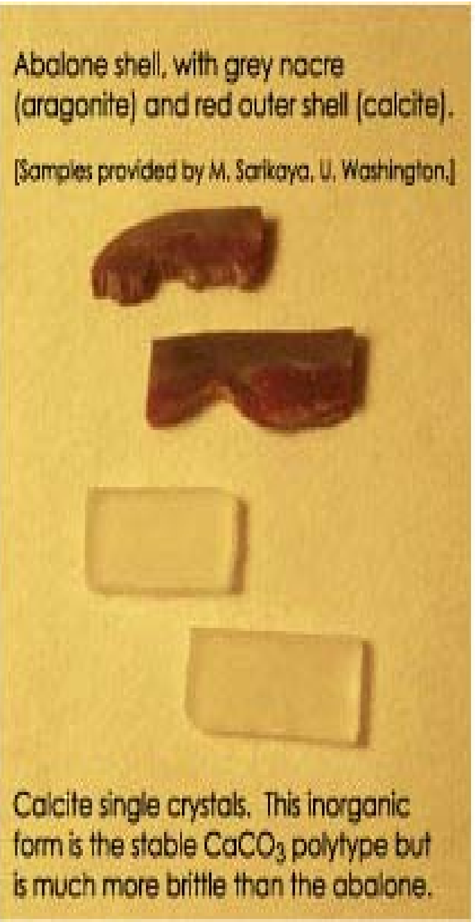
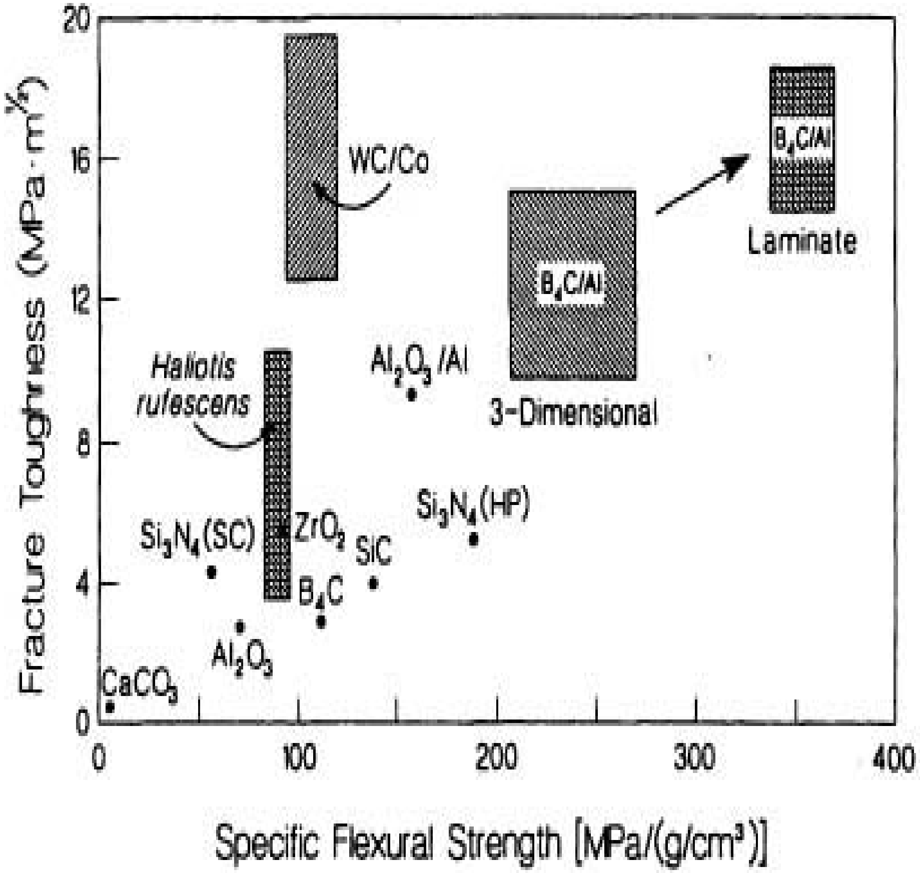
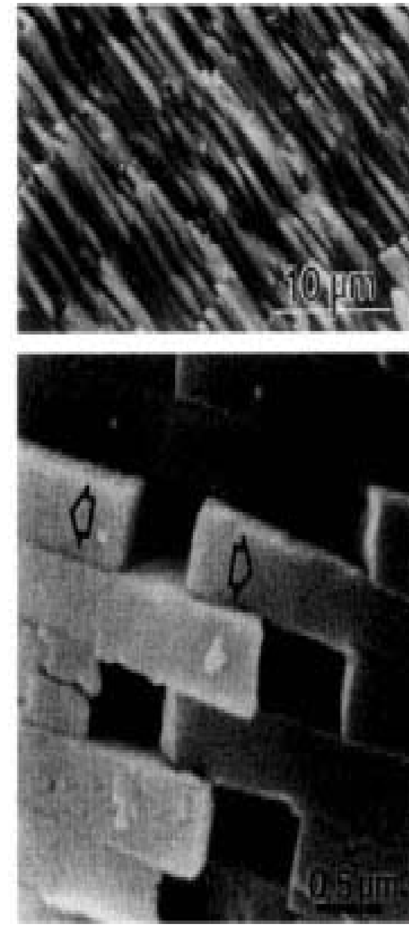
Biomineralization and In-situ Crystallization

- In the process of biomineralization, a living organism provides a chemical environment that controls the nucleation and growth of unique mineral phases.
- Often these materials exhibit hierarchical structural order, leading to superior physical properties, not found either in their inorganic counterparts or in synthetic materials.

- The abalone shell shown in the next is one of many examples.
- Mollusk shells are composite materials, where small amounts of organic material guide the nucleation of calcium carbonite into precise crystal polytypes and growth habits.
- The resulting brick-and-mortar architecture of abalone nacre lends it a strength far exceeding that of inorganic calcium carbonate.


Abalone shell, with grey nacre (aragonite) and red outer shell (calcite).
[Samples provided by M. Sarikaya, U. Washington.]
Calcite single crystals. This inorganic form is the stable CaCO3 polytype but is much more brittle than the abalone.


Fracture Toughness (MPa·m½)
Specific Flexural Strength [MPa/(g/cm³)]
0
4
8
12
16
20
0
100
200
300
400
WC/Co
B4C/Al
Laminate
B4C/Al
3-Dimensional
Al2O3 /Al
Haliotis rufescens
Si3N4(SC)
ZrO2
SiC
Si3N4(HP)
B4C
Al2O3
CaCO3


10 µm
0.5 µm

- One of the persistent questions that arises in trying to understand these structures concerns the interactions between organic molecules and the crystallizing mineral.
- And one of the reasons this question does persist is that many of the most important experimental techniques available -- optical and electron microscopy.
- It must be conducted after crystallization has been completed or interrupted. Therefore, structural information about very early growth times is not available.
- Yet this early stage, the transformation between the disordered assemblage of molecules and the macroscopic crystal, lies at the heart of the problem.

Synchrotron x-rays.

- Research program in biomineralization combines structural studies of biogenic materials with in-situ studies of "biomimetic" crystallization, using synchrotron x-rays.

Calcium carbonate nucleating from solution in a Langmuir trough at NSLS beamline X22B.

Calcium carbonate and fatty acid monolayer

- Calcium carbonate films can be grown from solution, mineralizing at a surface monolayer that serves as a nucleation region.
- But does it serve as an organic template?
- This question is answered by studying the film structure with liquid surface scattering techniques as the film nucleates and crystallizes.

- Nucleation can be strongly affected by acidic macromolecules similar to those found in biological systems.
- Synchrotron x-ray measurements provide structural information from the film's inception as a collection of calcium ions collected at a flat interface, through the amorphous stage and on to its final form as a macroscopic crystalline film.
- The dependence of film growth rate on the chemical conditions, rather than the template structure, leads us to conclude that this system is *kinetically directed*, and that *no strutural templating takes place*.l

Abalone shell at the beamline

- Surprisingly many well-studied biogenic composite materials still raise fundamental structural questions: is the mineral amorphous or crystalline?
- How do domain sizes change under these environmental conditions? What stabilized these nanocrystalline components? and so on.
- Synchrotron x-ray work is well poised to complement other techniques and answer such questions. Mysteries remain even for the well studied nacre structure.

Bone implant application

- Synthetic biomaterials for medicine have been important for a century, and this will continue in the future.
- Ti multilayer and TiO_2 samples used for calcium phosphate nucleation experiments under electrochemical control.
- Studies of model systems related to implant materials allow us to simultaneously address scientific questions and future applications.
- Soft-solution processing of industrial materials is another important motivation. Biomimetic materials are grown under environmentally friendly conditions.

Implant materials