BIOMINERALIZATION

Introduction

Frédéric MARIN
UMR CNRS 6282
Université Bourgogne Europe
Dijon

My career in (very) short…

Cursus Earth Sciences, Paris VI, 1984 to 1989 – DEA: bone collagen

PhD Thesis: 1989 to 1992: Paris-Orsay, lab. Paleontology: BIOMINERALIZATION

Military Service, 1992-1993

1st post-doc, ATER 1993-1994, Paris-Orsay, lab. Paleontology

2nd Post-doc: mar. 1994, dec. 2000, Leiden University, NL

Private Biotech Company, NL, 2001-2002

CNRS, CR1: Jan 2003 - DIJON

Habil: Jun 2009 – DR: Oct 2012

BGS BIOGÉOSCIENCES

UMR 6282 Biogéosciences, DIJON

≈ 150 permanent & non-permanent employees

Eco/Evo | **BioME** | **SAMBA** | **SEDS** | **CRC**

Biomineralization

2 permanent members: Irina BUNDELEVA (2013): microbialites

Frédéric MARIN: metazoan calcification

Since 2004, 8 PhD theses in biomineralization: ***B. Marie, N. Le Roy, P. Ramos-Silva, J. Sakalauskaite, M. Oudot, B. Khurshid, M. Martinho De Brito, C. Lutet-Toti***

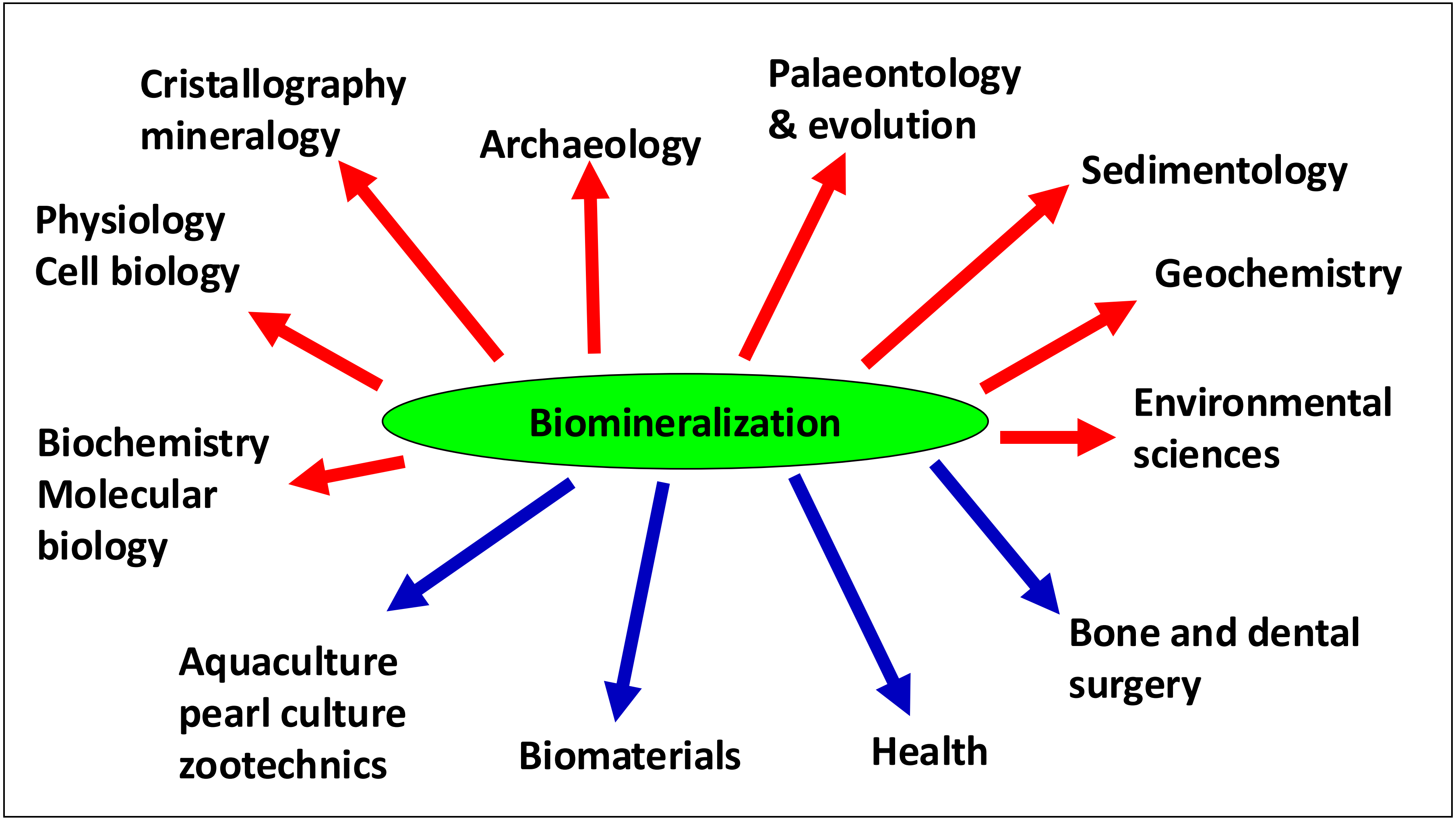
Biomineralization: different meanings…

Mineralized structures produced by living systems

Process by which living systems produce minerals

Scientific discipline in its own

Biomineralization: scientific discipline



A little pinch of history…

A brief history of biomineralization

Very first use of biominerals:
- Oldest ornaments: 142 000 yr,
- Bizmoune Cave, Morrocco

- Shells sewed on clothes, ornaments

Ex: Grimaldi children: 11000 years BP.

- Currency: cowries (*Cypraeidae*)

- 1st glue from bone and skin collagen

A brief history of biomineralization

1st dental implant in Mayas: 7-8th century BP

3 implants made from bivalve nacre (Bobbio, 1972). Completely osteointegrated in the jaw.

A brief history of biomineralization



Middle Age:

- Religious symbols

(Blister Buddhas, pilgrims scallop, font…)


From XVIIth century:

- Marquetery work



- Manufactured objects

A brief history of biomineralization

From XVIIth century:

- Jewels: pearls



- Industrial fabrication of glue from bone/skin collagen

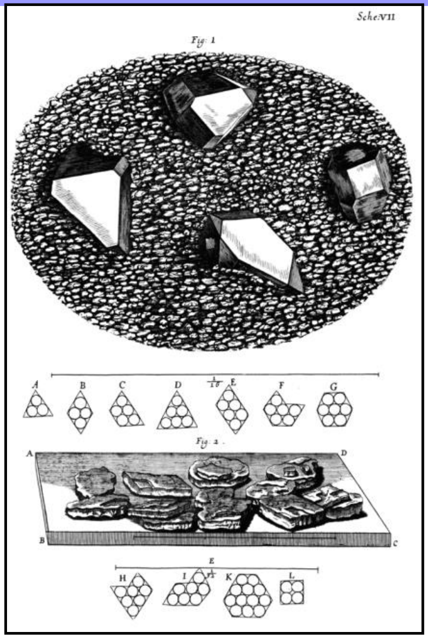
From XIXth century:

- Soil enrichment

A brief scientific history of biomineralization

Andreas Vesalius: the Basel skeleton (1543): **anatomical Museum of the Basel Univ.**

Jan Swammerdam / Anton van Leeuwenhoek: 1st optical microscopes, circa 1660…



Robert Hooke: *Micrographia* (1665): 1st observations of biominerals under microscope
('of gravels in urine ')

A brief scientific history of biomineralization

Clopton Havers (1657-1702): 1st description of bone microstructure
Osteologia nova, or some new Observations of the Bones, and the Parts belonging to them, with the Manner of their Accretion and Nutrition (1691).

De Lasone (1751): 1st experiments of bone calcining

1811-1823: Braconnot/Odier: chitin discovery

Frémy (1855): 1st chemical characterization of biominerals:

- Bone, teeth
- Crustacean teguments
- Gorgonian coral exoskeleton
- Mollusc shell (nacre) and cuttlefish bone

A brief scientific history of biomineralization

2nd half of XIXth century – 1st half of XXst century

- Several chemical analyses of biominerals.
- Several observation with optical microscope (Schmidt, Boggild)

After War period:

- Development of biochemistry and of several techniques for separating biomolecules:
    - *Amino acid analysis: bone, teeth, shells (1953-1955).*

- XRD of biomolecules: *3D structure of bone collagen (1954, G. N. Ramachandran).*

A brief scientific history of biomineralization

The Sixties:

- Several biochemical characterizations of biominerals.

- Development of electron microscopy: TEM, SEM.

The Seventies:

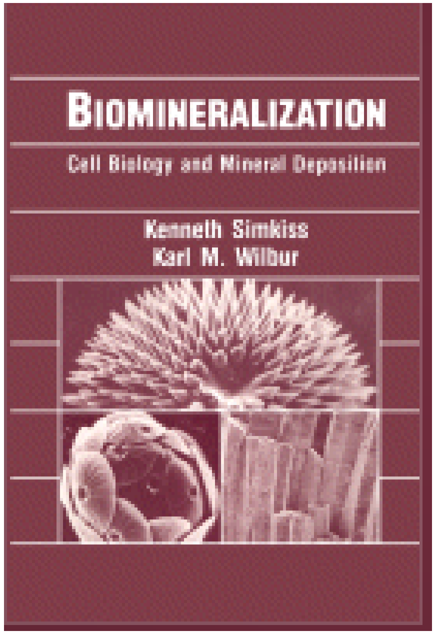
- 1st International Symposium on Biomineralization: 1970.
  17th Symposium in Saint-Etienne, in august 2023: BIOMIN XVII

- 1st molecular models on biomineralization.

A brief scientific history of biomineralization

H. Lowenstam, K. Simkiss, A. Veis, M. Glimcher, W. Traub, B. Landis, A. Salleudin, J. Oldak, K. Wilbur, S. Weiner, H. Mutvei, M. Crenshaw, P. Westbroek, L. Addadi...

Lowenstam & Weiner (1989)



Simkiss & Wilbur (1989)

A brief scientific history of biomineralization

TODAY...

Beside the Int. Symp. on Biomineralization, several important scientific events:

- ***Gordon Research Conference (GRC) on Biomineralization***

- ***ICCBMT (International Conference on the Chemistry & Biology of Mineralized Tissues)***

Several international or national conferences have sessions dedicated to biomineralization: *Goldschmidt Conference, Int. Marine Biotech Conf., Int. Sclerochronology Conf., ...*

Biomineralization, a widespread phenomenon

Bacteria → **Vertebrates**

Biomineralization:

55 phylums

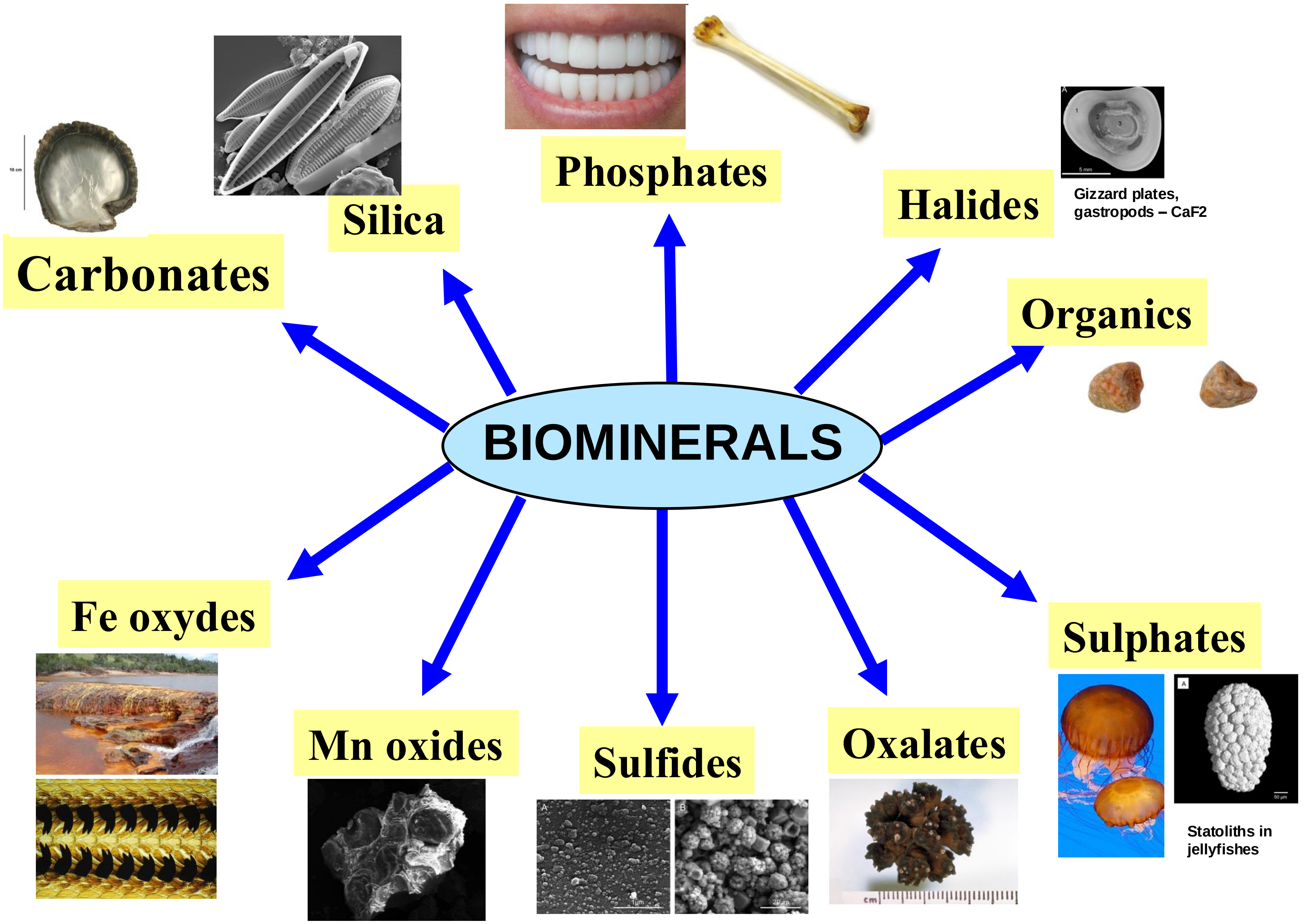
(living or fossils)

Bacteria

Archaea

Eucarya

About 70 different minerals!!


BIOMINERALS
Carbonates
Silica
Phosphates
Halides
Gizzard plates,
gastropods – CaF2
Organics
Sulphates
Statoliths in
jellyfishes
Oxalates
Sulfides
Mn oxides
Fe oxydes

2 types of biomineralizations

Biologically-induced

Biologically-controlled

Biologically-induced mineralizations

- *No specific macromolecular machinery*
- *Formed crystals = look like chemically-precipitated crystals*
- *Depend on environmental conditions*
- *No control on the shape & layout of the crystals*

Who, what ? Bacteria, fungi, protists, algae, pathological mineralizations in metazoans

A well-known example: stromatolites

Photo Ch. Pomerol.

Stromatolites

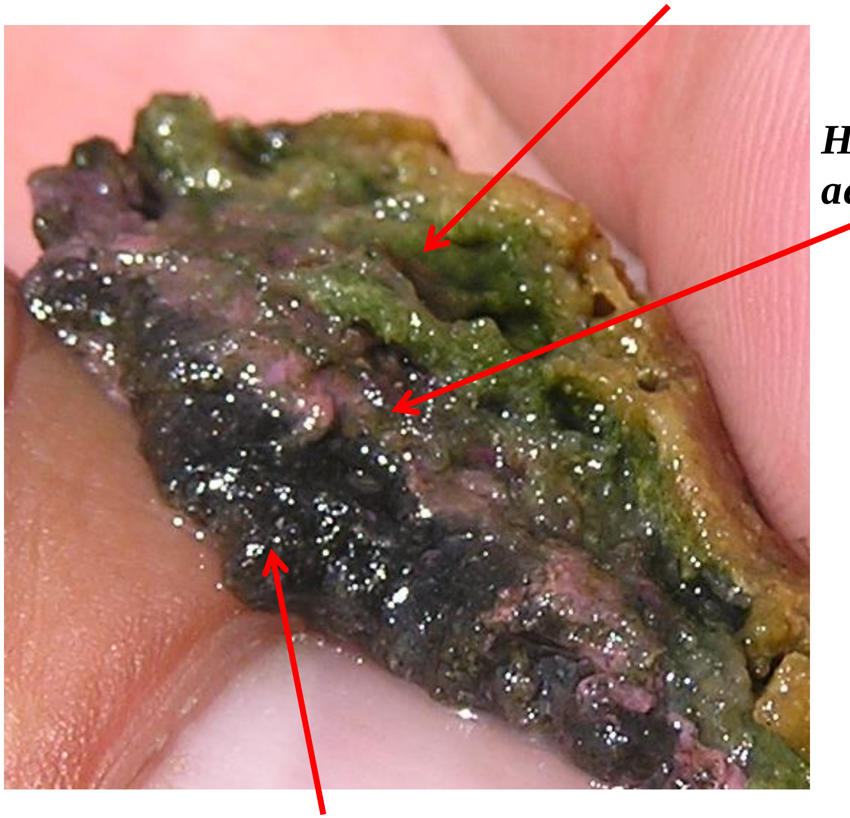
Carbonates predominantly formed by bacterial communities

Bahamas

Salda Lake (Turkey)

Laminar structure of stromatolites

Microbial communities in biofilm forming different layers



www.mnhn.fr/mnhn/mineralogie/histoire/index/collections/sedimentaires.htm

Fossil stromatolite, Tumbiana formation

A very old origin…

Most ancient stromatolites: 3.5 billion years (Australia & South Africa)
Formed in anoxic terrestrial atmosphere.

Stromatolites from Australia (Shark Bay)

http://www.routard.com/images_contenu/communaute/photos.jpg

Slow growth - 0,4 mm per year

Modern stromatolites

Bahamas

Salda Lake (Turkey)

Salt Lake (EU)

Biologically-controlled mineralizations

1. Very specific molecular & cellular machinery

2. Space delineation (where crystallization takes place)

3. Formed crystals = different from their chemical counterparts

4. Multi-scale organization

5. Far less dependent on environmental conditions

6. Mineral deposition = controlled by an organic matrix

WHO ? Magnetotactic bacteria, «protists», «algae», metazoans

Biologically-controlled mineralizations

1. Very specific molecular & cellular machinery

- **Specialized cells. For bone: osteoblasts, osteocytes, osteoclasts**

- **Specialization of cells in organs: the mollusk mantle**

- **This kind of organ appears early during Development (cell differentiation)**

- **Gene regulatory network (GRN) far upstream the formation of the specialized organ**

Biologically-controlled mineralizations

1. Very specific molecular & cellular machinery: the mollusk mantle

Edible pacific oyster *Crassostrea gigas / Magallana gigas*

Calcifying mantle

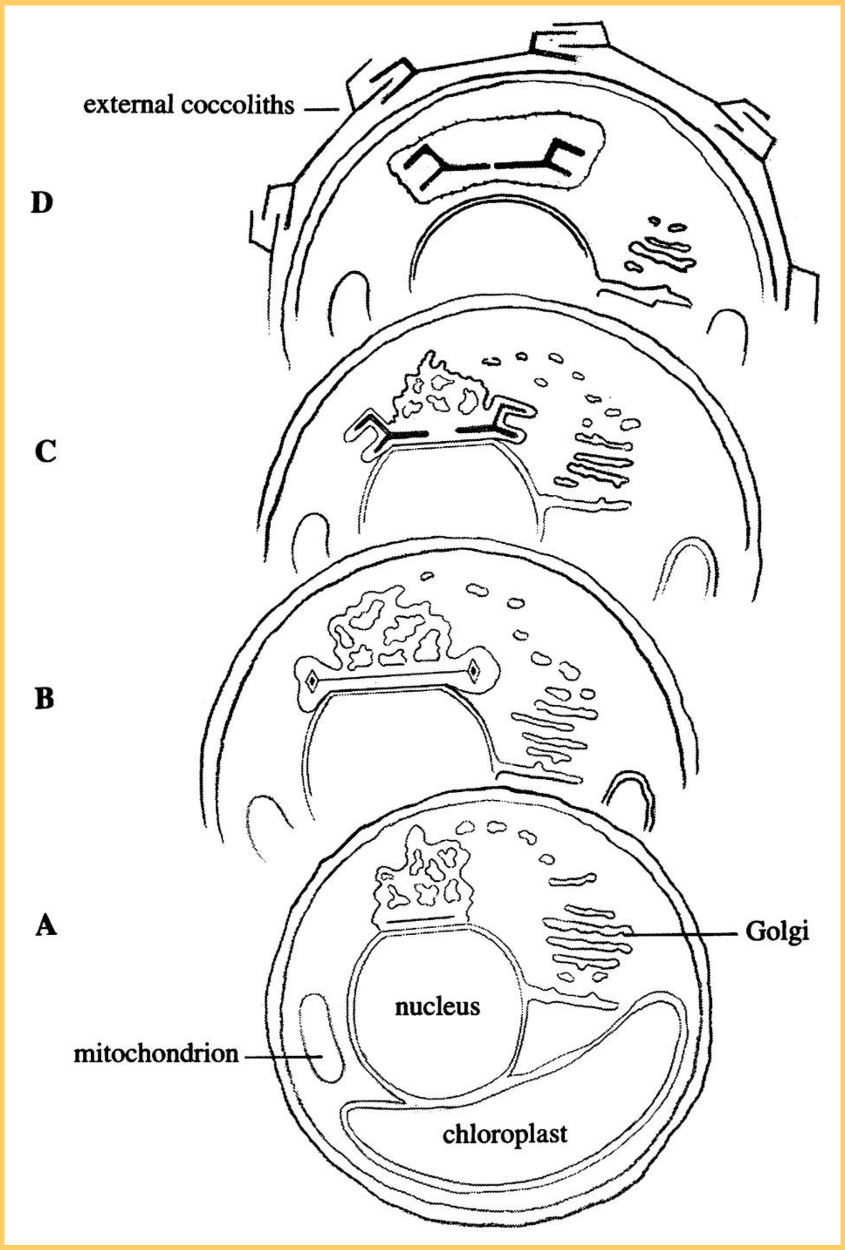
$$HCO_3^- + Ca^{2+} \longrightarrow CaCO_3 + H^+$$

- **Translocation of precursor inorganic ions and secretion**
- **Secretion of amorphous granules**
- **Shell matrix secretion**
- **Proton reabsorption**

Biologically-controlled mineralizations

2. Space delineation

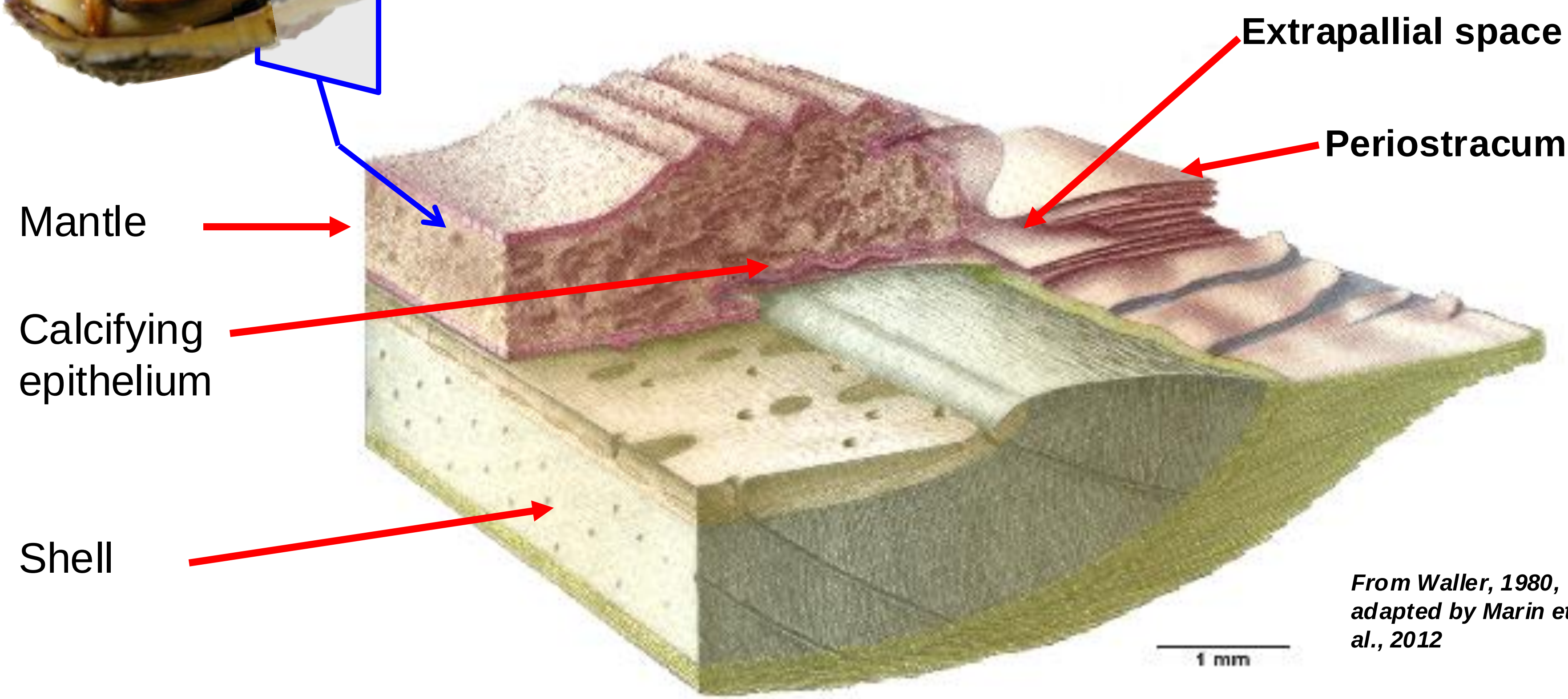
1st example: coccolithophore algae
Formation of coccoliths in a vesicle



Biologically-controlled mineralizations

2. Space delineation

2nd example: the mollusk shell
Confinement by an organic membrane

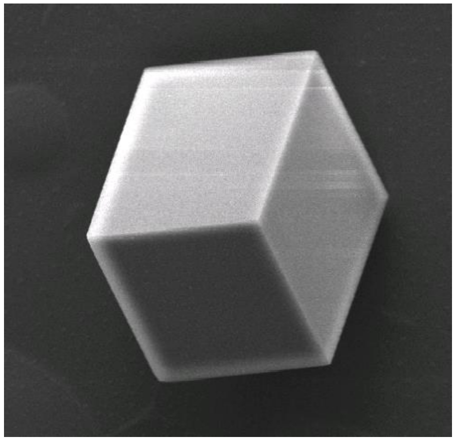


From Waller, 1980, adapted by Marin et al., 2012

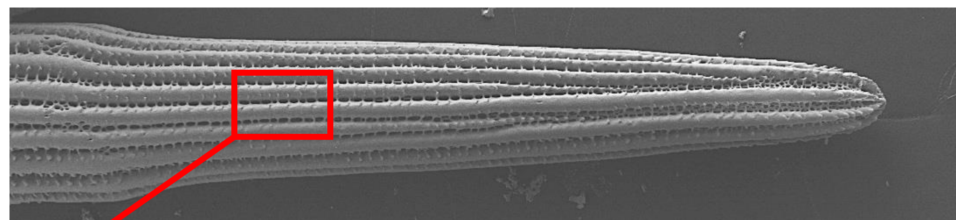
Biologically-controlled mineralizations

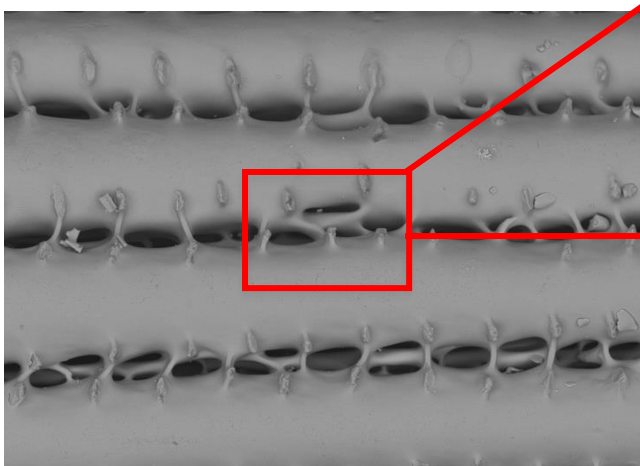
3. Formed crystals = different from their chemical counterparts

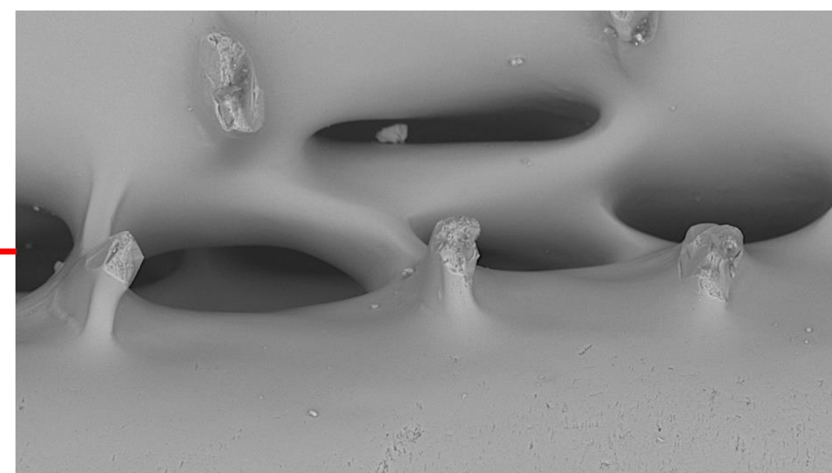
Abiotic calcite



Biological calcite





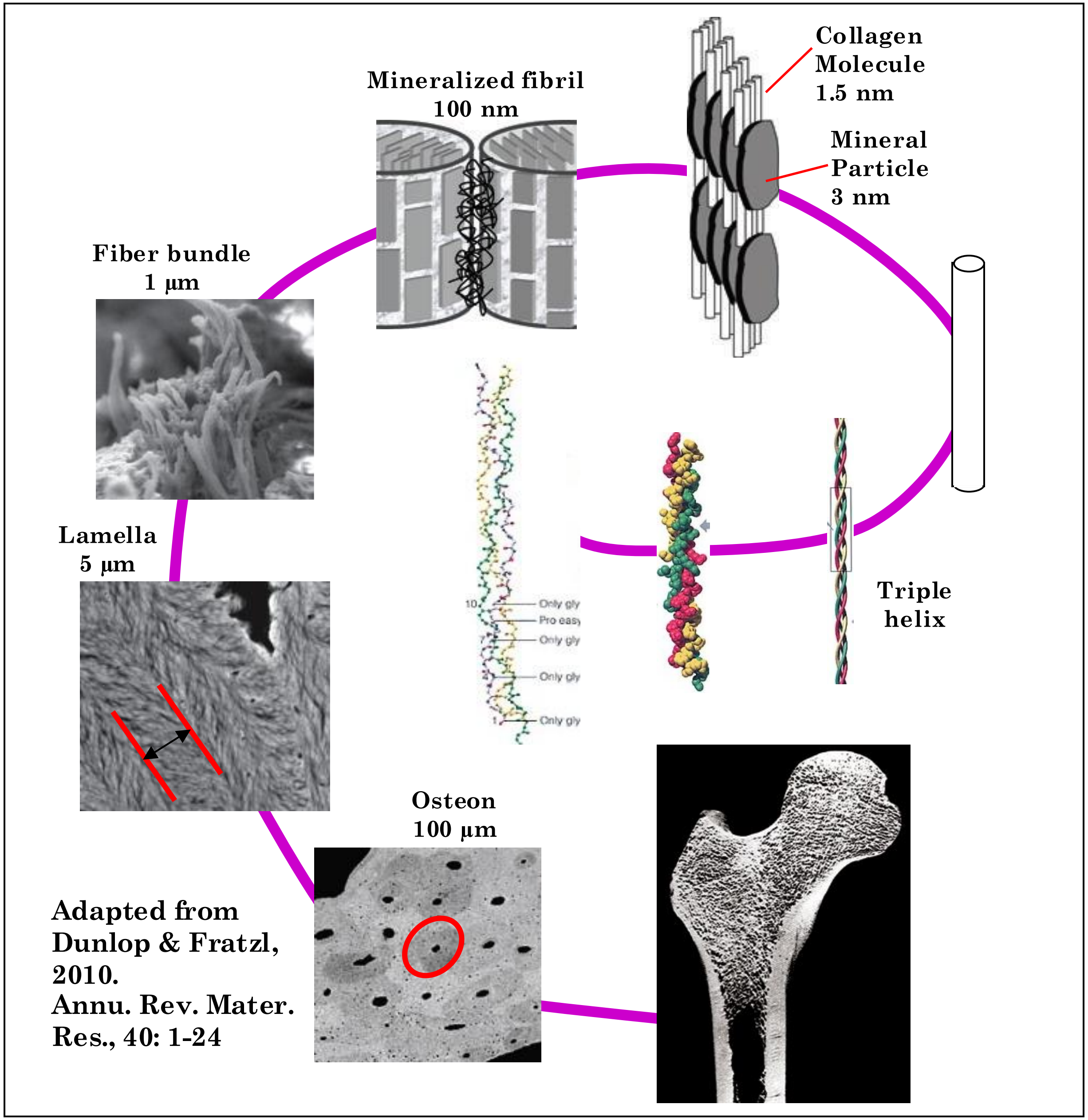


Biologically-controlled mineralizations

4. Multi-scale organization

Vertebrate bone:

At least 7 levels of hierarchy, from nm to cm



Adapted from Dunlop & Fratzl, 2010. Annu. Rev. Mater. Res., 40: 1-24

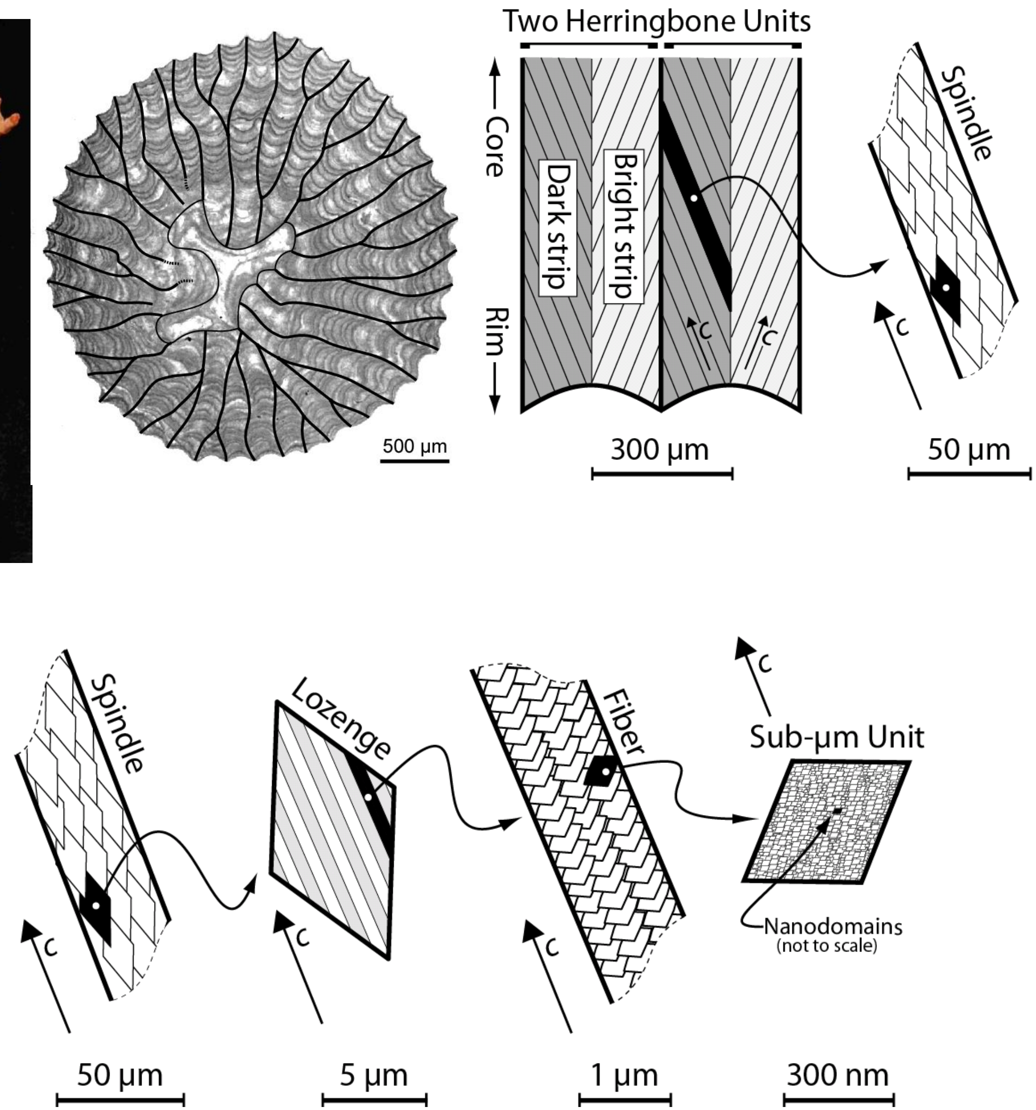
Biologically-controlled mineralizations

4. Multi-scale organization

Red coral

(Corallium rubrum) - Mg Calcite

http://www.uco.es/dptos/zoologia/zoolobiolo_archivos/practicas/practica_3/C_Corallium_rubrum.jpg



7 levels of hierarchy, from nm to cm

Vielzeuf et al., 2008. Am. Mineralogist, 93: 1799-1815. Vielzeuf et al., 2010. Am. Mineralogist, 95: 242-248.

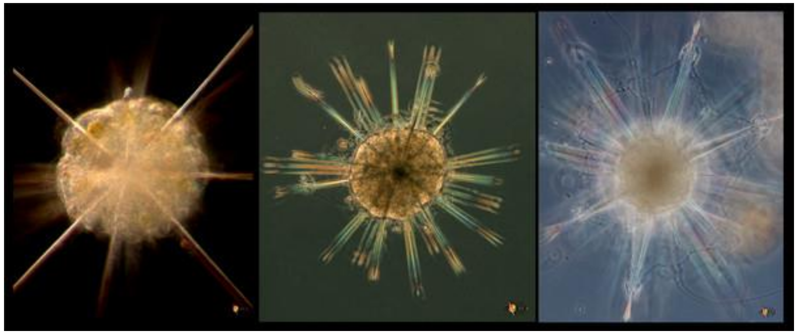
Biologically-controlled mineralizations

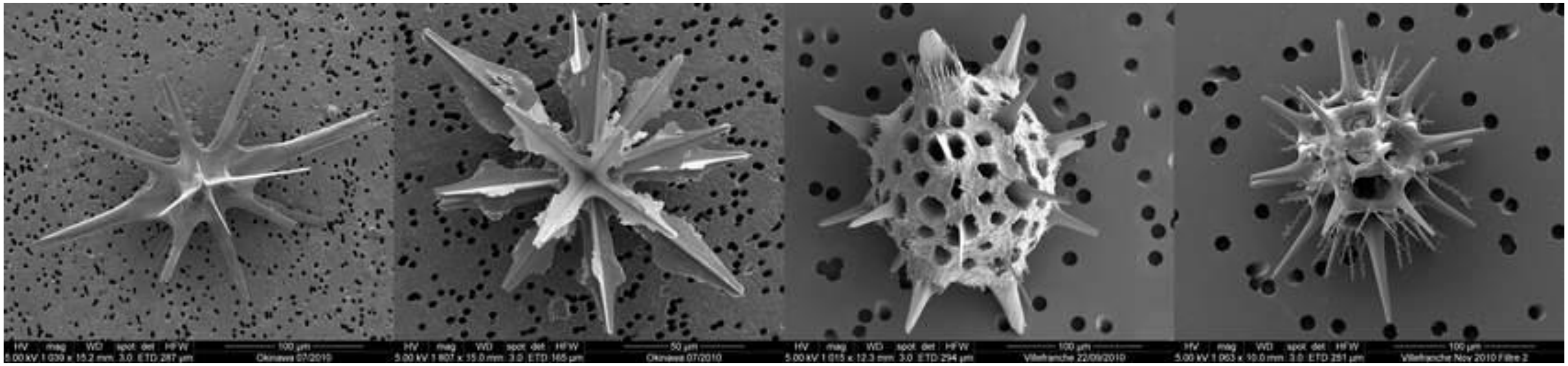
5. Far less dependent on environmental conditions

The example of Acantharians: planctonic marine protists

$SrSO_4$: celestite

Very undersaturated in marine environment = highly unstable





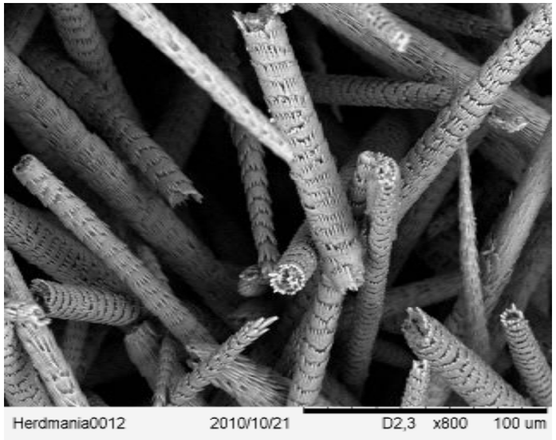
Biologically-controlled mineralizations

5. Far less dependent on environmental conditions

The example of freshwater mussel

Acidic water, under-saturated in $CaCO_3$

The example of the ascidian, *Herdmania momus*



Spicules made of vaterite (unstable polymorph of $CaCO_3$)

Biologically-controlled mineralizations

6. Controlled by an organic matrix

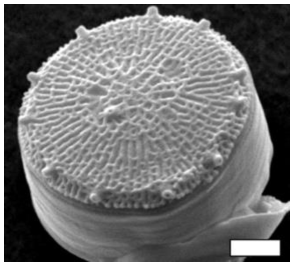
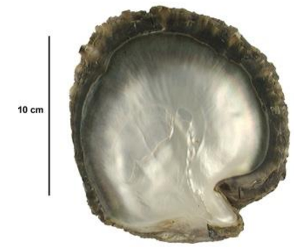


Photo M. Hildebrand

Photo A. Frijsinger & M. Vestjens

http://en.academic.ru/dic.nsf/enwiki/6124580



	Silica		$CaCO_3$		Ca-P
	Diatoms	**Demosponge**	**Sea urchin**	**Mollusk**	**Chordate**
	Thalassiosira pseudonana	***Suberites domuncula***	***Strongylocentrotus purpuratus***	***Pinctada sp.***	***H. sapiens sapiens***
PROTEINS	Silaffins, Frustulins SITs ($Si(OH)_4$ transporters)	Silicateins Galectins Collagens Selenoprot. M Silicase…	SpSM50, SpSM32, SpSM37, SpSM29, SPU_005989-91-92, SpPM27, SPU_027906, SpSM30-A to F SpC-lectin MSP130…	Aspein, MSI31, Prismalin-14, N19 Nacrein / N66, N14 / N16 / Pearlin, MSI60, MSI7, Pfty1-2, KRMP1-4, Shematrins 1-7 Prismin, Pif177, Prisilkin-39, mpn88 pfp-16, msi25 Several ESTs…	DSPP MEPE + ASARM pept. DMP1, DMP2 DPP Amelogenin Ameloblastin Enamelin Amelotin Biglycan Kallikrein-4 MMP20 Enamelysin Collagen…
OTHER COMPONENTS	LCPAs (long chain polyamines); PTMs	PTMs	PTMs	PTMs + Pol	PTMs + Pol

An example of biologically-controlled mineralization: magnetotactic bacteria

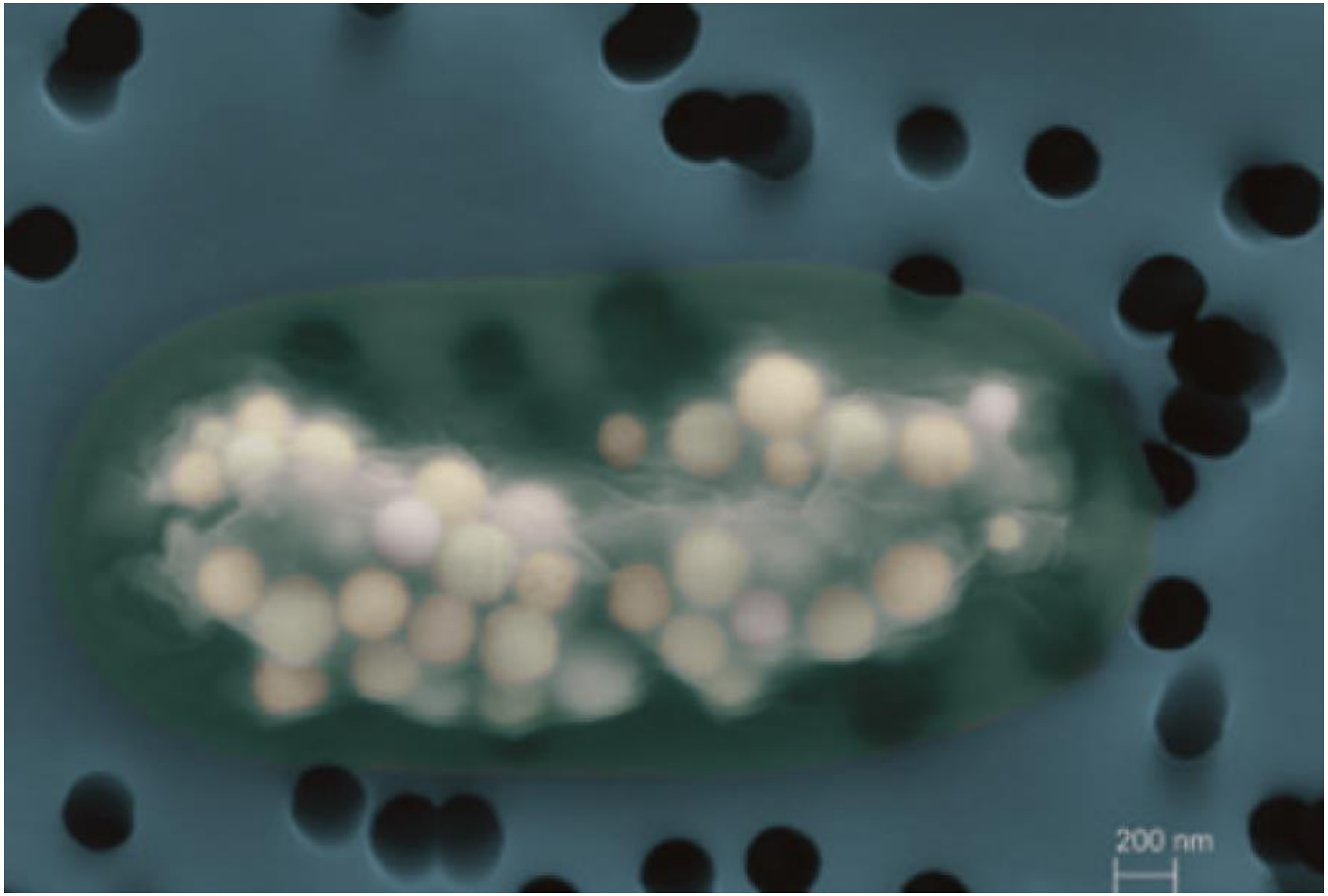
- **Magnetite nanograins (25-100 nm)**

synthesized in an organite (vésicule), the magnetosome
*** Processus = controlled by about 20 different proteins, the «Mam family ».**

Another example of controlled mineralization:

Photosynthetic bacteria with intracellular Ca nodules

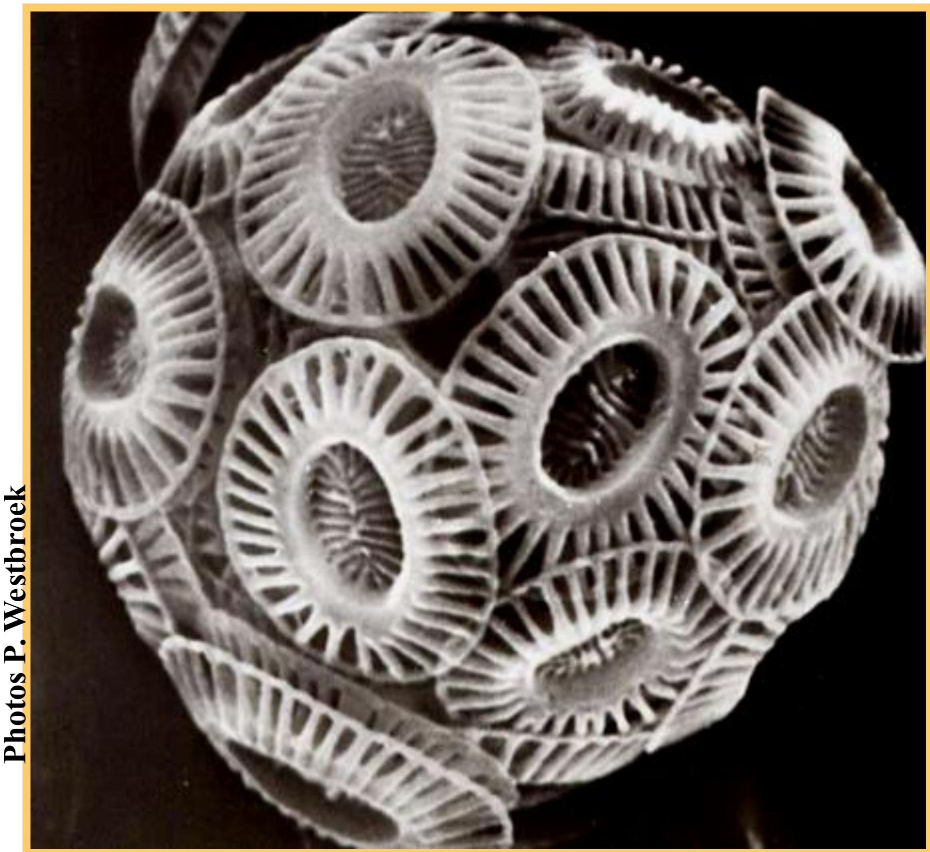
Function: ballast ?



Couradeau et al., Science, 2012

Another example of controlled mineralization: coccolithophore algae

Calcite plates secreted by unicellular algae, coccolithophorids (Haptophytes)

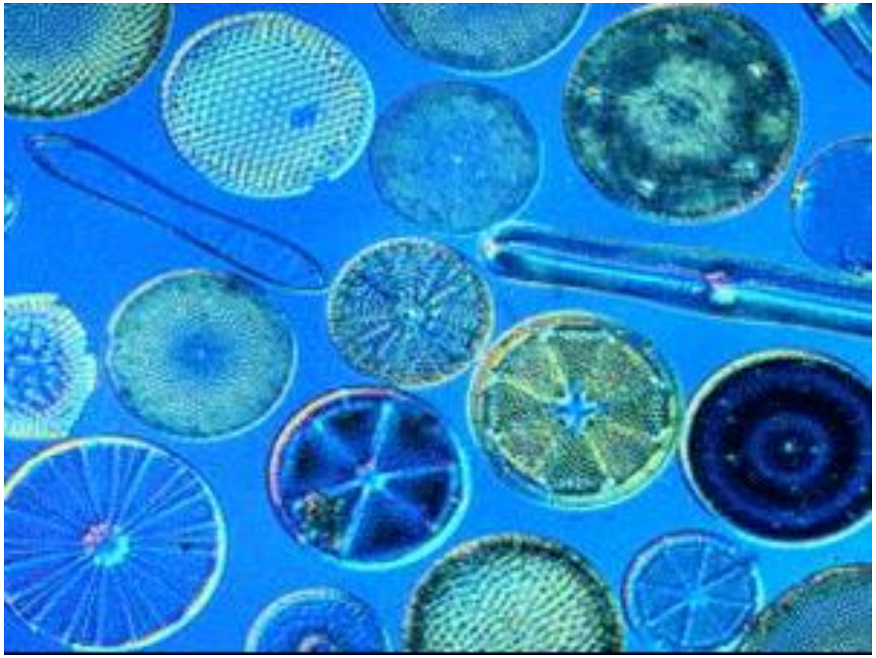


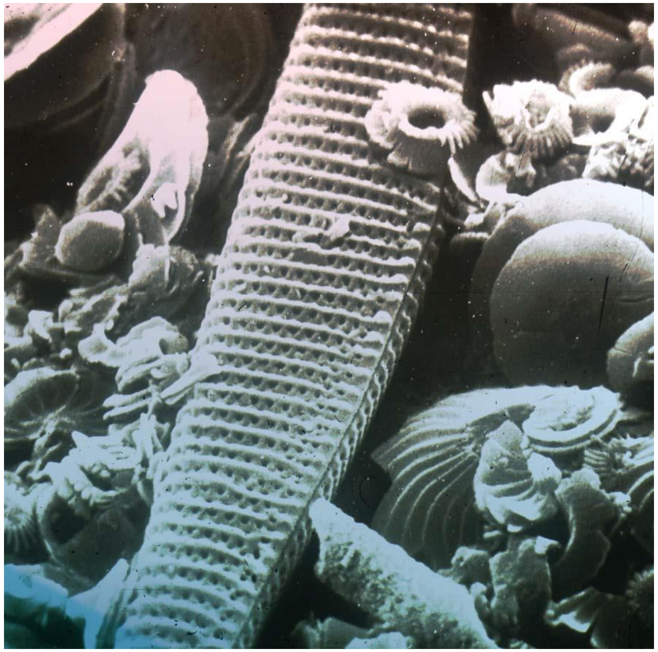
Photos P. Westbroek

Photos P. Westbroek

Photos P. Westbroek

Another example:
diatoms (bacillariophyte algae): Trias to now

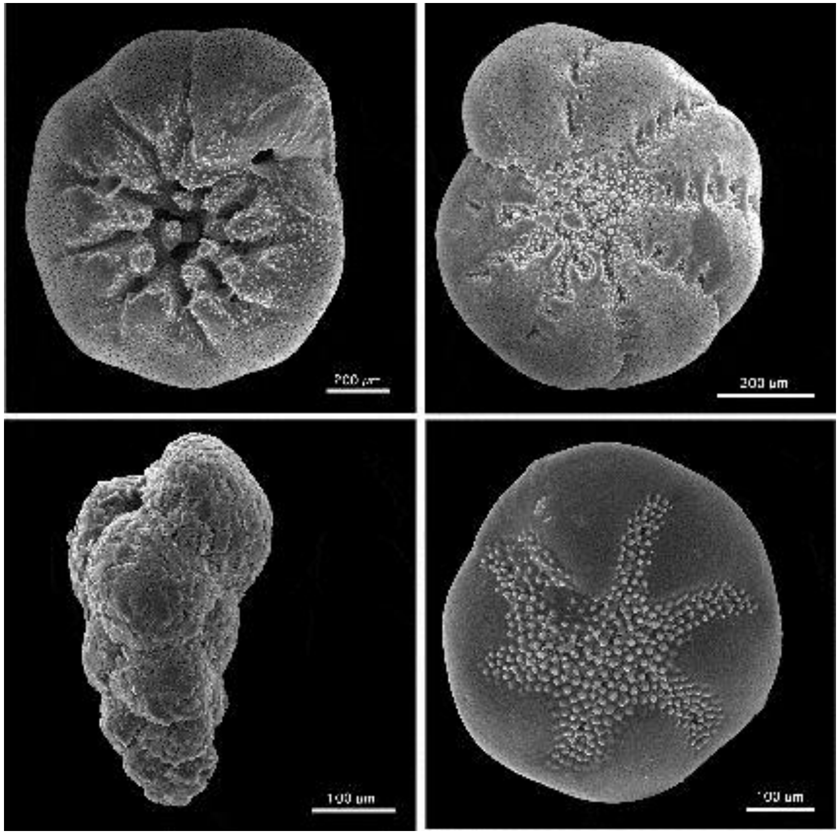




- Freshwater and marine water: diatomites

- Key-player in the regulation of silica at global scale

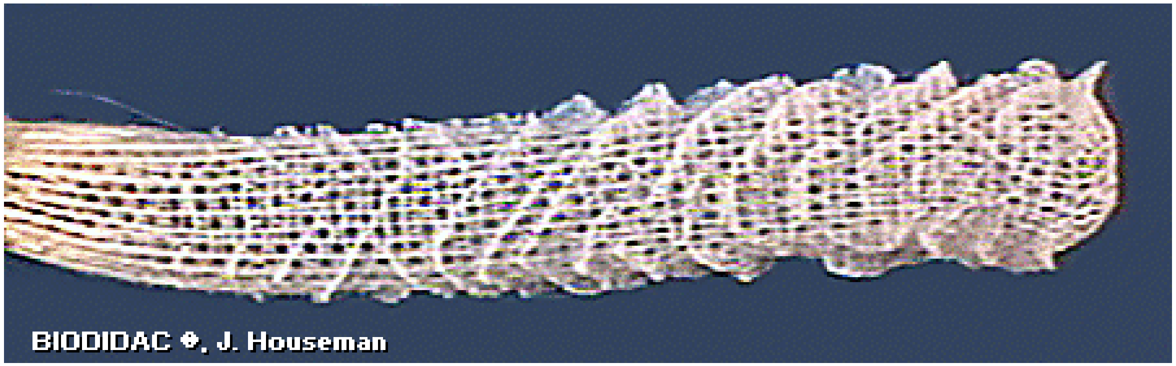
Another example: Foraminifera



Nummulites

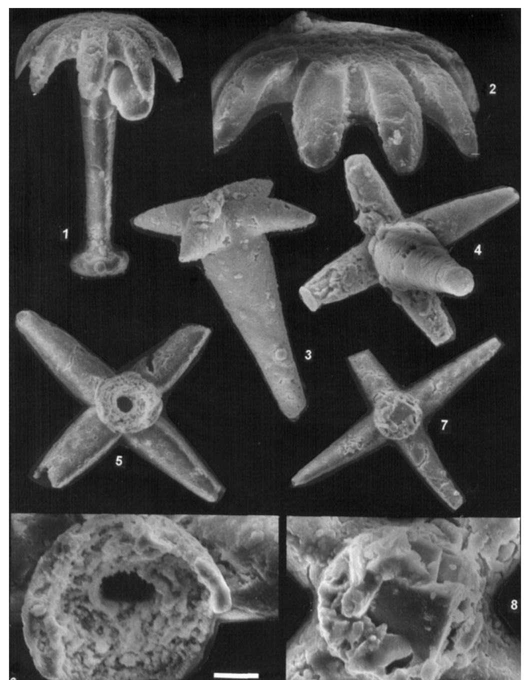
Calcite or aragonite

Another example: sponges (Porifera)



2 mineralogies:

$CaCO_3$
Calcarea)



SiO_2 =
Hexactinelles
(glass sponges)
& Demosponges

$SiO_2 + CaCO_3$
Few demosponges

Another example: cnidarians

In cnidarian, 2 polymorphs of $CaCO_3$

Octocorallia

Scleractinia

CALCITE

ARAGONITE

The example of brachiopods and bryozoans

Brachiopods

CALCITE

Exception: lingulid = Ca-phosphate !

Bryozoans

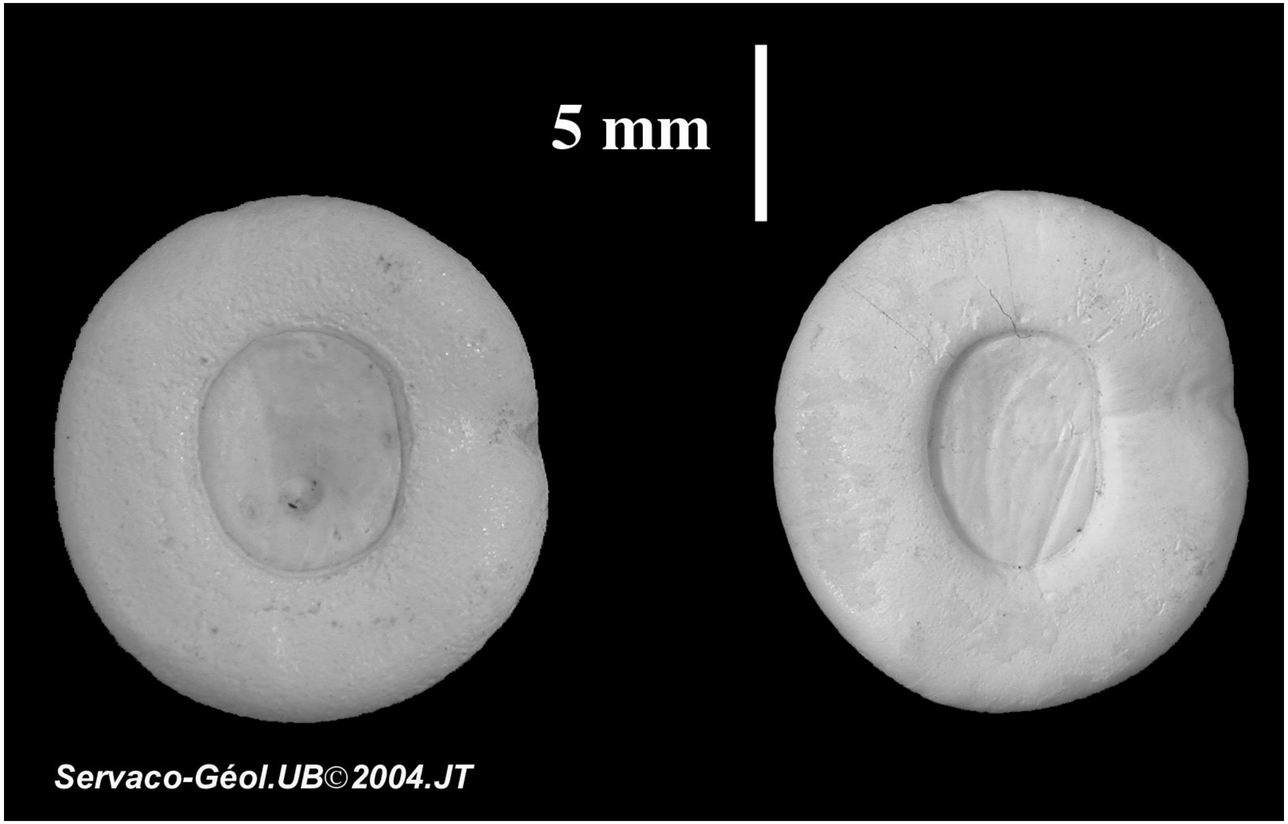
CALCITE
(+ aragonite)

Example in arthropods (crustaceans)

Lobster, crayfish, shrimp, prawn, crab…

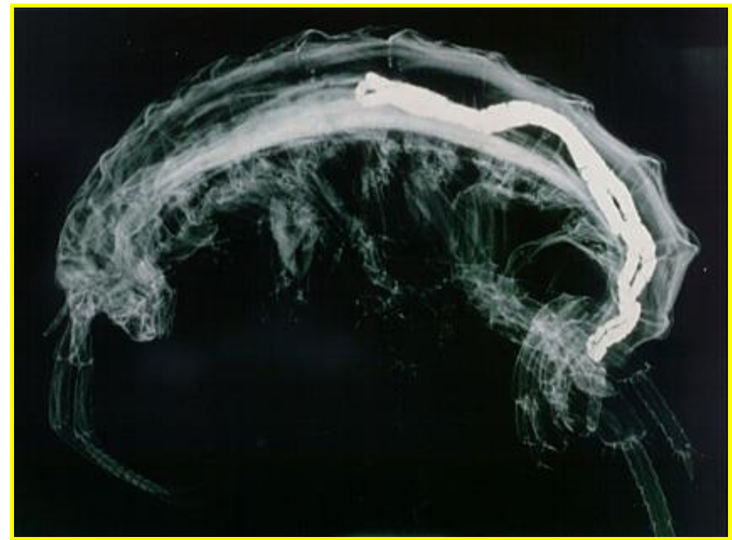
Mineralized cuticle + Ca-storage structures

In crustaceans: gastroliths

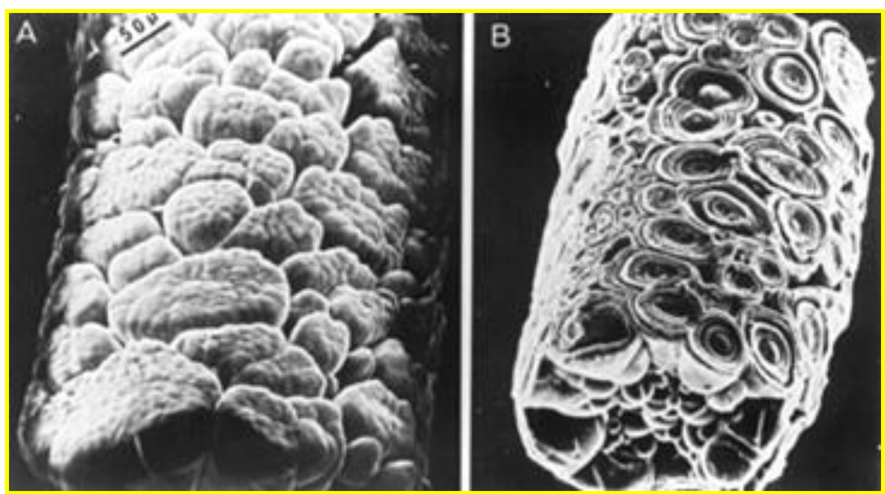


Biologically-controlled mineralization in crustaceans: calcium storage structures

***Orchestia cavimana*, terrestrial amphipod crustacean**



During the molting process (ecdysis)



10 hours after molting

Biologically-controlled mineralization: the mollusk shell

Biologically-controlled mineralization: the mollusk shell

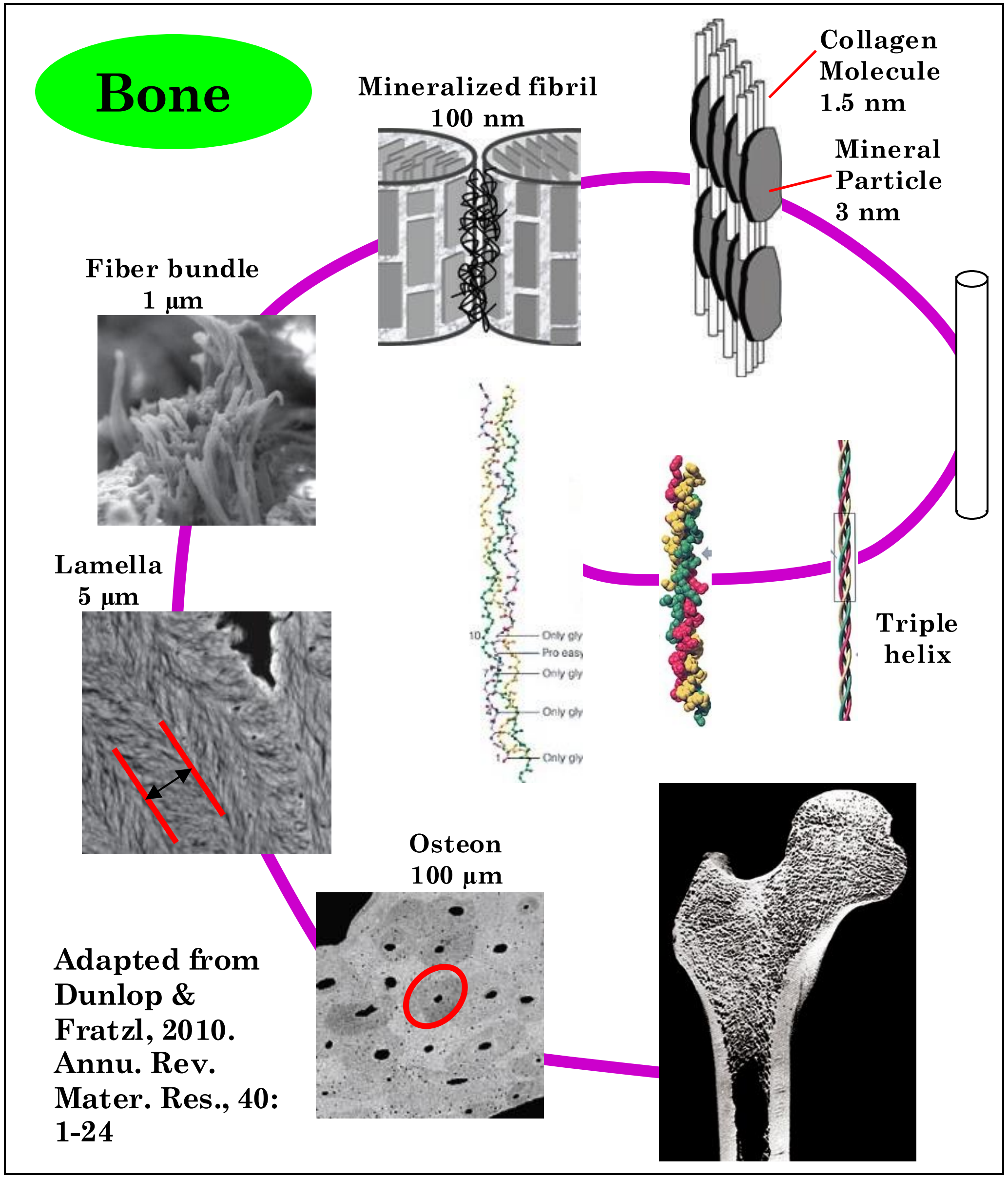

Photo H. Girardi

Thanatocenosis

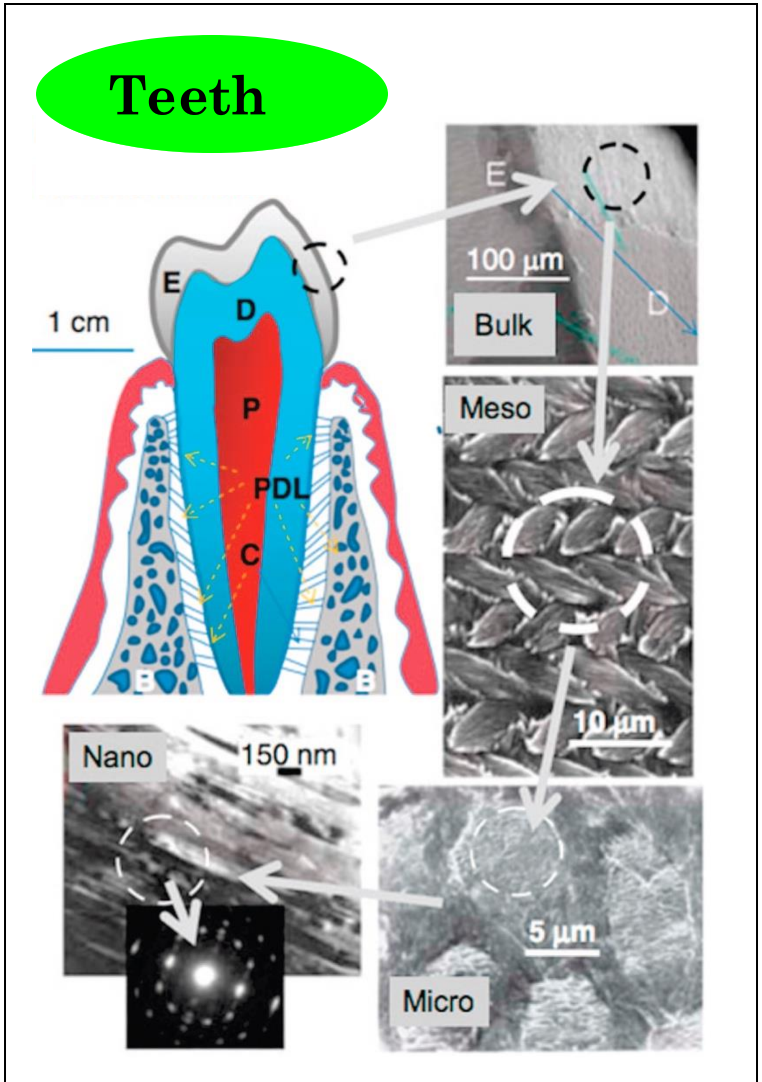

Photo Schumann & Steuber

Reef from Upper Cretaceous:
Rudist bivalves

The vertebrates…



Adapted from Dunlop & Fratzl, 2010. Annu. Rev. Mater. Res., 40: 1-24



Adapted from Palmer et al., 2008. Chem. Rev. 108: 4754-4783 and from Tamerler & Sarikaya, 2008. MRS Bull., 33: 504.