

A kink-site limited model for growth and inhibition of biominerals

J.J. DE YOREO¹, A.A. CHERNOV², L.A. ZEPEDA-RUIZ¹,
L.E. WASYLENKI³, S. ELHADJ³, C.A. ORME, G. GILMER¹
AND P.M. DOVE³

¹Lawrence Livermore National Laboratory, Livermore, CA
(deyoreo1@llnl.gov, zepedaruiz1@llnl.gov,
orme1@llnl.gov, gilmer1@llnl.gov)

²NASA Marshall Space Flight Center, Huntsville, AL
(alex.chernov@msfc.nasa.gov)

³Virginia Polytechnic Institute, Blacksburg, VA
(dove@vt.edu, elhadj@vt.edu, waz@asu.edu)

One forefront of biomineralization science is the need for a fundamental understanding of kinetic and thermodynamic controls on the morphology and compositional signatures of minerals formed in complex systems. Conventional analysis of mineral growth from aqueous solutions has been based on application of the Gibbs-Thomson (GT) effect, a thermodynamic principle relating the size of atomic features on a crystal face to the driving force for crystallization. Experimental results obtained in recent years using atomic force microscopy (AFM) call into question the basic GT requirement that the thermal fluctuations along step edges on a crystal face are fast enough to assure that step growth is controlled by molecular incorporation at kink sites along the steps. Rather, the generation of the kinks themselves by so-called "1D nucleation" appears to become the rate limiting step.

Abandoning the GT effect helps to explain numerous anomalies observed during growth of sparingly soluble biominerals. Here we present the results of AFM studies of calcite and brushite growth that are best explained by assuming step motion is limited by kink availability. We show how they impact analyses of growth rates, extraction of thermodynamic parameters, and interpretation of impurity effects. We then show that, during the growth of calcite in the presence of inorganic and organic constituents important in the biogenic carbonates such as Sr²⁺ and a wide variety of aspartic acid-rich peptides, the dependence of step kinetics on impurity content and saturation state differs dramatically from that expected from the GT effect.

To explain these results we replace the GT-based analysis with a kinetic description in which the essential step in stopping growth is the blocking of newly formed kinks. Finally, we show the results of kinetic Monte Carlo simulations that predict behaviour similar to that seen in the AFM experiments, and explicitly reveal the importance of 1D nucleation and kink-site blocking during growth and inhibition.

Free energy of adsorption of molecules and ions at the calcite-water interface

SEBASTIEN KERISIT^{1,2} AND STEPHEN C. PARKER²

¹Pacific Northwest National Laboratory, 902 Battelle Blvd,
P.O. Box 999, K8-96, Richland, WA 99352, USA
(sebastien.kerisit@pnl.gov)

²Chemistry Department, University of Bath, Claverton Down,
Bath, BA2 7AY, UK (s.c.parker@bath.ac.uk)

A full atomistic understanding of adsorption and growth thermodynamics and kinetics requires the evaluation of the free energies of adsorption in aqueous solution. Currently, studies of adsorption and growth of inorganic solids have focused on computing the energetics of these processes.

In this presentation, we will show that these free energies can be calculated and we illustrate this by modeling the free energy profile of water on the surfaces of calcite. The approach uses molecular dynamics with parameterized equations to describe the interatomic forces. These simulations predict that the free energy of adsorption of water is relatively small (~3 kJ mol⁻¹) compared to the enthalpy of adsorption (~45 kJ mol⁻¹) calculated in a previous paper (Kerisit and Parker 2003). Hence, this suggests that a large change in entropy is associated with the water adsorption on the surface. To investigate this further, we computed the effect of the mineral surface on the water orientation and diffusion.

Next, we will present results obtained from the simulation of the adsorption of three metal ions (magnesium, calcium, and strontium) on the (10.4) calcite surface in aqueous solution. First, we will demonstrate that the potential model is able to reproduce the interactions between water and the metal ions regardless of whether they are at the mineral surface or in bulk water. Next, we will show that the free energy profile of an ion adsorbing on the surface correlates with the solvent density and that the formation of an inner-sphere complex is associated with a large free energy barrier, which is mainly electrostatic in nature. In addition, these calculations allow us to begin to address the rates of adsorption and desorption, which are essential for studying growth and dissolution. Our calculations of the rate of desorption from the surface suggest that magnesium has a much longer residence time on the surface than calcium and strontium due to its strong interactions with both water and the surface.

References

Kerisit S. and Parker S.C. (2003), *J. Phys. Chem. B* **107**, 7676-7682