Polymer Controlled Growth of an Amorphous Mineral Film

Beamline: X22B

Technique: Reflectivity and Grazing Incidence X-ray Diffraction from a Liquid Surface

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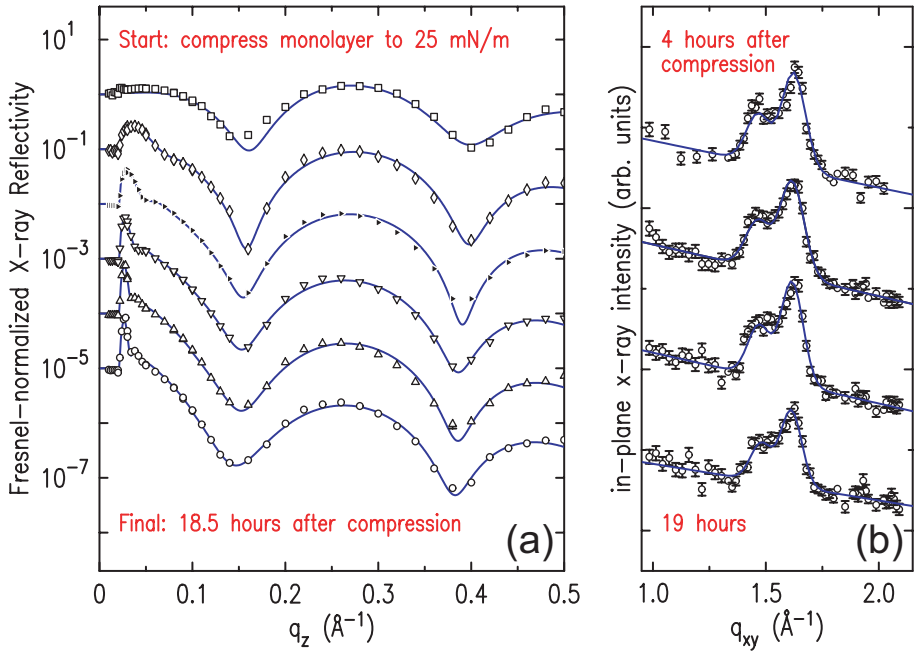
E. DiMasi, et al. "Polymer-controlled growth rate of an amorphous mineral film nucleated at a fatty acid monolayer" *Langmuir* **18** (2002) 8902.

Motivation:
Biomineralization, in which mineralization is controlled by proteins and other organics, produce phases which are not stable in ambient conditions. For example, $CaCO_3$ is abundant geologically as calcite but can be stabilized by marine organisms in amorphous, hydrous forms. To study the effects of acidic polypeptides on $CaCO_3$ mineralization in a systematic way, we have studied nucleation at fatty acid films from solutions containing polyacrylic acid additives. Such soluble polymers may mimic the effects of proteins affecting biological mineralization.



(a) Time series of reflectivity curves from initial preparation of the sample through the growth of the mineral film. Fits to the oscillations in the data allow us to extract the time-dependent density, thickness and roughness of the amorphous $CaCO_3$ phase. (b) In-plane diffraction patterns show that the fatty acid structure is affected by the charged polymer additives, but not by the time-dependent film growth.

Results: One effect of the polyacrylic acid (PAA) is to remove Ca^{2+} cations from solution. Analysis of x-ray reflectivity shows that the binding of Ca^{2+} to the surface film is reduced fivefold compared to cases without polymer. With the lower surface charge, the in-plane structure of surfactant molecules is affected. Instead of calcite crystals nucleating directly from solution, the polymer forces mineralization through an amorphous $CaCO_3$ phase. The growth rate of this film depends mainly upon supersaturation rather than PAA concentration; however, PAA lengthens the life of the amorphous film.