Natural and synthetic biomineralization

Last time: enzymatic recognition of biomaterials
Cytokine signaling from biomaterials

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

Reading: Stephen Mann, 'Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry,' Ch. 3 pp. 24-37, Oxford Univ. Press (2001)

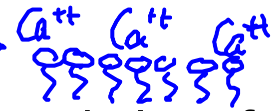
Supplementary Reading: -

ANNOUNCEMENTS: REMINDER: NO CLASS NEXT TUESDAY

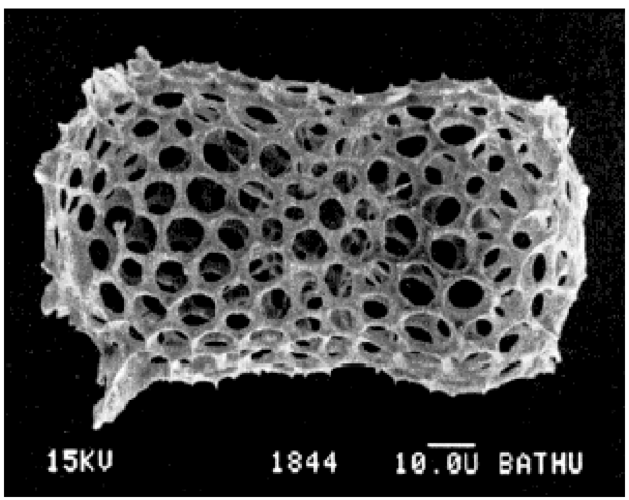
Complex macro- and microstructures of biological inorganic materials

Central tenets of biomineralization:

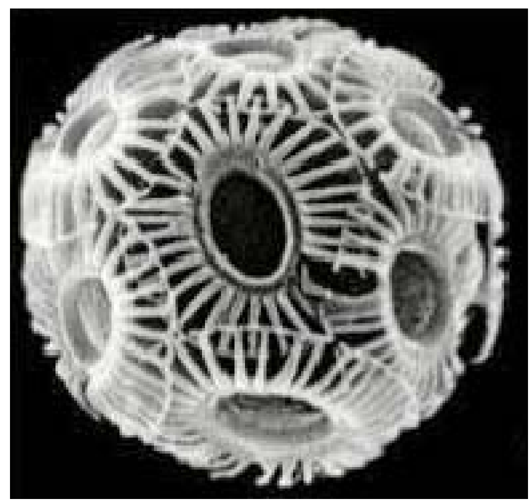
--organic molecules regulate nucleation, growth, morphology, and assembly of inorganic materials



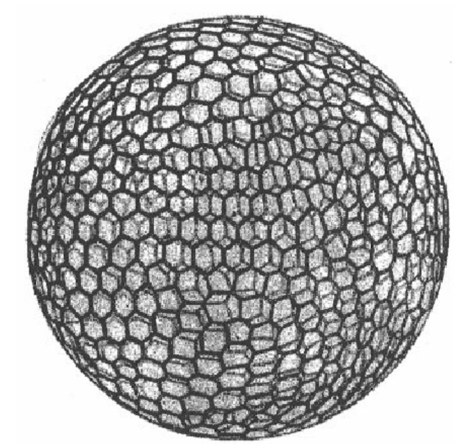
--often employ molecular recognition at organic-inorganic interfaces to control syntheses



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

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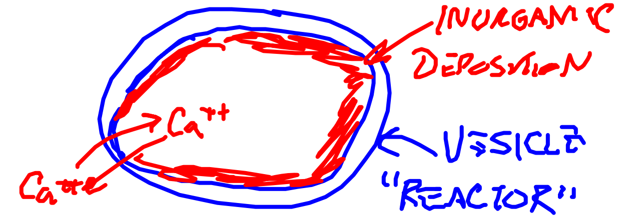
Please see: Table 2.2 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

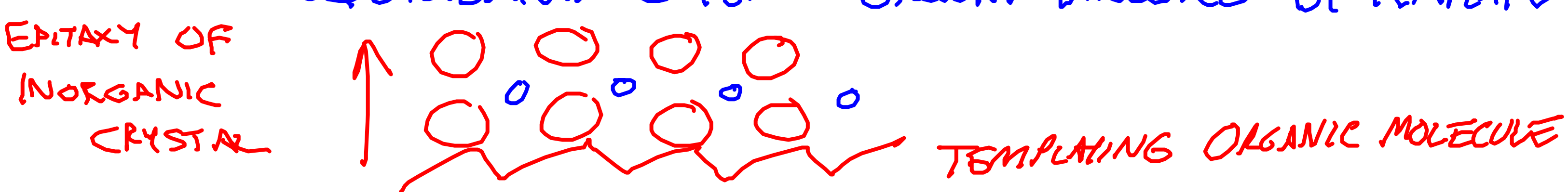
Paradigms in biomineralization

Two mechanisms of templating complex natural crystals:



1. INTERFACIAL INORGANIC GROWTH
   - NUCLEATION AT/WITHIN ORGANIZED BOUNDARIES
   - KINETICALLY CRYSTAL GROWTH

2. EPITAXIAL INORGANIC (CRYSTAL) GROWTH
   - GROWTH FROM TEMPLATE BIOMOLECULES
   - EQUILIBRIUM CRYSTAL GROWTH DIRECTED BY TEMPLATE



Interfacial inorganic deposition

interfacial inorganic deposition

UTILIZATION OF 2-PHASE SYSTEMS FOR COMPARTMENTALIZED DEPOSITION

4 main classes:

- VESICULAR MINERALIZATION
- MICROEMULSION "
- MICELLE "
- DENDRIMER "

Vesicular biomineralization

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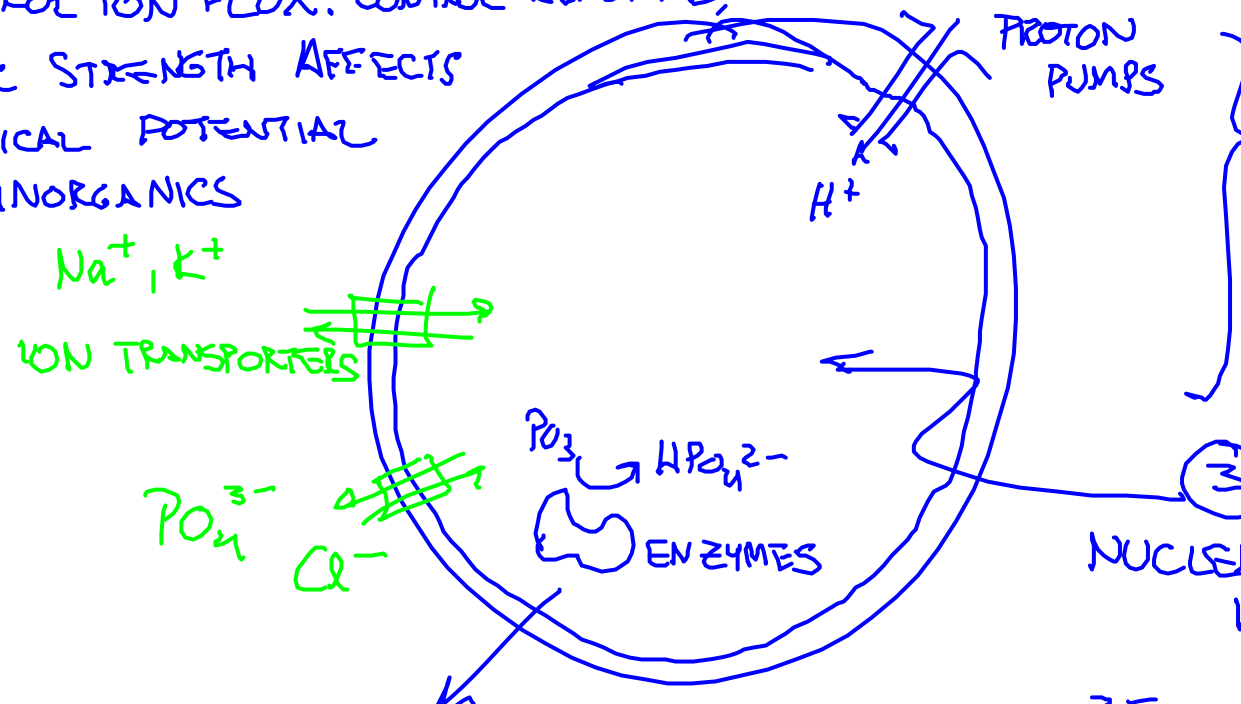
Please see: Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

Vesicular biomineralization

VESICLES PROVIDE CONTROL OF:

① CONTROL pH: ION SOLUBILITY VARIES w/ pH

② CONTROL ION FLUX: CONTROL REACTANTS, IONIC STRENGTH AFFECTS CHEMICAL POTENTIAL OF INORGANICS



④ CRYSTAL STRUCTURE AND MORPHOLOGY

③ NUCLEATION KINETICS

e.g. ALKALINE PHOSPHATASE: PRODUCE HPO_4^{2-}
CARBONIC ANHYDRASE: REMOVES H_2CO_3 ...

Vesicular biomineralization

$$M^{z+}_{\nu+} X^{z-}_{\nu-} \rightleftharpoons \nu_+ M^{z+} + \nu_- X^{z-}$$

SOLID — IONS IN SOLUTION

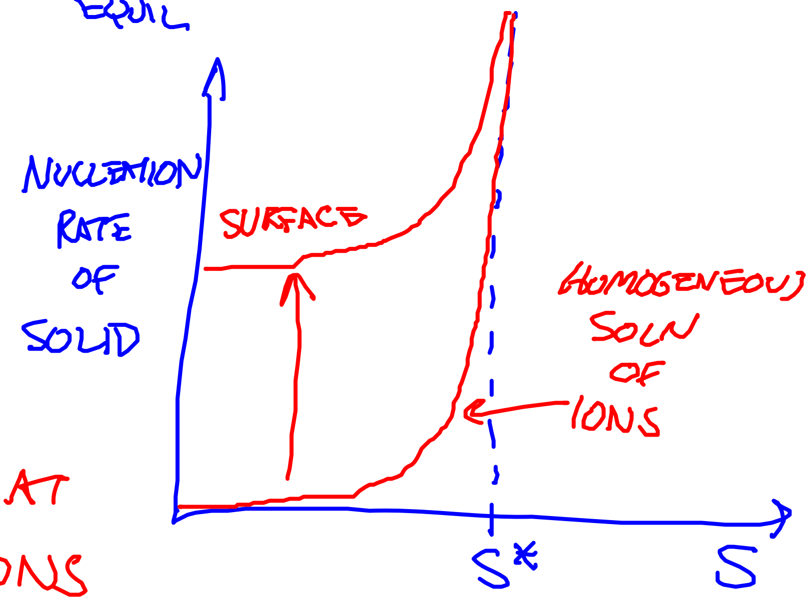
$$K_{sp} = \text{SOLUBILITY PRODUCT} = \left[[M^{z+}]^{\nu+} [X^{z-}]^{\nu-} \right]_{\text{MAX EQUIL}}$$

$$S = \text{RELATIVE SUPERSATURATION} = \frac{[M^{z+}]^{\nu+} [X^{z-}]^{\nu-}}{K_{sp}}$$

$S > 1$ FAVORS SOLID FORMATION

↓

VESICLE SURFACES ALLOW HETEROGENEOUS NUCLEATION AT LOW TOTAL ION CONCENTRATIONS



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

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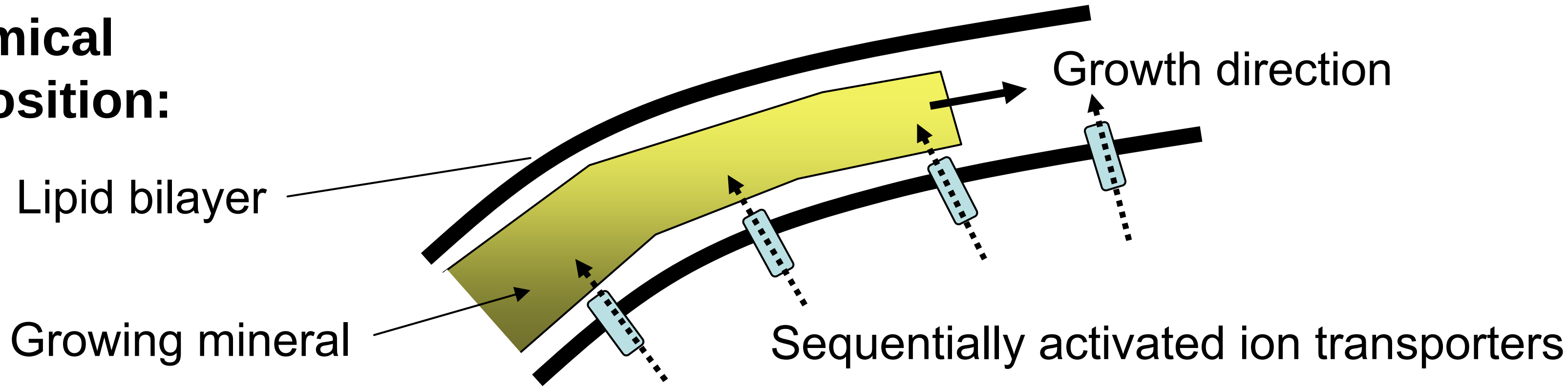
Please see: Figure 7.6 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*.
New York, NY: Oxford University Press, 2001.

Spatial control of chemical deposition:



Example biological mineralization: diatom and radiolarian microskeletons

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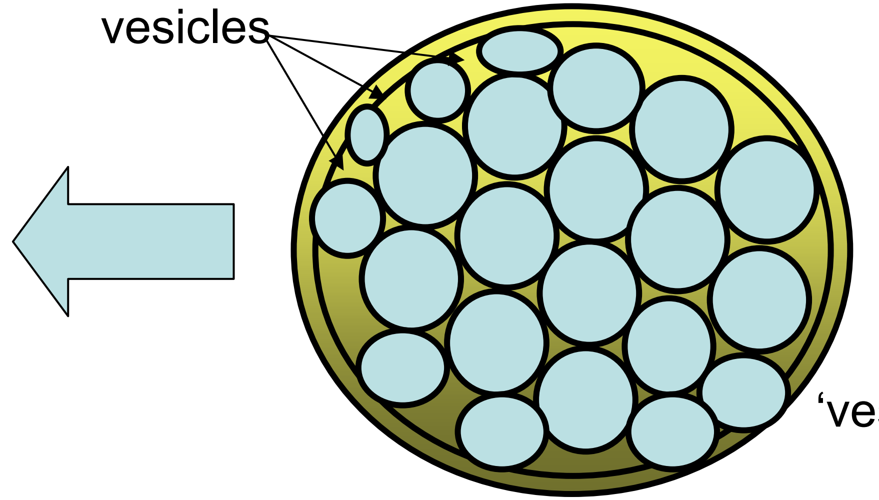

Example biological mineralization: diatom and radiolarian microskeletons

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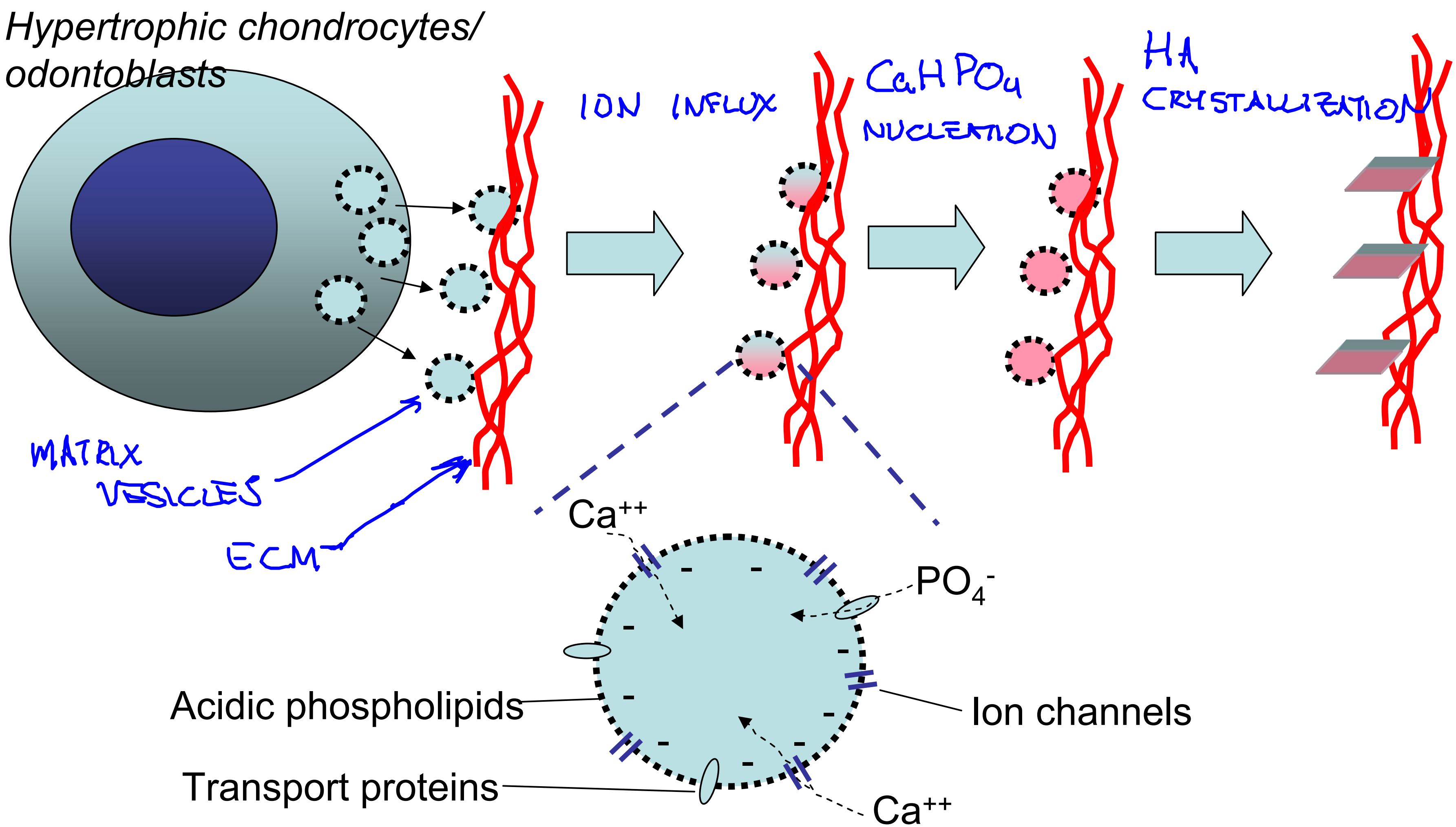
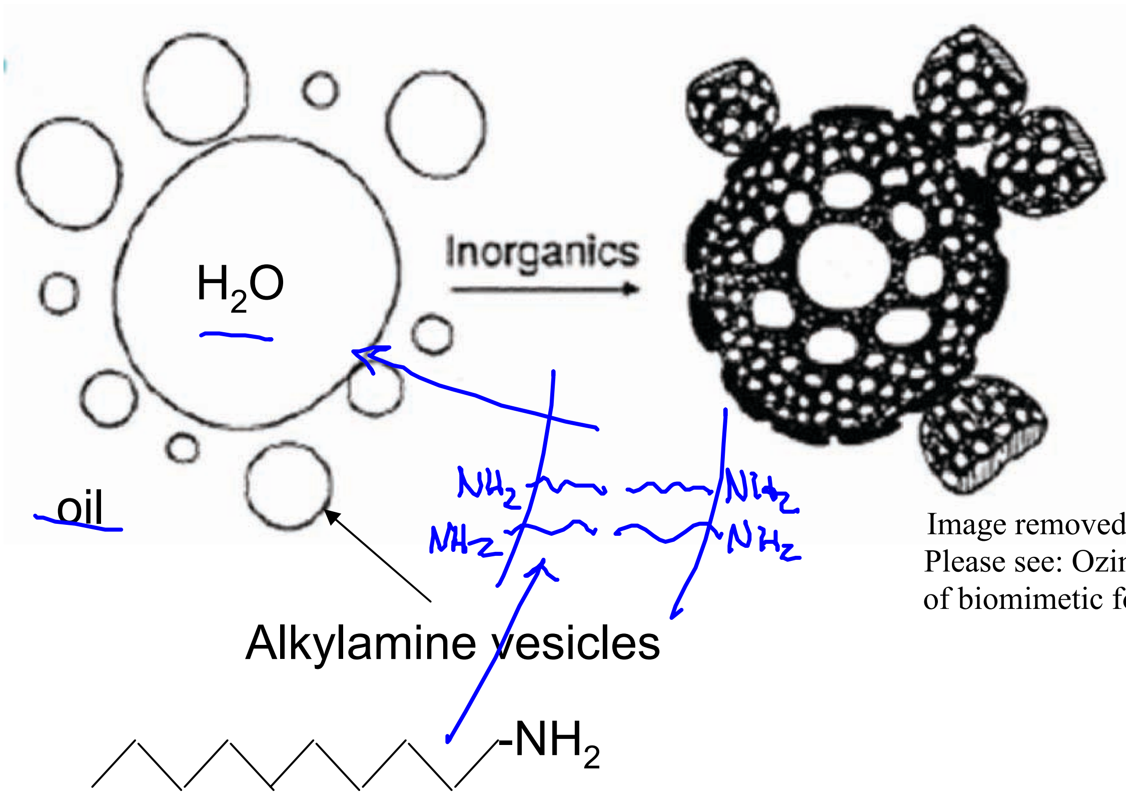
Please see: Figure 7.16 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

Biological vesicular mineralization: human growth plate cartliage and tooth dentine



Synthetic vesicular mineralization

Vesicular mineralization



Please see: Ozin, G. A. "Morphogenesis of biomineral and morphosynthesis of biomimetic forms." *Acc Chem Res* 30 (1977): 17.

Natural and synthetic vesicular biomineralization

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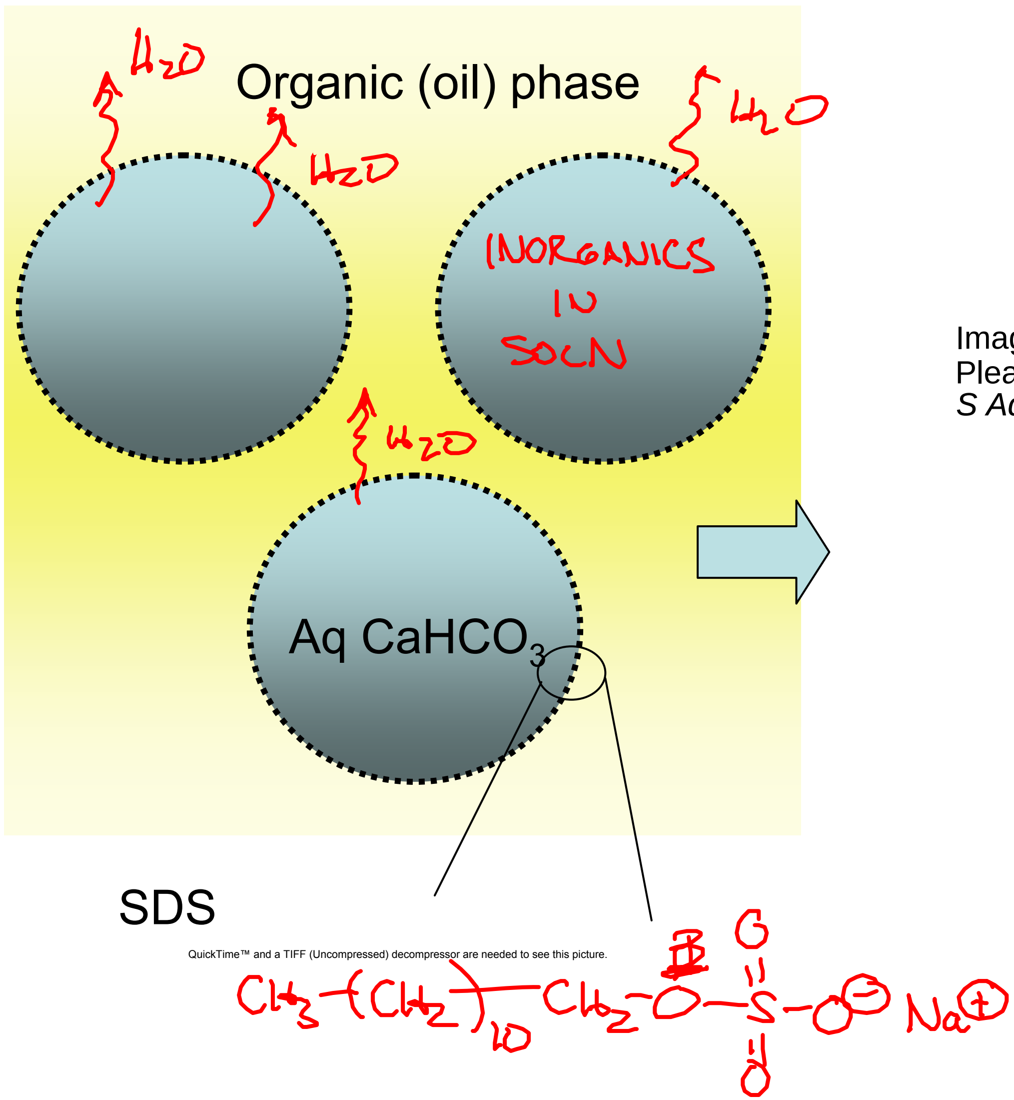
Please see: Ozin, G. A. "Morphogenesis of biomineral and morphosynthesis of biomimetic forms." *Acc Chem Res* 30 (1997): 17.

Microemulsion biomineralization



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Please see figure 3 in Walsh, D., B. L. Lebeau, and S. Mann, *S Adv Mater* 11 (1999): 324-328.

Gas-evolving microemulsion biomineralization

Microemulsion mineralization

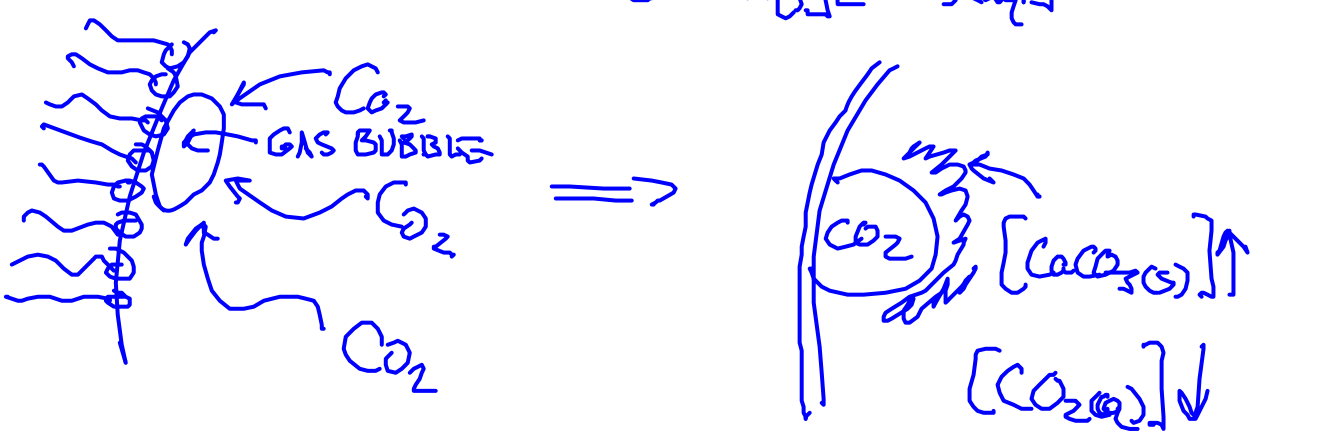
Chemistry of $CaCO_3$ deposition in vesicles:

$$Ca^{++}(aq) + 2HCO_3^{-}(aq) \longrightarrow CaCO_{3(s)} + CO_{2(aq)} + H_2O$$

(DISSOLVED GAS)

AT EQUILIBRIUM:

$$K_{eq} = \frac{[H_2O][CO_{2(aq)}][CaCO_{3(s)}]}{[Ca^{++}(aq)][HCO_3(aq)]^2} = \text{CONSTANT AT GIVEN } T, P$$



Mineralizing bicontinuous microemulsions

(1) UNSTABLE BICONTINUOUS MICROEMULSION → (2) FREEZE STRUCTURE IN PLACE (IONS STILL MOBILE IN Aq PHASE) → (3) GROW $CaHPO_4$ IN NANOCHANNELS

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Please see: Figure 9.33 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

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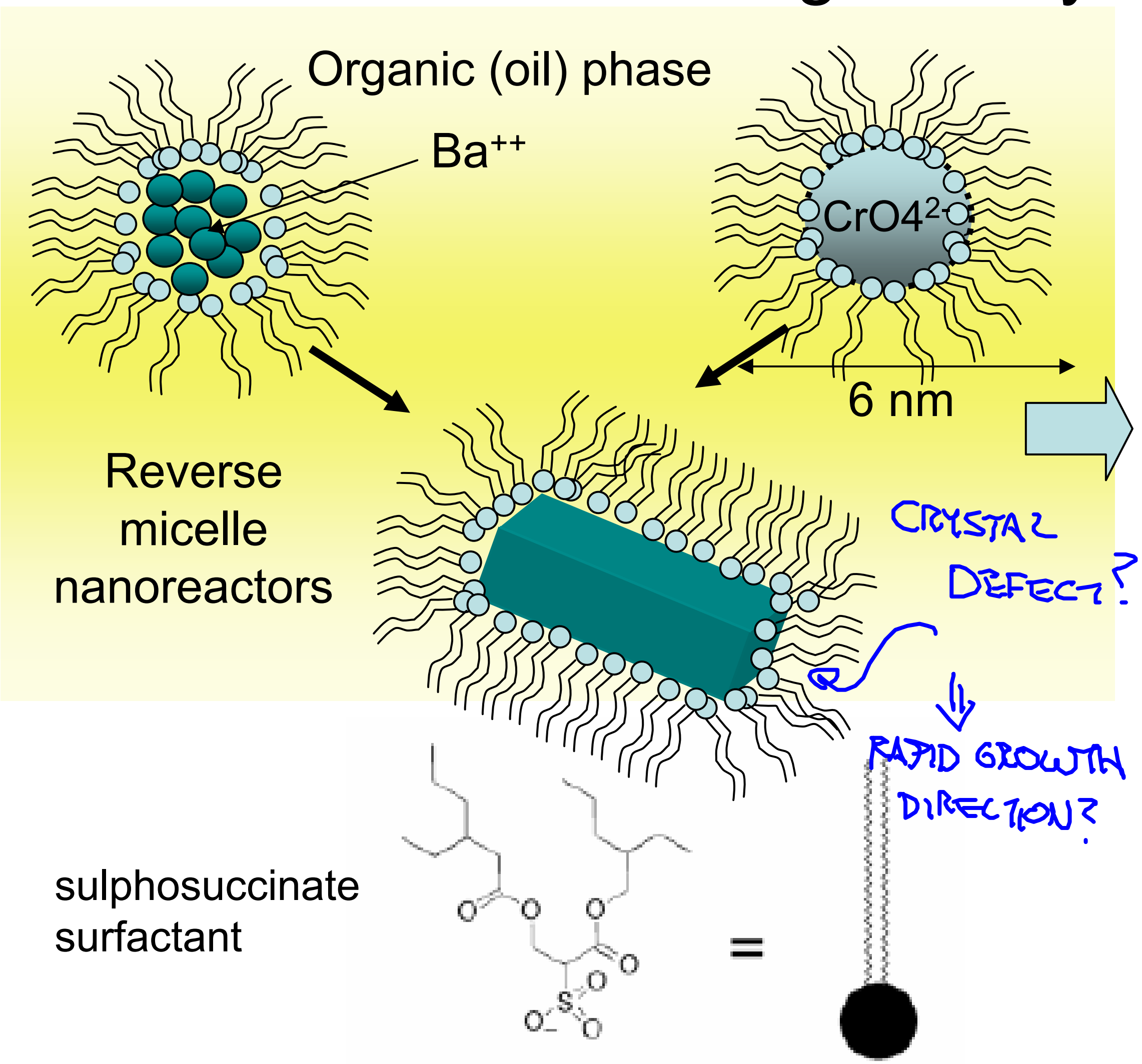
Please see: Figure 9.32 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

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

LIPID INTERDIGITATION DRIVEN BY VdW FORCES



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Please see: Li, M., H. Schnablefer, and S. Mann. "Coupled synthesis and self-assembly of nanoparticles to give stuctures with controlled organization." *Nature* 402 (1999): 393-395.

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 Stuctures 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 Stuctures with Controlled Organization." *Nature* 402 (1999): 393-395.

Organic templating of inorganic materials

EPITAXY OF INORGANICS

Optimization of inorganic biomaterial properties- nature does it better

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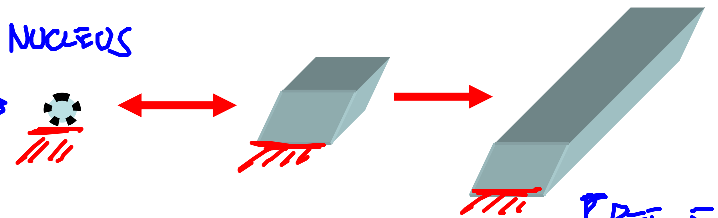
Please see: Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

Organic template control of inorganic nucleation

Nucleation of solid phase:

IONS IN SOLUTION → SOLID NUCLEUS



$$\Delta G_{NUC} = \Delta G_{SURFACE} - \Delta G_{BULK}$$

$$= 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \frac{\Delta \bar{G}_{form}}{\bar{V}}$$

σ: SURFACE ENERGY OF NUCLEATING CRYSTAL

$\sigma > 0$

↓ MODIFIED BY THE PRESENCE OF A NUCLEATING SURFACE

r: RADIUS OF NUCLEUS

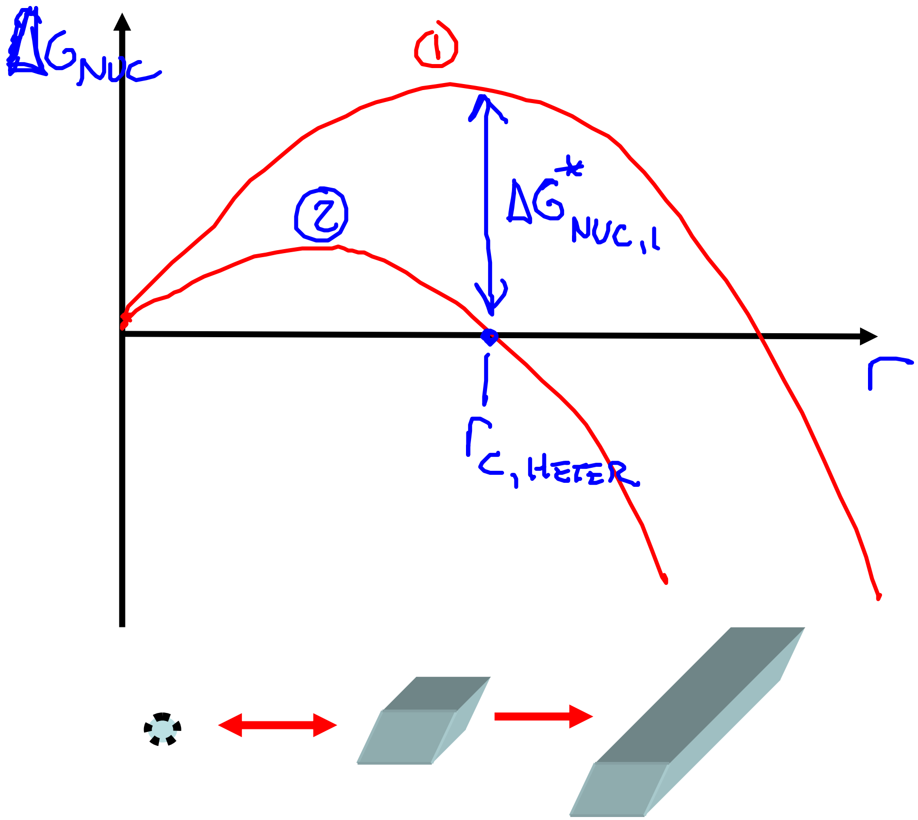
$\Delta \bar{G}_{form}$: FREE ENERGY CHANGE TO FORM SOLID FROM FREE IONS

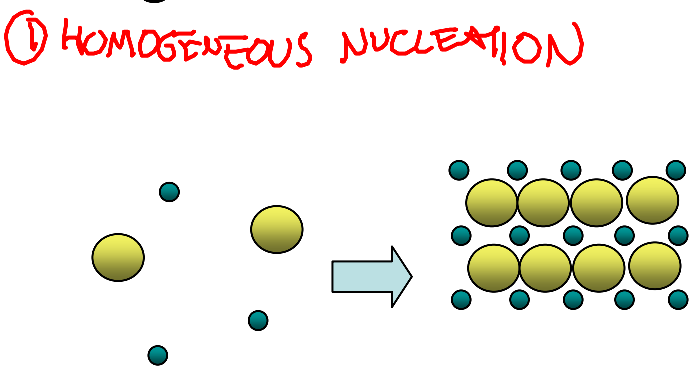
↓ FIXED BY CHEMISTRY OF SYSTEM

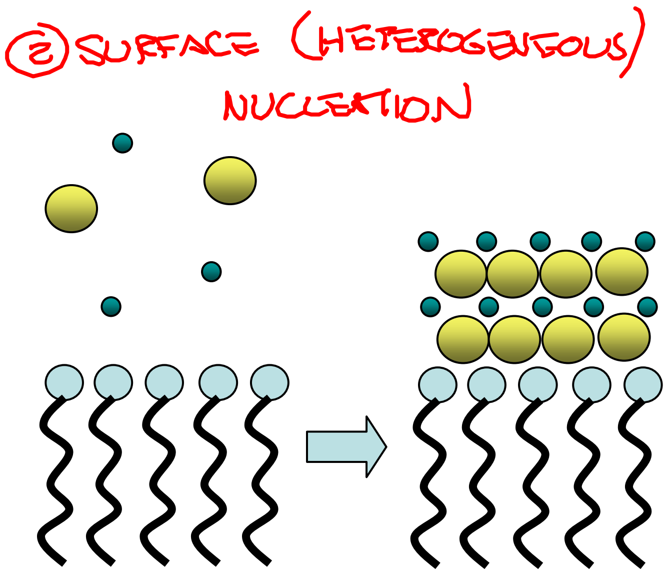
$\bar{V}$: MOLAR VOLUME

Organic template control of inorganic nucleation

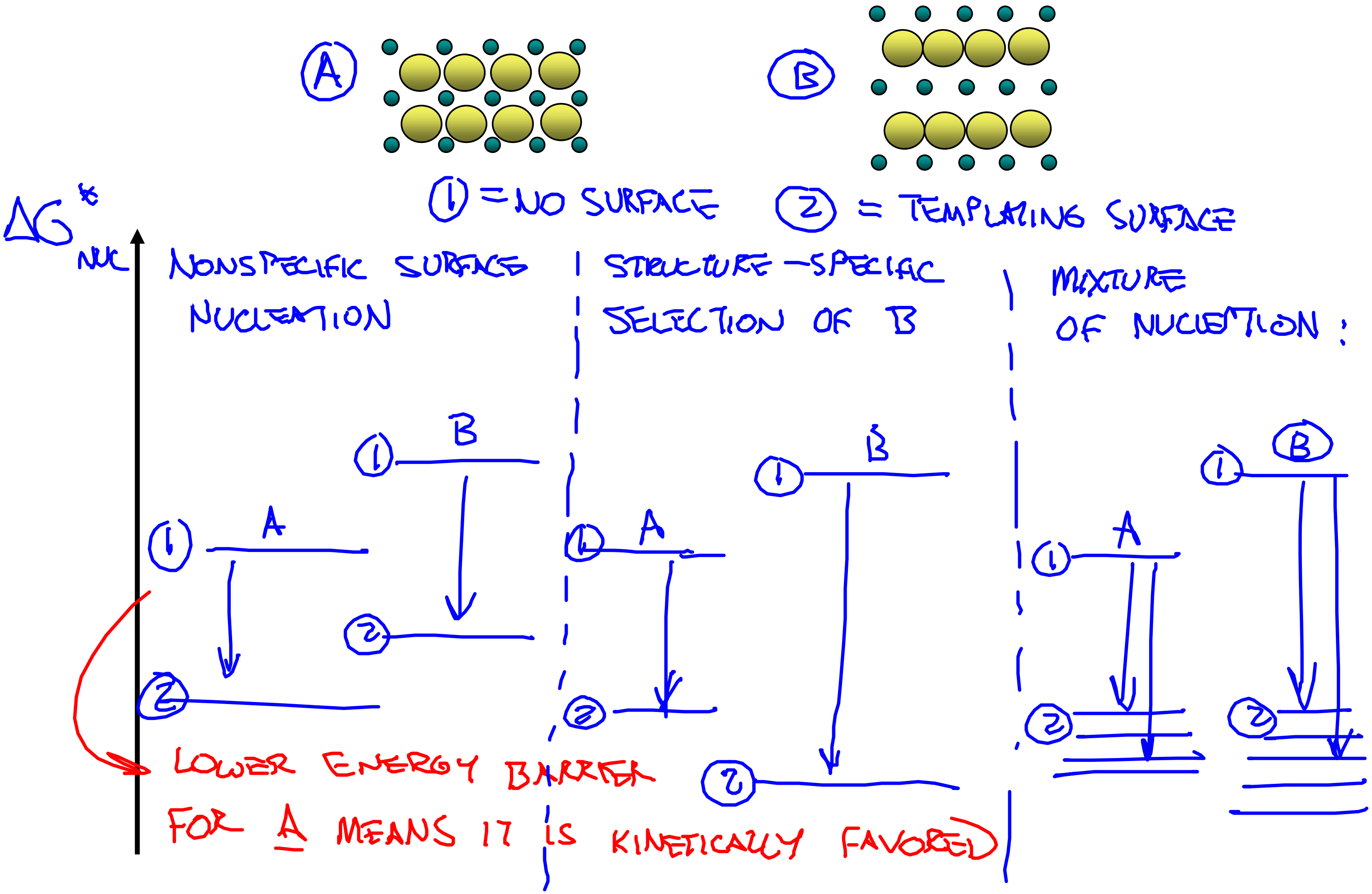
Nucleation of solid phase:





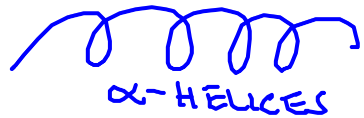


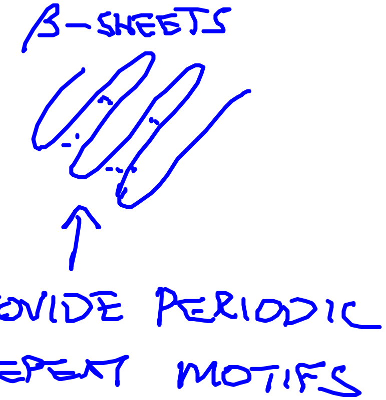
Organic templates can select crystal structures



What are the organic templates?

Templates used by nature:





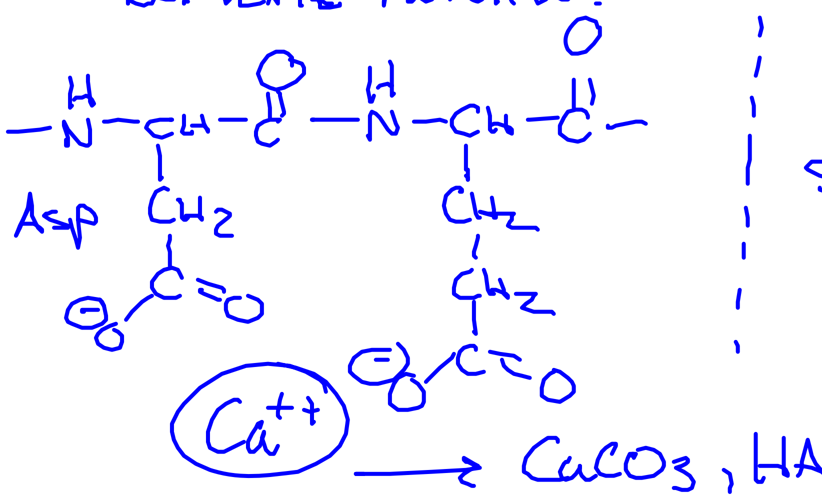
PROTEINS → FORM HIGHER-ORDER STRUCTURES

POLYSACCHARIDES

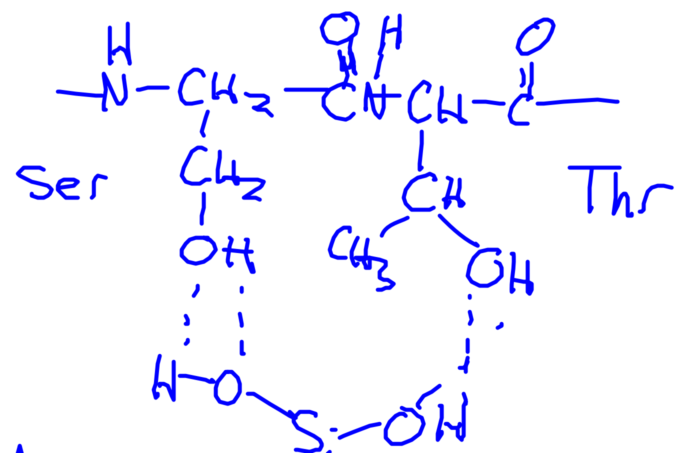
LIPIDS → LESS SELECTIVE: 2D FLUIDS

Template functional groups correlate with structure to be nucleated:

CARBOXYLATE MOIETIES:



H-BONDING MOIETIES:



How are free energy barriers modified by organic templates?

Lattice matching for epitaxial nucleation of inorganic:

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Please see: Figure 4A in Mann, et al. 1993.

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Please see: Figure 4B in Mann, et al. 1993.

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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Please see: Figure 4.23 in Mann, S.
Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry. New York, NY: Oxford University Press, 2001.

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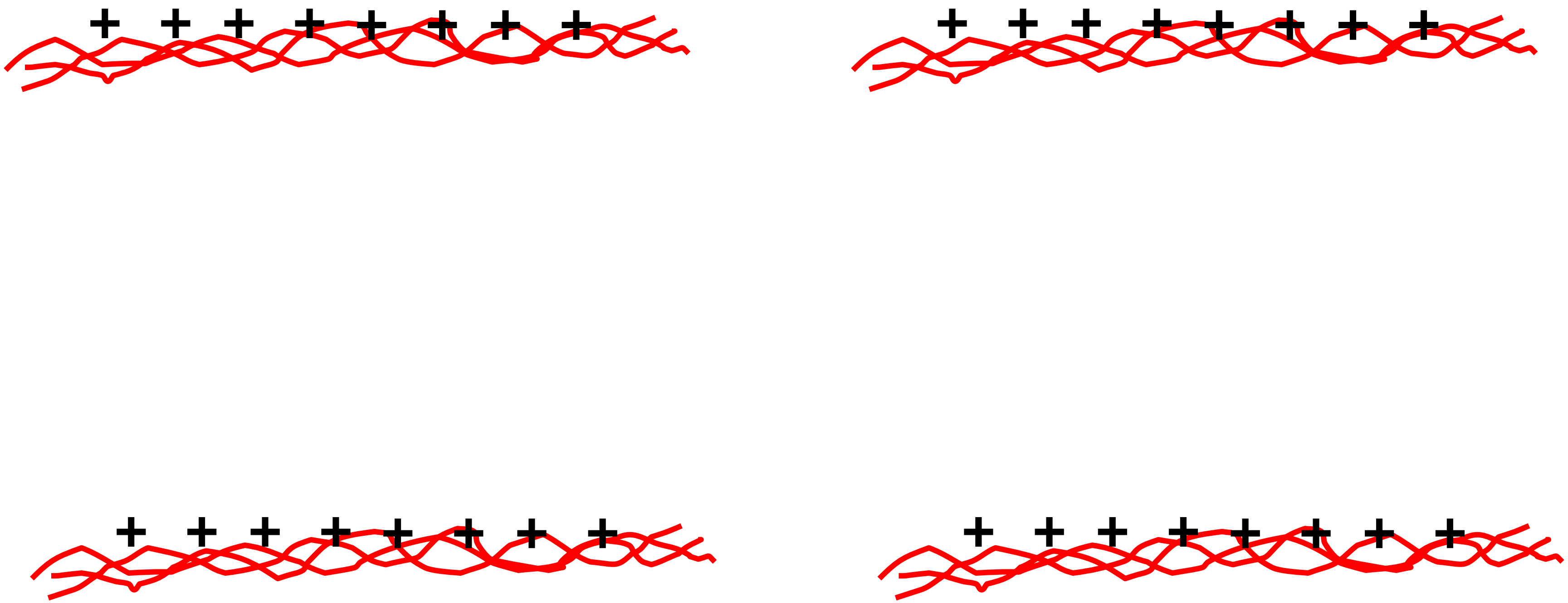
Please see: Figure 4.20 in Mann, S.
Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry
New York, NY: Oxford University Press, 2001.

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

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

    - Obtaining periodicity in organic templates:

Further Reading

1. Estroff, L. A. & Hamilton, A. D. At the interface of organic and inorganic chemistry: Bioinspired synthesis of composite materials. *Chemistry of Materials* **13**, 3227-3235 (2001).
2. Ozin, G. A. Morphogenesis of biomineral and morphosynthesis of biomimetic forms. *Accounts of Chemical Research* **30**, 17-27 (1997).
3. Green, D., Walsh, D., Mann, S. & Oreffo, R. O. C. The potential of biomimesis in bone tissue engineering: Lessons from the design and synthesis of invertebrate skeletons. *Bone* **30**, 810-815 (2002).
4. Almqvist, N. et al. Methods for fabricating and characterizing a new generation of biomimetic materials. *Materials Science & Engineering C-Biomimetic and Supramolecular Systems* **7**, 37-43 (1999).
5. Walsh, D., Hopwood, J. D. & Mann, S. Crystal Tectonics - Construction of Reticulated Calcium-Phosphate Frameworks in Bicontinuous Reverse Microemulsions. *Science* **264**, 1576-1578 (1994).
6. Walsh, D., Lebeau, B. & Mann, S. Morphosynthesis of calcium carbonate (vaterite) microsponges. *Advanced Materials* **11**, 324-328 (1999).
7. Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry* (Oxford Univ. Press, New York, 2001).
8. Young, J. R., Davis, S. A., Bown, P. R. & Mann, S. Coccolith ultrastructure and biomineralisation. *J Struct Biol* **126**, 195-215 (1999).
9. Li, M., Schnablegger, H. & Mann, S. Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization. *Nature* **402**, 393-395 (1999).
10. Donners, J. J. J. M. et al. Amorphous calcium carbonate stabilised by poly(propylene imine) dendrimers. *Chemical Communications*, 1937-1938 (2000).