Innovative Technologies and Sustainable Use of Mediterranean Sea Fishery and Biological Resources (FishMed-PhD)

Teaching week 2025

Crystallization in biomineralization and in the environment

2. Calcium Carbonates

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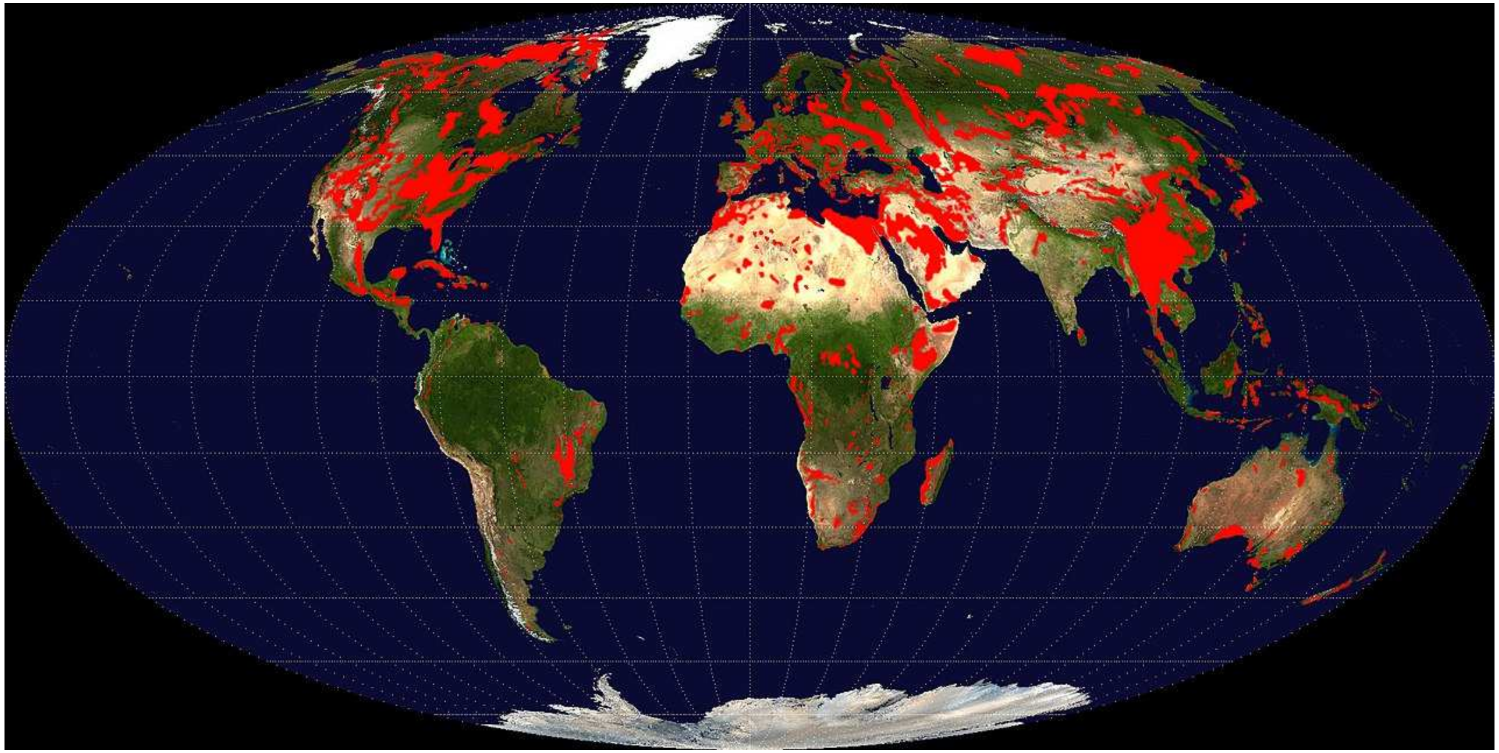
Calcium carbonate: ordinary mineral

… $CaCO_3$ is one of the most abundant mineral ...

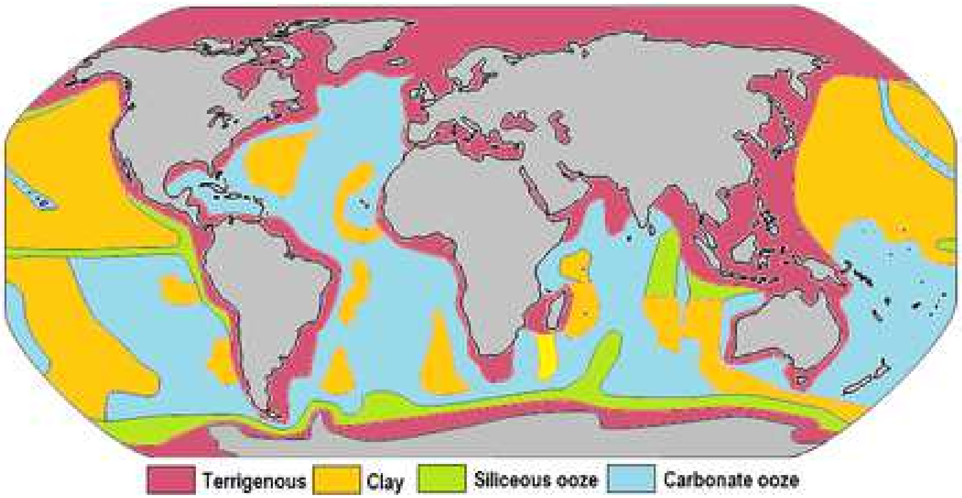
4% Earth crust, 20% sedimentary rocks – chalk, limestone, tufa, travertine ...



Global distribution of limestone

https://en.wikipedia.org/wiki/Karst

25% seafloor sediment – containing more than 30% $CaCO_3$



http://en.wikipedia.org/wiki/

Geological $CaCO_3$

Karst / limestone

Tufa

Travertine

Chalk

Stalactite, stalagmite

Biominerals

Limescale

Properties	
Molecular formula	$CaCO_3$
Exact mass	100.0869 g/mol
Appearance	Fine white powder
Density	2.71 g/cm^3 (calcite) 2.83 g/cm^3 (aragonite) ?????
Melting point	825 °C (aragonite) 1339 °C (calcite)
Boiling point	decomposes
Solubility in water	0.00015 mol/L (25°C)
Solubility product, K_{sp}	4.810^{-9} ?????
Solubility in dilute acids	soluble
Acidity (pK_a)	9.0
Refractive index (n_D)	1.59
Structure	
Crystal structure	Trigonal
Space group	2/m

http://en.wikipedia.org/wiki/Calcium_carbonate)

Calcite – Iceland spar

aragonite

marble

travertine, tufa

Calcium Carbonate Phases at Environmental Conditions

POLYMORPHS

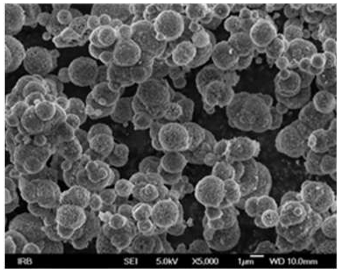
Vaterite	$CaCO_3$
Aragonite	$CaCO_3$
Calcite	$CaCO_3$

HYDRATES

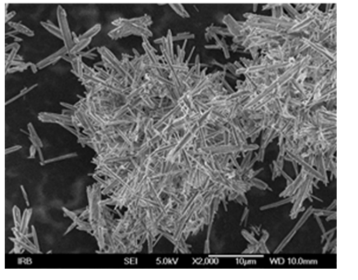
Calcium Carbonate Hexahydrate (Ikaite)	$CaCO_3 \cdot 6H_2O$
Calcium Carbonate Monohydrate	$CaCO_3 \cdot H_2O$

AMORPHOUS

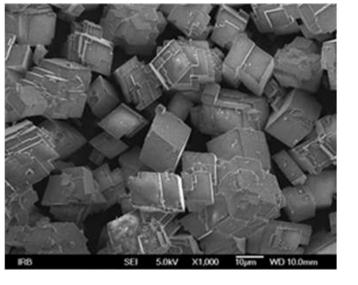
Amorphous Calcium Carbonate	$CaCO_3 \cdot nH_2O$



vaterite



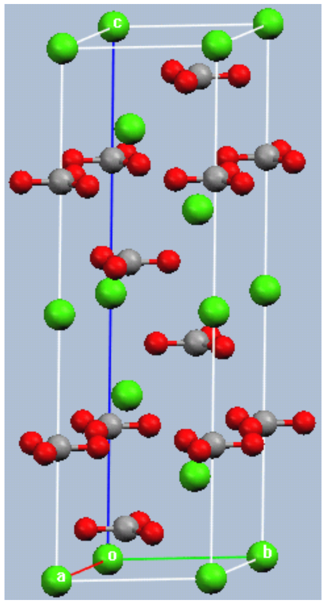
aragonite

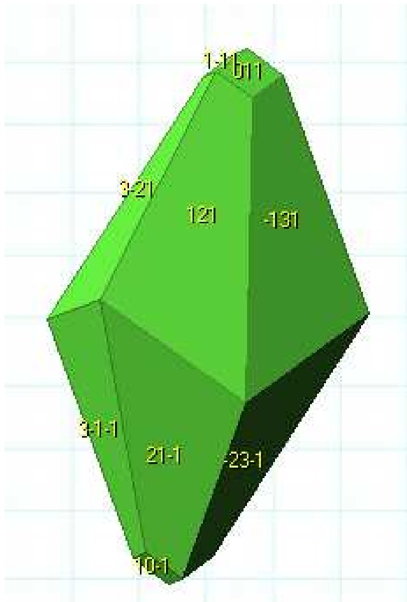


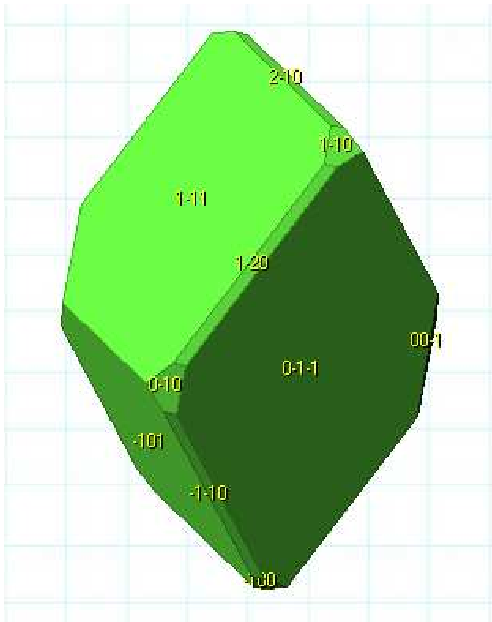
calcite

Calcite

Most stable polymorph
Wide spread mineral (≈ 4 % Earth crust)
Formation during different periods of Earth history
More than 800 crystal forms
Trigonal crystal system, hexagonal lattice system, Ca coordinated with 6 CO_3^{2-}
Unit cell: a = 4.9896(2) Å, c = 17.0610(11) Å;







http://en.wikipedia.org/wiki/Calcium_carbonate)

Typical crystal habit

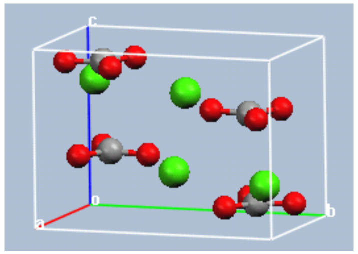
scalenohedral

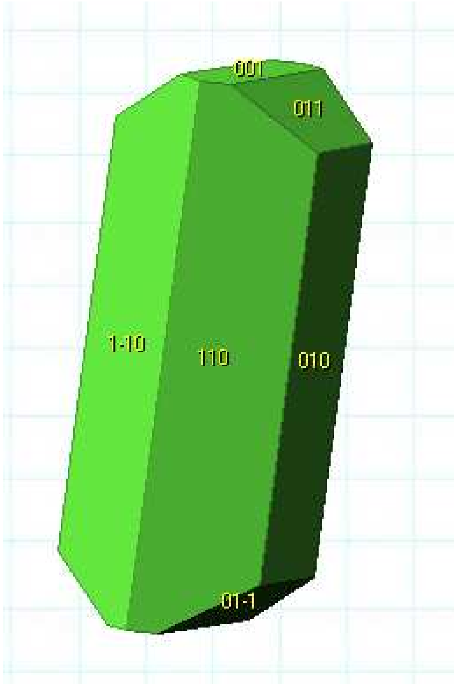
microcrystalline aggregate

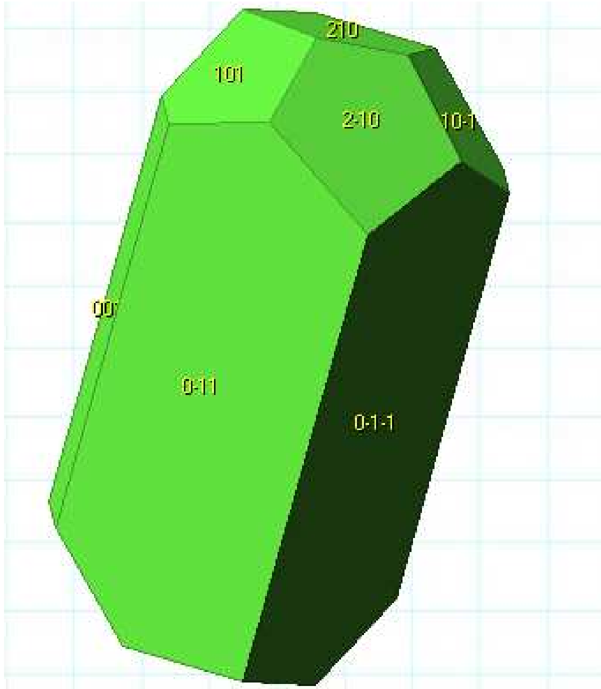
rhombohedral

Aragonite

Less stable modification (high pressure, high temperature modification)
Formation in presence of Mg^{2+}
Slow transformation of geological deposits to calcite (10 to 100 M years)
Important biomineral – corals, mollusk shell (nacreous layer or entire) ...
Orthorhombic crystal system, dipyramidal crystal class, Ca coordinated with 9 CO_3^{2-}
Unit cell: a = 4.95 Å, b = 7.96 Å, c = 5.74 Å;







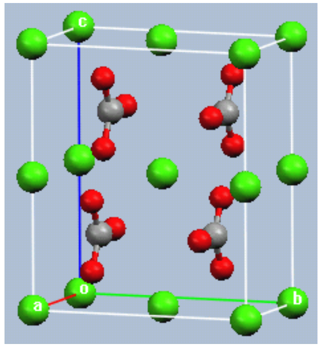
http://en.wikipedia.org/wiki/Calcium_carbonate)

Typical crystal habit

Prismatic, acicular, columnar, globular

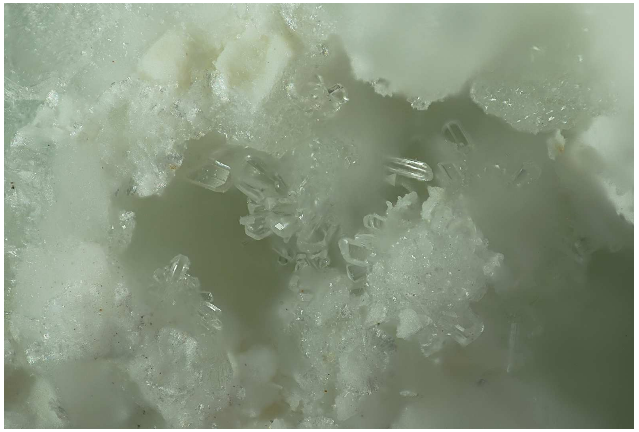
Vaterite

Least stable $CaCO_3$ polymorph
Uncommon in nature (fast transformation in aqueous environment)
Stabilized by organic macromolecules – biomineralization (fish otoliths), pathological mineralization (gallstone)
Hexagonal crystal system; dihexagonal dipyramidal crystal class, Ca coordinated with 8 CO_3^{2-}
Unit cell: a = 4.13 Å, c = 8.49 Å



http://en.wikipedia.org/wiki/Calcium_carbonate)

Typical crystal habit



Calcium carbonate: "Extraordinary mineral" ??

(*Do you know that...)*

… the highest man-made structure is made of calcium carbonate (limestone)

Great pyramid (Pyramid of Khufu) (2550 – 2500 p.n.e)

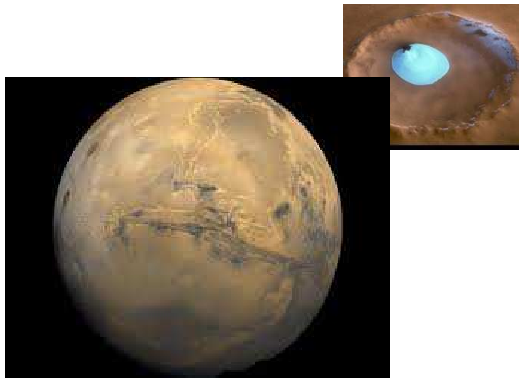
Tura - the finest and whitest limestone of all Egyptian quarries

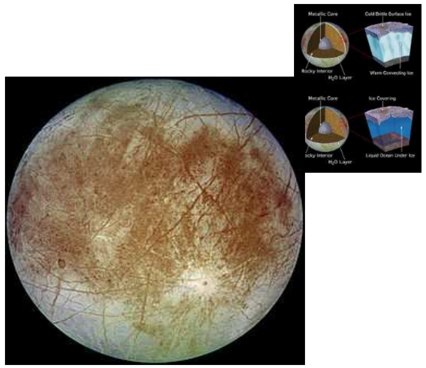
… the calcium carbonate is found only on Earth…

Formation only in aqueous solution:

$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrows CaCO_3\,(s)$

What about Mars, Europa, ... ??





$CaCO_3$ - search for extraterrestrial life

SNC (Martian) meteorites (**S**hergottites, **N**akhlites, **C**hassignites)

Elemental and isotopic compositions similar to Mars' rocks and atmosphere

Shergotty meteorite

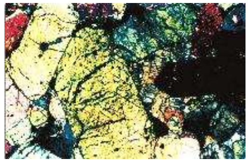
Shergotty, Bihar, India (1865)

Nakhla meteorite

Nakhla, Aleksandria, Egipat (1911)

Chassigny meteorite

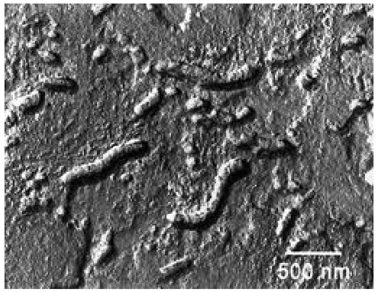
Chassigny, Francuska (1815)

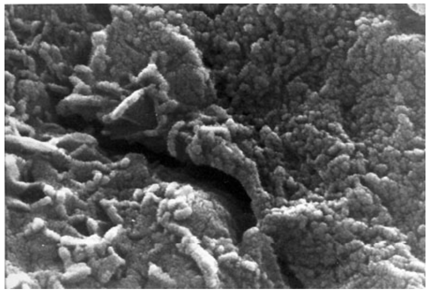


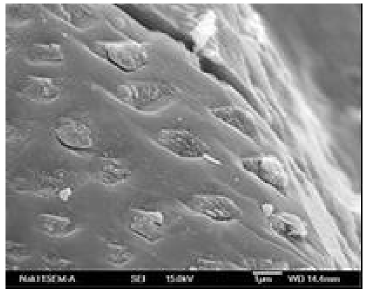
http://en.wikipedia.org/wiki/

ALH 84001 meteorite

Allan Hills, Antarctica (1984)







David S. McKay et al.: Search for Past Life on Mars: Possible Relic Biogenic Activity in Martian Meteorite ALH84001

Science, 1996, Vol. 273 no. 5277 pp. 924-930

Calcium carbonate in seawater and oceans

Origin of seawater and oceans

Water: Volcanoes – degassing from molten rocks (and/ or comets)

Minerals

Majority of minerals	→	rainfall washout of the ground (continental weathering)
Na^+	→	additionally leached out from ocean floor
Cl^-, SO_4^{2-} HCO_3^-, ...	→	outgassing from Earth interior (volcanos, hydrothermal vents)
Salinity	→	stable during the Earth's history
Ca^{2+}/ Mg^{2+}	→	variable during the Earth's history

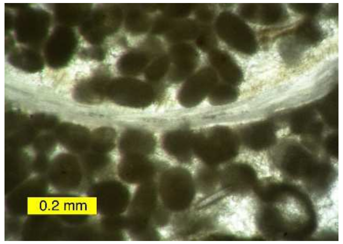
http://en.wikipedia.org/wiki/

$CaCO_3$ precipitation - inorganic

Dominant during the early time of Earth history (Precambrian) (+ microorganisms - stromatolites)

Modern seawater - supersaturated with respect to $CaCO_3$

Ooids, peloids



$CaCO_3$ precipitation – biological

Dominant during the Phanerozoic (last 540 million years of the Earth's history)

Mineralogical composition

- Low-magnesium calcite (brachiopods, planktonic foraminifera, coccoliths)
- High-magnesium calcite (benthic foraminifera, echinoderms, coralline algae)
- Aragonite (mollusks, calcareous green algae, stromatoporoids (sponges), **corals,** tube worms)

http://en.wikipedia.org/wiki/

$CaCO_3$ precipitation during the Earth's history

Calcite sea

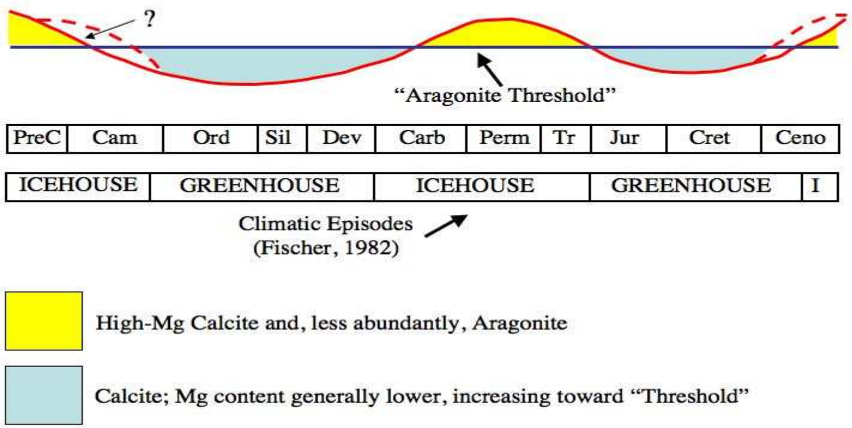
Low magnesium calcite dominant inorganic $CaCO_3$ precipitate

Formation of carbonate hardground, calcitic ooids, calcite cements, dissolution of aragonite shell

Aragonite sea

Aragonite and high-magnesium calcite dominant inorganic $CaCO_3$ precipitate

High magnesium content in seawater



After Sandberg (1983)

Why calcite sea ?

Rapid seafloor spreading at mid-ocean ridges

Seawater cycling through hydrothermal vents

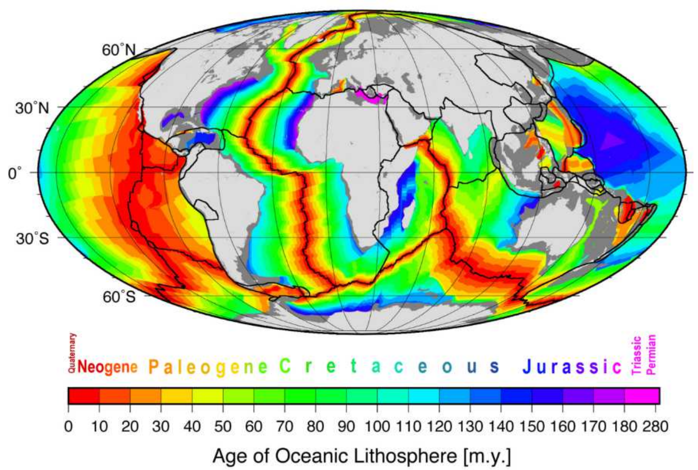
Reduction of Mg by metamorphosis:

(Ca-rich minerals → Mg-rich basalt or clays (hydrothermal alteration)

Low Mg content → Favors calcite precipitation

Global greenhouse conditions

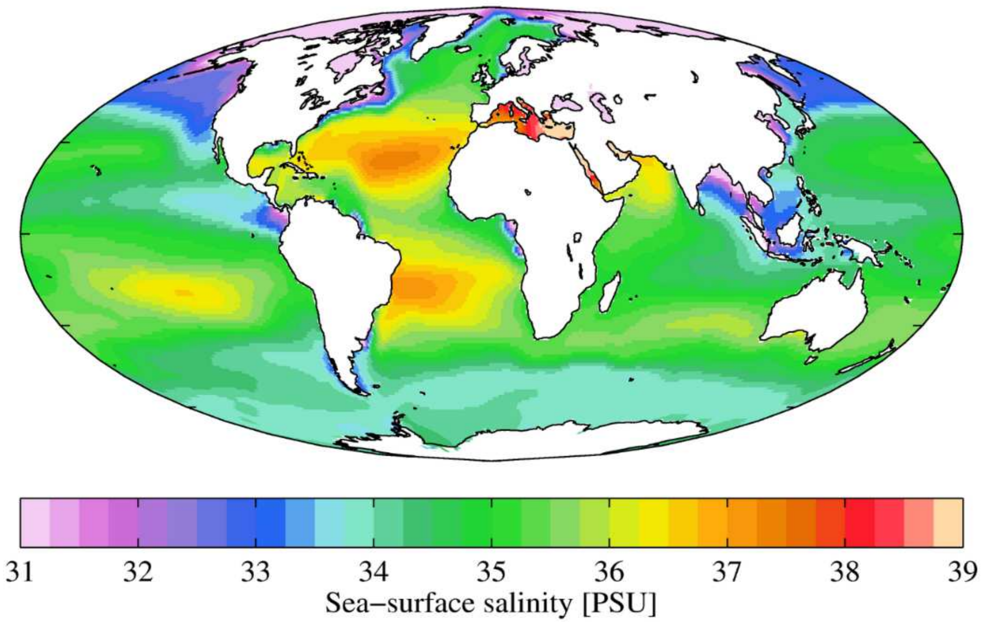
Volcanism → High CO_2 content → Favors calcite precipitation



http://en.wikipedia.org/wiki/

Composition of modern (aragonitic!) seawater

Salinity = quantity of dissolved salts in water



pH = 7.5 - 8.4

http://en.wikipedia.org/wiki/

Chemical composition (average)

(35 ‰ salinity)

Component	Concentration (mol/kg)
Cl^{-}	**0.546**
Na^{+}	**0.469**
Mg^{2+}	**0.0528**
SO_4^{2-}	**0.0282**
Ca^{2+}	**0.0103**
K^{+}	**0.0102**
HCO_3^{-}	**0.00206**
Br^{-}	0.000844
$B(OH)_3$	0.000416
Sr^{2+}	0.000091
F^{-}	0.000068

Seawater as $CaCO_3$ precipitation system

Relevant ionic species

H^+, OH^-, **Ca^{2+}**, $CaCO_3^0$, $CaHCO_3^+$, $CaCl^+$, $CaSO_4^0$, $H_2CO_3^*$, HCO_3^-, **CO_3^{2-}**,
Mg^{2+}, $MgCO_3^0$, $MgHCO_3^+$, $MgSO_4^0$, SO_4^{2-}, Cl^-, NO_3^-, Na^+, $NaCO_3^-$, K^+

Mass balances

$$[\mathbf{Ca}]_{\mathbf{tot}} = [Ca^{2+}]+[CaCO_3^0]+[CaHCO_3^+]+[CaSO_4^0]+[CaCl^+]$$

$$[\mathbf{CO_3}]_{\mathbf{tot}} = [H_2CO_3^*]+[HCO_3^-]+[CO_3^{2-}]+[CaCO_3^0]+[CaHCO_3^+]+[MgCO_3^0]+[MgHCO_3^+]+[NaCO_3^-]$$

$$[\mathbf{Mg}]_{\mathbf{tot}} = [Mg^{2+}]+[MgCO_3^0]+[MgHCO_3^+]+[MgSO_4^0]$$

Ionic equilibria

$$H_2CO_3^*(aq) \leftrightarrow 2\ H_2O + 2\ CO_2\ (g)$$

$$H_2CO_3^*\ (aq) \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^-\ (aq) \leftrightarrow H^+ + CO_3^{2-}\ (g)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s)$$

$$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+$$

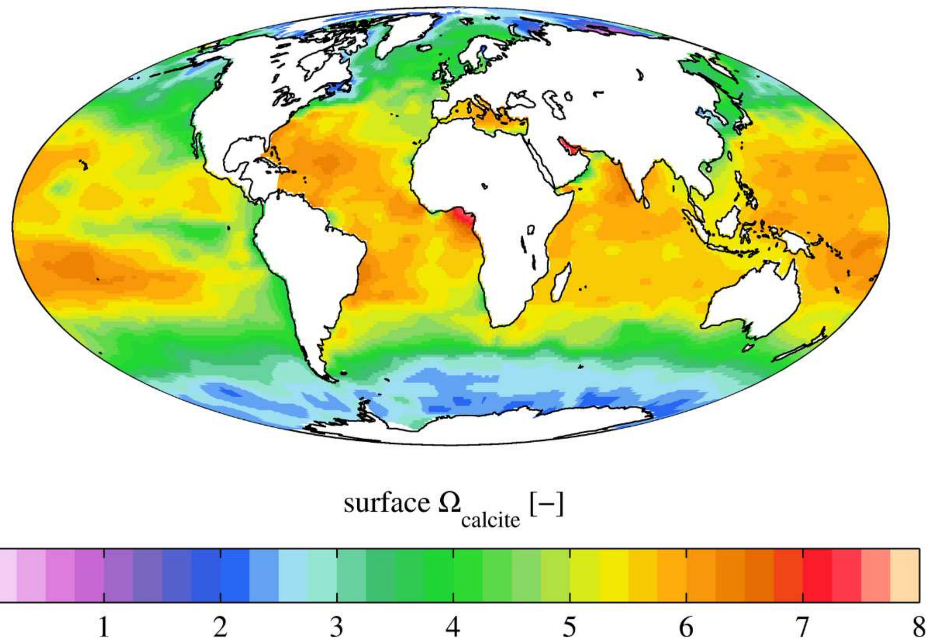
$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3^0$$

....

Calcium carbonate equilibrium in seawater

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3(s)$$

$$\Omega = \frac{[Ca^{2+}]\cdot[CO_3^{2-}]}{K_{sp}}$$



http://en.wikipedia.org/wiki/

Role of Mg and temperature in $CaCO_3$ precipitation (in seawater)

Precipitation of calcite or aragonite depends on Mg/Ca ratio and temperature:

Low Mg/Ca and low temperatures → **Calcite**

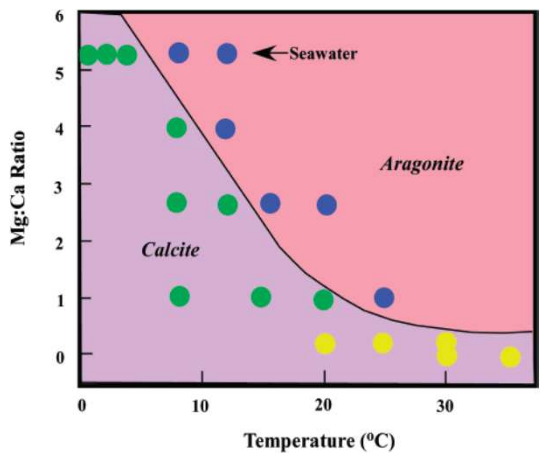
Mg/Ca > 5 and $t < 8$ °C → Calcite (seawater, salinity = 35 ‰)

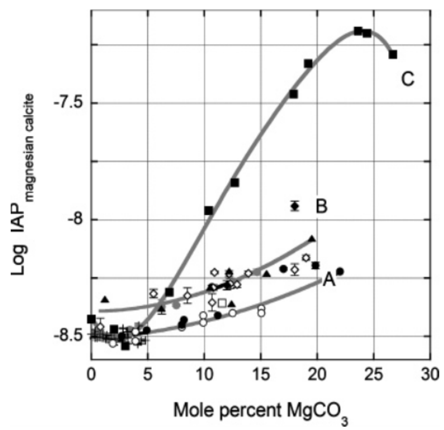
Mg/Ca = 0 and t > 60 °C → Aragonite

Explanation:

(a) Preferential adsorption of Mg^{2+} on calcite → inhibition of calcite and promotion of aragonite

(b) Incorporation of Mg^{2+} into calcite lattice → Increase of calcite solubility





J. W. Morse, R. S. Arvidson, and A. Luttge: Calcium Carbonate Formation and Dissolution. Chemical Reviews, 2007, 107, 342-381.

S. Fermani, B. Njegić Džakula, M. Reggi, G. Falini, D. Kralj: Effects of magnesium and temperature control on aragonite crystal aggregation and morphology, CrystEngComm, 2017, 19, 2451-2455

Vertical distribution of $CaCO_3$ saturation (Ω)

Shallow water - supersaturated with respect to $CaCO_3$ polymorphs (calcite, aragonite, vaterite)

- $CaCO_3$ shells of dead marine organisms preserved in the water column
- No significant spontaneous precipitation of $CaCO_3$ (!!!!)
  - High Mg^{2+} concentration - inhibition of calcite nucleation (precipitation)
  - Organic phosphate – inhibition of aragonite nucleation (precipitation)

Deep waters - undersaturated with respect to $CaCO_3$ polymorphs (calcite, aragonite, vaterite)

- Solubility increases with increasing pressure and salinity, and decrease with temperature
- Dissolution of calcitic and aragonitic shells

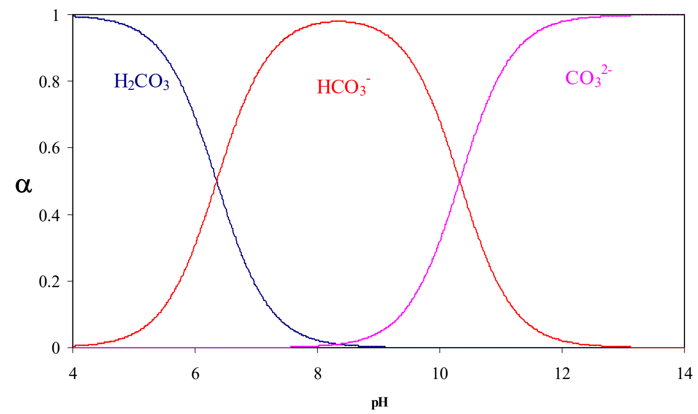
Sediment

- **Mid-depth zone**: 0 - 3.5 km → sediment contains 85-95% $CaCO_3$
- **Transition zone**: few hundred meters below 3.5 km → $CaCO_3$ content drop to around 10%
- **Abyssal depth** → 0% $CaCO_3$

Lysocline = depth in the ocean below which the rate of dissolution of calcite dramatically increases (d ≈ 3.5 km)

Calcite compensation depth = depth at which calcite deposition is completely compensated with dissolution

Role of calcium Carbonate in seawater



$CaCO_3$ precipitation / dissolution → major buffering mechanism in seawater

$$Ca^{2+}(aq) + HCO_3^-(aq) \leftrightarrow CaCO_3(s) + H^+$$

$$H_2CO_3^0(aq) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+$$

Regulate the intensity of CO_2 exchange at the interface water / atmosphere

Global warming and seawater acidification by CO_2

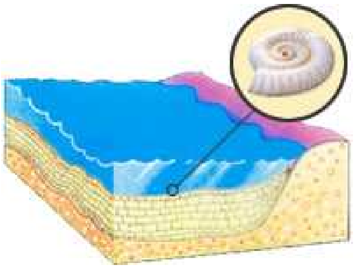
$\mathbf{p_{CO2} \approx 3,30 \cdot 10^{-4}}$ **atm** → pH = 8,21 → supersaturated (**calcite, aragonite**)

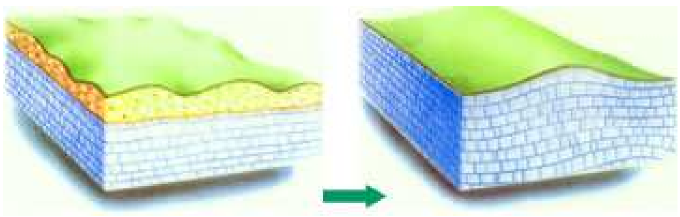
$\mathbf{p_{CO2} \approx 6,60 \cdot 10^{-4}}$ **atm** → pH = 7,96 → supersaturated (**calcite, aragonite**)

$\mathbf{p_{CO2} \approx 1,65 \cdot 10^{-3}}$ **atm** → pH = 7,61 → supersaturated (**calcite**), saturated (aragonite)

Calcium carbonate on mainland and karst topography

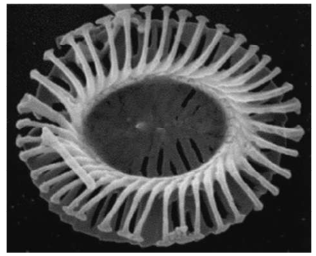
Formed by diagenesis of seawater sediments

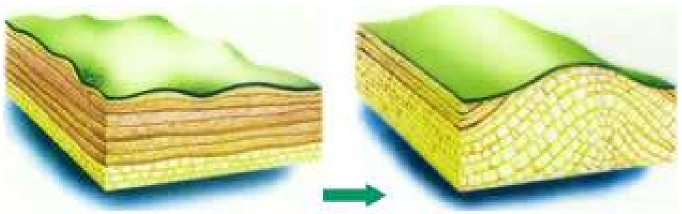




Chalk, 70 – 120 M years

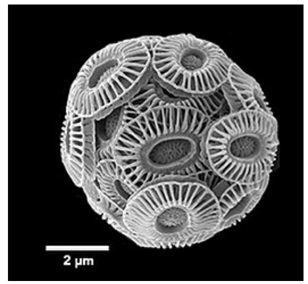
Planktonic or benthic protista (Foraminifera)

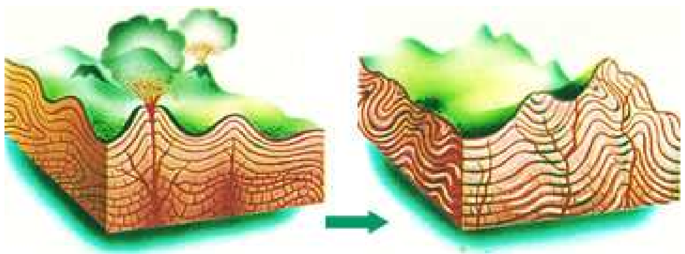




Limestone, 340 M years

Phytoplankton (coccolithophores (algae))



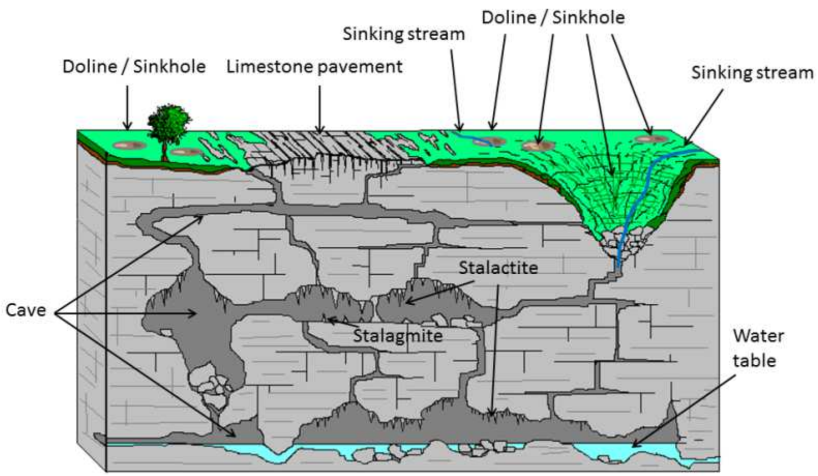


Marble = metamorphic limestone or chalk

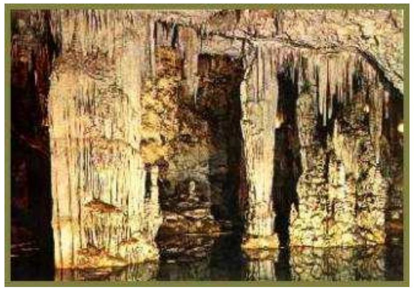
http://en.wikipedia.org/wiki/

Calcium carbonate on mainland and karst topography

Karst landscape → Earth's surface erosion of dense carbonate rock (limestone (calcite, aragonite) or dolomite)

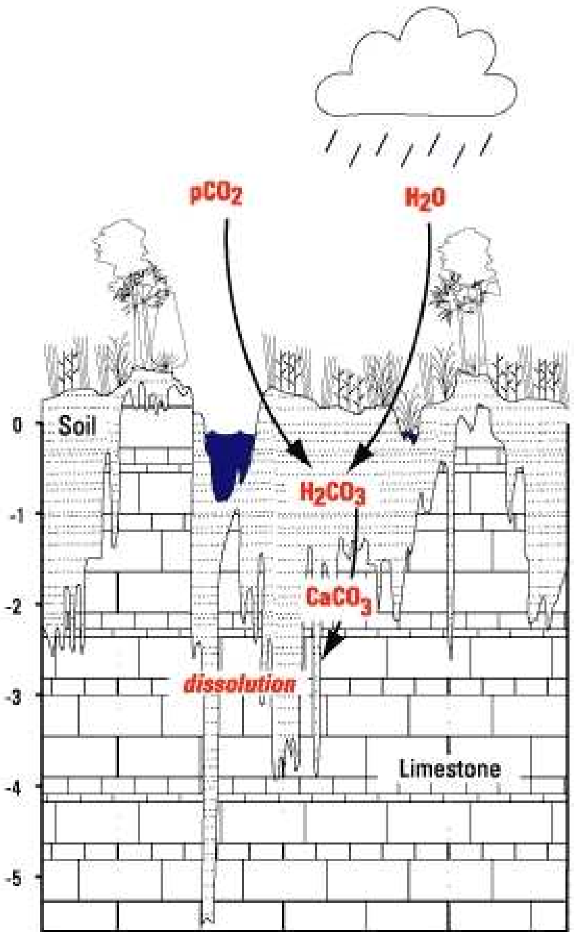


Typical karst landforms



http://en.wikipedia.org/wiki/

Mechanism of limestone dissolution and precipitation in karst



CO_2 absorption

atmosphere → $\boldsymbol{p_{CO2}} \approx \mathbf{10^{-3.4}}$ **atm**

$H_2O + CO_2\,(g) \leftrightarrows H_2CO_3\,(aq) \leftrightarrows H^+ + HCO_3^-$

$CaCO_3$ dissolution

underground → $\boldsymbol{p_{CO2}}$ **>> $\mathbf{10^{-3.4}}$ atm**

$H_2O + CO_2\,(g) \leftrightarrows H_2CO_3\,(aq) \leftrightarrows H^+ + HCO_3^-$

(CO_2 dissolution, pH decrease)

$CaCO_3(s) + H^+ \leftrightarrows Ca^{2+} + HCO_3^-$

($CaCO_3$ dissolution)

$CaCO_3$ precipitation

(atmosphere → $\mathbf{p_{CO2}} \approx \mathbf{10^{-3.4}}$ **atm**)

$H_2CO_3\,(aq) \leftrightarrows H_2O + CO_2\,(g)$

(CO_2 degasification, pH increase)

$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3(s)$

($CaCO_3$ precipitation)

stalactite, stalagmite, tufa, lake sediment...