# Biomineralisation

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# Biomineralisation

- Biomineralisation is the process by which living organisms produce mineral products, usually skeletal

- What? Who? Where? When? How?
- How do we know?
- Why? At what cost?  Who cares?

# What?

- Biominerals:  almost 60 known
  - Carbonates, phosphates, halides, sulfates
  - Silicate, Fe oxides, Mn oxides, sulfides
  - Metals, citrate, oxalates and more
- About 50% of all precipitated minerals are based on Ca
- Most common marine biominerals are calcium carbonate and silicate

## Calcium carbonate $CaCO_3$

- Crystalline or amorphous
- Often contaminated with other elements (Sr, Mg)
- Many polymorphs
- Commonly precipitated by:
  - Foraminifera
  - Nannoplankton
  - Invertebrates

## Silicate $SiO_2$

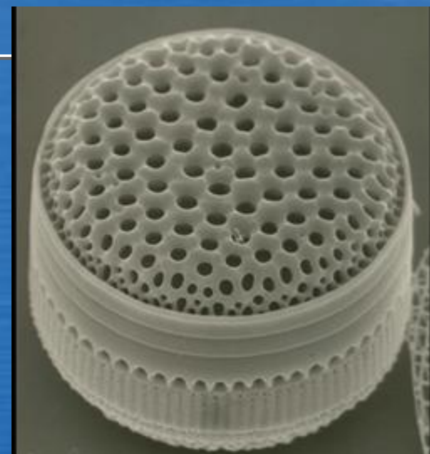
- Amorphous opaline silicate
- Generally nearly pure
- Commonly precipitated by:
  - Radiolarians, diatoms
  - Some other plants
  - Silicosponges and a few other invertebrates

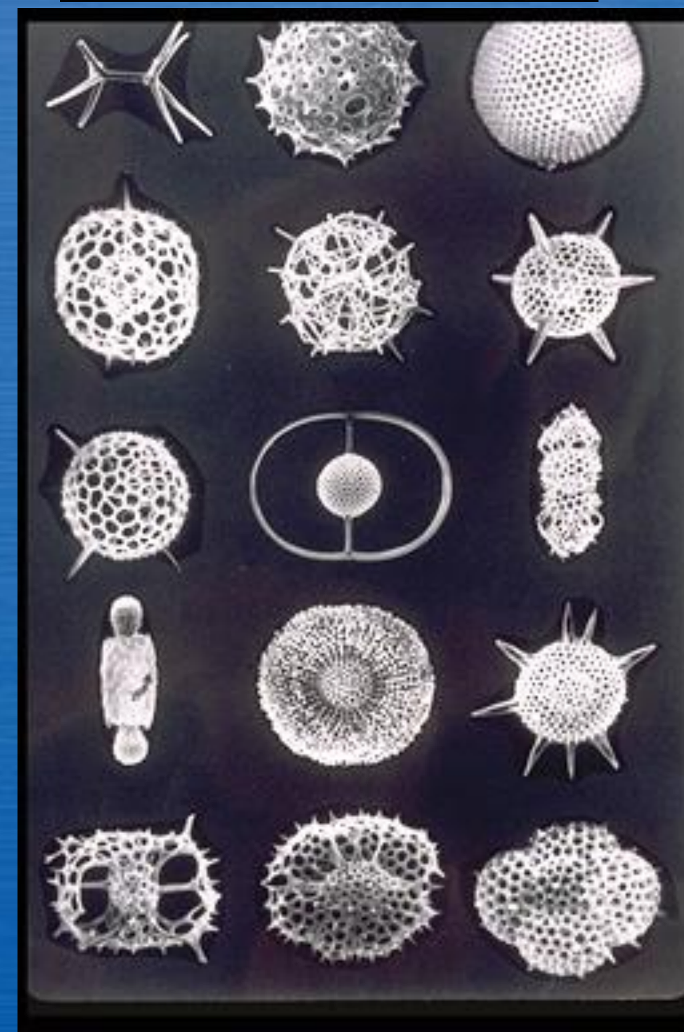
# Silicate is glass

- $SiO_2$ is the mineral quartz, the most common mineral in Earth's crust
- Silicate is the main mineral in glass
- Biomineral silicate is usually transparent & glassy, often in needle shapes
- $SiO_2$ is used in cement, drilling muds, various ore processing methods, also grinding, leaching, pumps, and as absorbents, lubricants, thickeners

# Mineral $SiO_2$

# Biomineral $SiO_2$





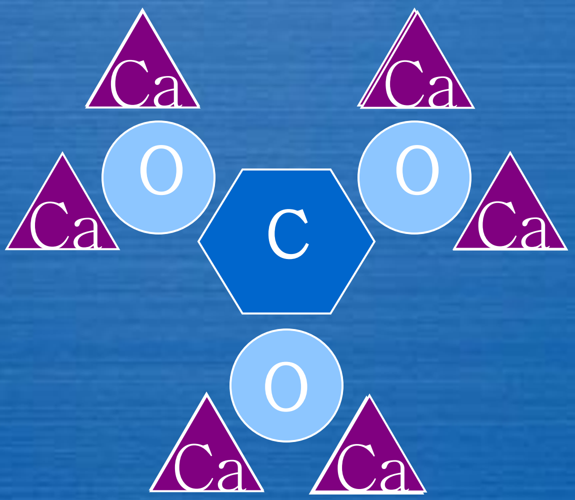
# $CaCO_3$: an important biomineral

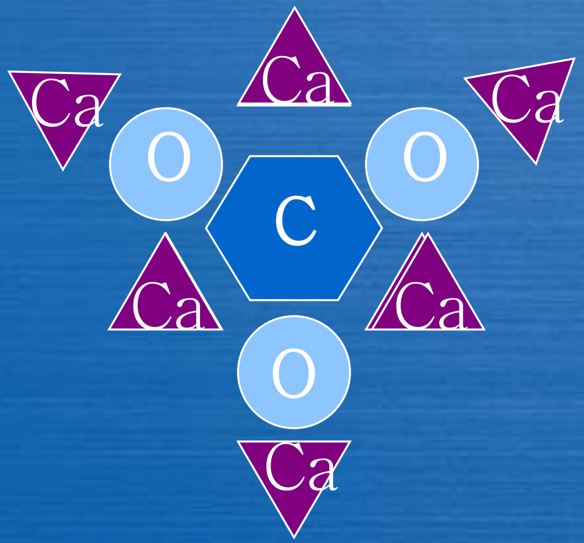
- Calcium carbonate (a.k.a. lime)
- Common on the Earth’s crust (4% by wt)
- Used in cements, mortars, lime, glass-making, ornamental stone
- Fossils, mineral cements, limestones, marbles, cave formations, mexican onyx, iceland spar, “tv rock”
- Several different crystal structures

# $CaCO_3$ polymorphs

**Calcite** (trigonal)

**Aragonite** (orthorhombic)

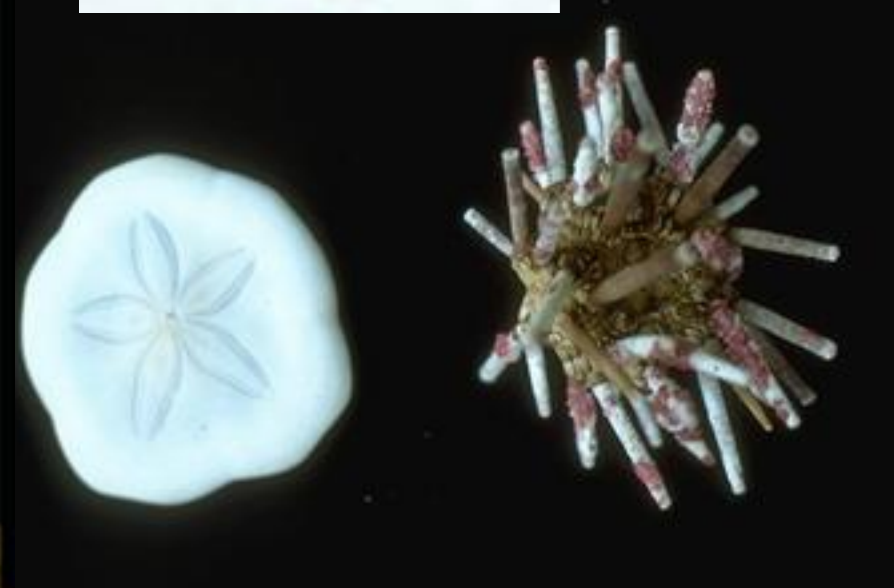


| Calcite | Aragonite |
| --- | --- |
| Easy, cheap to make | Expensive to make |
| Resistant to dissolution | Resistant to mechanical stress |
| Stable over time | Metastable |
| Mg substitution (< 22%) | Sr substitution (< 2%) |
| Common in cool waters | Common in warm waters |

# Mineral Calcite

# Biomineral Calcite



# Mineral Aragonite

# Biomineral Aragonite

# Bio-Mineralogical Space


(Smith et al, 2006)

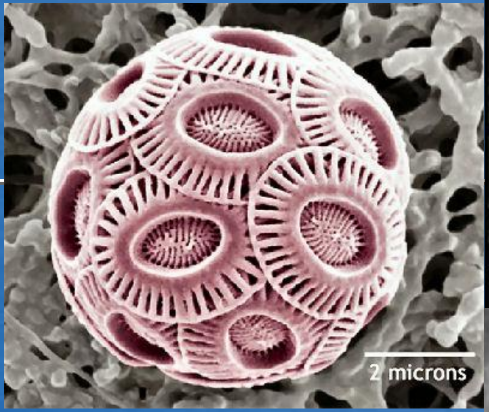
# Who?

- Bacteria, fungi, protists
- Algae, phytoplankton, plants
- Invertebrates
  - Sponges, worms, bryozoans, brachiopods,
  - Molluscs, arthropods, echinoderms…
- Vertebrates
  - Ascidians, chordates
- In all, 55 phyla have at least some mineralisers (thus some hard parts)

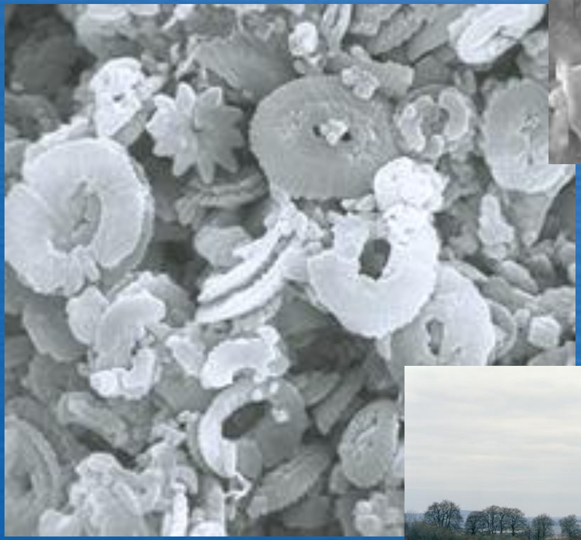
# Microfossils

# Coccolithophores

- Haptophyta: Prymnesiophyceae: Coccolithales
- Marine calcareous nannoplankton
- *Coccolithus huxleyi*
- Coccoliths (~ 1 µm) form sediment, chalk
- Low-Mg calcite



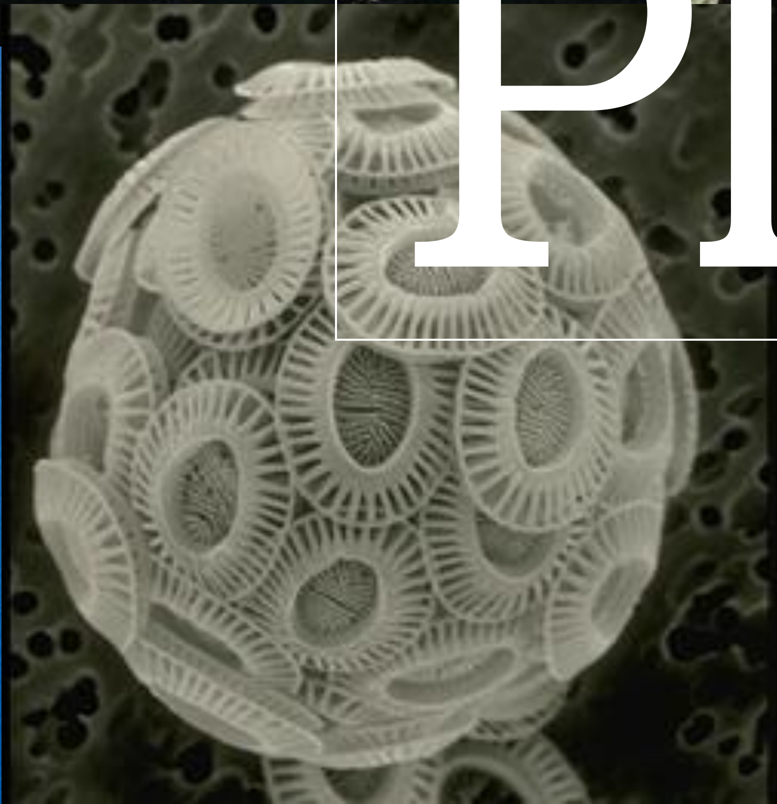




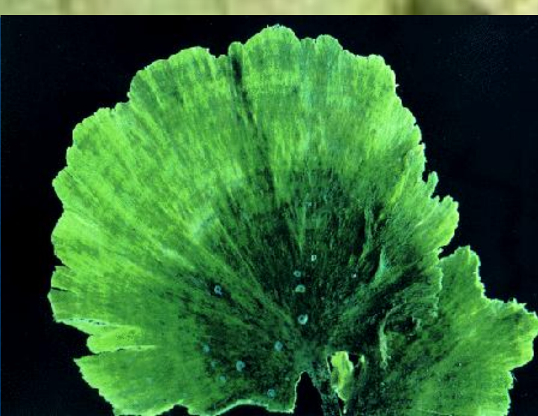
# Foraminifera

- Amoeboid protozoa
- Pelagic marine
- Consumers
- *Globigerina, Orbulina*
- Tests (1 mm) form sediment
- Important in deep sea cores & paleoceanography
- Almost all calcite

# Plants







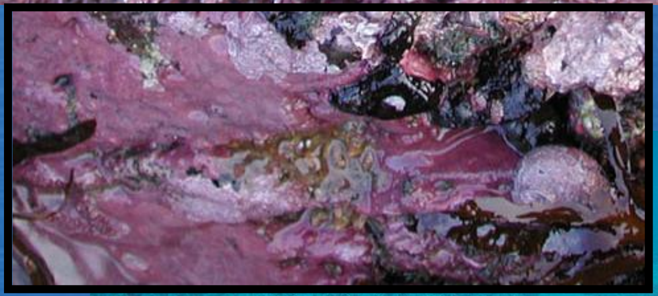
# Codiacean Green Algae

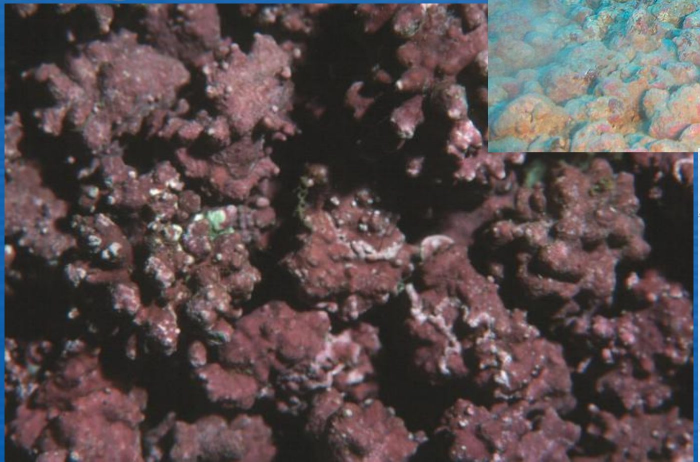
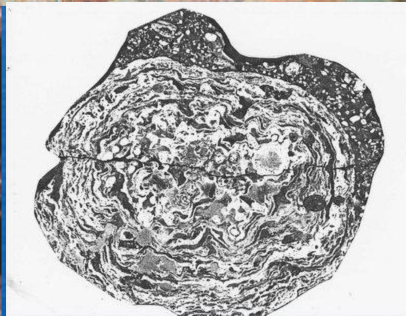
- Chlorophyta: Bryopsidales
- Tropical marine
- *Halimeda, Penicillus*
- Rapid sediment production, lime mud
- Usually aragonite

# Coralline Algae

- Rhodophyta: Corallinales
- Tropical to temperate marine shallow water
- Geniculate or non-geniculate
- *Corallina, Lithothamnion*
- Rhodoliths
- Fossils, Limestone
- High-Mg calcite






Invertebrates

# Corals -- solitary and colonial

- Coelenterata: Anthozoa
- Soft vs hard corals
- Reef-building (tropical) vs solitary
- *Porites, Flabellum*
- Reefs, biodiversity, sea-level research
- Aragonite

# Brachiopods -- lamp shells

- Brachiopoda
- Benthic marine
- *Calloria, Notosaria, Terebratella*
- Long fossil record
- Usually calcite or fluorapatite (Ca phosphate)



# Bryozoans -- moss animals

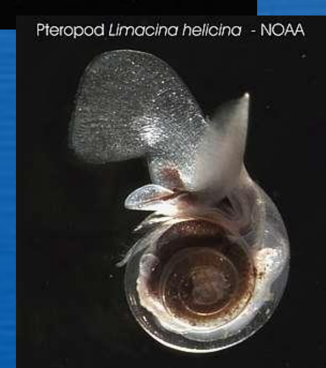
- Bryozoa
- Marine benthic colonies
- *Bugula, Cellepora*
- Thickets, encrusting
- Important sediment-formers, long fossil record
- Variable mineralogy

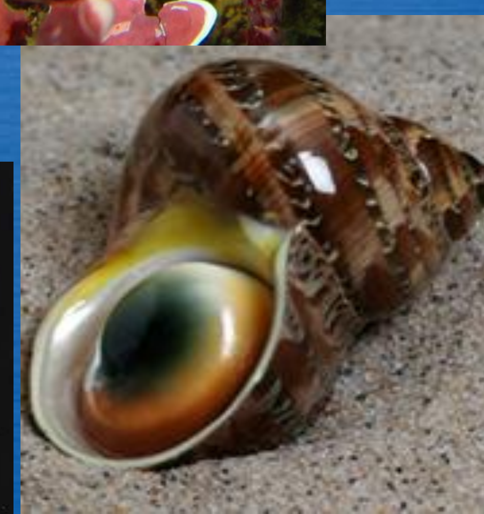
# Molluscs - clams, snails, squids

- Pelecypods: clams, scallops, oysters
- Gastropods: snails, limpets, paua
- Cephalopods: squid, octopus
- Chitons, tusk shells, pteropods
- Highly variable mineralogy





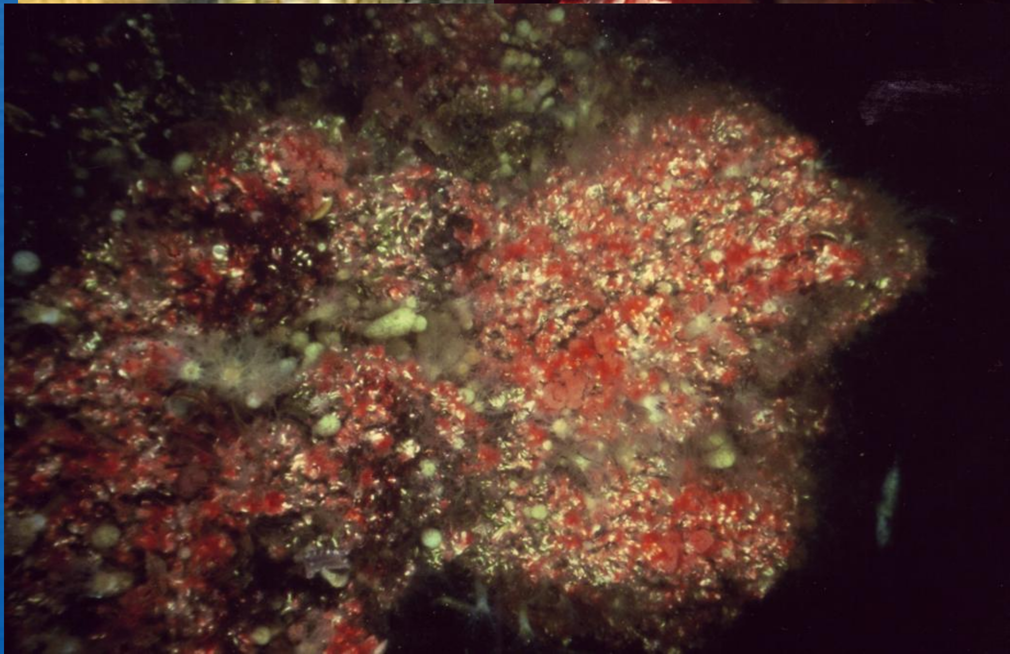




# Annelids -- worms

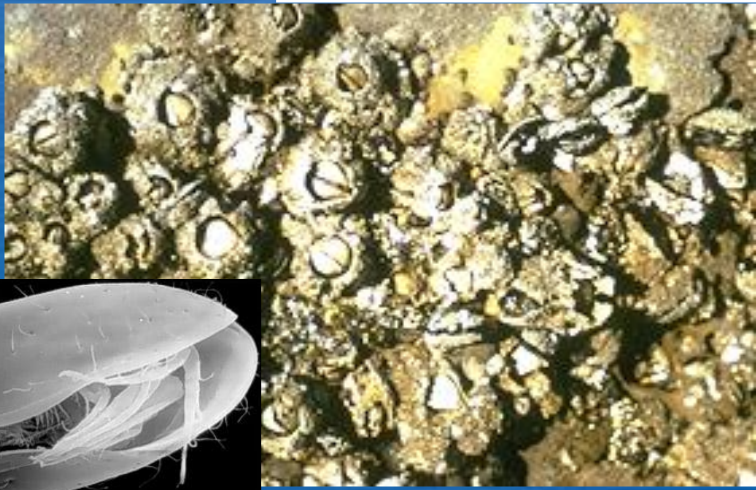
- Annelida: Serpulidae
- Marine benthos
- Tubes, reefs
- *Galeolaria, Serpula*
- High-Mg Calcite





# Arthropods: crabs, barnacles

- Arthropoda:
  Crustacea (crabs)
  Cirripedia (barnacles)
  Ostracoda
- *Cancer, Balanus*
- Mobile, consumers
- Usually calcite



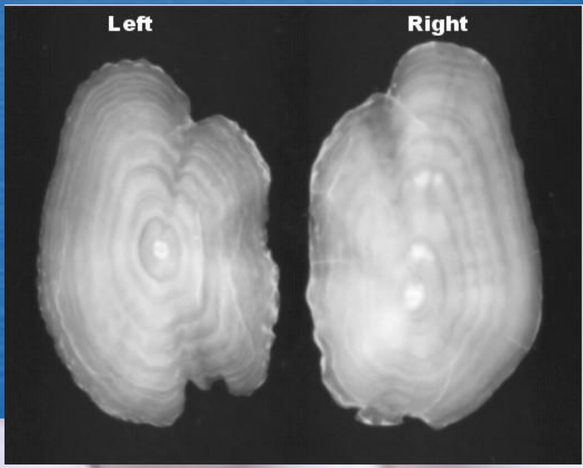
# Echinoderms -- urchins, stars

- Echinodermata: Echinoidea (urchins), Asteroidea (stars)
- *Evechinus*
- Mobile, consumers
- High-Mg calcite

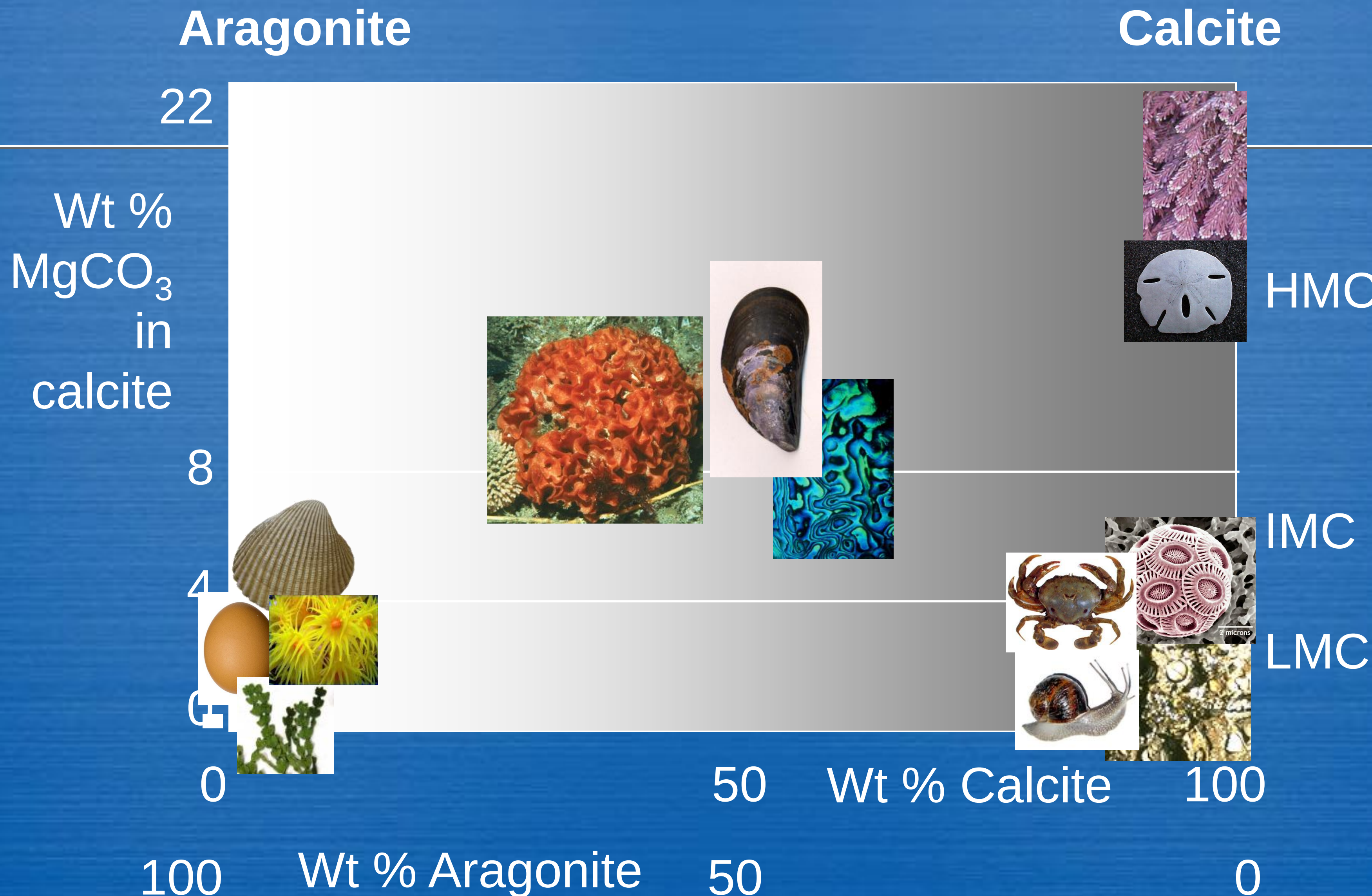
# Vertebrates

# Vertebrates -- bone, eggs

- Most bones are calcium phosphate (Dahllite or Francolite):
  $Ca_5(PO_4, CO_3)_3OH$
- Otoliths & Eggshells: $CaCO_3$




# Bio-Mineralogical Space




(Smith et al, 2006)

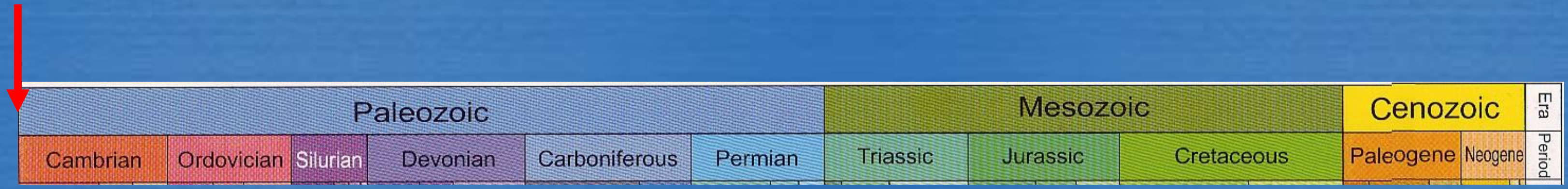
# Where?

- Shallow tropical environments are dominated by aragonite and high-Mg calcite
- In shallow temperate/polar environments, low-Mg calcite dominates
- Moderate deep waters -- calcite oozes
- Deep high-productivity ocean -- silicate

# When?

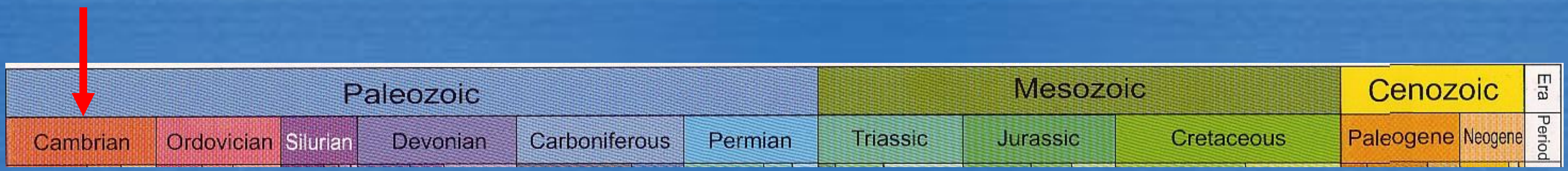
- 5 billion years ago -- Earth
- 2.7 Bya -- First biological precipitation in sulfides
- 1.6 Bya -- Encrusting bacteria produce Mn crusts
- 1 Bya -- metazoans (unmineralised fossils such as tracks, burrows)
- 1 Bya -- lightly calcified cyanobacteria

# Proterozoic - Phanerozoic



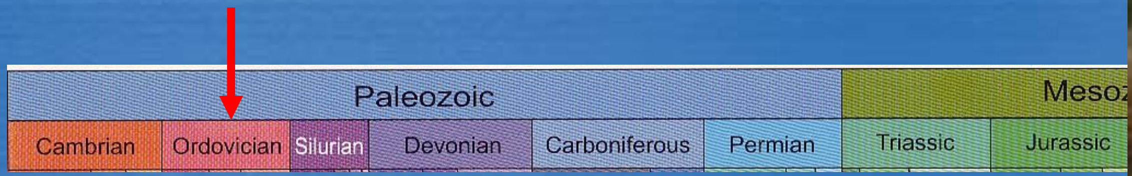

- Phanerozoic means "visible life."
- 570 Mya -- beginning of Cambrian Period
- A major extinction
- Onset of truly shelled organisms
  - Plants, animals, bacteria
  - Carbonates, phosphates, silicates

# Cambrian Period

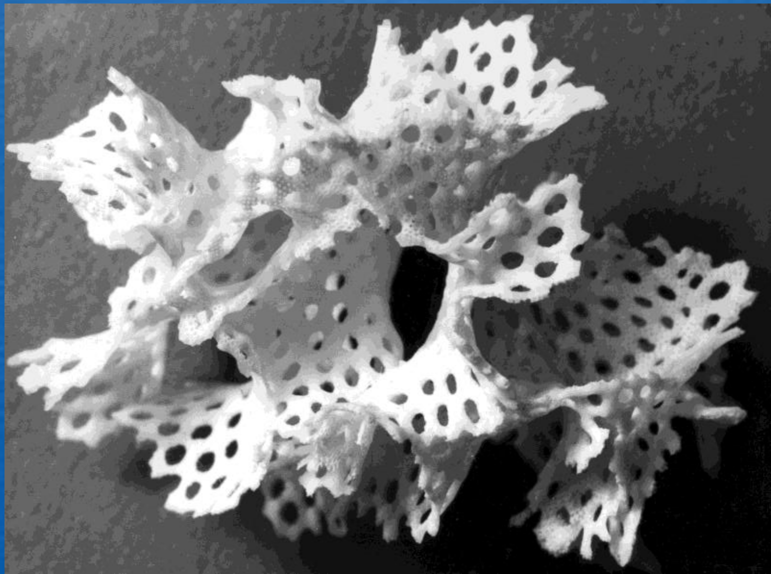



- 570 to 490 Mya
- "Problematica" experimenting with minerals and structures, most died out by end of Cambrian

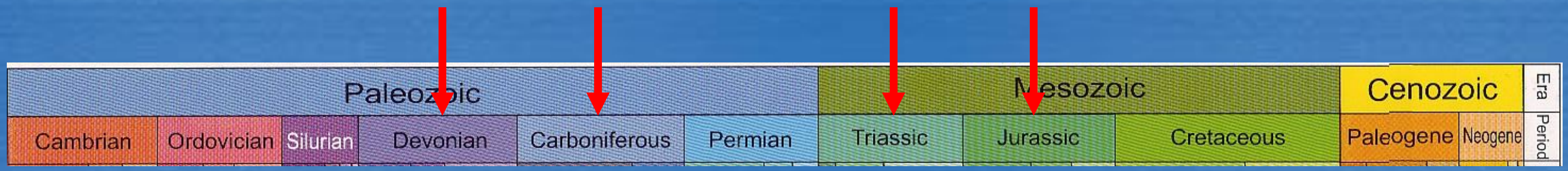
# Ordovician Period



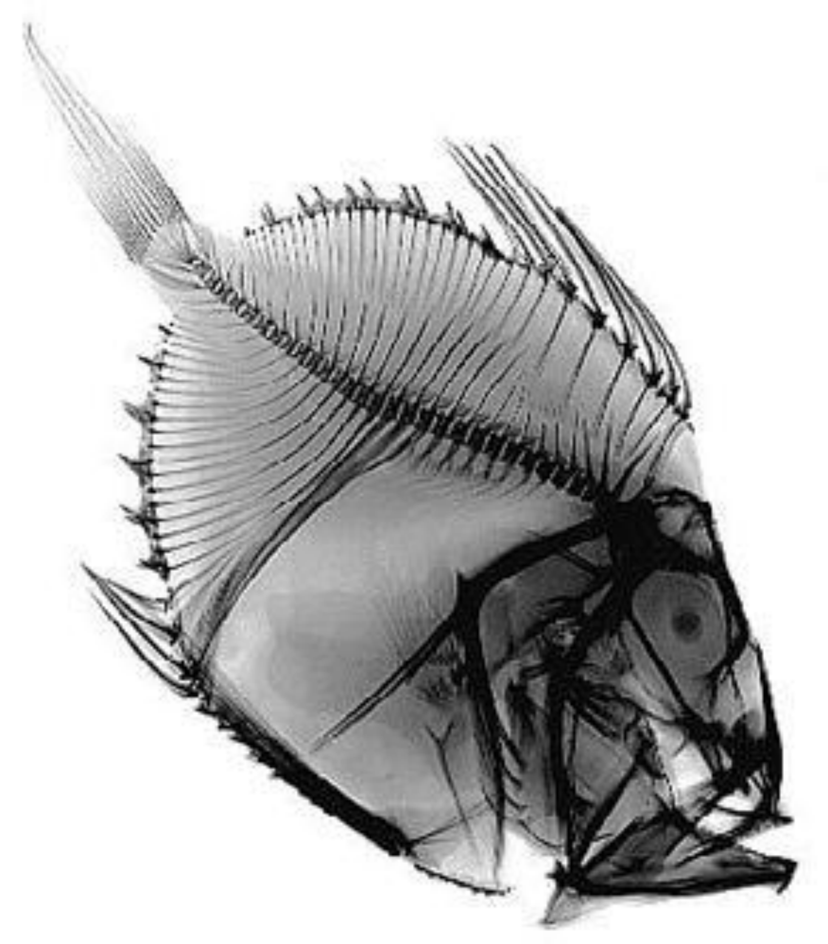

- 490 to 434 Mya
- Phosphatic minerals became limited to vertebrates
- Silicates precipitated by sponges, radiolarians
- By 434 Mya, all major mineralising taxa had arisen and were well-established.



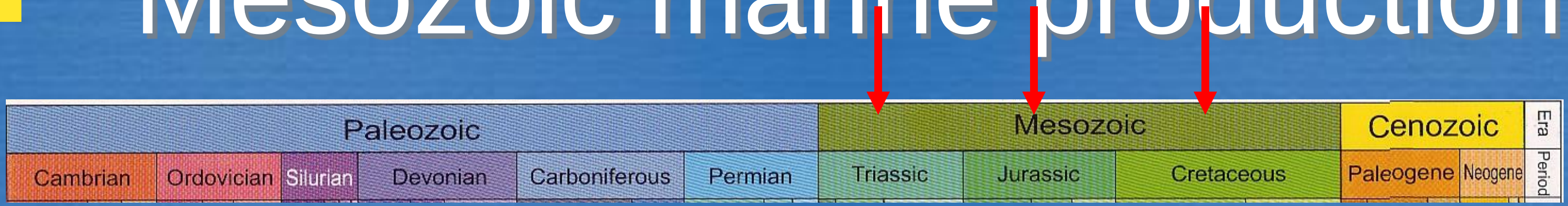
# Vertebrates and bone




- Devonian 395 Mya -- bony fish arise
- Carboniferous 285 Mya -- reptiles
- Triassic 200 Mya -- mammals on land
- Mid-Jurassic 170 Mya -- birds evolve last of the vertebrates



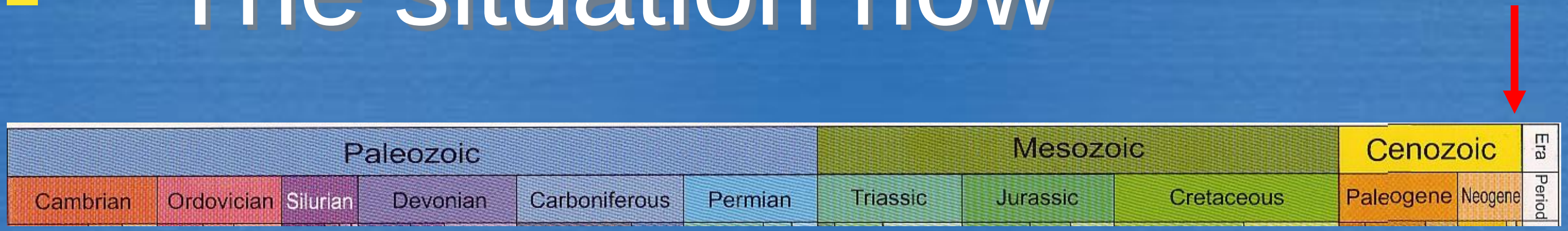
# Mesozoic marine production




- Triassic reef-building time 230 Mya
- Carbonate producers (forams, coccoliths) invaded the open ocean at about 195 Mya
- Silicate producers (radiolarians, diatoms) became important in the ocean in the Cretaceous

  (100 - 65 Mya)
- Mollusc reef-building

# The situation now




- Open ocean undersaturated with silica, much lower in calcite than before the Jurassic.
- Carbonate and silicate “stored” in solid form in sea floor sediments
- Huge and diverse aragonitic reefs in the tropics
- Large tracts of cool-water shelf gravels,
- But remember -- it hasn’t always been this way.

# How?

- Silicification and Calcification are complicated and poorly understood
- People want to know, though, because of the many medical uses to which such information could be put

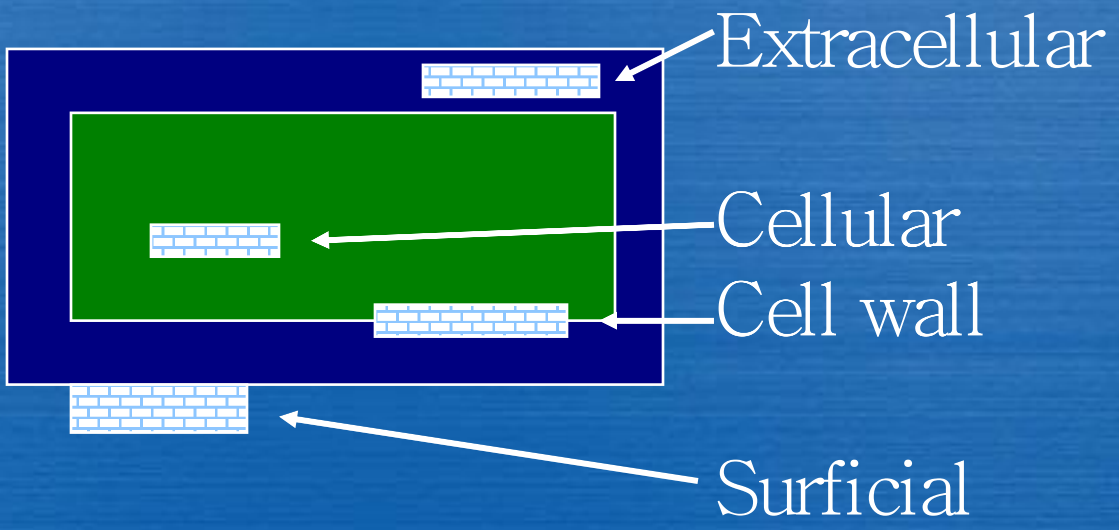
# Calcification

- $CO_2$ (gas) + $H_2O$ --> $CO_3^{=}$ + $2H^+$
- $CO_3^{=}$ + $2H^+$ + $Ca^{++}$ --> $CaCO_3$ + 2 $H^+$

- Does not require an organism -- if water is warm and supersaturated

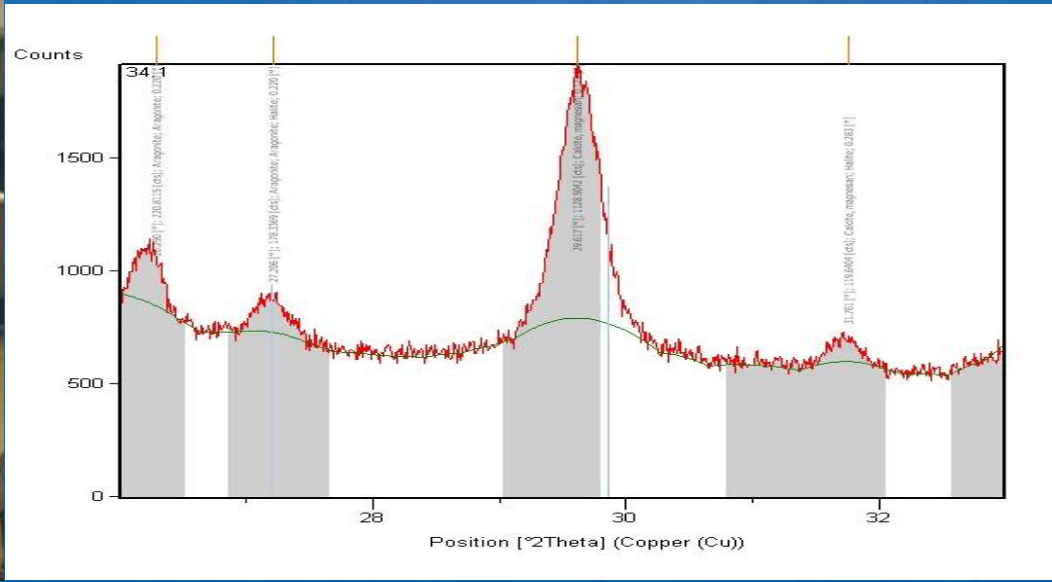
# Sites of Mineralisation

- Surficial, Extracellular, Cell wall, cellular



# How do we know?

- Staining, titration
- X-ray diffractometry
- Raman laser spectrometry

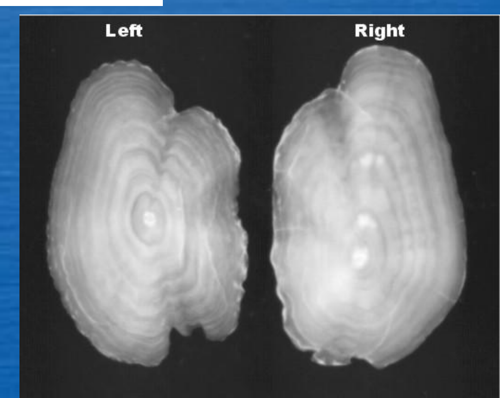


# Biomineralisation costs

- It takes up energy
- It makes you heavier, maybe slower
- It gets in the way of physiological functions

# Why Biomineralise?

- Protection
- Structural support, doors
- Food gathering
- Reproductive protection
- Navigation, Gravity reception
- Detoxification, mineral storage

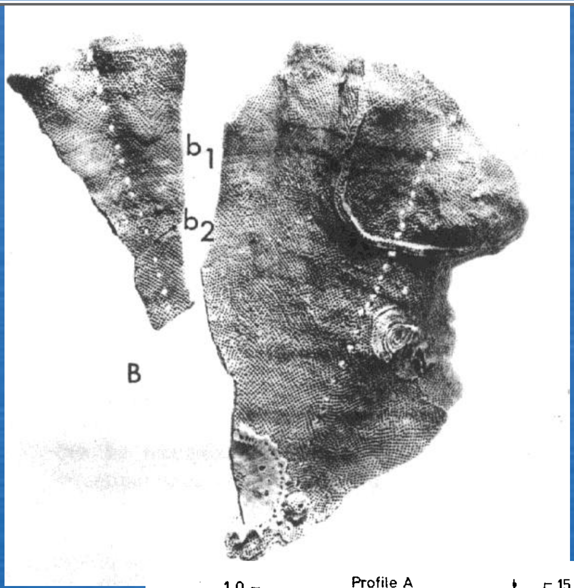


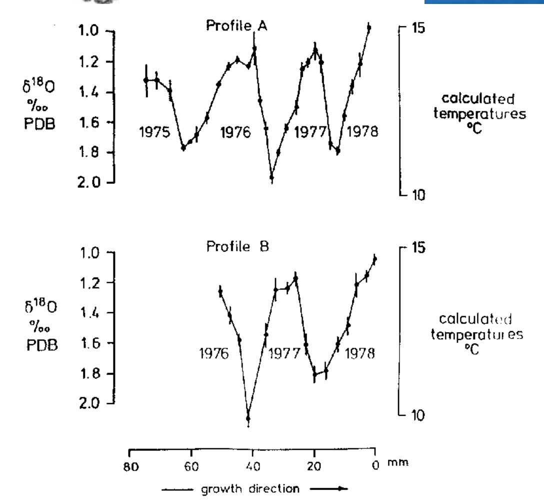
# So what?

- Biomineralisation produces shells
- Shells break down into sediment
- Sediments lithify into fossils, limestones, marble
- A permanent record

# A permanent record of what?

- Chemistry of sea water
- Marine sedimentation
- Storage of solid carbonate in the carbon cycle
- Biodiverse environments such as reefs
- Fossilisation, preservation
- Record of evolution over time



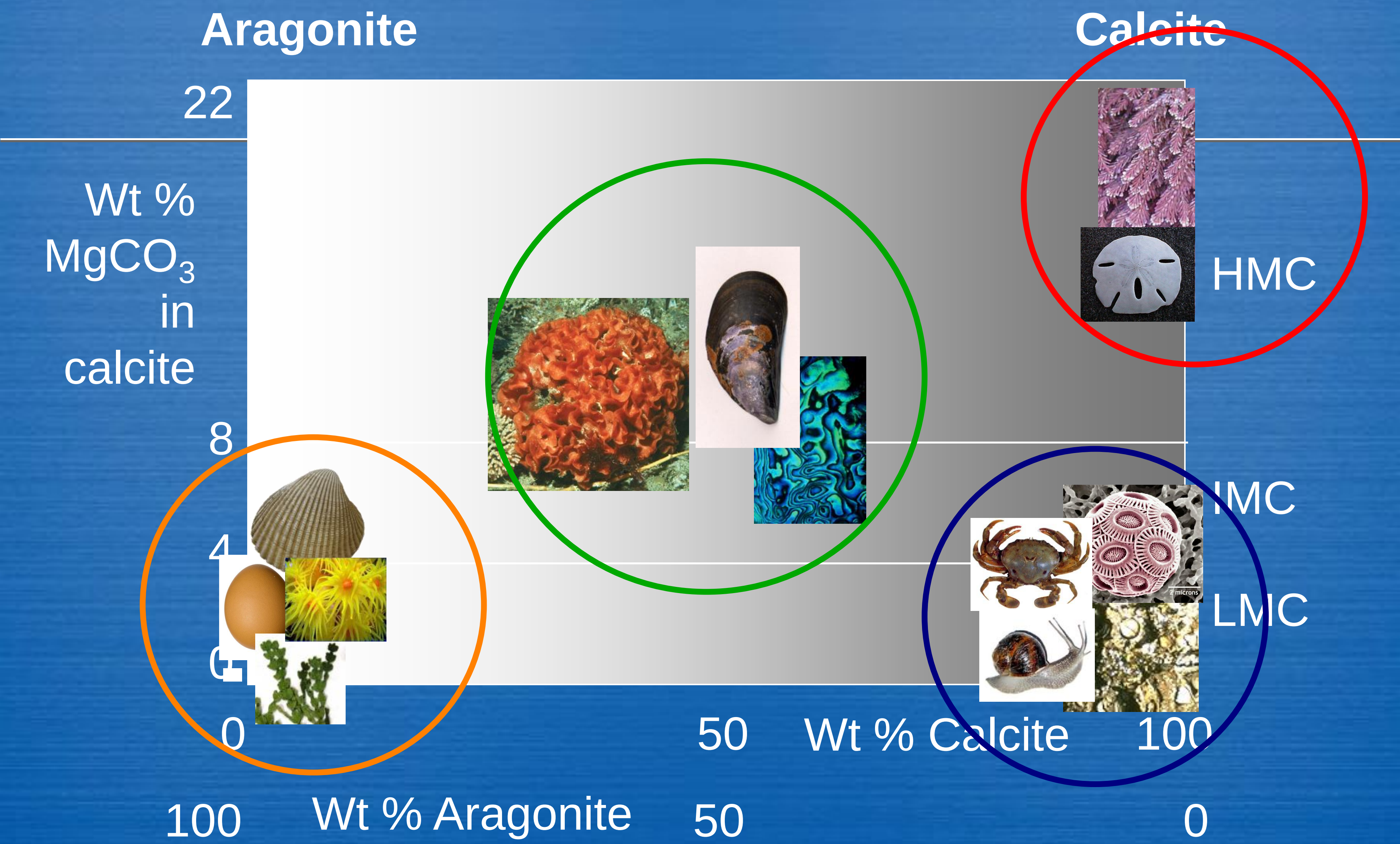
# Mineralogy and sea-water chemistry

- Aragonite is less stable than calcite
- High-Mg calcite is even less stable

- High-Mg calcite producers may be at greatest risk from acidification, especially in cool waters

(Andersson et al., 2008)

# Bio-Mineralogical Risk




(Smith et al, 2006)

# So who cares?

- Calcifying organisms
  - Life could get a lot harder for shell-formers
- Marine food chains & reef dwellers
  - If calcifying organisms are struggling, so will others who rely on them
- Us
  - Implications for fisheries, conservation, carbon cycle, marine geological history

# In Summary,

- Many different kinds of marine organisms make shells from many different biominerals
- $CaCO_3$ (calcite and aragonite) is the most common biomineral, and the most likely to be affected by ocean acidification
- Understanding the mineralogy of marine shells allows evaluation of risk