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**Dissolution Dynamics of the Calcite-Water Interface
Observed In Situ by Glancing-Incidence X-ray Scattering**

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Abstract

Glancing-incidence X-ray scattering measurements made at the National Synchrotron Light Source were used to investigate dissolution dynamics *in situ* at the calcite-water interface. The relation between calcite saturation state and roughness of the calcite (10 $\bar{1}$ 4) cleavage surface as a function of time was examined during pH titrations of an initially calcite-saturated solution. Systematic variations in roughness were observed as a function of saturation state as pH was titrated to values below that of calcite saturation. Different steady-state values of roughness were evident at fixed values of ΔG_r , and these were correlated with the extent of undersaturation. A significant increase in roughness begins to occur with increasing undersaturation at a ΔG_r value of approximately $-2.0 \text{ kcal} \cdot \text{mol}^{-1}$. The dissolution rate corresponding to this increase is about $1.5 \times 10^{-7} \text{ mmol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. This increase in roughness is attributed to a transition in the principal rate-determining dissolution mechanism, and is consistent with both powder-reaction studies of dissolution kinetics and single-crystal dissolution studies by atomic force microscopy. These data indicate some important potential applications of GLXS in the study of mineral-water interface geochemistry.

Introduction

It has long been recognized that the phenomena of crystal growth and dissolution are controlled by the presence of crystal defects and associated microtopographic features at the crystal surface (Burton et al., 1951; Cabrera and Levine, 1956; Hirth and Pound, 1957). The surface microtopography of a crystal reflects the history of surface reactions (involving chemical bond generation or destruction) that occurred as new material was added to and/or removed from the crystal. Observations of surface microtopography can be used to identify important constraints on reaction kinetics and mechanisms at mineral-fluid interfaces (e.g., Hillner et al., 1992; MacInnis and Brantley, 1992; Gratz et al., 1993; Dove and Hochella, 1993; Paquette and Reeder, 1995).

The kinetics of crystal growth and dissolution in aqueous solution are generally measured in powder reaction experiments. In such experiments, surface reaction mechanisms are not directly observed but may be inferred from empirical rate laws (e.g., Plummer et al., 1978). This approach has provided much accurate kinetic data, but more detailed information on reaction mechanisms is required to achieve a comprehensive understanding of mineral-fluid interface processes. Such information is available only through direct observation of these interfaces at the microscopic scale using modern analytical tools, complemented by application of appropriate theory.

Elucidation of the relations between microtopography and surface reactions can be accomplished with *in situ* observations of crystal surfaces while the solution composition is being controlled independently. Some advantages of the *in situ* approach over conventional powder-reaction techniques were demonstrated in experiments performed by Ohmoto et al. (1991), who used optical microscopy to observe single-crystal mineral surfaces during dissolution and growth reactions at elevated temperatures and pressures. However, the spatial resolution of their observations were limited by the wavelength of visible light to micron-scale features. *In situ* observations at a much smaller scale have become feasible since the advent of the atomic force microscope (AFM) equipped with a fluid-flow reaction cell (e.g., Hillner et al., 1992; Gratz et al., 1993; Dove and Hochella, 1993; Stipp et al. 1994; Liang et al., 1995). Most of the *in situ* AFM studies performed to date on minerals have been on calcite, because of its availability as large, high-quality single crystals, its perfect (10 $\bar{1}$ 4)

cleavage surface and its relatively rapid reaction kinetics.

An ultrasensitive *in situ* technique that has clear potential for time-resolved mineral-water interface studies is glancing-incidence X-ray scattering (GIXS) (Chiarello et al., 1993). This technique provides information that is distinct from, yet complementary to, that provided by AFM observations. The intensity of X-rays scattered from an interface at glancing incidence is sensitive to angstrom-scale variations in root-mean-square interface roughness. Variations in interface roughness as a function of mineral saturation state can be measured precisely by GIXS (Chiarello et al., 1993), and such measurements can yield important constraints on both surface reaction kinetics and mechanisms, as well as equilibrium thermodynamics, in aqueous environments. To demonstrate the technique, in this paper we present preliminary time-resolved GIXS data concerning the roughness of the calcite-fluid interface as a function of calcite saturation state. We give evidence for layer-by-layer dissolution as well as widespread etch hole nucleation on terrace areas on calcite, and we show that there is an apparent transition in dissolution mechanism at a certain degree of undersaturation. The same technique can be used for growth studies as it can potentially distinguish adsorption, spiral growth, and two-dimensional nucleation mechanisms (Nielsen, 1983).

Experimental Description

X-ray scattering measurements were made at the National Synchrotron Light Source using beamline X10B. The incident X-ray beam wavelength ($\lambda = 0.967 \text{ \AA}$) was selected by a Ge(220) monochromator that was asymmetrically cut for focusing in the horizontal direction. A flat platinum-coated Zerodur mirror was bent to focus in the vertical direction. The incident beam was focused to a 1-mm^2 area at the sample position, and the incident X-ray flux was 2×10^{11} photons/second. The intensity of the incident X-ray beam was monitored by a NaI scintillation detector, and the intensity of the scattered X-ray beam was monitored by another NaI scintillation detector with a Ge(111) analyzer crystal positioned in front of it.

Measurements were made at room temperature using a Teflon reaction cell having X-ray transparent Teflon-coated Kapton windows. The X-ray pathlength through this cell was 3 mm and the fluid volume was 0.93 mL. Optically clear single crystals of Iceland spar calcite

from Chihuahua, Mexico, were used for the experiments. The calcite was cut into rectangular blocks (providing 3 mm x 8 mm cleavage faces) and ultrasonically cleaned with acetone, methanol, and deionized water. These blocks were cleaved in a glovebag under flowing N_2 . A (10 $\bar{1}$ 4) cleavage surface free of visible steps and defects was selected for use in this experiment. The calcite block with this cleavage surface was loaded into the reaction cell in the glovebag without being exposed to air. X-ray scattering measurements were first made under flowing N_2 , and then the surface was exposed to a dilute, synthetic groundwater-like solution that was calcite-saturated at pH = 8.5. The solution pH was subsequently cycled seven times from pH = 8.5 to pH = 4, and back to pH = 8.5, by autotitration (Mettler DL-70) using 0.01 M HNO_3 and 0.05 M NaOH. The solution was circulated using a peristaltic pump at a rate of 6 mL/minute through a closed, airtight loop including the reaction cell and the autotitrator. The tubing used was 1/16-inch inner diameter silicone and all other surfaces exposed to the fluid were made of Teflon.

Experimental Results and Discussion

Insights regarding the microtopographic evolution of the calcite-water interface during dissolution were gained by monitoring changes in the scattered X-ray intensity over time at a fixed glancing incidence angle ($\theta = 0.44^\circ$) during the pH titrations. In this geometry, variations in the scattered X-ray intensity indicate angstrom-scale changes of the calcite surface roughness (Chiarello et al., 1993; Chiarello and Sturchio, 1995). The incident beam size was about 1-mm² and the X-ray coherence length was about 1 micron, thus the measured intensity represents an ensemble average at the micron scale.

Figures 1 and 2 show the scattered X-ray intensity and the values of ΔG_r as a function of time for two representative titrations performed during this experiment. The thermodynamic quantity, ΔG_r , is the Gibbs free energy of reaction, a measure of the deviation of the calcite-fluid system from thermodynamic equilibrium. At equilibrium, $\Delta G_r = 0$. The ΔG_r values were calculated from our bulk solution chemical data (pH, Ca, alkalinity) using SOLMINEQ.88 (Kharaka et al., 1988). According to Plummer et al. (1978), the composition of the fluid at the bottom of the hydrodynamic boundary layer (i.e., at the calcite surface) in a well-stirred batch reactor is near that of the bulk solution during dissolution, except at low pH

(≤ 4). This is because of the slow rate of surface-controlled reactions relative to diffusion of solutes through the boundary layer. At low pH (≤ 4), transport of protons through the boundary layer controls the calcite dissolution rate.

Layer-by-layer dissolution

The data in Fig. 1 were obtained while the pH was being ramped from 8.5 to 4. The surface had previously been cycled once to pH = 4 for 5 minutes and back again to pH = 8.5. The scattered X-ray intensity clearly shows short-period (~ 44 seconds) oscillations during the first 300 seconds of this titration. These oscillations begin when the ΔG_r value decreases below about $0.2 \text{ kcal} \cdot \text{mol}^{-1}$ and continue, with somewhat increasing frequency, until the ΔG_r decreases below about $-2.0 \text{ kcal} \cdot \text{mol}^{-1}$ and the intensity begins to fall off more rapidly with decreasing ΔG_r . These oscillations were observed repeatedly in similar titrations during this experiment, and comparable oscillations have been observed in other X-ray scattering experiments involving crystal growth (Vlieg et al., 1988; Fuoss et al., 1992). We calculated from our chemical data, using the calcite dissolution rate equation of Plummer et al. (1978), that the frequency of each oscillation corresponds to the removal of an amount of calcite equivalent to approximately 6 monomolecular layers (a monomolecular layer is $3.04 \text{ \AA}$ thick). Etch pits that had formed during the first pH = 4 reaction step were already present during this titration. Considering that about 85% of the net steady-state calcite dissolution occurs on inclined surfaces such as etch pit walls (MacInnis and Brantley, 1992), the frequency of these oscillations is consistent with layer-by-layer dissolution (by monomolecular step migration) on terrace areas; one layer equivalent was dissolved from terrace areas with each oscillation and the other five layer equivalents were dissolved at etch pit walls. The scattered X-ray intensity at glancing incidence in this case is sensitive mainly to the roughening of the terrace areas, because of the large size of the etch pits relative to the X-ray coherence length.

A computer simulation of the scattered X-ray intensity (using Eqn. 1 from Chiarello and Sturchio, 1995) from a surface undergoing layer-by-layer dissolution is represented by the dotted line at the top of Fig. 1. In this simulation, which agrees well with the measured intensity for the first 300 sec, a local minimum in the scattered X-ray intensity corresponds to the removal of half a monomolecular layer from a surface having an initial roughness of $3 \text{ \AA}$.

A local maximum in the scattered X-ray intensity corresponds to the completion of the removal of one monomolecular layer.

Transition in dissolution mechanism

As the ΔG_r value during the titration decreased below $-2.0 \text{ kcal} \cdot \text{mol}^{-1}$ (and the dissolution rate increased above $1.5 \times 10^{-7} \text{ mmol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$), the short-period oscillations were no longer evident, and the scattered X-ray intensity decreased rapidly (Fig. 1). This change may have signified that the dominant process controlling surface topography changed from layer-by-layer dissolution to the spontaneous nucleation and growth of etch features as the deviation from equilibrium increased. Such behavior is predicted by theories of crystal dissolution and etching (Sangwal, 1987) and could produce the observed decrease in the scattered X-ray intensity.

The inferred transition in dissolution mechanism occurs at a ΔG_r value of approximately $-2.0 \text{ kcal} \cdot \text{mol}^{-1}$. This value is significantly more negative than that calculated by Nagy and Lasaga (1992) [from the experimental data of Berner and Morse (1974)] for the opening of dislocation cores to form etch pits on calcite. This difference indicates that another process having a higher activation energy, perhaps etch hole nucleation at non-dislocation sites such as impurities or point defects (cf. Blum et al., 1990; "etch pinholes" of Hillner et al., 1992; "G2 etch pits" of MacInnes and Brantley, 1992), became increasingly rapid as the value of ΔG_r became more negative with decreasing pH. Such nucleation and growth of etch holes on terrace areas could account for the observed decrease in scattered X-ray intensity with decreasing pH.

Plummer et al. (1978) studied the kinetics of calcite dissolution as a function of temperature, pH, and pCO_2 . They defined three dissolution "regions" at 25°C as a function of dissolution rate, pH, and pCO_2 . Our experimental conditions were within their regions 2 and 3. Region 2 extends from $\text{pH} = 3.5$ to $\text{pH} = 5.5$ at 1 atm pCO_2 , and from $\text{pH} = 4.5$ to $\text{pH} = 6.5$ at 0.03 atm pCO_2 . Region 3 extends from the high-pH end of Region 2 to higher pH values. Plummer et al. (1978) the dominant forward reaction mechanism in region 2 to carbonic acid attack, via

and the dominant forward reaction mechanism in region 3 to water attack, via

In both regions, calcite dissolution is surface-controlled.

The rapid decrease in scattered X-ray intensity observed during the titrations from pH = 8.5 to pH = 4 (Figs. 1 and 2) occurred at a pH value of approximately 7; this is approximately the boundary between regions 2 and 3 for a solution at atmospheric $p\text{CO}_2$ (Plummer et al., 1978). Accordingly, the X-ray data provide evidence for a transition in the surface etching mechanism, with increasing deviation from equilibrium, that may correspond to a transition from water attack to carbonic acid attack.

Steady-state roughness and defect layering

Figure 2 shows data for the final, and longest, pH = 4 reaction step that lasted for 3600 seconds. Two effects are illustrated by Fig. 2. First, the scattered intensity approaches a steady-state value when the pH is held constant at pH = 4 ($\Delta G_r = -6.11 \text{ kcal} \cdot \text{mol}^{-1}$). This was observed in all of the titrations at pH = 4, as well as in another experiment we performed at pH = 6. Second, the scattered X-ray intensity during the pH = 4 reaction time exhibits oscillations with equal or greater amplitude but much lower frequency than those shown in Fig. 1. Assuming a dissolution rate at pH = 4 of $10^{-5.2} \text{ mmol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (Plummer et al., 1978), these long-period oscillations correspond to the removal of 3.5 to $8.8 \mu\text{mol} \cdot \text{cm}^{-2}$ of calcite (an equivalent thickness of 2 to 5 μm) per oscillation. We speculate that compositionally distinct layers may have developed parallel to the (10 $\bar{1}$ 4) surface during the natural growth of the crystal (Paquette and Reeder, 1990). As dissolution proceeded at constant ΔG_r , variations in the concentration of impurities or other point defects (e. g. vacancies) within these layers may have acted as a temporally variable source of etch hole nucleation. The long-period oscillations observed in the scattered X-ray intensity may thus be correlated with the concentrations of these impurities and point defects in layers parallel to the (10 $\bar{1}$ 4) surface.

Surface healing effect

The scattered intensity increased slowly after the pH was titrated back from pH = 4 to pH = 8.5 (Fig. 2). This was observed to some extent, with a similar time constant, in all of the titrations and may indicate that the dynamically rough surface maintained by rapid dissolution at pH = 4 was smoothed at pH = 8.5. This may occur by a surface process analogous to Ostwald ripening, whereby surface free energy of a rough surface is minimized by local redistribution of material to "heal" the surface. This effect has been documented a number of times with crystal truncation rod measurements in near-equilibrium calcite-water systems (Chiarello and Sturchio, 1995). The surface healing effect may have been accelerated by a slight undersaturation during this experiment, because the solution had become slightly undersaturated with calcite by dilution with titrant (final value of $\Delta G_r = -0.3 \text{ kcal} \cdot \text{mol}^{-1}$). After titration to pH = 8.5, etch holes nucleated at the surface at pH = 4 may have grown laterally and intersected by step migration. This process would cause a gradual increase in the scattered intensity (decrease in roughness), as was observed, until enough additional calcite had dissolved to reduce the undersaturation at pH 8.5 to zero. The leveling off of the scattered intensity at about 7000 seconds (Fig. 2) indicates that the undersaturation had approached zero by this time. There was, however, an irreversible net decrease in scattered intensity because of macroscopic etch pit formation. Figure 3 is a scanning electron microscope image of the surface reacted at pH = 4. This figure shows that geometric etch pits had formed on the reacted surface. They ranged in size from 50 to 350 μm in their longest dimension and covered about 25% of the surface area.

Summary and Conclusion

Time-resolved glancing-incidence X-ray scattering measurements were made to investigate the dissolution dynamics of the calcite (10 $\bar{1}$ 4) cleavage surface. Variations in scattered X-ray intensity at fixed incidence angle were used to investigate angstrom-scale changes in root-mean-square interface roughness as a function of solution saturation state. The results of the measurements presented here are consistent with a transition in rate-determining dissolution mechanism at a ΔG_r value near $-2.0 \text{ kcal} \cdot \text{mol}^{-1}$. Above this value of ΔG_r , we infer that dissolution occurred layer-by-layer by the migration of monomolecular steps.

Below this value of ΔG_r , we infer that dissolution was accelerated by the spontaneous nucleation and growth of etch features. These inferences are consistent with both kinetic studies (Plummer et al., 1978) and with atomic force microscopy studies (Hillner et al., 1992) of calcite dissolution. Comparison with the results of Plummer et al. (1978) indicates that the inferred transition in dissolution mechanism may correspond to a transition from water attack to carbonic acid attack.

Studies of mineral-fluid interfaces that combine *in situ* synchrotron X-ray scattering with precise control and monitoring of solution composition have enormous potential to resolve fundamental questions in geochemistry. The increased X-ray flux and brilliance available at new third-generation synchrotron radiation sources (such as the European Synchrotron Radiation Facility, the Advanced Photon Source, and SPRing-8) will enable such measurements to be performed on much smaller samples with time resolution of less than a millisecond. These measurements will be complemented by simultaneous surface-sensitive fluorescence-based measurements involving X-ray standing waves and reflection-geometry X-ray absorption spectroscopy. It is anticipated that increased use of such synchrotron-based experimental approaches will lead to rapid progress in our understanding of the atomic-scale processes occurring at mineral-fluid interfaces.

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Figure Captions

Figure 1: Reflected X-ray intensity at $Q_{\perp} = 0.1 \text{ \AA}^{-1}$ (open circles) and ΔG_r (dashed line) plotted as a function of reaction time as pH was titrated from a value of pH = 8.5 ($\Delta G_r = 0.0 \text{ kcal} \cdot \text{mol}^{-1}$) to pH = 4.0 ($\Delta G_r = -6.1 \text{ kcal} \cdot \text{mol}^{-1}$). The dotted line is a simulation (see text) of the effect of layer-by-layer dissolution upon the scattered X-ray intensity (this curve is offset upward by approximately 0.05 units on the intensity scale for clarity).

Figure 2. Reflected X-ray intensity at $Q_{\perp} = 0.1 \text{ \AA}^{-1}$ (open circles) and ΔG_r (dashed line) plotted as a function of reaction time as pH was titrated from a value of pH = 8.5 ($\Delta G_r = 0.0 \text{ kcal} \cdot \text{mol}^{-1}$) to pH = 4.0 ($\Delta G_r = -6.1 \text{ kcal} \cdot \text{mol}^{-1}$) and then back again to pH = 8.5. Note that the time scale of Fig. 2 is nearly 20 times greater than that of Fig. 1.

Figure 3: Scanning electron microscope image of calcite ($10\bar{1}4$) surface after net dissolution of $26 \text{ } \mu\text{mol} \cdot \text{cm}^{-2}$ (an equivalent layer thickness of $14.8 \text{ } \mu\text{m}$) of calcite. This is the post-reaction surface of the crystal used in this experiment. Small white specks are surface contamination from evaporated solution residue.

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Fig. 1