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***In-Situ* Atomic Force Microscope Imaging of Calcite Etch Pit Morphology Changes in Undersaturated and 1-Hydroxyethylidene-1,1-diphosphonic Acid Poisoned Solutions**

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Abstract

Morphology changes in etch pits formed on the (10 $\bar{1}$ 4) cleavage plane of calcite were induced by varying the ratio of [Ca²⁺] to [CO₃²⁻] in the bulk solution as well as through the addition of the crystal poison 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). Three distinct morphologies were noted: symmetric rhombic, asymmetric rhombic, and triangular with a rough curved hypotenuse. The latter represents a transient morphology which is only observed during the actual dissolution process, while the former morphologies persist after dissolution is halted.

Introduction

The growth and dissolution mechanisms of calcium minerals have important implications in many phenomena such as rock weathering, scale formation in cooling towers, and biomineralization processes. Calcium minerals account for almost 50% of all known biogenic minerals and are widely studied.¹ Still, a better understanding of the surface processes controlling these mechanisms, and how to encourage or inhibit them from occurring, is wanting.

The atomic force microscope (AFM) is a high-resolution microscope which has demonstrated its potential for studying dynamic mineralization processes *in situ*. Calcite, CaCO₃, growth and dissolution mechanisms in supersaturated and undersaturated solutions, respectively, have been elucidated on the atomic-scale using the AFM.^{2–7} AFM analysis of crystal growth in the presence of inhibitors such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP or etidronic acid) has also been reported.^{8,9} The morphology of surface features on the (10 $\bar{1}$ 4) cleavage plane of calcite is generally rhombic.^{2–4,6,8–10} Both positive surface features (terraces and hillocks) and negative surface features (pits) display this rhombic morphology. Furthermore, the orientation of all the rhombic features on the (10 $\bar{1}$ 4) cleavage plane is the same, with the short and long diagonals of the rhomboid running parallel to the [2 $\bar{2}$ 1] and [010] crystal indices, respectively as shown in Figure 1. Under dynamic conditions of growth or dissolution, this orientation of the rhomboids is preserved, indicating preferred planes for growth and dissolution which correspond to the periodic bond chains (PBC) for calcite.^{11–13} The four calcite (10 $\bar{1}$ 4) PBCs are illustrated in Figure

1A. Deviation from these preferred growth planes under varying conditions of saturation or in the presence of inhibitors does not appear to occur; however, changes in the growth and dissolution rates along nonequivalent planes do occur, which can cause the rhombic surface features to grow or dissolve asymmetrically. Figure 1 illustrates the formation of two striking features in calcite etch pits: First, the formation of the rounded corner at the intersection of the two fast steps; second, the fleeting presence of the rough [010] step during dissolution. Recently, a number of papers have been published which address the rounding of the fast-fast corner under certain reaction conditions.^{6,14,15–17} Factors influencing the asymmetry include the presence of impurities which selectively impair kink propagation^{14,15} as well as experimental effects such as flow rate which determine whether the dissolution process is controlled by diffusion through the unstirred boundary layer or by surface reaction.^{6,14} Baer *et al.* have observed the rounded fast-fast corner in nearly saturated solutions as well as in the presence of impurities and have attributed this phenomenon to the quenching of kink motion.^{14,17}

We demonstrate here that changes in the composition of the bulk solution (i.e., the $[\text{Ca}^{2+}]$: $[\text{CO}_3^{2-}]$ ratio) also lead to a rounding of the fast-fast corner in calcite [10 $\bar{1}$ 4] etch pits; furthermore, the fleeting presence of the rapidly dissolving [010] step is observed. The changes in etch pit morphology are attributed to changes in the activity of calcium ions in the bulk solution, which, in turn, alter the dissolution rates between nonequivalent steps of the etch pits. It is also shown that the inhibitor HEDP displays step-specific binding which retards etch pit expansion unequally on the different steps of the etch pit.

Experimental Section

The following solution media were used: (1) a saturated calcite solution containing 1 mM ethylenediamine tetraacetic acid (EDTA), (2) an undersaturated calcite solution (saturation ratio $S = 0.9$), and (3) an undersaturated calcite solution containing 1 μM HEDP. Saturated calcite solutions were prepared by dissolving crystals of naturally occurring calcite in double-distilled water and allowing the system to equilibrate over several days (equilibrium pH 8.5). Undersaturated calcite solutions (saturation ratio $S = 0.9$) were prepared by dilution (9:1) of a saturated calcite solution with double-distilled water. EDTA solutions (1 mM) were prepared in a saturated calcite solution, while HEDP solutions were prepared in an undersaturated calcite solution. *In-situ* crystal dissolution was recorded in the constant force mode using a Digital Instruments Nanoscope II with a polycarbonate flow cell. A triangular Park Scientific silicon nitride cantilever with a nominal stiffness of 0.37 N/m and a probe radius of curvature of about 20 nm was used as received. The normal force imparted on the calcite by this probe was typically around 50 nN for the scans shown here. Nucleation and growth of symmetric rhombic etch pits on the (10 $\bar{1}$ 4) face of a freshly cleaved, naturally occurring calcite specimen were achieved by flowing the 1 mM EDTA solution through the flow cell. The EDTA solution was replaced with the saturated calcite solution to halt dissolution. Etch pit nucleation and growth was reinitiated by introducing the undersaturated calcite solution. Retardation of etch pit growth was achieved with the 1 μM HEDP solution. All solutions were flowed at 0.05 mL/s, and AFM images were recorded every few minutes without interrupting solution flow. This flow rate corresponds to a complete exchange of the solution in the flow cell about every 2 s, favoring dissolution which is surface reaction

limited, not diffusion limited.¹⁴ The image acquisition time was 20 s/frame. All images were flattened and plane-fitted before further analysis.

The purity of the calcite specimen was determined using an HP 5950B X-ray photoelectron spectrometer (XPS).

Results

Exposing the cleaved crystal to the saturated calcite solution containing 1 mM EDTA (solution 1) produced symmetric rhombic etch pits, as shown in Figure 2A. Exchanging solution 1 for a flowing saturated calcite solution immediately halted etch pit nucleation and growth. Injecting the undersaturated calcite solution (solution 2) into the flow cell reinitiated growth of the rhombic etch pits, as seen in Figure 2B–D. After 30 min of dissolution (Figure 2D), the etch pit morphology has changed significantly from the symmetric rhombic shape seen in Figure 2A. Only one interior angle has remained unchanged at $\sim 97^\circ$ throughout this process; two angles have decreased from $\sim 85^\circ$ to $\sim 77^\circ$, while the remaining angle increased from $\sim 95^\circ$ to $\sim 114^\circ$. The nucleation of additional asymmetric and triangular etch pits also was noted under these conditions of undersaturation, as shown in Figure 3A–H. In the presence of 1 μ M HEDP (solution 3; Figure 3I–L), the general etch pit morphology reassumes that of a more symmetric rhombus; notice the interior angles marked in Figure 3K are similar ($\pm 5^\circ$) to those in Figure 2A.

XPS analysis indicates impurity levels are below 2 atomic %, as determined by the ratios of Ca:C:O 1s peaks. An XPS survey scan showed no unexpected peaks, and narrow scans show no Mg or P impurities.

Discussion

The dependence of the etch pit dissolution mechanism, and hence morphology, on the activity of calcium ions in the bulk solution is demonstrated in Figure 2. Exchanging solution 1 with solution 2 increases the bulk $[\text{Ca}^{2+}]$ concentration, which results in a transition from symmetric to asymmetric etch pit morphology. This transition is attributed to differences in the ratio of $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ in the bulk solution. Paquette and Reeder have demonstrated that increasing the $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ ratio enhances the asymmetry of rhombic growth hillocks.^{18,19} Exchanging solution 1 with 2 increases the $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ ratio in the bulk solution by about 5%, assuming that the calcite solution is in equilibrium with atmospheric CO_2 . The pH of 8.5 measured for the saturated calcite solution is close to the calculated pH value of 8.4 for a calcite solution in equilibrium with CO_2 at ambient conditions of 1 atmosphere and 25 $^\circ\text{C}$.²⁰

In Figure 3 it is seen that etch pits formed in the undersaturated solution can be very asymmetric, appearing as distorted rhomboids or triangles with rough, convex hypotenuses. Once the flow of undersaturated solution was stopped, only the asymmetric rhombic morphology was retained. This suggests that the triangular and very irregular-shaped etch pits are rapidly changing, very transient morphologies, while the asymmetric and symmetric rhombic etch pit morphologies are able to persist for much longer times (several days) once dissolution is halted. The roughness and orientation of the fleeting edge (Figure 3A–F)

suggest that this is the highly kinked [010] step predicted by the PBC theory for calcite.¹³ PBC theory predicts that straight-chain PBCs exist parallel to the $[441]$ and $[481]$ directions while relatively rougher PBCs exist parallel to the $[221]$ and $[010]$ directions due to an increased kink density along these latter two directions. These predictions are borne out in the results presented here.

PBC theory, however, fails to explain the rounded corner which persists after dissolution is halted (Figure 2D). Ives postulates the existence of a stable kink configuration at maximum kink density for rock-salt type crystal.²¹ For such a configuration to be stable, the kink motion must be greatly retarded. Liang *et al.* demonstrate that this can be accomplished through the addition of impurities which bind preferentially to kinks moving toward the intersection of the two fast steps.¹⁴ It is unlikely that impurities, present at less than 2 atomic % in the calcite sample used here, contribute significantly to kink retardation. The rounding effect observed in response to the increased calcium concentration in solution may result from a near-equilibrium situation in which bulk calcium ions readsorb to favorable kink sites, selectively retarding kink propagation. Paquette and Reeder demonstrate a nonequivalence of kink sites in calcite by bond coordination and steric arguments.¹⁹ Similarly, Liang *et al.* predict an activation energy difference of 22 meV for the nucleation of double kinks on the slow versus fast steps.¹⁴ Thus, the rounded fast-fast corner observed in solutions near saturation may be a kinetic effect, most readily observed when the dissolution kinetics are slow. These step-specific kinetics explain why the rounding phenomenon is observed in only one corner of the etch pit. A return to a less rounded corner morphology occurs in the presence of HEDP as discussed below.

The crystal poison, HEDP, was used at a concentration which is considered a “threshold” limit for inhibition.⁹ While dissolution was not totally inhibited, the effects of the poison are visible. As seen in Figure 3H–L, the dissolution mechanism and/or rate has changed in the presence of HEDP; the etch pit morphology is approaching that of a symmetric rhomboid. HEDP appears to be less effective at retarding dissolution from the rounded steps. This apparent reduced HEDP affinity for the rounded steps may arise from an increased kink density and/or bond character along these steps. At the concentration used here, HEDP also appears unable to inhibit the nucleation of new etch pits: Figure 3I–L demonstrates the nucleation of several etch pits in an undersaturated solution containing HEDP. Notice that these etch pits (excluding the pits which have coalesced) all have a more symmetric rhombic morphology as compared to the etch pits nucleated solely in an undersaturated solution (Figure 3A–H).

The morphology changes presented here demonstrate that the lateral expansion rate of the etch pit steps depends on the ratio of $[Ca^{2+}]$ to $[CO_3^{2-}]$ in the bulk solution and the presence of the crystal poison HEDP. These morphologies appeared to be independent of experimental factors such as sample rotation, scan rate, or scan direction. However, Park *et al.* have recently demonstrated that probe-sample contact forces lead to strain-enhanced nucleation of double kinks on calcite steps as manifested by dissolution rates which increase exponentially with contact force.^{15,16} Furthermore, they show that fast steps are much more susceptible to scanning-enhanced dissolution than slow steps, but only at higher contact force.¹⁶ While the 50 nN contact forces used here may enhance dissolution somewhat, it is

unlikely that this is the sole cause of the morphologies reported here. The raster scanning technique used in AFM can also lead to distortion of dynamic features (such as dissolving etch pits) due to the temporal nature of AFM data acquisition. A correction for the temporal nature of AFM image acquisition is given by Hillner *et al.*⁴ but was not used in the data presented here.

Conclusion

AFM imaging of transient pit morphologies offers a unique method for studying the effects of crystal growth and dissolution modifiers. We have demonstrated a transition from symmetric to asymmetric rhombic pit morphology through an increase in the ratio of $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ in the bulk solution; furthermore, a reverse transition has been demonstrated through the addition of HEDP. Thus, two pathways leading to a symmetric rhombic morphology have been shown to exist. Changes in etch pit morphology during dissolution in EDTA and undersaturated solutions are attributed to differences in the ratio of $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ in the bulk solution. These morphology changes are a manifestation of the non-equivalence in kink nucleation and/or mobility on the various steps. The morphology changes in the presence of the crystal poison HEDP may result from the selective inhibition of nonequivalent steps on the (10 $\bar{1}$ 4) cleavage plane. A decreased HEDP affinity for the transient, curved edges over the straight edges of the etch pits is apparent. In all, three different etch pit morphologies were observed: a symmetric rhombic pit, an asymmetric rhombic pit with a rounded corner, and a rough, triangular-shaped pit. The triangular pits were transient, present only during dissolution; once dissolution was halted, these pits assumed an asymmetric rhombic morphology. In undersaturated solutions asymmetric rhombic pits were formed from existing symmetric rhombic pits and were also nucleated *de novo*. Symmetric rhombic etch pits were only formed using EDTA solutions and never with undersaturated solutions, presumably due to the differences in the $[\text{Ca}^{2+}]$ to $[\text{CO}_3^{2-}]$ ratio.

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Figure 1.

Calcite etch pit morphology changes in response to the depicted changes in bulk solution composition. (A) Symmetric rhombic etch pit nucleated in a saturated calcite solution containing 1 mM EDTA. (B) Asymmetric etch pit expansion in an undersaturated calcite solution. (C) Continued expansion of etch pits in an undersaturated solution. The transient triangular morphology is superimposed on the asymmetric rhombus. (D) Return to a symmetric rhombic morphology through addition of 1 μ M HEDP, which preferentially retards the straight steps over the curved steps.

Figure 2.

Changes in calcite etch pit morphology during dissolution in an undersaturated ($S=0.9$) calcite solution. Step heights = 0.4 nm. Numbers correspond to etch pit interior angles. (A) $t = 0$; eccentric rhombic etch pits formed in a 1 mM EDTA solution, imaged in a saturated calcite solution. (B) $t = 6$ min after introducing a flowing (0.05 mL/s) undersaturated ($S = 0.9$) calcite solution; the uppermost interior angle is becoming rounded. (C) $t = 12$ min. The most superficial etch pit is demonstrating enhanced expansion toward the right of the image as evidenced by the partially dissolved step. (D) $t = 30$ min. Only the deepest etch pit is still “intact”; the upper three etch pits have expanded beyond the scanned area of the crystal,

except at the rounded (114°) interior angle, where the steps have piled up. All images are $3 \times 3 \mu\text{m}$.

Figure 3.

(A–H) Nucleation and growth of asymmetric and triangular etch pits in flowing (0.05 mL/s) undersaturated ($S = 0.9$) solution. (A) $t = 0$ min. (B) $t = 2.5$ min. A pit has just nucleated above the existing triangular etch pit. (C) $t = 3.0$ min. (D) $t = 4.5$ min. Another nucleating pit. (E) $t = 6.5$ min. (F) $t = 9$ min. F is an expanded view of E; the three etch pits seen in E are labeled i, ii, and iii, in F. (G) $t = 12$ min. Pits i and ii have coalesced. (H–L) Dissolution in an undersaturated solution ($S = 0.9$) containing 1 μM HEDP. (H) $t = 0$. H is a zoomed view of the two leftmost etch pits seen in G. (I) $t = 1$ min. The two etch pits have coalesced, and two etch pits have nucleated within. (J) $t = 10.5$ min. (K) $t = 14$ min. (L) $t = 30$ min. Dissolution in the presence of HEDP has led to a more symmetric rhombic etch pit morphology in contrast to the rounded triangle and asymmetric rhombic morphologies seen in A–H. All images are $4 \times 4 \mu\text{m}$ except for F and G which are $8 \times 8 \mu\text{m}$.