General Principles of Biomineralization

- *Information is available about the structures of biominerals*
- *How they vary in different organisms*
- *Little is known about the detailed molecular interactions governing their construction*
- *However, there are some "general principles"*

Outline

- *Biologically induced biomineralization*
- *Biologically controlled biomineralization*
- *Site-directed biomineralization*
- *Control mechanisms*
- *General model*

Biologically induced biomineralization

- *Inorganic minerals are deposited by adventitious precipitation, which arises from secondary interactions between metabolic processes and the surrounding environment*
- *Example: $CaCO_3$ precipitation in types of green algae*

  $$Ca^{2+} + 2HCO3^{-} \leftrightarrow CaCO_3 + CO_2 + H_2O$$

- *Metabolic removal of CO2 during photosynthesis*
- *Extrusion of metabolic products across or into the cell wall of bacteria can result in precipitation, by reaction with extraneous metal ions*

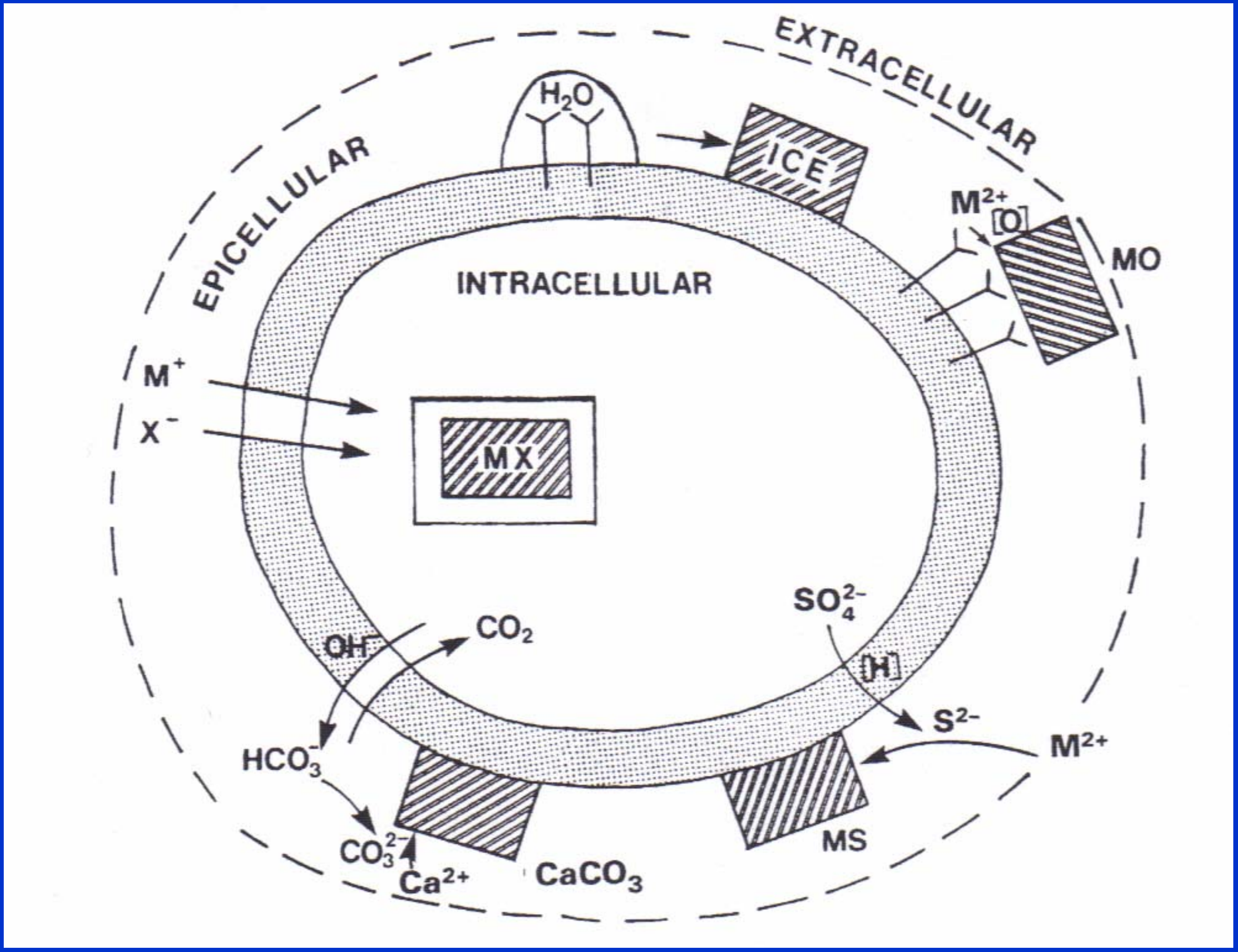
Biologically induced biomineralization

- *OH^- fluxes are involved with precipitation of oxides, carbonates and phosphates*
- *H_2S and electrons induce precipitation of sulfides and mixed-valence iron oxides*
- *Some bacteria are able to accumulate and passivate toxic metal ions, such as UO_2^{2+}, Pb^{2+}, Cd^{2+}*
- *Biologically induced biomineralization could have an important role in clean up of polluted waters and soils*

Biologically induced biomineralization

Mechanism	Mineral	Examples
Soluble biopolymers	Mn/FeOOH	*Leptothrix*
		Pedomicrobium
Spore coats	MnOOH	*Bacillus*
Gas/ion exchange		
H_2S	Fe/CuS	*Desulfovibrio*
CO_2/pH	$CaCO_3$	*Calothrix*
pH	$MgNH_4PO_4$	*Proteus*
Membrane transport	$Ca_{10}(PO_4)_6(OH)_2$	*Streptococcus*
Enzyme activity	$(UO_2)_3(PO_4)_2$	*Citrobacter*
Electron transfer	Fe_3O_4	GS-15
	UO_2	GS-15
	Au	*Pedomicrobium*
Nucleation proteins	H_2O (ice)	*Pseudomonas*
Surface layer proteins	FeOOH	*Leptothrix*

Biologically induced biomineralization



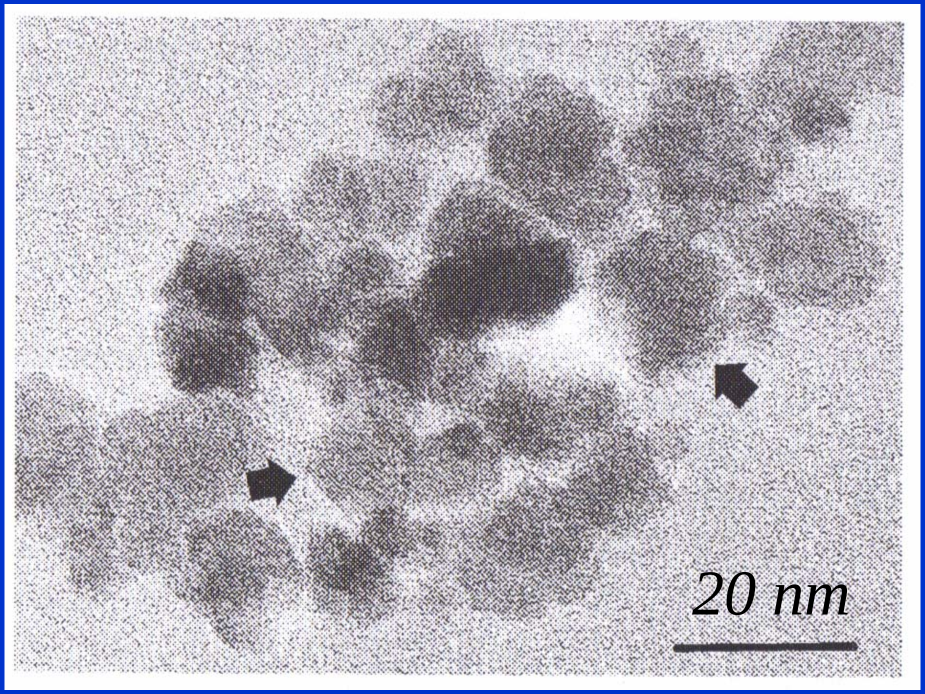
Epicellular biomineralization

Epicellular biomineralization

- *Minerals form along the surface of the cell*
- *They remain firmly attached to the cell wall*
- *In some cases individual cells become totally encrusted in the mineral deposit. They increase in weight and sink to the bottom of the ocean forming sediments*
- *Organic components (lipids, proteins, polysaccharides) of the cell wall are involved, by creating surfaces for precipitation*

Control and Morphology in Epicellular biomineralization

- *There is no strict cellular control*
- *Size, shape, structure, composition and organization are poorly defined and heterogenous*



Irregularly shaped Fe_3O_4 (magnetite) particles Produced by a bacterium Called GS-15

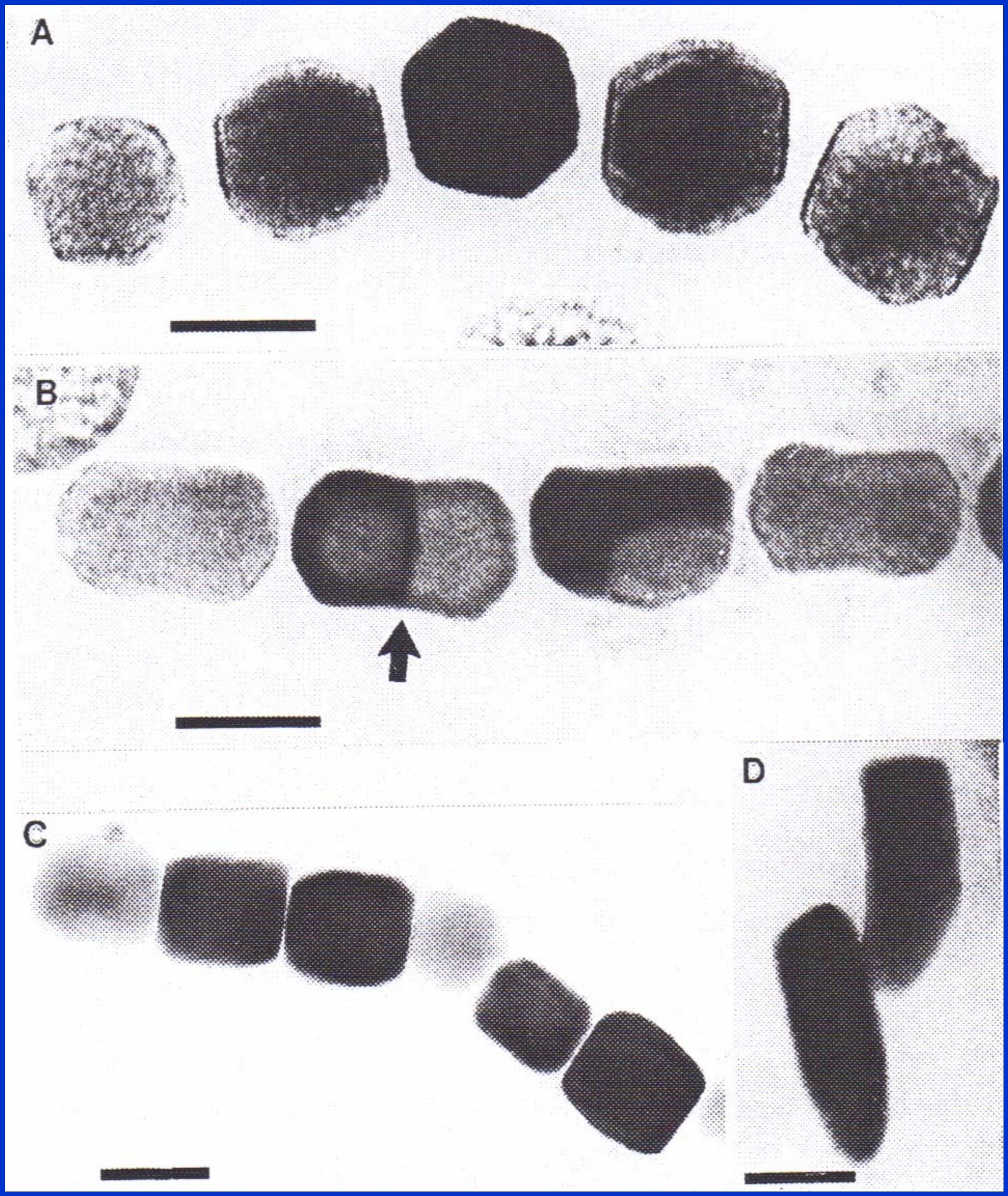
Biologically Controlled biomineralization

- *Biologically controlled biomineralization is a highly regulated process*
- *It produces minerals such as bones, shells, and teeth that have specific biological functions and structures*
- *These biominerals are identified by their species-specific crystallochemical properties*

Characteristics of these biominerals

- uniform particle sizes
- well-defined structures and compositions
- high levels of spatial organization
- complex morphologies
- controlled aggregation and texture
- preferential crystallographic orientation
- higher-order assembly into hierarchical structures.

Example: Magnetotactic Bacteria



Site-directed biomineralization: it occurs At specific sites

- *Epicellular*

  (on the cell wall)

- *Intercellular*

  (in the spaces between closely packed cells)

- *Intracellular*

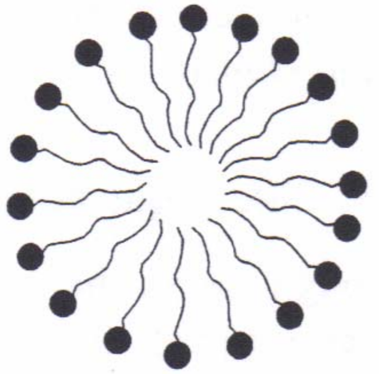
  (inside enclosed compartments within the cell)

- *Extracellular*

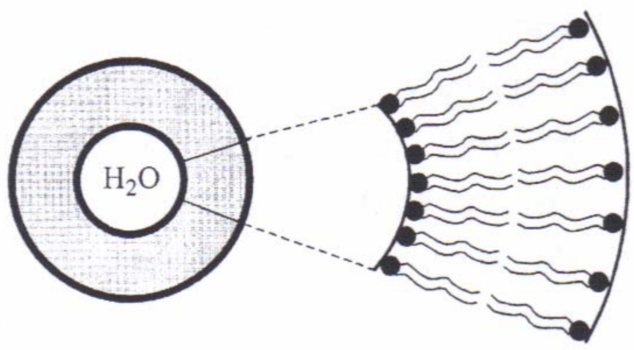
  (on or within an insoluble macromolecular framework outside the cell)

Lipid Vesicles

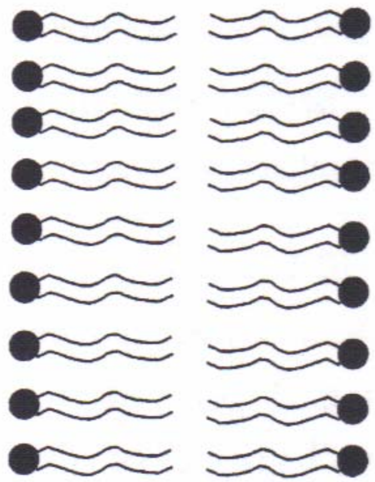
Mineralization in small spaces



Surfactant micelle with polar headgroups exposed.



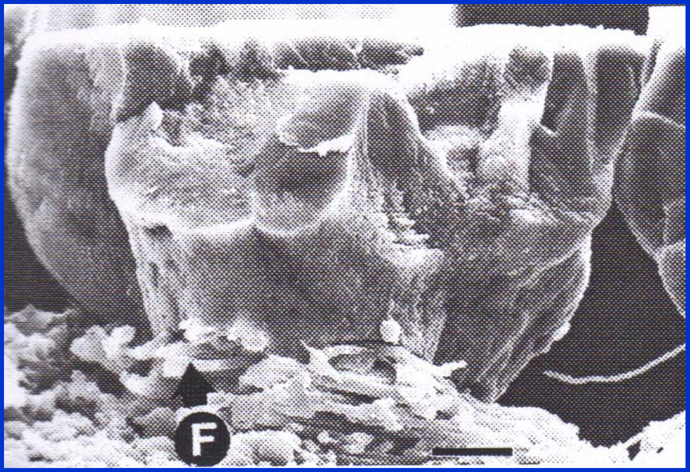
Lipid vesicle with aqueous inner compartment and bilayer shell.



Planar lipid bilayer (lamellar phase). The sheet is 4 to 5 nm in width.

Macromolecular frameworks

- *Vesicles are not suitable for building large structures such as bones, shells or teeth*
- *An organic matrix is needed*
- *It is composed of insoluble proteins and polysaccharides such as collagen or chitin*
- *The mineral phase is deposited in close association with the organic matrix*



Early stages of egshell Formation showing calcite Crystals and macromolecular fibers

Site Requirements

Although the mechanisms that govern the biological control of Biomineralization vary enormously in different systems, there are Four basic requirements associated with mineralization sites, such As vesicles and macromolecuar frameworks

- *Spatial delineation*

  For size and shape control

- *Diffusion-limited ion flow*

  For controlling solution composition

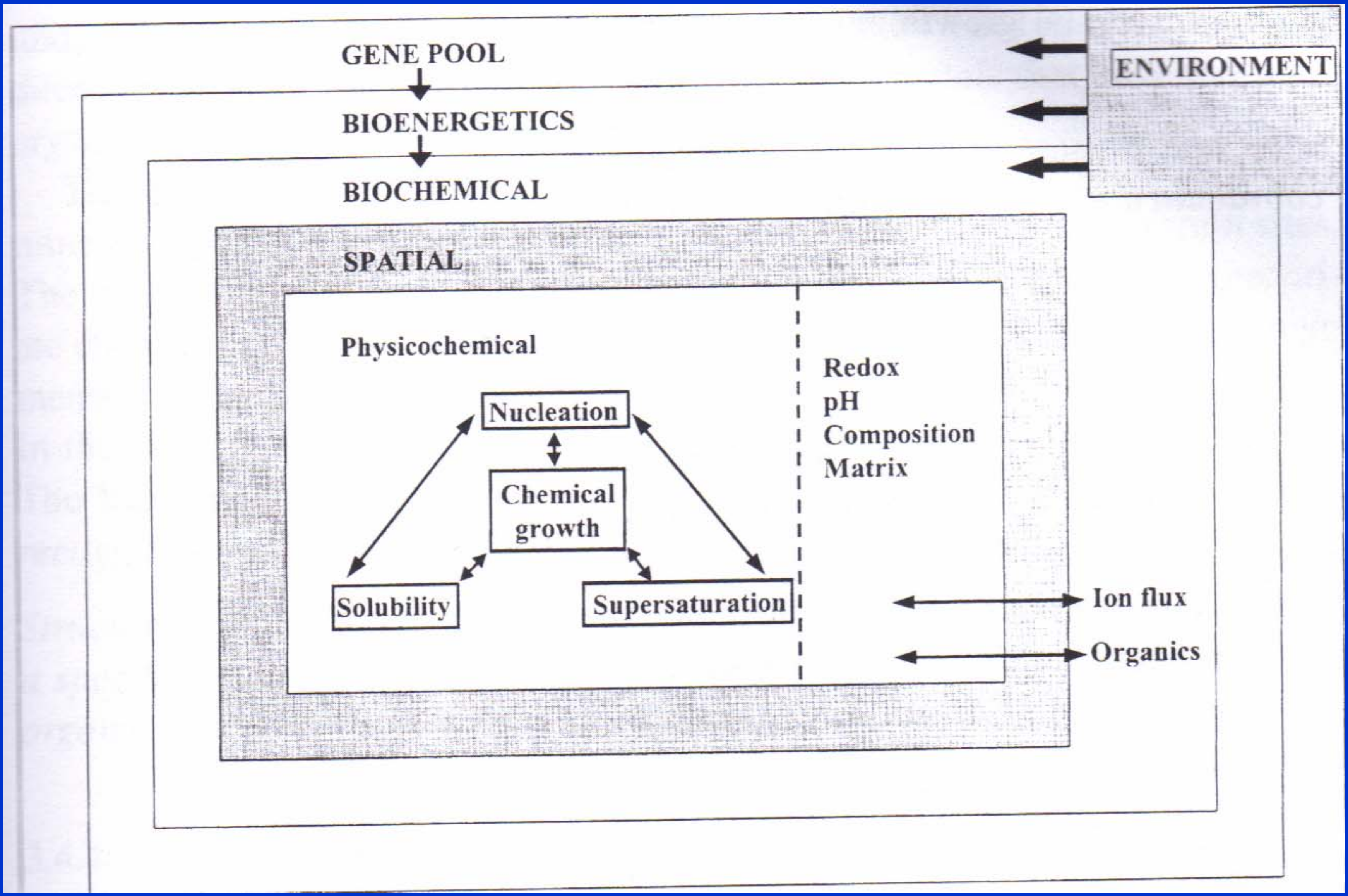
- *Chemical regulation*

  for increasing ionic concentrations

- *Organic surfaces*

  For controlling nucleation

Control mechanisms: regulation of chemistry, space, structure, morphology, and construction



Chemical control

Four fundamental physicochemical factors

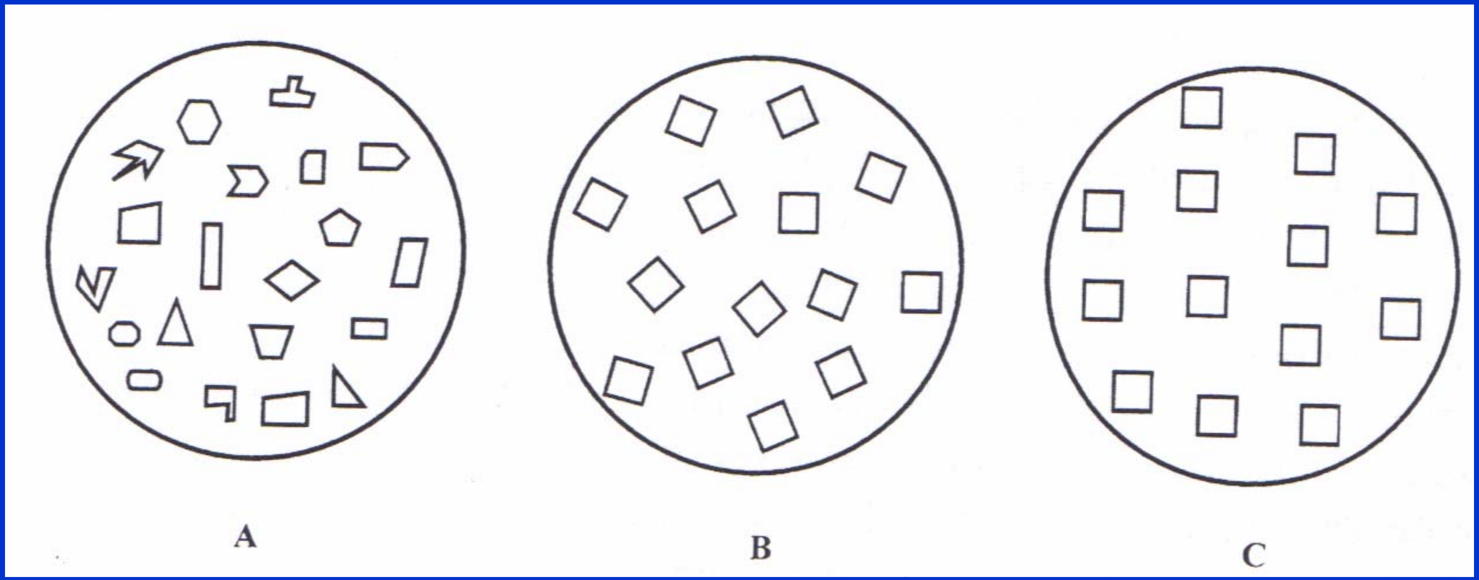
- *Solubility*
- *Supersaturation*
- *Nucleation*
- *Crystal growth*

These are chemically controlled in biomineralization by coordinated ion transport and molecular-based inhibitors and promoters

Spatial control

The control of space in biomineralization occurs through the supramolecular pre-organization of organic molecules, and impacts on the size and shape of mineral deposits and the chemical mechanisms of their deposition

Structural control

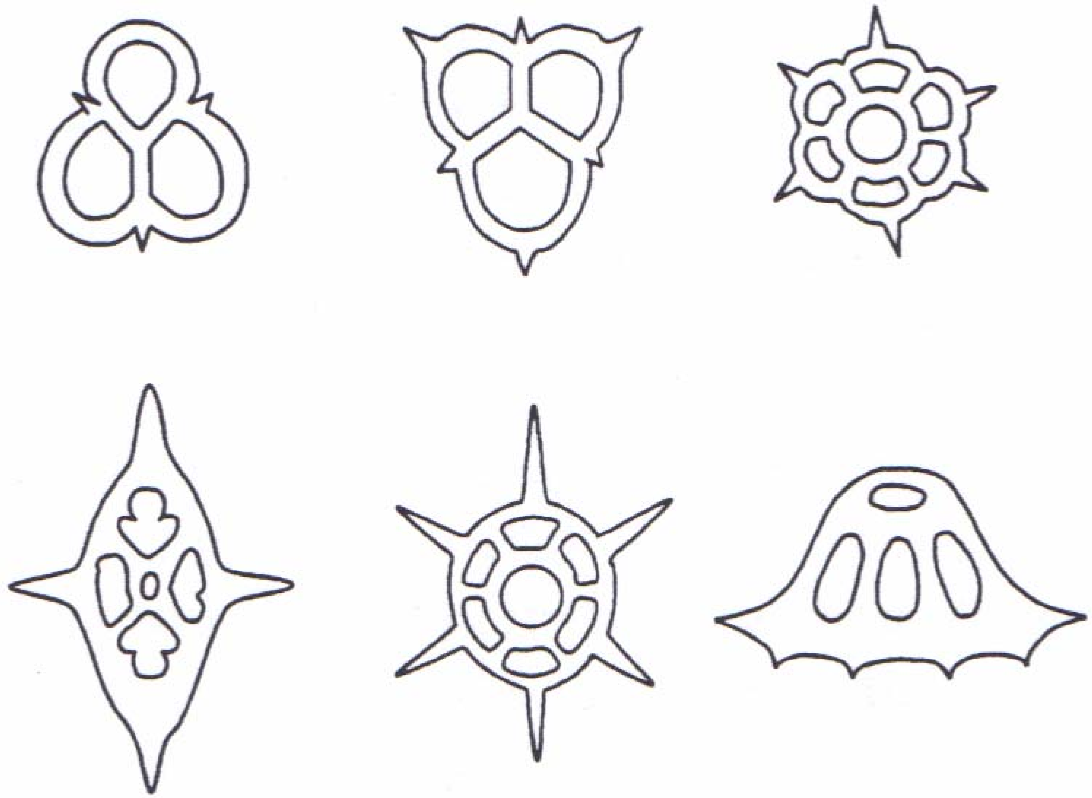


Non-oriented *mosaic* *Iso-oriented*

The organic matrix acts as an organic template for inorganic nucleation

Interfacial molecular recognition

Morphological control



Silica scales produced in *silicoflagellates*.

Morphological control

- *Vectorial regulation*
- *Mineral growth process is controlled by organic boundaries that change in size and shape with time*
- *The inorganic phase is progressively routed along specific directions set by a biological program*
- *Patterning program… morphogenesis*

Constructional control

- *Controlled construction of hierarchical structures*
- *Assembly of mineral-based building blocks into a series of progressively higher-order structures*
- *In bone, tiny crystals of hydroxyapatite are interwoven with collagen fibers*
- *Biomineral tectonics*

General model