Face-Selected Orthoclase Dissolution Kinetics Measured with X-ray Reflectivity

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Introduction

Feldspar dissolution rates have normally been studied using macroscopic approaches (e.g., batch powder measurements) whose data represent an ensemble average over a potentially broad range of surface orientations, defect distributions and particle sizes. The extent to which the measured powder dissolution rates and the effective energy barriers derived from the variation of the dissolution rate with temperature are representative of actual molecular-scale processes is unclear. Here we describe recent investigations in which we probe directly the dissolution rate of the orthoclase (001) surface as a function of temperature using x-ray reflectivity.[1]

Methods and Materials

We examined the evolution of dissolving orthoclase (001) cleavage surfaces from a gem-quality crystal (Or$_{94.5}$Ab$_{4.5}$, monoclinic, Itrongay, Madagascar). Real-time measurements were obtained at the first "anti-Bragg condition," which is highly sensitive to the evolution of structure, roughness and termination of the dissolving mineral. Measurements were made in flowing solutions of 0.1 M NaOH and HCl solutions (at pH = 12.9 and 1.1, respectively) at temperatures ranging from 50 to 85° at beamlines 12-ID and 12-BM (BESSRC-CAT, Advanced Photon Source) using monochromatic x-rays with a typical photon energy of E ~ 18 keV.

Results

Real-time x-ray reflectivity data obtained *in situ* during dissolution at pH 12.9 are shown in Fig. 1a for three temperatures. Each oscillation corresponds to the removal of a single orthoclase layer. The dissolution rate increases rapidly with increasing temperature. If we scale the time axis, we find that the data at all three temperatures collapse onto a single curve implying that the dissolution process is unchanged as a function of temperature, albeit with substantially variable rate. Plotting the time scale factor as a function of 1/KT we find data are well-described by an Arrhenius behavior with an effective energy barrier of 0.65 ± 0.05 eV. Similar data have been obtained for dissolution at acidic pH.

Discussion

These data provide the first precise measurements of face-selected dissolution rates of feldspar minerals. The derived effective energy barrier is roughly similar to that derived by powder dissolution studies for the dissolution of related potassium feldspar minerals (0.54 eV), although relatively little data is available. In this context, it is interesting to note that orthoclase (001) dissolution at pH 12.9 involves at least two separate fundamental processes whose active sites are steps and terrace areas with the step process dominating.[2] Consequently the effective energy barrier will be the result of the interplay of these fundamental processes. Finally, we note that the rough agreement in derived effective energy barriers between the x-ray and powder dissolution measurements is not universal as measurements at acidic pH (not shown) reveal substantial discrepancies in the Arrhenius behavior.[1]

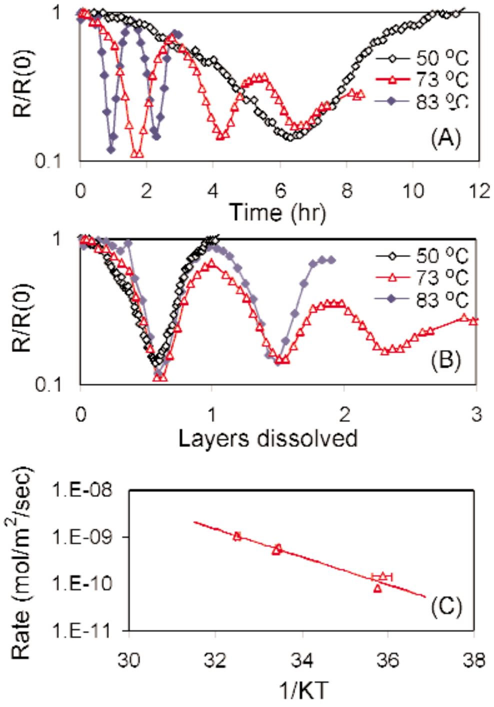

FIG. 1. (a) In situ x-ray reflectivity versus time (measured at the orthoclase anti-Bragg condition, $Q = 0.48$ Å^{-1}) during exposure to pH = 12.9 NaOH. The intensity maxima correspond to the removal of successive 6.48-Å-thick atomic layers. (b) Same data as in (a) after scaling the time axis to correspond to the number of dissolved monolayers. (c) The measured dissolution rate as a function of temperature at pH = 12.9.

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References

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