Barite-Water Interface Structures: X-ray Reflectivity Results

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Introduction

Barite precipitates when sulfate-rich seawater reacts with Ba-rich sedimentary formation waters, forming scale deposits that restrict flow in pipes used in petroleum production. Most relevant studies to date have concentrated on understanding the mechanisms of barite crystal growth in the presence and absence of growth inhibitors.[1] Relatively little is known, however, about the Å-scale structure of the barite-water interface. Here, we report recent results on the structure of the barite(001)- and (210)-water interfaces at 25°C as measured by high-resolution specular x-ray reflectivity and atomic force microscopy.[2]

Methods and Materials

X-ray scattering is an ideal probe of mineral-fluid interface structure because x-rays penetrate macroscopic quantities of fluids (such as water) with limited attenuation, and x-ray reflectivity is directly sensitive to the atomic arrangement of an interface.[3] The x-ray reflectivity measurements were performed at bending-magnet station 1-BM (SRI-CAT, Advanced Photon Source) using monochromatic x-rays ($\lambda = 0.775$ Å). Single crystals of optically clear, natural barite were cleaved to expose (001) and (210) surfaces. Experiments were performed in a static thin-film configuration,[3] with a water layer having a typical thickness of ~60 μm at the barite surface contained by a thin Kapton film.

Results

Representative x-ray reflectivity data are shown in Fig. 1 for freshly cleaved (001)- and (210)-water interfaces. In each case the data follow the form of a crystal truncation rod (CTR), in which the reflectivity is maximum (R~1) at the bulk Bragg peak positions and is much lower ($R \sim 10^{-10}$) between the Bragg peaks. It is the slow continuous variation of the CTR between bulk Bragg peaks that provides direct sensitivity to the structure of the barite-water interface. The solid lines in Fig. 1 correspond to our best-fit models of the (001)- and (210) barite-water interfaces. In both cases we find that a quantitative description of the reflectivity data requires inclusion of symmetry-allowed displacements of near-surface atomic locations, roughness due to individual steps on the barite surface, and the adsorption of water molecules to the barite surface. The substrate structural relaxations include vertical motion of both Ba and sulfate ions (~0.4 Å and ~0.07 Å, respectively), as well as rotation of the sulfate ions. These displacements decay rapidly into the crystal. We also find that a layer of water molecules (or OH^-, H_3O^+) adsorbs to the barite surface consistent in both number and height with the saturation of broken Ba-O bonds created during cleavage of the surface.

Discussion

The present results are similar in many respects to those obtained previously for the calcite-water interface[4] as might be expected on the basis that both calcite and barite are ionic minerals. In the case of calcite, each Ca ion exposed by cleavage has only one broken Ca-O bond, and consequently the derived structure in that case is simpler than that reported here for barite. Together, these data suggest that the adsorption of water molecules to terminate the metal-oxygen bonds broken during cleavage is a general characteristic of these surfaces.

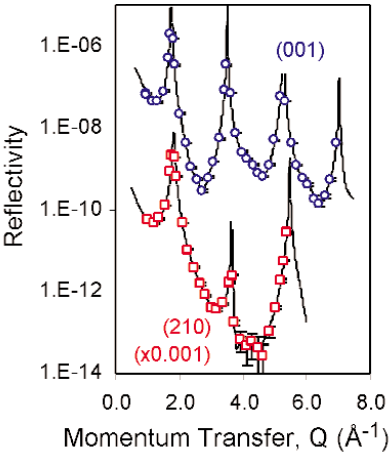

FIG. 1. The reflectivity of the barite(001)- and (210)-water interfaces are shown as a function of momentum transfer, Q. The solid lines are calculations of optimized structures described in the text.

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