

## Altered layers on dissolving albite – 1. Results

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**ABSTRACT:** Single albite crystals were hydrothermally altered at 225°C and then compositionally depth profiled using X-ray photoelectron spectroscopy (XPS) and calibrated Ar ion beam sputtering. We found that Na, Al and O are preferentially removed from the structure during hydrolysis, resulting in leached layers up to ~ 1000 Å thick. The depth of leaching decreased with pH in the acidic range (pH 0.5–6) and increased with pH in the basic range (pH 7–10). Angle resolved XPS (ARXPS) revealed that the uppermost monolayers are extremely depleted in Na and Al. Leaching depths were also found to be related to the overall rate of Si release. The XPS spectra indicated the presence of Cl<sup>-</sup> and Ba<sup>2+</sup> over the entire depth of the leached layer for samples altered in acidic and basic solutions, respectively. This is indicative of electrostatic adsorption at charged sites within the leached layer. The presence of Cl<sup>-</sup> and Ba<sup>2+</sup> also shows that leached layers are subject to the large scale influx of water and other aqueous molecules. The openness of the structure suggests that transport of reactants and products within the leached layer is not diffusion limited. By comparing calculated depths of preferential leaching from both the XPS and solution chemistry results, hydrolysis reactions are probably not spatially uniform, but probably occur preferentially at specific sites (dislocation outcrops, etc.) of elevated surface strain energy.

### 1. Preferential leaching and altered layers

The mechanism of silicate hydrolysis reactions has been the subject of much controversy; presently two models exist- the surface reaction model and the leached layer-diffusion model. The surface reaction model describes hydrolysis reactions occurring at specific surface sites of elevated strain energy. The presence of etch pits and the dependence of reaction rates on surface area are used as evidence in support of this model. However, many previous studies, mostly based on aqueous solution data from feldspar studies (see Chou and Wollast 1985; and references therein) have shown the preferential leaching of alkalis and some network forming elements during the initial, incongruent phase of dissolution. The preferential leaching process is hypothesized to lead to the formation of leached layers, where the diffusion of hydrolysis products through the layer is the rate-limiting process during dissolution. However, until recently, surface spectroscopic results had not yielded evidence for the presence of leached layers more than ~10 to 20 Å thick (see Berner and Schott, 1982; and references therein). Within the past few years, however, the application of various spectroscopic techniques (such as RNR, ERD, AES and SIMS) has demonstrated the formation of leached layers in silicates up to 1000 Å in thickness (Petit et al. 1987; Casey et al. 1988; Mogk and Locke 1988; Nesbitt and Muir 1988).

The purpose of this study was to further elucidate the nature and properties of leached layers in albite. We utilized X-ray photoelectron spectroscopy (XPS) because this technique offers superior analytical depth resolution, as well as chemical environment information. We subjected single crystals of albite to hydrothermal alteration at 225°C in solutions ranging in pH from 0.5 to 10.1. These conditions allowed us to collect aqueous solution data and

compare it directly to the XPS results. Using our XPS and solution chemistry data in conjunction with published theoretical molecular orbital studies, important inferences regarding the mechanisms of dissolution could be drawn with respect to the mechanisms of feldspar dissolution. These results are discussed in detail in Part II of this extended abstract (Eggleston et al., this volume).

### 2. Methods

Single crystals of Amelia albite were reacted up to a maximum of 15 hours in a titanium flow-through reactor at 225°C at solution pH's ranging from 0.5 to 10.1 (HCl and Ba(OH)<sub>2</sub> were the acid and basic media, respectively). Effluent solutions were collected concomitantly and analyzed for Na, Al and Si. Al levels were always well below the saturation limit of boehmite (AlO(OH)). Reacted surfaces were examined with SEM to verify the absence of precipitates. Surfaces were analyzed with a VG ESCALAB Mk II XPS instrument using non-monochromatic Al K $\alpha$  (1486.6 eV) radiation. Depth profiles were obtained by sputtering with a calibrated Ar ion beam. The effect of differential sputtering rates for Na, Al, O and Si was taken into account when determining leaching depths. The preferential leaching depths were normalized to Si since Si concentrations generally remained invariant throughout the leached zones. The surface area covered by the X-ray beam was 10mm<sup>2</sup>, the analysis depth (representing 95% of the total signal) was approximately 78 Å (this is based on attenuation lengths of electrons traversing SiO<sub>2</sub> measured by Hochella and Carim 1988). Increased depth resolution within the upper 80 Å was achieved (up

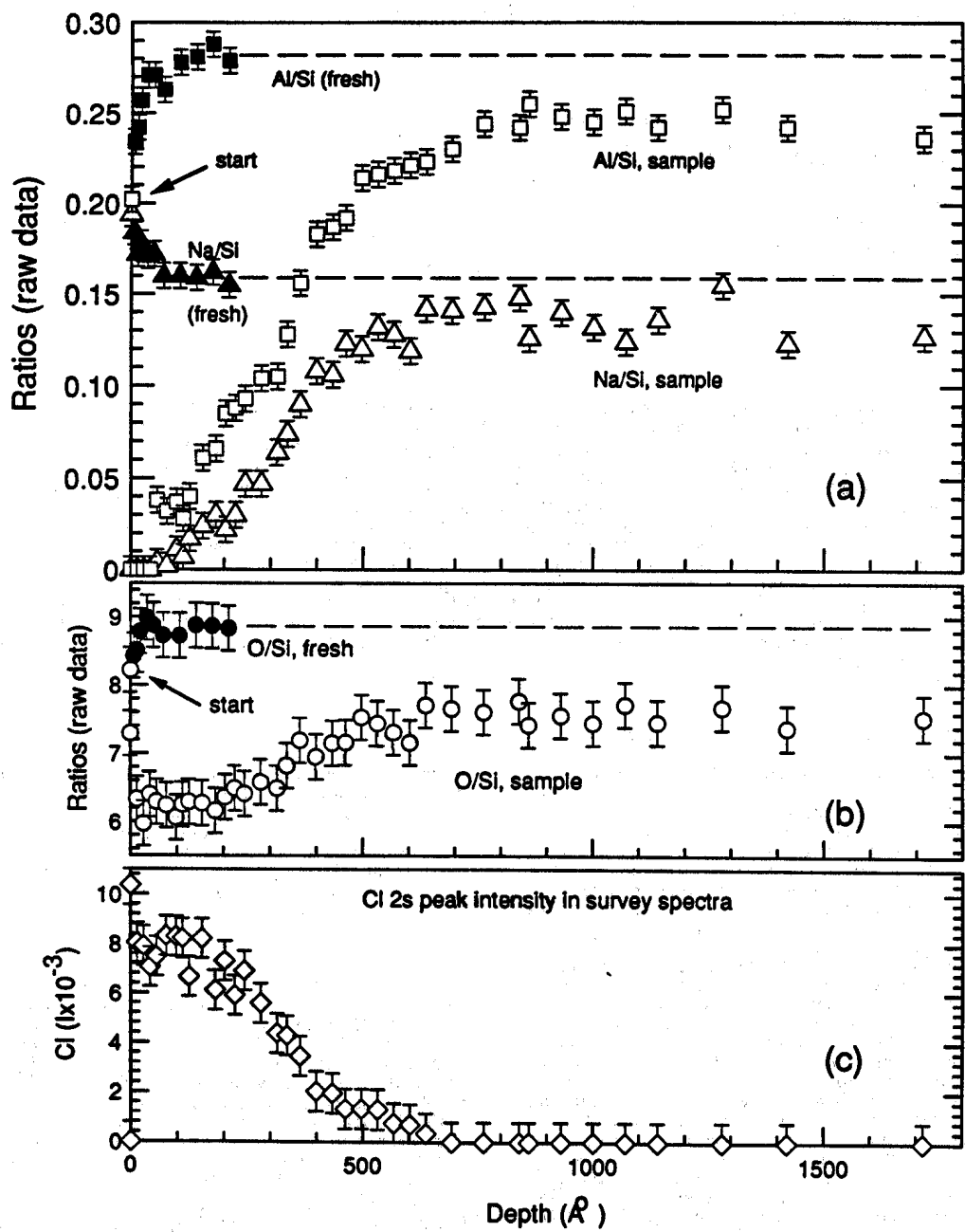


Fig. 1 XPS sputter depth profiles (open symbols) of Al/Si and Na/Si (top), O/Si (middle), and Cl (bottom) for a sample reacted at pH 0.5 and 225°C for 4 hours. The solid symbols represent the sputtering profiles for fresh albite, these have been extended out to 1000 Å. The error bars represent 2σ values from replicate analyses of both fresh and altered samples. The depths of leaching of Na, Al and O are approximately 700-900 Å, this is also the approximate depth of Cl invasion into the leached structure. (Fig. taken from Hellmann et al., 1989)

to 34 Å at 65° tilt) by utilizing angle resolved XPS (ARXPS) on certain non-sputtered sample surfaces.

### 3. Results

The depths of leaching are estimated from the intersection of sputtering curves, represented by Na/Si, Al/Si and O/Si ratios from altered surfaces, with the differential sputtering curves of fresh, unaltered albite. The differential sputtering curves serve as a calibration tool- they were extended to 1000 Å on the assumption that steady state was achieved with respect to differential sputtering after only 20-50 Å were sputtered from the surface. In most cases, the sputtering curves intersect the calibration curves. Occasionally, however, the ratios plateau out at values below the calibration curve. Possible reasons for this are fully discussed in Hellmann et al. (1989).

The figure below shows the depletion of Na, Al and O to depths ranging from 700-900 Å for a sample run at pH 0.5 for 4 hours at 225°C. The uppermost 50 Å are almost totally depleted in Na and Al. From 50 to 900 Å the ratios steadily climb to values representative of fresh albite. The XPS spectra also showed the invasion of Cl<sup>-</sup> into the structure; it is remarkable that the influx of Cl occurs to depths equal to leaching of Na, Al and O. The depletion of Na, Al and O for samples run at higher pH's (all at 225°C) show similar profiles except that leaching depths were much shallower. At intermediate pH's, leaching was only on the order of 10 Å. At pH 10.1, leaching depths were on the order of 100-200 Å (Na) and 500 Å (Al). As was the case with Cl under acidic conditions, the XPS spectra revealed the presence of Ba to 500 Å, this being the deepest extent of leaching at pH 10.1.

Within the resolution of the data, Al was leached to greater depths than Na at all pH's (see Fig. 1, as an example). However, the ARXPS results showed that Na was far more leached from the uppermost monolayers than was Al. The leaching depth dependence on pH was mirrored by a similar dependence of the rate of Si release on pH; this points to a direct correlation between leaching depth and Si release rate.

XPS spectra can also reveal changes in chemical environment, oxidation state and structure. Due to the destructive nature of ion sputtering, changes in chemical environment could only be documented between unaltered and altered, non-sputtered surfaces. We noted that binding energies changed in a systematic way for nearly all peaks, this was attributable to charging. However, changes in the full width at half maximum (FWHM) for the Na, Al, Si and O peaks indicated that altered surfaces contain more unique chemical environments than found in fresh surfaces. Thus, these results and the ARXPS results show that the near surface (the uppermost 80 Å) of leached layers contain both structural and chemical gradients. Unfortunately, the effects of sputtering hide these types of changes over the entire depth of leaching.

The solution data directly corroborated the XPS results by revealing the preferential release into solution of Al and Na with respect to Si. At the beginning of each experiment, an initially high, but transitory, release of Na was always measured and could be directly correlated with a concomitant sharp increase in H<sup>+</sup> consumption, as measured by the difference between H<sup>+</sup><sub>in</sub>-H<sup>+</sup><sub>out</sub>. After Na levels assumed steady state, H<sup>+</sup> consumption did not drop to zero, indicating that hydrolysis reactions are a sink for H<sup>+</sup>. The solution results also showed that at acidic pH, H<sup>+</sup> consumption due to hydrolysis

reactions far exceeds the equivalents of Na<sup>+</sup> and Al<sup>3+</sup> released.

### 4. Discussion

The formation of leached layers is related to the susceptibility of Na-O, Al-O and Si-O bonds to hydrolysis. The rapid, initial loss of Na from surface sites at the beginning of hydrolysis can be attributed to ion exchange reactions with H<sup>+</sup>. Electrostatically bound Na ions are by far the most easily removed member of the albite structure. The preferential leaching of Al over Si can be explained by the fact that Al-O bonds are slightly weaker and are thus more easily broken than Si-O bonds. The preferential removal of Al from the structure leaves behind silanol groups. Adjacent silanol groups may repolymerize, this resulting in the production of free water molecules. The depletion of O from leached layers could be indicative of repolymerization reactions (see Casey et al. 1988, for example).

The pH dependence of leached layer depths seems to suggest that the formation of leached layers is correlated to the overall rate of hydrolysis since the calculated Si release rates also show the same dependence on pH. This is possibly attributable to the pH-dependent reactivity of bridging oxygen sites (O<sub>br</sub>) in the feldspar structure. The stronger the reaction between adions or admolecules and O<sub>br</sub> sites, the weaker the Si-O<sub>br</sub> and Al-O<sub>br</sub> bonds become. MO calculations (de Jong and Brown, 1980) actually show that O<sub>br</sub> groups in silicate dimers display the following affinity sequence: H<sup>+</sup>>H<sub>3</sub>O<sup>+</sup>>OH<sup>-</sup>>H<sub>2</sub>O; thus, H<sup>+</sup>-O<sub>br</sub> interactions are most effective in hydrolyzing Si-O and Al-O bonds, and conversely, H<sub>2</sub>O molecules are least effective. This affinity sequence qualitatively corroborates the finding that the depth of leaching is directly related to the rate of dissolution.

The adsorption of Cl<sup>-</sup>, as revealed by the XPS spectra for samples run at pH<2.4 (and not at pH>2.4), suggests electrostatic adsorption at positively charged sites within the leached structure. This also indicates that the zero point of charge (ZPC) of the leached layer is ~ 2.4. The imbalance between H<sup>+</sup> consumed and equivalents of Na<sup>+</sup> and Al<sup>3+</sup> released at acidic pH's indicates that H<sup>+</sup> is used in the creation of positively charged sites within the leached layer. The adsorption of Ba<sup>2+</sup> within the leached layer at pH 10.1, in turn, reveals the presence of negative adsorption sites at pH>pH<sub>ZPC</sub>. The presence of adsorbed species over the entire depth of leaching indicates that the formation of leached layers opens up the structure and thus allows the influx of water and other molecules to the alteration front. Structural changes within the leached layer, as suggested by the broadening of XPS spectral peaks, may serve to create pathways for the advance of water into the leached zone. Preliminary calculations indicate that the structure of leached layers is porous enough such that it is not diffusion limiting to the outward flux of product ions.

By comparing the calculated thickness of the leached layers based on both the XPS and the solution chemistry results, the formation of leached layers is not spatially uniform. This may indicate that dissolution and the formation of leached layers occurs preferentially at sites of elevated surface strain energy. SEM micrographs, showing the presence of etch pits (with minimal, lateral surface expression), would seem to corroborate this.

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