

Exploring the role of ions and amino acids in directing the growth of minerals from solution.

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## Abstract

The influence of both sulphate ions and aspartic acid on directing the growth of barite has been explored using computer simulation. Both species are found to significantly reduce the activation free energy to growth under appropriate conditions, with the influence of sulphate being surface specific. This offers the potential for a new approach to morphology control without inhibition that may have implications for biomineralisation.

## Introduction

Nature is able to exhibit phenomenal control over the growth of minerals from aqueous conditions through biomineralisation, including manipulation of the composition, polymorph, and most spectacularly the crystal morphology. Although structures of considerable complexity have now been synthesized through biomimetic self-assembly and there have been extensive investigations of biomineralisation, a full picture at the atomic scale of how nature achieves such a degree of control has yet to emerge. Important factors are known to include the local manipulation of ion concentration and pH, as well as the direct influence of interactions with biomolecules.

Valuable insights into mineral formation have been provided over the last few years through the use of atomic force microscopy to image growing surfaces *in situ*. However, the unambiguous interpretation of such images is not always straightforward. Here computer simulation can be a useful complement to experiment since it is capable of providing atomic detail regarding the mineral-solution interface at the nanoscale. With the exponential increase in computing power, as well as the development of new algorithms for exploring complex potential energy surfaces, it is now increasingly possible to probe the kinetics of mineral surface growth.

It has long been recognised that the growth of minerals can be manipulated through the use of additives to inhibit crystal growth through binding to steps and kinks at the surface. Conceptually, this represents the simplest model for the role that organics can play in altering the morphology of crystals during biomineralisation. However, it has recently been recognised that species, such as amino acids, can actually accelerate crystal growth under appropriate conditions, rather than just inhibit it. In the present work we aim to explore the atomic details of how this new mechanism for promoting mineral crystallisation occurs for both an inorganic ion and one of the most common amino acids.

## Methods

The most widely studied material in the field of biomineralisation is calcium carbonate. However, it represents a challenging system to study since nucleation and crystal growth is complicated by the existence of several polymorphs, including hydrates and an amorphous precursor, in addition to the speciation of the carbonate ion. For this reason, the initial focus is barite ( $\text{BaSO}_4$ ), which exists as a single anhydrous polymorph with the sulphate ion being unprotonated under relevant conditions of pH, and has been found to be biomineralised by some molluscs.

Simulations of the barite-solution interface are performed based on an atomistic force field, using an ionic formalism to describe barium and sulphate, while water is treated using the SPC model. Parameters are fitted in order to accurately reproduce the structure and lattice energy of barite, as well as the hydration free energies of the component ions. The three thermodynamically favoured surfaces of barite have been studied, namely (001), (210) and (010), by representing the system as a 2-D system with water separating the slabs normal to the surface.

First principles simulations of the calcite (10-14) surface have also been performed using the SIESTA methodology, employing the PBE functional with a soft-confined DZP basis set and norm-conserving pseudopotentials. Molecular dynamics is used to explore the time evolution of the systems with timesteps of 2 and 0.5 fs for the atomistic and first principles methods, respectively. Simulations are performed in the NPT ensemble for the aqueous interface and NVT for calcite at 298 K. Energy profiles for the addition of ions to the surface are determined by umbrella sampling. Full details of the methods employed can be found elsewhere (Piana et al, 2006, 2007).

[1<sup>st</sup> level] Results and discussion

[2<sup>nd</sup> level] Barite growth from aqueous solution

Barite has three important surfaces under most conditions, which are (001), (010) and (210). Based on simulation of the hydrated surfaces, the energies of these facets are 0.241, 0.193 and 0.194  $\text{Jm}^{-2}$ , respectively. At equilibrium it would be expected that the (010) and (210) surfaces should be equally dominant in the morphology. However, when grown at low to moderate supersaturation the (010) face is experimentally

observed to be completely absent, thus indicating that there must be a significant difference in the kinetics of growth for this surface.

Because the unbiased rate of growth of most minerals occurs on a timescale longer than that presently accessible to most atomistic simulations, it is not feasible to directly obtain the rates for all growth steps. Despite this, it is possible to map out the free energy profile for ions diffusing from solution to the crystal surface, which allows the activation energy for individual growth steps to be estimated. In the case of barite at low supersaturation, nucleation on the flat surface is likely to be rate-limiting. This contrasts with calcite where screw dislocations ensure that step growth dominates. For barite we have examined the free energy profile for barium ions to be added to all three surfaces under consideration, both in the presence and absence of a sulphate ion on the surface. Simulations of the interface between barite and a solution of barium and sulphate ions demonstrated that the desolvation of the barium cation is the slowest step since sulphate was found to adsorb on the mineral surface without the application of any bias.

Figure 1 shows the free energy profiles for the three different surfaces, both with and without a pre-adsorbed sulphate anion. Here the constrained barium ion migrates from aqueous solution on the left of each panel in Figure 1 towards the surface adsorbed state at the right, with all free energies being relative to the ion being in solution. Considering first the adsorption of barium on to the clean surface (green curve), the free energy increases as the ion gets closer to the surface before passing through an activation barrier at distances of 4.26, 2.43 and 2.53 nm for the (001), (010) and (210) surfaces, respectively. In all cases, the activation energy to adsorb barium at the clean surface lies in the range 20-30 kJ/mol, while the local minimum at the surface (i.e. to the right of the transition state in Figure 1) is unstable with respect to the ion in solution.

In the presence of sulphate, there is a marked change in the energy landscape. Firstly, the formation of an ion-pair on the surface leads to the adsorbed state being stabilised with respect to solution, as shown by the right hand minimum for the red curve lying below zero. The binding energy, given by the depth of the right hand minimum in the red curve relative to the solution state, is almost identical on all three surfaces, suggesting that interaction with the adsorbed sulphate is dominant. Secondly, and more significantly, the activation barriers are substantially modified in two cases, though the effect is highly surface specific. The dominant (001) face experiences only a small change in barrier height, though the transition state occurs further from the surface. For the (210) surface the barrier is reduced by greater than a factor of 2, while for (010) the barrier is reduced to being of the order of ambient thermal energy. When allowing for the exponential dependence of rate on barrier height, this is consistent with the experimentally observed fast growth of the (010) surface relative to the (210). Indeed, during 1 ns of simulation the emergence of a line of barium and sulphate ions appears on the (010) surface spontaneously (Figure 2), suggesting the beginning of nucleation; an observation that is not duplicated for the other faces studied. Hence, it appears that the sulphate ion assists in the desolvation of the barium cation and thereby accelerates the growth, but only in a surface specific manner, which may be related to the orientation of the sulphate when aligned with the crystal structure below.

## [2<sup>nd</sup> level] Barite growth in the presence of aspartic acid

Motivated by the observation that the sulphate ion is able to catalyse the desolvation of barium, it is interesting to explore what influence an amino acid might have on the rate of crystal growth. Elhadj *et al* (2006) have demonstrated that peptides containing aspartic acid residues increase the step speed for the basal plane of calcite, prior to the onset of growth inhibition at high concentration.

For barite, the (001) surface was chosen for the study of the effect of aspartic acid since this surface possesses the highest activation barrier to barium addition. The modified free energy profile for this simulation is shown in Figure 1a according to the blue curve. While aspartic acid increases the complexity of the potential energy surface, the important effect is the reduction of all activation barriers to less than approximately 6 kJ/mol, representing more than a four-fold reduction relative to the situation in the absence of this molecule. Examination of the trajectories demonstrates that aspartic acid is able to coordinate the barium ion in solution and shuttle the cation to the surface, thereby lowering the resistance to desolvation. Critical to the acceleration of this process is that aspartate only exhibits moderate complexation strength to barium, and thus removal of the ligand does not introduce a further barrier to growth.

## [2<sup>nd</sup> level] Calcite (10-14) surface

Having characterised a new pathway for mineral growth acceleration for barite, the challenge is to determine whether the same mechanism might operate for step propagation at the surface of calcite. Preliminary calculations have been performed quantum mechanically to examine the interaction of water and aspartic acid with a step on the (10-14) surface. Through the use of limited first principles dynamics it is possible to determine whether there are any speciation issues to consider before undertaking force field studies in which the protonation state is typically fixed.

The calcite surface has been represented by a slab containing six layers, reconstructed to generate steps on both sides, in a cell of dimensions 10.1 x 25.2 x 40.0 Å, where the *c* axis repeat is set to ensure vacuum separation of images. Four molecules of water were introduced with one at each obtuse and acute step. After energy minimisation, the system was evolved dynamically for 1 ps. While no significant dissociation of water was observed during this time, there was rapid evolution of the system. Both water molecules initially coordinated to the obtuse step diffused away from this location, becoming coordinated to calcium ions on the flat surface, while those at the acute step remained strongly bound and failed to exhibit even rotational freedom on this timescale.

Although the above represents a small statistical sample, it is strongly suggestive of the carbonate terminated obtuse step being hydrophobic, while the acute step is strongly hydrophilic. Elhadj *et al* (2006) have noted an experimental correlation between hydrophilicity of peptides and rate acceleration. This suggests that the acceleration may be linked to competition with the acute step aiding desolvation of the growth site. The effect will also occur for the obtuse step since growth involves addition of calcium ions, which will alter the solvation characteristics.

## Conclusions

Computer simulation has been used to identify mechanisms by which both sulphate ions and aspartic acid can accelerate, rather than inhibit, the growth of barite from aqueous solution. Furthermore, the catalytic desolvation of barium is surface specific, at least for the case of sulphate ions. This suggests further mechanisms through which biomineralisation might manipulate mineral morphology. Work is currently in progress to examine whether the same pathways operate for calcite step growth.

## Acknowledgements

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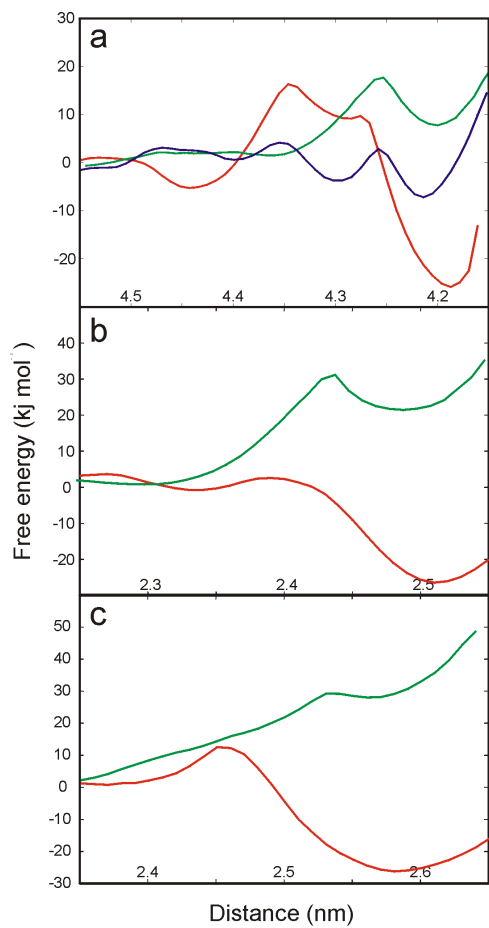


Figure 1: Free energy profiles for the constrained migration of a barium cation from aqueous solution (left) to the (a) (001), (b) (010), and (c) (210) surfaces of barite (right). Here the green line is for the case where barium is approaching the clean surface, red is for where there is a sulphate ion already adsorbed, and blue, for the (001) surface, is in the presence of aspartic acid.

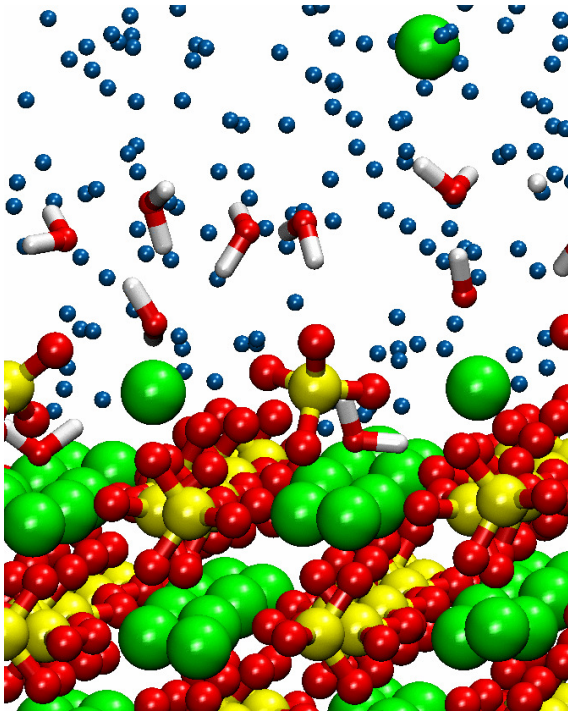


Figure 2: Formation of a 1-D growth line of  $\text{BaSO}_4$  on the (010) surface of barite. Atoms are coloured green, yellow, red and white for barium, sulphur, oxygen and hydrogen, respectively. For clarity, water molecules remote from the solvation of the surface nucleus are illustrated by a blue particle situated at the position of oxygen.