Effects of magnesium ions on near-equilibrium calcite dissolution: Step kinetics and morphology

Man Xu *, Steven R. Higgins

Department of Chemistry, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA

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Abstract

Dissolution kinetics at the aqueous solution-calcite (10 ^ 14) interface at 50 °C were investigated using in situ atomic force microscopy (AFM) to reveal the influence of magnesium concentration and solution saturation state on calcite dissolution kinetics and surface morphology. Under near-equilibrium conditions, dissolved Mg ^ 2+ displayed negligible inhibitory effects on calcite dissolution even at concentrations of 10 ^ -4 molal (m). Upon the introduction of 10 ^ -3 M Mg ^ 2+, the solution saturation state with respect to calcite, \( \Omega_{\text{calcite}} = \frac{a_{\text{Ca}^{2+}}}{a_{\text{CO}_2}^{0.5}} \), acted as a “switch” for magnesium inhibition whereby no significant changes in step kinetics were observed at \( \Omega_{\text{calcite}} < 0.2 \), whereas a sudden inhibition from Mg ^ 2+ was activated at \( \Omega_{\text{calcite}} > 0.2 \). The presence of the \( \Omega \)-switch in dissolution kinetics indicates the presence of critical undersaturation in accordance with thermodynamic principles. The etch pits formed in solutions with 10 ^ -3 M Mg ^ 2+ exhibited a unique distorted rhombic profile, different from those formed in Mg-free solutions and in de-ionized water. Such unique etch pit morphology may be associated with the anisotropy in net detachment rates of counter-propagating kink sites upon the addition of Mg ^ 2+. © 2010 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Interactions between impurities and minerals have significant environmental and geochemical implications. By partitioning among aqueous and mineral phases or incorporating into minerals, impurities may exert marked effects on the rates of mineral growth and dissolution processes and have significant influences on the morphology of natural mineral crystals. Carbonate minerals are ubiquitous in soils, aquifers, and marine deposits and are known to adsorb and incorporate metal impurities of environmental and geochemical interest. Being one of the most common rhombohedral carbonate minerals, calcite, and its growth and dissolution in the presence of divalent metal impurities have attracted much attention, particularly in regard to calcite’s role in potentially large-scale geologic trapping of CO2.

The inhibitory effects of magnesium ions on calcite growth and dissolution have been extensively investigated because of their importance in carbonate geochemistry and the relevance to marine chemistry (Berner, 1975; Compton and Brown, 1994; Deleuze and Brantley, 1997; de Leeuw, 2002; Morse and Arvidson, 2002; Lopez et al., 2009; Ruiz-Agudo et al., 2009). In recent years, the usage of microscopic techniques such as atomic force microscopy (AFM), enabling direct and in situ measurements of growth and dissolution processes at mineral surfaces, has enhanced the understanding of inhibitory mechanisms of foreign ions. During calcite growth processes, the observed reduction in step speeds and changes in surface morphology in the presence of magnesium have been proposed to reflect enhanced mineral solubility associated with Mg ^ 2+ incorporation, which reduces the driving force for growth (Davis et al., 2000, 2004; Wasylchenki et al., 2005a).

When impurity interactions are important, dissolution may not follow an exactly opposite process of growth. For example, the growth-inhibiting mechanism of Mg ^ 2+, which in part involves a change in the equilibrium point...
due to substitution of Ca\(^{2+}\) with Mg\(^{2+}\) in calcite, cannot be identical for describing the inhibitory effects of Mg\(^{2+}\) on pure calcite dissolution. Though it is generally accepted that Mg\(^{2+}\) retards calcite dissolution through competitive adsorption with Ca\(^{2+}\) at surface sites (Sjöberg, 1978; Compton and Brown, 1994), the mechanisms that control the effectiveness of magnesium as a dissolution inhibitor remain unclear. Sjöberg (1978) fitted calcite dissolution rates obtained from free-drift and pH-stat experiments to Langmuir adsorption isotherms and found that [Mg\(^{2+}\)] and [Ca\(^{2+}\)] up to 5 × 10\(^{-5}\) molal (m) and 10\(^{-3}\) m, respectively, the combined effects of Mg\(^{2+}\) and Ca\(^{2+}\) on calcite dissolution followed the theory of competitive adsorption and the effectiveness of Mg\(^{2+}\) inhibition increased with increasing degree of saturation with respect to calcite, \(\Omega_{\text{calcite}}\). Here \(\Omega_{\text{calcite}}\) is defined as the ratio of the ion activity product to the solubility product of calcite

\[
\Omega_{\text{calcite}} = \frac{Q}{K_{sp}(\text{calcite})} = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{sp}(\text{calcite})}
\]

where \(Q\) is the ion activity product, \(a_{\text{Ca}^{2+}}\) and \(a_{\text{CO}_3^{2-}}\) are activities of ions, and \(K_{sp}(\text{calcite})\) is the solubility product for calcite at the temperature of interest. If it is generally true that Mg\(^{2+}\) effects increase with increasing calcite saturation, the results from Sabbides and Koutsoukos (1995) and those from Gutjahr et al. (1996) are somewhat contradictory. Sabbides and Koutsoukos (1995) observed a three-fold reduction in calcite dissolution rate at [Mg\(^{2+}\)] = 4 × 10\(^{-3}\) M and \(\Omega_{\text{calcite}} = 0.004\)–0.02, whereas Gutjahr et al. (1996) reported no Mg\(^{2+}\) inhibition at [Mg\(^{2+}\)] ≤ 3 × 10\(^{-4}\) M and \(\Omega_{\text{calcite}} = 0.5\). Such diversity and inconsistency in experimental results make it difficult to draw conclusions regarding the role of magnesium as an inhibitor and the possible mechanisms of magnesium inhibition on calcite dissolution.

AFM studies of dissolution at calcite-aqueous solution interfaces have given insight into the effects of Mg\(^{2+}\) by directly measuring step movement and etch pit morphology on the mineral surface. AFM and vertical scanning interferometry (VSI) studies by Arvidson et al. (2006) demonstrated that under far-from-equilibrium conditions, when [Mg\(^{2+}\)] < 5 × 10\(^{-5}\) m significant inhibition of calcite dissolution was found in carbonate-buffered solutions ([NaHCO\(_3\)] = 4.4 × 10\(^{-3}\) m), although no change in etch pit morphology was observed. The reduction in dissolution rate was proposed to be due to step pinning by Mg\(^{2+}\) adsorption and slow dehydration. As [Mg\(^{2+}\)] increased to 0.8 × 10\(^{-3}\) m, unique etch pit profiles were observed in both AFM and VSI experiments. Arvidson et al. (2006) attributed the change in etch pit morphology to the selective step pinning and the accumulation of excess kinks along positive (i.e., obtuse) step edges. However, little is known about the detailed mechanisms of magnesium effects on calcite dissolution kinetics and morphology; whether Mg\(^{2+}\) impurities irreversibly adsorb onto calcite surfaces and act as static site-blocking points inhibiting the retreat of step edges, or Mg\(^{2+}\) impurities retard the step motion through the reversible adsorption and the formation of a mobile “fence” at calcite surfaces.

To obtain more insight into the dissolution-inhibiting mechanism of magnesium, a systematic study of how magnesium concentration and solution saturation state influence the effectiveness of Mg\(^{2+}\) as a calcite dissolution inhibitor was carried out. In this study, we investigated step kinetics and etch pit morphology at calcite-aqueous solution interfaces during dissolution in the presence and the absence of magnesium ions. Experiments were conducted in both near-equilibrium solutions and far-from-equilibrium solutions with respect to calcite, the former of which mimics the conditions of natural water systems, especially on long time scales (Morse and Mackenzie, 1990; Morse and Arvidson, 2002; Gaus et al., 2005). Near-equilibrium conditions are defined in this work based on the Gibbs energy of reaction (\(\Delta G_{\text{rxn}} > -kT \iff \Omega > 0.37\)). The effects of magnesium concentration and solution saturation state on calcite dissolution kinetics and morphology at a temperature of 50 °C are explored through detailed analysis of time-sequential AFM images on calcite surfaces. Due to the relatively slow kinetics of calcite dissolution in near-equilibrium solutions at room temperature, the elevated temperature employed in this work decreased the timescale for step edge motion such that it was observable over a practical AFM image sequence timescale of approximately 10–100 min. Possible mechanisms that lead to magnesium inhibition and changes in calcite step morphology are discussed.

2. EXPERIMENTAL

2.1. Preparation of aqueous solutions

Aqueous solutions used in calcite dissolution studies were prepared from high-purity (99.99 + %) NaHCO\(_3\), CaCl\(_2\), NaCl, and MgCl\(_2\) dissolved in de-ionized water (resistivity ~ 18 M\(\Omega\) cm). Stock solutions were first prepared in appropriate proportions according to the desired compositions and were then incrementally diluted by using 0.1 m NaCl with 0, 10\(^{-4}\), and 10\(^{-3}\) m MgCl\(_2\). Calcium concentration and alkalinity in stock solutions were analyzed by using Inductively Coupled Plasma optical emission spectrometry (ICP-OES) (Varian 710-ES) and standard HCl titration at room temperature (23.5 °C). pH at room temperature was measured for each experimental solution. Saturation states of experimental solutions with respect to calcite (\(\Omega_{\text{calcite}}\)), ionic strengths, activities of ions, and pH values at the temperature of interest (50 °C) were determined using Visual MINTEQ software. Details of MINTEQ calculations can be found in our previous publication (Xu et al., 2010). Briefly, in the MINTEQ calculations, aqueous solutions were first treated as partially open systems at room temperature, i.e., the partial pressure of CO\(_2\) (P\(_{\text{CO}_2}\)) was modified for an open system such that the MINTEQ predicted pH agreed with the measured pH since the preparation of fresh NaHCO\(_3\) solutions were in a state of disequilibrium with respect to atmospheric CO\(_2\). At the experimental temperature of 50 °C, aqueous solutions were then treated as systems closed to the atmosphere and total inorganic carbon values obtained from the previous partially open system calculations were utilized in the calculation. MINTEQ calculations showed that our experimental solutions have \(\Omega_{\text{calcite}}\) varying from 0.04 to 1.2, ionic strength at ~ 0.1 M, and pH values in the range 7.8–8.3 at 50 °C, as listed in Table 1. As to the solution
saturation state with respect to magnesite, MINTEQ calculations yielded $\Omega_{\text{magnesite}}$ from 0.0018 to 0.070, based on $K_{sp}(\text{magnesite}) = 10^{-3.2}$ at 50 °C. The reported $K_{sp}(\text{magnesite})$ values varied in the range of $10^{-8.2} - 10^{-7.2}$ (Konigsberger et al., 1992; Langmuir, 1997). If $K_{sp}(\text{magnesite}) = 10^{-8.2}$ was employed in the calculations, $\Omega_{\text{magnesite}}$ was in the range of 0.018–0.70. Regardless of the $K_{sp}(\text{magnesite})$ used, the experimental solutions were undersaturated with respect to magnesite upon the addition of $0$–$10^{-3}$ m Mg$^{2+}$.

2.2. In-situ nanoscale measurements of calcite dissolution

Optically clear calcite (CaCO$_3$) crystals used in this study originated in Chihuahua, Mexico and were purchased from Ward’s Natural Science Est., Inc. Calcite crystals were rinsed with reagent grade methanol, dilute hydrochloric acid, and de-ionized water before usage. Specimens of $\sim 4$ mm $\times 4$ mm $\times 1$ mm in size were cleaved with a razor blade along calcite (10 14) surfaces.

Direct observation and measurements of calcite dissolution were made by using a self-constructed AFM (Higgins et al., 1998; Bose et al., 2008). With a closed fluid cell, this AFM allowed a continuous flow of solution to interact with the mineral specimen and enabled the instrument to be operated at elevated pressure and temperature. In the present study, the fluid cell was pressurized to $\sim 0.3$ bar above ambient using N$_2$ and heated to 50 °C. The calcite specimen was mechanically fixed in the titanium AFM fluid cell with a gold wire. A “wall-jet” was employed in the AFM fluid cell where the fluid was due to a fluid jet impinging normally on the mineral surface and spreading radially over the surface (Compton et al., 1990a,b; Bose et al., 2008). A mass flow controller (Porter Instrument) downstream of the cell was used to control fluid flow rate. A previous study (Xu et al., 2010) under similar experimental conditions demonstrated that step speed was independent of fluid flow rate at and above 1.4 $\mu$g/s. Thus a flow rate of 1.4 $\mu$g/s was used throughout our AFM experiments, ensuring that dissolution was limited by surface reaction instead of diffusive transport under our experimental conditions. AFM experiments were performed in contact mode by using uncoated silicon cantilevers (Nanosensors, force constant of 0.02–0.77 N/m, typically 0.2 N/m). The externally applied load was below 15 nN in order to minimize lateral forces. Scanning frequency was 3–6 Hz, with 512 sampling points per scan line and scanning areas ranging from 4 $\mu$m $\times 4$ $\mu$m to 12 $\mu$m $\times 12$ $\mu$m. Speeds of step retreat were determined from time-sequential AFM images by quantifying step positions with respect to a fixed surface landmark as a function of time. Images scanned in the same directions were employed for the step speed determination. The consistency of step speeds was verified using different steps and images obtained under the same experimental condition. All step speed data presented in this paper were averaged from two to six replicate measurements.

Positive (+) and negative (−) step speeds at calcite (10 14) surfaces were measured in aqueous solutions with saturation state $\Omega_{\text{calcite}}$ ranging from 0.04 to 1.2 and magnesium concentration from 0 to $10^{-3}$ m at 50 °C. Magnesium in experimental solutions arising from impurities in the reagent chemicals NaHCO$_3$, CaCl$_2$, and NaCl was on the order of $10^{-6}$–$10^{-5}$ m, as indicated in Xu et al. (2010), and thus the “Mg-free” solutions contained trace magnesium impurities. The actual magnesium concentration in the aqueous solution was the summation of the amount of magnesium added to the system and magnesium as impurities from chemicals, plus the amount of magnesium dissolved from the calcite crystal, the latter of which was negligible. To simplify this issue, the concentration of magnesium throughout this paper only represents the concentration of added magnesium.

3. RESULTS

Upon the introduction of aqueous solutions or de-ionized water into the AFM fluid cell, dissolution at the calcite (10 14) surface proceeded as a layer-by-layer process through the formation of etch pits, the retreat of step edges, and the intersection of etch pits. Calcite etch pits formed in de-ionized water at 50 °C have a characteristic rhombic shape and are surrounded by straight steps oriented parallel to the [4 4 1] and [4 8 1] directions (see Fig. 1a in Xu et al. (2010)). The two inequivalent steps along these two directions intersect the calcite (10 14) surface at obtuse and acute angles (nominally 102° and 78°) and are referred to as positive (+) and negative (−) steps. In this paper, positive and negative steps will be denoted by “+” and “−” subscripts, respectively. The positive step pair [4 4 1]_+ and [4 8 1]_+, of the etch pit are bisected by the c-glide plane, which is also true for the negative step pair [4 4 1]_− and [4 8 1]_−. However, no symmetry operation relates the + and the − steps.

3.1. Step kinetics

Step speed data obtained at calcite (10 14) surfaces in this study are summarized in Table 2 and plotted as a function of saturation state $\Omega_{\text{calcite}}$ in Fig. 1. To clarify the effects of Mg$^{2+}$ on speeds for + and − steps (V_+ and V_−), step speeds are also plotted as a function of fluid magnesium concentration in Fig. 2. Uncertainties in step speed are estimated to be $\pm 0.3$ nm/s for V_+ and $\pm 0.1$ nm/s for V_−. In Mg-free solutions, V_− decreases linearly from 1.9 nm/s to 0 nm/s at $\Omega_{\text{calcite}} = 0.05$ to 1.2, and V_+ varies from 0.2 to 0.01 nm/s over the same interval, as shown in Fig. 1 and Table 2. With the addition of $10^{-4}$ m Mg$^{2+}$ to the aqueous solutions, step speeds are similar to those of the Mg-free experiments within uncertainty (Figs. 1 and 2). At $\Omega_{\text{calcite}} = 1.2$, calcite step motion ceased or, in some experiments, steps continued to retreat although bulk thermodynamics predicts the direction of step motion to reverse. The discrepancy may be due to the uncertainty in $K_{sp}$(calcite) values, trace impurities in solid minerals, or possibly effects of step edge energies on the net driving force for dissolution (Teng et al., 1999; Davis et al., 2000; Jensen et al., 2002; Wasylentki et al., 2005a; Fan et al., 2006; Saldi et al., 2009; Stack and Grantham, 2010; Xu et al., 2010).

When the concentration of Mg$^{2+}$ was further increased to $10^{-3}$ m, step speeds decreased markedly at $\Omega_{\text{calcite}} \geq 0.2$,
Table 1
Composition and chemistry of aqueous solutions used in calcite dissolution experiments.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>NaCl (mol/L)</th>
<th>MgCl₂ (mol/L)</th>
<th>pH (23°C)</th>
<th>aCO₂ (atm)</th>
<th>aNa⁺ (10⁻⁶)</th>
<th>aMg²⁺ (10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.1</td>
<td>0.1</td>
<td>7.95</td>
<td>0.009</td>
<td>3.11</td>
<td>0.53</td>
</tr>
<tr>
<td>A2</td>
<td>0.1</td>
<td>0.1</td>
<td>7.81</td>
<td>0.008</td>
<td>3.12</td>
<td>0.59</td>
</tr>
<tr>
<td>A3</td>
<td>0.1</td>
<td>0.1</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>A4</td>
<td>0.1</td>
<td>0.1</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>B1</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.95</td>
<td>0.009</td>
<td>3.11</td>
<td>0.53</td>
</tr>
<tr>
<td>B2</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.94</td>
<td>0.008</td>
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<td>B3</td>
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<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>B4</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>B5</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>B6</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>C1</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.95</td>
<td>0.009</td>
<td>3.11</td>
<td>0.53</td>
</tr>
<tr>
<td>C2</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.94</td>
<td>0.008</td>
<td>3.12</td>
<td>0.59</td>
</tr>
<tr>
<td>C3</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
<tr>
<td>C4</td>
<td>10 x 10⁻³</td>
<td>10 x 10⁻³</td>
<td>7.81</td>
<td>0.009</td>
<td>3.12</td>
<td>0.6</td>
</tr>
</tbody>
</table>

where the + and − steps ceased to migrate. The saturation state, Qcalcite, acts as a “switch” for the Mg²⁺ inhibitory effects in the presence of 10⁻³ m Mg²⁺. That is, at Qcalcite < 0.2, Mg²⁺ has insignificant influence on V⁺ and V−, whereas a large inhibition of step motion is activated at Qcalcite ≥ 0.2 (Figs. 1 and 2). The zero or near-zero step speeds suggest that the threshold value of Mg²⁺ concentration is somewhere between 10⁻⁴ and 10⁻³ m for aqueous solutions with Qcalcite ≥ 0.2. For Qcalcite < 0.2, however, the data indicate a higher than 10⁻³ m threshold value for effective Mg²⁺ inhibition.

3.2. Morphology of etch pits

Fig. 3a–c presents AFM topographic images of the calcite (1014) surface during dissolution in aqueous solutions with Qcalcite ≈ 0.05 and [Mg²⁺] = 0, 10⁻⁴, and 10⁻³ m, respectively. Three representative time-sequential AFM image sets showing the progressive expansion of etch pits on calcite surfaces are illustrated in Fig. 4a–c. As shown in Fig. 3a and discussed in Xu et al. (2010), calcite dissolution in Mg-free CaCl₂–NaHCO₃ aqueous solutions at 50°C under near-equilibrium conditions leads to expansion of existing etch pits with straight + steps along [441] and [481] and curvilinear − steps oriented approximately along the [010] direction. The incremental addition of magnesium to the aqueous solution did not change the shape of etch pits formed on the calcite surface (Figs. 3b and 4b) until the concentration of magnesium in the aqueous solution reached 10⁻³ m, where significant changes in the morphology of calcite etch pits are observed, as illustrated in Figs. 3c and 4c. The curvilinear − steps formed in Mg-poor ([Mg²⁺] ≤ 10⁻⁴ m) systems become straight in Mg-rich ([Mg²⁺] = 10⁻³ m) solutions, approximately following [441] and [481] directions, and the −/− step boundaries are sharp and well defined. The + steps formed after the introduction of 10⁻³ m Mg²⁺ are slightly mis-oriented compared to the characteristic rhombic etch pits, resulting in a +/+ corner angle of 95 ± 1°. Additionally, significant quantities of surface blebs are observed in Figs. 3 and 4. Although the Mg-free images in Figs. 3a and 4a appear to show fewer of these blebs, the blebs observed in Figs. 3b and 4b were present before the introduction of the Mg-containing solutions, showing that there is not a direct correlation between the presence of aqueous Mg²⁺ and the appearance of the blebs. Similar surface features were reported previously in a study performed exclusively in Mg-free solutions (Xu et al., 2010).

4. DISCUSSION

4.1. Effects of Mg²⁺ and Qcalcite on step kinetics

As presented in Figs. 1 and 2 and Table 2, the retreat speeds of + and − steps remain constant when 10⁻⁴ m Mg²⁺ is introduced. This observation is in good agreement with previous pH-stat studies by Gutjahr et al. (1996) that showed no inhibitory effect of Mg²⁺ on calcite dissolution at Qcalcite ≈ 0.5 when fluid Mg²⁺ concentration was less than 3 x 10⁻⁴ mol/L. However, in solutions with
10^{-3} \text{ m Mg}^{2+}$, the inhibitory effects of magnesium on calcite dissolution became pronounced and both $+$ and $-$ steps ceased to propagate at $\Omega_{\text{calcite}} \geq 0.2$ (Figs. 1 and 2). When $\Omega_{\text{calcite}} < 0.2$, no significant inhibition from $\text{Mg}^{2+}$ was
observed. \( \Omega_{\text{calcite}} \) therefore acts as a “switch” for Mg\(^{2+}\) inhibition when [Mg\(^{2+}\)] in the aqueous solution reaches 10\(^{-3}\) m.

4.1.1. Magnesium inhibitory effects as a function of \( \Omega_{\text{calcite}} \)-kink density variations

To better understand how \( \Omega_{\text{calcite}} \) could alter the inhibitory action of magnesium, we first consider how the density of kink sites on moving step edges may vary with solution saturation. The theoretical step edge kinetic model developed by Zhang and Nancollas (1990) predicts the kink density of a dissolving step as a function of saturation state where at high undersaturation, kink densities are maximized, whereas near-equilibrium step edges become smoother. Although the reduction in kink density with increasing \( \Omega_{\text{calcite}} \) could be an important factor in the general trend of increasing Mg\(^{2+}\) inhibition as equilibrium is approached, the kink density model could not provide a satisfactory explanation for the presence of the \( \Omega_{\text{calcite}} \)-switch where a sudden change in step speed is observed. According to Zhang and Nancollas (1990), kink density varies by a factor of \( \sqrt{2} \) in the range of 0 \( \leq \Omega \leq 1 \). In the case of our study where the solution \( \Omega_{\text{calcite}} \) changes from 0.1 to 0.2, the variation of the kink density is estimated to be less than 5%. A 5% variation in kink density could not cause any significant change in step kinetics, as step speed is proportional to kink density according to step kinetic models (Temkin, 1969; Zhang and Nancollas, 1990). Investigations by Wasylenki et al. (2005b) and additional observations by De Yoreo et al. (2009) however suggest that calcite growth inhibition by Sr\(^{2+}\) is consistent with a kink-limited growth model, such as that of Zhang and Nancollas (1990) whereby the efficacy of Sr-blocking at kink sites is a strong function of supersaturation.

4.1.2. Kinetic inhibition through site-blocking

Step pinning mechanisms may contribute to the observed kinetic behavior of step retreat in the presence of magnesium impurities. Pinning occurs when impurity molecules or ions adsorb to step edges or accumulate on terraces ahead of retreating steps and inhibit detachment. In dissolution processes, impurities from both the solution and within the crystal may cause pinning and contribute to the decrease in step speeds. Assuming homogeneous distribution of magnesium impurities in the calcite specimen, if impurities from the calcite crystal played an essential role in the step pinning effects, one would expect insignificant...
Fig. 3. AFM topographic images of etch pits formed on the calcite (10\text{1}4) surface during dissolution at 50 °C in (a) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.048$, (b) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.047$ and $[\text{Mg}^{2+}] = 10^{-4}$ m, (c) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.044$ and $[\text{Mg}^{2+}] = 10^{-3}$ m. Image sizes are 10 $\mu$m $\times$ 10 $\mu$m for (a) and 4.33 $\mu$m $\times$ 4.33 $\mu$m for (b) and (c).

Fig. 4. Sequence of AFM topographic images of calcite (10\text{1}4) surface during dissolution at 50 °C in (a) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.048$, (b) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.047$ and $[\text{Mg}^{2+}] = 10^{-4}$ m, (c) an undersaturated aqueous solution with saturation state $\Omega_{\text{calcite}} = 0.044$ and $[\text{Mg}^{2+}] = 10^{-3}$ m. Image sizes are 11.6 $\mu$m $\times$ 11.6 $\mu$m for (a), 4.61 $\mu$m $\times$ 4.61 $\mu$m for (b), and 8 $\mu$m $\times$ 8 $\mu$m for (c). These images show the expansion of dissolution etch pits with time. Time intervals are 422 s for (a), 211 s for (b), and 337 s for (c).
difference in step speeds between Mg-free and Mg-rich solutions, contrary to the observations.

Magnesium impurities from aqueous solutions could adsorb to terraces, steps, or kink sites through reversible or irreversible processes. Reversible adsorption is assumed in the Langmuir–Volmer model (Reddy and Wang, 1980; Meyer, 1984; Gutjahr et al., 1996)

\[ \frac{\theta_i}{1 - \theta_i} = \frac{v - v_i}{v_i} = K_i c_i \]

(2)

where \( \theta_i \) is the fraction of impurity-occupied adsorption sites, \( v \) and \( v_i \) are the growth or dissolution rates (or step speeds) in the absence and the presence of impurities, respectively, \( K_i \) is an equilibrium constant for adsorption of the impurity, and \( c_i \) is the concentration of impurities in solution. Applying the Langmuir–Volmer model, surface coverage by \( \text{Mg}^{2+} \) is a function of \([\text{Mg}^{2+}]\) in aqueous solutions. A plot of \( \log \frac{\theta_i}{1 - \theta_i} \) versus \( \log c_i \) should follow a straight line with a slope of one. This trend is not observed at \( \Omega_{\text{calcite}} = 0.2 \) in the present study (plot not shown), therefore the Langmuir–Volmer model may not apply to \( \text{Mg}^{2+} \) inhibition in this set of conditions. The model described by Cabrera and Vermilyea (Cabrera and Vermilyea, 1958; Berner and Morse, 1974; Meyer, 1984; Gutjahr et al., 1996) deals with immobile impurity adsorption on surfaces and may be associated with the inhibition by \( \text{Mg}^{2+} \) on calcite dissolution processes. Whereas the Cabrera and Vermilyea model is applicable when steps are rough enough that they contain a maximum density of kinks (e.g., a line sink/source for adsorption/desorption), the kink-limited model of Zhang and Nancollas (1990) and its extension by De Yoreo et al. (2009) assumes that kinks are minority sites along steps. In the present work, the – steps, in the absence of impurities, follow a curvilinear path (e.g., Figs. 3a and 4a), indicating the presence of a highly kinked segment roughly parallel to [010]. Therefore, in the case of the – steps, it is reasonable to assume that the Cabrera and Vermilyea model is applicable. For the + steps, it is more difficult to assess the kink density of the resolution of the images in Figs. 3 and 4, but here we will make the assumption that the roughness of the + and – steps will be comparable. The following section therefore discusses the Cabrera and Vermilyea model as it relates to the present investigation.

4.1.3. \( \Omega \)-switch: critical length considerations

It has been well established that during growth processes, in order for growth to occur spontaneously, the energy required for solid–liquid interface formation, which can be described in terms of the Gibbs–Thomson equation, has to be exceeded by the favorable free energy of solute deposition (Burton and Cabrera, 1951; Tang et al., 2004). This thermodynamic treatment gives a critical size, \( L_c \), the minimum length at which a step can advance without increasing the Gibbs energy. In the present dissolution study, a critical length analogue to that in the growth process may account for the presence of the \( \Omega \)-switch, a critical undersaturation at which the inhibitory effects of \( \text{Mg}^{2+} \) impurities change dramatically. Crystal growth theories (Cabrera and Vermilyea, 1958; Teng et al., 1998; Dove et al., 2005; Tang et al., 2005) state that the critical length, \( L_c \), is inversely correlated with \( \ln \Omega \) by

\[ L_c = \frac{2 \beta c_j}{K_j T \ln \Omega} \]

(3)

where \( \beta \) is the intermolecular distance along the step, \( c_j \) is the distance between rows, \( (\gamma) \) is the average step edge free energy, \( k_B \) is Boltzmann constant, and \( T \) is the absolute temperature. In case of dissolution processes, there should also be a critical length for step edges, in accordance with thermodynamic treatment of the dissolution reaction at steps:

\[ L_c = - \frac{2 \beta c_j}{K_j T \ln \Omega} \]

(4)

In the presence of \( \text{Mg}^{2+} \) impurities, although \( \text{Mg}^{2+} \) does not stay permanently at the calcite surface, its adsorption can be treated as immobile, or irreversible, as long as the residence time of \( \text{Mg}^{2+} \) at the surface sites is significantly longer than that of \( \text{Ca}^{2+} \) (Pokrovsky et al., 1999; Arvidson et al., 2006). Based on the model of Cabrera and Vermilyea (Cabrera and Vermilyea, 1958; Berner and Morse, 1974; Meyer, 1984; Gutjahr et al., 1996), impurity ions adsorbed on crystal surfaces fix or “pin” steps at some points between which the step can retreat or advance only with a curvature. As the step retreats, the curvature increases and the diameter of curvature, whose minimum value is the distance between the adjacent adsorbed impurities, becomes smaller. If on the crystal surface the distance between the adsorbed immobile impurity ions is less than the critical length, step retreat would stop completely.

The Cabrera and Vermilyea model, based on the presence of critical phenomena, predicts the presence of the \( \Omega \)-switch behavior. The inhibitory effects of \( \text{Mg}^{2+} \) on calcite dissolution undergo a dramatic enhancement upon reaching a certain critical undersaturation, \( \Omega_c \), which corresponds to a critical length, \( L_c \), as shown in Eq. (4). Due to the inverse correlation between \( L_c \) and \( -\ln \Omega \), we expect \( \Omega_c \) to decrease as the distance between \( \text{Mg}^{2+} \) impurities decreases on the calcite surface.

From our AFM experiments, a critical undersaturation \( \Omega_c \) of \( \sim 0.2 \) is estimated for fluid containing \( 10^{-3} \) \( \text{Mg}^{2+} \) at 50°C. This corresponds to a critical length \( L_c \) of \( \sim 22 \) nm using the step free energy values in Teng et al. (1998). Therefore, by taking \( L_c \) to approximate the mean distance between immobile impurities at the \( \Omega \)-switch, the number density of immobile \( \text{Mg}^{2+} \) ions at the calcite surface, in experiment C3, is roughly 1 \( \text{Mg}^{2+} \) ion per 400 nm\(^2\) (i.e., \( L_c^{-2} \)). According to Pokrovsky et al. (1999) and Van Cappellen et al. (1993), the maximum surface site density is \( \sim 4000 \) sites per 400 nm\(^2\) for \( \text{MgCO}_3 \), \( \text{MnCO}_3 \), and \( \text{FeCO}_3 \). We expect similar surface site density for the calcite (10 14) surface, and therefore, \( \sim 0.05\% \) of the total cation sites are estimated to be occupied by the irreversibly adsorbed \( \text{Mg}^{2+} \) cations at \( \Omega_{\text{calcite}} = 0.2 \) and \( [\text{Mg}^{2+}] = 10^{-3} \) m. As a result of the low immobile ion coverage, the majority of \( \text{Mg}^{2+} \) adsorbs onto calcite surfaces through reversible adsorption. Compton and Brown (1994) demonstrated that the adsorption constant of \( \text{Mg}^{2+} \) on calcite surfaces was 1/4 of that of \( \text{Ca}^{2+} \). Considering the concentrations of \( \text{Mg}^{2+} \),...
and Ca\(^{2+}\) in our aqueous solutions, a ratio of \([\text{Mg}^{2+}]_{\text{surface}}/ [\text{Ca}^{2+}]_{\text{surface}} = 1.7\) is obtained, implying \(\sim 60\%\) of adsorbed cations as Mg\(^{2+}\). Although the coverage of Mg\(^{2+}\) determined from the relative adsorption constants of Mg\(^{2+}\) and Ca\(^{2+}\) (Compton and Brown, 1994) might be different from other estimations (for instance, (Meyer, 1984) and references therein), it is apparent that only a small fraction of Mg\(^{2+}\) adsorbed to the calcite surface is immobile under our experimental conditions. It is likely that Mg\(^{2+}\) irreversibly adsorbs to the sites at step edges that make up a small fraction of the surface sites. The irreversibly adsorbed Mg\(^{2+}\) exhibits strong inhibitory effects on step retreat and calcite dissolution. At terraces where the majority of the surface sites are located, the adsorbed Mg\(^{2+}\) is expected to be mobile and exhibit minimal influence on calcite dissolution at concentrations up to \(10^{-4}\) m.

### 4.1.4 Step dissolution at \(Q_{\text{calcite}} \geq 1\)

The observations in Fig. 1, that steps continued to dissolve even in solutions with \(Q_{\text{calcite}} \geq 1\) (i.e., in equilibrium to supersaturated solutions), are not well understood due to three important calcite properties that are not well characterized. Firstly, the ubiquitous presence of minor and trace impurities in high quality Iceland Spar (e.g., 0.6% Mg cation basis) (Xu et al., 2010) is extremely difficult to characterize on the microscale, thus preventing a direct correlation with AFM images. The substitution of \(\text{Mg}^{2+}\) for \(\text{Ca}^{2+}\) in calcite increases the solubility constant of the solid (Busenberg and Plummer, 1989; Davis et al., 2000). Therefore, it is reasonable to expect that the previously determined impurity levels of the calcite material that sourced the samples for the present study could contribute to a larger solubility constant compared with a pure calcite specimen. Secondly, the thermodynamic quality of standard Gibbs energy of reaction for calcite dissolution is not known to sufficient precision to ignore uncertainties in \(Q_{\text{calcite}}\). Specifically, \(K_{\text{eq}}(\text{calcite})\) is known to 2 significant digits at best (e.g., \(10^{-8.46} = 3.3 \times 10^{-9}\) is a commonly reported 25°C \(K_{\text{eq}}\) calcite value), and furthermore, the range of reported \(K_{\text{eq}}(\text{calcite})\) values at room temperature extends from \(10^{-3.90}\) to \(10^{-8.85}\) (Jensen et al., 2002). Thirdly, the finite Gibbs energy associated with step edges (i.e., step edge free energy) may shift the apparent equilibrium point of a solution based on the observation of step edge motion. Recent observations of calcite-water interfaces with AFM provide some evidence supporting the expected influences of edge energy on the direction of step migration in near-equilibrium solutions (Fan et al., 2006; Stack and Grantham, 2010). This third possibility, while plausible, is the most difficult to evaluate due to the limited number of experimental measurements of calcite step energies (Teng et al., 1998) and the difficulty in performing those measurements (Higgins and Hu, 2006).

### 4.2. Effects of Mg\(^{2+}\) on etch pit morphology

One of our most striking observations is the change in etch pit morphology with the addition of Mg\(^{2+}\). Upon the introduction of \(10^{-3}\) m Mg\(^{2+}\) into near-equilibrium aqueous solutions, the etch pits display a unique distorted rhombic profile. The \(-/+\) rounding in Mg-poor ([Mg\(^{2+}\)] \(\leq 10^{-4}\) m) systems disappeared in Mg-rich solutions and the \(+/-\) corners became smaller than that of a characteristic rhombic etch pit.

#### 4.2.1 Negative step edges

As presented in Fig. 3a & b and Fig. 4a & b, when \(Q_{\text{calcite}} = 0.05–1.2\) and \([\text{Mg}^{2+}] \leq 10^{-4}\) m, the \(-/+\) corners of the etch pits formed on calcite surfaces are curvilinear, approximately following the \([010]\) direction. Our previous AFM study at comparable saturation states and temperatures revealed similar etch pit morphology, a phenomenon attributed to the backward reaction that preferentially occurs at the \(-/+\) kink sites rather than the \(+/-\) kinks in near-equilibrium systems (Xu et al., 2010).

If \(r_{-/+}\) and \(r_{+/-}\) refer to the \(-/+\) and \(+/-\) kink detachment rates (Fig. 5) in far-from-equilibrium systems, the net cation detachment rates near-equilibrium are \(r_{-/+}^\text{net} = r_{-/+} - r_{+/-}\) and \(r_{+/-}^\text{net} = r_{+/-} - r_{-/+}\), where \(r_{-/+}\) and \(r_{+/-}\) represent rates of backward reaction (i.e., attachment) at the two types of kink sites in Mg-free near-equilibrium systems. \(r_{-/+}\) is usually considered to be less than \(r_{+/-}\) (Liang et al., 1996; McCoy and LaFemina, 1997).

Teng et al. (1999) reported an inversion in step advancement rates, i.e., \(v_{+} < v_{-}\), for systems approaching equilibria. The near-equilibrium step speeds observed by Teng et al. reflect the net attachment rates \(r_{-/+}^\text{net}\) rather than the attachment rates \((r)\) at kink sites, and thus are not in conflict with the inequality of \(r_{-/+} < r_{+/-}\). As demonstrated by Kinetic Monte Carlo (KMC) simulations (Jordan et al., 2001) and illustrated in Fig. 6, a large anisotropy in detachment rates of counter-propagating kink sites could lead to a step viscosity through the accumulation of the slower detaching kink sites. KMC simulations investigating the variation in step orientation upon the change in kink detachment rates are discussed later in this paper. The observed curvilinear – steps that orient approximately along \([010]\) (Figs. 3a and 4a) thus may originate from the small net detachment rate ratio \(R^\text{calcite} = r_{-/+}^\text{net}/r_{+/-}^\text{net}\) and the accumulation of excess \(-/+\) kinks along step edges under near-equilibrium conditions. Consequently, the preferential backward reaction at the \(-/+\) kink sites, \(r_{-/+}(\text{Ca}^{2+}) > r_{+/-}(\text{Ca}^{2+})\), would result in a smaller \(R^\text{calcite}\) in near-equilibrium systems compared to that of far-from-equilibrium systems.

An alternative explanation for the \(-/+\) rounding is due to the greater influence of the backward reaction on the \(-/+\) kink detachment rate than on the \(+/-\) kink detachment rate. That is, if the backward reaction rates are comparable at \(-/+\) and \(+/-\) kink sites, \(r_{-/+}(\text{Ca}^{2+}) \approx r_{+/-}(\text{Ca}^{2+})\), \(R^\text{calcite}\) near-equilibrium may still be less than \(r_{+/-}/r_{-/+}\) at far-from-equilibrium, resulting in the orientation and morphology change of the – steps. Therefore, it may be assumed that \(r_{-/+}(\text{Ca}^{2+}) \approx r_{+/-}(\text{Ca}^{2+})\) in order to arrive at the conclusion that as equilibrium is approached, \(R^\text{calcite} = r_{-/+}/r_{+/-}\).

Upon the introduction of \(10^{-3}\) m Mg\(^{2+}\), the etch pits displayed straight, rhombic – steps intersecting at a sharp
−/+ corner (Figs. 3c and 4c). This change in stable step direction may be associated with the attachment or adsorption of Mg$^{2+}$ cations onto kink sites along −/+ steps. It is generally accepted that impurity effects are highly direction-specific with preferential incorporation of ions with radii smaller than Ca$^{2+}$, such as Mg$^{2+}$, into step edges along −/+ directions during calcite growth as a result of kink site structure and coordination geometry (Paquette and Reeder, 1995; Reeder, 1996; Teng et al., 1999; Astilleros et al., 2000; Davis et al., 2000, 2004; Wasylenki et al., 2005a). Similar direction-specific impurity adsorption is plausible in dissolution processes. Mg$^{2+}$ present in the aqueous solutions will attach to −/+ and −/+/+ kink sites in competition with Ca$^{2+}$. Here, the net cation detachment rates at −/+ and −/+/+ kink sites can be described as $r_{n/+/+} = r_{+/+} - r^b_{+/+/(\text{Ca}^{2+})} - r^b_{+/+/+(\text{Mg}^{2+})}$ and $r^{net}_{/+/+} = r_{+/+} - r^b_{+/+/(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}$, assuming that variations in $r_{+/+}$ and $r_{+/+}^{-}$ upon the introduction of Mg$^{2+}$ lead to insignificant change in $R^\perp$. The −/− step morphology change observed in Figs. 3 and 4 may arise from a variation in $R^\perp$. Fig. 7 illustrates the proposed kink attachment contributions to the −/− step morphology change. The cation detachment and backward reaction rates, shown as lines in Fig. 7 are approximated as zero-order and first-order, respectively in cation concentration or $Q^{1/2}$. Under Mg-free far-from-equilibrium conditions, contributions from backward reactions at −/− and −/+ steps are negligible, that is, $R = \frac{r_{+/+}}{r_{+/+}}$ (designated as $R_1$ in Fig. 7) and −/− steps are straight following the [441] and [481] directions, which is consistent with many previous investigations. For Mg-free solutions approaching equilibrium with respect to calcite, as discussed above, backward reaction of Ca$^{2+}$ becomes significant and $R^\perp$ (designated as $R_2$ in Fig. 7) becomes smaller than $r_{+/+}$.

$$\frac{r_{+/+}}{r_{+/+}^{-}} < \frac{r_{+/+}^{-} - r^b_{+/+/(\text{Ca}^{2+})}}{r_{+/+}^{-} - r^b_{+/+/(\text{Ca}^{2+})}} \quad (5)$$

resulting in curvilinear −/− steps along [010] (Figs. 3a and 4a). Upon the addition of sufficient Mg$^{2+}$ ($[\text{Mg}^{2+}] = 10^{-3}$ m in the present study) into near-equilibrium solution, the one again straight, rhombic −/− steps shown in Figs. 3c and 4c suggest an $R^\perp$ value (designated as $R_3$ in Fig. 7) similar to the ratio of $\frac{r_{+/+}}{r_{+/+}^{-}}$ (i.e., $R_1$ in Fig. 7).

$$\frac{r_{+/+}}{r_{+/+}^{-}} = \frac{r^b_{+/+/(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}}{r^b_{+/+(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}} \approx \frac{r_{+/+}}{r_{+/+}^{-}} \quad (6)$$

Combining inequalities (5) and (6) gives

$$\frac{r_{+/+}}{r_{+/+}^{-}} = \frac{r^b_{+/+/(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}}{r^b_{+/+(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}} < \frac{r_{+/+}^{-} - r^b_{+/+/(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}}{r_{+/+}^{-} - r^b_{+/+(\text{Ca}^{2+})} - r^b_{+/+(\text{Mg}^{2+})}} \quad (7)$$

As suggested by the near-equilibrium etch pit morphology in the absence of Mg$^{2+}$, $r^b_{+/+(\text{Ca}^{2+})} / r^b_{+/+(\text{Mg}^{2+})}$. Kink attachment rates and $R^\perp$ would follow the same trend whether this inequality or the equality holds and thus, Fig. 7 only shows the situation of $r^b_{+/+(\text{Ca}^{2+})} / r^b_{+/+(\text{Mg}^{2+})}$. Since $r^b_{+/+(\text{Ca}^{2+})} / r^b_{+/+(\text{Mg}^{2+})}$ and $r_{+/+}^{-} < r_{+/+}^{-}$ (Liang et al., 1996; McCoy and LaFemina, 1997), $r_{+/+}^{-} - r^b_{+/+(\text{Ca}^{2+})} < r_{+/+}^{-} - r^b_{+/+(\text{Mg}^{2+})}$ is predicted. Consequently, in order to satisfy the condition presented in inequality 7, the backward reaction rate of Mg$^{2+}$ at the −/− kink sites has to be smaller than that at the −/+/+ kink sites. Moreover, compared to Ca$^{2+}$, the anisotropy in backward reaction rates for Mg$^{2+}$ at the two counter-propagating kink sites is more significant. The anisotropy of Mg$^{2+}$ attachment rates therefore may play an essential role in the observed morphology change of −/− steps edges.

### 4.2.2. Positive step edges

As to the slight mis-orientation of the +/− steps observed in our Mg-rich solutions ($[\text{Mg}^{2+}] = 10^{-3}$ m), similar mis-orientation has been reported by Arvidson et al. (2006) in their VSI and AFM study of calcite dissolution in NaHCO$_3$ buffered solutions with $0.8 \times 10^{-3}$ m Mg$^{2+}$. They attributed the mis-oriented +/− steps to the severe step pinning along +/− steps upon the introduction of Mg$^{2+}$. In that same study, the addition of Mg$^{2+}$ brought the speed of +/− steps to zero and the expansion of etch pits reflected only the migration of −/− steps. In the present study, however, such severe reduction in +/− step speed in response to the introduction of $10^{-3}$ m Mg$^{2+}$ was not observed at $Q_{calcite} = 0.05$ and $Q_{calcite} = 0.1$ (Figs. 1 and 2 and Table 2) where the AFM images of etch pits were collected (Figs. 3 and 4).

The discrepancy in +/− step kinetics of the present study from the prior work may be due to chemistry differences of the input solutions. The aqueous solutions employed in the study of Arvidson et al. (2006) were Ca-free and therefore were far-from-equilibrium with respect to calcite, although the concentrations of NaHCO$_3$ ($4.4 \times 10^{-3}$ m) and MgCl$_2$ ($0.8 \times 10^{-3}$ m) were comparable to the present study. Mg$^{2+}$ as well as CO$_3^{2−}$ slowed the retreat of the +/− steps by substantially reducing the detachment rates at +/− and +/+/− kink sites (Arvidson et al., 2006; Lea et al., 2001). Under our near-equilibrium conditions, the presence of Ca$^{2+}$ together with CO$_3^{2−}$ and Mg$^{2+}$ complicates the adsorption and dissolution processes. Near-equilibrium dissolution in the absence of Mg$^{2+}$ revealed more significant effects of backward reaction on the −/− steps (Xu et al.,...
Fig. 6. Sketch showing the relation between the ratio of net kink detachment rates and the orientation of – step edges: (a) $R^- \equiv \frac{r_{-/-}}{r_{+/-}} = 1$; (b) $R^- < 1$; (c) $R^- \ll 1$.

Fig. 7. Sketch showing the kink detachment rates ($r_{-/-}$ and $r_{+/-}$), backward reaction rates ($r^{b}_{-/-}$ and $r^{b}_{+/-}$), and the net detachment rate ratios ($R$) of $-/-$ to $+/-$ kink sites. Detachment and backward reaction rates are shown in lines; net detachment ratios are shown in markers.

For Mg-free near-equilibrium calcite dissolution, the $+/+$ angle is $101 \pm 1^{\circ}$ (Figs. 3a and 4a), very close to the typical crystallographically defined angle of $102^\circ$ between [441] and [481] directions. Thus the backward reaction has only a minor effect on $R$ in Mg-free near-equilibrium systems:

$$\frac{r_{+/-} - r^{b}_{+/-}(\text{Ca}^{2+})}{r_{+/-} - r^{b}_{+/-}(\text{Mg}^{2+})} \approx \frac{r_{+/-}}{r^{b}_{+/-}}$$  \hspace{1cm} (9)

Combining inequality 8 and Eq. (9) gives $r^{b}_{+/-}(\text{Mg}^{2+}) \succ r^{b}_{+/-}(\text{Ca}^{2+}) \approx \frac{r_{+/-}}{r^{b}_{+/-}}$ (see Appendix A for proof of this inequality), if $r_{+/-} \prec r^{b}_{+/-}$ is assumed (Liang et al., 1996; McCoy and LaFemina, 1997). Although it is difficult to predict the exact relationship between the backward reaction rates of Mg$^{2+}$ at $+/-$ and $+/-$ kink sites based on our AFM results, it is clear that the attachment of Mg$^{2+}$ has more pronounced influence on $R$ and the resultant $+$ step orientation compared to that of Ca$^{2+}$ under our experimental conditions.

The effects of Mg$^{2+}$ on kink rates and step speeds appear to be contradictory. As discussed above, the decrease in the $+/-$ angle indicates the influence of Mg$^{2+}$ on the backward reaction as well as the net kink detachment rates at the $+/-$ and $+/-$ kink sites. However, at the same saturation state, no significant variation in the $+$ step speed is observed upon the introduction of Mg$^{2+}$, as shown in Fig. 1a and Fig. 2a. One-dimensional KMC simulations were performed to test the sensitivities of step speed and step orientation upon the
variation in kink detachment rates. In our KMC simulations, the total number of sites was set to be 300, the double kink nucleation rate, \( i \), was 0.2, the +/+ kink detachment rate, \( r_{n+/+}^{\text{net}} \), was fixed at 2, and the +/− kink detachment rate, \( r_{n+/−}^{\text{net}} \), varied from 2 to 1.225. These values were chosen based on the previous literature (Liang et al., 1996; Jordan et al., 2001). In order to estimate the effects of the double kink nucleation rate, additional simulations were conducted at \( i = 0.02 \). Further details of the methods and assumptions employed in the KMC simulations can be found in Jordan et al. (2001). By KMC simulations, step slopes (tangent of angle between the orientation of the vicinal step and the close-packed step orientation) and step speeds (perpendicular to the vicinal step orientation) were computed and plotted in Fig. 8 as a function of the net detachment rate ratio \( R^+ \left( \equiv \frac{r_{+/+}^{\text{net}}}{r_{+/−}^{\text{net}}} \right) \).

Fig. 8a and c demonstrate the simulated steps as \( R^+ \) varies from 1 to 0.61 for \( i = 0.2 \) and 0.02, respectively. In Fig. 8b and d, the left axis refers to the percentage decrease in \( V \) as compared to the step speed \( V_0 \) at \( R^+ = 1 \).

As observed from our AFM images, the + step is slightly mis-oriented as a result of the introduction of Mg\(^{2+}\). At \( \Omega_{\text{calcite}} \leq 0.05 \), the +/+ angle decreases from 101±1° for the Mg-free solution to 95 ± 1° for the Mg-rich ([Mg\(^{2+}\)] = 10\(^{-3}\) m) solution, and thus, the average orientation change of one + step is \( \sim 3^\circ \), the tangent of which is \( \sim 0.05 \). For \( i = 0.2 \) (Fig. 8b), a step slope of 0.05 corresponds to an \( R^+ \) of 0.9, where the decrease in step speed is estimated to be less than 3%. Even if \( i \) is tenfold smaller, as shown in Fig. 8d, a step slope of 0.05 corresponds to a 12% decrease of the step speed. Our + step speed values obtained from AFM studies (Figs. 1a and 2a) have an uncertainty of \( \pm 0.3 \) nm/s, which equals approximately 15% of the step speed at \( \Omega_{\text{calcite}} = 0.05 \). In other words, under our experimental conditions where \( \Omega_{\text{calcite}} \leq 0.05 \) and [Mg\(^{2+}\)] varies from 0 to 10\(^{-3}\) m, the AFM is not sensitive enough to detect the inhibitory effects of Mg\(^{2+}\) on the step speed. Therefore, the morphological analysis shows a pronounced influence of Mg\(^{2+}\) on the orientation of + steps to which the AFM is sensitive, whereas the + step speed does not decrease by a statistically significant amount.

5. CONCLUSION

The systematic AFM study presented in this paper reveals the effectiveness of magnesium inhibition on calcite dissolution kinetics as a function of magnesium concentration and solution saturation state. Step speeds obtained from time-sequential AFM images show that at [Mg\(^{2+}\)] ≤ 10\(^{-4}\) m, the inhibitory effects of Mg\(^{2+}\) ions on calcite dissolution are insignificant at 50 °C in our concentration range (\( \Omega_{\text{calcite}} \leq 0.05–0.12 \)). Upon the addition of 10\(^{-3}\) m Mg\(^{2+}\), however, a sudden inhibition from Mg\(^{2+}\) is activated at \( \Omega_{\text{calcite}} \geq 0.2 \) where both + and − steps cease to retreat. No such kinetic change is observed at \( \Omega_{\text{calcite}} \leq 0.1 \). The presence of the \( \Omega \)-switch, a critical undersaturation at which the effectiveness of Mg\(^{2+}\) inhibition changes dramatically, indicates that at [Mg\(^{2+}\)] = 10\(^{-3}\) m and \( \Omega_{\text{calcite}} \geq 0.2 \) the distance between irreversibly adsorbed Mg\(^{2+}\) ions on the calcite surface is less than the critical length, corresponding to a critical \( \Omega_{\text{calcite}} \). Immobile Mg\(^{2+}\) ions adsorbed to the sites at step edges are expected to exert strong inhibitory effects on calcite dissolution processes.

The etch pits formed at calcite (1014) surfaces in the presence of 10\(^{-3}\) m Mg\(^{2+}\) have a unique distorted rhombic shape. Different from etch pits formed in Mg-poor ([Mg\(^{2+}\)] ≤ 10\(^{-4}\) m) near-equilibrium solutions, at [Mg\(^{2+}\)] = 10\(^{-4}\) m, the rounding at the −/− intersection of the etch pit disappears and the −/− corner becomes sharp. The + steps, on the other hand, are slightly mis-oriented compared to the characteristic rhombic etch pits, with a +/+ angle of \( \sim 95^\circ \). The morphology change of etch pits can be interpreted in terms of the variations in net detachment.
rate ratio of counter-propagating kink sites. The addition of \( \text{Mg}^{2+} \) ions into aqueous solutions affects the backward reaction and the net detachment rates at different kink sites, resulting in the orientation and morphology change of \(-\) and \(+\) step edges on the calcite (1014) surface.

The results of magnesium inhibition on calcite dissolution presented above can be used as part of a foundation for the development of robust geochemical models for the prediction of long-term calcite dissolution kinetics in natural water systems. Although relatively closed aqueous solution-calcite systems, especially on long time scales, are near-equilibrium with respect to calcite, the majority of previous experimental studies focused on systems far-from-equilibrium and therefore has not addressed the complexities of foreign ions as inhibitors to near-equilibrium calcite dissolution. According to our AFM results of magnesium inhibitory effects on near-equilibrium calcite dissolution processes, the existence of the \( \Omega \)-switch in magnesium inhibition indicates that the relationship between dissolution kinetics and saturation state is definitely nonlinear in the presence of magnesium impurities. Geochemical modeling that attempts to extrapolate the far-from-equilibrium data to near-equilibrium conditions using a single, and typically linear relationship, between dissolution rate and saturation state may lead to gross errors in the chemical flux due to dissolution near-equilibrium. The kinetics and morphology results as well as magnesium inhibitory mechanisms presented in this paper provide direct and accurate experimental data that demonstrate a need to consider fundamental surface interactions that may lead to highly nonlinear near-equilibrium behavior in natural systems containing significant degrees of chemical complexity.

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APPENDIX A

Given 
\[
\frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} < \frac{r_{+/-}}{r_{+/-}} \tag{A1}
\]

\[
\frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}} \tag{A2}
\]

We claim, and will prove, that 
\[
\frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}}
\]

**Proof.** Combine inequalities (A1) and (A2)

\[
\frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Ca}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}} \tag{A3}
\]

Let 
\[
R_1 = \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}}
\]

\[
\text{Let } R_2 = \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}}
\]

then \( r_{+/-} - r_{+/-(\text{Ca}^{2+})} = R_1 \times (r_{+/-} - r_{+/-(\text{Mg}^{2+})}) \) \hspace{1cm} (A4)

\[
\text{and } r_{+/-} - r_{+/-(\text{Ca}^{2+})} = R_2 \times (r_{+/-} - r_{+/-(\text{Mg}^{2+})}) \hspace{1cm} (A5)
\]

Substitute (A4) and (A5) to inequality (A3), the left hand side of (A3) equals

\[
\frac{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}}{r_{+/-} - r_{+/-(\text{Ca}^{2+})} - r_{+/-(\text{Mg}^{2+})}}
\]

The right side of (A3) equals \( R_1 \)

Inequality (A3) becomes

\[
\frac{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}}{r_{+/-} - r_{+/-(\text{Ca}^{2+})} - r_{+/-(\text{Mg}^{2+})}} < R_1
\]

Divide both sides of (A6) by \( R_1 \)

\[
\frac{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}}{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}} < 1
\]

Multiply both sides by \( r_{+/-} - r_{+/-(\text{Ca}^{2+})} - r_{+/-(\text{Mg}^{2+})} \)

\[
(r_{+/-} - r_{+/-(\text{Ca}^{2+})}) \times \frac{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}}{R_1 \times (r_{+/-} - r_{+/-(\text{Ca}^{2+})}) - R_2 \times r_{+/-(\text{Mg}^{2+})}} < r_{+/-} - r_{+/-(\text{Ca}^{2+})} - r_{+/-(\text{Mg}^{2+})}
\]

Subtract \( r_{+/-} - r_{+/-(\text{Ca}^{2+})} - r_{+/-(\text{Mg}^{2+})} \) from both sides

\[
\frac{R_2 \times r_{+/-(\text{Mg}^{2+})}}{R_1} < -r_{+/-} - r_{+/-(\text{Mg}^{2+})}
\]

Divide both sides by \( -r_{+/-} - r_{+/-(\text{Mg}^{2+})} \)

\[
\frac{R_2}{R_1} > 1
\]

Multiply both sides by \( R_1 \)

\[
R_2 > R_1
\]

Therefore

\[
\frac{r_{+/-} - r_{+/-(\text{Mg}^{2+})}}{r_{+/-} - r_{+/-(\text{Ca}^{2+})}} > \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \tag{A7}
\]

Combine (A7) and (A2)

\[
\frac{r_{+/-} - r_{+/-(\text{Mg}^{2+})}}{r_{+/-} - r_{+/-(\text{Ca}^{2+})}} > \frac{r_{+/-} - r_{+/-(\text{Ca}^{2+})}}{r_{+/-} - r_{+/-(\text{Mg}^{2+})}} \approx \frac{r_{+/-}}{r_{+/-}}
\]

REFERENCES


*Associate editor: Kevin M. Rosso*