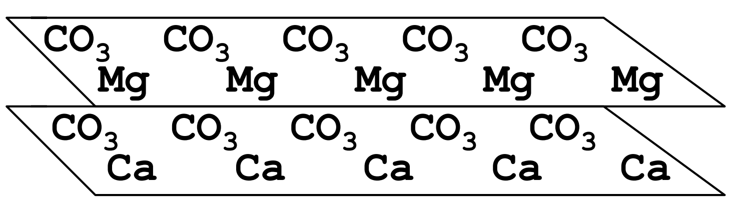
CARBONATE MINERALS

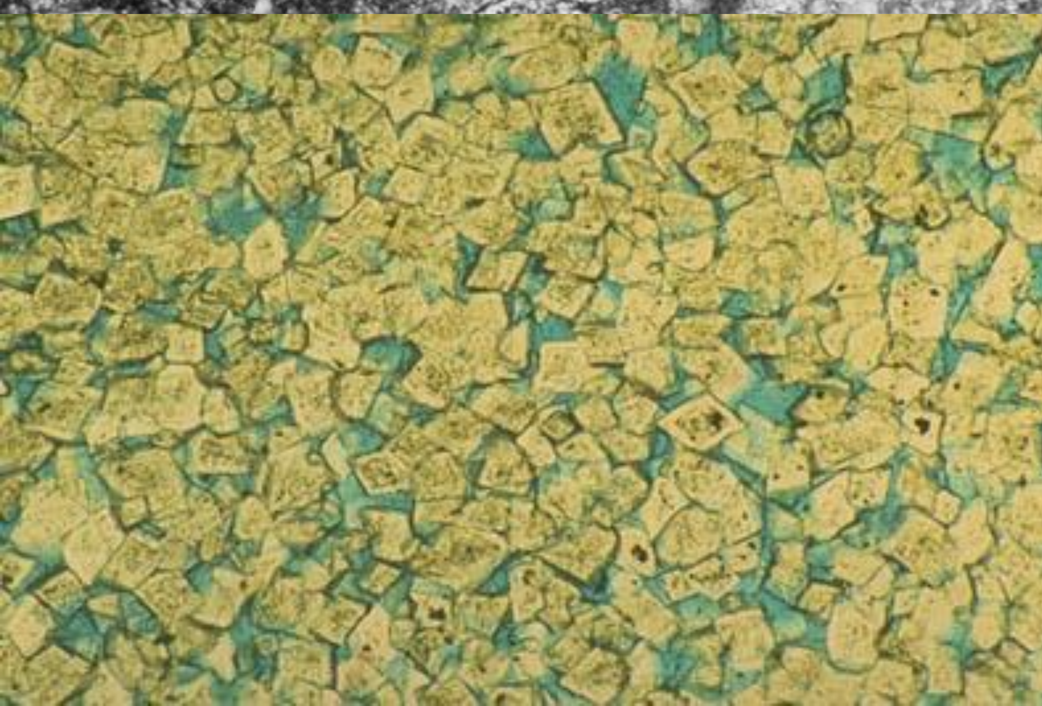
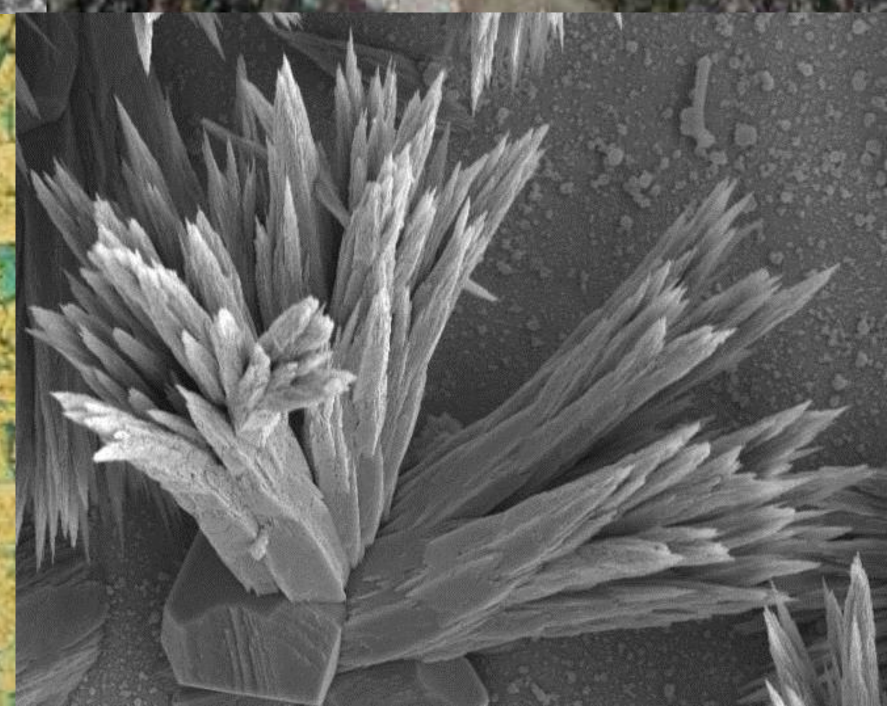
Name	Formula	Lattice
Calcite	$CaCO_3$	Rhombohedral
Aragonite	$CaCO_3$	Orthorhombic
Dolomite	$CaMg(CO_3)_2$	Rhombohedral

-Mg, Fe, & Sr are commonly substituted into crystal lattices for all these

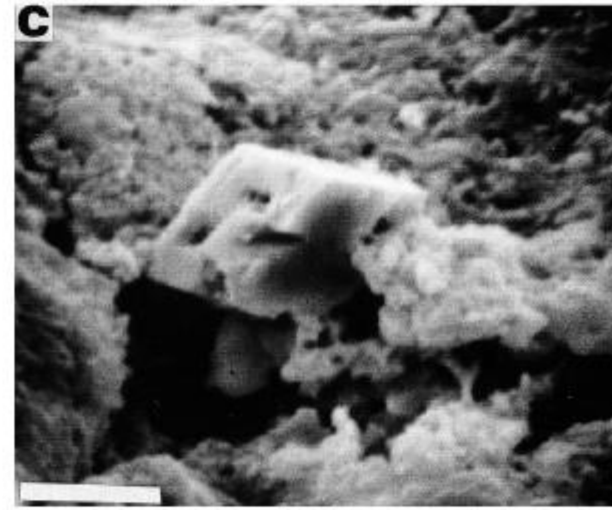
-Dolomite has alternating layers of calcite $CaCO_3$ and magnesite $MgCO_3$





Dolomite $CaMg(CO_3)_2$



Ordered / Unordered

Alternating cationic layers
vs.
Random cationic distribution

Stoichiometric / Non-stoichiometric

1:1 Ca:Mg Ratio
vs.
Substantial cationic substitution
(sometimes called Calcian Dolomite)

Primary / Secondary

Precipitation from open waters vs. Diagenesis

CARBONATE MINERALS

- **Modern Carbonates**
  - Mostly primary metastable marine minerals
  - Aragonite
  - High-Mg Calcite (HMC)
    - 5-18 mole% $MgCO_3$

- **Ancient Carbonates**
  - Mostly secondary minerals
  - Low-Mg Calcite (LMC) $CaCO_3$
  - Dolomite $CaMg(CO_3)_2$

Carbonate (Bio)Chemistry

Calcite dissolves in pH neutral water

$$CaCO_3 \quad == \quad Ca^{++} + CO_3^{--}$$

Solubility of Carbonate minerals is determined empirically

K_{sp} ≡ ***Solubility product constant*** = product of concentrations of both ions in solution ***in equilibrium*** with a solid

$IAP = [Ca^{++}]\,[CO_3^{--}]$ ***Ion Activity Product***

$K_{sp} > IAP$ undersaturated, will dissolve

$K_{sp} = IAP$ saturated, in equilibrium

$K_{sp} < IAP$ supersaturated, will precipitate

Carbonate (Bio)Chemistry

Oceanic *IAP*

Calcite	$K_{cal} = 10^{-8.35}$	$[Ca^{++}][CO_3^{--}] = 10^{-7.2}$
Aragonite	$K_{arag} = 10^{-8.22}$	
Dolomite	$K_{dol} = 10^{-17}$	$[Ca^{++}][Mg^{++}][CO_3^{--}]^2 = 10^{-13.9}$

Why do average ocean waters appear supersaturated with respect to carbonates?

IAP **depends on all the other ions in solution**

K_{sp} **depends on temperature, pressure, pH**

Precipitation from solution takes time and rates of precipitation are slow

Carbonate (Bio)Chemistry

-Carbon Dioxide from the atmosphere forms carbonic acid in water

Water + carbon dioxide yields carbonic acid

$$H_2O + CO_2 \quad == \quad H_2CO_3$$

-Carbonic acid in water will dissolve carbonates

Calcium carbonate + carbonic acid yields Calcium + 2 bicarbonate

$$CaCO_3 + H_2CO_3 \quad == \quad Ca^{++} + 2HCO_3^-$$

-so will most any other acid depending on pH

Calcium carbonate + acid yields Calcium + bicarbonate

$$CaCO_3 + H^+ \quad == \quad Ca^{++} + HCO_3^-$$

-Chemical equilibrium reaction can proceed in *either* direction

forward (right), dissolution of calcium carbonate

reverse (left), precipitation of calcium carbonate

Carbonate (Bio)Chemistry

Disturbances to equilibrium are met by "reversing" nature of disturbance-

Physical factors affecting equilibrium

- **-pCO_2**
  - **any process that $\uparrow$ pCO_2 promotes carbonate dissolution**
  - **any process that $\downarrow$ pCO_2 promotes carbonate precipitation**

$$H_2O + CO_2 == H_2CO_3$$

$$\Updownarrow$$

$$CaCO_3 + H_2CO_3 == Ca^{++} + 2HCO_3^{-}$$

Carbonate (Bio)Chemistry

Disturbances to equilibrium are met by "reversing" nature of disturbance-

Physical factors affecting equilibrium

-pH

any process that ↑ pH promotes carbonate precipitation

any process that ↓ pH promotes carbonate dissolution

$$CaCO_3 + H^+ \quad == \quad Ca^{++} + HCO_3^-$$

$$\updownarrow$$

$$-\log[H^+] = pH$$

Carbonate (Bio)Chemistry

Disturbances to equilibrium are met by "reversing" nature of disturbance-

Physical factors affecting equilibrium

-Pressure

any process that ↑ pressure promotes carbonate dissolution

any process that ↓ pressure promotes carbonate precipitation

This is a very weak affect that is much more important to metamorphism than to sediments

Carbonate (Bio)Chemistry

Disturbances to equilibrium are met by "reversing" nature of disturbance-

Physical factors affecting equilibrium

-Temperature

any process that ↑ temperature promotes carbonate dissolution

any process that ↓ temperature promotes carbonate precipitation

...but this requires all else to be *constant*

In nature, other factors are more dependent on Temperature than K_{sp}

Most important- cold water holds more carbon dioxide than warm water

cold water can therefore also dissolve more carbonate than warm

Warming == precipitating

Cooling == dissolving

$$CaCO_3 + H_2O + CO_2 == Ca^{++} + 2HCO_3^-$$

K_{cal} increases with increasing temperature

forward reaction = dissolution

pCO_2 decreases with increasing temperature

reverse reaction = precipitation

-On Earth's surface, temperature has a stronger effect on pCO_2 than on K_{cal} ...the net result is

warming == precipitating

cooling == dissolving

Carbonate (Bio)Chemistry

Disturbances to equilibrium are met by "reversing" nature of disturbance-

Biological factors affecting equilibrium

-Photosynthesis

uses carbon dioxide and removes it from the water

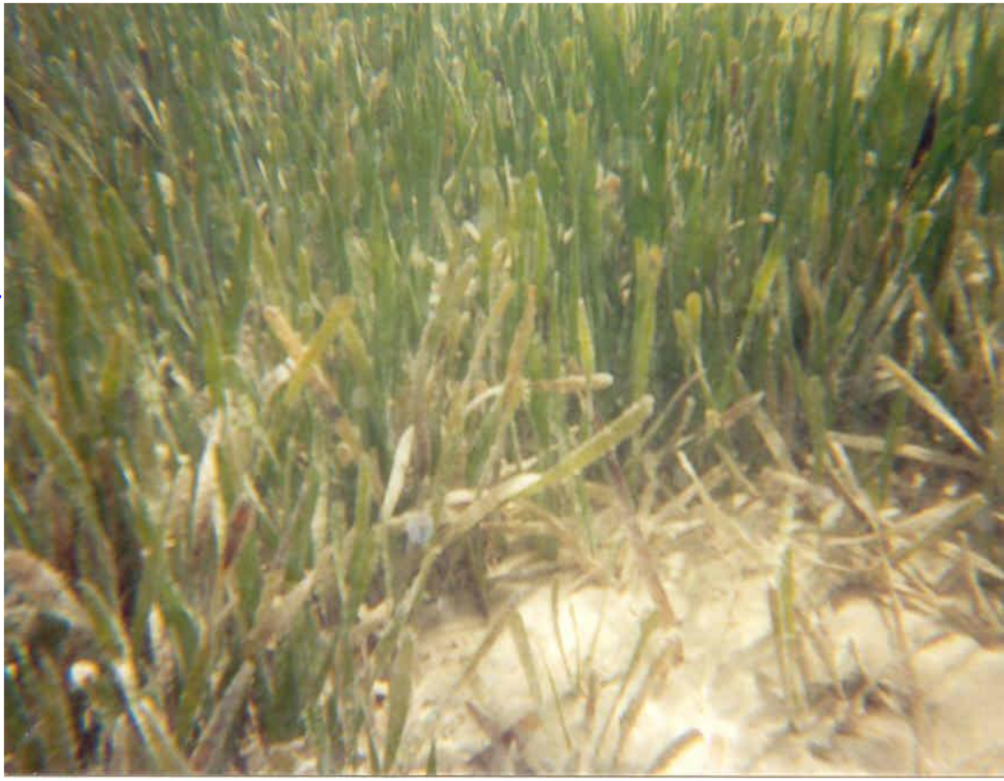
promotes carbonate precipitation

-Respiration (or death & decay)

releases carbon dioxide

adding it back into the water

promotes carbonate dissolution



Growing →

$$H_2O + CO_2 == CH_2O + O_2$$

← **Decaying**

Modes of Carbonate Precipitation

- **Abiotic – Precipitates where biotic effects are negligible**
- **Biotically Induced – Precipitates where the organism sets the process in motion, but where organismal influence ceases after the initial step**
- **Biotically Controlled – Precipitates where the organism determines the location, beginning and & of the process. Key in carbonates!**

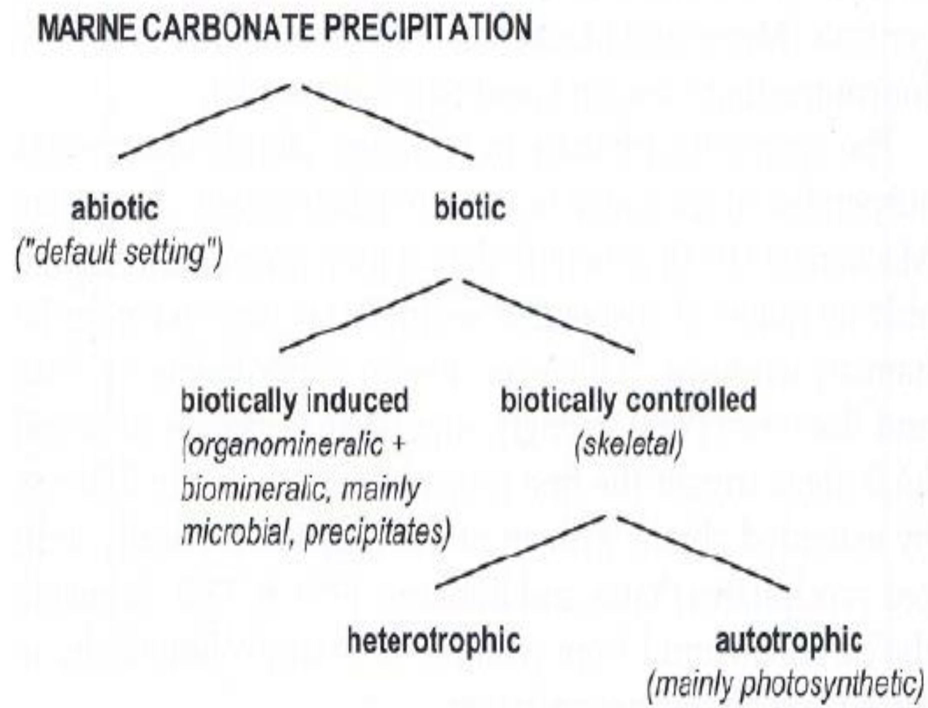


Fig. 2.1.– Pathways of carbonate precipitation in aquatic environments – a cascade of options governed by the degree of biotic influence. After Schlager (2000), modified.