

Template or kinetics directed
mineralization

Introduction

- Open questions concerning both the insoluble organic matrix and soluble entities such as the acidic proteins commonly associated with biominerals.
- Macromolecules may provide boundaries for compartmentalization of ions prior to nucleation, or charged surfaces which locally change the solution composition..

- An ordered insoluble organic template may direct crystallization *via* stereochemical alignment between functional groups or by epitaxial atomic-scale registry between charge positions in the organic and mineral structures.

- Protein may recognize and bind to specific crystal faces, affecting growth and morphology.
- It has been proposed that the acidic proteins may act as process-directing agents, in which the solution crystallization is transformed into a precursor process.

- Simplified experiments with well defined mineral or organic surfaces will allow these competing mechanisms to be distinguished, but many experiments suffer from a lack of *in-situ* structural information

- Observations of macroscopic crystal morphology or orientation relative to the organic are suggestive of epitaxial templating in many of these studies.
- At the same time, it has been remarked repeatedly that functionalized organic surfaces can influence both **structural and kinetic aspects** of mineral phase formation.
- Ion concentrations, temperature, and pH are known to affect the structures of such surfactant assemblies.

- It is crucial to monitor the structures of both template and mineral during nucleation, to correctly distinguish kinetic from epitaxial or stereochemical control.
- Only recently have *in-situ* methods such as synchrotron X-ray scattering and neutron reflectivity been applied to mineralizing film systems.

X ray scattering

- Surface-sensitive synchrotron X-ray scattering from Langmuir monolayers of fatty acids assembled on a supersaturated calcium bicarbonate subphase.
- Escape of carbon dioxide gas precipitates CaCO_3 , and in the absence of a monolayer film, the thermodynamically stable calcite polymorph is obtained in the form of rhomb-shaped crystals.
- A series of influential papers published showed that CaCO_3 nucleating at surfactant monolayers can crystallize as flattened calcite rhombs or polycrystalline florets of the less stable vaterite polytype.

- Previous studies made two essential points: (i) vaterite could be induced by a stearic acid monolayer, dependent upon the surface pressure of the film; (ii) macroscopic vaterite crystals observed by optical microscopy or harvested for electron diffraction appeared to be oriented with the c -axis normal to the monolayer plane.

- Stereochemical match between the orientations of the charged fatty acid headgroups and the carbonate groups in vaterite, combined with favorable cation positions in vaterite as opposed to calcite, promoted vaterite formation at the surface.
- The importance of a stereochemical or even epitaxial template is now sometimes taken for granted.

Monolayer role for polymorph

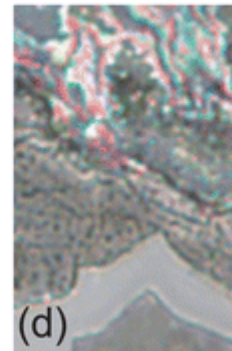
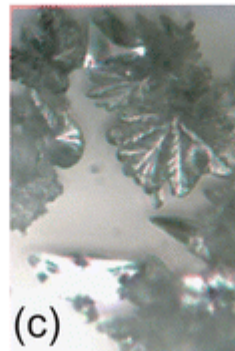
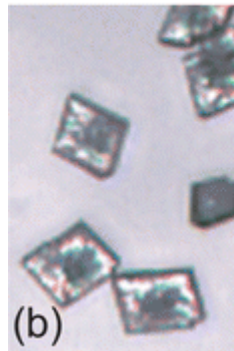
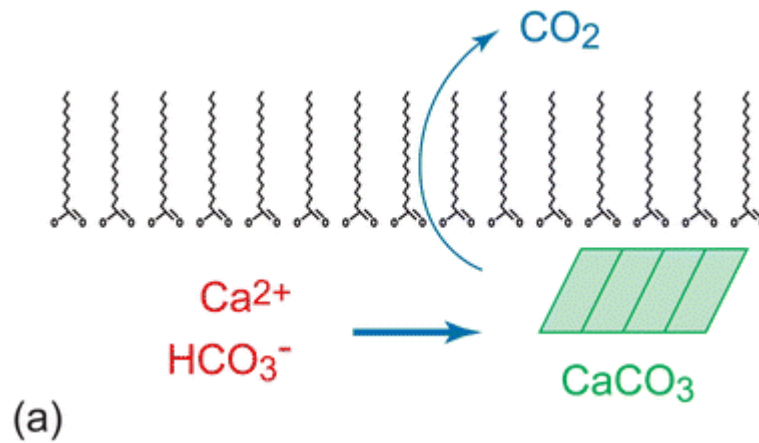


Figure explanation

- (a) Depiction of fatty acid template on the supersaturated calcium bicarbonate solution. CO₂ escape precipitates calcium carbonate, which nucleates preferentially at the monolayer.
- (b) Rhombohedral calcite favored during fast mineralization.
- (c) Vaterite florets obtained from rate-inhibited mineralization.
- (d) Birefringent calcite thin film grown through an amorphous precursor phase by the addition of poly(acrylic acid, sodium salt),

Kinetic effects

- *In-situ* X-ray scattering measurements demonstrate that the CaCO₃ polytype is determined primarily by kinetic effects and does not depend explicitly upon the structure of the monolayer film.
- Metastable amorphous precursor phase by the addition of poly(acrylic acid) to the subphase. The amorphous precursor films nucleate slowly enough to enable time-dependent measurements of film density and thickness, giving us direct access to kinetic parameters.

- The concepts of epitaxial control are prevalent in the biomimetics literature.
- In contrast to earlier reports, vaterite crystals nucleated by stearic and arachidic acid films are not oriented relative to the monolayer.
- X-ray reflectivity measurements of the cation binding find values of 4–8 molecules per Ca^{2+} at the monolayer.
- Not suggestive of an epitaxial mechanism for promoting the vaterite polytype.

Template independency

- Grazing-incidence diffraction from monolayers under a variety of solution conditions finds that a rectangular unit cell forms in the presence of these cations, essentially independent of applied surface pressure, solution supersaturation, or CO₂ overpressure.
- The template-independent variations in solution kinetics can select vaterite over calcite, the former being favored when mineralization occurs more slowly due to a change of stoichiometry of reactants near the monolayer.

Summary

- The dominant factor in polymorph selectivity was found to be the CO₂ escape rate.
- The *in-situ* structural information obtained in the experiments has allowed us to make very specific statements about kinetic *vs.* stereochemical or epitaxial mechanisms in this system for the first time.
- Synchrotron X-ray scattering techniques will play an important part in future studies of organic-mediated and structurally templated mineralization.