Synchrotron X-ray Scattering Studies at Mineral-Water Interfaces

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ABSTRACT

Synchrotron X-ray scattering techniques provide a powerful tool for the *in situ* study of atomic scale processes occurring at solid-liquid interfaces. We have applied these techniques to characterize and study reactions at mineral-water interfaces. Here we present two examples. The first is the characterization of the calcite (CaCO_3) ($10\bar{1}4$) cleavage surface, in equilibrium with deionized water, by crystal truncation rod measurements. The second is the *in situ* study of the heteroepitaxial growth of otavite (CdCO_3) on the calcite ($10\bar{1}4$) cleavage surface. The results of such studies will lead to significant progress in understanding mineral-water interface geochemistry.

INTRODUCTION

Reactions occurring at mineral-water interfaces play a crucial role in geochemical transport processes. Traditionally, atomic-scale structural information concerning these processes has been inferred from chemical measurements made in systems where powders are reacted with fluids. In these studies the initial condition of the surface is unknown, crystallographic control is lacking, reactive surface area is difficult to determine, and product characterization may be extremely tedious if not impossible. We have applied synchrotron X-ray scattering techniques in response to the need for high-resolution atomic scale structural information regarding mineral-water interface processes. To understand these processes, fundamental solid-liquid interface phenomena that occur at mineral-water interfaces need to be studied: dissolution and precipitation, adsorption, heterogenous nucleation, epitaxial growth, recrystallization, solid-solution formation, oxidation-reduction, and the electric double layer.

Here we present some results of X-ray scattering measurements made at mineral-water interfaces. We studied the structure of the calcite (CaCO_3) ($10\bar{1}4$) cleavage surface in equilibrium with deionized water using the crystal truncation rod (CTR) technique. The CTR arises from the termination of a single crystal at a surface or interface and can be used to determine its structure (e.g., surface reconstruction, relaxation, etc.) with monolayer sensitivity.[1] The CTR measurements showed that the calcite ($10\bar{1}4$) cleavage surface exhibits monomolecular and bimolecular steps. Also, we found no evidence for surface reconstruction or the presence of a disordered surface phase of hydrated calcium carbonate. We also studied the heteroepitaxial growth of otavite (CdCO_3) on the calcite ($10\bar{1}4$) cleavage surface.[2] X-ray reflectivity measurements were used to determine the otavite growth rate and diffraction measurements were used to characterize the otavite overgrowth and to determine the calcite-otavite heteroepitaxial relationship. This study demonstrated a new and accurate approach for measuring *in situ* precipitation rates and growth mechanisms in mineral-water systems.

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EXPERIMENTAL

Synchrotron X-ray scattering measurements were made at beamline X10B at the National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength of the incident X-rays (λ) was 0.967 Å and the incident X-ray beam was focused to a 0.5 mm x 0.5 mm spot. The experiments were performed using a solid Teflon reaction cell with Teflon-coated, X-ray transparent windows.[3] The cell was equipped with micro-pH and micro-thermocouple probes. All measurements presented here were made at 25 °C. The reaction cell was mounted to the Φ circle of a Huber six-circle diffractometer. This arrangement allowed sufficient access to the calcite and otavite reciprocal lattices to perform specular and off-specular X-ray reflectivity and diffraction measurements. The calcite samples were cut from large single crystals of optically clear "Iceland Spar" calcite from Chihuahua, Mexico. The surface area of the samples was 3.4 mm x 8 mm. The cut crystals were ultrasonically cleaned successively in acetone, methanol, and deionized water. The crystals were then cleaved in a glove bag under a flowing N₂ gas atmosphere, and the freshly cleaved calcite was loaded into the reaction cell without exposure to air.

RESULTS

Crystal Truncation Rod Measurement of the Calcite-Water Interface

The CTR of the calcite (10 $\bar{1}$ 4) cleavage surface in equilibrium with deionized water (DIW) is shown in Figure 1. Equilibrium was determined by monitoring the solution pH.[3] The DIW pH was initially 5.6 and after 100 minutes the solution pH was 8.2. During this time, 0.07 $\mu\text{mol}\cdot\text{cm}^{-2}$ of calcite had dissolved. The CTR was measured, after the pH had reached 8.0, by performing rocking curve (θ) scans at fixed values of perpendicular momentum transfer [$Q_{\perp} = (4\pi/\lambda)\sin\theta$] between 0.08 and 4.1 Å⁻¹. Each point of the CTR represents the integrated intensity of these rocking curve scans after background subtraction. The line labeled "ideal" in Figure 1 represents the calculated CTR of an ideally terminated calcite (10 $\bar{1}$ 4) surface, which was calculated using:[1]

$$I_{CTR} = I_0 \left| \frac{e^2}{mc^2} \frac{1}{R_0} F(Q) N_1 N_2 \right|^2 \frac{1}{2 \sin^2 \left(\frac{1}{2} Q_{\perp} a_3 \right)} \quad (1)$$

where I_0 is the incident X-ray beam intensity, e and m are the electron charge and mass, respectively, R_0 is a length related to the sample-detector distance, N_1 and N_2 are the number of unit cells, $F(Q)$ is the structure factor, $Q_{\perp}$ is the perpendicular momentum transfer, and a_3 (= 3.04 Å) is the d-spacing of the calcite (10 $\bar{1}$ 4) diffraction planes. This model obviously does not accurately describe the CTR. To accurately describe the CTR we had to use a model which describes the CTR from a stepped surface. The model we used may be written as:[4]

$$I_{\text{step}} = I_{\text{CTR}} \frac{\sinh^2(a_3 / h_{\text{step}}) - \cos(Q_{\perp} a_3)}{\cosh(a_3 / h_{\text{step}})} \quad (2)$$

Figure 1: Intensity (log scale) of the calcite $(10\bar{1}4)$ crystal truncation rod (open circles) plotted as a function of $Q_{\perp}$. The calcite surface was near equilibrium with water. The line labeled "ideal" represents the calculated CTR of an ideally terminated calcite-water interface. The line labeled "stepped" is the best fit result using the stepped-surface model described in the text. The line labeled "hydrated" is the expected CTR for a 3 Å-thick disordered surface phase of hydrated calcium carbonate at the calcite-water interface.

In this model [equation (2)] a Poisson distribution of step heights about an average step height (h_{step}) is assumed. Examination of the calcite structure reveals that step-heights must be integer multiples of 3.04 Å, the monomolecular layer thickness. We first attempted to describe the CTR by fixing h_{step} to be equal to 3.04 Å. Although this model described the data much better than equation (1), the best fit was obtained using a linear combination of the stepped-surface model with monomolecular and bimolecular steps, i. e.

$$I = xI_{step}(h_{step} = 3.04 \text{ Å}) + (1 - x)I_{step}(h_{step} = 6.08 \text{ Å}) \quad (3)$$

where x is restricted by $0 \leq x \leq 1$. For calcite in equilibrium with deionized water, we found $x = 0.66$. This implies that 66% of the steps have heights of one monomolecular layer and that 34% of the steps have heights of two monomolecular layers. The result of this calculation is the line labeled "stepped" in Figure 1.

Some authors have proposed that there is a disordered surface phase of hydrated calcium carbonate at the interface [5-7]. The line labeled "hydrated" in Figure 1 represents the calculated CTR for a 3 Å-thick hydrated surface phase of disordered calcium carbonate (bulk composition $\text{CaCO}_3 \cdot \text{H}_2\text{O}$) at the calcite-water interface. This calculation represents the concept invoked by these authors for describing kinetic models of carbonate mineral dissolution and precipitation. The calculated CTR for this hydrated surface layer, however, does not resemble any of the observed CTRs, and the fit quality using this model worsens with increasing layer thickness.

Heteroepitaxial Growth of Otavite on Calcite

X-ray reflectivity and diffraction were used to characterize an otavite overgrowth during its precipitation from aqueous solution onto the calcite (10 $\bar{1}$ 4) cleavage surface. Otavite growth was initiated when approximately 1 mL of an otavite-saturated solution, which had 100% CO_2 bubbled through it for two days prior to use, was added to the reaction cell. As CO_2 diffused out of the solution through a small vent at the top of the cell, otavite became oversaturated and precipitated on the calcite cleavage surface. X-ray reflectivity and diffraction scans were measured during 4585 min of growth. Specular X-ray reflectivity is measured by monitoring changes in the reflected X-ray intensity as a function of perpendicular momentum transfer. Reflectivity is used to determine the properties of thin films, including the film thickness (D), interfacial roughness (σ), and real-space electron density profile across interface(s). Therefore, reflectivity is ideal for determining thin film thickness as a function of time (growth rate). We determined the otavite growth rate to be 15 Å/hr during the first 540 min of growth from reflectivity measurements.[2]

The calcite structure is rhombohedral and can be discussed conveniently in terms of the hexagonal unit cell. The calcite lattice constants are $a = 4.99 \text{ Å}$ and $c = 17.059 \text{ Å}$. [8] Otavite has the calcite structure, and the otavite lattice constants are $a = 4.92 \text{ Å}$ and $c = 16.298 \text{ Å}$. [8] If the otavite overgrowth forms with the bulk otavite lattice parameters, then we expect the otavite (10 $\bar{1}$ 4) reflection to have a diffraction maximum at $Q_{\perp} = 2.13 \text{ Å}^{-1}$. The calcite (10 $\bar{1}$ 4) reflection has a

diffraction maximum at $Q_{\perp} = 2.07 \text{ \AA}^{-1}$. These correspond to d-spacings of $3.04 \text{ \AA}$ and $2.95 \text{ \AA}$ for calcite ($10\bar{1}4$) and otavite ($10\bar{1}4$), respectively.

The specular diffraction scans recorded during otavite growth are shown in Figure 2. The intense, narrow peak at $Q_{\perp} = 2.07 \text{ \AA}^{-1}$ is due to the diffraction maximum of the calcite ($10\bar{1}4$) reflection. The full width at half maximum (FWHM) intensity of this peak was limited by instrumental resolution. The second peak in Figure 2, which appears at higher $Q_{\perp}$, is due to diffraction from the otavite overgrowth. The peak position is nearest to otavite ($10\bar{1}4$), indicating that the otavite formed with its ($10\bar{1}4$) direction parallel to the calcite ($10\bar{1}4$) direction. With increasing time, the FWHM of this peak became narrower and the peak position shifted to lower $Q_{\perp}$.

Figure 2: Diffracted X-ray intensity (log scale) vs. $Q_{\perp}$. The data are offset for clarity. Vertical dashed lines at $Q_{\perp} = 2.07$ and $2.13 \text{ \AA}^{-1}$ indicate the ($10\bar{1}4$) reflections of calcite and otavite, respectively. The inset shows percent compression of the measured otavite overgrowth d-spacing (relative to bulk otavite) vs. the measured longitudinal coherence length (i.e., thickness) of the overgrowth.

To quantify these observations the otavite peaks were fit using a Voigt function. The relevant fit parameters were the otavite peak position and FWHM. The FWHM and peak position were used to estimate the average domain size (L) of the otavite in the direction perpendicular to the $(10\bar{1}4)$ diffraction planes (using the Scherrer equation [9]) and the d-spacing ($d_{10\bar{1}4}$) of the otavite in the direction perpendicular to the $(10\bar{1}4)$ diffraction planes, respectively. We found that L , determined from diffraction, and D , determined from reflectivity were in good agreement indicating that L provides an acceptable estimate of film thickness. After 173 min, $d_{10\bar{1}4}$ was equal to 2.885 Å ($L = 36.6$ Å). After 381 min of growth $d_{10\bar{1}4}$ was equal to 2.934 Å ($L = 63.4$ Å). This result indicates that at a thickness of 36.6 Å the otavite was compressed by 2.2% in the direction perpendicular to the calcite surface. The $(10\bar{1}4)$ compression served to relieve lateral strain in the overgrowth. The lateral strain occurred because the cadmium atoms in the otavite structure were aligned with calcium atom positions of the underlying calcite, i.e. the interface was coherent. At a thickness 63.4 Å, the lateral and longitudinal strain in the otavite was relieved. The relief of strain at a critical thickness is commonly observed in semiconductor systems.

Several off-specular diffraction scans were measured for the otavite after 4585 min of growth. The presence of off-specular diffraction maxima indicate that the otavite formed as a single crystal overgrowth. From rocking curve scans at off-specular diffraction peaks, the in-plane crystal mosaic was 0.45° . The out-of-plane crystal mosaic was determined to be 0.41° from rocking curve scans measured at the otavite $(10\bar{1}4)$ diffraction peak. The lattice constants determined from the off-specular peak positions were nearly identical to those of bulk otavite. These results indicate that the otavite grew as a single crystal heteroepitaxially on the calcite $(10\bar{1}4)$ cleavage surface.

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