

Cation Binding and the Effects of Acidic Soluble Polymers on Biomimetic Mineral Nucleation

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Introduction

In the process of biomineralization, an organism provides a chemical environment that directs the formation of mineral structures having precisely controlled morphologies and polytypes. Organic matter is always found in proximity to the biominerals, and it generally belongs to one of two categories: (1) insoluble material that provides a boundary surface or structural scaffold or (2) soluble, usually acidic, macromolecules that affect the kinetics. The precise mechanisms by which these organic species control mineralization are not known, but much of the present literature is concerned with whether or not stereochemical recognition occurs on particular crystal faces. Recognition by the insoluble organic is usually assumed to cause preferential nucleation of a given mineral through a templating effect, while recognition by a species in solution is often supposed to have an inhibitory effect on the crystal's growth. Both mechanisms may play a role, and, in fact, in some cases, proteins that seem to promote mineralization *in vivo* but act as inhibitors *in vitro* have been identified.

Methods and Materials

We are studying a model system of mineralization from solution at a Langmuir film, where the chosen surfactant monolayer takes the part of the insoluble organic and where the effects of acidic polymers in solution on mineralization can be studied at the air-water interface. A supersaturated calcium bicarbonate subphase was prepared by dissolving CaCO₃ powder in water with bubbled CO₂ gas, with the addition of polyacrylic or polyaspartic acids in amounts of 10-50 µg/mL. Arachidic acid monolayers were spread onto the surface from chloroform solution and compressed to surface pressures of 25 mN/m, after which the films were allowed to relax at a fixed area. X-ray reflectivity and grazing-incident in-plane diffraction were monitored to observe growth of the mineral film.

Results

Our experiments have found that an important effect of the soluble polymer is to change the amount of cations bound to the anionic headgroups of the fatty acid monolayer. Reflectivity measurements performed for a range of polymer concentrations, each within an hour of spreading the monolayer, were analyzed to quantify the electron density bound in the headgroup region. Excess density is attributed to Ca²⁺ bound to the headgroups (and to some water that also will occupy this volume). We find that both polyaspartic acid and polyacrylic acid additives decrease the cation binding by more than a factor of two when compared with a supersaturated calcium bicarbonate subphase that lacks any polymer additive.

Discussion

These *in situ* experiments allow us to make the crucial distinction between templating and kinetic effects in biomimetic mineralizing systems. Our further studies have shown that, in this type of system, physical conditions, such as the rate of CO₂ diffusion, drastically affect film growth. However, we have no strong evidence of interactions between the in-plane monolayer structure and that of the mineral film. Hence, we believe that this system is more properly described as kinetically driven than template driven. Control of biomimetic mineral films by a more direct effect of the surfactant template is presumably more important in other systems, which we hope to identify in the future.

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