Mineral Growth

International Edition: DOI: 10.1002/anie.201604357
German Edition: DOI: 10.1002/ange.201604357

A Microkinetic Model of Calcite Step Growth

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Abstract: *In spite of decades of research, mineral growth models based on ion attachment and detachment rates fail to predict behavior beyond a narrow range of conditions. Here we present a microkinetic model that accurately reproduces calcite growth over a very wide range of published experimental data for solution composition, saturation index, pH and impurities. We demonstrate that polynuclear complexes play a central role in mineral growth at high supersaturation and that a classical complexation model is sufficient to reproduce measured rates. Dehydration of the attaching species, not the mineral surface, is rate limiting. Density functional theory supports our conclusions. The model provides new insights into the molecular mechanisms of mineral growth that control biomineralization, mineral scaling and industrial material synthesis.*

Calcite is a simple compound but predicting its growth rate at low to intermediate supersaturation for varying solution composition is impossible with existing models. Rates vary substantially as a function of saturation index (SI), ratio of Ca^{2+} to CO_3^{2-}, pH, impurity species and local step edge structure (i.e. obtuse or acute).[1–6] Constructing a single model to account for all of these parameters has proven extremely difficult. This suggests incomplete understanding of the molecular scale processes responsible for crystal growth. Most existing step growth models are based on ion attachment and detachment rates,[7–10] while others include, for example, surface complexation models.[10,11]

The models are generally rather complex, with a number of free parameters, and they only provide a reasonable fit over a narrow range of experimental conditions. No model properly addresses the difference in growth rate for obtuse and acute steps and it has been particularly difficult to estimate step growth as a function of supersaturation state and the Ca/CO_3 activity ratio.[12] Also unexplained is the pH dependence of step growth rate as a function of Ca/CO_3.[6] At pH 9, step velocity is maximum at significantly lower Ca/CO_3 than at pH 8 and the absolute growth rate is also much lower. Finally, no model proposed to date has considered adsorption and incorporation of species that are more complex than ions or ion pairs, even though classical models of solute complexing in solution,[13] and the more recent "prenucleation cluster" approach,[14] imply that more complex species are involved in calcite growth. A general mineral growth model that can 1) predict step velocity over a wide range of solution composition, 2) account for pH effects, while 3) being consistent with the solute species distribution, would contribute significantly to fundamental understanding of crystal growth, contribute a predictive tool and provide insight for a range of applications, such as biomineralization,[8] designing mineral growth inhibitors and modelling the global carbon cycle.

Here we present a simple and expandable microkinetic model for calcite step growth that considers the role of polynuclear complexes.[13] It has been validated using experimental data from our own work[12] and that of others.[6,9] The model provides detailed atomic scale insight into step growth processes and explains the differences in growth rate observed for acute and obtuse steps as a function of Ca/CO_3, SI and pH.

In line with previous work, our first assumption is that kink nucleation is the rate limiting step for calcite growth when additives or foreign ions are absent (Figure 1 a).[15] Evidence is the regular rhombohedral shape of calcite growth spirals,[12] implying low kink density. In supersaturated systems, that is, SI ≥ 0.6, ion detachment from kink-free steps is minimal. Because the rate of detachment is very low compared with attachment, and we have no analytical expression, it was neglected for SI > 0.6, simplifying the model. Assuming a single rate limiting step, we can apply transition state theory to write a simple functional form for calcite growth, where kink nucleation is initiated by addition of an ion pair (IP) (Figure 1 d). IP model growth rate (in nm s^{-1}) can be expressed:[16]

$$r_{IP} = 0.32 \cdot \frac{K_{AB}[A][B]}{(1+K_A[A])(1+K_B[B])} \frac{kT}{h} e^{-\frac{\Delta G_{IP}}{RT}}, \qquad (1)$$

where 0.32 nm is the step height of calcite, K_A and K_B are equilibrium constants for binding Ca and CO_3 ions to the step and ΔG_{IP} represents a reaction barrier associated with dehydration of the Ca ion and the calcite surface.[17] K_{AB} is the equilibrium constant for $CaCO_3^0$ ion pair formation.[18] [A] and [B] represent the ion concentrations. The functional form for adding individual ions (Figure 1 b,c) is identical to Equation (1) so we need not distinguish between the two processes in considering the model fit to the experimental data.[16] Strictly speaking, the atomic attempt frequency used in Equation (1) would generally be modified by a diffusive barrier associated with the jump from solution to the step site[19] but this term cannot be separately determined and is

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Supporting information and the ORCID identification numbers for the authors of this article can be found under http://dx.doi.org/10.1002/anie.201604357.

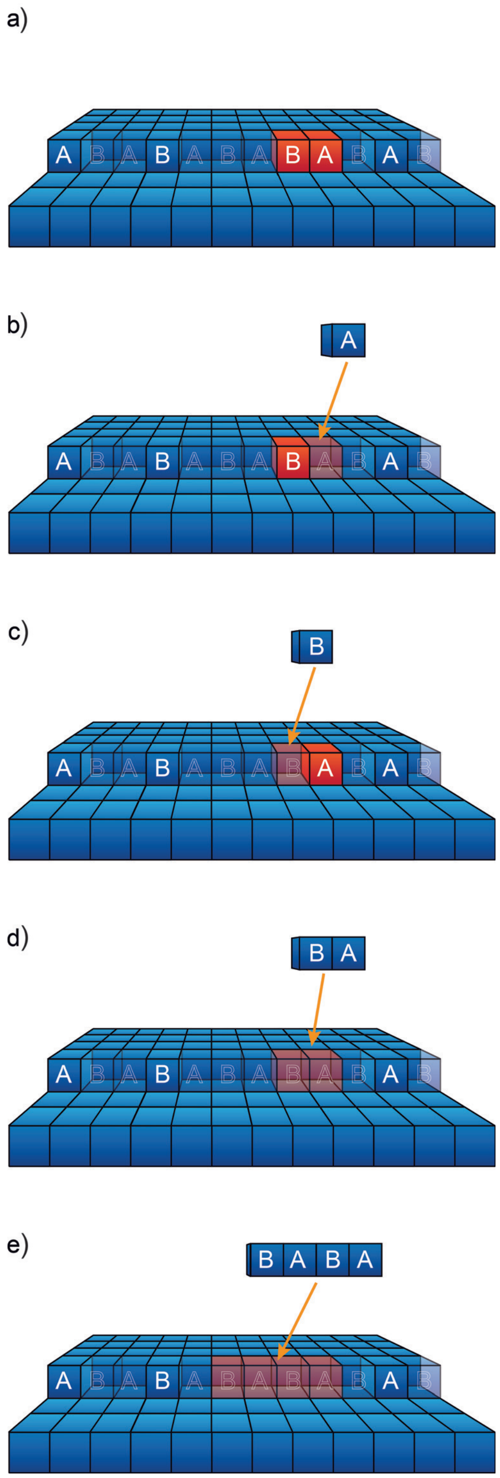

Figure 1. A schematic view showing key processes in the growth model. At the step (obtuse or acute), available sites for attachment have been drawn to appear translucent, while individual adsorbed ions, that block kink nucleation, are shown as boxes with solid white text. The rate determining step, that is, formation of a new kink that is indicated by the red structure (a), can occur by single ion attachment to already adsorbed ions (b, c) or by ion pair filling an empty site (d). At higher SI, structures such as (e) can form by direct addition of polynuclear complexes.

effectively incorporated in ΔG_{IP}.

At higher SI, where 2D surface nucleation dominates,[20,21] mineral growth models struggle to reproduce experimental data. Recent work[22–24] presents evidence for crystal growth by attachment of species larger than ions and ion pairs, ranging from fully formed particles to polymeric multi-ion complexes, originally known as polynuclear complexes.[13] We propose that polynuclear complexes control calcite growth by attaching directly at steps, nucleating a kink (Figure 1e). More sites are required to fit a larger ion aggregate so the function describing growth (in $\mathrm{nm\,s^{-1}}$) is:[16]

$$r_{\mathrm{PoNuC}} = 0.32 \cdot \frac{K_{\mathrm{AB},n}[\mathrm{A}]^n[\mathrm{B}]^n}{(1+K_{\mathrm{A}}[\mathrm{A}])^n(1+K_{\mathrm{B}}[\mathrm{B}])^n}\frac{kT}{h}e^{-\frac{\Delta G_n}{kT}}, \tag{2}$$

where n represents the number of ion pairs in the attaching unit and $K_{\mathrm{AB},n}$ is the equilibrium constant for $[\mathrm{AB}]_n$ complex formation in solution. $K_{\mathrm{AB},n}$ is not a free parameter in our study. We derived it from data from PHREEQC,[25] a geochemical speciation modelling program, and molecular modelling,[23] which also indicates that linear chains are the most stable form of polynuclear complexes. When both Equation (1) and (2) are required to describe the processes controlling the growth rate, we call it the polynuclear complex (PoNuC(n)) model, where n stands for the number of ion pairs in the complex.

Figure 2 shows the model fits for our experimental step growth data[12] with the ion pair (IP, blue) and the ion pair + polynuclear complex (PoNuC (2), red) models. At low saturation state, where polynuclear complexing is lower, the IP model performs well but for higher SI, where polynuclear complexes are expected, PoNuC(2) captures the nonlinear growth rate dependence on SI. It performs only slightly worse for low SI but we emphasize that our model is constrained to $n=2$ to minimize the number of parameters in our fit. The polynuclear complex with $n=2$ is present at the highest concentration of all polynuclear complexes for SI ≤ 1, which means that the dominant contribution from polynuclear complexes is accounted for in our PoNuC(2) model.[16] The free adsorption energies from the IP model for the acute step are $\Delta G_{\mathrm{Ca}} = -21 \pm 1\,\mathrm{kJ\,mol^{-1}}$ and $\Delta G_{\mathrm{CO_3}} = -18 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and for the obtuse, $\Delta G_{\mathrm{Ca}} = -16 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta G_{\mathrm{CO_3}} = -21 \pm 2\,\mathrm{kJ\,mol^{-1}}$ (Table S1). The subtle difference in the adsorption energies at the two steps is enough to explain the difference in maximum growth rate as a function of Ca/$\mathrm{CO_3}$ (Figure 2). For IP, maximum step velocity[16] occurs at:

$$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{K_{\mathrm{B}}}{K_{\mathrm{A}}} \tag{3}$$

Thus the relative stability of Ca vs. $\mathrm{CO_3}$ on a particular step determines the maximum growth rate and the corresponding ion activity ratio. The presence of polynuclear complexes [Eq. (2)] is only important at higher SI (Figure 2), where n in the denominator leads to a slightly narrower growth curve, as for SI = 1.0. All fit parameters are introduced as free energies and the derived reaction barriers for r_{IP} and r_{PoNuC} agree reasonably well with predictions by density functional theory (DFT; Table S3 in the Supporting Informa-

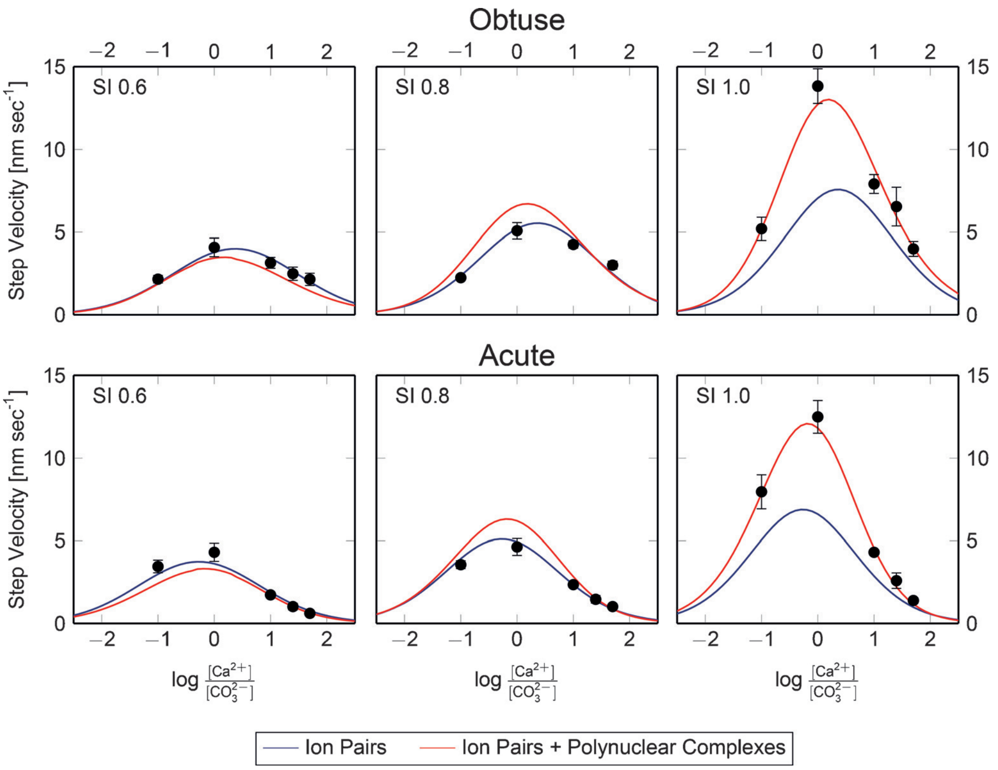

Figure 2. Step growth rates as a function of log$[Ca^{2+}]/[CO_3^{2-}]$, SI and step type. The ion pair (IP) attachment model (blue) fails to fit the data at higher SI whereas the ion pair and polynuclear complexes model (PoNuC(2)) fits all data.

tion). The activation barrier is lower for a polynuclear complex than for an ion pair, which in turn is predicted to be lower than for the free ion. This further supports our use of ion pairs as the attaching unit at low SI. Notably, we see very good fits using the same reaction barrier for the acute and obtuse steps, which is consistent with our assumption that dehydration of the attaching unit, not the step, is rate limiting.

Our IP model also fits experimental calcite step growth data published by others[96] (Figures S1 and S2). An important point is that combining data from all the fits demonstrates that Ca adsorption energy is different for acute and obtuse sites (Tables S1 and S2). Stronger Ca adsorption on acute steps blocks more step sites, leading to fewer acute sites available for an ion pair to nucleate a kink (Figure 1 d). This explains the faster growth observed for obtuse steps (Eq. S21). This is an important result. Behavior of the Ca ion differentiates growth on the two step types. In contrast, within fit uncertainties, CO_3 interacts equally on both steps (Table S2).

Figure 3 shows fits for acute step velocity as a function of Ca/CO_3 from Hong and Teng.[6] Our model captures the strong pH dependence of the growth rate. Fits with the IP model are reasonable, even for pH 9, where growth rate increases monotonically with decreasing Ca/CO_3. From our fit, we conclude that free energy of adsorption for Ca is significantly higher than for CO_3 (Table S2) and this shifts the maximum of the growth curve to a lower Ca/CO_3 activity ratio for higher pH [Eq. (3)]. DFT calculations for water behavior on the two steps can help explain. The pK_a of water bound to Ca is 8.5 at the acute step and 13.0 at the obtuse step (Table 3 in Ref. [26]). Thus at $pH > 8.5$, the acute step is negatively charged because OH^- adsorbs preferentially to water on calcite. Ca^{2+} binding to acute steps becomes stronger at pH 9 than 8, explaining the large shift in the maximum on the growth curve. On obtuse steps, surface charge is virtually unaffected by this slight pH increase and no shift in Ca/CO_3 or absolute value for the maximum step velocity is observed (Figure S1).

The concept and construction of our model also allows for studying growth inhibition, such as competitive adsorption of

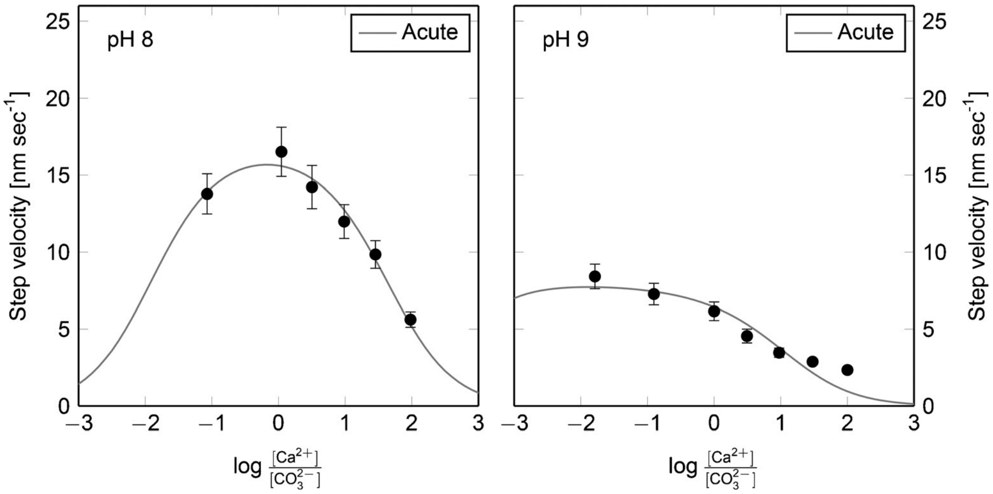

Figure 3. Experimental data for the acute step from Hong et al.[6] and our IP model. Fits with PoNuC(2) are identical because $SI < 1$.[16]

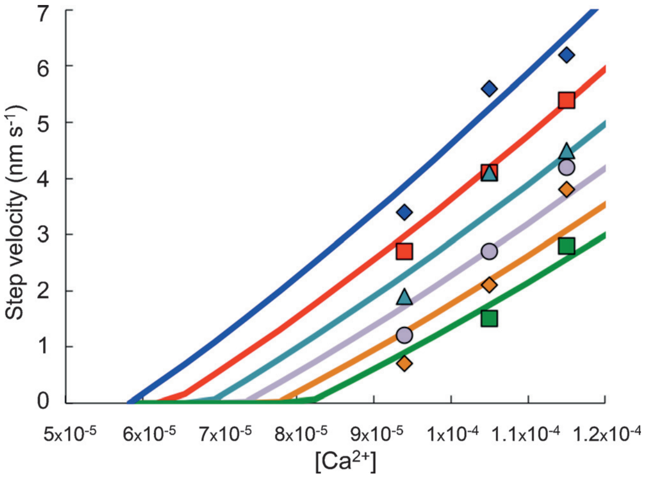

Figure 4. Calcite growth rate in the presence of Mg^{2+}, predicted by our IP model for $[Ca^{2+}]/[CO_3^{2-}]=1$. The points are experimental data from Davis et al.[2] Step velocity decreases as Mg^{2+} concentration increases: 0 M Mg^{2+} (blue), 3.2×10^{-5} M (red), 6.4×10^{-5} M (light green), 9.6×10^{-5} M (light purple), 1.3×10^{-4} M (orange) and 1.6×10^{-4} M (dark green).

Ca^{2+} and Mg^{2+} on calcite steps.[27] Figure 4 tests our IP model for calcite growth inhibition by Mg^{2+} with experimental results.[2] For $0 < SI < 0.6$, where detachment rates cannot be ignored, we included a constant backward rate, such that the net growth rate was 0 for pure calcite at $SI = 0$ with our values for adsorption energy and dehydration barrier from the IP model (Tables S1 and S3). As a second step, we decreased the reaction barrier (to compensate for the backward rate) to get good agreement for the growth rate in the absence of Mg. The third step was to increase the adsorption energy of Mg to obtain the set of curves for predicted growth rate in Figure 4. The good agreement suggests that Mg step blocking is the dominating growth inhibition mechanism for acute steps. More details are presented in the Supporting Information.

The success of a kinetic model for step growth, that includes polynuclear complexes, has implications for modelling the dynamics of complexes in solution. The form of the equilibrium constant, $K_n = [(AB)_n]/([A]^n[B]^n)$, for formation of polynuclear complexes of size n (Eq. S5), implies that for $[Ca^{2+}] = [CO_3^{2-}]$, $[(AB)_n] = K_n[Ca^{2+}]^{2n}$. That is, the number of polynuclear complexes of size n, relative to the number of free ions, scales as $[(CaCO_3)_n] \propto [Ca^{2+}]^{2n}$. In the classical formulation for complex formation, which dates back to Gibbs and Smith (1874),[28] the number of complexes of size n is proportional to $\exp(-n\Delta\mu/kT)$, where $\Delta\mu$ represents the chemical potential of the solution, given by $kT\ln\{[Ca^{2+}][CO_3^{2-}]/K_{sp}\}$ (details presented in the Supporting Information). Thus, for $[Ca^{2+}] = [CO_3^{2-}]$, the classical model predicts $[(CaCO_3)_n] \propto [Ca^{2+}]^{2n}$, consistent with the polynuclear complex model presented above. In contrast, in the prenucleation cluster model, the number of clusters is a constant fraction of the total Ca^{2+}.[14] Thus the concentration of clusters would be $\propto [Ca^{2+}]$, which conflicts with a polynuclear complex model of growth.

In summary, our microkinetic model is robust and flexible, describing calcite growth based on attachment of ion pairs and polynuclear complexes. The model explains how calcite growth depends on ion activity ratio, saturation index, pH and the presence of impurities such as Mg^{2+}. An important point is that it follows naturally from classical complex formation statistics. Our results demonstrate that polynuclear complexes play a role, not only for calcite nucleation, but also for regular calcite step growth, particularly at $SI > 1$.

Acknowledgements

We thank K. Dideriksen and the NanoGeoScience group members for discussion. Funding was provided by Maersk Oil, through Nano-Chalk and the Research and Technology Centre, by the Materials Interface with Biology (MIB) Consortium (UK EPSRC grant, EP/I001514/1) and by the Materials synthesis and simulation across scales initiative, of the LDRD program at Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated for the Department of Energy by Battelle (Contract No. DE-AC05-76RL01830). The computational resources were provided by the Danish e-Infrastructure Consortium (DeIC).

Keywords: calcite · calcium carbonate · microkinetic model · mineral growth

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11086–11090
Angew. Chem. **2016**, *128*, 11252–11256

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Received: May 4, 2016
Revised: June 29, 2016