Biomineralization

- The processes by which organisms form minerals
  - The control by many organisms over mineral formation distinguishes these process from abiotic mineralization
- Until the 1980s the field was known as calcification reflecting the large number of biologically formed calcium-containing minerals

Calcium

- Calcium is the cation of choice for most organisms comprising 50% of known biominerals
  - Calcium phosphate, carbonate, oxalate and other mineral types
- 25 % of the minerals are non-crystalline
- 25 % of biogenic minerals are phosphates
- Calcium carbonates are the most abundant biogenic minerals

Calcium Carbonate

- Eight known polymorphs
  - Seven crystalline and one amorphous
  - Three are pure calcium carbonate; aragonite, calcite, and vaterite
  - Two contain one water molecule per calcite; monohydrocalcite and amorphous calcite
  - Calcium carbonate hexahydrate

Other Biominerals

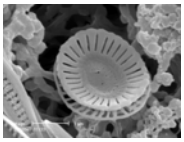
- Calcium phosphate
  - Bone
  - Teeth
- Celestite- Acantharians
- Barite- Loxedes
- Silica-Diatoms Radiolarians
- Iron Oxides-magnetic bacteria
  - Iron teeth-limpets and chitins

Uses

- Skeletons
- Gravity Sensors- otoliths
- Lenses- Trilobites
- Vaterite- Ascidians, some inner ears of fish, repair in molluscs
- Amorphous calcium carbonate-storage of Ca in plants

Biominerals

- Biominerals meet the criteria for being true minerals but they can possess other characteristics
  - Unusual external morphologies; how do organisms do this
  - Actually composites of crystals separated by organic material



Saturation

- In order for a mineral to form, the product of the activity of the elements in the solution must exceed the thermodynamic solubility

$$IAP = \alpha Ca \,.\, \alpha CO_3^{2-} > Ksp$$

$$\alpha = \gamma m$$

γ = activity coefficient

Definitions

$$SI = IAP/Ksp$$

If SI =1 Solution is at saturation
Seawater is ~ 4 with respect to aragonite

Seawater

- Seawater
  - Ca 410 ppm 10 mM
  - CO_3^{2-} 12 ppm 0.2 mM
  - Mg 1200 ppm 55 mM

Ksp (aragonite) $= 10^{-8.301}$
Ksp (calcite) $=10^{-8.481}$
Ksp (HMC) $=10^{(-8.21 \text{ to } -7.43)}$

Why aragonite not calcite?

- Organisms which calcify internally and externally
  - Internal calcifiers tend to secrete calcite
  - External calcifiers tend to secrete aragonite
- Freshwater water environments do not secrete aragonite but rather calcite
- The mineralogy or inorganic cements and of different groups has changed through time

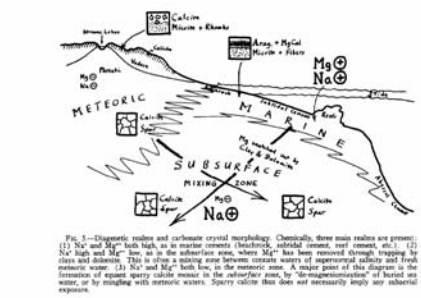
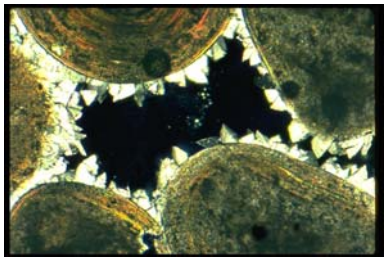
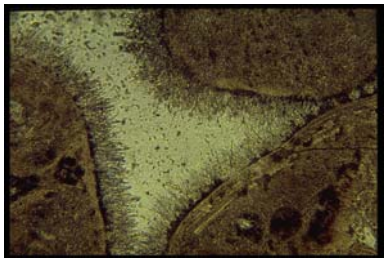


Fig. 5—Diagenetic realms and carbonate crystal morphology. Chemically, three main realms are present: (1) Na^+ and Mg^{++} both high, as in marine cements (beachrock, subtidal cement, reef cement, etc.). (2) Na^+ high and Mg^{++} low, as in the subsurface zone, where Mg^{++} has been removed through trapping by clays and dolomite. This is often a mixing zone between connate waters of supercrustal salinity and fresh meteoric water. (3) Na^+ and Mg^{++} both low, in the meteoric zone. A major point of this diagram is the formation of equant sparry calcite mosaic in the *subsurface* zone, by "de-magnesiumization" of buried sea water, or by mingling with meteoric waters. Sparry calcite thus does *not* necessarily imply any subaerial exposure.

Folk 1974





Why aragonite?

- Has to do with the Mg/Ca ratio; present day the molar ratio is 5:1
- Several hypotheses
  - The high Mg favors the formation of HMC which is actually more soluble than aragonite
  - Mg poisons the side ward growth of crystals forming the acicular habit
  - Calcite growth is prevented by the obstructive presence of hydrated Mg ions

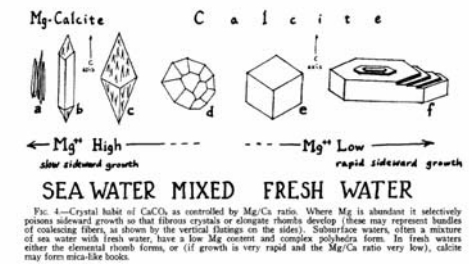
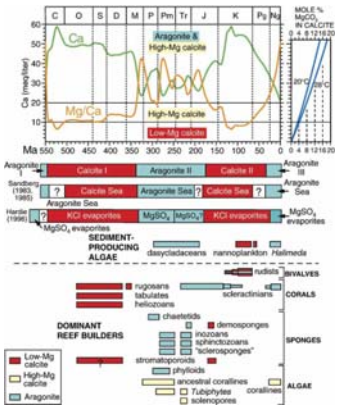
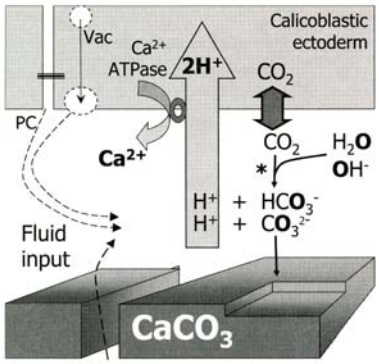


FIG. 4.—Crystal habit of $CaCO_3$ as controlled by Mg/Ca ratio. Where Mg is abundant it selectively poisons sideward growth so that fibrous crystals or elongate rhombs develop (these may represent bundles of coalescing fibers, as shown by the vertical flutings on the sides). Subsurface waters, often a mixture of sea water with fresh water, have a low Mg content and complex polyhedra form. In fresh waters either the elemental rhomb forms, or (if growth is very rapid and the Mg/Ca ratio very low), calcite may form mica-like books.





Cohen and McConnaughey (2005)

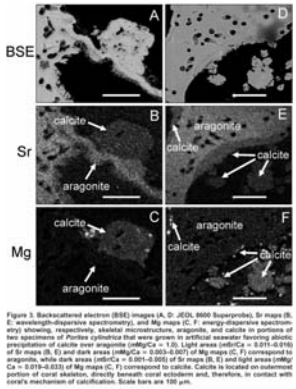


Figure 3. Backscattered electron (BSE) images (A, D: JEOL 8600 Superprobe), Sr maps (B, E; wavelength-dispersive spectrometry), and Mg maps (C, F; energy-dispersive spectrometry) showing, respectively, skeletal microstructure, aragonite, and calcite in portions of two specimens of *Porites cylindrica* that were grown in artificial seawater favoring abiotic precipitation of calcite over aragonite (mMg/Ca = 1.0). Light areas (mSr/Ca = 0.011–0.016) of Sr maps (B, E) and dark areas (mMg/Ca = 0.003–0.007) of Mg maps (C, F) correspond to aragonite, while dark areas (mSr/Ca = 0.001–0.005) of Sr maps (B, E) and light areas (mMg/Ca = 0.019–0.033) of Mg maps (C, F) correspond to calcite. Calcite is located on outermost portion of coral skeleton, directly beneath coral ectoderm and, therefore, in contact with coral's mechanism of calcification. Scale bars are 100 μm.

Suggested Titles

- The Geological Record of Biomineralization
- Models of Biomineralization
  - Coelenterates
  - Molluscs
  - Foraminifera
  - Procaryotes
  - Other
- Trace Elements
- Stable Isotopes

References

- Biogeochemical cycling of mineral-froming elements, Trudinger and Swaine, Elsevier,1979
- Biomineralization, Dove, De Yoreo, Weiner, MSA, 2003
- Biomineralization