Resolving Orthoclase Dissolution Processes with X-ray Reflectivity

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Introduction

Feldspar weathering is one of the most important geochemical processes in near-surface environments. Evidence from field and laboratory studies indicate that the mechanisms of feldspar-water interfacial reactions may be distinct under acidic and alkaline conditions. Despite these extensive studies, we have gained little knowledge about the actual surface processes of feldspar dissolution. Here we describe recent investigations in which we directly probe the dissolution of orthoclase (001) surface using x-ray reflectivity and atomic force microscopy.[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 in flowing solutions of 0.1 M HCl and 0.1 M NaOH solutions having pH values of 1.1 and 12.9, respectively, at T ~ 50°C. The x-ray reflectivity measurements were performed at beamlines 12-ID and 12-BM (BESSRC-CAT, Advanced Photon Source) using monochromatic x-rays (E = 18 keV).

Results

Real-time x-ray reflectivity data obtained *in situ* during dissolution are shown in Fig. 1. The measured x-ray reflectivity versus time did not decrease monotonically during dissolution, as would be characteristic of random dissolution (e.g., where all exposed tetrahedral sites dissolve at the same rate). Instead, the reflectivity exhibited an oscillatory pattern for both acidic and alkaline pH. This implies that there are two distinct dissolution processes (e.g., terrace and step dissolution) in both pH regimes. The full recovery of the reflectivity at pH 12.9 upon dissolution of the first layer implies that dissolution at alkaline pH is fully stoichiometric and dominated by lateral dissolution processes producing layer-by-layer dissolution. At pH 1.1, we observed a damped oscillatory pattern indicative of a more random dissolution process in which substantial disruption of the orthoclase surface lattice occurs.

We have also obtained "snapshots" of the dissolution process through high-resolution x-ray reflectivity measurements[2] of previously reacted surfaces. Crystal truncation rod (CTR) data are shown (Fig. 2) for the freshly cleaved orthoclase surface and after dissolution of approximately one and 15 monolayers at pH = 2.0, and two monolayers at pH = 12.9 (1 monolayer = 5.7×10^{-10} mol cm^{-2}). The lines are calculations of the optimized structures for each data set and show that the alkaline-reacted surfaces are indeed fully stoichiometric with a modest increase in surface step density. The acid-reacted surfaces show a substantial change in the surface termination, including step proliferation and local etching described by an error function profile of the atomic occupation factors that is nonstoichiometric in only the outermost unit cell.

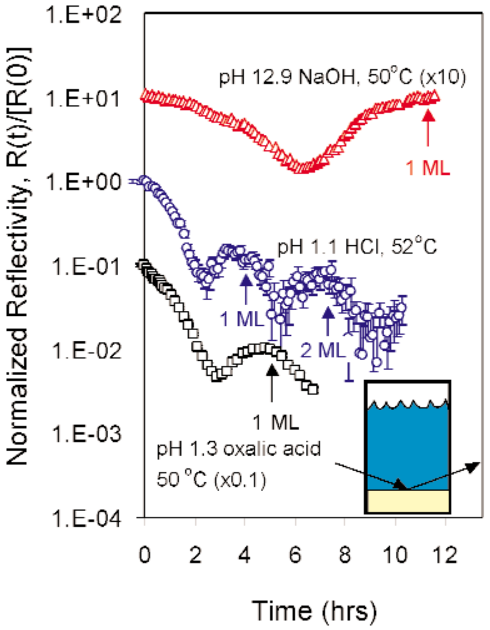

FIG. 1. In situ x-ray reflectivity versus time (measured at Q = 0.48 Å^{-1}) during exposure to pH = 1.1 HCl, pH = 1.3 oxalic acid, and pH = 12.9 NaOH. The removal of successive monolayers (ML) is noted for each set of data.

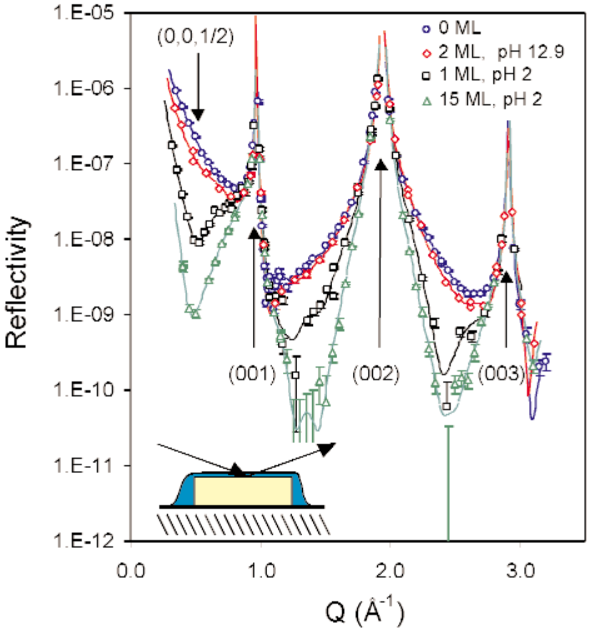

FIG. 2. CTR profiles for the freshly cleaved surface (circles) and surfaces reacted at pH = 2.0 (1 and 15 ML dissolved), and pH = 12.9 (2 ML dissolved). CTR profiles were measured in deionized water at room temperature (T = 25 ± 2°C).

Discussion

These x-ray reflectivity data coupled with parallel atomic force microscopy measurements reveal a detailed new picture of the dissolving orthoclase (001) surface that resolves both the lateral and vertical aspects of this process.[1] We have also distinguished the separate roles of steps/defects versus terraces in orthoclase dissolution at different pH conditions, providing direct evidence for distinct elementary dissolution reactions and reaction sites.

Acknowledgments

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