Topographic Analysis of Calcite (104) Cleavage Surface Dissolution in Ethanol–Water Solutions

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Abstract: The interaction of organic molecules with calcite surfaces plays a key role in many geochemical, industrial, and biomineralization processes, and exploring the influences of organic molecules on calcite reactions is crucial for a fundamental understanding of the reaction mechanisms. Here, we used digital hologram microscopy to explore the in situ evolution of the calcite (104) surfaces when dissolved in ethanol–water solutions, and total organic carbon analysis was applied to confirm the adsorption of ethanol by calcite. The results showed that the bulk dissolution rate of calcite decreases as the volume fraction of ethanol increases, and the topographic features of etch pits were also altered by the presence of ethanol. When exposed to too much ethanol, the etch pits’ growth was inhibited and their shapes tended to change from rhombuses in ultrapure water to triangles. Our results provide insights into the interaction between adsorbed ethanol and evolving calcite crystal, which highlights the dissolution regulation of calcite by organic molecules that could benefit a broad range of fields.

Keywords: calcite; dissolution; ethanol; etch pit; adsorption

1. Introduction

Calcite is ubiquitous in natural systems and presents as an important carbon reservoir, greatly contributing to the global carbon cycle due to its dissolution and growth [1,2]. Most modern calcite is precipitated by calcifying organisms through the biomineralization process [3], where organic molecules play a significant role in modifying calcite reactivity, thus regulating its surface reactions [4]. Depending on the surrounding environment, calcite is often out of equilibrium and reacts rapidly, resulting in different surface morphologies and properties. A better understanding of the regulation of organic molecules on calcite surface reactions, including dissolution and growth, would help to unravel the mechanisms of biomineralization and benefit a broad range of fields, such as biomimetic material design [5], nanoengineering [6] and environmental sustainability [7].

In recent decades, how organic molecules interact with calcite surfaces has attracted much attention, and organic molecules have been confirmed to affect the growth and dissolution processes of calcite [8,9]. Based on the surface chemistry and crystal structure of calcite, organic molecules are likely to adsorb on calcite surfaces through processes including electrostatic accumulation, structural correspondence, and stereochemical requirements [10]. The adsorption affinities of organic molecules largely originate from their functional groups [11]. For example, the –OH and –COOH functional groups in molecules like sugars [12], alcohols [13,14], and carboxylic acids [15] could adsorb tightly on calcite surfaces, while molecules with –NH2 functional groups [16] often have a much weaker adsorption affinity. Substantial efforts have been expended to investigate the organic compounds’ influence on calcite growth in particular [8,9,17,18], but there is a significant lack of understanding of organic molecules’ controlling mechanisms during calcite dissolution. Although a few studies have investigated how several types of organic molecules...
affect the calcite dissolution process, the inherent complexity of macromolecules and the complicated calcite surface geometry often result in conflicting findings [8,15,19–21]. Therefore, there is a huge demand to isolate and determine single functional group impacts on calcite dissolution.

As one simple organic chain molecule, ethanol with a –CH$_3$ group on one end and a –OH group on the other end is suitable to serve as a model organic molecule to investigate the interaction between calcite and molecules with simple functional groups. In the last decade, the spatial configuration of ethanol on calcite surfaces has been confirmed by both computational simulations and experimental results [22–26]. Specifically, ethanol tends to form a highly ordered monolayer on calcite surfaces rapidly as a barrier for solute motion. Although some studies have found that ethanol is able to inhibit calcite dissolution [21,27], there is still a lack of accurate and quantitative data regarding calcite dissolution rate, especially in circumstances that are far from equilibrium.

The aim of this work is to measure calcite dissolution rates in ethanol–water solutions and monitor the evolution of calcite’s surface morphology using digital hologram microscopy (DHM). DHM allows for in situ nanoscale observations of calcite surface evolution and has been successfully applied in dissolution research concerning other minerals [28,29]. This paper monitors the dissolution behaviors of calcite at (104) cleavage surfaces submerged in flowing ethanol–water solutions, and the results show that ethanol inhibited calcite dissolution and altered the topographic features of the etch pits. Additionally, the adsorption of ethanol by calcite was determined by the total organic carbon (TOC) analysis. Significantly, our results suggest that ethanol adsorption has a stronger inhibiting effect on calcite dissolution than lowering the water activity alone.

2. Materials and Methods

Clear, optically transparent, and pure Iceland spar crystals originating from China were cleaved with a razor blade along the (104) plane, confirmed by the X-ray diffraction patterns (Figure 1a). Immediately after cleaving, a portion of the crystal surface was sputter coated with a layer of approximately 20 nm of platinum (Q150T, Quorum Technologies, East Sussex, United Kingdom) to form a mask, serving as an inert reference plane for the dissolution experiments. The dissolution of crystals in flowing ultrapure water and ethanol–water solutions, at a flowing rate of 34 mL·min$^{-1}$, was monitored by the DHM (Model R-2203, Lyncée Tec, Lausanne, Switzerland), and the experimental details are similar to those described previously [28–30]. Simply, DHM tracked the holograms and phase images of calcite surfaces that were submerged in solutions every 1 min, and 3D height maps were produced by the numerical reconstruction of phase data. The average computed surface height change between exposed surface and the reference plane ($\Delta h$) at a time interval ($\Delta t$) can yield a retreat velocity, and then the dissolution rate can be obtained through dividing the velocity by the molar volume ($V_{mol}$) of calcite, $3.693 \times 10^{-5}$ m$^3$·mol$^{-1}$, and is in the unit of moles per unit area per unit time:

$$r = \frac{\Delta h}{\Delta t} \times \frac{1}{V_{mol}}, \quad (1)$$

Ethanol–water solutions with ethanol volume fractions of 10%, 20%, and 50% were prepared in this study, and their water activities ($\alpha_H$) were calculated as 0.9667, 0.9404, and 0.8570, respectively, using the nonrandom two-liquid (NRTL) model [31]. All DHM experiments were conducted at a temperature of 23 ± 1 °C, and at least three replicate experiments were performed at each solution. Specifically, crystals intended for the dissolution rate measurements were imaged by the DHM equipped with a 20× immersion objective lens, which is able to monitor a regional surface of approximately 194 µm × 194 µm with a lateral resolution of 299 nm, while crystals intended for the investigation of the ethanol effect on the etch pits’ growth were first stored in a 20% ethanol–water solution for 12 h and then were exposed to flowing solutions and imaged by the DHM equipped
with a $40 \times$ immersion objective lens for higher resolution imaging, whose field of view is approximately $97 \mu m \times 97 \mu m$ with a lateral resolution of 150 nm.

![Figure 1. X-ray diffraction pattern of (a) cleaved calcite and (b) crushed calcite powders.](image)

TOC analysis was used to determine the adsorption of ethanol on the calcite powders. Polycrystalline calcite powders, confirmed by X-ray diffraction patterns (Figure 1b), were obtained by crushing single crystals and were passed through sieves smaller than $50 \mu m$ (fine powder) and $75 \mu m$ (coarse powder). The coarse and fine powders have median particle sizes ($D_{50}$, $\mu m$) of $28.60 \mu m$ and $11.27 \mu m$, respectively, and their specific surface areas were analyzed by the Blaine method ($150 m^2/Kg$ for the coarse powder and $241 m^2/Kg$ for the fine powder). Calcite powders were firstly added into a 50% ethanol–water solution at a liquid to solid mass ratio of 1:1, and the suspensions were stored in sealed tubes to prevent $CO_2$ adsorption and liquid evaporation. The suspensions were stirred strongly by a vortex mixer for 4 h, and then the solids were quickly filtrated, and the amount of ethanol in the remaining liquid was measured by a TOC analyzer (MultiN/C 3100, Analytik Jena, Jena, Germany) as soon as possible. The adsorption of ethanol by calcite powders was expressed as dividing the difference of total organic carbon between the pure ethanol liquid and the filtrated liquid by the total organic carbon in the pure ethanol liquid.

3. Results

3.1. Bulk Dissolution Rate

Bulk dissolution rates for crystals dissolving in flowing solutions were computed from the measurements of their average surface height changes according to Equation (1). Figure 2a shows the measured rates as a function of water activity, exhibiting that water activity has a negative effect on calcite dissolution. Under an ultrapure water environment ($\alpha_H = 1$), the average dissolution rate of calcite at the (104) surface is estimated to be $0.501 \pm 0.116 \mu mol-m^{-2} s^{-1}$. As the water activity reduced from 0.9667 to 0.8570, the dissolution rates of calcite decreased from $0.217 \pm 0.025 \mu mol-m^{-2} s^{-1}$ to $0.043 \pm 0.052 \mu mol-m^{-2} s^{-1}$. Figure 2b shows the dissolution rate distribution spectrum of calcite in a 50% ethanol solution by frequently recording the dissolution rates of $3 \mu m \times 3 \mu m$ regions among an area that is not smaller than $50 \mu m \times 50 \mu m$, and it can be seen that a small tail with negative dissolution rates exists, which refers to the growth. Normally, it is rare for calcite to grow in undersaturated environments, and the reason for calcite to possibly grow at a 50% ethanol–water solution ($\alpha_H = 0.8570$) could be attributed to the transient thermal expansion during the initial dissolution process [30].
Normally, local dissolution rates strongly depend on the types and densities of reactive sites on the calcite surfaces. Thus, a statistical sampling of dissolution rates over randomly selected regions would provide a deeper understanding of the ethanol effect on calcite dissolution [32–34]. Figure 3 shows the frequency distributions of dissolution rates of crystals with initially smooth, flat surfaces at different conditions. The peak rate values are in the range of 0.1 \( \mu \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) to 0.5 \( \mu \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), and the values shift left with the reduction of water activity.

The inhibition of calcite dissolution by ethanol is accompanied by the changes in the topographic features, i.e., the shapes and densities of the etch pits. Figure 4 shows a series of topographies of calcite when dissolving in ultrapure water and ethanol–water solutions. The initial topography of freshly cleaved calcite surface (Figure 4a) consists of a smooth surface with some minor, nanoscale undulations, which can serve as a base for comparing the surface evolutions under different conditions. When dissolving in ultrapure water, where water activity is the highest, for 5 min (Figure 4b), several etch pits had merged and had well-defined openings in the shape of a rhombohedron, which is consistent with the morphology that was observed in the previous study [35]. With the dissolution time extended to 20 min (Figure 4c), these pits became much deeper and wider. Obviously, the surfaces presented differently when ethanol was present. After dissolving in a 10% ethanol–water solution for 20 min, fewer and smaller etch pits were observed, and the shapes of pits were slightly changed, as shown in Figure 4d. Figure 4e shows that in a solution with an even lower water activity, the DHM image offered no clear evidence for etch pit development, which indicates that the surface energy may be too low to keep the
etch pits active [36]. We also characterized the etch pits that formed after immersing calcite crystals in a 20% ethanol–water solution for 12 h (Figure 4f). The shapes of pits changed significantly and were characterized as shallow, triangular shapes. Similar morphologies for etch pits formed on calcite surfaces have been observed when exposed to organic molecules [37].

![Figure 4](image)

**Figure 4.** Digital hologram microscopy (DHM) images of the topography of crystals in solutions for different times. (a–c) Dissolving in flowing, ultrapure water for 0, 5, and 20 min; (d) dissolving in a flowing 10% ethanol–water solution for 20 min; (e) dissolving in a flowing 50% ethanol–water solution for 20 min; (f) dissolving in a static 20% ethanol–water solution for 12 h. The size of each picture is 35 µm × 35 µm.

3.2. Etch Pits Growth after Pre-Immersion in 20% Ethanol–Water Solution for 12 h

Etch pit development is a fundamental step and contributes significantly in the dissolution of calcite. Higher-resolution imaging was also applied to monitor the evolution of etch pits on calcite after pre-immersion in a 20% ethanol–water solution for 12 h. Figure 5 provides a closer view of the etch pit growing on pre-dissolved crystals with time. Though all beginning with etch pits with triangular shapes (Figure 4f), the topographies of crystals differed greatly after re-dissolving in solutions for 1 h. Etch pits with triangular and rhombohedral shapes were observed when crystals were dissolved in ultrapure water, while in ethanol–water solutions, etch pits still had triangular shapes but had a larger depth after 1 h of dissolution.

![Figure 5](image)

**Figure 5.** DHM images of the topography of pre-dissolved crystals dissolving in different solutions for 1 h. (a) Dissolving in flowing ultrapure water; (b) dissolving in a flowing 10% ethanol–water solution; (c) dissolving in a flowing 20% ethanol–water solution. The size of each picture is 35 µm × 35 µm.
The time dependence of a deepening and spreading of etch pits was investigated in this work. For crystals dissolving in ultrapure water, the newly formed rhombohedral etch pits were of great interest. Based on the angles between the intersecting walls, the etch pit formed was bounded by the $[441]_+$ and $[48\bar{1}]_+$ directions, consistent to the observation in previous studies [37]. The time dependence of a deepening and spreading of etch pits is shown in Figure 6, which clearly shows the dimensional information for the pits. Figure 6a displays the sequence of crystal surfaces evolving with time, exhibiting the merging and coalescence of etch pits. By drawing 1D profiles of the edge of the central etch pit along the $[441]_+$ direction (Figure 6b), its depth increased by about 40 nm over the first 12 min but changed slightly over the next 20 min, consistent with the argument of Arvidson et al. [38] that fast dissolution rates at etch pits can only persist for a short time. A similar phenomenon was observed at the edge along the $[48\bar{1}]_+$ direction, but the deepening rate was slower. During the whole dissolution measurement, the profile changes also provided clear evidence for etch pit formation and coalescence.

Figure 6. (a) Magnified view of the development of the etch pit of calcite that dissolved in ultrapure water for different times; (b) etch pit edge cross section (arrow line) profile along the $[441]_+$ direction; (c) etch pit edge cross section (arrow line) profile along the $[48\bar{1}]_+$ direction.

Figure 7 shows the time dependence of a deepening and spreading of an existing etch pit in a 10% ethanol–water solution. Different from crystals in ultrapure water, no obvious changes of the topography of calcite surfaces were observed during the 30 min dissolution, and the profile of etch pit edges along the $[441]_+$ and $[48\bar{1}]_+$ directions remained almost the same, as shown in Figure 7b,c. Comparing to the inhibition of etch pit spreading by inorganic compounds for carbonate minerals [39], the inhibition effect of ethanol seems to be much stronger, resulting in no obvious pit spreading. Similar results were obtained for crystals dissolving in a 20% ethanol–water solution for a time as long as 44 min (Figure 8).
Figure 7. (a) Magnified view of the development of the etch pit of calcite that dissolved in a 10% ethanol–water solution for different times; (b) etch pit edge cross section (arrow line) profile along the [441] direction; (c) etch pit edge cross section (arrow line) profile along the [481] direction.

Figure 8. Magnified view of the development of the etch pit of calcite that dissolved in a 20% ethanol–water solution for different times.

3.3. Adsorption of Ethanol by Calcite Powders

The adsorption of ethanol by calcite with different fineness was checked by the TOC experiments, and the results confirmed the ethanol adsorption phenomenon by calcite.
After immersing and stirring powders in ethanol liquid for 4 h, about 10% ethanol was adsorbed by fine powders with a size smaller than 50 µm, while only less than 2% ethanol could be adsorbed by powders with a size slightly larger than the fine powders, as shown in Figure 9, indicating the adsorption of ethanol to calcite surfaces; this adsorption becomes stronger with the increase of surface area or defect densities [40].

![Figure 9. Carbon adsorption on powder calcite with different fineness.](image)

4. Discussion

During the dissolution process of calcite, the interfacial structure is of fundamental importance in determining the dissolution behaviors and providing a molecular level of understanding for dissolution mechanisms. The current DHM experiments focus on the evolution of interfaces and exhibit an influence of ethanol on calcite dissolution behaviors. With the increased ethanol volume fraction, the dissolution rate of calcite greatly decreased, with a reduction of about 90% for calcite in a 50% ethanol–water solution compared with that of ultrapure water. As expected, the increased fraction of ethanol could result in the reduced chance of calcite being exposed to water. In other words, the reduced water activity should be responsible for the deceleration of calcite dissolution, similar to research focusing on other minerals [41,42]. Since calcite consists in rhombohedral cells, and organic molecules could bind toward calcite with their hydroxy groups—specifically, through the hydrogen of the hydroxy group binding toward the carbonate group (Figure 10) [26], so one carbonate group in calcite is able to interact with one water molecule [43] at the same time if ethanol does not affect calcite’s reaction with water—the maximum reduction extent of the dissolution rate, caused by the presence of 50% ethanol, should be calculated as one subtracts the water activity and thus equals to 0.14. It is obvious that the calculated value is much smaller than the measured inhibition extent obtained by DHM experiments, which indicates that some other interactions should exist during calcite dissolution. One possible reason is the competitive adsorption of water and ethanol on calcite surfaces. Our TOC results and previous studies all suggest the interaction of ethanol with calcite [22–25,44], and it is predicted that ethanol adsorbs more strongly on the calcite surface than water. Once ethanol dominates the adsorption layer that forms on the calcite surface and is able to displace the pre-existing water, the chance and ability for calcite to interact with water would reduce, resulting in a stronger dissolution inhibition compared with lowering the water activity alone.
Figure 10. Atomic structure of the (104) surface of a calcite cell with additional, surrounding O atoms and the possible interaction between calcite and water through the hydrogen bond, top view.

Normally, etch pit development plays a key role in controlling calcite dissolution. The current work shows that ethanol could lead to the alteration of the topographic features of etch pits. The reduced openings and density of etch pits can be either attributed to the reduced undersaturation degree or the tight protecting layer formed by ethanol [45]. When the volume fraction of ethanol is high, etch pits tend to form in a triangular shape. This phenomenon is likely related to the specific adsorption of ethanol molecules on calcite surfaces [44]. Previous studies have shown that some inorganic and organic compounds are able to adsorb on specific sites and have a profound effect on calcite’s morphology [46,47]. Once an organic molecule adsorbs to the etch pit edge and remains intact throughout the dissolution, they can become anchoring points and alter the shape of the etch pits [8].

5. Conclusions

Organic molecules are able to influence the calcite dissolution behaviors, and in situ nanoscale measurements were performed by DHM to measure dissolutions and observe topographic changes of calcite (104) cleavage surfaces submerged in ethanol–water solutions. This work confirms the adsorption of ethanol by calcite and reveals that the dissolution behaviors are sensitive to the amount of ethanol. The bulk dissolution rate decreased with the increased ethanol fraction, and the etch pits’ growth was inhibited by ethanol and their shapes could be altered. Such an inhibition effect of ethanol is more related to the adsorption of ethanol, rather than the reduction of water activity. The results obtained in this study may provide some new insights to the mineral–organic molecule interactions, which could be beneficial to a broad range of fields including geochemistry, environmental science, the food industry, etc.

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