Biomineralization: The role of inorganic materials in Life

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What is the definition of “Biomineralization”?

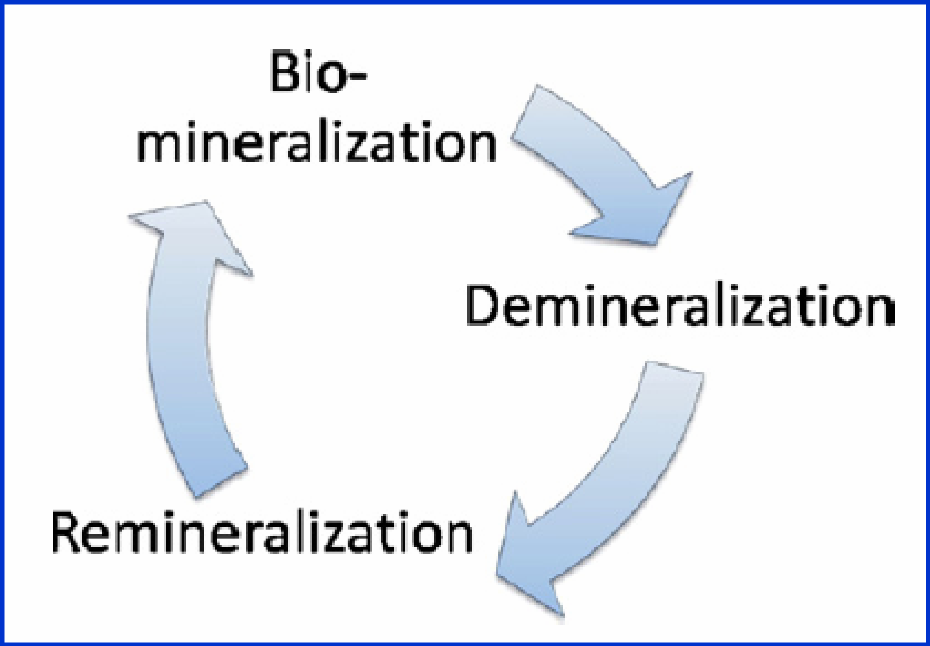
Biomineralization: the study of the formation, structure and properties of inorganic solids deposited in biological systems

Stephen Mann “Biomineralization: Principles and concepts in Bioinorganic materials chemistry, Oxford University Press, 2001

BIOMINERALIZATION: Formation of Inorganic Complex Structures in Biological Systems

E. Brunner, *Nature Mater.* **2007**, *6*, 398.

Demineralization: the other side of the same coin



Biomineral types and functions

(1) Calcium carbonate

a. Calcite and vaterite (shells, gravity sensors, lenses)

b. Amorphous phases (calcium storage)

(2) Calcium phosphate

a. Bone

b. Teeth

(3) Silica (unique amorphous nature)

(4) Iron oxides

a. Magnetic bacteria

b. “Rusty” proteins

c. Iron teeth

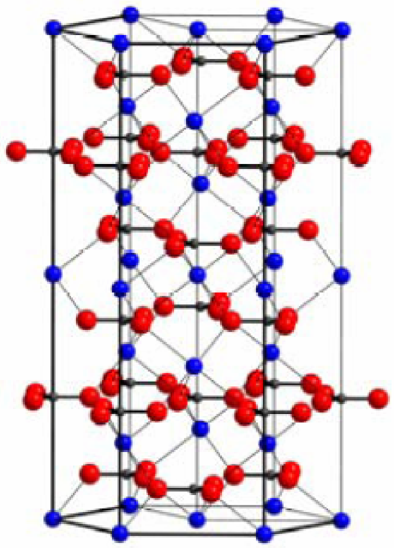
(5) Metal sulfides

Calcium Carbonate: a ubiquitous biomineral

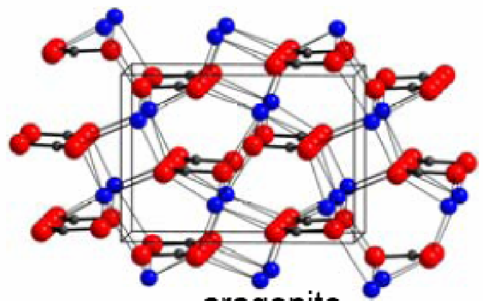
3 crystalline polymorphs of $CaCO_3$:

Calcite, Aragonite and Vaterite

Calcite is stable form under normal conditions



calcite



aragonite

Mg is readily incorporated, up to ~30% seen in calcite

Two hydrates as well: 1 H_2O & 6 H_2O

Amorphous $CaCO_3$ seen in some cases

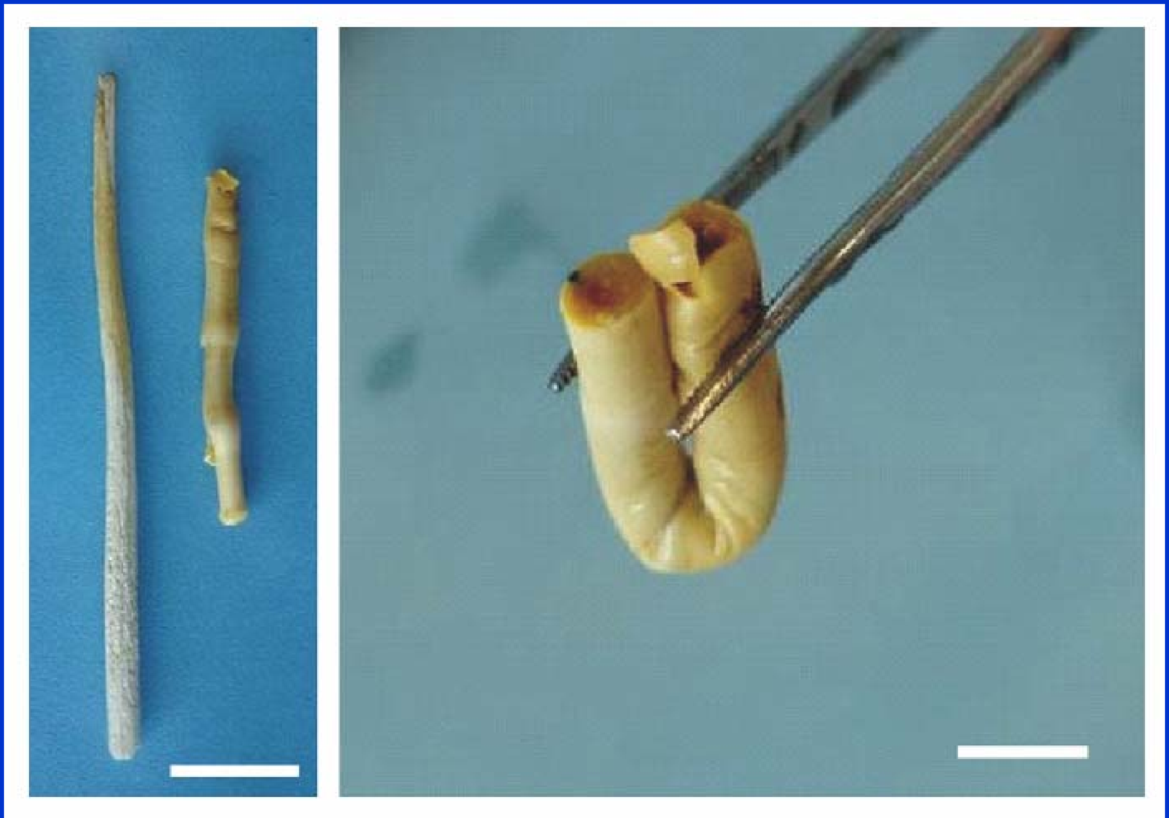
Calcium Carbonate: several uses by Nature

Mineral	Formula	Organism	Location	Function
Calcite	$CaCO_3$	Coccolithophores	Cell wall scales	Exoskeleton
		Foraminifera	Shell	Exoskeleton
		Trilobites	Eye lens	Optical imaging
		Molluscs	Shell	Exoskeleton
		Crustaceans	Crab cuticle	Mechanical strength
		Birds	Eggshells	Protection
Mg-calcite	$(Mg,Ca)CO_3$	Octocorals	Spicules	Mechanical strength
		Echinoderms	Shell/spines	Strength/protection
Aragonite	$CaCO_3$	Scleractinian corals	Cell wall	Exoskeleton
		Molluscs	Shell	Exoskeleton
		Gastropods	Love dart	reproduction
		Cephalopods	Shell	Buoyancy device
		Fish	Head	gravity receptor
Vaterite	$CaCO_3$	Gastropods	Shell	Exoskeleton
		Ascidians	Spicules	Protection
Amorphous	$CaCO_3 \cdot nH_2O$	Crustaceans	Crab cuticle	Mechanical strength
		Plants	leaves	Ca store

Echinoderms: seastars, sea urchins…
Cephalopods: octopuses…in mollusc family

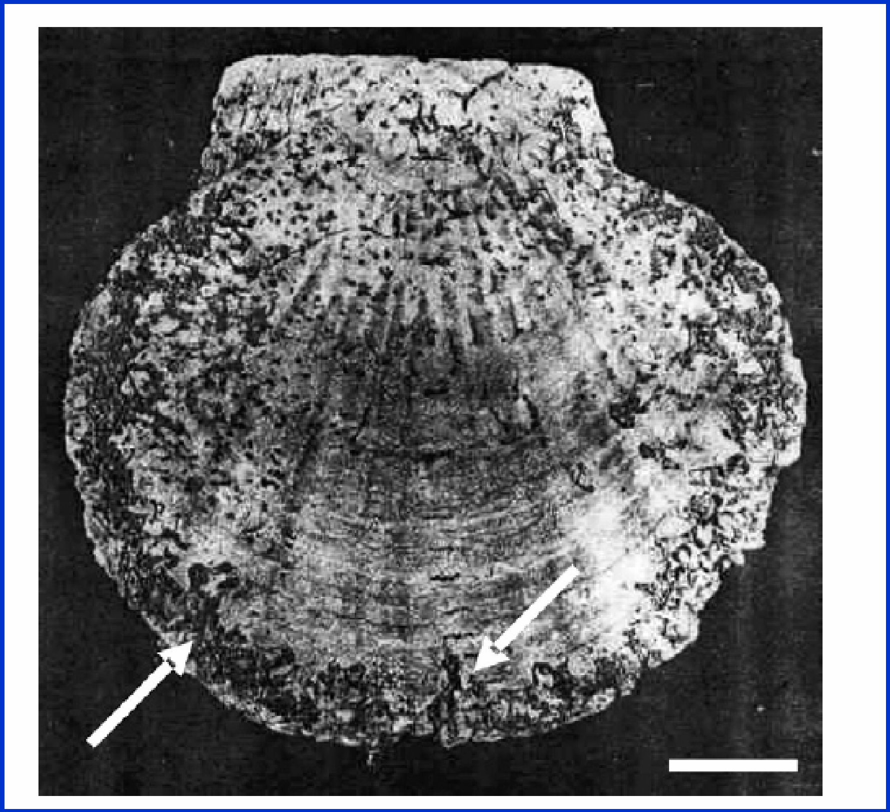
Ascidians: sea squirt (sessile coral looking animals)
Gastropods:snails, abalone, limpets…

Calcium Carbonate: Used for “protection”



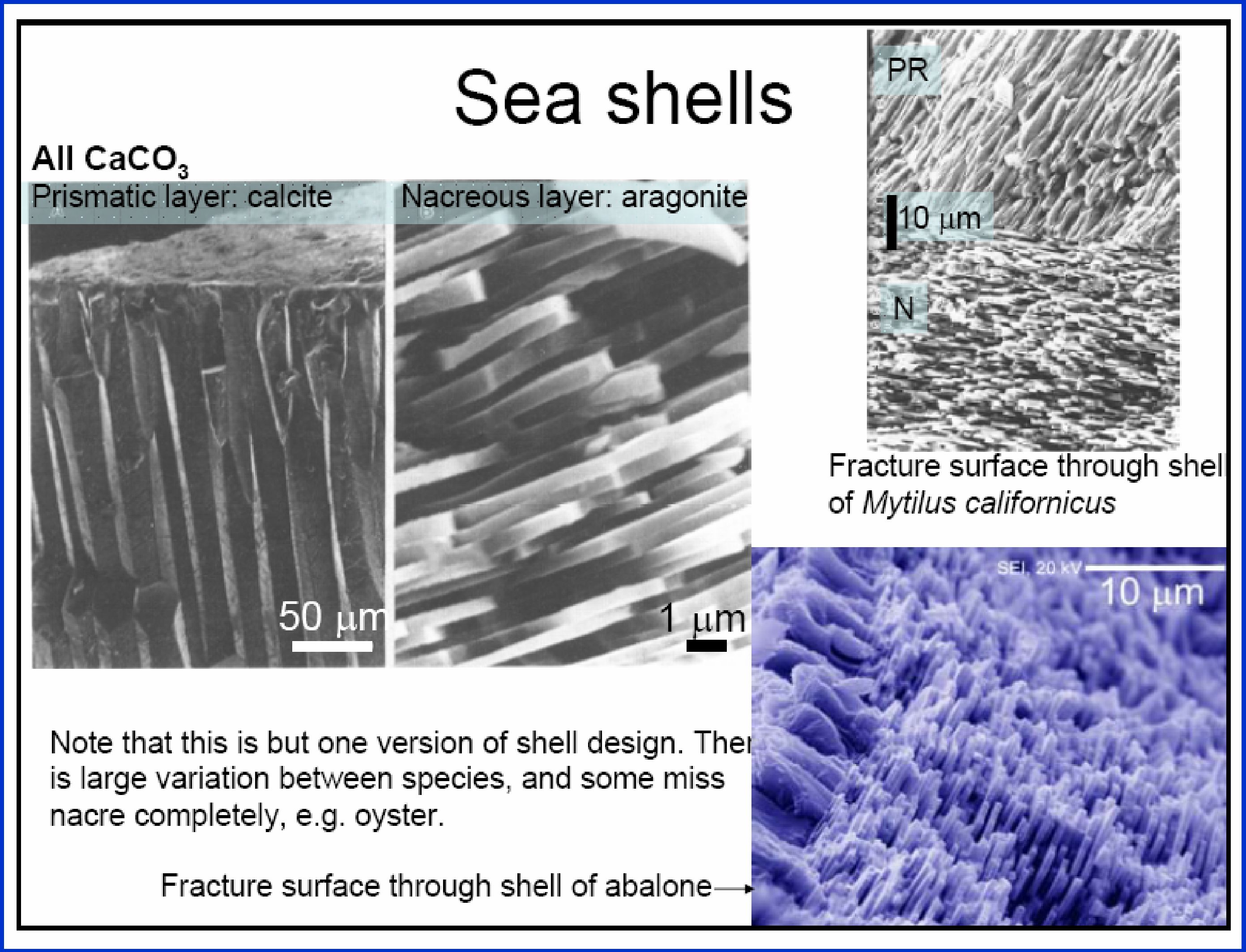
Demineralization in vitro of the stony hard calcite skeleton of the sea pen coral (Pennatulaceae) in vitro. Demineralization using Osteosoft (EDTA) solution led to loss of mineral phase (left), after that highly flexible organic matrix (right) could be obtained

Calcium Carbonate: Used for "protection" but… vulnerable



Boring worms: the outer surface of the scallop Patinopecten yessoensis (Jay) shell eroded (arrows) by polychaete worm Polydora brevipalpa

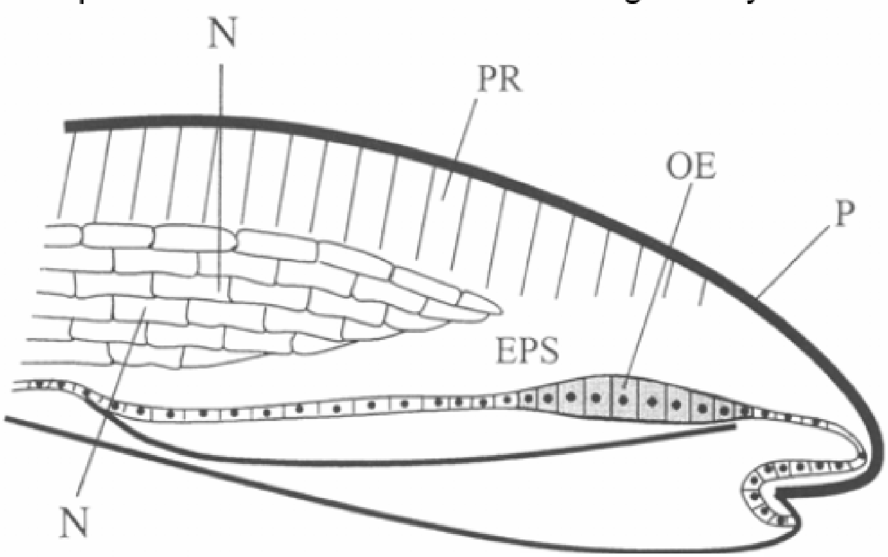
Calcium Carbonate in shells: why is it preferable?



Calcium Carbonate in shells: mechanical strength

Sea shells #2

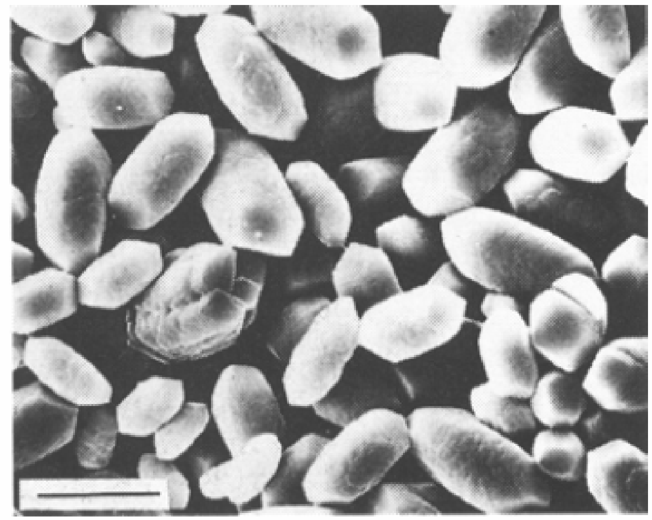
N:	nacre	aragonite, 0.5 μm thick tablets, 30 nm organic linker
PR:	prismatic region	calcite rods
OE:	outer epethilium	close packed cells, control mineralization
EPS:	Extrapallial space & fluid	water filled region
P:	periostracum	outer organic layer



Nacre: brick structure & combination of organic with inorganic ➔ **fracture toughness 3000× larger than for pure aragonite**

Calcium Carbonate: gravity sensor

- Aragonite & calcite used as gravity sensors in both land and marine animals
  - Statoliths, statoconia, otoliths or otoconia
- Function by transferring linear acceleration to hair-like extensions on sensory cells ➔ electrical signal
- Akin to fluid in the semicircular canals which are for angular momentum



8 μm

In humans (above) calcite is used in form of spindle shaped crystals

Calcite eyes in trilobites

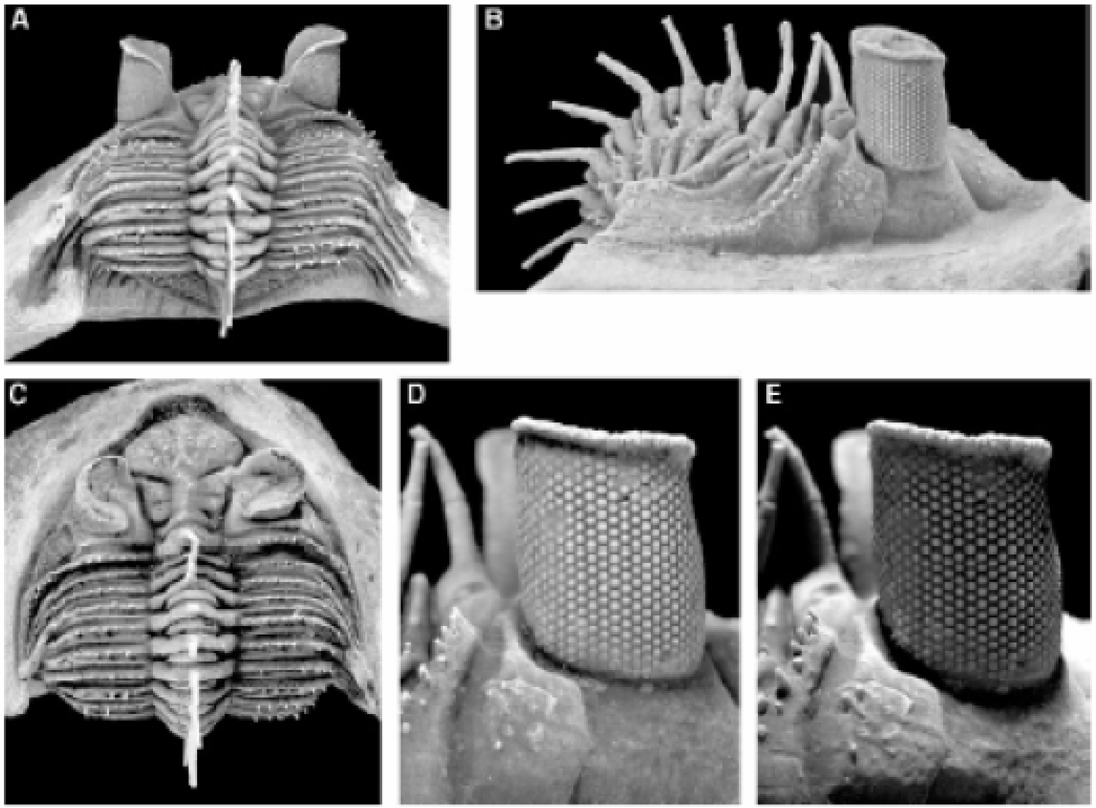


Fig. 1. *Erbenochile erbeni* (Alberti). Devonian (Emsian) Timrahrhart Formation (Jebel Gara el Zguilma, near Foum Zquid), southern Morocco. (A) Posterior view showing overhanging eyeshades. (B) Lateral view. (C) Dorsal view. The headshield is 32 mm across. (D) Side view detail of right eye showing lenses under optimum illumination, and (E) how the eyeshade cuts out light from above, when directed as a parallel beam above the palpebral lobe.

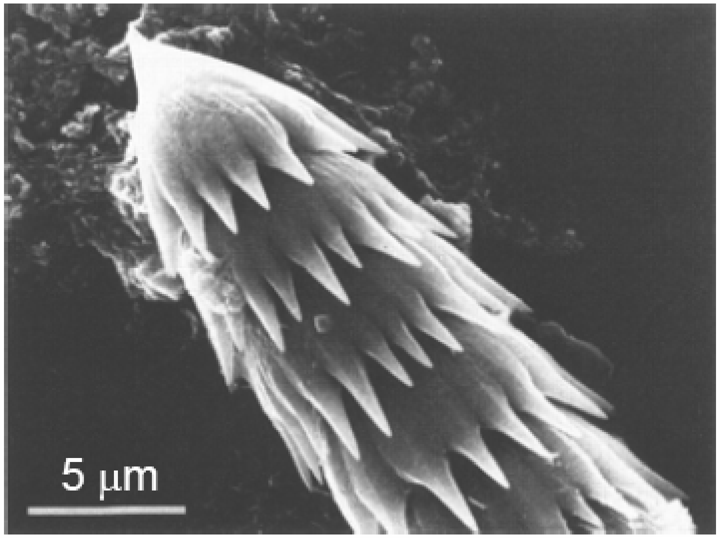
R. Fortey & B. Chatterton, 'A Devonian Trilobite with an Eyeshade' *Science* **2003**, *301*, 1689

The high position of the eyes afford 360° vision.

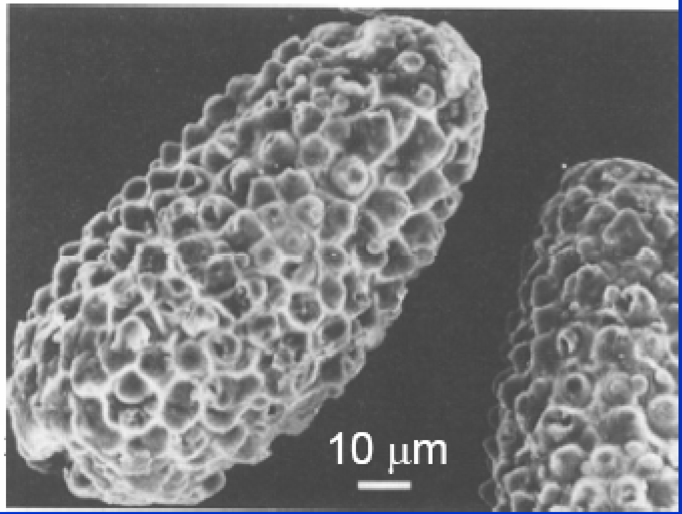
Eyeshade protects against glare from surface (peculiar to this species)

Vaterite & amorphous $CaCO_3$ phases

Vaterite: least thermodynamically stable form of the 3 non-hydrate crystal forms
Used by Ascidians, observed in inner ear of 2 species of fish



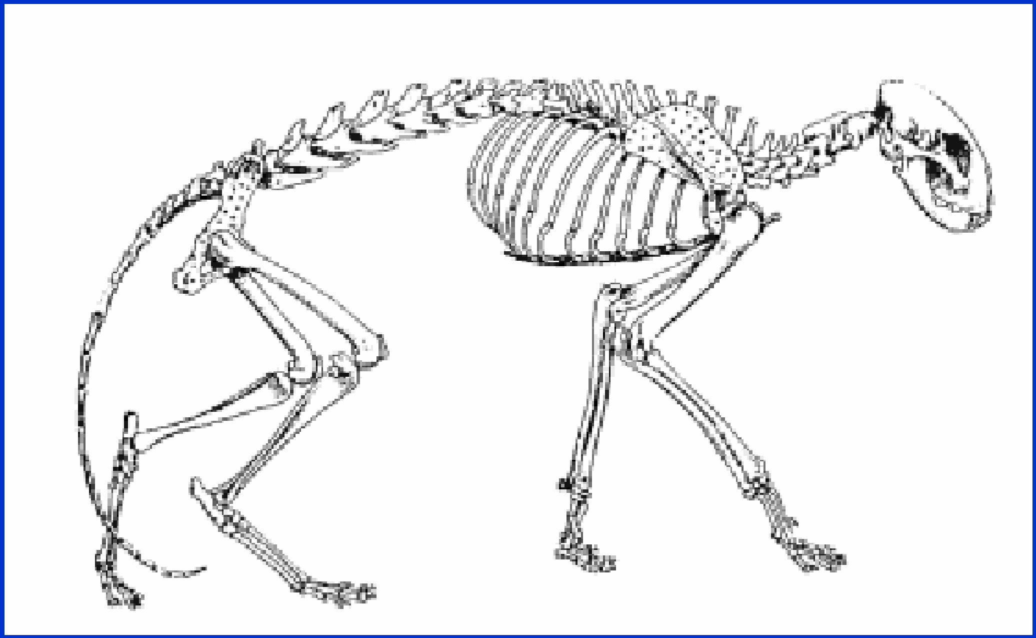
Amorphous $CaCO_3$:
Used as Ca store in leaves of many plants, cystoliths
Cannot be stabilized without organic stabilizers – still hard in the lab



Calcium Phosphates: they are everywhere!!!

Mineral	ideal formula	organism	location	function
Hydroxyapatite	$Ca_{10}(PO_4)_5(OH)_2$	Vertebrates	Bone	Endoskeleton
		Mammals	Teeth	Cutting/grinding
		Fish	Scales	Protection
Octacalcium phosphate	$Ca_8H_2(PO_4)_6$	Vertebrates	Bone & teeth	precursor phase
Amorphous	variable	Chitons	Teeth	precursor phase
		Gastropods	Gizzard plates	Crushing
		Bivalves Gills	Ion store	
		Mammals	Mitochondria	Ion store
		Mammals	Milk	Ion store

Vertebrates skeleton: made of Calcium Phosphate



Bone: a unique biocomposite based on hydroxyapatite

Bone

- Constant remodelling
  - Stress response
  - Pregnancy
- Bone cells:
  - Osteoblasts: bone builders
  - Ostoclasts: bone removers
  - Osteocytes: incrusted in bone – may act as strain gauges
- Piezoelectric
  - Strongest when dry (nonbiological), role uncertain
- Hierarchical structure

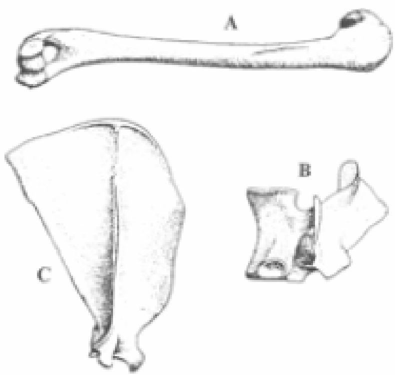
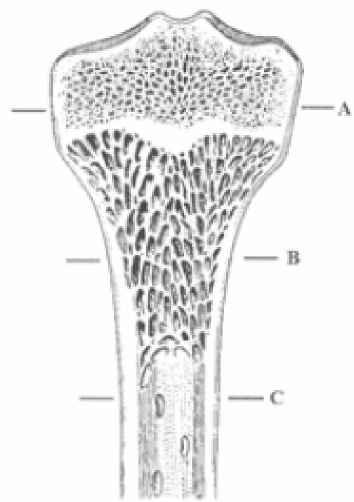
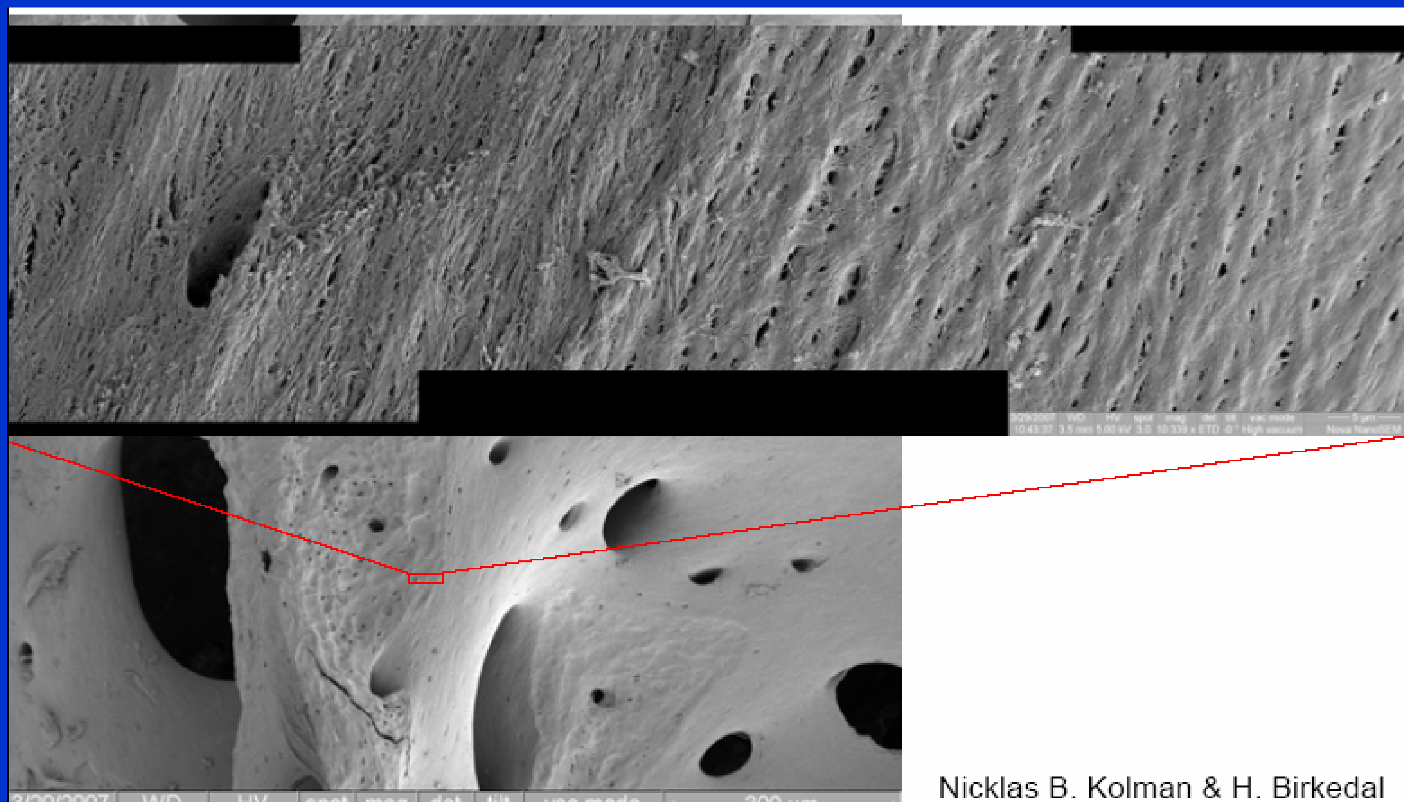


Fig. 2.8 Bone types: (A) long bone; (B) short bone; (C) flat bone.



Bone growth and remodeling

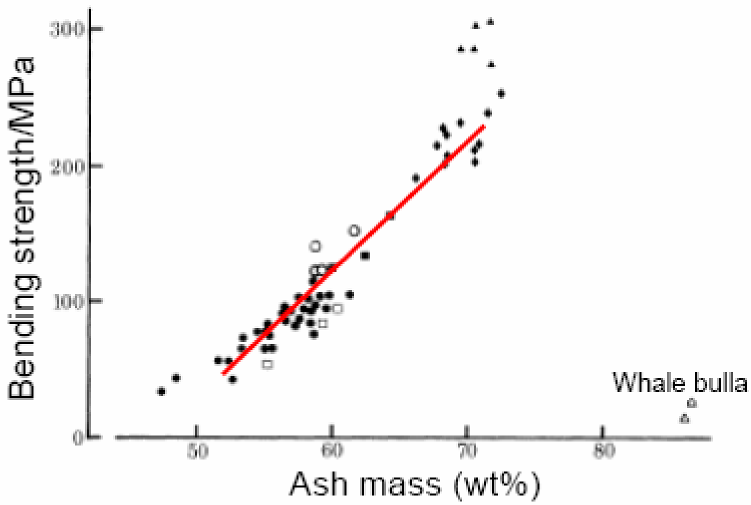


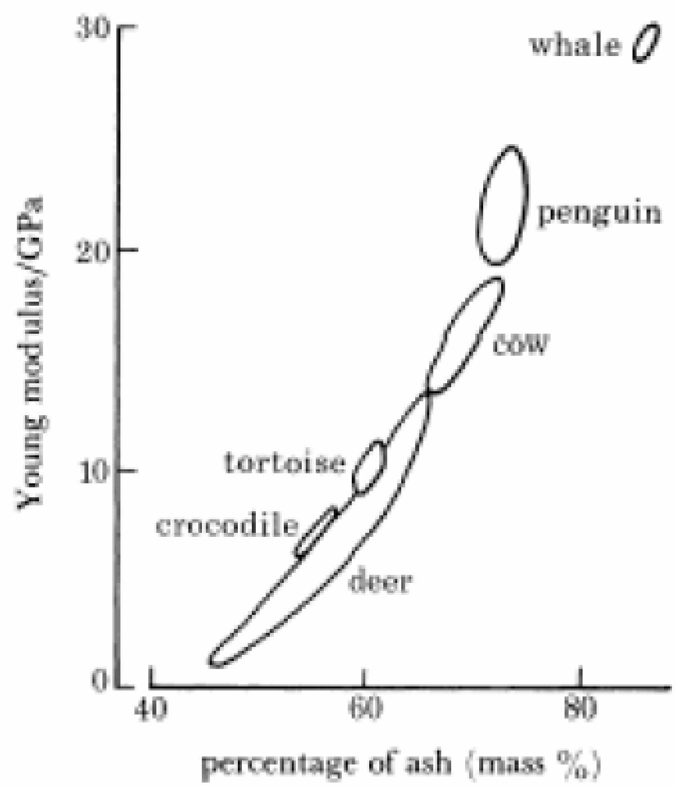
Nicklas B. Kolman & H. Birkedal

Bone's exquisite mechanical properties

Mechanical properties: from mix of xtals & collagen fibers + glycoproteins

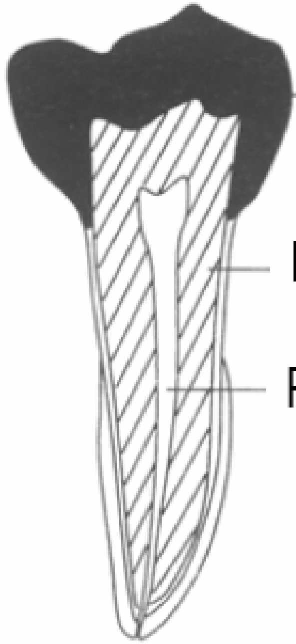
Stiffness & fracture resistance scales with mineral content in interspecies comparisons





Currey, *Phil. Trans. R. Soc. Lond.* B **1984**, *309*, 509

Teeth: another unique biocomposite



Enamel, 95 wt% mineral, hard but brittle

Dentine, collagen containing, closer to bone

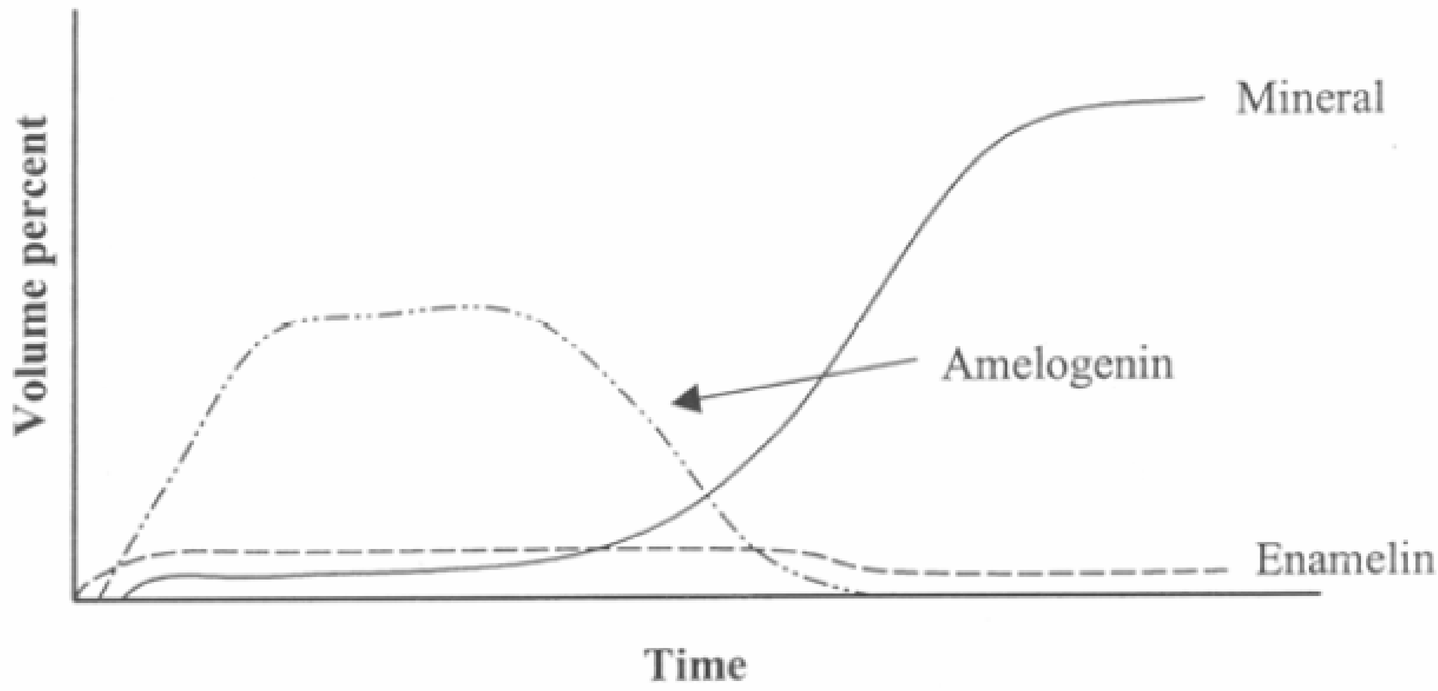
Pulp, organic

Hard outer surface with softer inner core → crack propagation can be stopped

Enamel rods are single crystals, several µm long

Enamel formation in teeth

1. Organic matrix of amelogenin & enamelin is deposited
2. Organic matrix is mineralized and removed



Why "fluoride treatment"???

- F-apatite has 10^3 lower sol. prod. than HAP
  - This is why F^- in tooth paste works
    - And why you can get joint pain when drinking too highly fluorinated water

Fish also have AP teeth, but F-AP:

Composition/wt%	Human enamel	Shark enameloid
Ca^{2+}	37.55	37.26
Na^+	0.75	0.76
Mg^{2+}	0.27	0.32
PO_4^{3-}	17.68	17.91
CO_3^{2-}	3.6	1.1
F^-	0.02	3.65

Iron Oxides: various types for various functions

Mineral	Formula	Organism	Location	Function
Magnetite	Fe_3O_4	Bacteria	Intracellular	Magnetotaxis
		Chitons	Teeth	Grinding
		Tuna/salmon	Head	Magnetic navigation
Geothite	α-FeOOH	Limpets	Teeth	Grinding
Lepidocrocite	γ-FeOOH	Sponges	Filaments	Unknown
		Chitons	Teeth	Grinding
Ferrihydrate	$5Fe_2O_5 \cdot 9H_2O$	Animals/plants	Ferritin	Fe storage protein
		Chitons	Teeth	Precursor phase
		Beaver/rat/fish	Tooth surface	Mechanical strength
	+phosphate	Bacteria	Ferritin	Fe storage protein
		Sea cucumber	Dermis	Mechanical strength

Magnetotactic Bacteria

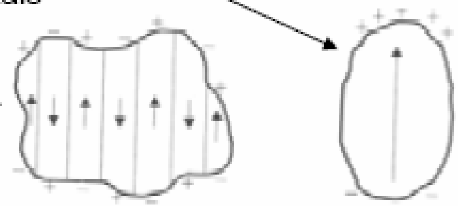
Magnetite: $Fe_3O_4 = Fe^{III}_2Fe^{II}O_4$

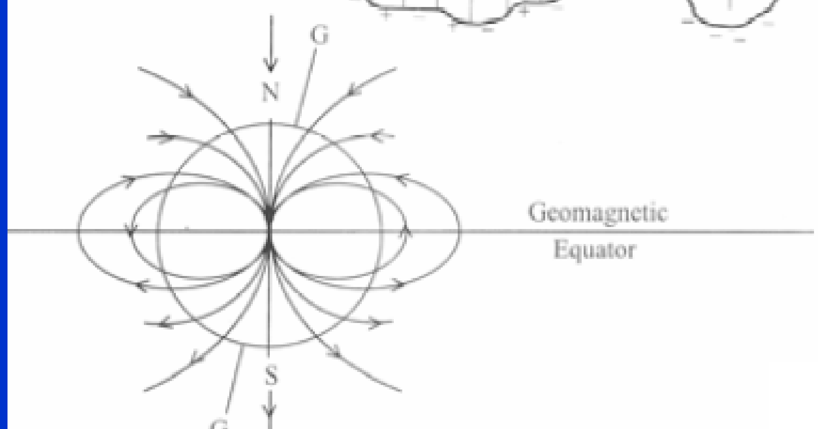
Magnetic:

Large xtals	ferrimagnet
<35 nm	superparamagnet
>120 nm	multidomain

35-120 nm: **single domain** nanomagnets!

Sizes for cubic crystals





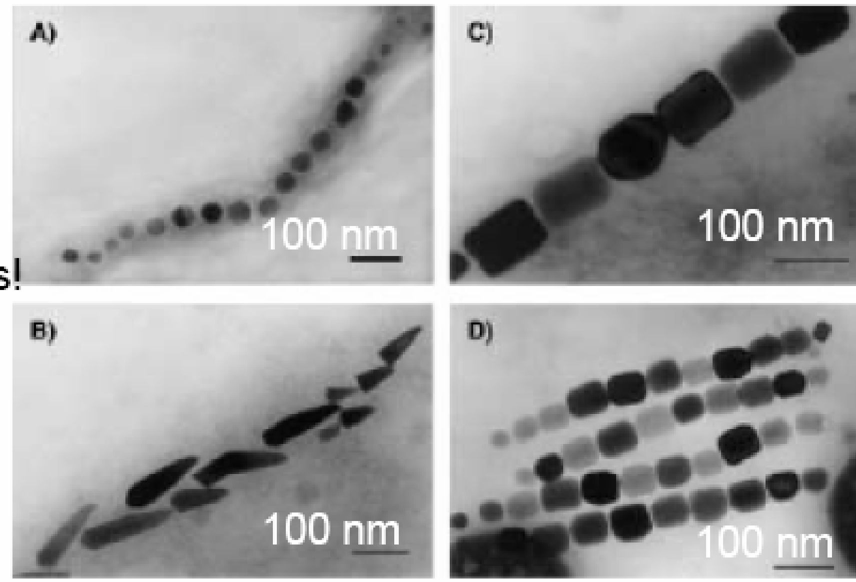


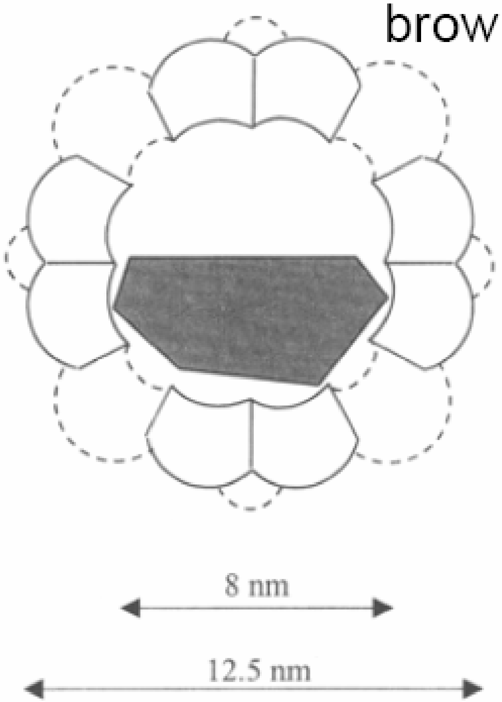
Figure 5. Crystal morphologies and intracellular organization of magnetosomes from magnetotactic bacteria: A) cubooctahedral; b) bullet-shaped; c–d) pseudohexagonal. The magnetosomes are arranged in one (C) or more (D) chains. The lengths of the bars represents 100 nm.

Bäuerlein *Angew. Chem. Int. Ed.* **2003**, *42*, 614

“Rusty” proteins: Ferritin

Apoferritin: empty protein

Ferritin: Fe-containing, capacity ~4500 Fe atoms
~30 wt% Fe
Ferrihydrate: $5Fe_2O_3 \cdot 9H_2O$
brown, obtained by action of OH^- on Fe^{III} solution

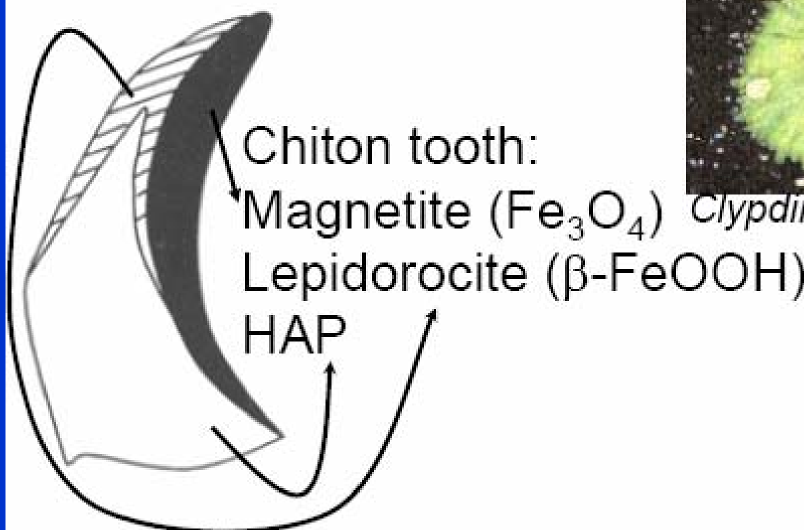


~solubilized iron oxide

Ferrihydrate is easy to condense/dissolve by slight changes of pH (dissolves at pH~5.5).

Release in lysosomes (intracellular vesicles)

Iron teeth: limpets & chitons

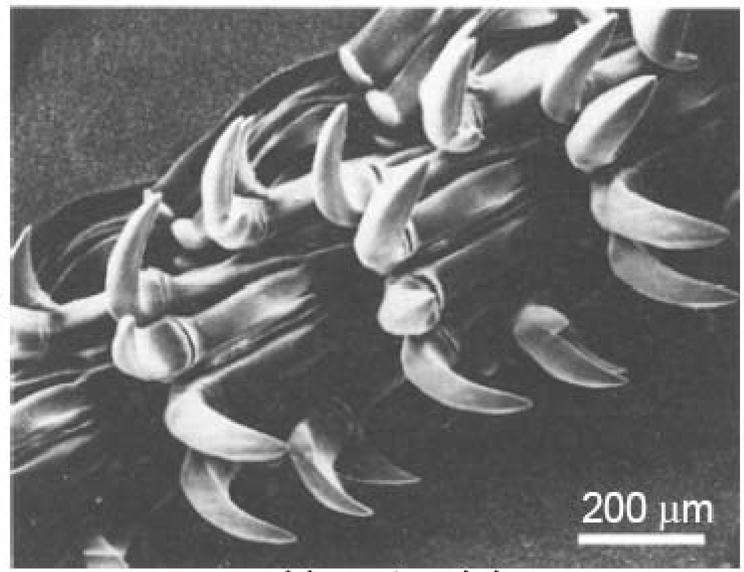



Clypdina rugosa


Ischnochiton australis

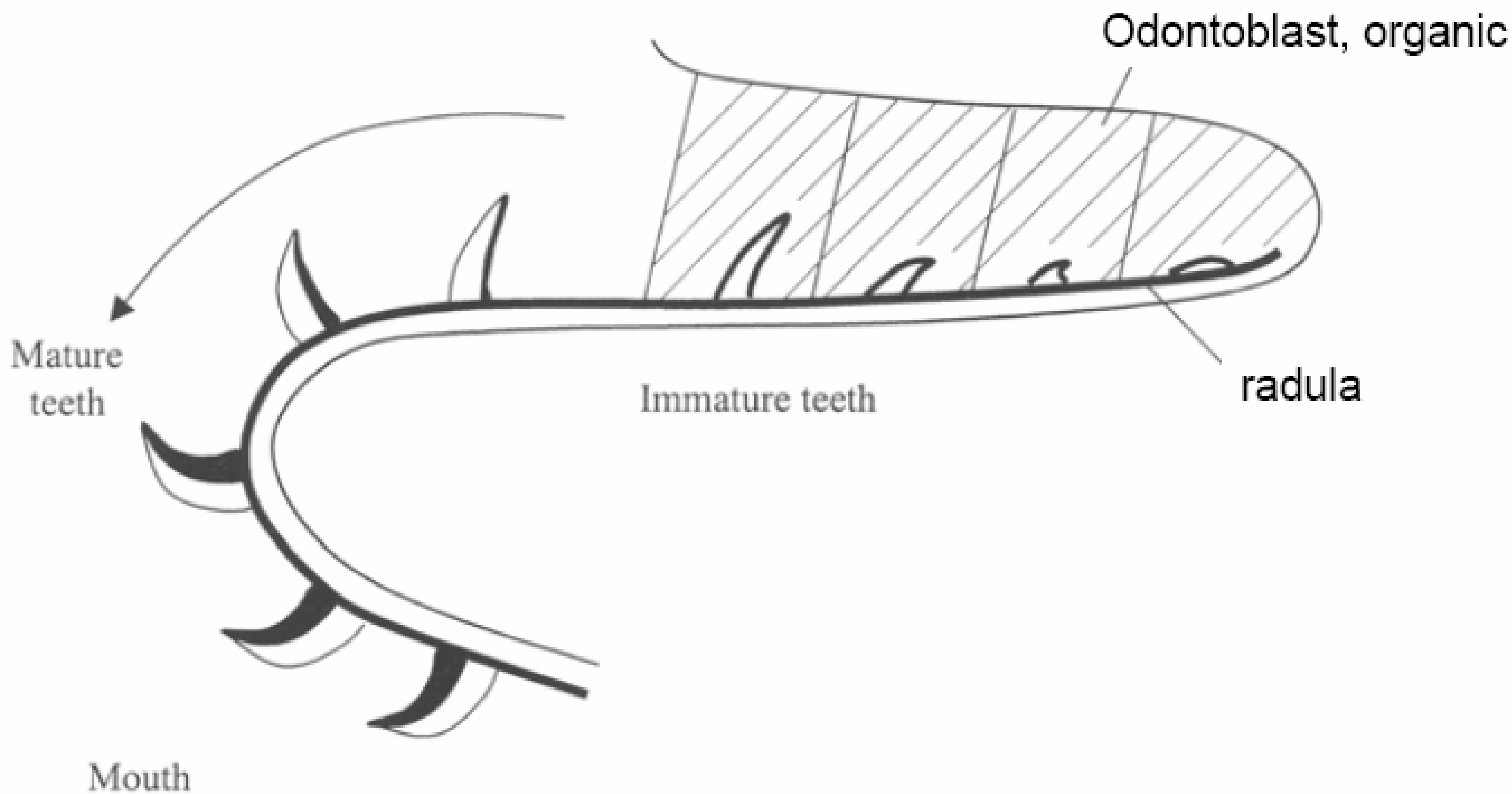
Limpet: goethite (α-FeOOH), no magnetite
silica core

Radula in limpet ~7 cm long!
Hundreds of teeth



Limpet radula

Iron teeth regeneration



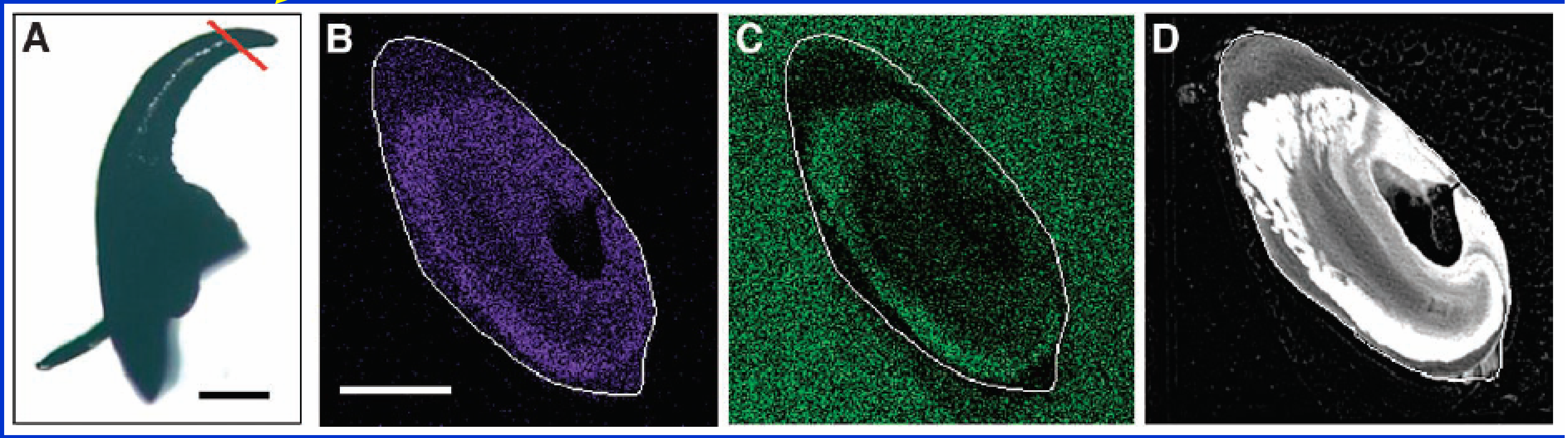
Conveyor belt construction mechanism: old & used are replaced by fresh

Mineralization upon exposure from odontoblast

Very complex mechanism, involving amorphous Ca-phosphate (chiton) or silica (limpet

Another biomineral used in teeth of *Glycera dibranchiata*

ATACAMITE, [$Cu_2(OH)_3Cl$], a copper based biomineral



Lichtenegger, et al. *Science* **2002**, *298*, 11