

Chemical alteration of feldspar: a comparative study using SIMS and HRTEM/EFTEM

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ABSTRACT: Here we report on the structural and chemical changes that occur at the surface and near surface of labradorite after dissolution at acid pH. These changes were measured with two different analytical techniques: secondary ion mass spectrometry (SIMS) and high resolution and energy filtered transmission electron microscopy (HRTEM and EFTEM, respectively). The main purpose of this comparative study is to show the similarities and differences in the data generated by these two analytical techniques. The SIMS results are in general compatible with the leached layer theory of dissolution, which is based on the preferential leaching of certain elements from the non-altered mineral. On the other hand, the higher resolution HRTEM/EFTEM data point to another mechanism of dissolution, one based on interfacial dissolution-reprecipitation.

1 INTRODUCTION

During water-rock interactions the fluid-solid interface plays the primordial role in the exchange of energy and matter between the aqueous fluid and the component minerals undergoing hydrolysis. Understanding how fluids interact with mineral surfaces requires analytical tools for measuring changes in the structure and chemistry of the surface and near-surface of the mineral; commonly used techniques include electron microscopy, X-ray diffraction and reflectivity, spectroscopy, and ion beam methods. Inherent to each technique are specific advantages and limitations with respect to the measurement of the structure or chemistry of hydrolyzed mineral surfaces. Among the key analytical parameters of any given technique are its elemental sensitivity and specificity, the spatial resolution (i.e. lateral, as well as depth), and the analysis area and volume. In this communication we compare the application of two different analytical techniques that were used to study the chemical alteration of feldspar.

We measured the structural and chemical changes that occur at the surface and near surface of labradorite after hydrolysis at 22 °C and pH 1 (the data are based in part on results given in Hellmann et al. 2003). The hydrolyzed feldspar was analyzed with two very different techniques: secondary ion mass spectrometry (SIMS) and high resolution and energy filtered transmission electron microscopy (HRTEM and EFTEM, respectively). SIMS was employed to obtain chemical depth profiles perpendicular to the altered surface. HRTEM and EFTEM were used to

determine structural and chemical changes of the altered region (extending from the surface through the altered region to the non-altered mineral); however, in this case, the samples were prepared in cross section by an ultramicrotome.

Analyses of the same altered labradorite sample by SIMS and HRTEM/EFTEM yielded similar and complementary data. Nonetheless, there were important differences in the two data sets, which are primarily a function of the resolution of the two techniques. By comparing these two techniques (including sample preparation) and their respective results, we will show the importance that the analytical method has with respect to the interpretation of results and how this affects the proposed mechanism of dissolution.

2 SAMPLE PREPARATION AND INSTRUMENTAL ANALYSES

Samples of labradorite ($\text{Na}_{0.39}\text{Ca}_{0.59}\text{Al}_{1.59}\text{Si}_{2.41}\text{O}_8$) were dissolved in HCl/H₂O solutions at pH 1 (500 h) at 22 ± 2 °C in flow-through reactors (for details, see Hellmann et al. 2003).

SIMS presents many advantages as an analytical tool for studying mineral surface alteration; perhaps its greatest asset is its versatility, because nearly all elements can be measured at trace concentrations (including their most important isotopes) to depths on the order of several hundred nm. Perhaps one of the most important elements that can be measured by SIMS is H, given that H⁺, H₂O, and OH⁻ are the key

aqueous species involved in bond hydrolysis (note that H cannot be measured by EFTEM). The depth resolution of SIMS generated profiles decreases with increasing depth, due mostly to the deleterious effects of ion sputtering and crater formation; this is a major limitation when profiles intercept chemical or structural interfaces at significant depths. An analytical artifact associated with SIMS and other ion beam methods is the tendency of ion beams to broaden the apparent width of interfaces, especially at depth (Hues & Williams 1986, Barbour & Doyle 1995). The exact degree of interface broadening is dependent on the method, analytical conditions, and the nature of the sample.

SIMS analyses were carried out with a Cameca IMS 3f instrument using a $^{16}\text{O}^-$ primary ion beam with the following instrument settings: 25 nA beam current, 12.6 kV accelerating voltage, $125 \times 125 \mu\text{m}$ raster area. Profile depths were determined from sputtering rates that were calibrated by the measurement of crater depths (Alpha step 200 Tencor Instruments profilometer). The reproducibility of crater depth measurements is approximately ± 20 -30 nm. Using a $^{16}\text{O}^-$ primary beam, the sputtering rate was determined to be ≈ 2.3 x faster in the altered zone than in non-altered labradorite.

High resolution images of the altered/non-altered interface were obtained with a JEOL 3010 TEM operated at 300 kV; its point resolution is 0.17 nm. EFTEM provides a convenient method for obtaining 2-D spatial distributions (i.e. concentration maps) of any chosen element at nm-resolution (with the exception of H). The ability to obtain nanometer-resolution chemical information is by far the greatest asset of this technique. In our study we determined jump ratio images based on electron energy loss spectroscopy (EELS) spectra that were obtained with a Gatan imaging filter attached to a JEOL 3010 TEM operated at 300 keV, with a dispersion = 0.2 eV/channel, and a collection angle $\beta = 6.5$ mrad. A jump ratio image is calculated by dividing the post-edge image by the pre-edge image. Each image is obtained by selecting a (20-30 eV width) part of the chosen core-loss ionization edge of the particular element (Ca $L_{2,3}$, O K, Al K, Si K edges used in this study).

3 RESULTS

3.1 Elemental depth profiles measured by SIMS

Chemical depth profiles of a sample reacted at pH 1 (Fig. 1) measured by SIMS, presented in terms of raw ion counts, reveal that the altered zone is depleted in Ca, K, Na, and Al, and enriched in H, Si, and B, as compared to the non-altered labradorite (boron was present as an impurity in the aqueous solutions). The profiles for depleted and enriched elements are sigmoidal and anti-correlated. The SIMS

results we report here are in good accord with previous SIMS and other ion beam and spectroscopy measurements of acid pH-altered near-surface zones on feldspars (e.g. Casey et al. 1989a, Hellmann et al. 1990, Petit et al. 1990, Inskeep et al. 1991, Muir & Nesbitt 1997, Schweda et al. 1997, Nesbitt & Skinner 2001). The average inflection point for all elements is located at approximately 480-500 nm, which corresponds to the depth measured from the surface to the interface between the altered zone and the non-altered labradorite. Note that the inflection points for the depleted elements are not the same, varying from 430 nm (K) to 500 nm (Na, Ca); the reason for this variability is not known. The apparent thickness (i.e. chemical gradient) of the interfacial boundary, as defined by the sigmoidal part of the profiles, is 100-150 nm (depending on the element). A significant proportion of the measured interfacial thickness is an artifact of the previously mentioned phenomenon of ion beam-induced interface broadening.

3.2 The altered/non-altered interface measured by HRTEM and EFTEM

As already mentioned, the electron transparent ultrathin sections of the altered zone examined by HRTEM/EFTEM were cut in cross section; this presents an important advantage because this provides a method for examining the interface directly, thus avoiding the deleterious effects of ion bombardment

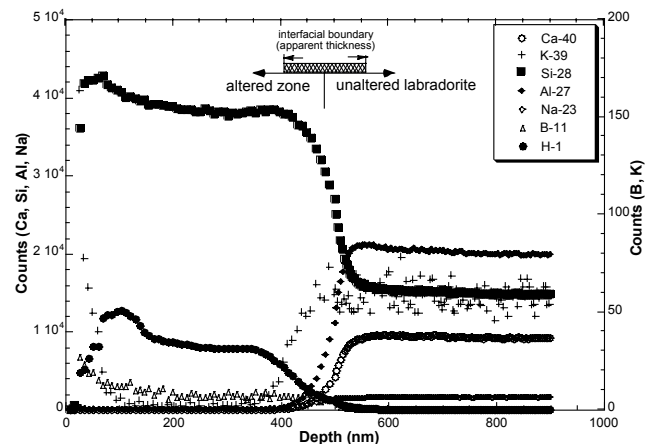


Figure 1. SIMS profile showing raw ion counts vs. depth for a labradorite sample hydrolyzed at pH 1 and 22 °C. The apparent interface between the altered zone and the non-altered mineral occurs at 480-500 nm. The thickness of the interfacial boundary ranges from 100-150 nm, depending on the element. Note that the altered zone is depleted in Ca, K, Na, Al, and enriched in Si, H, and B (the latter is present as an impurity in the hydrolyzing solution). The anti-correlated nature of the profiles for depleted and enriched elements is typically used as evidence for an interdiffusion process, which is an integral part of the leached layer hypothesis.

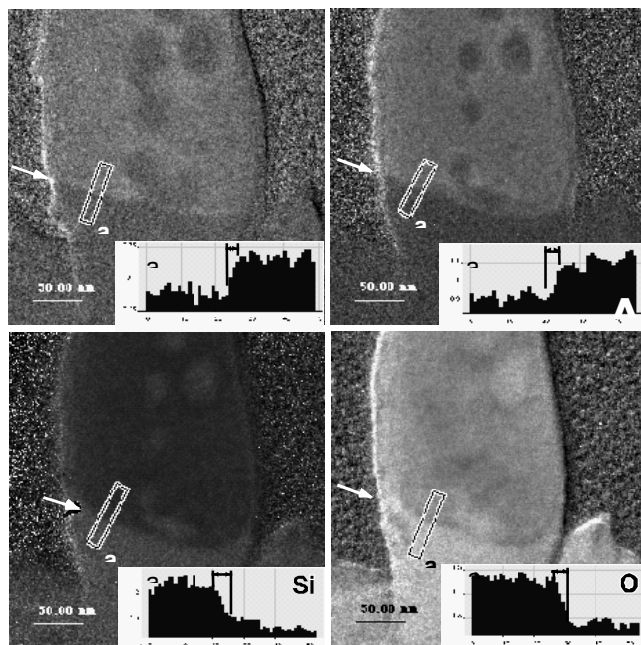


Figure 2. Single lamella of labradorite altered at pH 1 prepared in cross section with an ultramicrotome (using the same sample as in Figure 1). The four jump-ratio EFTEM images represent qualitative chemical concentration maps of Ca, Al, Si, and O (left to right, top to bottom, respectively; lighter tones represent higher concentrations; scale bar in lower left corner is 50 nm). In each case, the interface between the non-altered mineral (top) and altered zone (bottom) is very sharp and distinct (see white arrows). The insets show chemical profiles based on the diagonal rectangular areas; in each inset the profile extends (left to right) from the altered zone (bottom half of lamella) to the non-altered mineral. In contrast to the SIMS depth profile shown in Figure 1, the interfacial thicknesses are very sharp, and range between 3.8 and 6.8 nm (delimited by small bracketing lines in each inset), depending on the element. The sharpness of the spatially coincident chemical interfaces (which are also coincident with an even sharper structural interface - not shown) is consistent with an interfacial dissolution-precipitation mechanism, and not leached layer formation (see text for details). Figure 2 is modified from Hellmann et al. (2003).

and cratering. In addition, surface rugosity (which is very often present after hydrolysis) does not affect the results. Thus, the ultramicrotome sample preparation technique used in this case presents several distinct advantages over ion beam methods.

In general, our SIMS and EFTEM data are complementary and show the same chemical trends and depths of alteration. Nonetheless, there is a crucial difference between the data sets that is due to the inherently higher resolution of the EFTEM technique. The true chemical gradients of the interfacial boundary are significantly less thick than those estimated from the SIMS results, based on chemical profiles of the ultra-thin sections that we measured with EFTEM. EFTEM jump-ratio images of a typical interfacial region (reacted at pH 1) on a single lamella portray qualitatively the concentrations of Ca, Al, Si, and O (Fig. 2). Sharp, step-like changes in the concentrations of these four elements occur exactly at

the same interfacial boundary that marks the structural transition between the amorphous, altered zone and the non-altered, crystalline labradorite, based on HRTEM (not shown). Chemical profiles across and perpendicular to the interfacial region (Fig. 2) give the following interfacial boundary thicknesses (in nm): Ca \approx 3.8; Al \approx 5.1; Si \approx 6.8; O \approx 4.9.

4 DISCUSSION AND CONCLUSIONS

If we examine the SIMS results in Figure 1, these are at first glance compatible with the leached layer hypothesis that is currently invoked to explain aluminosilicate mineral dissolution at acid pH. Very briefly, this theory is based on the formation of an amorphous, altered near-surface zone that represents a relict 'structure', composed primarily of Si and O, that is created after certain elements (e.g. Na, K, Ca, and Al) are preferentially released from the non-altered mineral. Silanol groups in the leached layer may undergo condensation reactions (Casey et al. 1989a, b, Hellmann et al. 1997). The preferential release of elements occurs by interdiffusion with H^+ from the aqueous solution, thus keeping the leached layer electrically neutral. The anti-correlated, sigmoidal depth profiles shown here and in other studies appear to fit (but only qualitatively) with interdiffusion models (e.g. see details in Hellmann 1997, Hellmann et al. 2003).

On the other hand, the HRTEM/EFTEM results show that the structural and chemical gradients (Fig. 2) are spatially coincident and extremely sharp (structural gradient $<$ 2 nm, chemical gradients: 4-7 nm). These interfacial gradients are too sharp to have been produced by a volume interdiffusion process associated with leached layer formation; this is supported by interdiffusion modeling presented in Hellmann et al. (2003). In addition, the true interfacial gradients are in reality probably even less than those presented here (i.e. sharper gradients, see discussion in Hellmann et al. 2003).

Even though the sharpness of the interfacial gradients is the primary reason for the non-applicability of the leached layer theory, we also cite the following other reasons: 1. the enrichment of Si and O in the altered zone, which is difficult to explain based on preferential leaching; 2. equivalent depths of depletion for fast (Na, K, Ca) and slow (Al) diffusing species, based on leached layer formation and a volume interdiffusion process; and 3. the presence of B in the SIMS profiles after treatment with a strong B-complexing agent (i.e. identical profiles before and after treatment).

The mostly likely explanation for the results we show here is that the altered zones form via an interfacial dissolution-precipitation process. The interfacial nature of this process needs to be stressed because we hypothesize that bond breaking

(dissolution) and bond re-making (reprecipitation) occur in a thin solution film directly in contact with the interface. Thus, supersaturation occurs in an interfacial thin film, and not in the bulk solution. During hydrolysis of the labradorite the bulk solution was undersaturated with respect to all possible secondary phases (e.g. silica gel). The precipitate corresponds to a hydrated silica gel, based on the SIMS and EFTEM results. This altered zone most probably has a very high porosity (e.g. Casey et al. 1989b, Putnis 2002), thus allowing non-diffusion limited transport of dissolution products and aqueous species between the interface and the external fluid.

The absence of leached layers is crucial to the mechanistic pathway of the intrinsic dissolution process. The interfacial solution-reprecipitation mechanism implies that the intrinsic dissolution process is stoichiometric at acid pH conditions. It implies a single, pH-invariant mechanism that controls the release of all elements comprising the feldspar structure. Any measured deviations from stoichiometric dissolution behavior (e.g. as measured by solution analyses) can be attributed to precipitation that occurs after the initial, stoichiometric detachment of elements from the non-altered matrix.

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