

## Stereochemical recognition revisited: A step-specific model for shape control

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Living organisms produce crystal structures that exhibit morphologies differing dramatically from the simple shapes obtained during laboratory growth from pure solutions. Analyses of these biomineral structures typically reveal the presence of both inorganic and macromolecular species, with the latter containing a large fraction of acidic residues.

In the past, the paradigm of "stereochemical recognition" has been invoked to explain these observations. According to this model, stereochemical matching of macromolecules to the crystal lattice of otherwise unexpressed faces leads to their stabilization, presumably by lowering their surface energies, thereby generating a new crystal shape.

Here we review results from *in situ* AFM investigations of a number of crystal-impurity systems that argue for a change in this paradigm. The systems studied included: 1) calcite plus inorganic metal ions, simple amino acids, a series of poly-aspartates and dipeptides, and complete proteins from marine organisms, and 2) calcium oxalate plus citrate, a small organic modifier, and osteopontin, a naturally occurring protein.

For all systems, we find that the resulting growth kinetics and crystal habit are defined by modifications to atomic steps on existing crystal faces and that the degree of modification on a given face is step-specific. Moreover, changes in macroscopic crystal shape mimic the modifications seen at the atomic level. While the exact mechanism of growth modification differs in each system, the feature these systems have in common is that the important molecular-scale interaction that drives modification is between the impurity and a specific set of steps on the existing crystal faces. Molecular models that calculate the modifier-crystal interaction, energy support these conclusions in that 1) they predict that the binding energies are greatest at the step edges, and 2) they give relative values in accordance with the step-specificity observed in the experiments.

These results argue for a shift in the paradigm of stereochemical recognition away from stabilization of new facets through matching to their atomic planes, towards a model recognizing the paramount role of steps. In particular, the inherently non-planar nature of steps provides an environment in which multiple bonding accommodations provide a high degree of coordination and, consequently, a large binding energy for non-planar growth modifiers.

## Dynamic simulations of polypeptide networks to form Ca-carbonate seed crystals

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Over the years, there have been a number of attempts to form synthetic organic templates that mimic dynamic processes at the interface between organic matter and mineral surfaces. One approach has been to isolate the templating matrix from mineralized tissues and examine the growth of calcium salts in the presence of this matrix. Other experiments have focused on synthetic (bio-)organic templates, such as polymers, macromolecular complexes, phospholipid vesicles,  $\beta$ -pleated polyamino acids entrapped in gelatin self-assembled monolayers on gold substrates, and Langmuir films. In the case of Langmuir monolayers, the amphiphilic molecules can be designed in such a way that they act as artificial two-dimensional nuclei for the promotion of crystal nucleation. Such films have been used as templates to direct the crystal nucleation and growth of calcium carbonate. For example, Buijnsters et al. (2001) used Langmuir films of amide-containing phospholipids in the presence of calcium ions to form well-defined two-dimensional domains at the air-water interface.

This is the starting point of our molecular dynamics simulations. After deriving a pure-core potential set for fast molecular dynamics simulations, we have created different two-dimensional networks of amide-containing phospholipids that serve as templates for Ca carbonate seed formation. We can vary the distance and structural arrangement of the functional groups to control adsorption and seed formation. The molecular dynamics runs in these calculations contain water with different concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions.

We have chosen a slightly different approach for polypeptide chains as template formers. Hybrids of two and three-dimensional networks of these chains with varying connectivities (chemically and structurally) were used to simulate interfaces for early seed formation. Charged (mostly negatively) functional groups on the networks allow polar carbonate surfaces to be exposed at the interface whereas in air or water (without a template), typically the non-polar surface such as (104) is the most stable one.

The ultimate goal of this project is to provide systematic insight into template and, thus, seed formation control from a theoretical point of view. Ultimately, we want to understand which carbonate will form with which surface at the interface depending on the template provided.

### Reference

Buijnsters, P.J.J.A., Donners J.J.J.M., Hill S.J., et al. (2001) *Langmuir* **2001**, *17*, 3623-3628.