Face-specific Dissolution Kinetics: Orthoclase (001) Versus (010)

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Introduction

The chemical weathering of feldspars has been studied for many years by using a variety of macroscopic and microscopic approaches to gain insight into the associated microscopic processes, kinetics, and energetics [1]. The extent to which these results represent individual molecular-scale processes or an ensemble average of different processes (e.g., due to the distribution of surface orientations, morphologies, etc., associated with powder measurements) has not yet been thoroughly explored. Here we describe the use of x-ray reflectivity (XRR) to probe the face-specific dissolution of the (001) and (010) surfaces of orthoclase [2], revealing important and unexpected differences in the dissolution kinetics and associated apparent activation energies in the dissolution of these two structurally similar surfaces.

Methods and Materials

We examined the evolution of dissolving orthoclase (001) and (010) cleavage surfaces at pH 1.1 by using gem-quality homogeneous crystals having a nominal stoichiometry of $KAlSi_3O_8$. The vertical separations between equivalent cleavage planes correspond to the (001) and (020) Bragg planes: $d_{001} = 6.459$ Å and $d_{020} = 6.503$ Å, shown schematically in Fig. 1(A).

XRR data were collected *in situ* from 50° to 76°C in flowing solutions of 0.1 M HCl having a pH (at 25°C) of 1.1. Time-resolved measurements of dissolution kinetics and processes were performed in a flow-through Teflon® sample cell in transmission geometry through with a ~3.5-mm path-length of x-rays through water and two 0.13-mm Kapton® windows. The sample cell volume was 1.0 mL. The temperature was monitored continuously by a thermocouple positioned in the solution ~2 mm above the sample surface. We continued to supply fresh solution to the cell throughout the experiment by using a syringe pump at 3 mL h^{-1}.

Synchrotron XRR measurements were made at APS beamlines 12-ID, 11-ID, and 12-BM by using monochromatic x-rays ($\Delta E/E = 10^{-4}$). Photon energies ranging from 17.5 to 19.6 keV were used for different experiments. The background-subtracted reflectivity was measured with a rocking scan for all points. The sensitivity of XRR measurements to dissolution is shown schematically in Fig. 1(B). At the "anti-Bragg" condition, x-rays that are reflected from neighboring terraces are exactly out of phase. The reflectivity is maximized for a smooth surface and minimized for surfaces having a half-occupied surface layer (e.g., due to partial removal of the outermost layer). An oscillatory variation in the XRR therefore corresponds to a layer-by-layer dissolution process, in which the oscillation period corresponds to the time to remove a single layer. This approach has been widely used to study the growth of materials (e.g., through molecular-beam epitaxy) but has only recently been used to probe dissolution [3].

Results

Real-time reflectivities of the orthoclase (001) surface taken at a pH of 1.1 during dissolution at temperatures ranging between 50° and 76°C are shown in Fig. 2(A). These data reveal that the surface roughness increases during dissolution, resulting in a substantial (~10-fold)
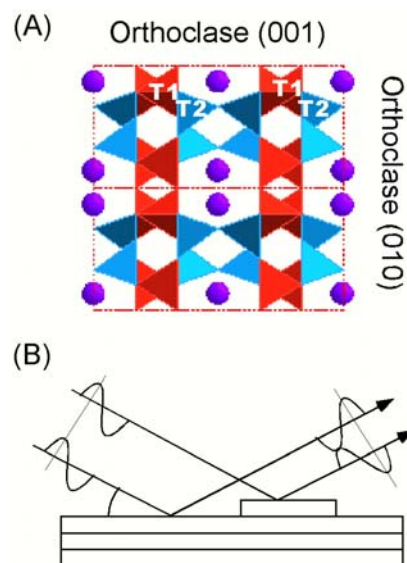

FIG. 1. (A) Schematic diagram of the (001) and (010) cleavage surfaces. Also labeled are the two distinct tetrahedral sites in the orthoclase lattice (T1 and T2). (B) Schematic diagram of the interference of x-rays reflected from neighboring terraces at the "anti-Bragg" condition.

decrease of the XRR at the first intensity maximum, with the reflectivity decreasing by as much as a factor of ~10³ with respect to the initial value. The dissolution rate variation as a function of temperature was determined by scaling the time axis to optimize the overlap of data obtained at separate temperatures. Similar data have been obtained for the (010) surface. The temporal variation of the reflectivity for the (010) surface was qualitatively similar to that of the (001) surface, in that the reflectivity was substantially damped, reflecting a strong increase in surface roughness during dissolution at acidic pH and suggesting a very similar process for the (001) and (010) surfaces.

The variation of the dissolution rate as a function of temperature is plotted as a function of the inverse temperature for both (001) and (010) surfaces in Fig. 2(B). In spite of the apparent similarity in the dissolution process as reflected in the temporal variation of the XRR, the apparent activation energies for dissolution of these two surfaces are different. The best-fit apparent activation energies for the (001) and (010) surfaces are 91.3 ±3 and 41 ±5 kJ/mol, respectively. These activation energies differ by more than a factor of two and bracket the value derived by Schweda for dissolution of K-feldspar (53.6 kJ/mol) from steady-state powder dissolution measurements.

Discussion

The substantial variation of the apparent activation energy for dissolution as a function of crystallographic orientation at a pH of 1.1 implies that that the dissolution rate is highly anisotropic and that the magnitude of the anisotropy is a strong function of temperature. For example, there is a ~40-fold change in the ratio of projected dissolution rates for the (001) and (010) surfaces between 25° and 90°C, in which the (001) surface dissolves faster at temperatures greater than 51°C and the (010) surface is projected to dissolve faster at temperatures less than 51°C.

The magnitude and temperature dependence of the dissolution anisotropy is surprising. The orthoclase (001) and (010) surfaces have similar structures. Each surface exposes a side of the tetrahedral ring shown schematically in Fig. 1(A); the (001) and (020) plane spacings are nearly identical (6.459 vs. 6.503 Å, respectively), as are the unit cell areas per tetrahedral ring (55.8 vs. 55.4 Å², respectively). The primary difference between these two surfaces is that there is an incomplete ordering of the Al and Si atoms distributed between the T1 and T2 sites, [shown in Fig. 1(A)]. The Al tetrahedral site is generally believed to be the primary reactive site at acidic pH, but the expression of the Al tetrahedral site differs for the (001) and (010) cleavage surfaces. This suggests that the different dissolution behavior of the two surfaces is associated with the incomplete ordering of Al in the orthoclase lattice.

References

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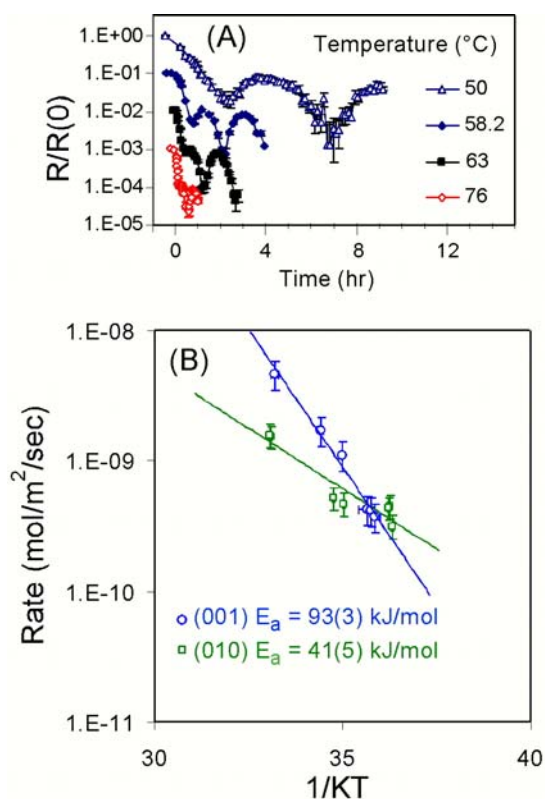[3] H. Teng, P. Fenter, L. Cheng, and N. C. Sturchio, Geochim. Cosmochim. Acta **65**, 3459-3474 (2001).

FIG. 2. (A) In situ XRR measurements of orthoclase (001) surfaces dissolving in pH 1.1 solution as a function of time at selected temperatures ranging from 50° to 76°C. Each data set is vertically offset by factors of 10, for clarity. (B) Plot of the measured orthoclase dissolution rate as a function of 1/KT at pH 1.1 for the (001) and (010) cleavage surfaces.