

Microbeam Diffraction from Abalone Shell

Beamline: X20A

Technique: X-ray
Microbeam Diffraction

Researchers:

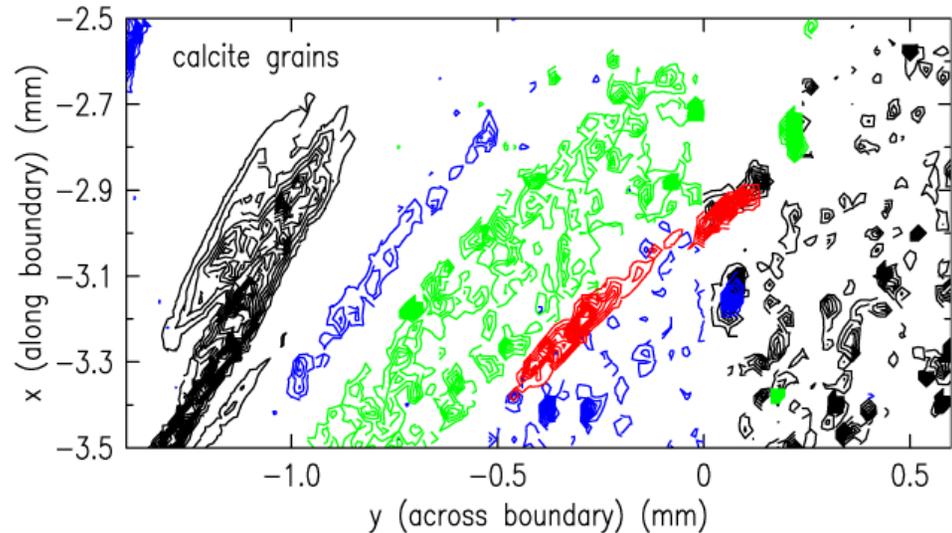
E. DiMasi (BNL),
M. Sarikaya (U.Washington),
I.C. Noyan and J.L. Jordan-
Sweet (IBM)

Publication:

E. DiMasi et al. "Synchrotron
X-ray Microbeam Diffraction
from Abalone Shell"
J. Materials Research **19**
(2004) 1471.

Motivation: The shell of the red abalone has a hierarchical microstructure that lends it strength orders of magnitude higher than that of its inorganic calcium carbonate building blocks. The nacre layer of the shell is composed of 40 nm thick aragonitic-CaCO₃ platelets, stacked in planes parallel to the shell's surface. The outer portion of the shell is composed of calcitic-CaCO₃ columns. Between these two crystal types, orientational correlations are expected close to the nacre-prismatic boundary, where the early growth stage of the crystals takes place.

Results: A large scale mapping in the x and y translations was performed at calcite peak positions, to identify these grains and find the boundary region. Contours of Bragg peak intensities from the calcite peaks show that the long axes of the calcite grains impinge the boundary at approximately 45 degree angles, suggesting nucleation on (104) faces and growth along the c-axis. Smaller calcite crystals are found in the boundary region, where a coarse powder texture is observed. No evidence for alignment of crystallization across the nacre-prismatic boundary was obtained, contrary to suppositions in the literature.



X-ray Bragg peak intensity maps for locations on abalone shell on the prismatic ($x < 0.2$) and nacre ($x > 0.2$) sides of the cut face containing the boundary line. Intensity contours at the calcite (300) (green) and (220) (other colors) peak positions, where each color corresponds to differently oriented sets of crystallites. The black contours also show aragonite (420) intensity on the nacre side of the boundary, with a texture of much smaller crystallites.

When is Mineralization Really Template Directed?

Beamline: X22B

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

Researchers:

E. DiMasi (BNL), M. J. Olszta and L. B. Gower (U. Florida, Gainesville)

Publication:

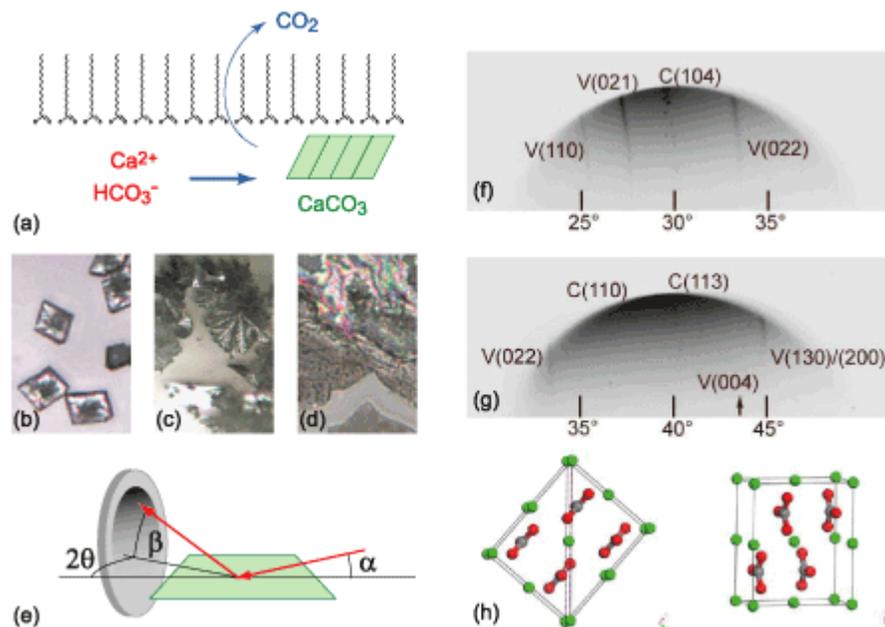
E. DiMasi, et al.

“When is template directed mineralization really template directed?”

CrystEngComm 5 (2003) 346.

Motivation: In biological mineralization, proteins and other macromolecules direct the formation of non-equilibrium morphologies and polytypes. In the case of CaCO_3 minerals, studies have shown that organic templates such as fatty acid monolayers can selectively nucleate certain polytypes. Very influential reports from 1988 attributed this to stereochemical templating, although no direct structural evidence could be obtained at early growth times. Using in-situ grazing incidence diffraction, we re-investigated these mineral recipes and looked for evidence of stereochemical recognition between crystal and template.

Results: Diffraction patterns from the mineralizing surface exhibit powder arcs and show conclusively that the vaterite polytype is not oriented to the organic template. Instead we found, by varying the supersaturation in template-independent ways, that kinetic effects are sufficient to select between calcite and vaterite. One way by which kinetics may be modified is the surface charge of the monolayer, which attracts Ca^{2+} cations from solution. The ratio of Ca^{2+} to surfactant molecules at the surface is much lower than the 1:2 ratio implied by stereochemical binding models.



CaCO_3 nucleation at monolayers (a) can produce calcite rhombs (b), vaterite florets (c), or an amorphous film (c), depending on kinetics. In-situ surface x-ray scattering (e) obtains diffraction patterns (f,g) showing that a range of vaterite orientations (h) are present at the monolayer.

Polymer Controlled Growth of an Amorphous Mineral Film

Beamline: X22B

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

Researchers:

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V. M. Patel, M. J. Olszta,
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and L. B. Gower (U. Florida,
Gainesville)

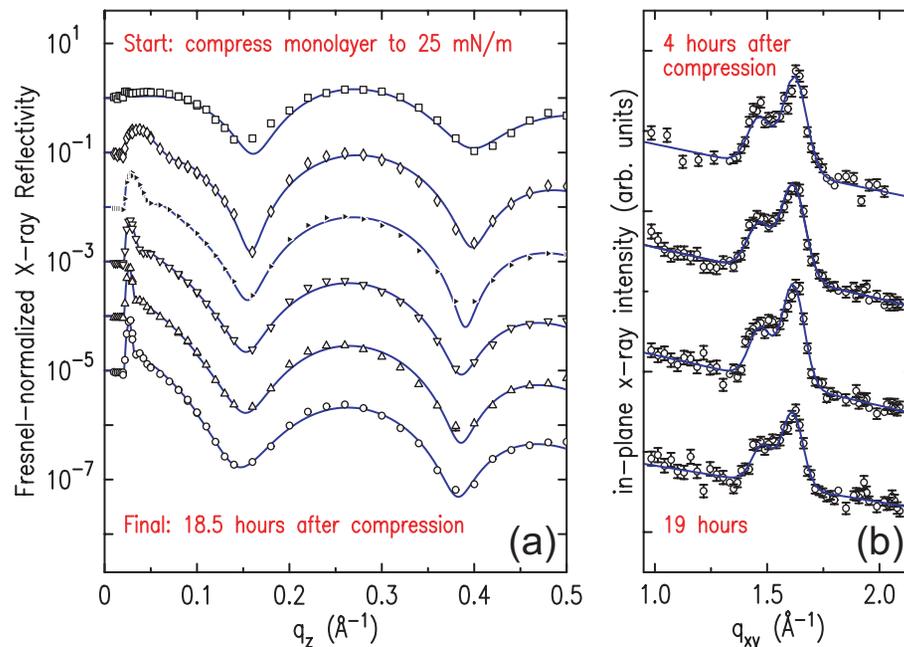
Publication:

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.

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.



(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.

Breaking the Gibbs Adsorption Rule in Liquid Metals

Beamline: X25

Technique: Resonant X-ray Reflectivity from a Liquid Surface

Researchers:

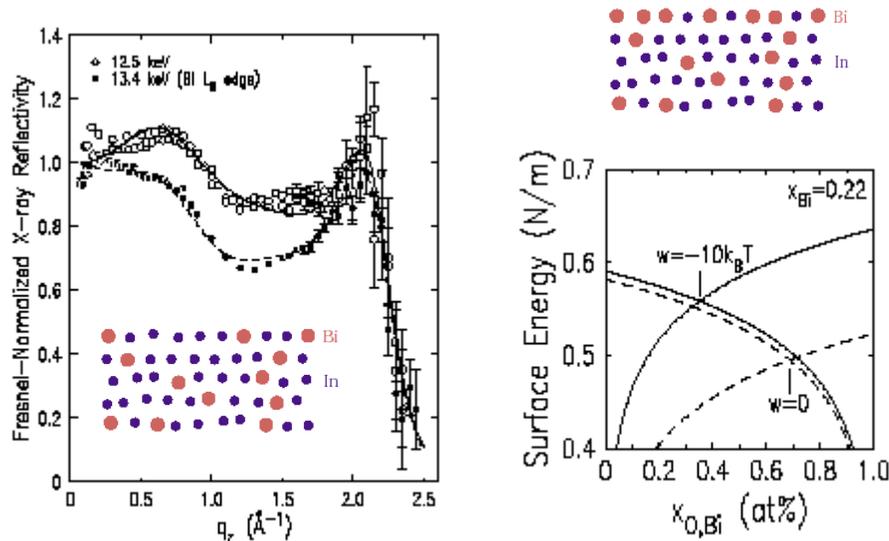
E. DiMasi, B.M. Ocko, L.E. Berman (BNL), H. Tostmann, O.G. Shpyrko, P. Huber, P.S. Pershan (Harvard), M. Deutsch (Bar-Ilan University, Israel)

Publication:

E. DiMasi et al. "Pairing Interactions and Gibbs Adsorption at the Liquid Bi-In Interface: Observations by Resonant X-ray Reflectivity." *Phys. Rev. Lett.*, **86** (2001) 1538.

Motivation: Binary liquids are supposed to follow a simple rule, formulated by Gibbs in 1878: the lowest surface tension species segregates at the surface. This picture assumes that interactions between atoms can be disregarded. What happens in liquids with attractive interactions? To answer this question, we performed resonant x-ray reflectivity measurements from a liquid 22% Bismuth – 78% Indium alloy. By tuning the incident x-ray energy through the Bi LIII absorption edge, we determined the ratio of Bi to In at the surface. The Gibbs prediction is 70% Bi for the non-interacting system.

Results: We find a Bi enrichment of 35 at% in the surface layer, compared to the 22 at% in the bulk. This is considerably less Bi than would be expected in the absence of attractive Bi-In interactions, which we find must be on the order of $10 k_B T$ to explain our data. This work quantifies, for the first time, the extent to which attractive interactions can compete with Gibbs adsorption. These are the first resonant x-ray reflectivity measurements ever achieved on a liquid surface, and were made possible by specialized instrumentation at the National Synchrotron Light Source at BNL.



Left: X-ray reflectivity from the liquid Bi-In surface as x-ray energy is varied near the Bi LIII edge. Inset schematically shows the observed surface segregation of 35 at% Bi. Right: in the absence of attractive interactions, predicted Bi enrichment is 70%. Attractive interactions must be of order $10k_B T$ to explain the observations.