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Mobile ions on carbonate surfaces

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Abstract—Surface ions move during the dissolution and growth of minerals. The present study investigates the density and the mobility of surface ions and the structure of the adsorbed water layer with changes in relative humidity (RH). The time evolution of the polarization force, which is induced by an electrically biased tip of an atomic force microscope, shows that the density and the mobility of surface ions increase with rising humidity, a finding which is consistent with increasing surface hydration. A marked change in the observations above 55% RH indicates a transition from a water layer formed by heteroepitaxial two-dimensional growth at low RH to one formed by multilayer three-dimensional growth at high RH. A comparison of the results of several rhombohedral carbonates (*viz.* $CaCO_3$, $FeCO_3$, $ZnCO_3$, $MgCO_3$, and $MnCO_3$) shows that a long relaxation time of the polarization force at high RH is predictive of a rapid dissolution rate. This finding is rationalized by long lifetimes in terrace positions and hence greater opportunities for detachment of the ion to aqueous solution (i.e., dissolution). Our findings on the density and the mobility of surface ions therefore help to better constrain mechanistic models of hydration, ion exchange, and dissolution/growth.

1. INTRODUCTION

The carbonate family of minerals is ubiquitous and plays many important roles (Morse and Arvidson, 2002). An understanding of carbonate mineral surface properties, however, remains incomplete, especially in response to hydration (Stipp et al., 1996; Fenter et al., 2000; Krueger et al., 2003). The high solubilities and the fast dissolution kinetics characteristic of carbonate minerals complicate efforts to characterize the chemical and electrical properties of the hydrated surface (Van Cappellen et al., 1993). Previous computational, spectroscopic, and imaging studies suggest that a cleaved calcite mineral surface prepared in vacuum is terminated by undercoordinated divalent metals and carbonate oxygens. In response to the unsatisfied charge, the surface relaxes, restructures, and, in the presence of water, hydrates (Stipp, 1999). X-ray reflectivity data show the formation of a 2-nm thick water film on freshly cleaved calcite under humid conditions (Chiarello et al., 1993). Atomic force micrographs collected for six days in humid air reveal a dynamic surface having changes in step positions and pit morphologies (Stipp et al., 1996). The inference is the presence of hydrated mobile ions on the surface of calcite and, presumably, of other members of the carbonate family. These mobile ions are also the active agents in kink-kink-annihilation (KKA) theory employed to describe mineral growth and dissolution (Liang et al., 1996a, 1996b; Jordan et al., 2001; Morse and Arvidson, 2002; Duckworth and Martin, 2003).

A missing link in experimental techniques is the ability to measure the density and the mobility of surface ions and thus to provide data to constrain mechanistic models of dissolution and growth. In the work reported in this paper, we employ a new approach to study the density and the mobility of surface ions. Namely, the time evolution of the electrical force between a biased atomic force microscope (AFM) tip and the mineral surface is monitored at various relative humidities (RH) (Hu et al., 1995a, 1995b). A large part of the force arises from charge induced (i.e., a polarization force) at the mineral surface by the nearby biased tip. When present, solvable surface ions are the main contribution to the induced charge (Hu et al., 1995b; Luna et al., 1998). These measurements are, therefore, sensitive to ion hydration, surface migration, and desorption, and new mechanistic insights of calcite dissolution may be gained. Specifically, we investigate connections between the density and mobility of surface ions and the dissolution rates of $CaCO_3$, $FeCO_3$, $ZnCO_3$, $MgCO_3$, and $MnCO_3$. We also investigate the structure and the thickness of adsorbed water at several relative humidities.

2. EXPERIMENTAL

2.1. Sample Preparation

Single crystal samples of calcite (variety Iceland Spar, Chihuahua, Mexico) were purchased from Ward's Geology (Rochester, New York). Rhodochrosite (sample no. 96030, Colorado), siderite (sample no. 134827, Ivigtut, Greenland), smithsonite (sample no. 115633, Broken Hill, Zimbabwe), and magnesite (sample no. 105090, Oberdorf, Austria) were obtained from the Harvard University Mineralogical Museum. Fresh $(10\bar{1}4)$ surfaces of each mineral were prepared by cleaving samples with a sharp razor blade. The samples were either mounted directly on a steel disk ("dry" preparation) or immersed in doubly distilled water for ten minutes and then mounted ("wet" preparation). In both cases, the samples were secured using silver paste (SPI, Inc., West Chester, PA) to ensure good electrical conductivity between the sample and the mount.

2.2. Polarization Force Measurements

2.2.1. *Principles*

When proximal to a mineral surface, an electrically biased atomic force microscope (AFM) tip experiences an attractive electrical force between the tip and the surface. The force originates from the polarization of substrate charges responding to the charge on the tip (Hu et al., 1995b). For example, when the tip is positively charged, mobile surface cations move away from the tip and anions accumulate beneath it, the combination of which results in a large attractive force. When the

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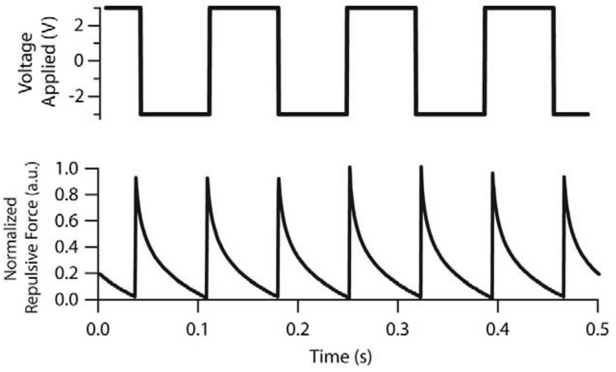

Fig. 1. (bottom) Repulsive force on tip in response to (top) the application of a square wave voltage (7 Hz, 6 V_{pp}). The repulsive force relaxes as anions (positive bias) or cations (negative bias) accumulate beneath the tip. The frequency of the force on the tip is 14 Hz, which is twice that of the driving voltage.

bias on the tip is cycled through a waveform such as a square wave, the time evolution of the polarization force can be monitored (Fig. 1 and Eqn. 2). Changes in tip polarity from positive to negative yield an instantaneous repulsive force from accumulated anions, which is followed by attractive decay resulting from the migration of anions away and cations to the tip position. From the sawtooth decays apparent in Figure 1 (i.e., "the mobile ion response"), three measurements are recorded, including the maximum repulsive force (F_{max}), the local contact potential (V_s), and the relaxation time (τ). These measurements quantify the density and the mobility of surface ions.

The maximum repulsive force F_{max} is proportional to the density of surface ions ($\Sigma\sigma_i$) for constant tip-sample separation distance. The local contact potential V_s depends on the difference between the density of cations (σ_+) vs. anions (σ_-) in the surface layer:

$$V_s = (\sigma_+ - \sigma_-)d/\varepsilon \tag{1}$$

where d is the distance between the mobile ions and the surface and ε is the electric permittivity across this distance (Luna et al., 1998). A Stern layer model can be employed to describe the separation d between the mobile ions and the surface.

The relaxation of the tip-sample separation occurs because of the movement of surface ions. The relaxation data can be fit to an exponential function:

$$F(t) = Ae^{-1/\tau} \tag{2}$$

A physical meaning of the relaxation time τ can be ascribed when a first-order approximation is made that the cantilever-tip-sample system is equivalent to an RC circuit. The cantilever/tip and the sample are treated as two plates of a capacitor, and the resistance ($R = (\sum\mu_i\sigma_i)^{-1}$) is described by the mobility (μ_i) and the density (σ_i) of the surface ions on the sample near the tip (Luna et al., 1998). It then follows that:

$$\tau = RC = \frac{1}{\sum \mu_i\sigma_i}C \tag{3}$$

The overall capacitance (C) of the system arises principally from the sample-to-ground and sample-to-cantilever components. Importantly, previous detailed calculations demonstrate the approximate invariance of both capacitances with tip-to-sample separation (Luna et al., 1998; Xu and Salmeron, 2001). We measure the sum of these two capacitances as 4 pF. In comparison, the tip-to-sample capacitance is negligible. Variability in the resistance arises from changes in the mobile ion response (e.g., because of increasing surface hydration at higher relative humidity). Therefore, high τ values indicate slow mobile ion responses (cf. Eqn. 3).

2.2.2. *Implementation*

Noncontact polarization force measurements were carried out on a Digital Instruments Nanoscope IIIa Multimode SPM with a Signal Access Module (SAM; Model SBOB-1). Specifically, a Pt-coated Si_3N_4 tip (Nanosensors, Inc.; nominal force constant of 0.19–0.40 N m^{-1}) was biased by 3 to 6 V with an AC square wave of 0.1 to 10 Hz. The AC waveform was applied to the tip by connecting the "ANA2" input port of the SAM to a function generator (Agilent Technologies Inc., Model 33120A, Palo Alto, CA). The AC signal was offset by a voltage equal to the opposite of the local contact potential between the tip and the surface. The offset provides a common baseline for the polarization force for both polarities of the AC cycle.

The mechanical deflection of the tip in response to the electrical polarization force was recorded by the photodiode in the optical head, and the voltage from the photodiode was directed from the "In0" output port of the SAM to an oscilloscope (Agilent Technologies Inc., Model 54621A, Palo Alto, CA) where it was displayed as the real-time tip deflection. The deflection data were transferred from the oscilloscope to a computer and converted to force units (Kendall and Hochella, 2003; Kendall and Lower, 2004) using a customized routine written in Igor Pro 5.0 (Wavemetrics, Inc., Lake Oswego, OR) for RS-232 communication.

2.2.3. *Protocols*

In three separate experiments, the mobile ion response was recorded for (1) calcite surfaces prepared "dry," (2) calcite surfaces prepared "wet," and (3) other carbonate mineral surfaces prepared "wet." For samples prepared "wet," the mobile ion response was first recorded at 95% RH. The RH was then decreased to 70% in increments of 5%, and the mobile ion response was recorded at each RH. For samples prepared "dry," the mobile ion response was monitored as RH was increased from 20 to 95% in increments of 5% RH. The mobile ion response required 10 to 15 min to stabilize at each RH increment. At a given RH, each measurement of the mobile ion response was an average of 100 individual traces. For all measurements, the tip was positioned over terrace regions of the surface.

2.3. Environmental Chamber

To control relative humidity, we provided a proportionated flow of water vapor and dry nitrogen to an environmental chamber housing the Nanoscope. The flows were thoroughly mixed before entering the chamber. The chamber was purged with N_2 before sample introduction, sealed with rubber *o*-rings, and maintained under continuous positive pressure throughout the experiments. A thermistor (Omega 44033, Stamford, CT; ±0.1°C accuracy) and a capacitive RH sensor (HC 610; Ohmic Instruments Co., Easton, MD; ±2% RH accuracy) were near the sample surface. RH was calibrated using saturated LiCl, KNO_3, and NaCl solutions as standards. The RH and the temperature data from the chamber were recorded using a stripchart module within the customized Igor code. Periodic comparison of the RH values from the capacitive sensor with RH values measured using an in-line chilled-mirror dewpoint hygrometer (Kahn, Wethersfield, CT) showed good agreement.

3. RESULTS AND DISCUSSION

3.1. Control Experiments

Control experiments conducted with NaCl and PTFE (Teflon) show the expected responses (Fig. 2). Specifically, the surface of NaCl should have a high density and a high mobility of surface ions, especially above 75% RH when a deliquescent aqueous layer forms. The collected data do show large changes in the polarization forces at 75% RH, which is the NaCl deliquescence point, and at 40% RH, which is the point at which infrared spectroscopy indicates monolayer surface coverage by water (Peters and Ewing, 1997; Luna et al., 1998). Increased water content and thus greater ion hydration result in