Natural and synthetic biomineralization

Last time: enzymatic recognition of biomaterials
            Cytokine signaling from biomaterials

Today: introduction to biomineralization and biomimetic inorganic/organic composites
       Interfacial biomineralization


Supplementary Reading: -

ANNOUNCEMENTS:
Complex macro- and microstructures of biological inorganic materials

Central tenets of biomineralization:

--organic molecules regulate nucleation, growth, morphology, and assembly of inorganic materials

--often employ molecular recognition at organic-inorganic interfaces to control syntheses

Radiolarian: Microskeleton of amorphous silica

Coccolith: CaCO$_3$ microskeleton

A. hexagona: Microskeleton of amorphous silica
HYDROXYAPATITE

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Please see: 
http://www.isis.rl.ac.uk/isis2000/highlights/boneScatteringH14.htm
Paradigms in biomineralization

Two mechanisms of templating complex natural crystals:
Interfacial inorganic deposition
interfacial inorganic deposition

4 main classes:
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Vesicular biomineralization
Vesicular biomineralization
Vesicular biomineralization

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Please see: Figure 1 and Figure 5.1 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.
Mechanisms for control of biomineral shape

Spatial control of chemical deposition:

- Lipid bilayer
- Growing mineral
- Growth direction
- Sequentially activated ion transporters

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Example biological mineralization: diatom and radiolarian microskeletons

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Mineralization nucleated at *exterior* surface of vesicles

‘vesicle foam’
Example biological mineralization: diatom and radiolarian microskeletons

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Biological vesicular mineralization: human growth plate cartilage and tooth dentine

**Hypertrophic chondrocytes/odontoblasts**

- Ion channels
- Transport proteins
- Acidic phospholipids
- \( \text{Ca}^{++} \)
- \( \text{PO}_4^- \)

Lecture 14 Spring 2006
Synthetic vesicular mineralization

Vesicular mineralization

H₂O

Oil

Alkylamine vesicles

-NH₂

Inorganics

Natural and synthetic vesicular biomineralization

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Microemulsion biomineralization

Organic (oil) phase

Aq CaHCO₃

SDS

Gas-evolving microemulsion biomineralization

Microemulsion mineralization

Chemistry of CaCO$_3$ deposition in vesicles:
Mineralizing bicontinuous microemulsions

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Coupling growth with self-assembly: micelle-directed inorganic crystallization

Coupling growth with self-assembly: micelle-directed inorganic crystallization

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Please see: Figure 1 in Li, M., H. Schnableffer, and S. Mann. “Coupled Synthesis and Self-Assembly of Nanoparticles to Give Structures with Controlled Organization.” *Nature* 402 (1999): 393-395.

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Please see: Figure 2 in Li, M., H. Schnableffer, and S. Mann. “Coupled Synthesis and Self-assembly of Nanoparticles to give Structures with Controlled Organization.” *Nature* 402 (1999): 393-395.
Organic templating of inorganic materials
Optimization of inorganic biomaterial properties—nature does it better

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Organic template control of inorganic nucleation

Nucleation of solid phase:
Organic template control of inorganic nucleation

Nucleation of solid phase:
Organic templates can select crystal structures
What are the organic templates?

Templates used by nature:

Template functional groups correlate with structure to be nucleated:
How are free energy barriers modified by organic templates?

Lattice matching for epitaxial nucleation of inorganic:
Charge distribution effects on templated nucleation

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Please see: Table 1 in Mann, et al. 1993.
Charge distribution effects on templated nucleation

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2 mechanisms of surface-mediated nucleation:
Controlled nucleation and growth vs. preferential nucleation and growth

• Organic templates can preferentially nucleate inorganics without ordering or aligning the crystals

• Templatized crystal growth requires both recognition of individual molecules and a larger underlying lattice to drive ordered nucleation

• Obtaining periodicity in organic templates:
Further Reading