

Interactions of Lithium-Bearing Solutions with Calcite during Dissolution

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INTRODUCTION.

Reactions between calcite and aqueous solutions have attracted a significant interest due to their central role in a wide range of natural and engineering processes. Solutions in contact with minerals often contain significant amounts of alkali and alkaline earth elements. Among them, Li is present in continental waters mainly due to mineral weathering. In the continental crust, it occurs in a number of pegmatitic minerals and clays. Biogenic carbonates incorporate Li from the surrounding seawater, and their Li/Ca ratio has recently been suggested as a proxy for describing ancient oceans. The major inputs of Li into seawater are rivers and hydrothermal interaction with oceanic crust, and therefore Li/Ca ratios in biogenic carbonates may provide information about past rates of weathering and hydrothermal processes (Hathorne and James, 2006). Li is known to significantly affect calcite growth. Rajam and Mann (1990) reported changes in calcite morphology in the presence of Li, consisting in the development of {0001} forms, additionally to the {10 $\bar{1}$ 4} rhombohedra. Since then, several growth studies have attempted to describe the mechanism controlling Li-calcite interactions. To our knowledge, however, there are no dissolution studies aimed at testing the mechanisms by which Li modifies the reactivity of calcite surfaces. As suggested by Teng and Dove (1997) dissolution features may represent an indication of the faces that become stabilized during mineral growth, with the advantage that dissolution experiments are less difficult and time-consuming than growth studies. It is the aim of this research to improve the understanding of the specific interactions of Li with calcite during dissolution, which may help to unravel the mechanisms by which ions mediate the nucleation and growth of minerals.

METHODOLOGY.

We investigated the nature of Li interactions with calcite surfaces using *in situ* Atomic Force Microscopy observations of changes in etch pit morphologies and spreading rate. Freshly cleaved calcite {10 $\bar{1}$ 4} surfaces were used as substrates for dissolution experiments. Three saline solution systems were used: LiCl, NaCl, and KCl. Ca-free saline solutions in concentrations ranging from 1 mM to 100 mM flowed continuously at 50 mL h⁻¹ from a syringe coupled to an O-ring-sealed fluid cell containing the sample crystal. The flow rate used guarantees that dissolution rates measured are surface controlled under the conditions of our experiments. *In situ* observations and measurements of calcite surfaces during dissolution were performed using a fluid cell of a Digital Instruments Nanoscope III Multimode AFM working in contact mode under ambient conditions of both *T* and *p*CO₂ (≈10^{-3.5} atm). AFM images were collected using Si₃N₄ tips. Images were analyzed using the NanoScope software (Version 5.12b48). The etch pit spreading rates were calculated by measuring the length increase per unit time between opposite parallel steps in sequential images.

RESULTS.

Dissolution Features on (10 $\bar{1}$ 4) Calcite Surfaces.

In contact with pure water, calcite dissolution at high undersaturation (no calcium in the inlet solution) occurs via etch pit formation and propagation on (10 $\bar{1}$ 4) surfaces. Dissolution pits were shallow and displayed the typical rhombohedral shape that has been thoroughly described (Astilleros et al., 2006). The four step edges of the etch pits formed on {10 $\bar{1}$ 4} faces during dissolution in pure water are parallel to [441]₋: i.e. they are parallel [441]₊, [48 $\bar{1}$]₊, [441]₋ and [48 $\bar{1}$]₋ directions,

being the diagonals of the rhombus parallel to [2 $\bar{2}$ 1] and [010]. [441]₋ and [48 $\bar{1}$]₋ steps are acute and intersect the bottom of the etch pit at 78° angle, while [441]₊ and [48 $\bar{1}$]₊ steps are obtuse and intersect the bottom of the etch pit at 102° angle. The morphology of etch pits developed in the presence of NaCl or KCl was very similar to that of etch pits developed in the presence of water. When dissolution occurs in solution containing LiCl, a new step edge develops parallel to [010] intersecting [441]₋ and [48 $\bar{1}$]₋ steps (Fig. 1). This effect is ascribed to the presence of Li⁺, as it was not observed in other Cl-bearing solutions.

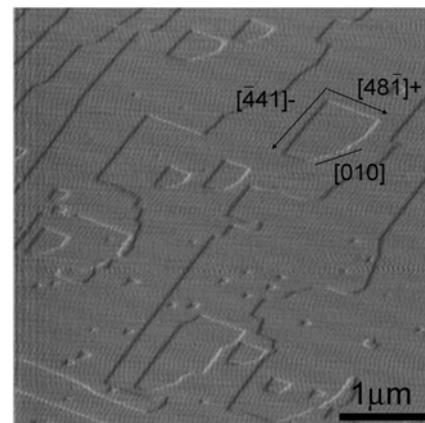


fig 1. Morphology of etch pits developed on calcite cleavage planes in the presence of 100 mM LiCl.

Etch Pit Spreading Rates.

The average velocity of etch pit spreading (i.e., the rate of change in etch pit length along [441]₋ or [48 $\bar{1}$]₋) in deionized water was 1.99 ± 0.14 nm s⁻¹. The step retreat rate increases generally with increasing concentration for all the salts tested. The etch pit spreading rate on the calcite cleavage surface changes under conditions of constant ionic strength (IS), depending on the background electrolyte tested. It increases in the order LiCl < NaCl < KCl at low IS. In these conditions, the presence of Li seems to inhibit calcite dissolution.

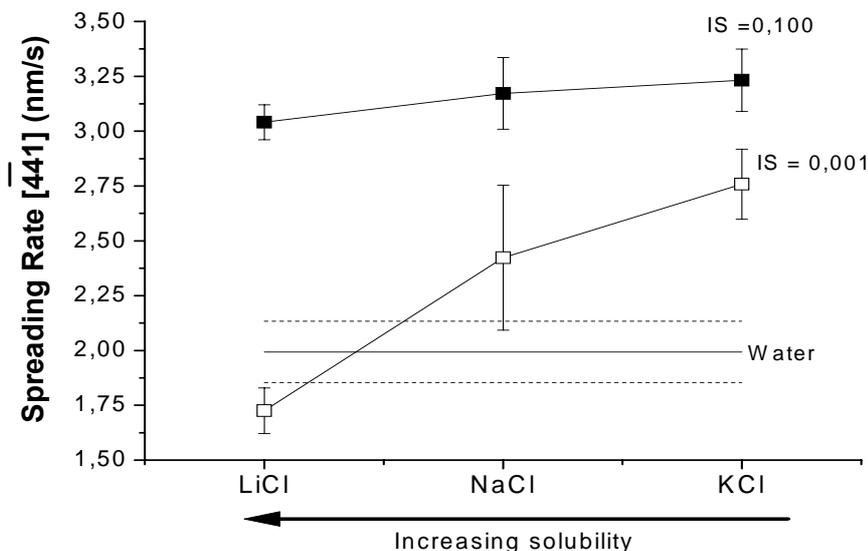


Fig. 2. Calcite etch pit spreading rate for the different electrolytes tested at different ionic strengths.

In more concentrated saline solutions, the etch pit spreading rate is similar for all the electrolytes tested (Fig. 2).

DISCUSSION.

Li-Induced Changes in Etch Pit Morphology.

In the presence of lithium, the observed change in etch pit morphology may be explained by considering stabilization of (0001) faces. This is in agreement with the observation of a new edge parallel to [010] on calcite etch pits during dissolution. This direction corresponds to the intersection of the {0001} form with the cleavage rhombohedron {10 $\bar{1}$ 4}. Atomistic simulations have shown that the basal (0001) face, unstable under normal growth conditions, becomes stable in the presence of Li⁺ (Titiloye et al., 1993). The dipolar (0001) face consists of alternate layers of Ca²⁺ and CO₃²⁻ ions in successive planes. CO₃²⁻ ions are in a non-close packed arrangement and leave interstices of 0.60 Å in which Li may accommodate (Ionic Radius = 0.59 Å), partially neutralizing the surface dipole of the basal faces and therefore stabilizing them (Rajam and Mann, 1990). The size of Na⁺ (0.99 Å) or K⁺ (1.52 Å) is too large for these ions to be accommodated in (0001) interstices; this is in agreement with the fact that no significant changes in etch pit morphology were observed in the experiments where NaCl or KCl were used as background electrolytes. Energy calculations suggested that during growth Li cannot incorporate in the bulk of the crystal, but it will be incorporated into surface interstitial sites (Titiloye et

al., 1993).

Effect of Electrolytes on Dissolution Kinetics.

In figure 2, etch pit spreading rate has been plotted for the three salts tested at two different IS. At low IS, water molecules in ion hydration shells are stabilized by the addition of electrolytes as a consequence of the electrostatic attraction between water dipoles in solvation shells and counterions present in solution. This effect should in principle assist calcite dissolution (Kowacz and Putnis, 2008). However, Ca²⁺ hydration during dissolution causes significant ordering in the solvent molecules, thereby lowering the entropy of the system, leading to a less negative change in free energy compared for example with Ba²⁺ or Sr²⁺ carbonates. Additional stabilization of hydration waters by background salt augments the unfavourable entropic effect upon dissolution. The tendency of ions to form pairs in solution will reduce the ability of salts to stabilize ion solvation shells. The closer the ions the more screened are their electric fields and consequently the electrostatic influence on solvation water diminishes. For simple 1:1 electrolytes, solubility was used as a proxy of ion separation in solution (Kowacz and Putnis, 2008). Calcite dissolution rates at low IS decrease with increasing solubility (increasing ion separation in solution) and thus, with increasing stabilization of water dipoles in cation hydration shells (Fig. 2). At higher IS (100 mM), the effect of background ions on water structure dynamics will determine the salt-specific

effects on calcite dissolution. Dissolution kinetics should increase with decreasing water affinity of the background anion, as it will determine solvent structure around Ca²⁺ cations and the removal of the cation from the crystal structure is the rate limiting step for dissolution of calcite. Therefore, salts with a common anion (LiCl, NaCl and KCl) have similar effects on calcite dissolution rate at high ionic strengths.

CONCLUSIONS.

In this dissolution study, we show that calcite {0001} surfaces, unstable in pure crystals, are developed in the presence of Li and, as a consequence, etch pits show new edges parallel to [010] direction. These surfaces are the same as those formed in Li-doped crystals during growth experiments. Additionally, the decrease in entropy occurring during calcite dissolution in the presence of non-paired LiCl at low IS due to stabilization of water molecules in the hydration shells of calcite building units leads to a reduction in etch pit spreading rate compared with pure water and other Cl-bearing salt solutions.

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