998a; b) are considered adequate for addressing heterogeneity in samples analyzed here.

Fig. 3A shows that for the unleached crystal, the surface ratio of Al/Si increases from 0.21 at a take-off angle of 10° to 0.36 at 90° , which is well within the estimated range of sample heterogeneity. The ratio of Na/Si on the unleached crystal, however, is consistently higher than the bulk value (0.32) at all depths except for the very top surface (Fig. 3B). These high values are also outside the expected range of variability.

Results presented in Fig. 3A and B show a significant temperature-dependence of leaching. The departure from stoichiometry (as defined by EM analyses and the range in XPS analyses on blanks), increases when temperature decreases: Al/Si and Na/Si ratios progressively decrease from 90° to 50° to 5°C for all take-off angles. At 90°C , Fig. 3A and B show that the Al/Si and Na/Si ratios of the 90°C sample at depth only differ slightly from the EM value, and are within or close to the range of estimated heterogeneity. In addition, at shallow take-off angles, the Al/Si ratio of the 90° leached sample is closer to the stoichiometric value than the ratio measured for the unleached sample.

XPS results from albite leaching experiments conducted at 90°C and pH 2.9 for different durations are plotted in Fig. 4 and tabulated in Table 3. To show the changes of Al and Na concentrations as a function of depth, data are plotted as Al/Si and Na/Si ratios vs. take-off angle, along with EM ratios and range estimates. Differences in Al/Si as a function of leaching time from 1 to 6 weeks are probably not significant, considering that each measurement was completed on a different crystal. However, all leached samples show higher Al/Si ratios nearer the surface (take-off angles $< 20^\circ$) and lower Al/Si ratios at depth (at take-off angles $> 30^\circ$) relative to the unleached sample, suggesting that both dissolution and leaching has occurred. The Na/Si data suggests that measurable leaching occurs in the first two weeks,

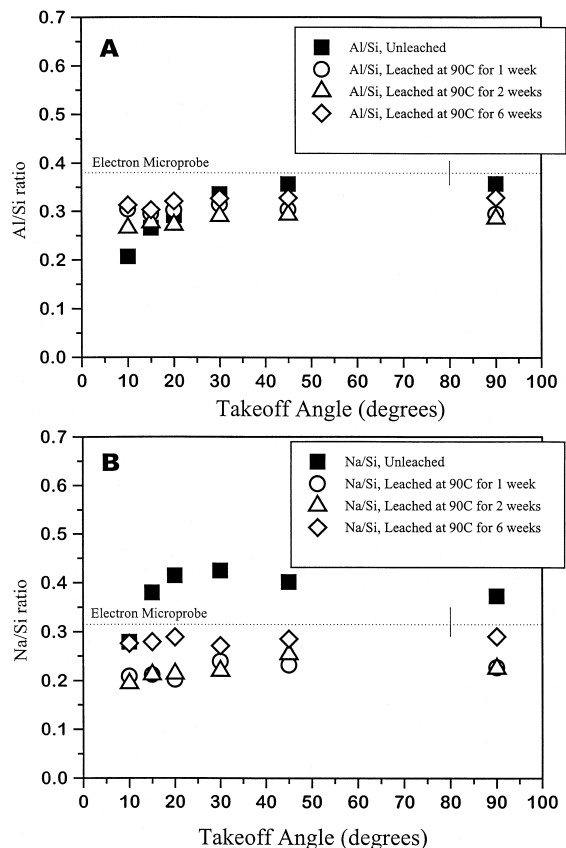


Fig. 4. (A) Change of Al/Si mole ratio with take-off angle for unleached albite and albite leached under conditions as indicated. EM value and range as in Fig. 3A. (B) Change of Na/Si mole ratio with take-off angle for unleached albite and albite leached under conditions as indicated. EM value and range as in Fig. 3A.

but that after six weeks the surface has dissolved such that the Na/Si ratio becomes almost stoichiometric.

Adventitious carbon on the surface of samples was analyzed by XPS and compared for the two sets of samples. Among Group I, the relative amount of C on the surface varied as $\text{AB90-6W} = \text{AB50-1} > \text{AB5-2}$. The relative amount of C on the 90°C samples (Group II) decreased from $\text{AB90-6W} > \text{Ab90-1W} \geq \text{AB90-2W}$.

4. Discussion

The Al/Si and Na/Si ratios measured on the unleached blank sample showed significant deviation

at shallow take-off angles from the EM values, even given the range in composition for 10 Quebec albite sample blanks measured at a take-off angle of 90°. Differences between XPS and EM measurements can be explained by: (1) the use of sensitivity factors for XPS measurements that are not measured directly for the phase of interest (2) differences in the information depths of XPS and EM. EM measures over much larger depths and so differences in surface chemistry due to preparation protocol will be revealed by XPS but not by EM. It is well-known that polishing affects the chemistry of most surfaces, and the decreased Al and increased Na at the feldspar blank surface (shallow take-off angle) is therefore attributed to such an artefact. As the ratios measured on leached samples (Figs. 3 and 4) differed significantly from unleached samples, we infer that mechanical and chemical effects of polishing were removed during dissolution, as expected.

Na and Al leaching was indicated by the solution chemistry during dissolution at 5 and 50°C (Na and Al release rates were > Si release rates early in dissolution, Fig. 2A,B). At 90°C, the initial release at 20 h showed enhanced Na and Al in comparison to Si release, but release rate ratios over the whole 1000 h experiment averaged 1.19 ± 0.10 (Si release rate/ $3 \times$ Na release rate) and 1.04 ± 0.11 (Si release rate/ $3 \times$ Al release rate). Therefore, little indication of enhanced release of Na and Al was observed at the higher temperature (Fig. 2C). As indicated previously, precipitation of secondary phases probably did not occur at any temperature since the saturation indices calculated for kaolinite, gibbsite, and halloysite were all < 0.

No attempt was made to calculate leached layer depths from these solution chemistry data as most of the experiments contained both powder and polished crystal (surface area of powder \gg polished crystal). The depths of leaching on powder and polished surfaces might not be similar due to differences in surface topography, porosity, defect density, etc. Furthermore, as pointed out by Hellmann (1995) and discussed in a later section, there is no reason that leached layer depths calculated from solution chemistry should equal depths measured spectroscopically.

We have, however, integrated total leached Na and Al from comparison of release rate data in Fig.

2. Note that data from experiment 6-90a, the flow-through experiment described by Chen and Brantley (1997) most similar to the batch experiment here was integrated for the 90°C calculation. (Remember that this original flow experiment did not yield intact albite crystals for analysis, and a repeat at 90°C was completed in a batch reactor in which the solution was changed every other day to provide the leached sample analyzed here). Total excess Na (or Al) released from the surface for each experiment was calculated by subtracting the Si release rate (mol feldspar $\text{cm}^{-2} \text{s}^{-1}$) from the Na (or Al) release rate, and then integrating over the experimental duration. In contrast to the ARXPS data, these calculations were inconclusive for Na leaching ($2 \pm 1 \times 10^{-9}$, $9 \pm 100 \times 10^{-11}$, and $-2.1 \pm 2.8 \times 10^{-8}$ mol Na cm^{-2} leached at 5, 50, and 90°C, respectively) and Al leaching ($7.3 \pm 0.7 \times 10^{-10}$, $4 \pm 1 \times 10^{-9}$, and $-4.4 \pm 5.7 \times 10^{-9}$ Al cm^{-2} at 5, 50, and 90°C, respectively). Large propagated errors in this calculation (small differences in relatively large numbers) make interpretation of solution chemistry problematic.

Analysis of the surface concentration of carbon showed that, for Group I samples, higher adventitious carbon was found on samples dissolved at the higher temperatures (50°, 90°C). Because higher C reduces the information depth, the difference in leaching between the 5°C and the 50 and 90°C samples is conservative. Consequently, the presence of adventitious C does not compromise the interpretation that leaching increases with decreasing *T*. Assuming that the leach profile shapes are independent of temperature, it follows that the depth of leaching increases with decreasing temperature. It is also reasonable to suggest that the leach depth for the 6 week 90°C sample is < 90 Å. It is not possible, however, to estimate the absolute depth of leaching using ARXPS due to the presence of adventitious C, some degree of surface roughness, and the calculated 90 Å information depth limit for XPS analyses of feldspars.

The temperature dependence of albite leaching represents a balance among at least three surface processes: penetration of hydrogen or water into the surface, diffusion of cations (Na and Al) from the leached layer into the solution, and detachment from the surface layer. Repolymerization of the Si tetrahe-

dral network also occurs, presumably affecting the rates of the other processes (Casey et al., 1988; Hellmann et al., 1990). Chen and Brantley (1997) have also argued that Al adsorption may be significant at temperatures above 50°C, and Hellmann et al. (1990) showed that anions may penetrate into the feldspar surface layer. The thickness of the leached layer at a given temperature and pH depends on the relative rates of these processes.

In this paper, we will argue that, for steady state dissolution, the rate of cation diffusion must slow to the point where the rate of cation leaching (diffusion and release to solution) equals the rate of net dissolution (dissolution minus surface adsorption or precipitation) of the outermost layer (e.g., Hellmann et al., 1990; Brantley and Stillings, 1996), and we will not address the rates of polymerization nor adsorption directly. We presume that the rates of these latter processes affect the observed net rate of dissolution, and are therefore implicitly included in this analysis. The rate of each of these processes is assumed to be temperature-dependent with different activation energies, thus affecting the observed activation energy of net dissolution. In this paper, we also do not assume any nonlinear effects, including the idea that the rate of dissolution, R , is directly related to the leached layer thickness (Hellmann, 1995; Brantley and Stillings, 1996). We argue that, if the apparent activation energy for net dissolution is greater than the activation energy for diffusion, then the dissolution rate will increase faster than the rate of leaching as temperature increases. The result would be a decreased leached layer thickness at higher temperature for both Na and Al, as observed in this study based on ARXPS data.

Experimental results indicate that at temperatures between 5° and 90°C in acid solutions, the activation energy of cation diffusion in the near surface layer of albite is lower than the net activation energy of albite dissolution. Chen and Brantley (1997) reported an apparent activation energy for net albite dissolution of 65 ± 3 kJ mol⁻¹ at temperatures from 5° to 300°C. In comparison, the activation energies of diffusion of Na in albite crystal and glass are reported to equal 176 ± 8 kJ mol⁻¹ (Kasper, 1975, as reported in Smith and Brown, 1988), and 56 ± 13 kJ mol⁻¹ (Jambon and Carron, 1976, as cited in Smith and Brown, 1988) respectively. Smith and Brown

(1988) infer, based upon indirect evidence, that the diffusion coefficient for Al is much lower than that of Na, perhaps by several orders of magnitude, and that the activation energy may be as high as 400 kJ mol⁻¹.

A broad estimate for the activation energy of diffusion through the leached layer on our samples may be made using a few assumptions. Assuming that, at steady state, the rate of release of Si from albite, r (mol feldspar cm⁻² s⁻¹) is equal to the rate of diffusion of either Na or Al across the leached layer (thickness l at steady state), then:

$$r = D\rho\Delta C/l \quad (1)$$

where D is the coefficient of cation diffusion, ρ is the atom density ((mol Na + mol Al + mol Si)/volume of the surface layer), and ΔC is the change in concentration C (at.% as defined in Table 3) of the cation (Na or Al) across the surface layer. Assuming that the values of r and D may be written with an Arrhenius temperature dependence, and that ρ and ΔC are constant with temperature (i.e., that $C = 0$ at the interface and $C =$ the bulk Quebec feldspar value at the bottom of the leached layer, e.g., Hellmann, 1995), we can derive:

$$l = \frac{A_{\text{diff}} \exp(-Q_{\text{diff}}/RT) \Delta C \rho}{A_{\text{diss}} \exp(-Q_{\text{diss}}/RT) \{H^+\}^n} \quad (2)$$

Here, Q_x or A_x is the activation energy or pre-exponential constant for dissolution ($x = \text{diss}$) or diffusion ($x = \text{diff}$), and R and T are the universal gas constant and absolute temperature, respectively. In addition, we have assumed that $r = k_{\text{diss}}\{H^+\}^n$, as modelled by many workers, including Chen and Brantley (1997). According to this simple model and the observation (Chen and Brantley, 1997) that $n = 0.5$ over the temperature range of interest, an Arrhenius plot ($\ln l$ vs. $1/T$) for one pH value should yield a slope equal to the value, $(Q_{\text{diss}} - Q_{\text{diff}})/R$. The predicted slope for such a plot (after correction for R) would therefore approximately equal -110 kJ mol⁻¹ or $+10$ kJ mol⁻¹, depending upon whether diffusion through the leached layer is more similar to Na diffusion in albite crystal or glass, respectively.

Unfortunately, the exact thicknesses of leached layers (l) in this study are impossible to determine. Given the uncertainty in the concentration vs. depth

data due to surface carbon and developed surface topography, extrapolation of the ARXPS to determine leached layer thicknesses was not attempted. Instead, we have chosen to plot a proxy for leached layer thickness (Fig. 5). In particular, we assumed that the leached layer thickness (depth such that $C = C_{\text{bulk}}$) could be approximated by the following function, Z , of C_{90} (the concentration of Na or Al integrated over 90 Å depth as measured by XPS at a 90° take-off angle):

$$Z = \frac{C_{\text{bulk}} 90}{C_{90}} \quad (3)$$

Here, C_{bulk} is the concentration of Na or Al as measured at a 90° take-off angle using XPS on the unleached sample (Table 3). Using this model we are implicitly assuming $C_{\text{surf}} = 0$ (concentration at a depth of 0 Å), $C_{\text{bulk}} = \text{value of unleached sample}$ (concentration at a depth of Z Å), and $C_{90} = \text{concentration of Na or Al at a depth of 90 Å}$. We assume that these three points lie on a concentration profile that varies linearly with respect to depth (= take-off angle). With these assumptions, Z equals the thickness of the leached layer, and is therefore equal to l in Eq. (3). As is obvious from Fig. 5, the slope of a plot of $\ln Z$ vs. $1/T$ is positive, and $Q_{\text{diss}} - Q_{\text{diff}}$ equals approximately 10 kJ mol^{-1} . Both of these conclusions are consistent with diffusion

through a leached layer which is structurally more similar to albite glass ($Q_{\text{diff}} \sim 56 \text{ kJ mol}^{-1}$) than to albite crystal ($Q_{\text{diff}} \sim 176 \text{ kJ mol}^{-1}$). The difference between the activation energies for Na and Al is insignificant based upon Fig. 5, suggesting that, if our analysis is correct, each can move through the leached layer as easily as the other.

The trend in temperature-dependent leaching we observed is in agreement with the data of Hellmann (1995) for albite leached at pH 2 between 100° and 300°C. In his experiments, the depth of Na leaching relative to Si at pH 2 decreased as temperature increased from 100° to 300°C. However, the rest of his data for albite leached at pH values other than 2 revealed no obvious temperature-dependence to the extent of cation leaching.

Hellmann (1995) modelled the leached layer composition by using solution chemistry data and by assuming linear concentration vs. depth profiles and Fick's law (assuming, as we have done here, that $C_{\text{surf}} = 0$ and that $C = C_{\text{bulk}}$ at the deepest extent of the leached layer). He concluded that the activation energy for diffusion of Na and Al was less than that for diffusion in albite crystal, but greater than that for glass. Although our calculated Q_{diff} is approximately equal to the Q_{diff} for glass, without better constraint on the leached layer depth we cannot conclude that our results differ from those of Hellmann. In addition, qualitatively, the activation energy of diffusion must be smaller than that of dissolution to explain our observations. Hellmann also concluded that the rate of diffusion through the leached layer of Na was close in value to that of Al, corroborated by our observations. However, his calculated leached layer depths were on the order of 1000 Å at 100°C, which appear qualitatively to be deeper than depths we might infer from Fig. 3 (for the 90°C data). His experiments also differed from ours in that our crystals were dissolved to an approximation of steady state (600 h) whereas his were dissolved < 20 h at 100°C. It may be possible that early in dissolution thick leached layers form that are removed later during steady state dissolution. Thicker Na-leached layers early in dissolution are possibly indicated by data of Fig. 4B.

These observations can also be compared to an analysis of Na and Al leaching on albite crystal dissolved in flow reactors at 25°C described by

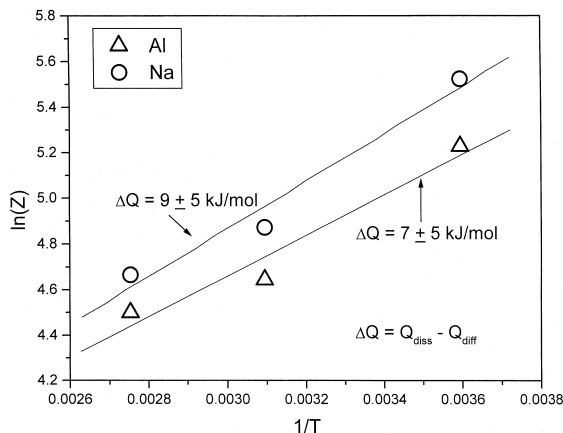


Fig. 5. Plot of the natural log of Z (see Eq. (3) in text) on samples leached at 5, 50 and 90°C, plotted vs. inverse temperature (K). Slopes of the Na and Al data were multiplied by R to estimate the value for $\Delta Q (= Q_{\text{diss}} - Q_{\text{diff}})$.

Hamilton (1999). Hamilton's results showed leached layer depths $< 500 \text{ \AA}$ for albite crystals dissolved at pH 2 at 25°C . This conclusion was based upon the similarity of concentration vs. depth data based upon SIMS measured for leached and unleached samples, where the depth resolution of SIMS analysis is approximately $200\text{--}500 \text{ \AA}$. Based upon Hamilton's observation, we must conclude that our samples, dissolved at 90°C , should have leached layer depths $< 500 \text{ \AA}$, since they were dissolved at a higher temperature and pH than those described by Hamilton (1999). Obviously, calculated leached layer depths based on solution chemistry ($\approx 1000 \text{ \AA}$ at 100°C , Hellmann, 1995) differ significantly from those constrained by surface spectroscopy ($< 500 \text{ \AA}$ at 90°C as indicated in Hamilton, 1999 and our own observations).

The results for albite (this work; Hellmann, 1995) also differ from the observations of Schweda (1990) for microcline in which leaching of K^+ increased with increasing temperature. The results of Schweda (1990) were based on solution chemistry measurements, and not on spectroscopic surface analysis. Again, however, it should be remembered that results based on the total leached cations from solution data such as Schweda (1990) and Hellmann (1995), and those based on spectroscopic measurements such as ours, should be expected to (and commonly do) differ. For example, the information depth of XPS is about 90 \AA for albite and we do not know how cation concentrations change with depth greater than this value, nor did we measure any depth where 100% leaching had occurred. In contrast, the thicknesses of the leached layers as calculated from solution chemistry often represent the theoretical depths over which the cations of interest must have been 100% leached in order to explain the stoichiometries of the leaching solutions. Alternately, to make a calculation of leaching depth based upon solution chemistry, the concentration-depth profile may be assumed to be linear; however, there is no reason to assume the profile is linear. In fact, diffusion profiles are commonly not linear (e.g., see Hellmann, 1997), and there is often evidence that 100% leaching of Na and/or Al is never attained. Inherently then, solution data and spectroscopic data can only be compared qualitatively. Nonetheless, some of the inconsistencies in comparing solution and spectro-

scopic data summarized from our results and from the literature are puzzling.

In addition to temperature, solution chemistry also influences the rate of cation leaching. As observed by Stillings et al. (1995), the exchange of H^+ for K^+ on the surface of K-feldspar is a function of salt concentration: the extent of exchange decreases as NaCl concentration increases in solution. Our experiments were run in dilute solution to steady state conditions at all temperatures. Solution chemistries from our experiments, listed in Table 2, show that concentrations of cations measured at 5° and 50°C (experiments used polished crystals and powder samples and had fluid residence times of 496 h (50°C) and 1051 h (5°C)) are higher than the maximum concentrations of the corresponding cations calculated for the 90°C experiments (in which only polished crystals were used in reactors with fluid residence times of 48 h), and yet the samples leached at 90°C show the least extent of leaching. Therefore, the observed difference in leaching extent in our experiments is most likely a function of temperature, rather than solution chemistry. Furthermore, the expected increase in ion pairing or complexing at the higher temperatures should decrease the activities of Na or Al in solution, and would therefore promote leaching at the elevated temperatures: therefore, the lack of observed enhancement of leaching with temperature is presumably not related to changes in ion pairing in solution with temperature.

While Na concentrations in the albite surface continued to change between 2 and 6 weeks, XPS measurements of crystal surfaces dissolved at pH 2.9 at 90°C showed that Al/Si did not change measurably during dissolution from ~ 1 to 6 weeks. Relatively rapid attainment of a steady state Al surface chemistry (i.e., by the first week of dissolution) may imply that the long periods needed for attainment of steady state dissolution in rate experiments (Blum and Stillings, 1995; Chen and Brantley, 1997) is related more to slow reactions such as (1) repolymerization or structural re-equilibration (Hellmann, 1995) or (2) development of etch pits and porosity, as compared to fast reactions such as cationic diffusion. However, the slightly longer times needed to reach a steady state Na/Si concentration of the albite surface might imply that the concentration of this ion in the surface may be related to the long

periods necessary for attainment of steady state dissolution rates for albite.

5. Conclusions

In this study we used angle-resolved XPS to study the composition of albite surface layers leached in solutions of pH 2.9 at temperatures of 5°, 50° and 90°C, at different reaction times. Albite was dissolved in flowing (or continuously replaced) solutions until steady state was achieved. All solutions contained low concentrations of Na, Al, and Si, and were under-saturated with respect to kaolinite, gibbsite, halloysite, and pure silica phases.

The experimental results from ARXPS demonstrate that cation leaching of albite in acid solution is temperature-dependent. Extent of Na- and Al-leaching as observed by ARXPS was greater at lower temperatures than at 90°C. These results indicate that the activation energy for cation diffusion through the albite surface is lower than the activation energy for albite dissolution by about 10 kJ mol⁻¹ under the experimental conditions, in agreement with published literature values for diffusion of cations through albite glass, and in agreement with a glass-like surface for the leached feldspar surface.

Relatively rapid attainment of a steady state Al surface chemistry (i.e., by the first week of dissolution) may imply that the long periods needed for attainment of steady state dissolution in rate experiments (Blum and Stillings, 1995; Chen and Brantley, 1997) is related more to slow reactions such as repolymerization or structural re-equilibration (see Hellmann, 1995) or development of etch pits and porosity, as compared to fast reactions such as cationic diffusion. More such surface spectroscopic studies could be used to investigate such questions.

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