Boundary-Organized Biomineralization

The delineation of biological environments is of key importance In boundary-organized biomineralization because it provides sites Of controlled chemistry that are spatially defined

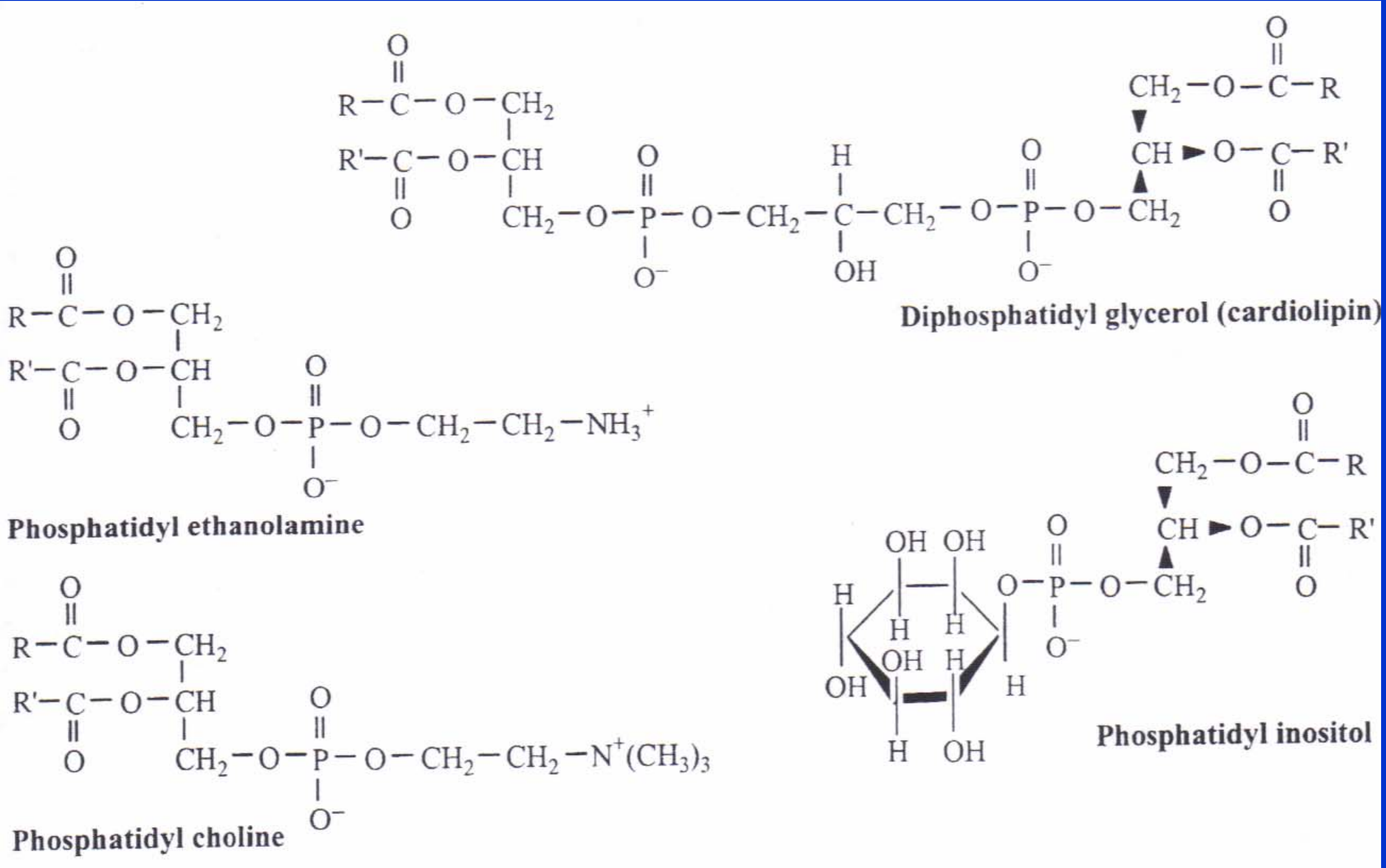
Outline

- *Spatial Boundaries*
- *Supersaturation control within spatial boundaries*
- *Ion transport*
- *Ion fluxes in calcification*

Phospholipid Vesicles

- *Vesicles are fluid-filled compartments enclosed by a continuous bilayer*
- *They form spontaneously under specific conditions*
- *Their spontaneous self-assembly arises from balancing hydrophilic and hydrophobic interactions*
- *They frequently adopt spherical structure (minimum total surface energy for a given volume)*

Phospholipid Vesicles

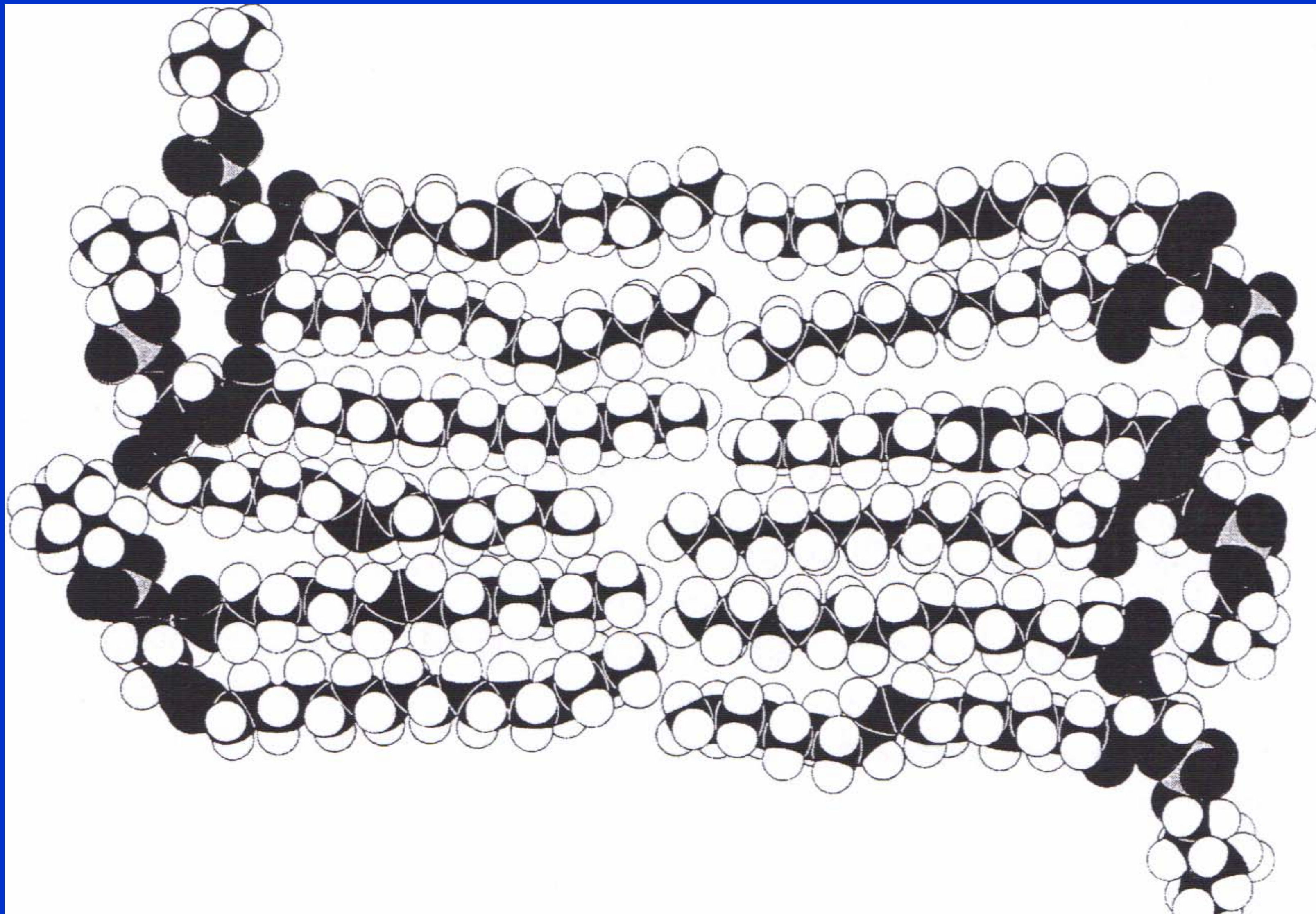


Phospholipids (R and R′ are long-chain moieties).

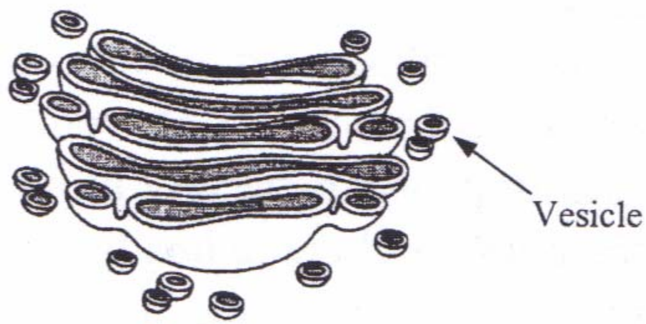
Phospholipid Vesicles

- *Phospholipids are key membrane constituents of biological vesicles*
- *They readily form self-sealing biomolecular sheets*
- *Packing of the molecules in the bilayer is quite loose*
- *High degree of lateral fluidity for moving of molecules into or outside the vesicle*
- *Proteins are also present in the vesicle membrane that may span the entire 4 to 5 nm thickness of the bilayer*

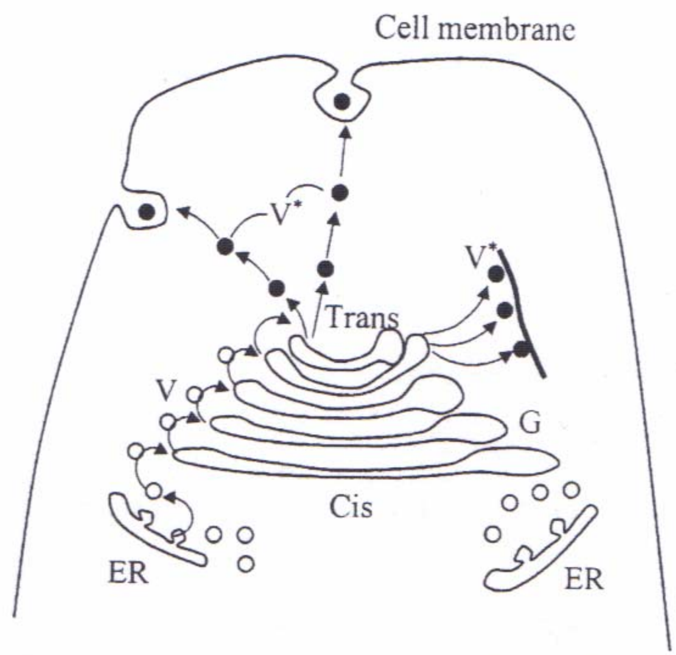
Phospholipid Bilayer Membrane



Golgi Complex and Surrounding Vesicles

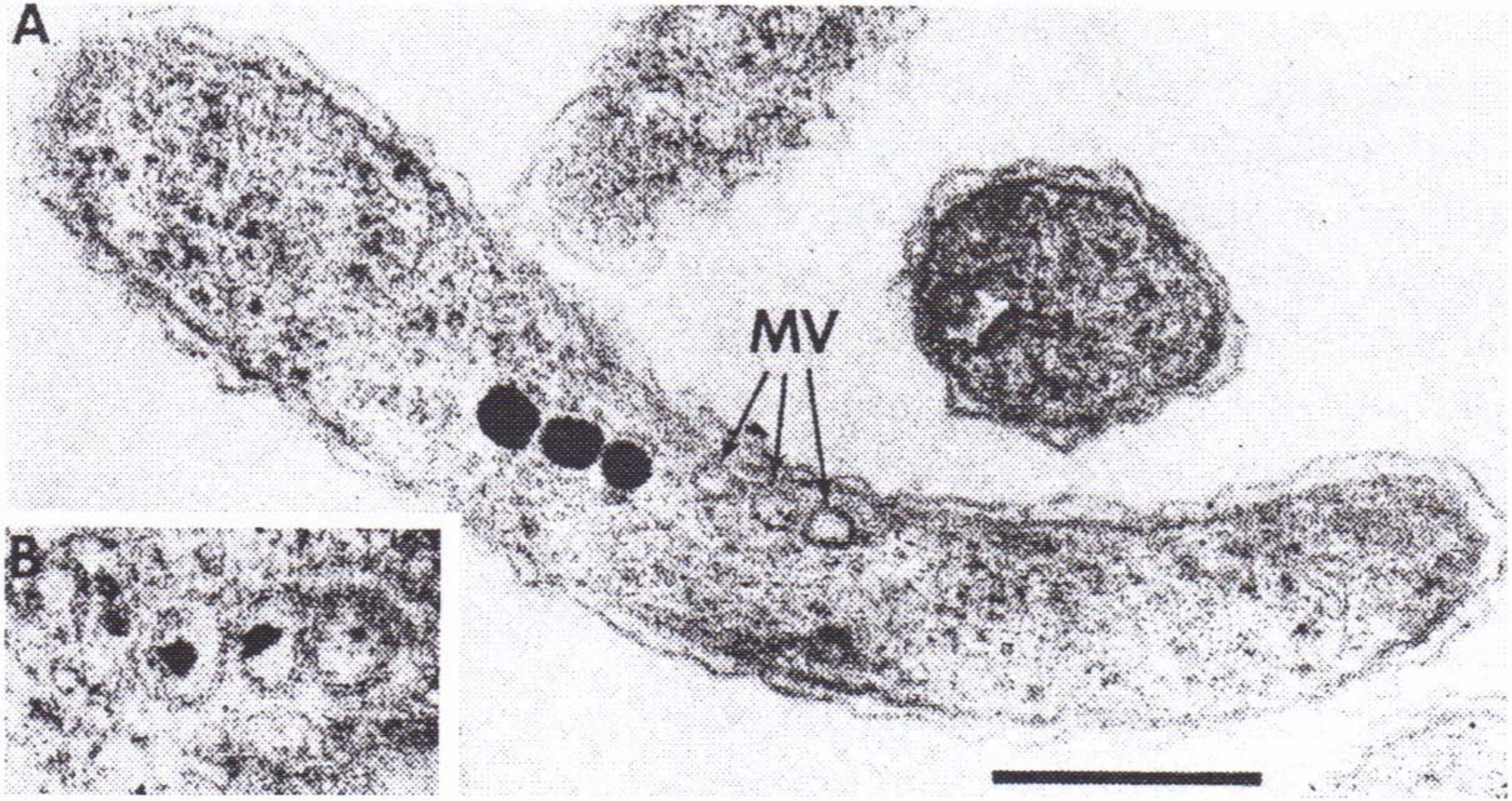


Golgi complex and surrounding vesicles drawn in cross-section.



Vesicles associated with the Golgi complex. ER, endoplasmic reticulum; G, Golgi complex; V, imported vesicles; V*, exported vesicles.

Inorganic Mineralization in Vesicles: Magnetotactic Bacteria

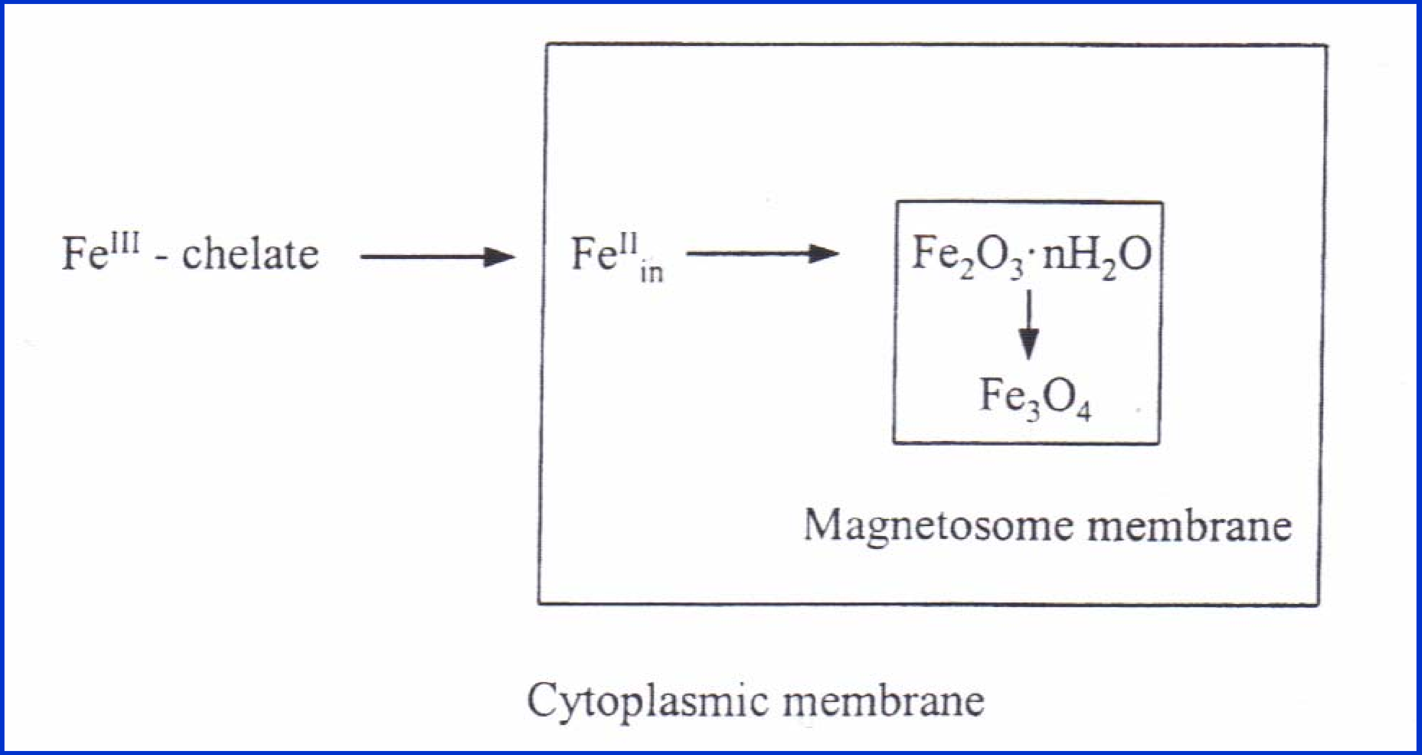


Section through a magnetotactic bacterial cell showing: (A) three mature magnetite crystals and three empty magnetosome vesicles (MV); (B) vesicles containing immature magnetite particles. Scale bar, 250 nm.

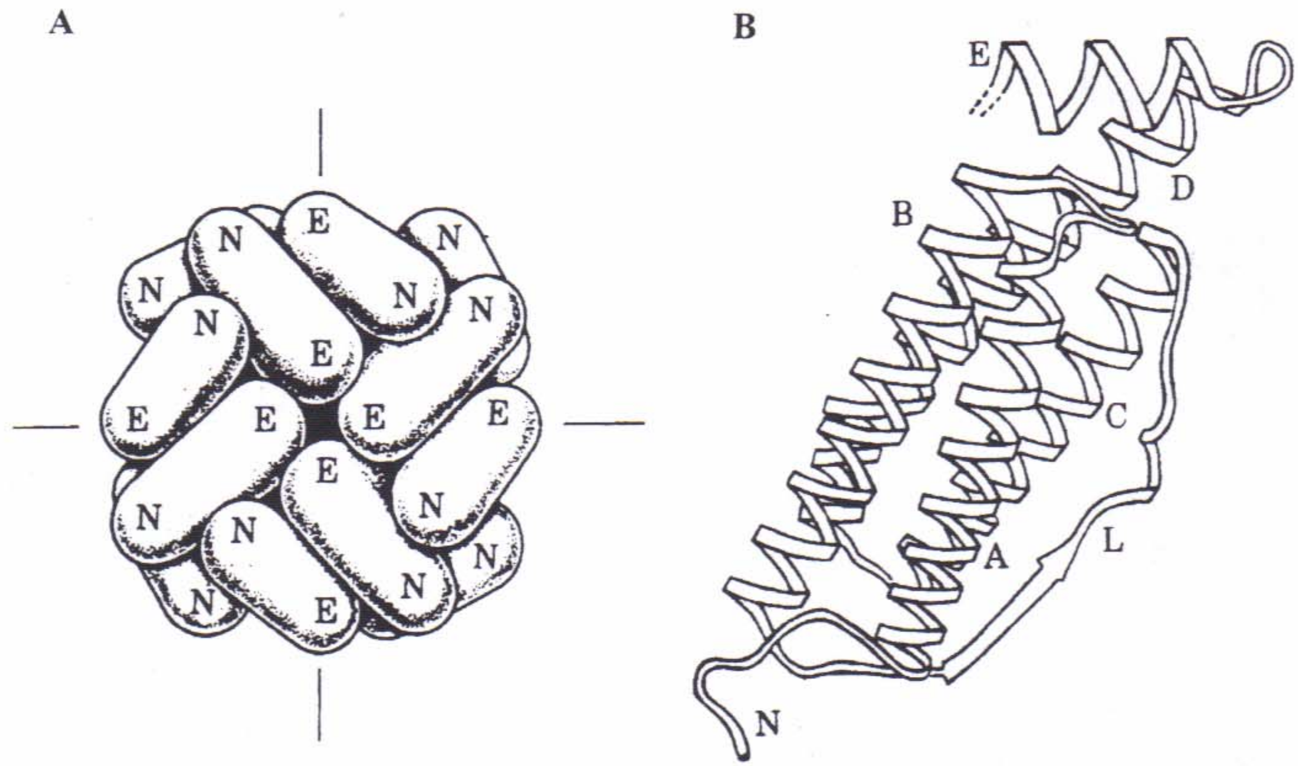
Formation of bacterial magnetite crystals

- *Uptake of Fe(III) ions from the environment*
- *Reduction of Fe(III) to Fe(II) ions during transport across the cell membrane*
- *Transport of Fe(II) ions to and across the vesicle membrane (the magnetosome membrane)*
- *Preciitation of amorphous hydrated Fe(III) oxide within the vesicle*
- *Transformation of the amorphous phase to magnetite by surface reactions involving mixed-valence intermediates*

Formation of bacterial magnetite crystals

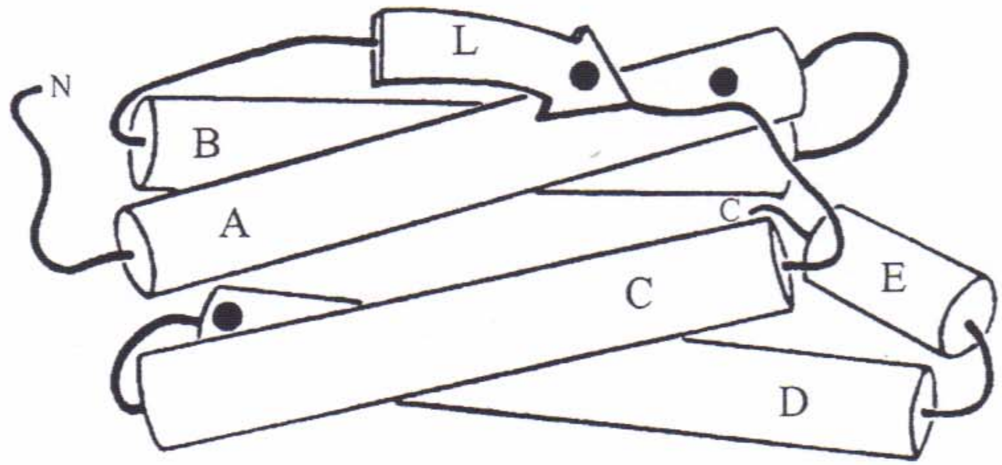


Protein Vesicles: Ferritin



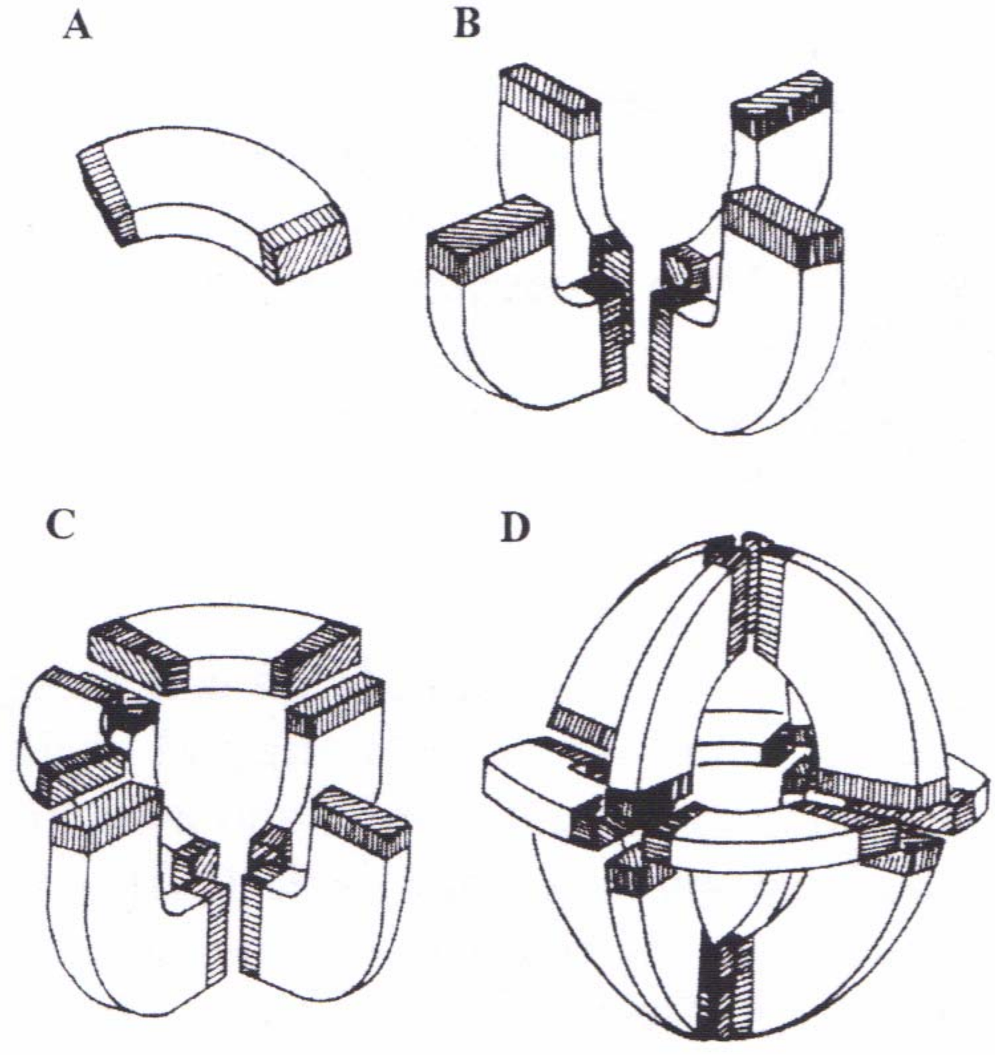
Ferritin. (A) Protein shell and arrangement of subunits: N, amino-terminus; E, carboxy-terminus of polypeptide chain. (B) Single subunit showing bundle of four α-helical domains (A–D), loop region (L), and small helix (E) of the polypeptide chain.

Protein Vesicles: Ferritin



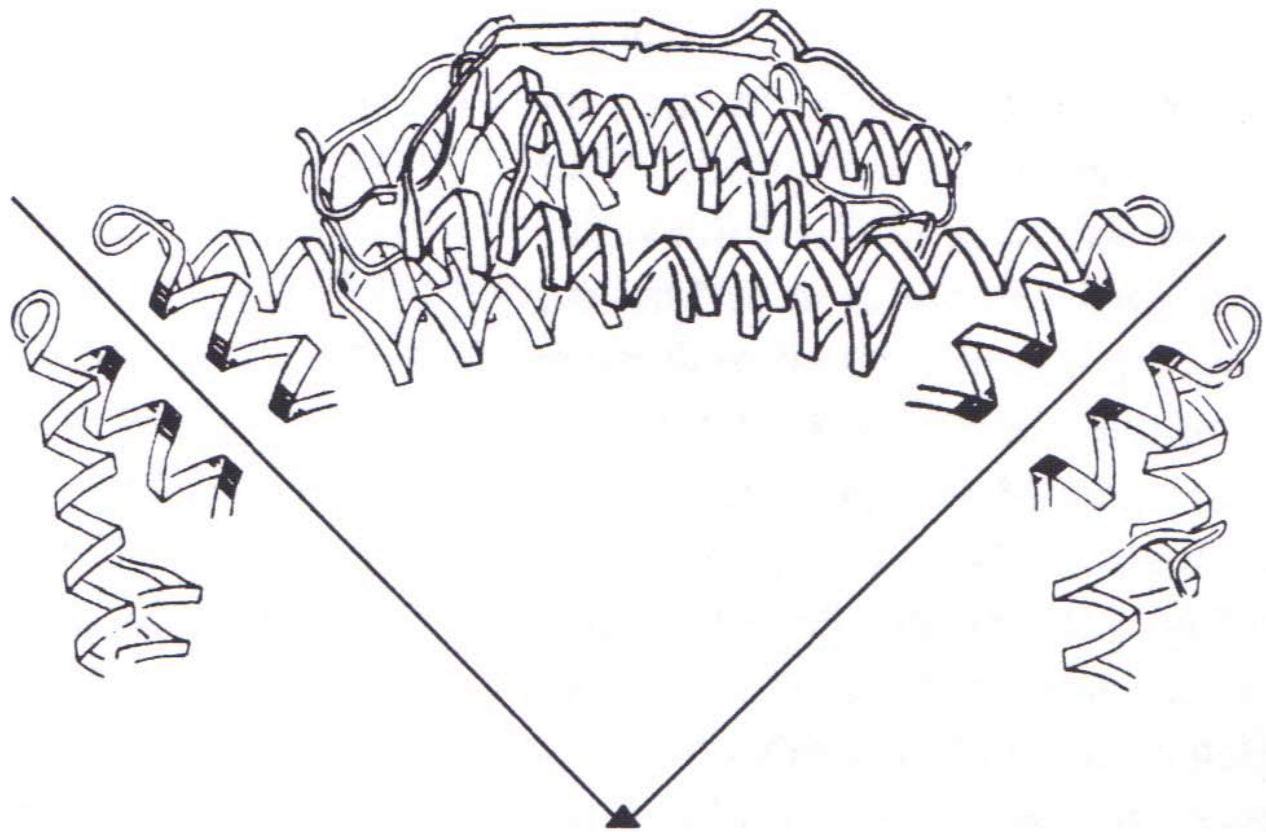
Simplified representation of ferritin subunit structure in which the α-helices are shown as cylinders.

Protein Vesicles: Ferritin



Self-assembly of ferritin shell from subunit dimers.

Protein Vesicles: Ferritin

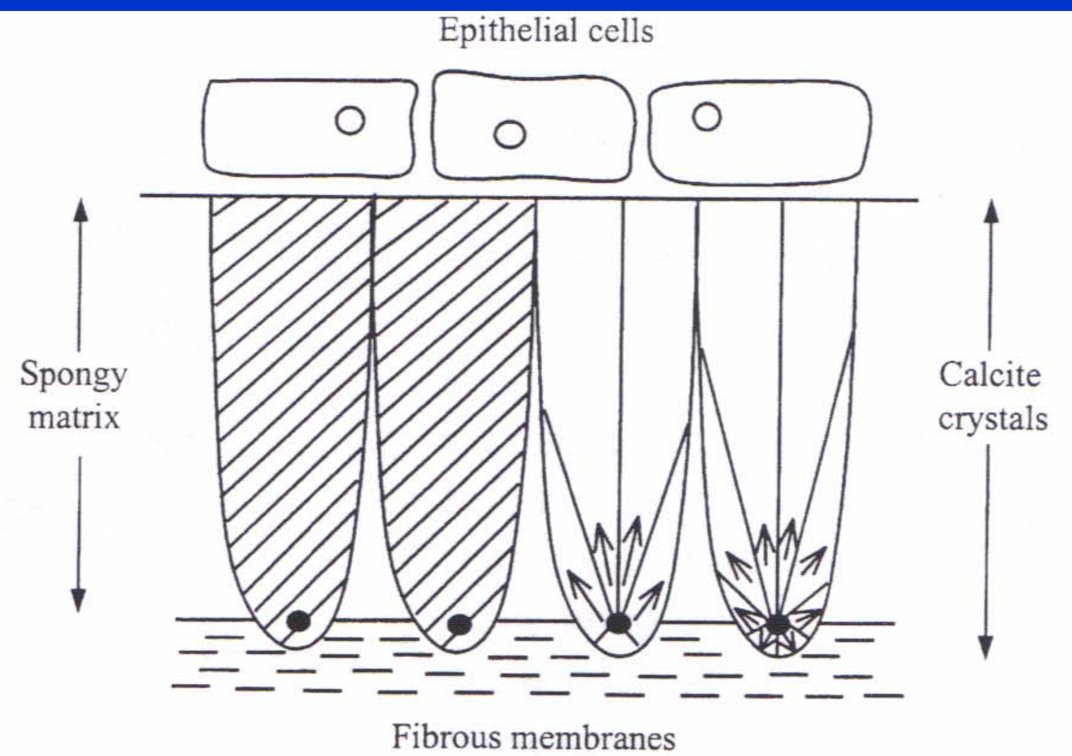


Cross-section of ferritin shell showing hydrophobic channels and associated E helices of the subunit dimers.

Macromolecular Frameworks

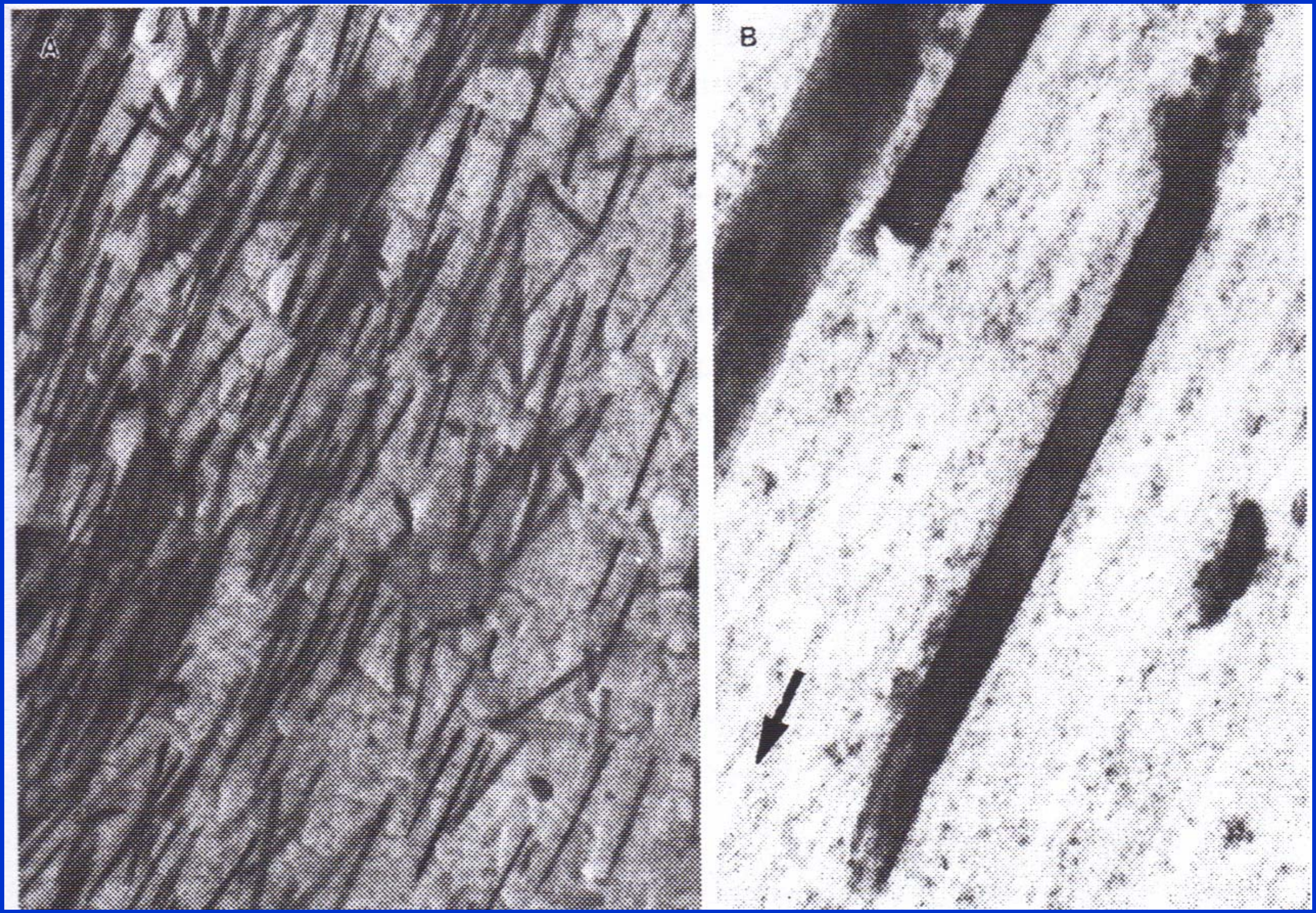
- *Cells are often tens of micrometers in size (very large)*
- *Disadvantage: mineral growth can get out of control*
- *Organisms often partition the mineralization space into smaller enclosures*
- *Semi-permeable organic matrices with open framework structures*
- *Mineral growth becomes contained at a more local level where it can be spatially organized*

Growth of calcite in Avial Shell



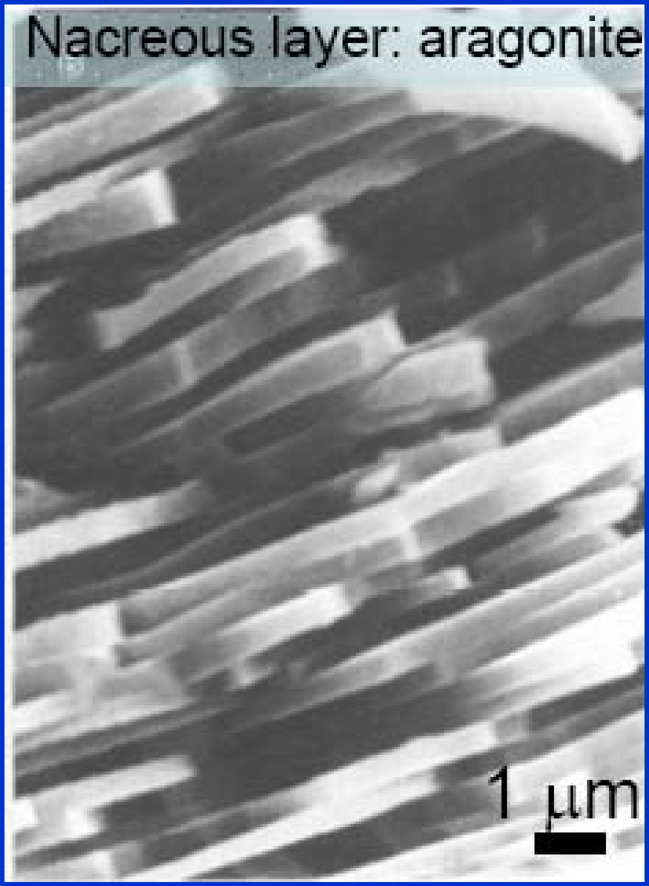
Eggshell formation. Arrows indicate directions of calcite *c* axes in the polycrystalline outgrowths.

Growth of Goethite (α-FeOOH) on Limpet Teeth

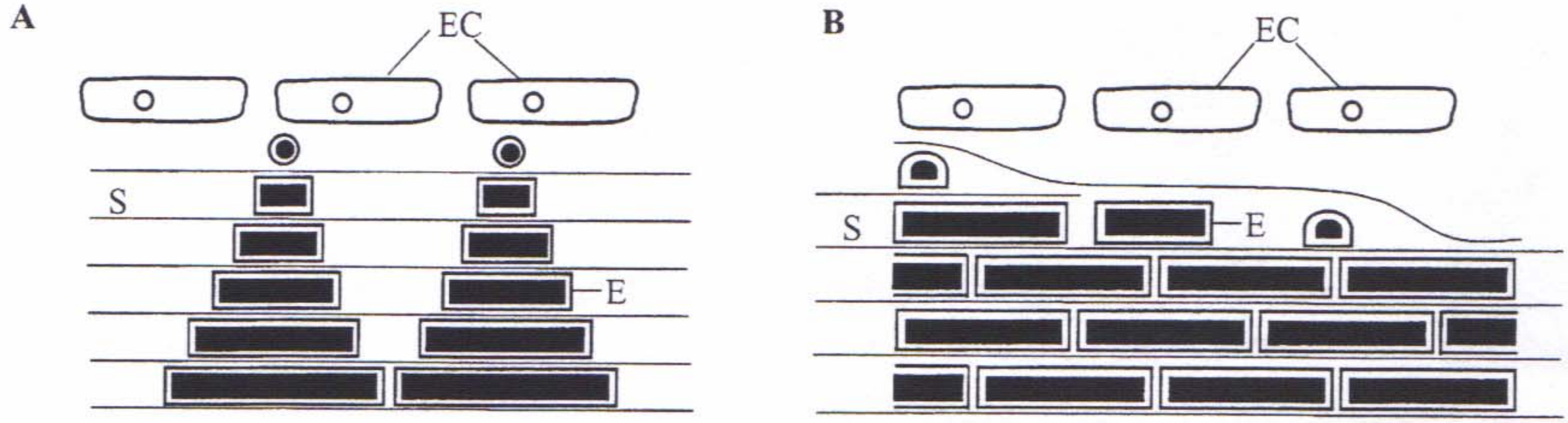


Chitin is the template for goethite growth

Aragonitic Nacreous Layer of Seashells



Aragonitic Nacreous Layer in Gastropods



Nacre formation in (A) gastropod and (B) bivalve seashells. Aragonite crystals are shown in black. EC, epithelial cells; S, sheets; E, envelopes.

Aragonitic Nacreous Layer in Seashells