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## Uncovering the atomistic mechanism for calcite step growth

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**Abstract:** Determining a complete atomic level picture of how minerals grow from aqueous solution remains a challenge since macroscopic rates can be a convolution of many reactions. For the case of calcite ( $\text{CaCO}_3$ ) in water, computer simulation has been used to map the complex thermodynamic landscape leading to growth of the two distinct steps, acute and obtuse, on the basal surface. The carbonate ion is found to preferentially adsorb at the upper edge of acute steps, while  $\text{Ca}^{2+}$  only adsorbs after  $\text{CO}_3^{2-}$ . In contrast to the conventional picture, ion pairs prefer to bind at the upper edge of the step with only one ion, at most, coordinated to the step and lower terrace. Migration of the first carbonate ion to a growth site is found to be rate-limiting for kink nucleation with this process having a lower activation energy on the obtuse step.

Crystallization is one of the most fundamental and important physical processes, being widely used for the preparation of materials and purification of chemicals. Hence it is unsurprising that understanding the molecular mechanisms by which crystals grow and dissolve from solution has been a long-standing topic of study.<sup>[1,2]</sup> Previous work has identified the key role of kink sites in the rate of both growth and dissolution when ion diffusion in solution is fast.<sup>[3]</sup> In the absence of extended defects, such as dislocations, curved or rough steps, nucleation of the initial kink site is postulated to be rate-limiting. However, it has been difficult to identify the thermodynamics or rate constants for individual atomic or molecular events, especially for multi-species materials. This is because most available experimental data represents a macroscopic convolution of several individual mechanistic reactions (e.g., rates of step propagation).

Calcium carbonate, and specifically calcite, represents one of the most studied cases for crystal growth and dissolution. Not only is this system of both fundamental and industrial significance, since calcium carbonate is an abundant biomineral and a common scale in pipelines and vessels, but it is also convenient for experimental study. The morphology of calcite crystals is dominated by the stable  $(10\bar{1}4)$  surface, leading to the availability of large, clean terraces that are amenable to techniques such as

X-ray reflectivity<sup>[4]</sup> and atomic force microscopy (AFM).<sup>[5]</sup> In particular, AFM is capable of following the rates of growth or dissolution of calcite steps *in situ*.<sup>[6]</sup>

Given the availability of growth and dissolution data for calcite there have been many studies that proposed models for the speciation at the surface<sup>[7]</sup> and ultimately the kinetics as a function of environmental conditions.<sup>[8-10]</sup> These models have often taken the form of coupled rate equations. Since pioneering work two decades ago,<sup>[11]</sup> there has been increasing interest in using kinetic Monte Carlo to simulate the growth/dissolution of the calcite surface.<sup>[12]</sup> This valuable approach makes a numerical connection between rates for individual ion additions/removals at specific crystal sites and overall macroscopic changes. To date, the rates for each step have largely been treated as empirical parameters that are adjusted to obtain good agreement with observations. Often simplifications are needed (i.e. assumptions about the equivalence of rates between sites) due to insufficient ability to separate contributions.

In this study we lay the foundation for an alternative route to obtaining rate constants for calcite, and ultimately other systems, by using atomistic molecular dynamics to provide the free energy landscape for individual ion addition events involved in nucleating a kink site at the two possible distinct steps, namely the acute or obtuse. This yields both the thermodynamics and activation energies for each mechanistic step. As shown for barite,<sup>[13]</sup> this produces accurate rates for multi-step reactions in the presence of aqueous solution.

Given that computing free energies from molecular dynamics is now routine, why does mapping the free energy for growth of calcite represent such a challenge? A requirement when producing a free energy landscape is that all degrees of freedom not explicitly mapped must be rapidly explored. If there are slow degrees of freedom, beyond those explicitly studied, then this can lead to incorrect results. For crystal growth from aqueous solution, the rate-limiting step is believed to be desolvation so that an ion from solution can bind to the step. While it has been argued<sup>[14]</sup> that the loss of water from the incoming ion is rate-limiting, previous work<sup>[15]</sup> has shown that water exchange at the step edge can be more than three orders of magnitude slower than for  $\text{Ca}^{2+}_{(\text{aq})}$ . While slow water exchange can be handled for a single ion by including the cation coordination number in the free energy landscape,<sup>[16]</sup> for a step edge this is non-trivial. Here we have used bias acceleration for the hydration of cations near each adsorption site at the step to overcome this problem and ensure reliable sampling of the free energy. Details can be found in the supporting information (SI).

Here molecular dynamics has been performed using a force field parameterized to reproduce the solvation free energy of ions in solution and the bulk properties of calcite.<sup>[16]</sup> In particular, the model was fitted to reproduce the solubility, and therefore should give accurate results for ions at the calcite-water interface. The free energy landscape at 300 K has been mapped for each of the 8 distinct cases of single ion adsorption (i.e. two symmetry unique positions on each acute and obtuse step edge for  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ ). Representative free energy landscapes perpendicular to the step

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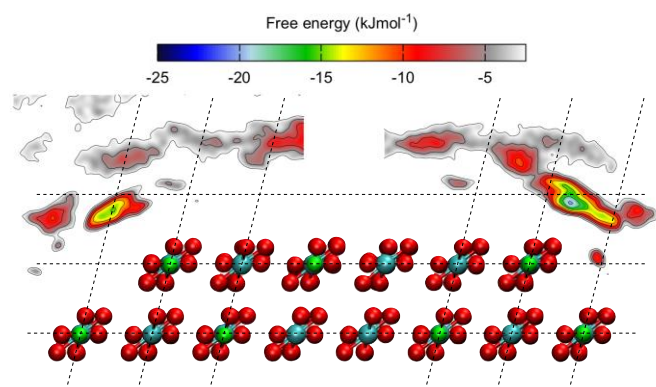
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direction are shown in Figure 1, while all contour plots can be found in the SI and key values are given in Table 1.



**Figure 1.** Free energy iso-surfaces for carbonate adsorbing at the obtuse (left) and acute (right) calcite steps for position 1 (see Figure S1 for definition). The calcite structure is shown with calcium, carbon and oxygen in green, blue and red, respectively. Dashed lines represent lattice planes; where these lines cross represents the position of ions that match the underlying bulk structure.

The first significant observation from the thermodynamics of single ion binding is that only carbonate will adsorb exothermically at either the acute or obtuse calcite steps. Given that  $\text{Ca}^{2+}$  is more strongly hydrated than  $\text{CO}_3^{2-}$ , the binding to the step edge is insufficient to compensate for the loss of water for the cation. At one of the two positions on the acute step, there is an exothermic calcium site, though this is for a solvent-shared state and the binding is only comparable to thermal energy. This picture differs from that of Andersson et al.<sup>[14]</sup> where the free energies for  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  are similar at both acute and obtuse steps. Despite the discrepancy for  $\text{Ca}^{2+}$ , our magnitude for the strongest binding site of  $\text{CO}_3^{2-}$  lies in the same quantitative range as fitted in this previous study (-16 to -21  $\text{kJmol}^{-1}$ ).

The second key finding concerns the preferred binding site for  $\text{CO}_3^{2-}$ . It might be expected that the ion at the step forms a continuation of the bulk structure, which we will refer to as a “growth site”, but this is not the case. Instead carbonate favors coordinating to the top step edge, to maximize hydration, with a preference for the acute over the obtuse step. While the growth site is also a free energy minimum, it is 10-20  $\text{kJmol}^{-1}$  less stable.

Examining the free energy for both ions as they move away from the step edges, either on the upper or lower terrace, then this only occurs for solvent shared or separated states (i.e., direct coordination to calcite is only found in proximity to the steps). This agrees with earlier results for adsorption of ions onto the terraces of calcite.<sup>[17]</sup> The only exception is for carbonate near the acute step on the upper terrace. Here a contact minimum is found one row away from the edge that has a free energy of -15.9  $\text{kJmol}^{-1}$ . This minimum corresponds to a position along the acute step where  $\text{CO}_3^{2-}$  at the upper edge is less stable. Therefore migration to the step edge from one row away will occur along a pathway that lies at an angle to the step direction, following the underlying calcium ion row. Aside from this site, our results show that surface diffusion of adsorbed ions is unlikely to significantly enhance

calcite growth relative to direct binding of ions from solution, in contrast to *in vacuo* and previous solution models.<sup>[18]</sup>

Our data also provides information regarding the kinetics of single ions reaching their growth site. The initial adsorption of carbonate at the upper step edge has effectively no barrier, and so the jump to a growth site would be rate-limiting for a single ion. The activation free energies for this migration are given in Table 1. Despite the difference in adsorption energies between acute and obtuse steps, the average kinetic barrier for carbonate to reach a growth site is remarkably similar in both cases.

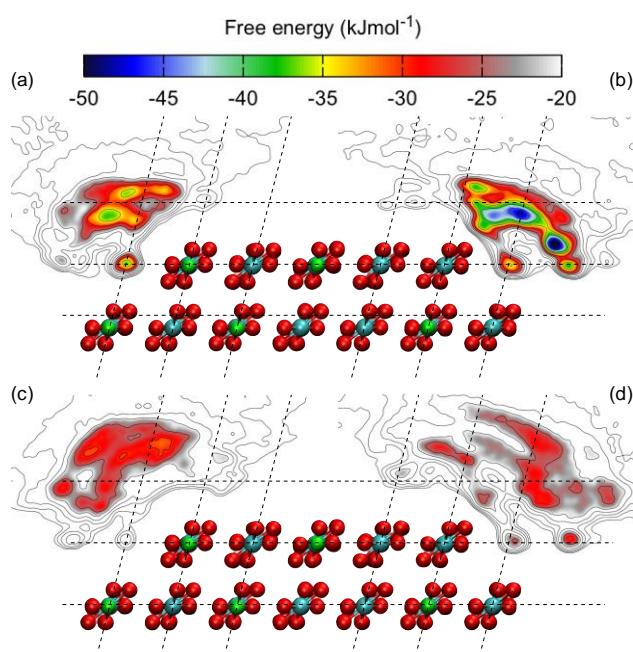
**Table 1.** Free energies of ion adsorption at two key sites at the acute and obtuse steps of calcite:  $\Delta G_{\text{top}}$  and  $\Delta G_{\text{bottom}}$  represent the values for the top edge of the step and the bottom growth site, respectively.  $\Delta G_{\text{act}}$  represents the activation barrier to move from the top to bottom site. For the definition of the positions parallel to the step edge (A/B,1/2) see Figure S1.

Ion	Step	Position	$\Delta G_{\text{top}}$ ( $\text{kJmol}^{-1}$ )	$\Delta G_{\text{bottom}}$ ( $\text{kJmol}^{-1}$ )	$\Delta G_{\text{act}}$ ( $\text{kJmol}^{-1}$ )
$\text{Ca}^{2+}$	Acute	A	6.8	5.5	29.1
		B	5.7	42.0	45.2
	Obtuse	A	3.5	25.9	46.6
		B	7.0	37.5	47.9
$\text{CO}_3^{2-}$	Acute	1	-20.2	-10.0	35.1
		2	-7.5	12.2	24.6
	Obtuse	1	-12.6	0.3	27.9
		2	-7.7	9.5	28.1

Having shown that carbonate is first to bind to the calcite step edge, this begs the question as to where  $\text{Ca}^{2+}$  prefers to bind after this? To explore this  $\text{CO}_3^{2-}$  was constrained to each minimum and then the free energy to add  $\text{Ca}^{2+}$  was computed in the region near the anion (Figures 2, S5 & S6). This creates a complex thermodynamic landscape with up to eight minima per carbonate site. Calcium binding is now exothermic, with one exception, as expected for an edge with a net negative charge. For the acute and obtuse steps, the most exothermic adsorption energies are -52.3 and -40.2  $\text{kJmol}^{-1}$ , respectively. Again the acute step is the favored region for adsorption, though the strongest binding of  $\text{Ca}^{2+}$  doesn't occur adjacent to  $\text{CO}_3^{2-}$  in its' most stable position, but when it is at the bottom of the step with  $\text{Ca}^{2+}$  near the upper edge. Full details of the  $\text{Ca}^{2+}$  adsorption free energies are in Table S2 along with the positions of the minima.

When analyzing the most stable configurations for calcium and carbonate ions in the vicinity of the steps, there are several structural motifs common to many of the states. The majority of the structures involve the formation of a contact ion pair between  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . In the standard model of crystal growth this would be anticipated, with the ion pair being adjacent to the step edge and occupying sites that grow the underlying lattice. This ion pair, or perhaps some multiple of adjacent ion pairs forming a chain, would then nucleate the growth of the step. However, the mechanism of ion addition that emerges here is far more complex. Instead of being parallel to the step edge, ion pairs are often orthogonal to this with  $\text{CO}_3^{2-}$  either being at the top of the step and  $\text{Ca}^{2+}$  lying above the lower terrace in a solvent shared position or, if  $\text{CO}_3^{2-}$  is in the growth site at the bottom of the step, then  $\text{Ca}^{2+}$  can bind at the top of the step next to the anion.

From all of the stable permutations of ion pair position and orientation, states can be identified that correspond to the classical model for nucleation of the next row of each step. For both steps the classical configuration is not the most stable one and therefore the critical nucleus for step growth must be larger than a single ion pair. While there is a significant thermodynamic difference between the most stable minima for an ion pair at the acute and obtuse steps ( $-62.3$  vs  $-42.2$   $\text{kJmol}^{-1}$ ), the energetics for nucleating two kink sites shows less discrimination ( $-45.3$  vs  $-36.7$   $\text{kJmol}^{-1}$ , respectively). These values are consistent with the solubility of calcite, but unsurprisingly are very different to previous calculations under dry conditions.<sup>[19]</sup> Since our free energies are concentration-independent, a shift must be applied to determine the thermodynamic driving force at given conditions. For a saturated solution this equates to an offset of  $+48$   $\text{kJmol}^{-1}$ , resulting in a nucleation barrier for step growth as expected.



**Figure 2.** Free energy iso-surfaces for a calcium ion adsorbing at the obtuse (a,c) and acute (b,d) calcite steps when carbonate is present at either the growth site (a,b) or step edge (c,d). Details as per Figure 1. The colored energy scale represents where  $\text{Ca}^{2+}$  is more stable than in an ion pair in water.

In principle, an ion pair parallel to either step can have two distinct orientations relative to the step direction. Here we find, for both the acute and obtuse case, that one orientation is lower in free energy than the other by up to  $29$   $\text{kJmol}^{-1}$ . This implies that the kink sites that emerge during step growth are likely to be dominated by half of the possible types.

For the two states that lead to nucleation of kink sites we can also assess the likely kinetics. Based on  $\text{CO}_3^{2-}$  addition followed by  $\text{Ca}^{2+}$ , the sequence of barriers is  $35.1$  then  $32.9$   $\text{kJmol}^{-1}$ , or  $27.9$  then  $21.9$   $\text{kJmol}^{-1}$  at the acute and obtuse steps, respectively. This is consistent with faster growth at the obtuse steps, as experimentally observed,<sup>[6]</sup> and is close to the activation energy measured for calcite growth,  $33$ – $39.2$   $\text{kJ/mol}$ .<sup>[20,21]</sup> Recently it was

proposed that ion pairs and pre-nucleation clusters play a role in the growth of calcite on the basis of a kinetic model fitted to experimental data.<sup>[14]</sup> Our results indeed support the formation of ion pairs at the step edge, thereby lowering the barrier to calcium migration to the growth site, and it is likely that further association of adsorbed ion pairs may explain the proposed role of pre-nucleation clusters.

In conclusion, we have shown that it is now feasible for simulation to accurately map complex free energy landscapes for the initial stages of step growth. By identifying competing atomic level pathways, alongside the thermodynamics for individual steps, this paves the way for validating and improving models of crystal growth. For calcite we have shown that growth proceeds first via anion addition, then cation, but that the initial states formed are not commensurate with the underlying crystal structure. The rate-limiting step is then for the ions to move from the preferred adsorption sites to those required for growth. At the acute step we find evidence that ion pairs may lower the barrier to growth through concerted motion. Future work is needed to identify how many contiguous ion pairs are required to reach the critical size for nucleation of the next step row, and to determine transmission coefficients for the pathways presented in order to provide a full predictive kinetic model.

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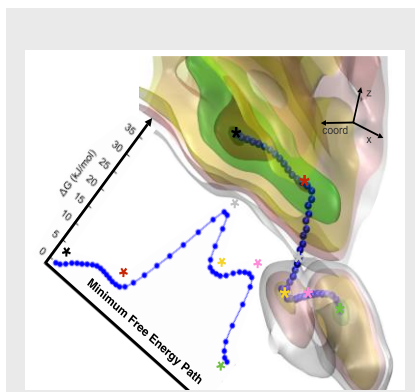
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## Entry for the Table of Contents

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Computer simulation has been used to map the initial thermodynamics for growth of steps on the calcite surface from aqueous solution leading to identification of the competing atomic pathways. This reveals that growth is limited by the rearrangement of adsorbed ion pairs from the step edge to nucleate kink sites.



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