

Studying the Structure of the Orthoclase (001)-Water Interface and the (010)-Water Interface by High-resolution X-ray Reflectivity

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Introduction

The reactivities of silicate mineral surfaces have been widely studied because of their importance in hydrothermal alteration, low-temperature weathering processes, soil formation, and various geochemical cycles. In the past few decades, numerous experimental and theoretical studies have addressed the rates and mechanisms of feldspar dissolution [1]. A major obstacle to achieving a better fundamental understanding of the feldspar dissolution process, however, has been the paucity of direct, *in situ* structural measurements of the feldspar-solution interface at the atomic scale. A previous *in situ* structural study of the feldspar-water interface that used x-ray reflectivity revealed the structure of the orthoclase (001)-water interface in deionized water [2]. The results showed that the outermost K⁺ ions were removed by interaction with deionized water and that the silicate lattice exhibited small structural displacements of the near-surface region.

Recent observations revealed significant differences in the apparent activation energy for dissolution at the (001) and (010) surfaces of orthoclase [3]. These suggest either that the actual terminations of these two nominally similar cleavage surfaces are unexpectedly different or that the dissolution mechanism is sensitive to the subtle structural differences in these two terminations of the orthoclase lattice. Here we compare the terminations, interfacial water structures, and structural displacements of these two cleavage surfaces and find only minimal structural differences between the interfacial structures of these two orthoclase surfaces [4].

Methods and Materials

We described our experimental procedures and details previously [2, 5]. We use gem-quality homogeneous crystals from Itrongay, Madagascar [6]. The vertical separations between orthoclase layers, corresponding to the d-spacings of the (001) and (020) planes, are $d_{001} = c \cdot \sin(\beta) = 6.459 \text{ \AA}$ and $d_{020} = b/2 = 6.5003 \text{ \AA}$, respectively. High-resolution x-ray reflectivity measurements of the freshly cleaved orthoclase (001) and (010) surfaces were performed at room temperature ($25 \pm 2^\circ\text{C}$) in deionized water by using a thin-film cell. Within a minute after cleavage of a fresh surface, each sample was placed under deionized water and promptly

loaded into the thin-film cell. Synchrotron x-ray reflectivity measurements were made at APS beamline stations 12-ID-D and 11-ID-D with monochromatic x-rays ($\Delta E/E = 10^{-4}$). Photon energies of 15.48 and 16.00 keV were used for measurements of the (010) and (001) surfaces, respectively.

Results

The specular x-ray reflectivities of the orthoclase (001)-water interface and the orthoclase (010)-water interface exhibit the same strong asymmetry for Q values about the first-order Bragg reflections [the (001) and (020) reflections, respectively]. This asymmetry, which, in each case, shows a substantially lower reflectivity minimum just above the first Bragg reflection than just below it, indicates that both surfaces cleave approximately at the K⁺ plane. This corresponds to the plane that involves minimal bond breaking. Direct comparisons of the experimental reflectivity results with the structure factor calculations allow interfacial models to be tested and optimized.

We show the laterally averaged electron density profile, plotted along the surface-normal direction, corresponding to the best-fit structures for the (001) surface [Fig. 1(A)] and the (010) surface [Fig. 1(B)]. These data are calculated directly from the best-fit structures and include a spatial broadening that is due to the limited Q -range of the reflectivity data [5]. Aspects of the interfacial structure (e.g., locations and occupations of individual atomic layers) resolved in this plot can be determined uniquely by x-ray reflectivity data. The surface structures for these two cleavage surfaces appear to be similar on the basis of the plots in Fig. 1. Each surface shows the substantial structure of the interfacial water above the surface, as evidenced by an oscillatory electron density profile within $\sim 5 \text{ \AA}$ of the surface that converges to the featureless fluid water density expected for bulk water (with an electron density of $0.33 \text{ e}^-/\text{\AA}^3$). Each surface also shows evidence for small ($< 0.1 \text{ \AA}$) structural displacements of the near-surface aluminosilicate layers.

Discussion

The orthoclase (001)-water interface exhibits a nearly ideal surface termination, as seen in the electron density plot in Fig. 1(A). The nonbridging oxygen

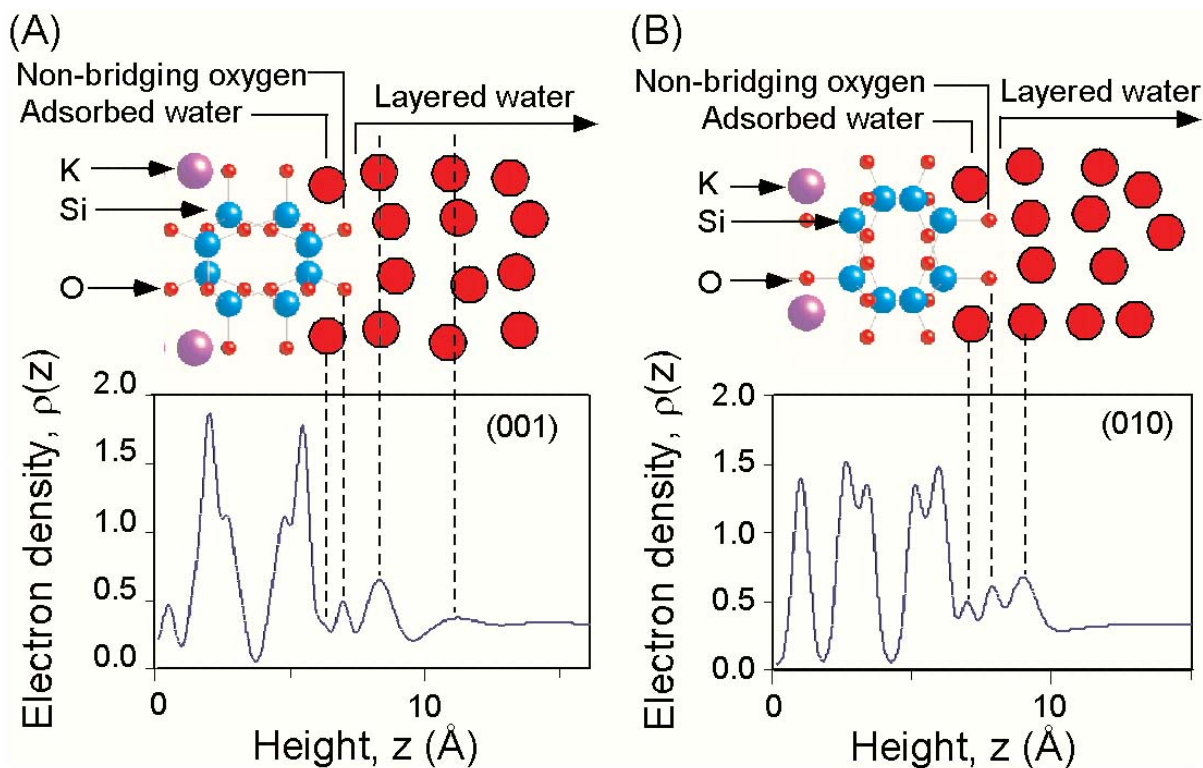


FIG. 1. The laterally averaged electron densities (plotted as a function of z , the coordinate along the surface-normal direction) for (A) the orthoclase (001)-water interface and (B) the orthoclase (010)-water interface, with structural schematic showing the derived interfacial structures. Water molecules are drawn as large filled circles.

(NBO) is located near the bulk-like position at a height of 1.4 ± 0.15 Å above the tetrahedral site. Additional “peaks” occurring on the fluid side of the interface indicate that water molecules near the orthoclase-water interface are not entirely fluid but instead have preferential positions above the mineral surface due to layering (as observed in other mineral-water interface systems) [7-11]. These peaks correspond to the layered-water structure factor having a water layer spacing of $c_w = 2.6 \pm 0.3$ Å, with the first layer at a height of 2.75 ± 0.1 Å above the outermost tetrahedral site, and $u_{bar} = 0.98 \pm 0.2$ Å. If we assume that the surface potassium ion is replaced by a water molecule, we derive an occupation of 1.35 ± 0.5 water molecules at a height of 0.7 ± 0.3 Å above the tetrahedral site, as compared with the bulk value for the K^+ ion of 0.55 Å, consistent with the 1:1 substitution of hydronium for K^+ , and referred to as an “adsorbed” water layer.

The orthoclase (010)-water interface [Fig. 1(B)] is similar in most respects to that of the orthoclase (001)-water interface [Fig. 1(A)]. The adsorbed water molecule is found to be 0.80 ± 0.15 Å above the tetrahedral site, with an occupation of 2.0 ± 0.4 water molecules per unit mesh, again consistent with a 1:1 substitution of H_3O^+ for K^+ ions. The second peak in the density profile is associated with a NBO, completing

the coordination shell of the surface tetrahedral cation, at a height of 1.75 ± 0.15 Å above the tetrahedral site. We again allowed for layered interfacial water and found the first layer at a height of 3.0 ± 0.15 Å above the tetrahedral site, with a layer spacing of $c_w = 1.8 \pm 0.2$ Å and $u_{bar} = 2.4 \pm 0.3$ Å. This produced a near-surface water structure that is similar to, but has less layering than, that found for the (001) surface.

The primary motivation for this study was to understand the sensitivity of dissolution kinetics to the cleavage orientation of orthoclase crystals at acidic conditions [3]. In particular, a twofold difference was observed in the apparent activation energies derived from the Arrhenius behavior of the initial dissolution kinetics for the (001) and (010) surfaces. Two distinct possibilities arose from this observation: either these two mineral surfaces are structurally distinct, or their reactivities are inherently different.

The present results indicate that the two surfaces are essentially similar in all aspects of the vertical interface structures that were probed in the current measurements, including the cleavage of the mineral to create surfaces terminated by NBO sites, the structuring of interfacial water within 5 Å of the orthoclase surface, the replacement of K^+ by water (presumably in the form of H_3O^+) at the interface, and the substrate relaxations

(information about the lateral structure can be obtained through nonspecular reflectivity measurements).

These results also reveal that the orthoclase (001)-water interface and the orthoclase (010)-water interface display more extensive water order than do the molecular ionic (calcite, barite) and quartz surfaces, and that this water order includes the completion of the surface tetrahedral coordination shell, an adsorbed water layer, and some limited structure of the fluid water above the mineral surface, but without the longer-range, weakly ordered, hydrogen-bonded water layer observed on muscovite. Hence, the degree of ordering at mineral-water interfaces is apparently a sensitive function of the mineral structure and composition. Interestingly, we have not yet observed substantial differences in interfacial water structure for distinct crystallographic orientations of a given mineral, even though we have looked for such differences on distinct surface orientations for the minerals orthoclase [2], quartz [10], and barite [12].

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