

Available online at www.sciencedirect.com



JOURNAL OF CRYSTAL GROWTH

Journal of Crystal Growth 307 (2007) 116-125

www.elsevier.com/locate/jcrysgro

Kinetic inhibition of calcite (104) dissolution by aqueous manganese(II)

Michael D. Vinson^a, Rolf S. Arvidson^a, Andreas Luttge^{a,b,*}

^aDepartment of Earth Science, Rice University, MS 126, Houston, TX 77251-1892, USA ^bDepartment of Chemistry, Rice University, Houston, TX 77251-1892, USA

Received 30 May 2006; received in revised form 18 April 2007; accepted 31 May 2007 Communicated by S. Veesler Available online 15 June 2007

Abstract

This study presents evidence of calcite (104) dissolution inhibition by dissolved manganese(II) through detailed observations of crystal surface morphology. Rates of dissolution have been quantified by direct measurement of surface-normal retreat and etch pit growth at far-from-equilibrium conditions using vertical scanning interferometry. The approach provides new insight into the control that dissolved inorganic carbon (DIC) exerts on manganese inhibition kinetics. Our results show that at 2×10^{-6} molal manganese, the rate of overall calcite dissolution is suppressed to close to zero, but only when sufficient CO_3^{2-} is available in solution. The near arrest of surface-normal dissolution is brought about by the likely reduction in step retreat, inferred through observed variation of etch pit and surface morphology. The inhibition mechanism likely reflects the strong affinity of Mn^{2+} for carbonate ion. In solution, this affinity is expressed by formation of a strong complexing ligand (MnCO₃⁰). On the (104) surface, this affinity may govern formation of a similar surface complex that stabilizes reactive sites, thereby inhibiting step movement and defect nucleation. Comparison with results from other metals suggests that inhibition may be understood in the context of the relative energetics of dehydration versus carbonation reaction steps. © 2007 Elsevier B.V. All rights reserved.

PACS: 07.60.L; 68.43.M; 82.20.Y; 82.60.L

Keywords: A1. Adsorption; A1. Etching; A1. Impurities; A1. Surface processes; B1. Minerals

1. Introduction

The carbonate mineral calcite $(CaCO_3)$ is ubiquitous in sediments, highly reactive over short time-scales, and can serve as both source and sink for metal cations of environmental significance. Adsorption, co-precipitation, and dissolution reactions at the calcite–water interface control the uptake and release of contaminant metals within aqueous environments (e.g., Refs. [1–6]). The interaction of foreign ions with the calcite crystal surface has a significant impact on its overall reactivity. Direct observations of the reacting calcite surface by atomic force microscopy (AFM) [5–11] and vertical scanning interferometry (VSI) [7,11–14] have yielded insight into the role of

E-mail address: aluttge@rice.edu (A. Luttge).

the crystal surface in terms of its interaction with dissolved species during growth and dissolution. In addition to experimental observations, recent molecular dynamics simulations have also constrained surface energies, bonding environments, and mechanisms that influence dissolution, precipitation, and sorption reactions (e.g., Refs. [15–17]).

The influence of impurity adsorption on calcite *dissolution* (e.g., Refs. [4,6,18–20]) has received much less attention compared to that directed at their influence on growth (e.g., Refs. [2,3,5,8,15–17,21–23]). The distinction between growth and dissolution is critical in terms of impurity interaction with the surface. For example, during crystal dissolution, the impurity ion may be only a temporary resident on the surface, whereas in growth impurities may become permanently incorporated within the growing bulk crystal. Incorporation within the crystal lattice involves inner sphere coordination of the adsorbing ion with the surface [17] at energetically favorable sites (i.e., kinks) along step edges [16]. Surface steric geometry and

^{*}Corresponding author. Department of Earth Science, Rice University, MS 126, Houston, TX 77251-1892, USA. Tel.: +1713 348 6304; fax: +1713 348 5214.

^{0022-0248/\$ -} see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jcrysgro.2007.05.059

the distribution of charge in dissolved species further mediate site preference [2,22]. Once coordinated at a step edge, an impurity cation can inhibit growth rate, thereby influencing the development of surface topography [8] and the impurity component's distribution within the growing crystal lattice [3].

Because of fundamental differences between growth and dissolution processes (but cf. Ref. [24]), we anticipate that the interaction of dissolved metal cations such as manganese(II) with the crystal surface during calcite dissolution may differ from those described above for growth. Current work demonstrates that adsorption of impurity cations influences rates of kink and step edge retreat, etch pit development, and surface morphology [6,7,10,11,25]. These relationships are complex, both in terms of the reactivity of individual surface features and the overall rate of crystal dissolution, and are specific to the impurity cation [7,25]. In addition, the effect of a given impurity on calcite dissolution may be dependent on the presence of additional solution components, most notably dissolved carbon species [6,7,11].

The effects of manganese(II) on calcite dissolution and growth are well documented. The results of previous work suggest irreversible chemisorption of manganese(II) on the calcite surface [2,3,21,26], and recent direct observations of the mineral surface itself document strong inhibition of the dissolution process [6,13]. These recent studies also indicate that surface uptake of manganese is favored on specific crystallographic directions (i.e., obtuse $[48\bar{1}]_+$ and $[\bar{4}41]_+$ step edges). Finally, at sufficient concentration, dissolution inhibition may derive from formation of a nascent (Mn,Ca)CO₃ phase [9].

As a general hypothesis, we suggest that the overall potential for inhibition can be understood by reconciling the energies of interactions between aqueous impurities (free ions and ligands), solvent water, and the structure of the crystal surface itself. Our goal is to present support for this hypothesis using the specific example of manganese(II) and calcite dissolution inhibition. We interpret our VSI results of calcite dissolution experiments in light of simple thermodynamic calculations describing the speciation of dissolved components. Because under certain conditions $MnCO_3^0$ is the most abundant species in solution, we also suggest this ion pair may be important mechanistically. Thus, the extent of manganese inhibition must be understood in the context of the collective interaction of manganese and carbonate with the calcite surface.

2. Experimental procedure

High purity reagents were used exclusively in all experiments (solvent water resistivity $\ge 18 \text{ M}\Omega \text{ cm}$), ultra high-purity gases were filtered and humidified prior to their introduction to solution, and solutions were freshly prepared for each experiment. Calcite crystals used for all VSI studies were >99.995% pure Icelandic spar from

Commercial Crystal Laboratories Inc. (Naples, FL, USA). The same material used by Lea et al. [6], Arvidson et al. [7,13] and Vinson and Luttge [11]. The majority of experiments were conducted at $23 \,^{\circ}$ C at pH 8.5–8.9. Supplemental experiments were performed at pH 7.8. Under these conditions, Sjöberg [19] argued that calcite dissolution was essentially a hydration reaction:

$$H_2O + CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}.$$
 (1)

In order to evaluate the role of dissolved carbon, reactant solutions were composed by adding MnCl₂ (standardized by chloride titration, 0.6% precision) to carbonated and CO₂-free solutions. Carbonated solutions contained $Na_2CO_3/NaHCO_3$ (total alkalinity $4.5 \times 10^{-3} eq kg^{-1}$ at pH 8.8 and 0.5×10^{-3} eq kg⁻¹ at pH 7.8, determined by HCl titration) sparged with a CO₂-N₂ gas mixture to fix pH and exclude free oxygen. It has been assumed that all manganese in solution added from MnCl₂ will remain divalent with exclusion of free oxygen. Solutions were allowed to either equilibrate with mixed gas to a pH 8.5-8.9 or were adjusted to pH 7.8 with aliquots of concentrated HCl. The Na₂CO₃/NaHCO₃ (2.2×10^{-3} molal) solutions are referred to in the text as "DIC-buffered". For CO₂-free experiments, NaCl $(4.4 \times 10^{-3} \text{ molal})$ solutions were sparged with pure N_2 to exclude both CO_2 and O_2 , and titrated with NaOH to set final pH. These solutions are referred to as "DIC-free" (the carbon derived from the dissolving crystal is quite small; see Section 4). Saturation states were computed from measured pH and titration alkalinity using MINTEQA2 [27].

Calcite dissolution rate was verified by time-lapse changes in mineral crystal surface topography, as mapped by VSI (MicroXAM MP-8, ADE Phase Shift). The instrument and basic approach have been previously described in detail [11,13,28,29]. Image data were collected using a white light source (vertical resolution $<2 \,\mathrm{nm}$, lateral resolution 0.5–1.2 µm). Calcite single crystal rhombs were cleaved along the (104) surface with a razor blade and mounted immediately to an oriented titanium holder using commercial epoxy resin. Cleavage surfaces typically consisted of broad, flat terraces several hundred microns in area bounded by macro-steps and ledges, the latter a common artifact of the cleaving process. Portions of the sample were masked with silicone to create a reference surface (cf. Refs. [13,28,29]). Samples were allowed to cure for 24 h under vacuum prior to use. The mounted sample was then placed into a fluid flow cell and reactant solution pumped through the cell (200 mL h^{-1}) for a fixed amount of time. The sample mount was then removed from the flow-cell, and the change in surface topography subsequently measured in the interferometer. The sample was then returned to the flow cell and the process repeated. The change in mean surface height over time gives the rate of reaction. Rates were measured in this fashion at total manganese concentrations from 0 to 2.0×10^{-6} molal for a total of 16h (DIC-free) and 20-24h (DIC-buffered). Rates of overall surface-normal retreat were reproducible within a factor of 2.

2.1. Calcite (104) surface

In Sections 3 and 4, we shall characterize steps on calcite (104) according to convention and refer to symmetry distinctions between nonequivalent $[48\overline{1}]$ or $[\overline{4}41]$ step pairs by denoting with (+) versus (-) subscripts (i.e., $[48\bar{1}]_+, [\bar{4}41]_+$ and $[48\bar{1}]_-, [\bar{4}41]_-$). Specifically, positive $([48\overline{1}]_+, [\overline{4}41]_+)$ step edges form an obtuse angle with the surface, whereas negative ($[48\overline{1}]_{-}, [\overline{4}41]_{-}$) step edges are acute with respect to the (104) surface. These crystallographic differences produce an anisotropic distribution of velocities between (+) versus (-) steps, observed under both growth and dissolution [30]. In pure water, the velocity ratio of (+) to (-) steps ranges from 1.5 to 2.3 [6]. Current work shows this ratio is highly sensitive to the ratio of framework ions in solution [12], the distance from equilibrium [31], and the concentration of impurities [5-7,11,32]. It has also been shown conclusively that variation in step velocity ratio during dissolution produces diagnostic changes in etch pit morphology; velocity distributions along a given step can also be related to kink formation and propagation dynamics [6,7,11,14]. We shall exploit these relationships by using etch pit morphology as an indicator of the relative velocities of (+) versus (-)steps.

3. Results

All reacted calcite (104) surfaces exhibited etch pits of variable distribution, development, and morphology, properties that were sensitive to the solution chemistry imposed at each experimental condition. Etch pits either terminated at a single point or were flat-bottomed (cf. Ref. [33]). These variations were also influenced by dissolved carbon (Na₂CO₃/NaHCO₃ DIC-buffer versus DIC-free NaCl solution) and manganese concentration (Fig. 1). Maximum observed etch pit depths over the course of all experiments decreased systematically from over 500 nm in DIC-free solutions to less than 20 nm in DIC-buffered solutions at the highest manganese concentration $(2.0 \times 10^{-6} \text{ molal})$. As detailed below, rates of overall dissolution (surface-normal retreat) and etch pit expansion (with respect to both depth and diameter) were strongly dependent on manganese and DIC concentrations as well as pH. No evidence of secondary surface phase growth was observed in any of our experiments.

3.1. DIC-free solutions

The VSI data obtained for DIC-free experiments $(4.4 \times 10^{-3} \text{ molal NaCl})$ show no reduction in dissolution rate as a function of manganese concentration (Table 1). Surprisingly, the surface normal retreat rate at 2.0×10^{-6} molal manganese is actually a factor of 3 greater than

that observed in manganese-free solutions. Manganese concentrations $\leq 2.0 \times 10^{-6}$ molal in DIC-free solutions had no influence on etch pit development throughout 16 h of dissolution, and results are otherwise consistent with previous work in manganese-free solutions (e.g., Ref. [30]). All etch pits were rhombic in plan view with euhedral corners and faces (Fig. 1A). Etch pits, whose deepest interior point was a well-defined apex (thus resembling an inverted pyramid), exhibited steep faces composed of (–) steps countered by gently sloping faces of (+) steps. Apices of pyramidal etch pits were thus always located nearer to the [48 \overline{I}]_/[$\overline{4}$ 41]_ corner (cf. Figs. 1A and 2).

3.2. DIC-buffered solutions ($pH \sim 8.8$, $4.5 \times 10^{-3} eq kg^{-1}$ total alkalinity)

In contrast to the results obtained at DIC-free conditions, dissolution rates in carbonated solutions were strongly reduced by manganese addition, but only at pH > 8.5. The rate observed in manganese-free solutions at pH \sim 8.8 (10^{-11.1} mol cm⁻² s⁻¹) agrees with dissolution rates in previous work [11,13]. Dissolution rates measured by surface-normal retreat drop by an order of magnitude between 0.5 and 1.5×10^{-6} molal manganese (Table 1; Fig. 3). Increase of manganese concentration to 2.0×10^{-6} molal results in a dissolution rate of zero within the error of measurement over the 24-h reaction interval. Addition of manganese to DIC-buffered solutions strongly influenced the development of etch pits and other dissolution features even at the lowest concentration $(0.5 \times$ 10^{-6} molal). Change in etch pit morphology became more pronounced with added manganese, which contrasted strongly with that observed in DIC-free experiments (Fig. 1). For example, with progressive increase in manganese concentration, etch pit apices developed much closer to the $[48\overline{1}]_+/[\overline{4}41]_+$ corner (cf. Figs. 1B to A and 2). Further increase in manganese concentrations to $\geq 1.0 \times 10^{-6}$ molal produced flat-bottomed etch pits characterized by shield-like morphologies with concave $[48\overline{1}]_+/[\overline{4}41]_+$ sloping faces (Fig. 4). At manganese concentrations $\ge 1.5 \times 10^{-6}$ molal, etch pit nucleation and growth were in effect completely arrested. Fig. 5 demonstrates a time-lapse progression of VSI data characteristic of surfaces observed at 2.0×10^{-6} molal manganese. After 21 h of reaction, only sparse, heterogeneous distributions of severely undersized etch pits separated by broad flat terraces were observed.

3.3. DIC-buffered solutions (pH 7.8, $0.5 \times 10^{-3} eq kg^{-1}$ total alkalinity)

Results obtained for pH \sim 7.8 DIC-buffered solutions contrast strongly with those observed at pH > 8.5, but more closely resemble those found under DIC-free conditions (Fig. 6). Rates of surface-normal retreat at 1.5×10^{-6} molal manganese at pH \sim 7.8 match within error to those at zero



Fig. 1. Three-dimensional VSI images of etch pits characteristic of calcite dissolution at $[Mn]_{Total} = 0.0, 0.5, 1.5, 2.0 \times 10^{-6}$ molal. Images in (A) are characteristic of dissolution under DIC-free conditions. Images in (B) are characteristic of DIC-buffered conditions. These images illustrate the variation in dissolution anisotropy between DIC-free and -buffered conditions and the influence of added MnCl₂ at each condition. Step retreat along obtuse (+) [48 \overline{I}]₊ and [$\overline{4}$ 41]₊ directions indicated by arrows in each frame. Etch pit depths in (A) are >400 nm. Depths in (B) vary from >200 to <20 nm, going from [Mn]_{Total} = 0–2.0 × 10⁻⁶ molal. Field of view is approximately 160 × 125 µm at 50 × magnification.

manganese (Table 1; Fig. 3). Etch pit morphology and growth were also similar to those formed at DIC-free conditions.

4. Discussion

Our purpose in independently varying total dissolved manganese and carbon in these experiments was to yield insight into the individual roles of these components (Table 2). In the case of experiments in which CO_2 was

eliminated from the input solution, the only source of dissolved carbon would have been from the dissolving mineral itself. This contribution is below detection in terms of changes in pH and titration alkalinity: based on cell residence time, flow rate, and observed dissolution rate we have estimated DIC concentration at $\sim 4 \times 10^{-7}$ molal, under our "DIC-free" conditions. Thus, for a given manganese concentration, we have measured rates as carbonate ion concentration varied from $\sim 1 \times 10^{-8}$ to $\sim 1 \times 10^{-4}$ molal.

Experiments	$[Mn]_{Total}$ ($\times 10^{-6}$ molal)	рН <i>T</i> (°С)		$-\log_{10} R_{\rm SNR} \ ({\rm mol} \ {\rm cm}^{-2} {\rm s}^{-1})$	$-\log_{10} R_{\text{etch pit}} (\text{mol}\text{cm}^{-2}\text{s}^{-1})$	
2.2×10^{-3} molal 1	Na ₂ CO ₃ -NaHCO ₃ solutions					
la	0.00	8.79	23.1	$11.09 \pm 44\%$	$11.16 \pm 19\%$	
1b	0.50	8.77	22.5	$11.69 \pm 20\%$	$11.46 \pm 29\%$	
1c	1.00	8.85	22.5	$12.52 \pm 47\%$	$11.79 \pm 37\%$	
1d	1.50	8.79	23.4	$12.77 \pm 26\%$	$13.38 \pm 68\%$	
1e	2.00	8.79	22.8	0	$12.85 \pm 60\%$	
2a	0.00	7.79	24.6	$10.73 \pm 15\%$	n/m	
2d	1.50	7.86	22.7	$10.70 \pm 21\%$	n/m	
4.4×10^{-3} molal 1	NaCl solutions					
3a	0	8.77	22.3	$10.94 \pm 45\%$	n/m	
3b	0.5	8.66	22.4	$10.94\pm61\%$	n/m	
3d	1.5	8.57	22.7	$10.55 \pm 30\%$	n/m	
3e	2.0	8.70	23.2	$10.44 \pm 23\%$	n/m	

Table 1Results of calcite (104) dissolution experiments

Rates of overall dissolution, R_{SNR} , and etch pit growth, $R_{etch pit}$, quantified from VSI measurements. Measured temperature and pH are also given. n/m: rate was not measured.



Fig. 2. Schematic illustration of the morphology of etch pits as a function of the relative velocities v of (+) and (-) steps. At lower right, in the etch pit forming at a single spiral dislocation, v_+ dominates over v_- , resulting in low angle vicinal faces composed of (+) step edges and steep vicinal faces composed of (-) edges. At upper left (e.g., under inhibition of (+) steps), v_- dominates, transposing the deepest point of the inverted asymmetric pyramid, and creating the opposite pattern (steep (+) vicinal faces and shallow (-) faces). If velocities are equal, interior angle created (ϕ) will be 180° . These relationships (in growth hillocks) are discussed in Ref. [31].

Our results provide evidence of complex, site-specific inhibition, and can be summarized as follows:

(1) In solutions containing abundant carbonate ion $(\sim 0.1 \times 10^{-3} \text{ molal} \text{ and above; Table 2})$, introduction



Fig. 3. Rates of (104) overall dissolution, R_{SNR} , versus manganese concentration for all experimental runs reported in Table 1. Rates are quantified from VSI measurements of crystal surface average retreat normal to a surface datum for each experimental condition.

of manganese at concentrations as low as 0.5×10^{-6} molal strongly depresses calcite dissolution. At manganese concentrations of 2.0×10^{-6} molal, dissolution is effectively arrested. Based on the progressive change in etch pit morphology (Fig. 2), this reduction in bulk rate is associated with a greater reduction in positive (v_{+}) versus (v_{-}) step velocities.

(2) As carbonate ion concentrations are decreased to $\sim 1 \times 10^{-6}$ molal, via reductions in pH and alkalinity, the dissolution rate becomes invariant with respect to manganese concentration.



Fig. 4. Three-dimensional VSI images of (104) etch pit deformation over time at [Mn]_{Total} = 1.0×10^{-6} molal, under DIC-buffered conditions. Each frame represents the same area of the (104) surface at a different time step within the experiment. Time interval is noted within each frame. White arrow indicates the location of the same etch pit at each time interval. Field of view is approximately $150 \times 120 \,\mu m$.







Fig. 5. Three-dimensional VSI images of inhibited (104) etch pit growth at [Mn]_{Total} = 2.0×10^{-6} molal, under DIC-buffered conditions. Each frame represents the same area of the (104) surface at a different time step within the experiment. There was no measurable surface normal retreat at these conditions. White arrow indicates the location of the same etch pit at each time interval. Field of view is approximately $150 \times 120 \,\mu\text{m}$.



Fig. 6. Three-dimensional VSI images of (104) etch pit growth at $[Mn]_{Total} = 1.5 \times 10^{-6}$ molal and DIC-buffered conditions after >20 h of dissolution. The top frame is an etch pit characteristic of dissolution at pH~7.8. The bottom frame illustrated etch pits characteristic of dissolution at pH~8.8. No inhibition is observed under DIC-buffered conditions at pH~7.8. This is in contrast to the strong inhibition observed under DIC-buffered conditions at pH~8.8. Field of view is approximately $160 \times 125 \,\mu\text{m}$ at $50 \times$ magnification.

(3) In solutions where carbonate ion concentration is decreased to extremely low values ($\leq 10^{-6}$ molal; Table 2), increase in manganese concentration to 2.0×10^{-6} molal results in a three-fold *increase* in dissolution rate, reflecting an increase in the obtuse (v_+) relative to acute (v_-) step velocities, opposite the pattern observed in 1).

We discuss the probable origin and implications of these results below.

4.1. DIC-free solutions

The fact that manganese addition to a DIC-free solution increases calcite dissolution rate can be explained by the surface interaction typical of cations that form strong hydration shells. For example, molecular dynamics model-

ing of calcite crystal growth by Kerisit and Parker [17] demonstrated that divalent cations which form strong bonds with oxygen in solvent water are more likely to form inner sphere coordination with the oxygens of crystal surface water, thus disrupting diffusion in the surface hydration layer. Similarly, de Leeuw [16] argued that a control on impurity uptake along steps at the calcite surface reflects "the relative strengths of the interactions between water and impurity ions at the surfaces compared to the calcium ions," thereby influencing surface stability and impurity cation affinity. These arguments should also apply to dissolution reactions. A key property mediating the behavior of ions in solution is the enthalpy of hydration, ΔH_{hyd} , which is a function of ionic charge and effective radius (r_{eff}). Mn²⁺ has a $r_{\text{eff}} = 83 \text{ pm}$ for six-fold coordination [34], giving rise to a hydration enthalpy $\Delta H_{\rm hyd} = -1845.6 \,\mathrm{kJ \,mol^{-1}}$ [35]. The $\Delta H_{\rm hyd}$ of $\mathrm{Mn^{2+}}$ is ~14% greater than that for $\mathrm{Ca^{2+}} \Delta H_{\rm hyd} = -1592.4 \,\mathrm{kJ \,mol^{-1}}$ [35]). The higher $\Delta H_{\rm hyd}$ of $\mathrm{Mn^{2+}}$ over that of Ca²⁺ adsorption possibly creates a competition for water molecules in the calcite surface diffusion layer, thereby resulting in an effective transfer of water away from surface calcium during manganese adsorption. This would allow Mn²⁺ to complete its primary hydration sphere. Manganese hydration would then cause surface destabilization. Specifically, thermochemical properties of Mn^{2+} produce an exchange constant of $k_{\mathrm{ex}} \approx 2.15 \times 10^7 \,\mathrm{s}^{-1}$ for water in its primary hydration sphere and a measured Mn–OH₂ bond length of \sim 191 pm [36]. By comparison, the bond lengths of the Ca²⁺_{calcite}–OH₂ are longer and thus weaker, at 237–238 pm [37]. In addition, the residence time of a water molecule in the Ca²⁺ primary hydration shell (Ca²⁺_(aq): $k_{ex} \approx 6.9 \times 10^8 \text{ s}^{-1}$ [36]) is about an order of magnitude less than that of Mn²⁺. Therefore, the slow rate with which Mn²⁺ exchanges water permits it to spend sufficient time on the surface (relative to surface diffusion) to destabilize (104) surface water, and ultimately enhance dissolution in DIC-free solutions.

4.2. DIC-buffered solutions

An important result of this study is the apparent dependence of dissolution inhibition on the presence of carbonate in solution. This dependency of manganese(II) inhibition effectiveness on dissolved carbon species is not unexpected and is anticipated by our previous work. For example, the addition of strontium [11] and magnesium [7] brings about a far greater reduction in step velocities and overall dissolution rate of calcite in the presence of dissolved carbon. Dissolved carbon (either as carbonate or bicarbonate) is also a significant inhibitor even in the absence of other dissolved cations (including calcium) [6]. The relevant work of Stumm and coworkers [1,38] has shown that the magnitudes of surface complex formation constants are correlative with those of the corresponding homogeneous system. These relationships provide a means of characterizing carbonate surface dissolution reactions in

log_{10} concentration (molal)											
Experiments	$Mn^{2+}_{(aq)}$	MnCO ₃ ⁰	MnHCO ₃ ⁺	$MnOH^+$	H ₂ CO _{3 (tot)}	HCO_3^-	CO_{3}^{2-}	$\log_{10} SI_{rhodochrosite}$			
la	_	_	_	_	-4.90	-2.39	-3.81	_			
1b	-7.04	-6.40	-8.26	-8.96	-4.90	-2.39	-3.81	-0.09			
1c	-6.74	-6.09	-7.96	-8.66	-4.90	-2.39	-3.81	0.21			
1d	-6.56	-5.92	-7.78	-8.48	-4.90	-2.39	-3.81	0.38			
1e	-6.44	-5.79	-7.66	-8.36	-4.90	-2.39	-3.81	0.51			
2a	_	_	_	_	-4.90	-3.44	-5.89	-			
2d	-5.84	-7.29	-8.11	-8.81	-4.90	-3.44	-5.89	-0.988			
3a	_	_	_	_	-9.35	-6.88	-8.34	-			
3b	-6.31	-10.19	-12.02	-8.27	-9.35	-6.88	-8.34	-3.89			
3d	-5.83	-9.34	-11.15	-7.81	-8.94	-6.49	-7.96	-3.04			
3e	-5.71	-9.11	-10.91	-7.69	-8.82	-6.38	-7.86	-2.81			

Table 2 Calculated concentrations of DIC species in solution and saturation index (SI) for rhodochrosite based on our experimental conditions

Saturation index is defined by the reaction, $SI = a(Ca^{2+})a(CO_3^{2-})/K_{rhodochrosite}$, where *a* is the activity of the ion and $K_{rhodochrosite} = 10^{-11}$ is the solubility product.

a constant capacitance model (e.g., Refs. [39,40]). Here, the calculated distribution of electrolyte species in the homogeneous system (HCO_3^- , CO_3^{2-} , OH_2^- , Mn^{2+} , $MnCO_3^0$, $MnHCO_3^+$, and $MnOH^+$) can be used to provide insight to the interaction of manganese with the dissolving calcite surface.

The distribution, with respect to pH, of metal-carbonate in solution can be compared with the efficiency of manganese as an inhibitor of calcite dissolution. Homogenous solution speciation calculations using MINTEQA2 [27] (shown in Fig. 7) indicate that at pH 8.8, $MnCO_3^0$ forms > 80% of total dissolved manganese, with the bulk of the remainder as free Mn^{2+} . In contrast, at pH 7.8, $MnCO_3^0$ is ~4% of total dissolved manganese, versus 95% as Mn^{2+} . The fractions of both $MnOH^-$ (<0.3%) and MnHCO₃⁺ (~1%) are comparatively quite small. The significance of this pattern is that the distribution of dissolved manganese strongly reflects the stability of the carbonate ion pair. The calculated K_{assoc} for MnCO₃⁰ $(\log K_{\rm assoc} = 4.70)$ is 2.5 orders of magnitude greater than that of MnHCO₃⁺ (log $K_{assoc} = 1.29$). These computed K_{assoc} values are consistent with the trend of published K_{assoc} constants, but vary from those of Langmuir [41] and Nordstrom et al. [42]. Our evidence for the significance of $MnCO_3^0$ stability to inhibition is consistent with recent work by Rouff et al. [43,44]. Their careful batch adsorption and X-ray spectroscopy work demonstrate that Pb(II) adsorption to calcite (104) varies with pH, resulting in greater Pb(II) uptake under conditions that favored higher $PbCO_3^0$ bulk solution concentrations. Similarly, our data demonstrate greater dissolution inhibition under conditions favoring higher bulk MnCO₃⁰ concentrations (cf. Figs. 3 and 7).

With the recognition of the significance of $MnCO_3^0$, we suggest that it may be relevant to the stability of the analogous surface complex, and this complex may in turn play a central mechanistic role in inhibition of calcite



Fig. 7. Distribution of aqueous manganese–carbonate species in DICbuffered homogeneous solution at 1.5×10^{-6} molal manganese versus pH (T = 23 °C) and calculated SI_{rhodochrosite}, as calculated by MINTEQA2. Both MnCO₃⁰ and Mn²⁺_(aq) vary from 0% to 99.9% across the pH range. By comparison, MnHCO₃⁺ reaches only 1.4% at its maximum and MnOH⁺ is less than 0.4% (not shown) across the pH range given.

dissolution. Although surface complexation can provide insight into the likely surface species distribution and equilibrium reactions involved, it should be emphasized that the theory itself does not account for any site-specific kinetic effect. We assume that the ratio of cation to anion surface sites is 1:1. According to the model of Van Cappellen et al. [39], at $7.8 \le pH \le 8.8$, the majority of active surface sites would be $>CO_3^-$ and $>CaOH_2^+$, both having surface concentrations of approximately $\sim 10^{-5} \text{ mol m}^{-2}$ [39]. In terms of manganese interaction with the surface, the distribution of surface complexes can be described by six relevant reactions (Table 3). At the moment, there is insufficient data to evaluate these reactions on a thermodynamic basis. However, the fact

Table 3 Selected calcite surface complex reactions in the system $MeCO_3(s)-H_2O-CO_2$

 $\begin{array}{ll} (1) > & CaOH_2^+ + MnCO_3^0 = > CaCO_3Mn^+ + H_2O \\ (2) > & CaHCO_3^0 + Mn^{2+} = > CaCO_3Mn^+ + H^+ \\ (3) > & CO_3H^0 + Mn^{2+} = > CO_3Mn^+ + H^+ \end{array}$

(4) $> CO_3Mn^+ + HCO_3^- = > CO_3MnCO_3^- + H^+$

(5) $> CO_3Mn^+ + H_2O = > CO_3MnOH^0 + H^+$

(6) $> CO_3MnOH^0 + HCO_3^- = > CO_3MnCO_3^- + H_2O$

Surface reactions (1)–(6) expected for DIC-buffered solutions of $7.8 \le pH \le 8.8$, T = 23 °C, ionic strength = 0.004.

that no change in rate is observed at low carbonate ion concentrations despite abundant free Mn^{2+} suggests that reaction (3) does not play a strong mechanistic role in terms of rate inhibition. Reactions (4)–(6) involve stepwise reactions of HCO_3^- with surface $>CO_3^-$ that has previously been bound with Mn^{2+} . Although the product sites of reactions (4)–(6) should be stable at a pH>7 [39] regardless of manganese concentration; because bicarbonate alone does not appear to exert much inhibition (i.e., at pH 7.8), it seems unlikely that reactions (4)–(6) would be important for inhibition.

We propose that reaction (1) may be mechanistically the most significant: despite the neutral charge on $MnCO_3^0$. Reaction (1) provides a means of surmounting the barrier imposed by dehydration. Formation of the metal carbonate complex in solution would involve the loss of at least some water molecules from the cation's first hydration shell, and thus reduce the energy penalty involved in subsequent surface attachment. In this way, carbonate ion may catalyze exchange of inner sphere solvent water, an avenue not available in reaction (2) (for example Table 3). This argument is supported by the work of Sternbeck [45], who concluded that dehydration of $MnCO_2^0$ on > MnHCO₃⁰ and > MnCO₃⁻ sites was the rate determining process for rhodochrosite growth. Similarly, Terjesen et al. [18] demonstrated that adsorption of Cu(II) to calcite decreased with decreasing solution pH, indicating that Cu(II) adsorbed mainly as CuHCO $_3^+$ or CuCO $_3^0$.

Alternatively, if successive stepwise reactions such as (4)–(6) are indeed important, especially at pH~8.8, the surface would require an induction period of some time before adsorption imposed a significant influence on the dissolution process. An expectation consistent with our assumption maintains that the strength of inhibition would increase with reaction time as the surface becomes stabilized. The lack of new etch pit formation after the initial stages of runs 1d–1e at $> 10^{-6}$ molal manganese (Fig. 5) supports this argument. Our results are analogous to those of Terjesen et al. [18], who found that cation adsorption had an increasingly stronger influence on inhibition over time, with little to no influence at the onset of an experiment. They concluded that adsorbed impurity cations increase surface carbonate ion concentration thus

increasing the rate of the reverse reaction and causing the formation of a protective adsorption layer [18]. The protective surface layer concept also supports our observations of a cessation in new etch pit nucleation at > 6 h total reaction time for DIC-buffered runs 1d–1e (Table 1). The lack of defect nucleation is important if we consider that surface-normal dissolution occurs through the retreat of monolayer steps across the crystal surface [11,46,47]. Absence of defect nucleation and lack of etch pit coalescence may effectively eliminate new step production. Coupled with strong inhibition of etch pit growth, this result would lead to the formation of broad, atomically flat, energetically stable terraces, thereby eliminating surface-normal dissolution.

However, we cannot unequivocally reconcile Terjesen et al.'s [18] concept of a protective surface adsorption layer with the site-specific nature of our observations. Consistent with recent AFM results [6], the pattern of etch pit morphology indicates that added manganese preferentially inhibits retreat of (+) versus (-) steps as etch pits develop (Figs. 1B and 4). While suppression of v_{\pm} is more obvious at low manganese concentrations, there is also clear evidence that both v_+ and v_- are inhibited, based on the appearance of severely undersized pits characteristic of higher manganese concentrations (Fig. 5). Reduced v_{\pm} and v_{-} caused by the reverse reaction along both (+) and (-) steps might be the essential factor leading to complete arrest of overall dissolution. By comparison, complete overall inhibition is not observed in other recent divalent cation adsorption studies (i.e., strontium and magnesium) even at metal concentrations orders of magnitude above those used here. For example, observations of dissolution inhibition by 800×10^{-6} molal magnesium [7] or 250×10^{-6} molal strontium [11] suggest that their overall influence on calcite dissolution is relatively minor compared to that of 2.0×10^{-6} molal manganese. Results of molecular dynamics modeling have shown the affinity of magnesium for the calcite surface is significantly larger than that of strontium [17]. Following the same reasoning, thermochemical relationships suggest that manganese would have a strong calcite surface affinity. For these ions, the extent of actual inhibition may reflect a balance between the penalty of dehydration (i.e., $Mg_{(aq)}^{2+} > Mn_{(aq)}^{2+} \gg Ca_{(aq)}^{2+} > Sr_{(aq)}^{2+}$) versus the benefit derived from carbonation, regardless of whether the metal–oxygen bond involves a lattice oxygen or solution component. In the case of manganese, the stability provided by a carbonate bond would be greater than that offered by hydration, resulting in essentially irreversible chemisorption of manganese [2], but only in the presence of significant dissolved carbonate (i.e., pH>8.5 in our experiments). The important observation here is that, contrary to strontium and magnesium adsorption where the formation of surface carbonate complexes is more selective because of preferential hydration, irreversible manganese adsorption apparently occurs along both the (+) and (-) step edges, thus facilitating greater inhibition.

5. Conclusions

This study demonstrates that the extent of calcite dissolution inhibition caused by adsorption of dissolved impurity cations depends critically on the carbonate ion concentration. We suggest that this relationship may reflect a key mechanistic role of the metal-carbonate complex in inhibition. For DIC-buffered bulk solutions, the $MnCO_2^0$ complex constitutes a major percentage of total dissolved manganese at pH > 8.5. We propose that this complex could also be kinetically important in terms of reducing the barrier to dehydration and surface attachment, thereby providing a pathway to overall dissolution inhibition. At pH < 8.5 or at DIC-free conditions this pathway is absent, and dehydration (or partial dehydration) of Mn^{2+} on the surface does not occur. Molecular dynamics simulations may be needed to reconcile the precise pathway of inhibition. However, our qualitative model explains experimental observations and fits the observed patterns of dissolution inhibition presented in other work. Employing a model that directly relates the stabilities of homogeneous manganese-carbonate complexes to overall calcite dissolution inhibition has allowed us to suggest potentially significant inhibition pathways. If correct, this would permit recognition of a systemic behavior of metal impurities with respect to the calcite surface, leading to a generalized model for their interaction with carbonate minerals and their role in dissolution kinetics.

Acknowledgements

The authors gratefully acknowledge Rice University as well as funding provided by the Department of Energy (DOE #DE FG07-01ER63295), the Office of Naval Research (ONR), the Department of Defense Multidisciplinary University Research Initiative (MURI) program, and the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0118007. The authors also wish to give thanks to two anonymous reviewers whose comments and criticism improved an earlier draft of this paper.

References

- [1] L. Sigg, W. Stumm, Colloids Surf. 2 (1981) 101.
- [2] J.M. Zachara, C.E. Cowan, C.T. Resch, Geochim. Cosmochim. Acta 55 (1991) 1549.
- [3] J. Paquette, R.J. Reeder, Geochim. Cosmochim. Acta 59 (1995) 735.
- [4] A. Gutjahr, H. Dabringhaus, R. Lacmann, J. Crystal Growth 158 (1996) 310.
- [5] K.J. Davis, P.M. Dove, J.J. De Yoreo, Science 290 (2000) 1134.
- [6] A.S. Lea, J.E. Amonette, D.R. Baer, Y. Liang, N.G. Colton, Geochim. Cosmochim. Acta 65 (2001) 369.
- [7] R.S. Arvidson, M. Collier, K.J. Davis, M.D. Vinson, J.E. Amonette, A. Luttge, Geochim. Cosmochim. Acta 70 (2006) 583.
- [8] J.M. Astilleros, C.M. Pina, L. Fernandez-Diaz, A. Putnis, Chem. Geol. 193 (2003) 93.
- [9] A.S. Lea, T.T. Hurt, A. El-Azab, J.E. Amonette, D.R. Baer, Surf. Sci. 524 (2003) 63.

- [10] S.J. Freij, A. Godelitsas, A. Putnis, J. Crystal Growth 273 (2005) 535.
- [11] M.D. Vinson, A. Luttge, Am. J. Sci. 305 (2005) 119.
- [12] R.S. Arvidson, K.J. Davis, A. Luttge, EOS Transactions, AGU 84(46), Fall Meeting Supplement, 2003, Abstract B12C-0793.
- [13] R.S. Arvidson, I.E. Ertan, J.E. Amonette, A. Luttge, Geochim. Cosmochim. Acta 67 (2003) 1623.
- [14] R.S. Arvidson, K.J. Davis, M. Collier, J.E. Amonette, A. Luttge, in: R.B. Wanty, R.R.P. Seal (Eds.), Proceedings of the 11th Symposium on Water–Rock Interactions, Saratoga Springs/Balkema Publishers, New York, 2004, p. 721.
- [15] K. Sangwal, J. Crystal Growth 203 (1999) 197.
- [16] N.H. de Leeuw, J. Phys. Chem. B 106 (2002) 5241.
- [17] S. Kerisit, S.C. Parker, J. Am. Chem. Soc. 126 (2004) 10152.
- [18] S.G. Terjesen, O. Erga, G. Thorsen, A. Ve, Chem. Eng. Sci. 74 (1961) 277.
- [19] E.L. Sjöberg, Stockholm Contrib. Geol. 32 (1978) 1.
- [20] D. Buhmann, W. Dreybrodt, Chem. Geol. 64 (1987) 89.
- [21] N.E. Pingitore Jr., M.P. Eastman, M. Sandidge, K. Oden, B. Freiha, Mar. Chem. 25 (1988) 107.
- [22] E.J. Elzinga, R.J. Reeder, Geochim. Cosmochim. Acta 66 (2002) 3943.
- [23] A.A. Rouff, E.J. Elzinga, R.J. Reeder, Environ. Sci. Technol. 38 (2004) 1700.
- [24] P.M. Dove, N. Han, J.J. De Yoreo, PNAS 102 (2005) 15357.
- [25] M.B. Hay, R.K. Workman, S. Manne, Langmuir 19 (2003) 3727.
- [26] M. Temmam, J. Paquette, H. Vali, Geochim. Cosmochim. Acta 64 (2000) 2417.
- [27] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQA2/ PRODEFA2, A Geochemical Assessment Model for Environmental Systems, Version 3.0 US EPA, Athens, GA, 1991, p. 106.
- [28] A. Luttge, E.W. Bolton, A.C. Lasaga, Am. J. Sci. 299 (1999) 652.
- [29] A. Luttge, U. Winkler, A.C. Lasaga, Geochim. Cosmochim. Acta 67 (2003) 1099.
- [30] P.E. Hillner, S. Manne, A.J. Gratz, P.K. Hansma, Geology 20 (1992) 359.
- [31] H.H. Teng, P.M. Dove, J.J. De Yoreo, Geochim. Cosmochim. Acta 63 (1999) 2507.
- [32] H.H. Teng, P.M. Dove, C.A. Orme, J.J. De Yoreo, Science 282 (1998) 724.
- [33] I.N. MacInnis, S.L. Brantley, Geochim. Cosmochim. Acta 56 (1992) 1113.
- [34] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
- [35] C.S.G. Phillips, R.J.P. Williams, Inorganic Chemistry 1, Oxford University Press, New York, 1965, p. 161.
- [36] D.T. Richens, The Chemistry of Aqua Ions, Wiley, Chichester, 1997, 592pp.
- [37] S. Kerisit, S.C. Parker, J.H. Harding, J. Phys. Chem. B 107 (2003) 7676.
- [38] P.W. Schindler, W. Stumm, in: W. Stumm (Ed.), Aquatic Surface Chemistry, Wiley, New York, 1987, p. 83.
- [39] P. Van Cappellen, L. Charlet, W. Stumm, P. Wersin, Geochim. Cosmochim. Acta 57 (1993) 3505.
- [40] O.S. Pokrovsky, J. Schott, Environ. Sci. Technol. 36 (2002) 426.
- [41] D. Langmuir, in: E.A. Jenne (Ed.), Modeling in Aqueous Systems, American Chemical Society, Washington, DC, 1979, p. 353.
- [42] D.K. Nordstrom, L.N. Plummer, D. Langmuir, E. Busenburg, H.M. May, B.F. Jones, D.L. Parkhurst, Chemical Modeling of Aqueous Systems II, Washington, DC, 1990, p. 398.
- [43] A.A. Rouff, E.J. Elzinga, R.J. Reeder, N.S. Fisher, Geochim. Cosmochim. Acta 69 (2005) 5173.
- [44] A.A. Rouff, R.J. Reeder, N.S. Fisher, J. Colloid Interface Sci. 286 (2005) 61.
- [45] J. Sternbeck, Geochim. Cosmochim. Acta 61 (1997) 785.
- [46] Y. Liang, D.R. Baer, J.M. McCoy, J.E. Amonette, J.P. LaFemina, Geochim. Cosmochim. Acta 60 (1996) 4883.
- [47] A.C. Lasaga, A. Luttge, Science 291 (2001) 2400.