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# The Effect of Hydrochloric Acid Strength on the Nanometer-Scale Dissolution Topography of Calcite Crystal Surfaces

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Jennifer Fruzzetti graduated from BSU in May 2012 with a Bachelor of Science degree in

Earth Sciences and a concentration in Environmental Geosciences. This research was conducted during the spring 2012 semester with her advisor Dr. Stephen E. Kaczmarek and was funded by the ATP Semester Grant Program. Her research was presented at the spring 2012 Undergraduate Research Symposium. Jennifer currently works as a geologist for an environmental engineering and consulting firm and is thankful for the opportunities provided to her through the Office of Undergraduate Research and her mentorship under Dr. Kaczmarek.

**T***he physico-chemical mechanisms by which rock-forming minerals dissolve in natural fluids are controlled by a number of environmental factors. In this study, we investigate dissolution mechanisms by observing how the nanometer-scale surface topography of calcite is affected by the acidity of etching solutions. Here we report atomic force microscope (AFM) observations of calcite crystal surfaces both before and after chemical etching for 10 seconds in 0.01%, 0.1%, and 1.0% HCl solutions. AFM observations show that unetched, freshly-cleaved calcite {10 $\bar{1}$ 4} crystal surfaces are characterized by flat layers separated by steps oriented parallel to calcite cleavage planes. Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 0.01% HCl are characterized by relatively flat surfaces with deep, well-defined V-shaped (pointed bottom) etch pits. Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 0.1% HCl are characterized by more irregular surfaces, with poorly-defined flat-bottom etch pits. Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 1.0% HCl are characterized by a highly irregular surfaces with a high density of poorly-defined, round-bottom etch pits. The findings from this study are consistent with previously published observations that indicate fluid acidity strongly controls the resultant surface topography of etched calcite. Agreement between the nanometer-scale observations made here and those from previous studies provides greater confidence that the new AFM on the campus of Bridgewater State University is fully calibrated and can accurately resolve nanometer-scale topographic features on the surfaces of natural materials.*

When exposed to Earth surface processes, minerals undergo chemical weathering, the physico-chemical process by which solid mineral material is removed (dissolved) from the solid mineral and transferred to an aqueous solution. Understanding the exact mechanisms by which dissolution occurs at the mineral-fluid interface is critical to calibrating both bulk laboratory dissolution rates and continental weathering rates as calculated using numerical models (MacInnis and Brantley, 1993). Previous studies investigating dissolution mechanisms in a wide variety of minerals have utilized atomic force microscopy (AFM) to characterize the nanometer-scale topography of dissolved crystal surfaces (Hochella et al., 1991; Teng 2004; Kaczmarek and Sibley, 2007).

Calcite, CaCO<sub>3</sub>, is one of the most abundant, and geologically important, rock-forming minerals on Earth. Because the dissolution topography of calcite crystal surfaces has been extensively characterized (Hillner et al, 1992;

MacInnis & Brantley, 1992; Rachlin et al, 1992; and Teng, 2004), the present study attempts to use observations from previous studies to calibrate Bridgewater State University's new AFM. The objective of this study is to replicate previous observations of calcite dissolution in solutions with variable acidities in order to confirm that the new AFM is capable of accurately recording nanometer-scale dissolution topography on calcite crystal surfaces. Calibrating the new AFM with previously acquired observations will minimize erroneous interpretation of artifacts and will provide greater confidence in observations of mineral surfaces where previously published studies do not exist.

### Methods

Three experiments were conducted to evaluate the effect of acid strength on calcite surface topography and to evaluate the accuracy of Bridgewater State University's new atomic force microscope (AFM). Three pieces of calcite (approximately 1 mm x 1 mm x 0.3 mm each) were obtained by cleaving a single large crystal of Iceland spar calcite (Wards Scientific) with a rock hammer. Freshly cleaved samples were briefly rinsed in distilled water to remove any particulate matter that may have adhered to the crystal surfaces. All AFM observations were performed on the {10 $\bar{1}$ 4} crystal surface using an atomic force microscope (Nanosurf easyScan2) using a sicona tip with a tip radius of approximately 20 nm.

Three different chemical etching solutions were prepared by diluting laboratory-grade hydrochloric acid (HCl) with distilled/deionized water; 0.01%, 0.1% and 1% (by volume). Calcite sample #1 was completely submerged in 15 ml of 0.01% diluted HCl for ten seconds. After ten seconds the sample was removed from the etching solution and rinsed with distilled water to halt the etching process. Calcite samples #2 and #3 were submerged for ten seconds in 15 ml 0.1% and 1.0% diluted HCl, respectively, and rinsed with distilled water. Etching times were chosen to best accentuate surface features and are based on previous experimental work with the mineral dolomite (Kaczmarek and Sibley 2007). All samples were dried, mounted face-up on metal AFM imaging disks and stored in a vacuum desiccator.

AFM images of calcite crystal surfaces were acquired using constant force mode. AFM images represent shaded relief (topography) maps of the crystal surface. Dark areas represent lower areas on the crystal surface while light areas are characteristic of higher elevations. Three different surface scan dimensions were acquired: 100 x 100  $\mu\text{m}$ , 50 x 50  $\mu\text{m}$ , and 16.6 x 16.6  $\mu\text{m}$ . Crystal surfaces were scanned at a rate of approximately 0.2 seconds per line with 512 sampling points per line and 0° rotation. The x- and y-slopes were set to 0° with an over scan of

5%. Z-Controller parameters, which control the force between the cantilever tip and the sample surface, were set to 25 nano-Newtons (nN) with a P-gain of 10,000 and an I-gain of 1,000. Tip voltage was set to -0.5 volts.

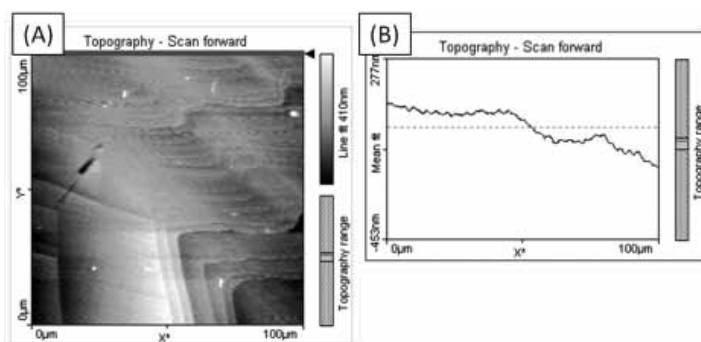
### Results

Unetched {10 $\bar{1}$ 4} calcite crystal surfaces are characterized by broad, flat layers with parallel steps that are approximately 25  $\mu\text{m}$  to 50  $\mu\text{m}$  high (Figure 1a). No pits were observed on the surface of the unetched calcite crystal. The cross-section of the crystal in Figure 1b shows relatively flat surfaces separated by steps.

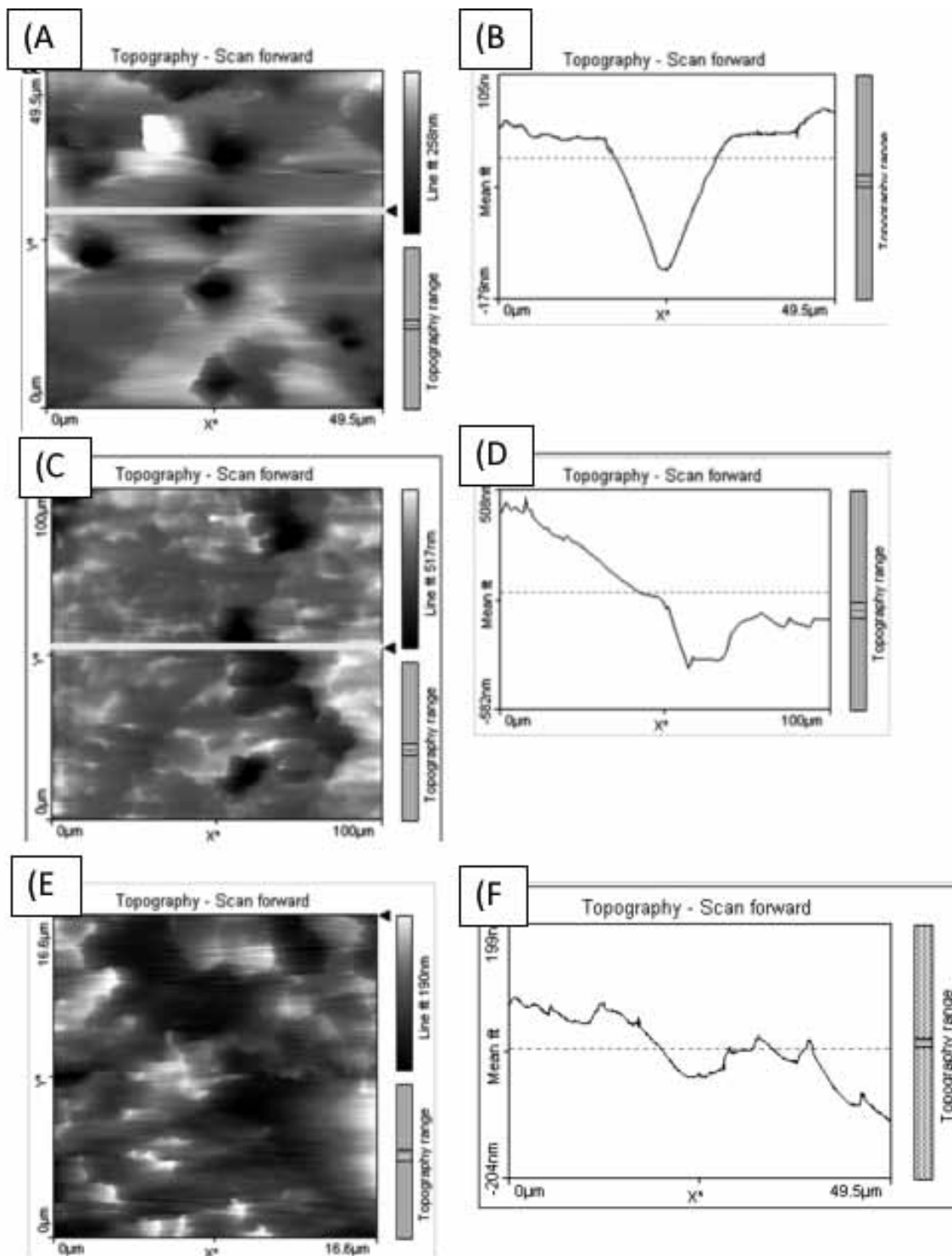
Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 0.01% HCl are characterized by relatively flat layers intersected by deep, V-bottom etch pits (Figure 2a). Etch pits are rhombic in shape and measure 7  $\mu\text{m}$  long by 7  $\mu\text{m}$  wide by 130  $\mu\text{m}$  deep. The cross section shown in Figure 2b shows a deep, V-shaped etch pit surrounded by a relatively flat surface.

Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 0.1% HCl are characterized by wider and deeper, but poorly-defined etch pits on a highly irregular inter-pit surface (Figure 2c). These etch pits measure approximately 16  $\mu\text{m}$  long by 20  $\mu\text{m}$  wide by 250  $\mu\text{m}$  deep. The cross section in Figure 2d shows pits have flatter bottoms, and lack the well-defined V-shape of Figure 2b.

Calcite {10 $\bar{1}$ 4} crystal surfaces etched in 1.0% HCl are characterized by a highly irregular topography with irregularly shaped, coalescing etch pits with poorly defined outlines. The etch pits measure approximately 25  $\mu\text{m}$  long by 20  $\mu\text{m}$  wide by 100  $\mu\text{m}$  deep. The cross section in Figure 2f shows a very shallow, bowl-shaped pit surrounded by a very irregular and jagged surface.



**Figure 1. Unetched calcite {10 $\bar{1}$ 4} crystal surface.** (A) Crystal surface is relatively flat and displays the intersection of two cleavage planes. The large, elongated black object in the center-left of the image is most likely from a piece of dust encountered by the AFM tip. (B) Cross section of horizontal line at the top of Figure 1a. Crystal topography is characterized by flat layers separated by steps.



**Figure 2. AFM observations of etched calcite {10ī4} crystal surfaces.** (A) Calcite {10ī4} crystal surfaces etched in 0.01% HCl showing well-defined rhombic etch pits on a relatively flat surface (B) Cross-section of horizontal line at the top of Figure 2a showing deep V-shaped etch pit with flat surrounding surface. (C) Calcite {10ī4} crystal surfaces etched in 0.1% HCl characterized by a more irregular surface and less defined etch pit shape. (D) Cross-section of horizontal line at the center of Figure 2c showing a bowl-shape etch pit. (E) Calcite {10ī4} crystal surfaces etched in 1% HCl showing several etch pits that are coalescing together. Pits are poorly defined and the surrounding surface is choppy and irregular. (F) Cross-section of line at the top of Figure 2E showing a highly irregular and choppy surface with round-bottom etch pit.

## Discussion

Calcite crystal surfaces etched in the lowest acid concentration are characterized by flat surfaces with well-defined, deep, V-shaped etch pits, whereas crystal surfaces etched in highly concentrated acid are characterized by a highly irregular surfaces with poorly-defined etch pits. In this respect, the results of the present study are consistent with previously published observations of etched calcite crystal surfaces (Hillner et al., 1992; MacInnis and Brantley, 1992; Teng 2004).

Hillner et al. (1992) showed that in mildly acidic fluids, when etched in solutions that are only slightly undersaturated with respect to calcite, crystal surfaces are characterized by deep, V-shaped etch pits. Hillner et al. (1992) observed that deep, V-shaped etch pits formed most readily where line defects intersected the crystal surface, and that with prolonged exposure to etching solutions, etch pits continue to grow in length, width and depth. Teng (2004) also showed that at higher acid concentrations, etch pits were absent from crystal surfaces. He interpreted this observation to be the result of the stronger acid attacking all areas of the crystal indiscriminately such that both vertical dissolution along crystal defects and lateral dissolution in inter-defect areas occurred at similar rates. Teng (2004) showed that with decreasing acid concentrations, calcite crystal surfaces were characterized by flat layers with V-shaped etch pits. He interpreted etch pit formation as faster dissolution at the defect compared to dissolution at defect-free areas.

The observation that linear defects are the site of preferred dissolution at low acid concentrations is not unique to calcite. Kaczmarek and Sibley (2007) used AFM to demonstrate that dislocations form preferentially at the intersection of linear defects and dolomite crystal surfaces when etched in dilute sulfuric acid. Aragonite etching experiments conducted by Kaczmarek (2005) also support a model of etch pit formation at low acid concentrations.

Observations from calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 0.01% HCl are consistent with previous studies. Etch pits are interpreted to form along linear crystalline defects, perpendicular to the crystal surface, where the surrounding topography remains relatively flat and unaffected by the acid. The pits formed in 0.01% HCl were small in size, but deep and V-shaped compared to the pits formed in higher HCl concentrations. This suggests that the acid targeted specific dislocations in the crystal and that the acid preferentially attacked these areas instead of dissolving the entire crystal surface at the same rate.

Calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 0.1% HCl have very deep, flat-bottom pits with an irregular surrounding surface. This is interpreted to represent a scenario where the acid targeted weak spots in the crystal (e.g., linear defects), but because the concentration of the acid was higher, the surrounding crystal surface area was also subjected to the acid's dissolving effects. Etch pit dimensions are also larger, which suggests that the acid attacked the crystal faster laterally than it did in the 0.01% diluted HCl sample.

It was much more difficult to distinguish between etch pits and the irregular surface layers in the calcite sample etched in 1% HCl. The pits were much shallower in these images. Therefore, the acid must have dissolved laterally as well as vertically, not giving pits as much time to develop before spreading to the surrounding surface. Also, observations indicate that etch pits coalesced by growing into one another laterally. Calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 1% HCl yield calcite surface that have low topographic relief but when comparing the extremely irregular area surrounding the pits to the flat, even surfaces of the calcite etched in 0.01% HCl, it is obvious that the acid has greatly affected most areas of the crystal surface.

## Conclusions

Dissolution topography of calcite crystal surfaces suggests that the acidity of a fluid dramatically affects mechanism by which calcite dissolves. Unetched calcite  $\{10\bar{1}4\}$  crystal surfaces are characterized by broad, flat surfaces with parallel steps and no etch pits. Calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 0.01% diluted HCl, are characterized by flat layers with deep, V-shaped etch pits that are interpreted to form at line defects. Calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 0.1% HCl are characterized by more irregular surfaces with flatter bottom, less well-defined etch pits. Calcite  $\{10\bar{1}4\}$  crystal surfaces etched in 1.0% diluted HCl are characterized by a very irregular surfaces with shallow, poorly-defined pits that were concave bottoms.

The results presented here are consistent with previous studies. This suggests that BSU's new AFM is capable of accurately characterizing nanometer-scale surface topography of natural mineral samples. These findings give greater confidence to future researchers who want to utilize the AFM to characterize mineral surfaces that have not been previously characterized.

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