Carbonate precipitation today

Precipitation occurs today in two main settings, ca. 50 / 50%:

- in superficial waters of the open ocean
- in shallow waters

Three common minerals.

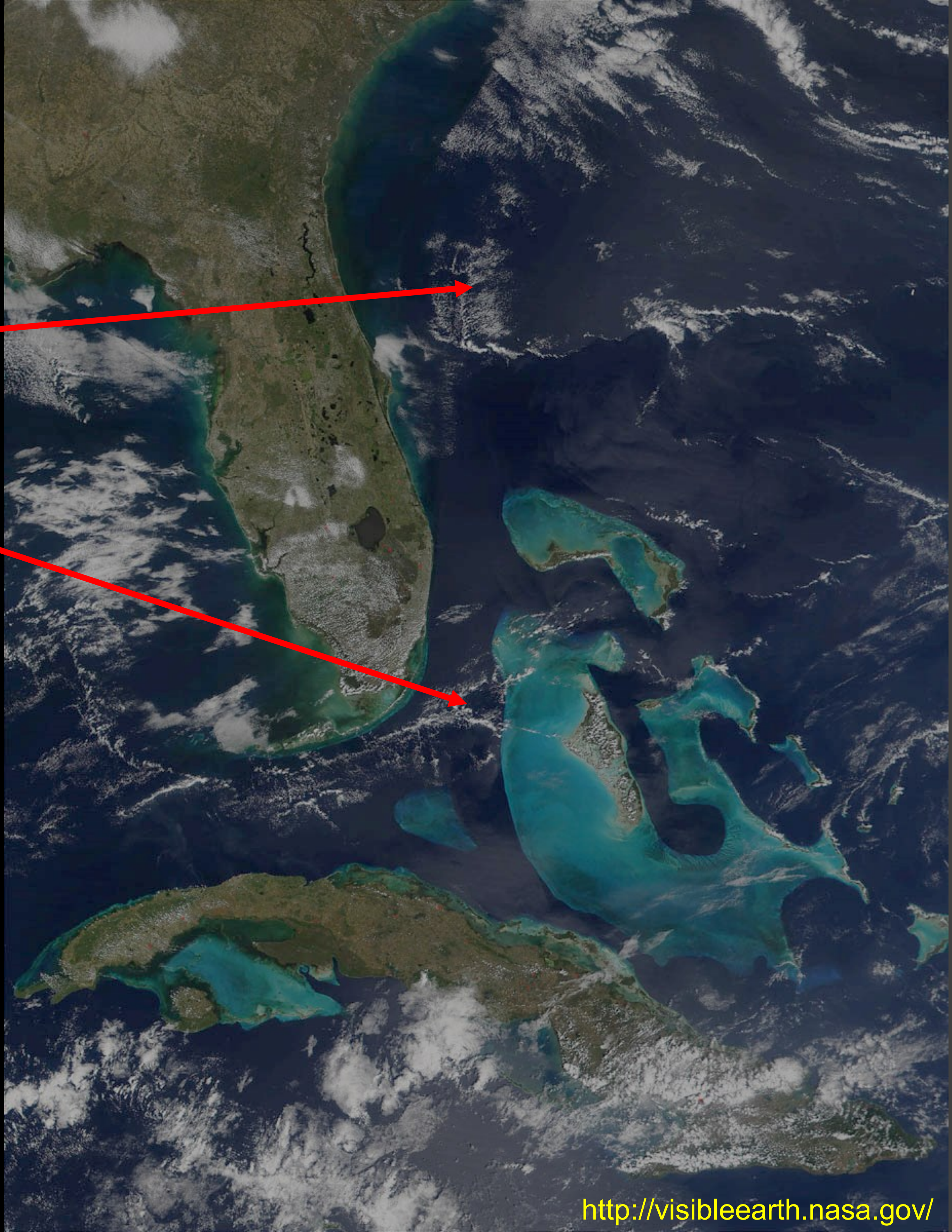
calcite occurs in two species:

- low-Mg calcite, stable during burial and resistant to dissolution
- high-Mg calcite ($MgCO_3 > 4\%$), much more soluble (metastable);

aragonite also is highly soluble;

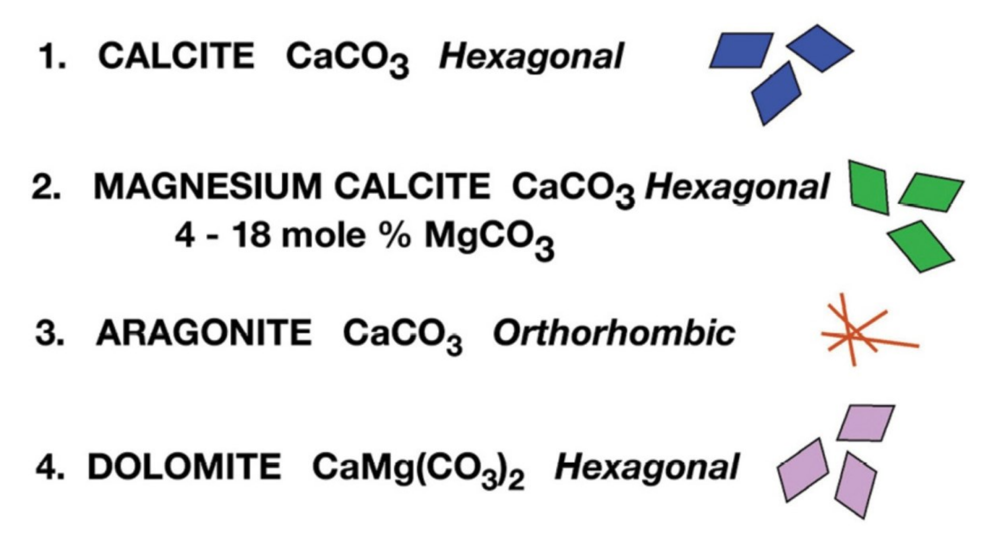
dolomite is rare as primary precipitate – but it would be most stable in seawater at ambient conditions.

Precipitation may result in accumulation and this is why ultimately carbonate sedimentology exists.



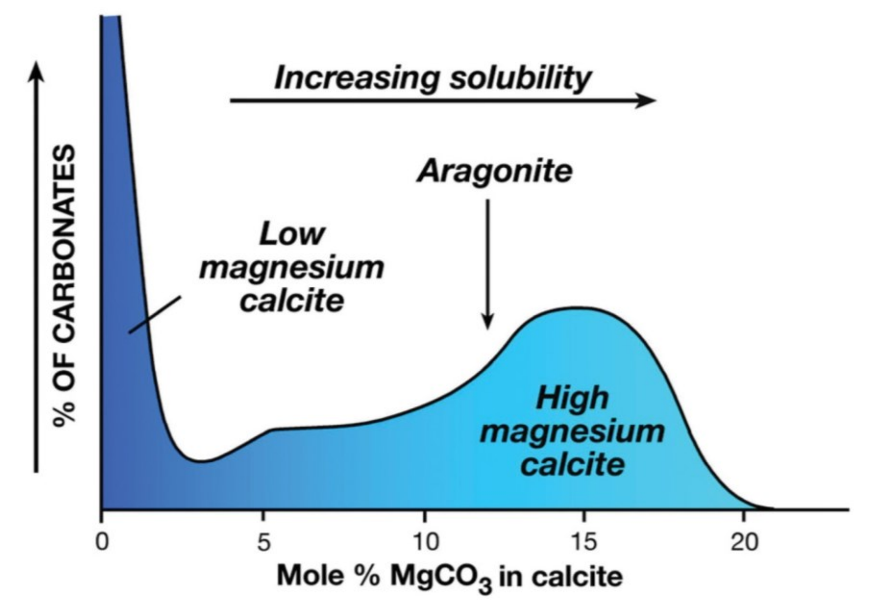
http://visibleearth.nasa.gov/

Carbonate mineralogy

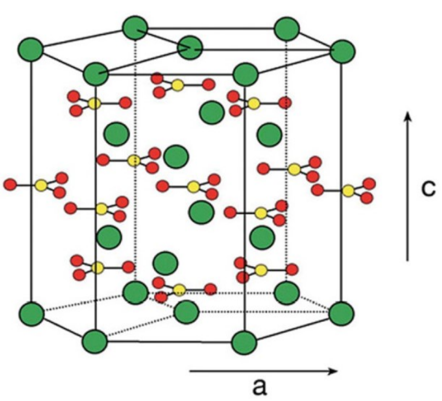


1. **CALCITE** $CaCO_3$ *Hexagonal*
2. **MAGNESIUM CALCITE** $CaCO_3$ *Hexagonal*
   4 - 18 mole % $MgCO_3$
3. **ARAGONITE** $CaCO_3$ *Orthorhombic*
4. **DOLOMITE** $CaMg(CO_3)_2$ *Hexagonal*

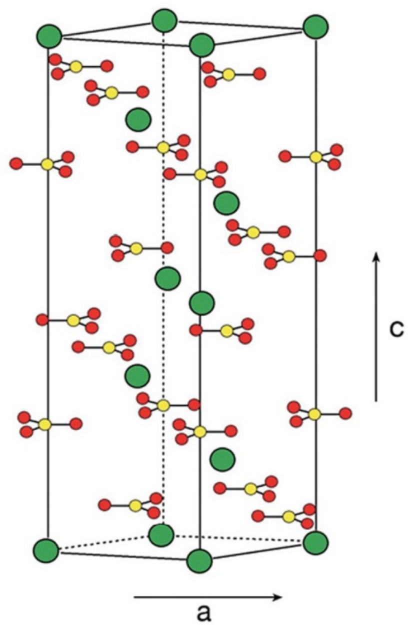
Crystallography and chemical composition of the four most common minerals in carbonate sediments



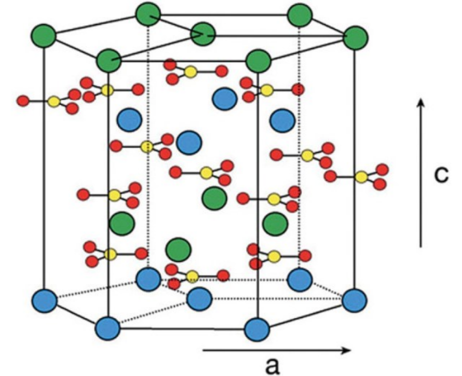
Relative solubility in calcite with increasing Mg content



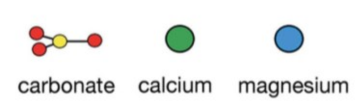
Calcite



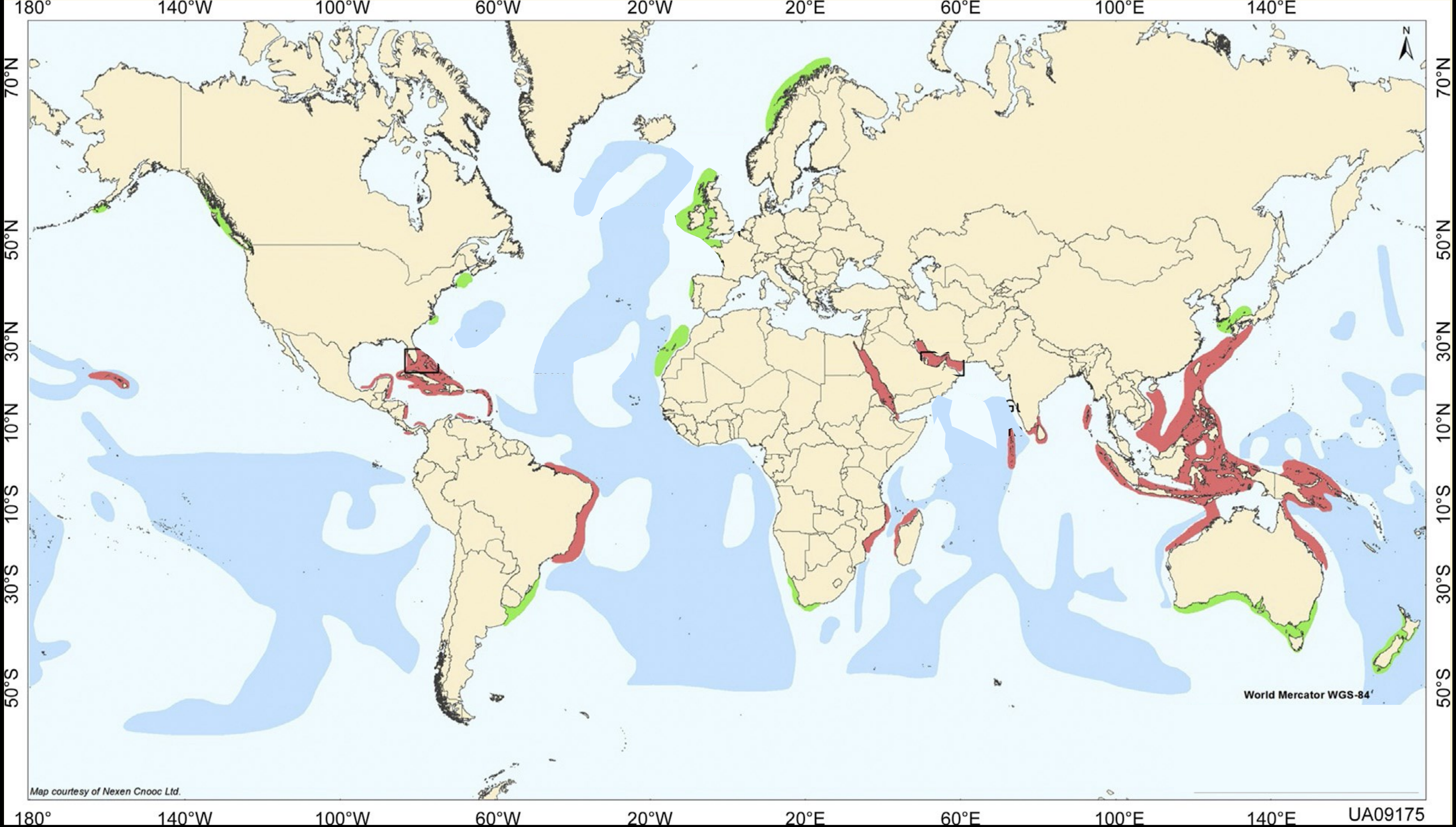
Aragonite



Stoichiometric dolomite



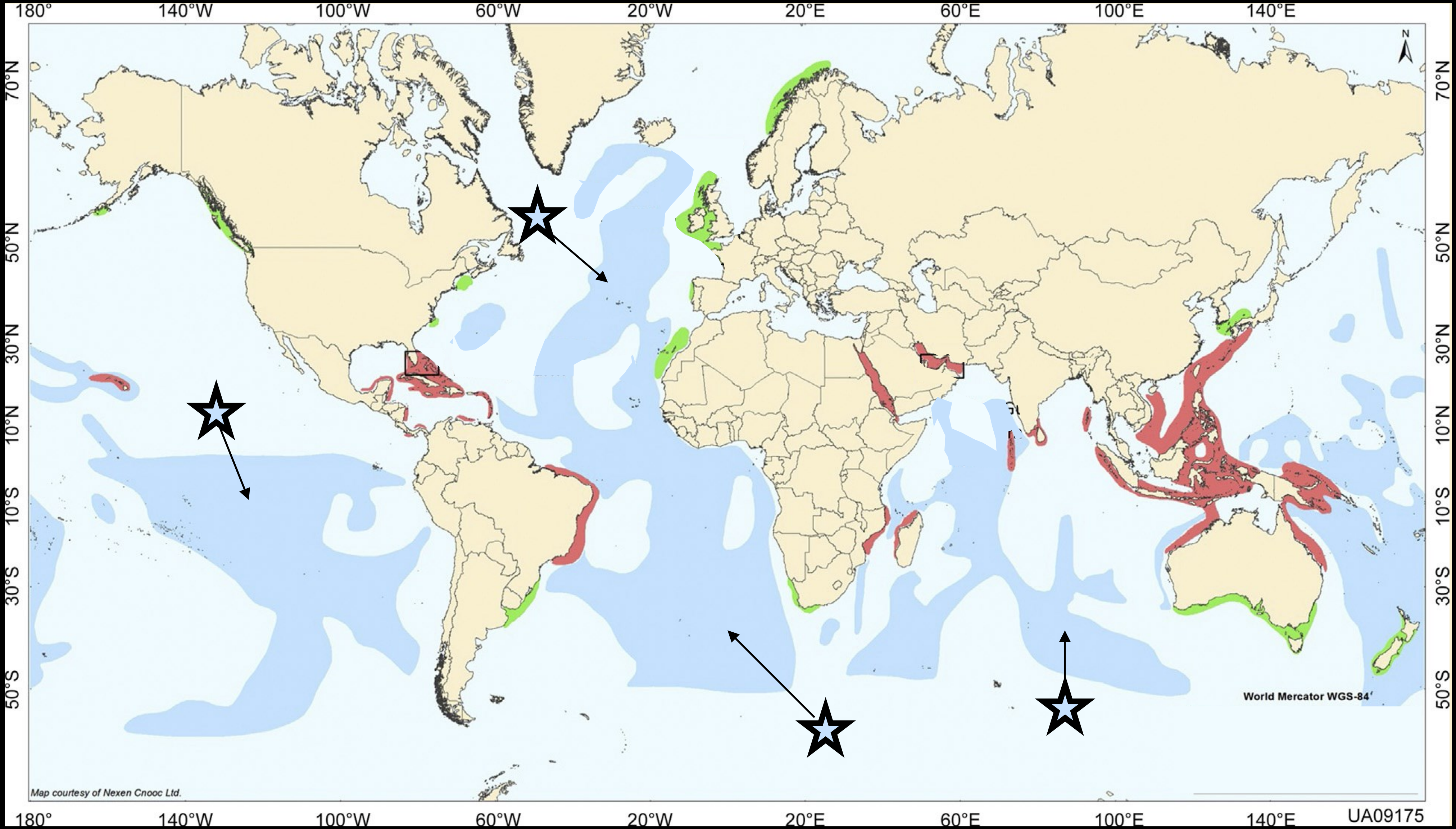
Carbonate precipitation today



Map courtesy of Nexen Cnooc Ltd.

Main areas of carbonate
precipitation in modern oceans:

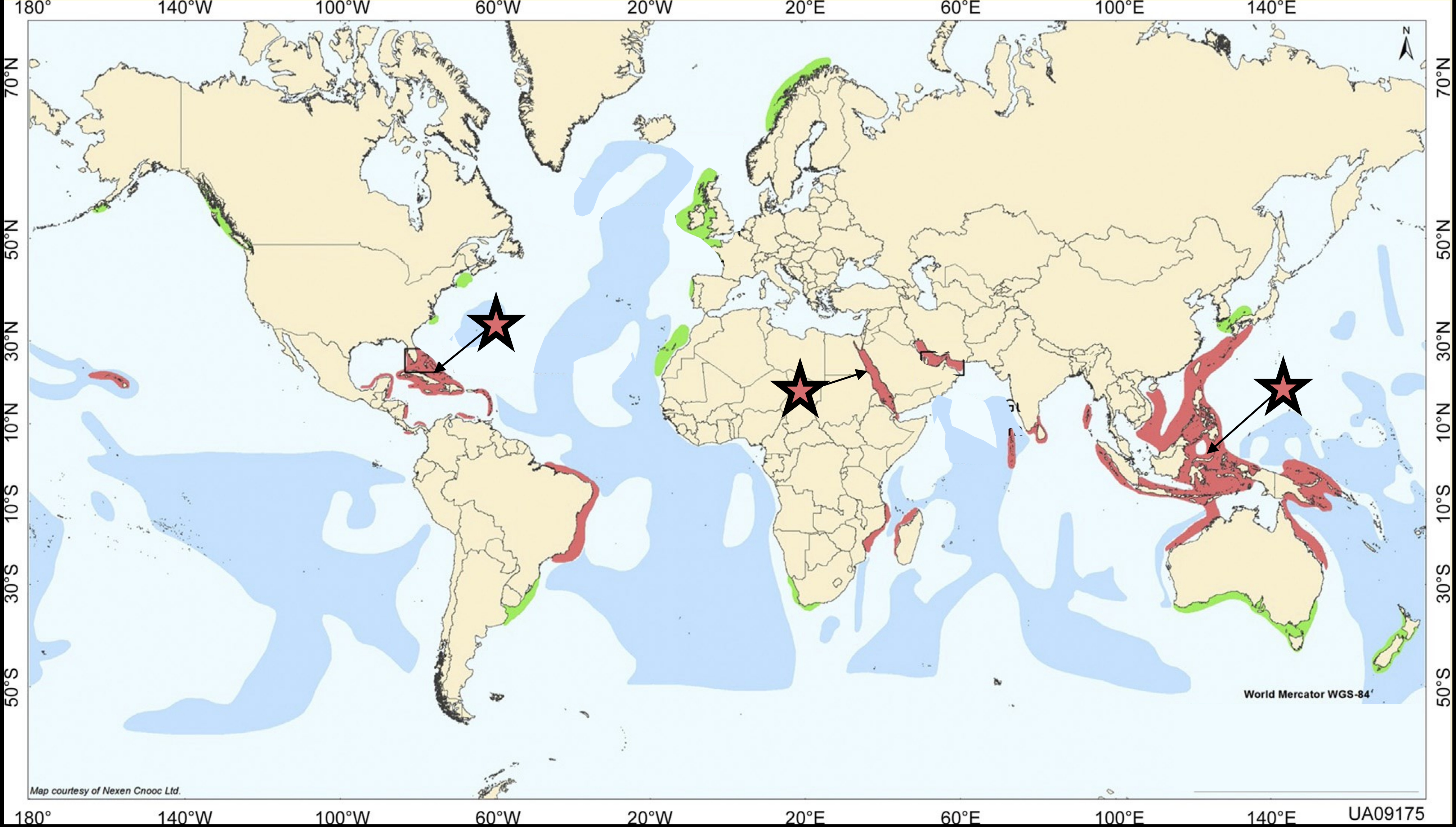
Carbonate precipitation today



Map courtesy of Nexen Cnooc Ltd.

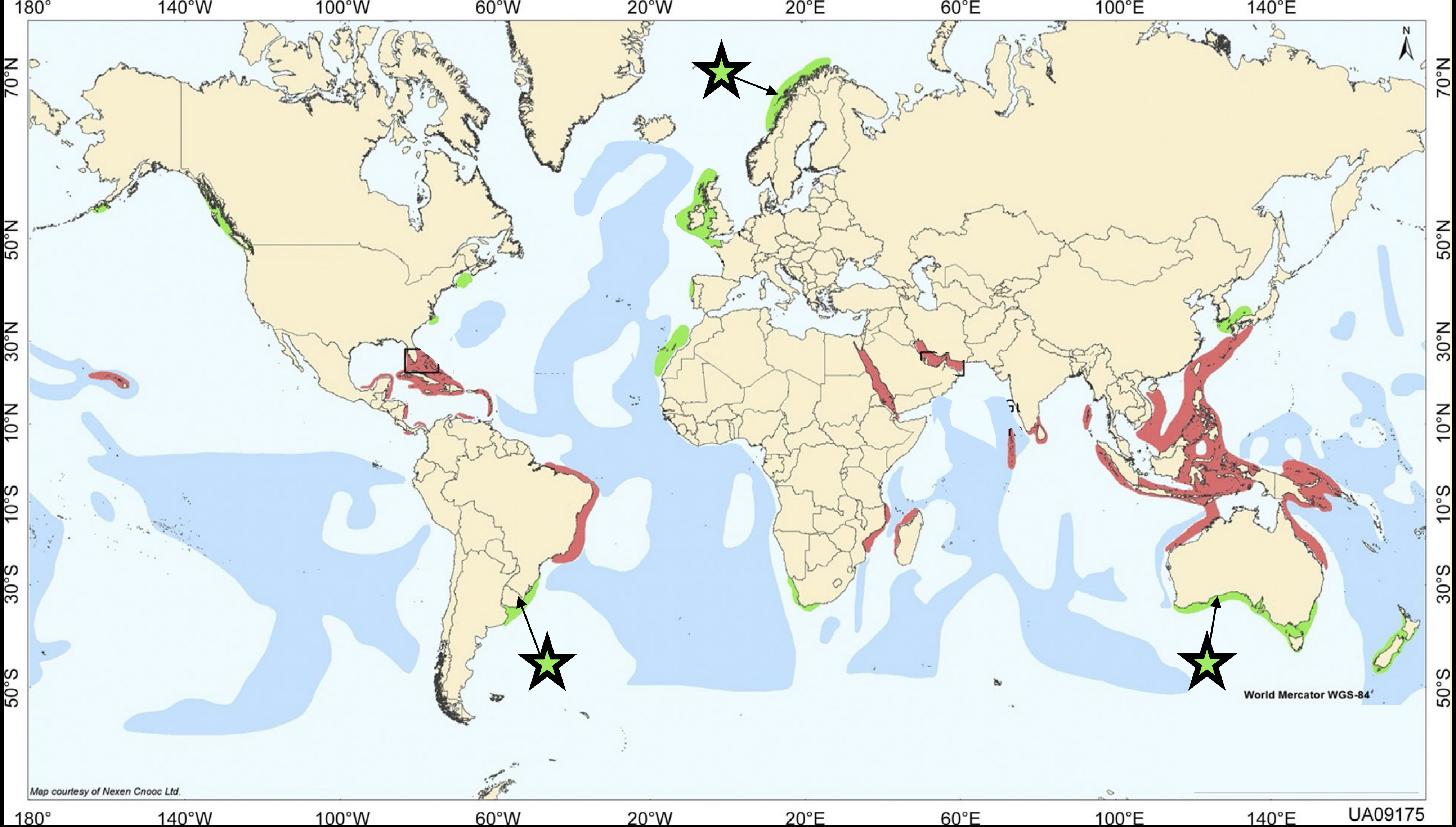
Main areas of carbonate precipitation in modern oceans:

Carbonate precipitation today



Main areas of carbonate
precipitation in modern oceans:

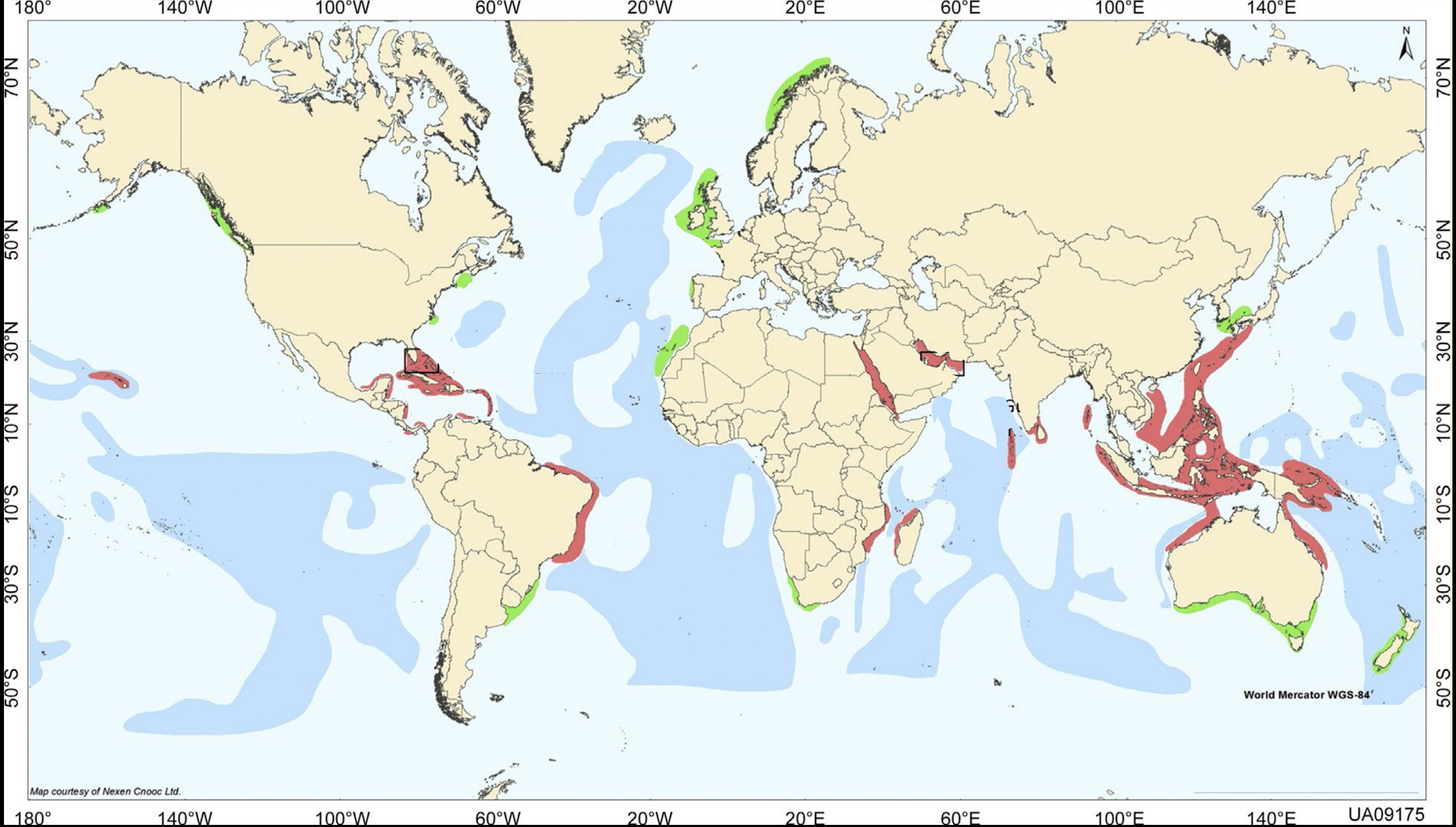
Carbonate precipitation today



Map courtesy of Nexen Cnooc Ltd.

Main areas of carbonate
precipitation in modern oceans:

Carbonate precipitation today

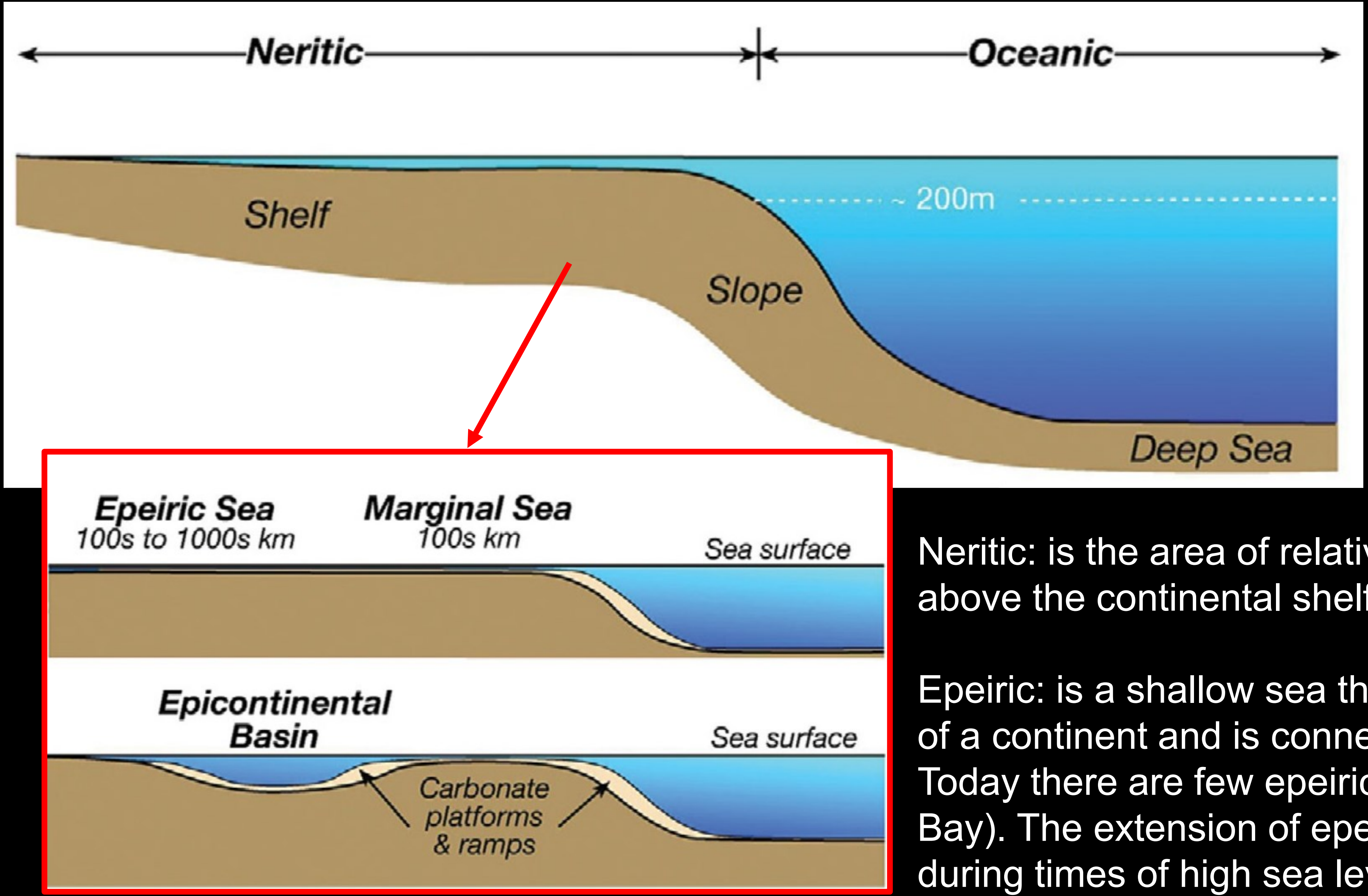


Map courtesy of Nexen Cnooc Ltd.

Main areas of carbonate precipitation in modern oceans:

- **DEEP WATER**
- **SHALLOW WATER** (**warm water**, **cool water**)

Carbonate precipitation today



From James and Jones, 2016

Carbonate accumulation zones

Neritic: is the area of relatively shallow water above the continental shelf

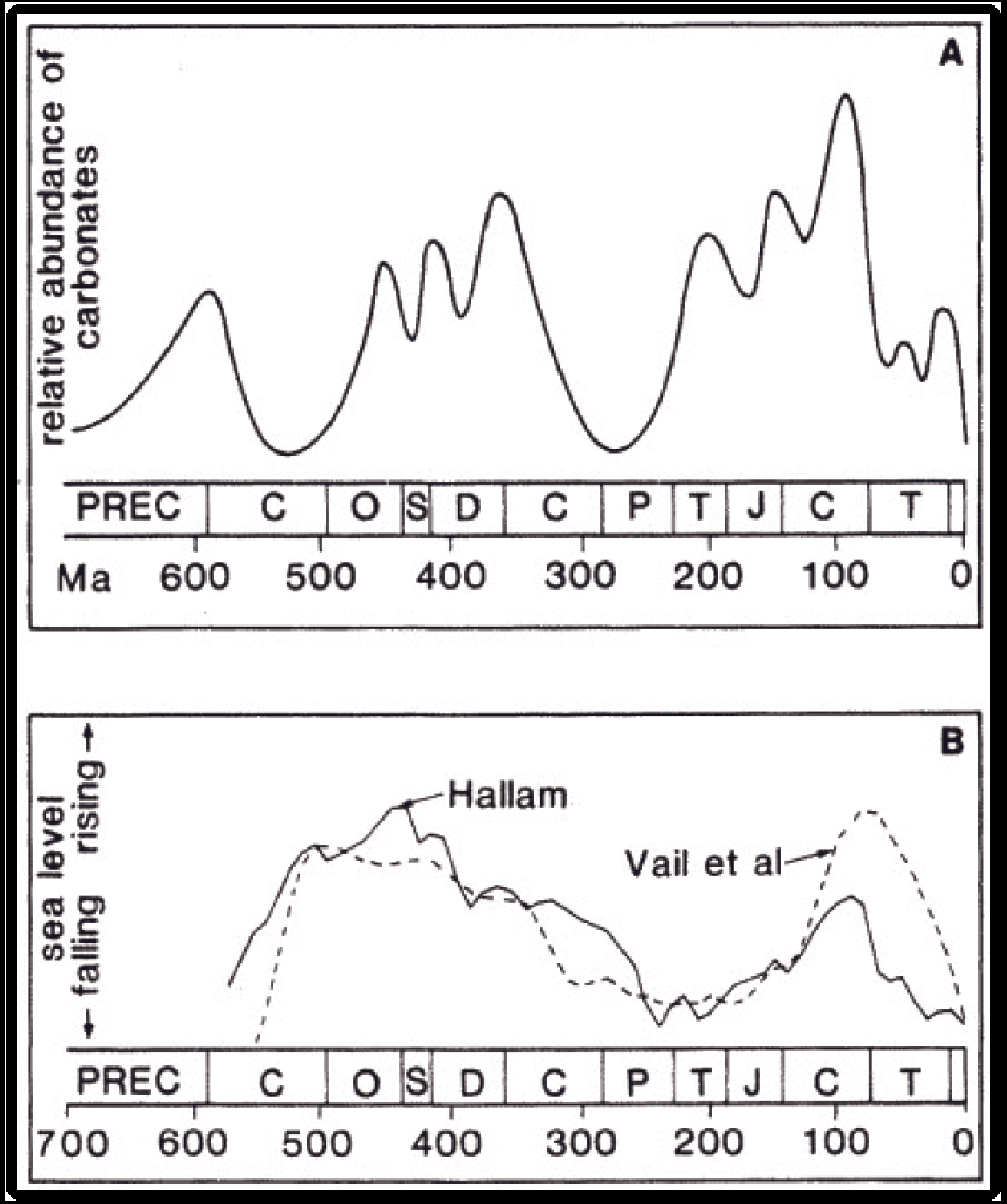
Epeiric: is a shallow sea that covers a large part of a continent and is connected to the ocean. Today there are few epeiric seas (e.g. Hudson Bay). The extension of epeiric seas is maximum during times of high sea level

Carbonates and sea level

Carbonates aboundance fluctuated through geological times and a broad correspondence is seen with large scale **osciallation of sea level**.

Carbonate abundance was high during times of high sea level and low in times of low sea level.

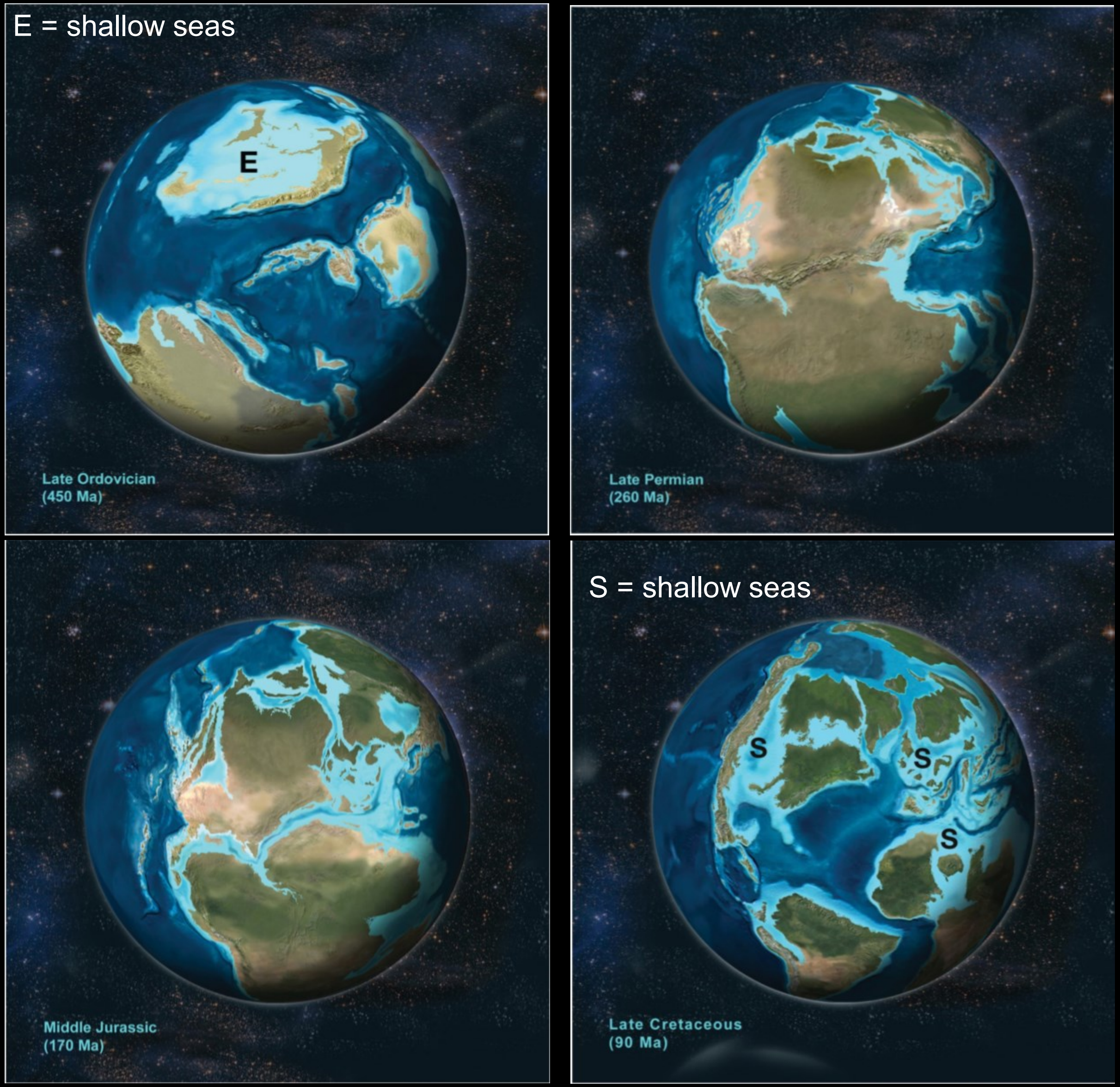
Can you guess why?

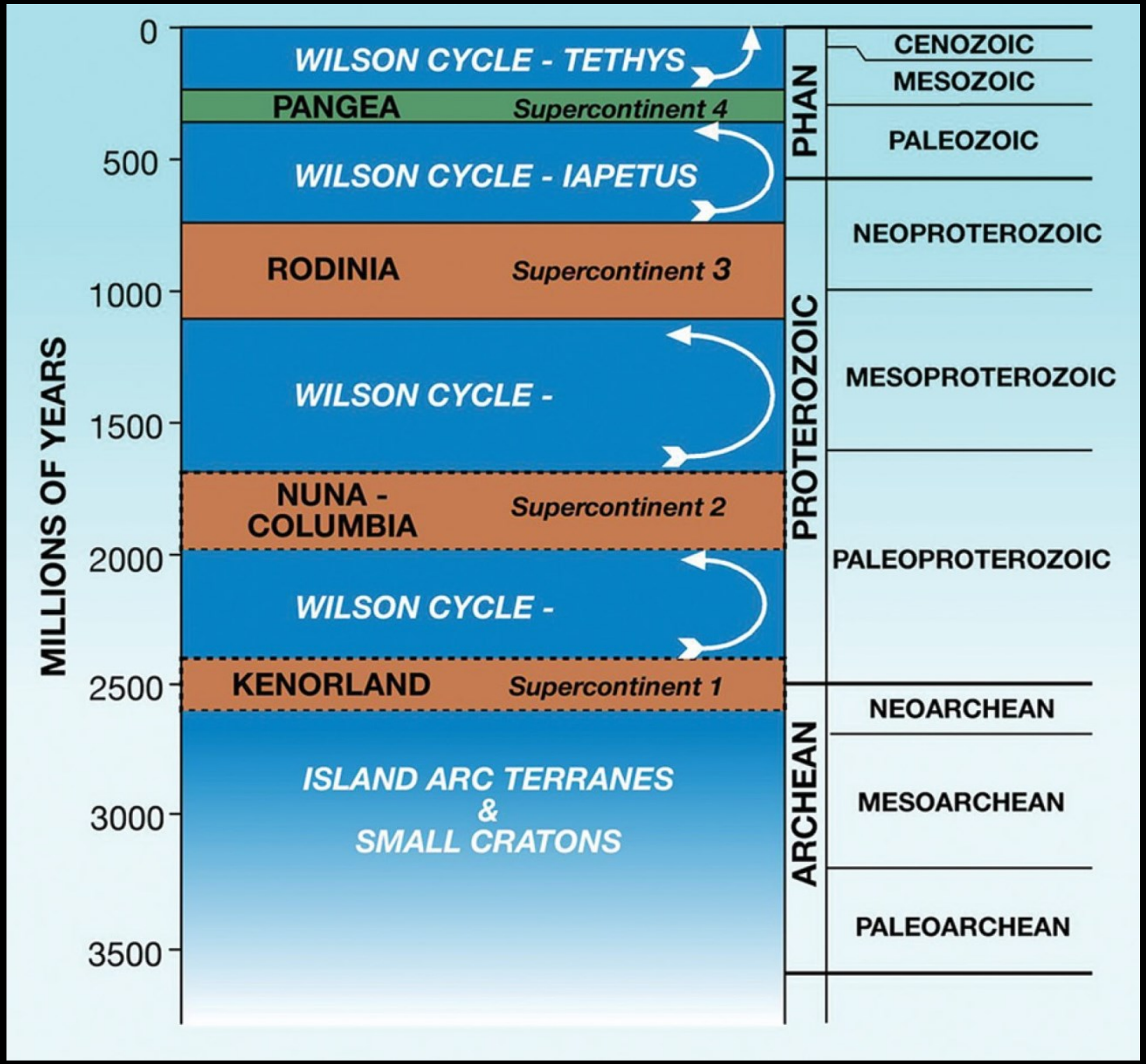


Tucker and Wright, 1990

Carbonates and sea level

Continental arrangement also plays a role

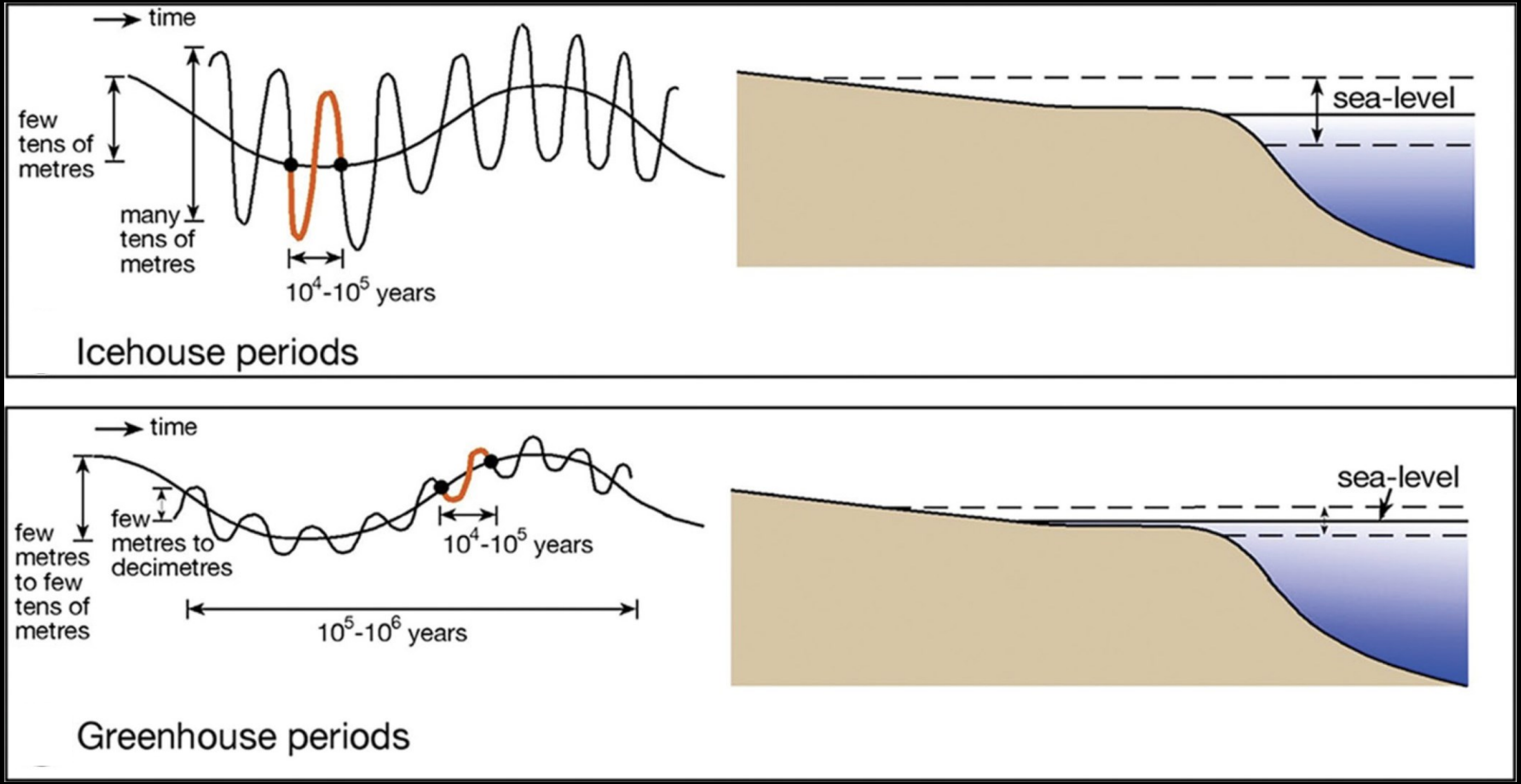




From James and Jones, 2016

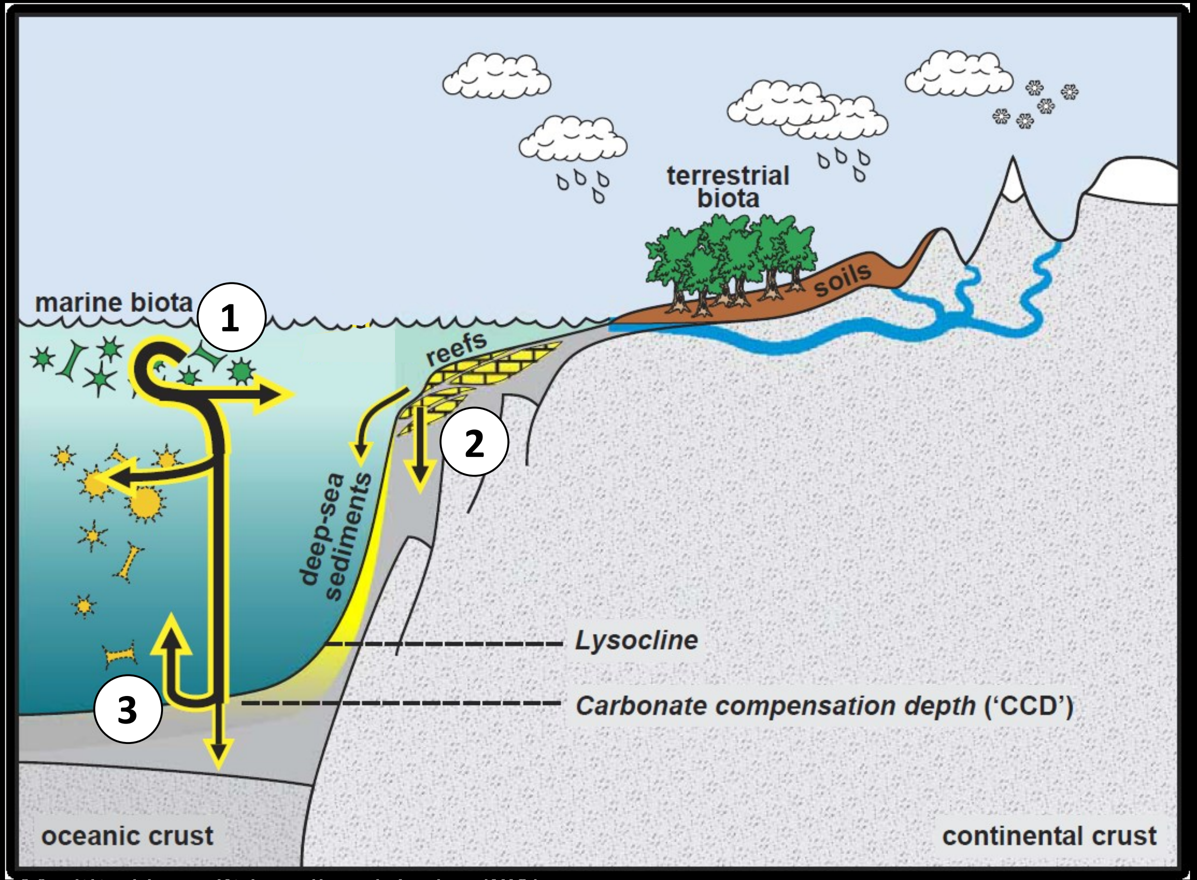
Carbonates and sea level

The link between sealevel change and carbonate deposition can be reflected in cyclicity of carbonate sediments and in their thickness



From James and Jones, 2016

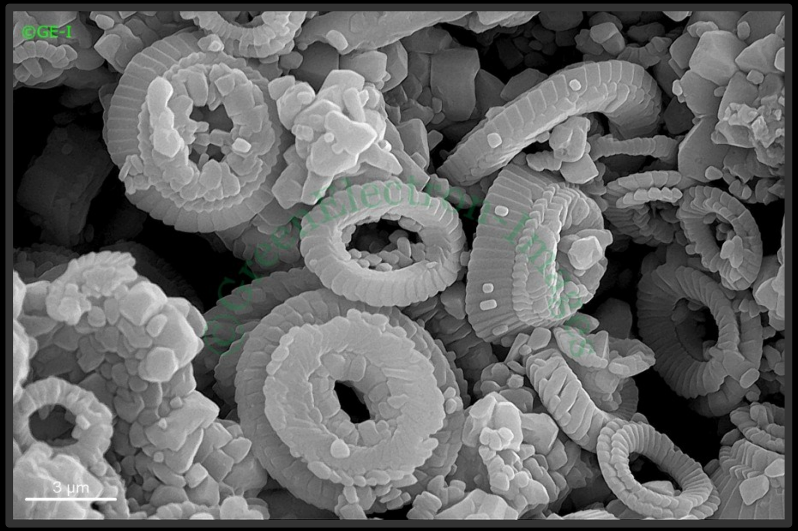
Carbonate precipitation today



Modified from Ridgwell and Zeebe, 2015

① Precipitation by **coccolitophores** and **foraminifera***

* also pteropods pracipitate carbonate but their contribution is minor with respect to cocoolithophores and forams

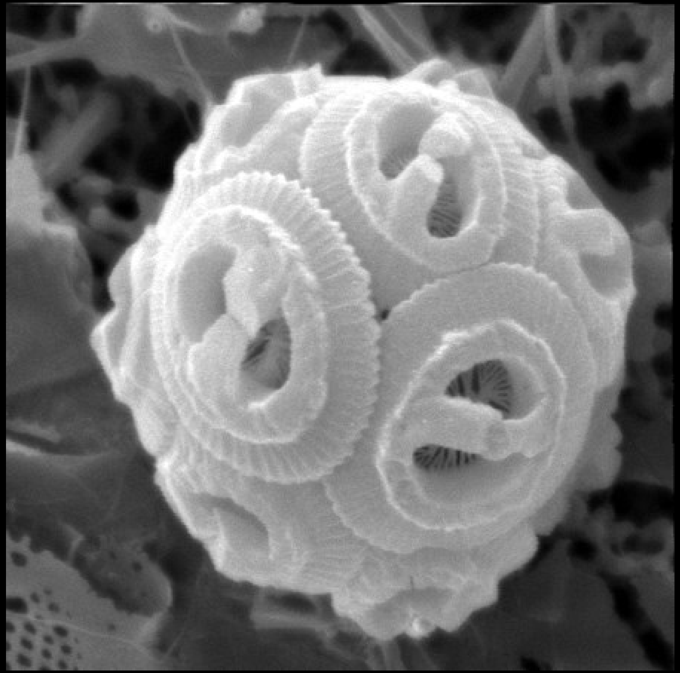


coccolithophores

Burke and Hull, 2017

foraminifera

Carbonate precipitation today



COCCOLITHOPHORES

Unicellular, eucaryotic algae. They are charcaterized by calcium carbonate plates called **coccoliths**.

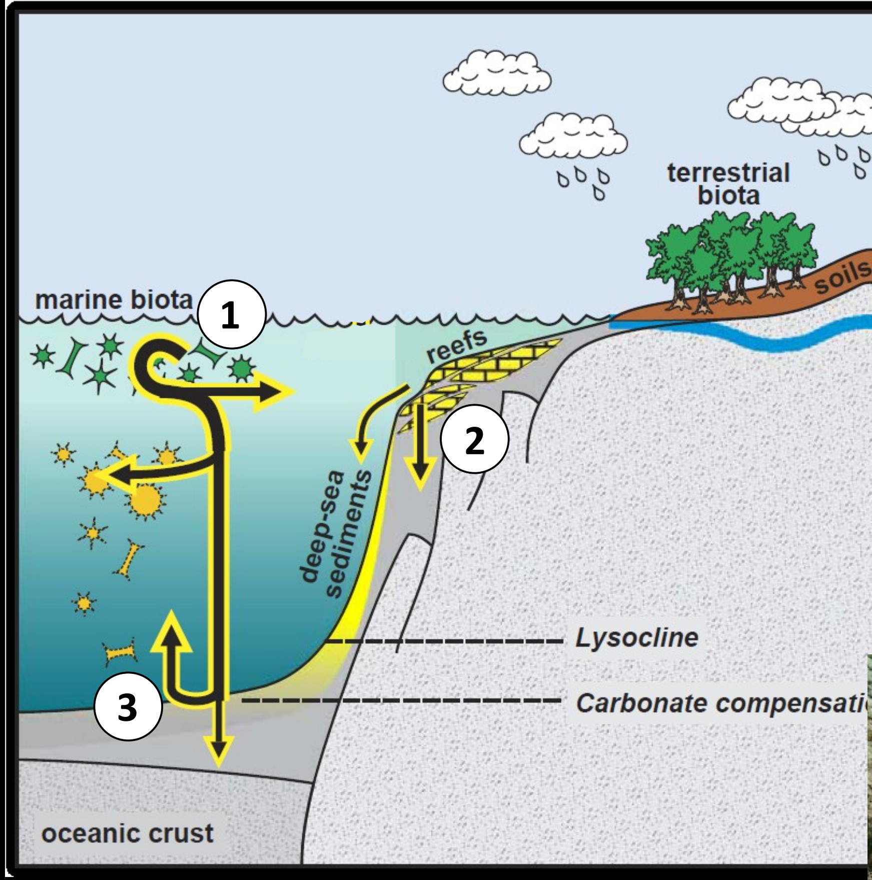
FORAMINIFERA

Unicellular animals (ameboid protists). They have an **external shell** that can be made of different materials, but mostly calcium carbonate.

*pteropods are gastropods

http://www.ucl.ac.uk/GeolSci/micropal/

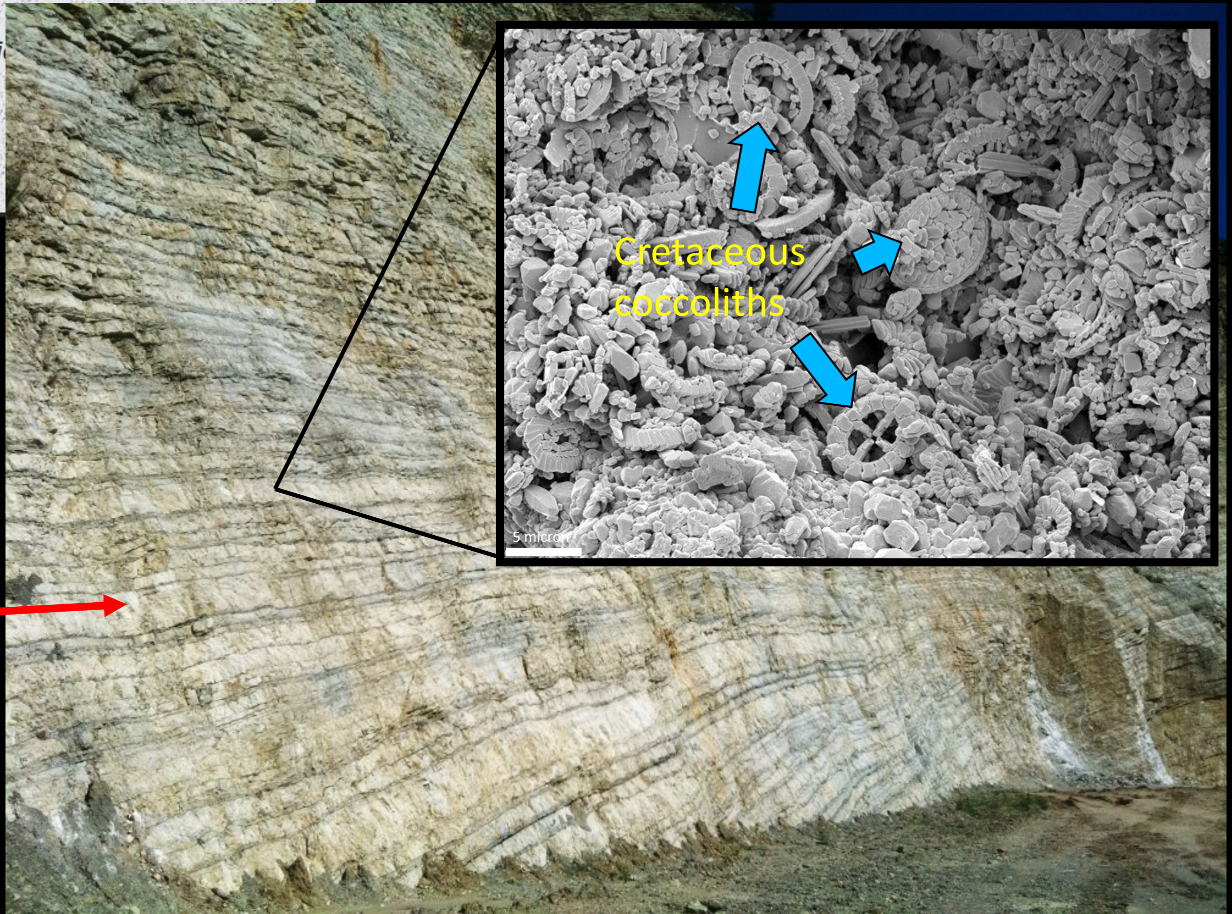
Carbonate precipitation today



① Precipitation by coccolitophores and planktonic foraminifera

Carbonate production by coccolithophores and foraminifera can be lithogenic.

Pelagic carbonate deposits made mainly of tiny fossils called nannoliths (= coccolith) (Maiolica, Cretaceous, Central Italy)

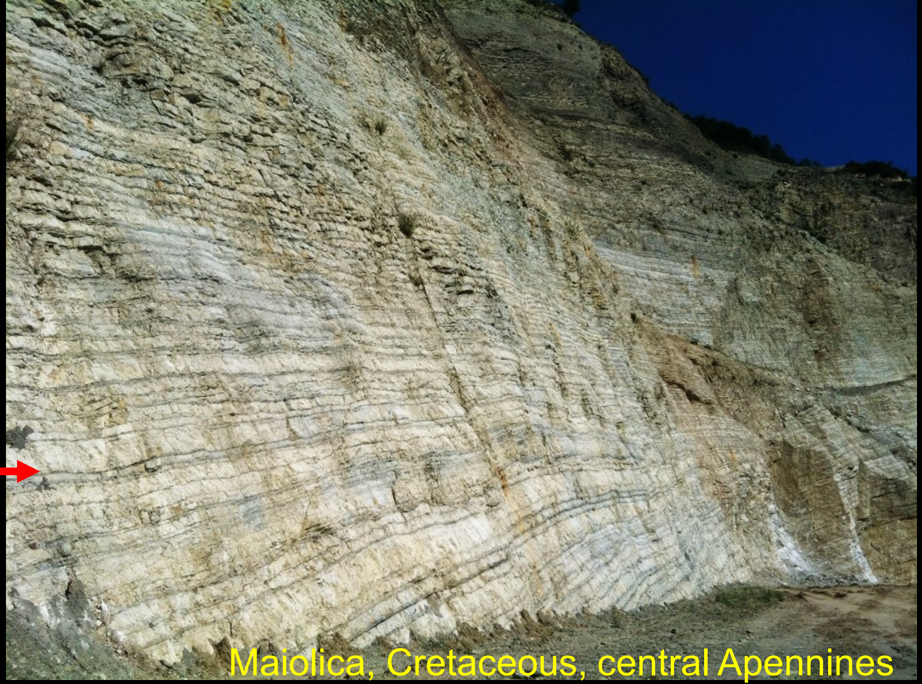


Carbonate precipitation today

Two types of deep-water sediments

- **Pelagic**: sediment deposited without influence (supply) from shallow water and continental sources

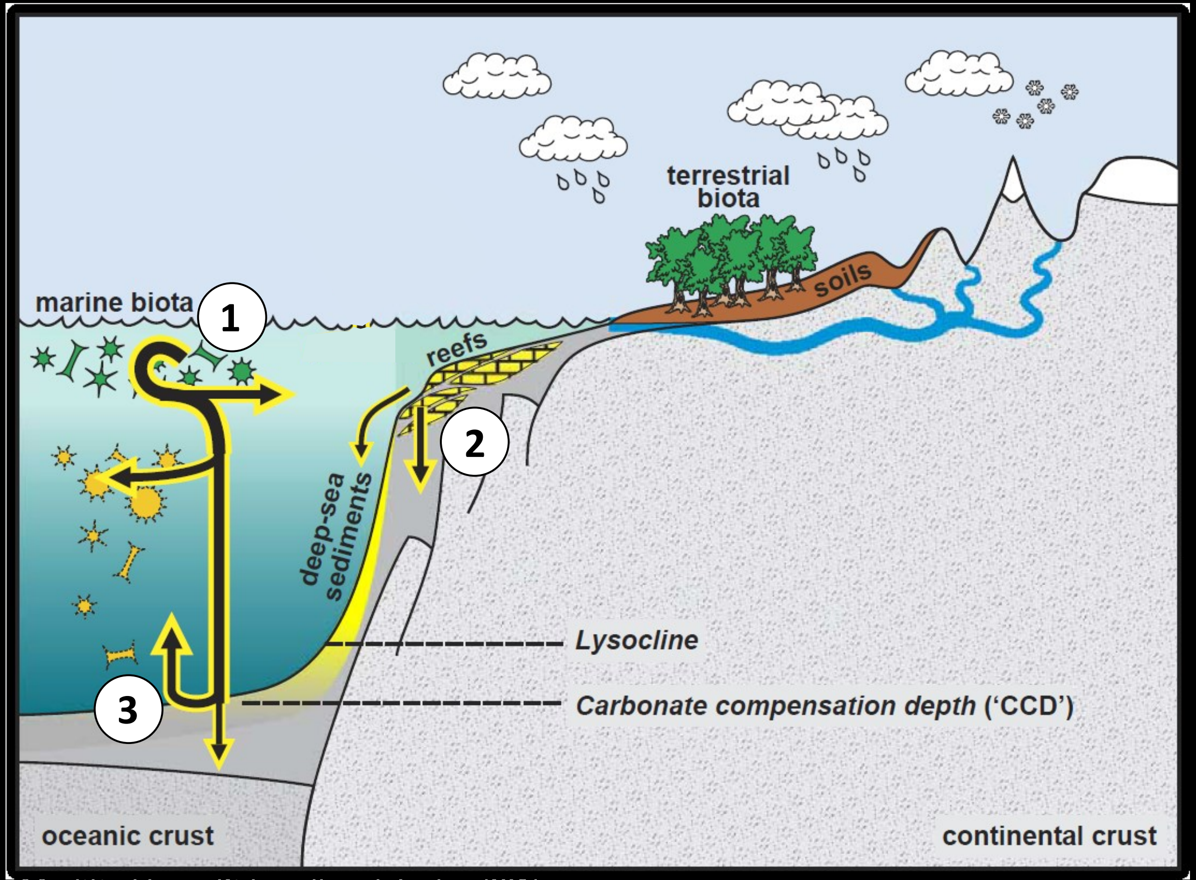
- **Hemipelagic**: mostly pelagic sediment, that includes, however, a component supplied from adjacent emerged lands or neritic platforms.



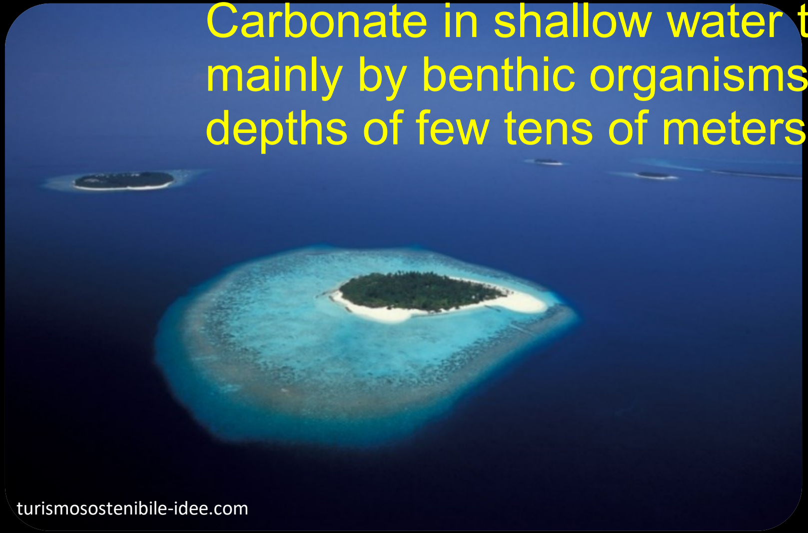
Maiolica, Cretaceous, central Apennines

Scisti a Fucoidi, Cretaceous, central Apennines

Carbonate precipitation today

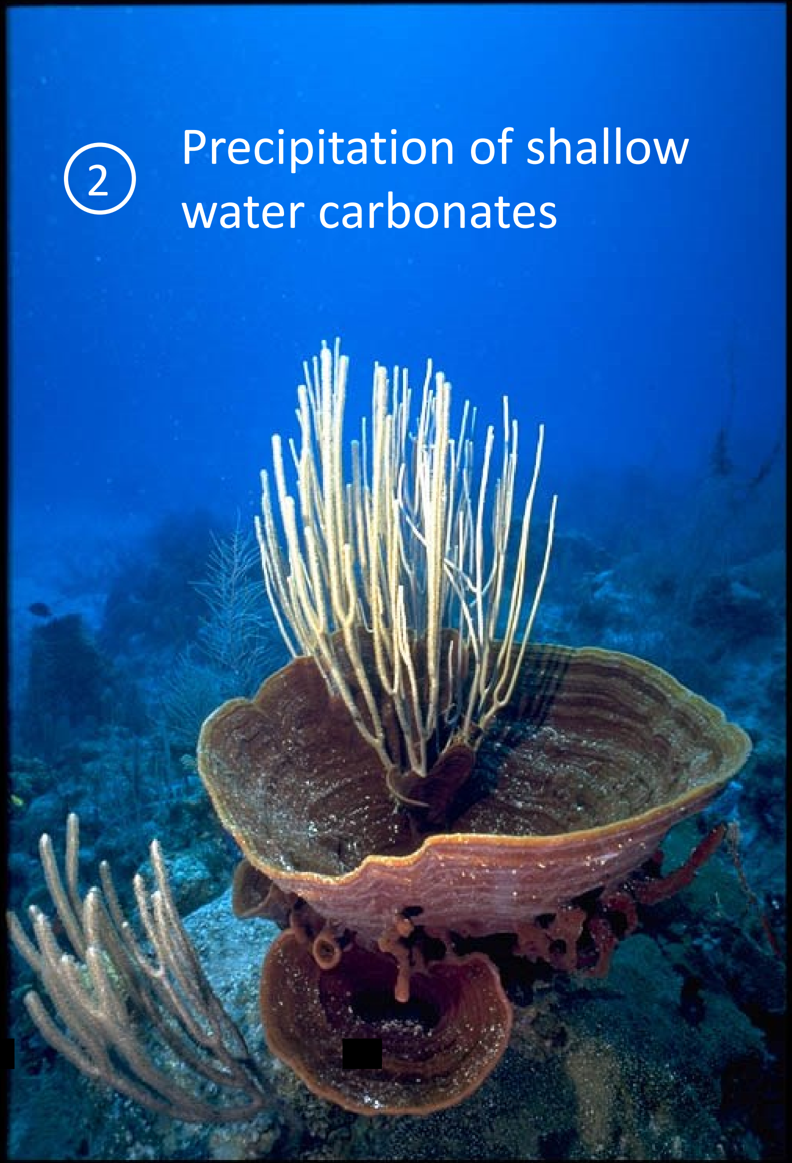


Modified from Ridgwell and Zeebe, 2015



Carbonate in shallow water today is precipitated mainly by benthic organisms that thrive up to depths of few tens of meters.

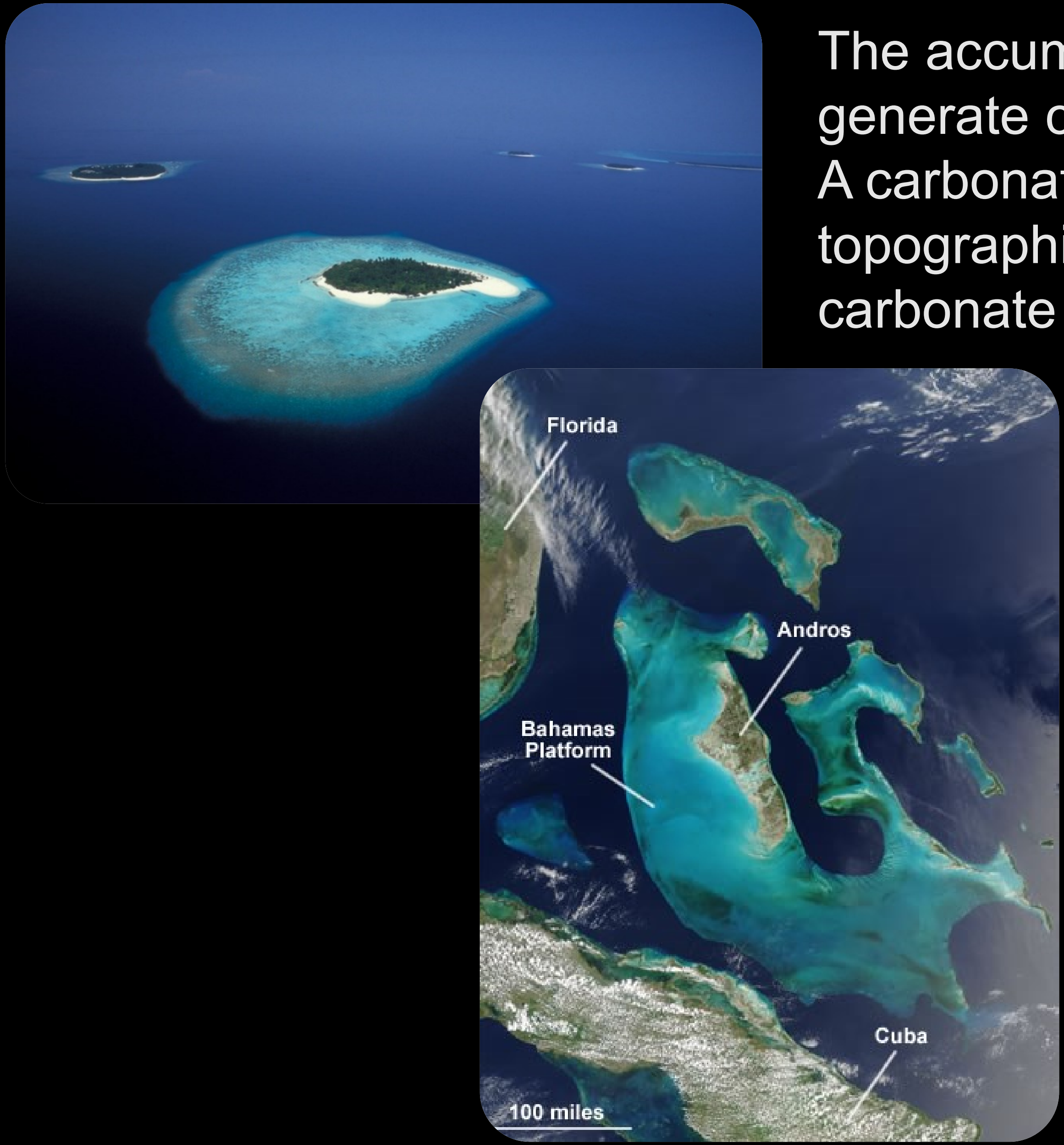
turismosostenibile-idee.com



② Precipitation of shallow water carbonates

Carbonate precipitation today

The accumulation of carbonate in shallow water can generate carbonate platforms.
A carbonate platform is a geological object that possess topographic relief and is made of parautochtonous carbonate deposits



Some modern examples of carbonate platform

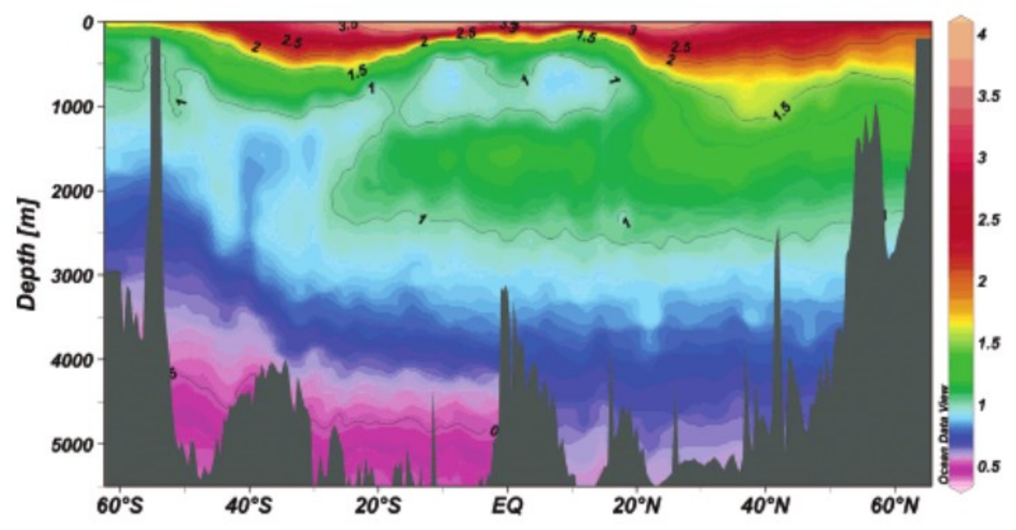
Carbonate precipitation today

The **saturation state** of seawater with respect to carbonate, **Ω**, indicates whether sea water tends to precipitate (**supersaturation**) or to dissolve (**undersaturation**) $CaCO_3$.
Seawater is undersaturated when $\Omega < 1$, supersaturated if $\Omega > 1$.
Today, tropical superficial waters are largely supersaturated (Ω is about 5 for calcite, and still 3 for aragonite). It gets worse in colder and deeper waters.

ION CONCENTRATIONS

$$\Omega = \frac{[\mathrm{Ca}^{2+}]_{\mathrm{sw}} \times [\mathrm{CO}_3^{2-}]_{\mathrm{sw}}}{K^*_{\mathrm{sp}}}$$

REACTION CONSTANT

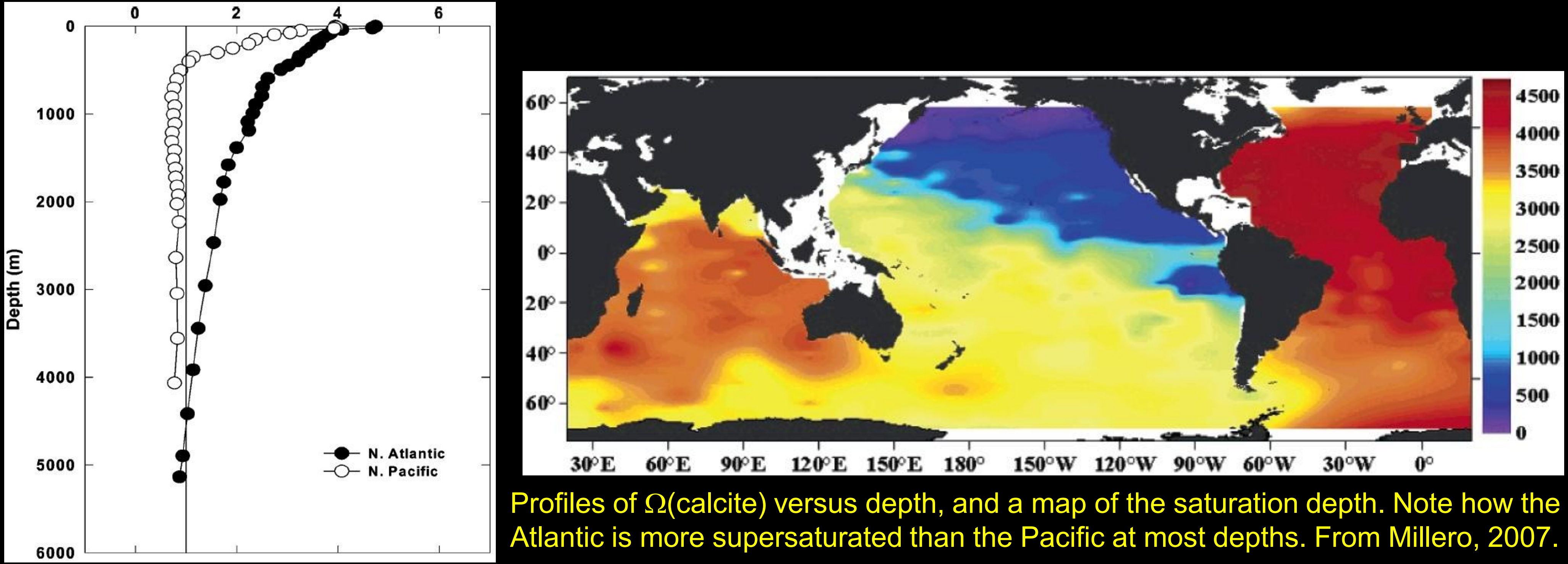


Saturation state (Ω) for aragonite in the Atlantic Ocean. Note that Ω diminishes (1) with depth and (2) with latitude, especially to the South. This is because of the combined effect of high pressure (depth) and temperature (depth and latitude) on solubility. From Millero, 2007.

Carbonate precipitation today

Ω lowers with depth, mostly because carbonates are more soluble at high pressures. Ω = 1 at the **saturation depth**.

Below the saturation depth, seawater is undersaturated. However, carbonate *does* accumulate in sediments anyway, as long as the flux of incoming carbonate is higher than the rate of dissolution.

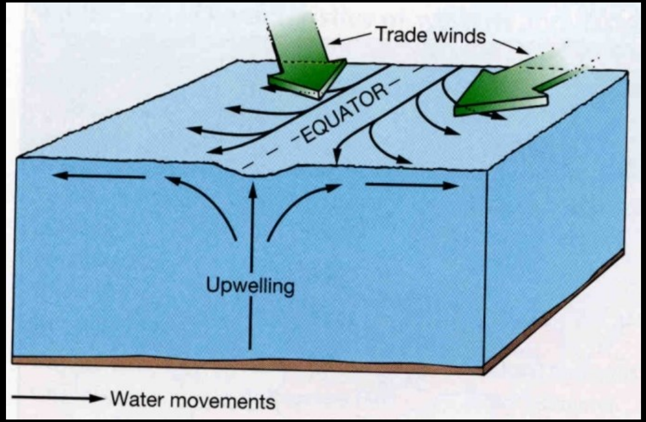


Profiles of Ω(calcite) versus depth, and a map of the saturation depth. Note how the Atlantic is more supersaturated than the Pacific at most depths. From Millero, 2007.

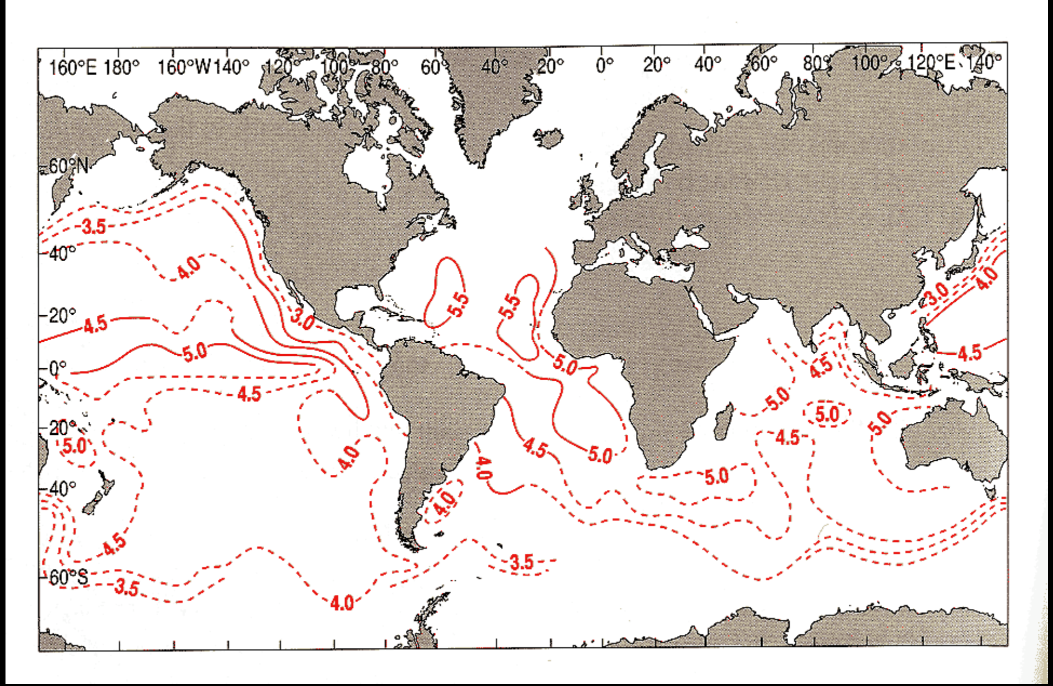
Carbonate precipitation today

Three surfaces can thus be defined.

- **Saturation depth**: surface at which Ω = 1;
- **Lysocline**: depth at which carbonate dissolution becomes recognizable in sediments. Sometimes, it is conventionally considered as the surface at which Ω = 0.8;
- **Carbonate Compensation Depth** (CCD): the surface at which the calcite flux to bottom sediments equals the dissolution rate, so that there is no net accumulation of carbonate.



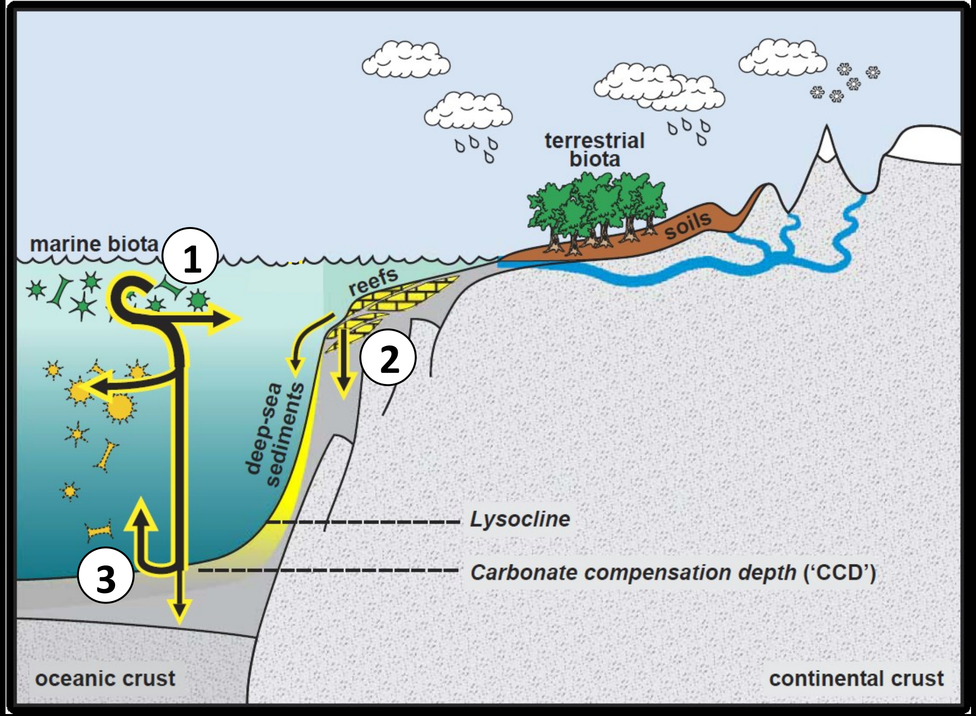
How the equatorial atmospheric circulation (the Hadley cell) steers equatorial upwelling. From http://www.i-cool.org/wp-content/uploads/2010/02/equatorial-upwelling.jpg



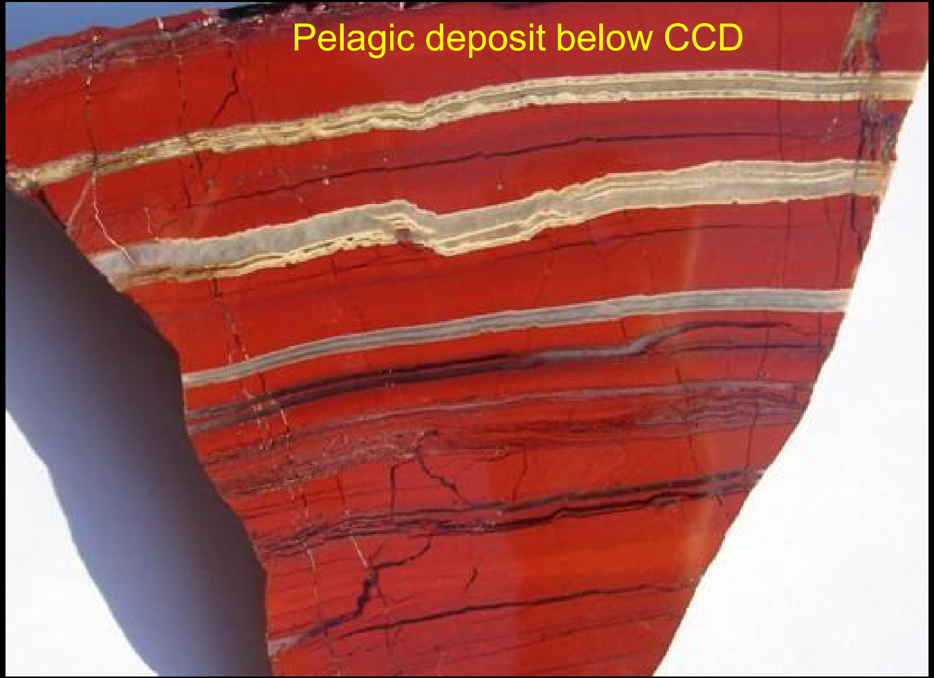
Depth to CCD, in km. Note how the CCD is deeper in the equatorial Pacific: this is due to high surface production and thus high flux of carbonate tests. Note also that the CCD is shallower in cold waters, because of both lower temperature and lower overall carbonate production. Again, the deepest CCD is in the Atlantic. From James, 2005

Carbonate precipitation today

Below the CCD carbonate is completely dissolved (3) and particular pelagic deposits can accumulate (e.g. radiolarites). Dissolution, however does occur also above the CCD (starts below the saturation depth) and also takes place within the sediment.



A *Harpoceras falciferum* "half ammonite". The flank on the left is presereved and clearly displays falcate ribs. To the right, instead, no sign of ornamentation is left. The dissolved side was likely in contact with undersaturated waters before the shell was buried completely. Image copyright Emily J. Swaby


Pelagic deposit below CCD

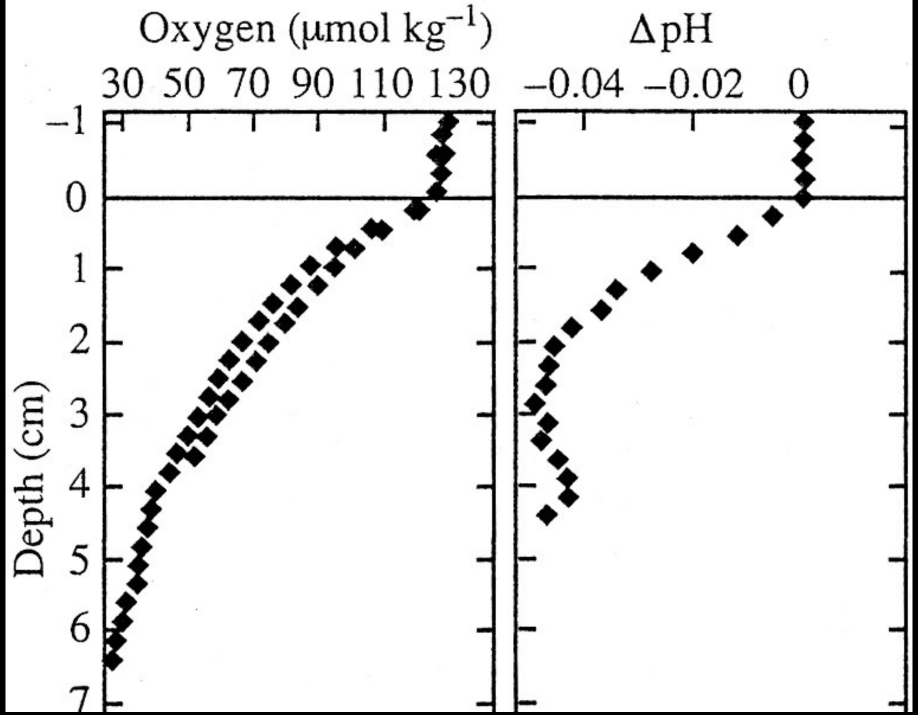
http://www.agatesandjaspers.com/big%20jasper%2002.jpg

Carbonate precipitation today

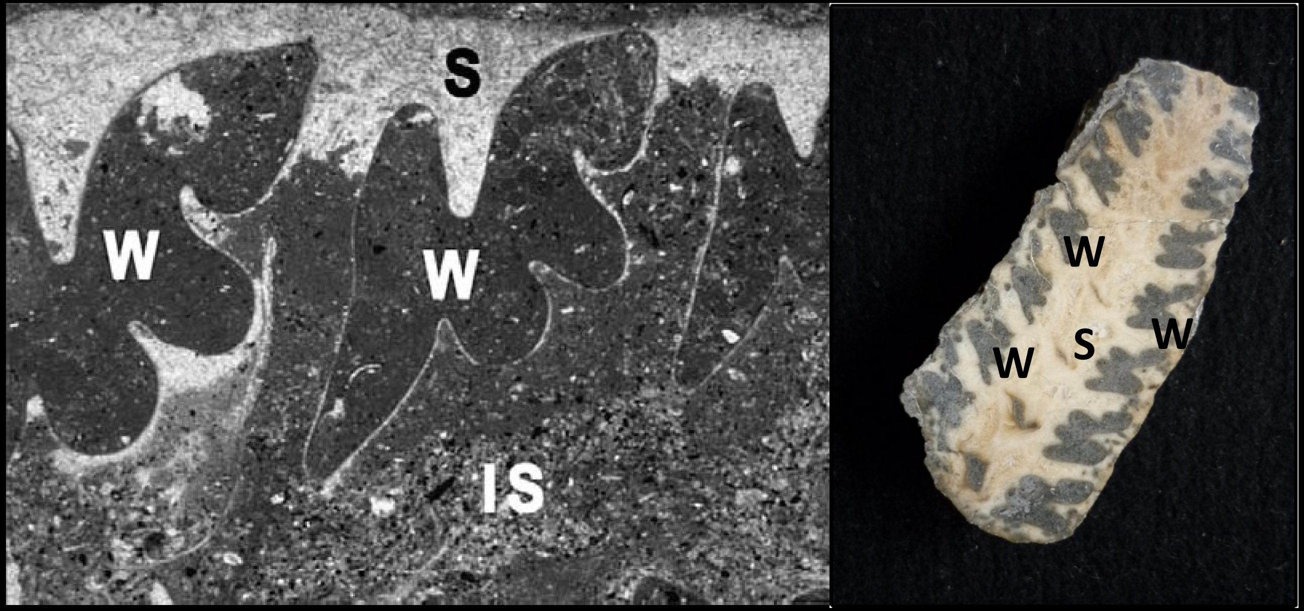
Superficial sediments are oxygenated thanks to bioturbation, and are thus inhabited by organisms which metabolism is based on aerobic respiration:

$$C_6H_{12}O_6 + 6\mathbf{O_2} \rightarrow 6\mathbf{CO_2} + 6H_2O + \text{energy}$$

If sediments are little porous (e.g., mud), CO_2 accumulates in pore waters, that quickly become undersaturated.



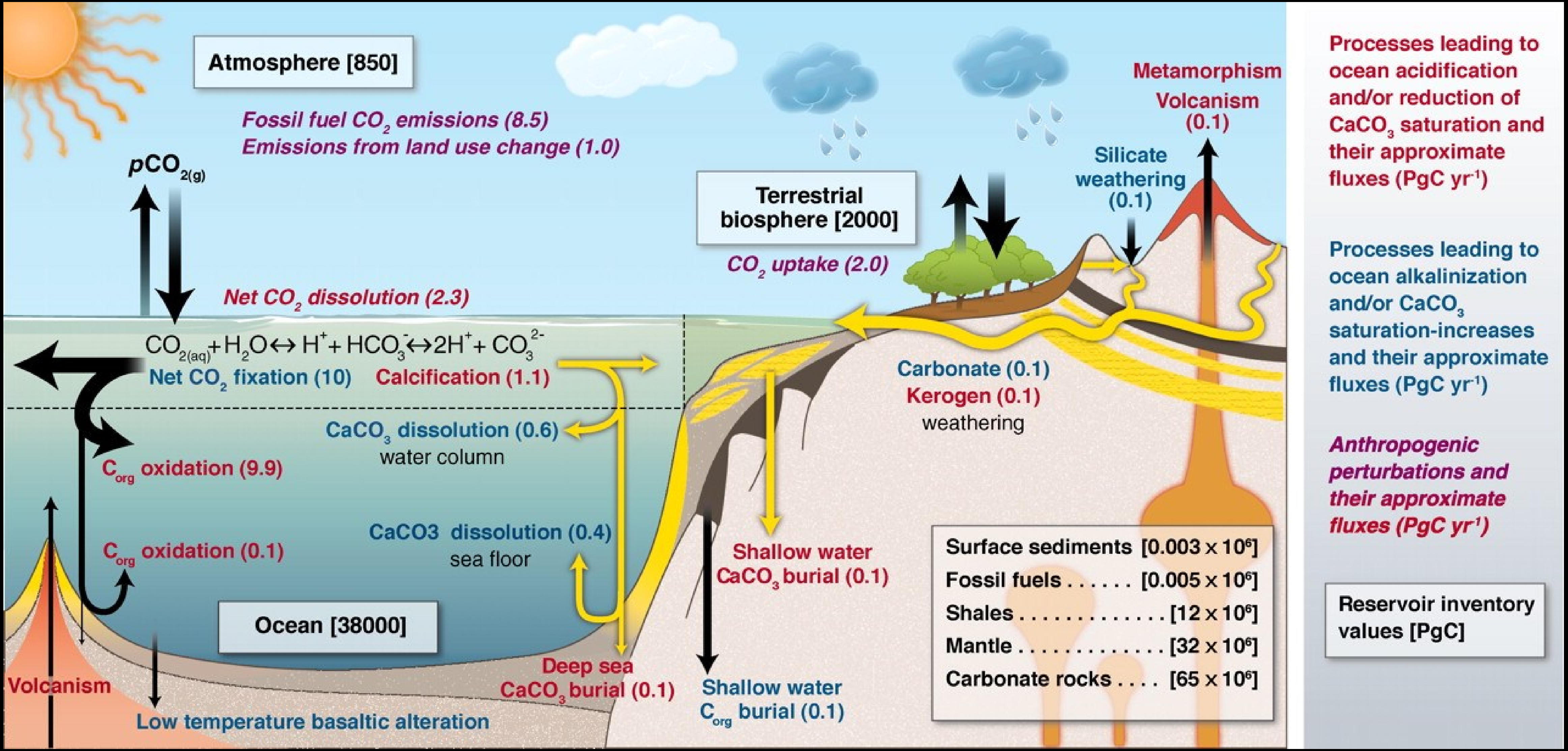
Oxygen and pH profiles in pore waters of the first 10 cm of sediment. Oxygen drops because it is consumed by respiration, while pH drops because pCO_2. increases. In a closed system as pore water, higher pCO_2 implies dissolution. From Broecker, 2006.



Left. Shallow water dissolution of a *Nerinea* shell (shallow water gastropod), and its partial substitution by sediment. From Sanders, 2003. Right. A *Nerinea* with preserved shell.

Carbonate precipitation today

Dissolution is a very relevant process. As little as **10%** of pelagic carbonate actually survives and ultimately becomes limestone



The carbon cycling in the oceans according to Hönisch et al., 2012.

Modes of carbonate precipitation

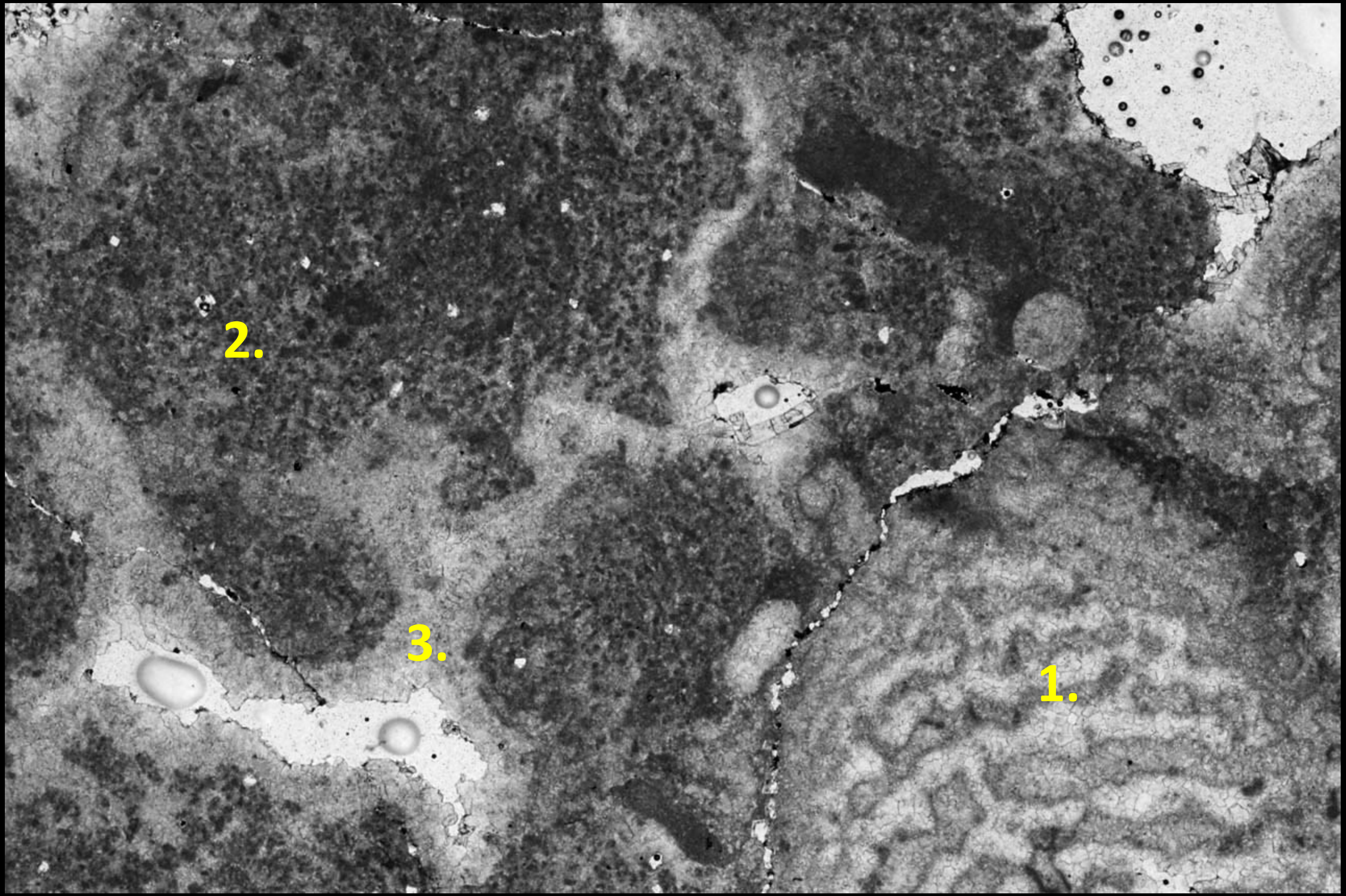
Precipitation of carbonate from seawater can be achieved fundamentally in three ways:

- 1. **Biotically controlled**
- 2. **Biotically induced**
- 3. **Abiotic**

1. Carbonate skeleton. Direct influence of organisms in the precipitation to produce structured skeletal components, shells etc.

2. Microbialite. metabolism of organisms (in this case microbs) creates the conditions for precipitation. Organisms does not produce carbonate directly.

3. Cements. Product of abiotic precipitation of carbonate

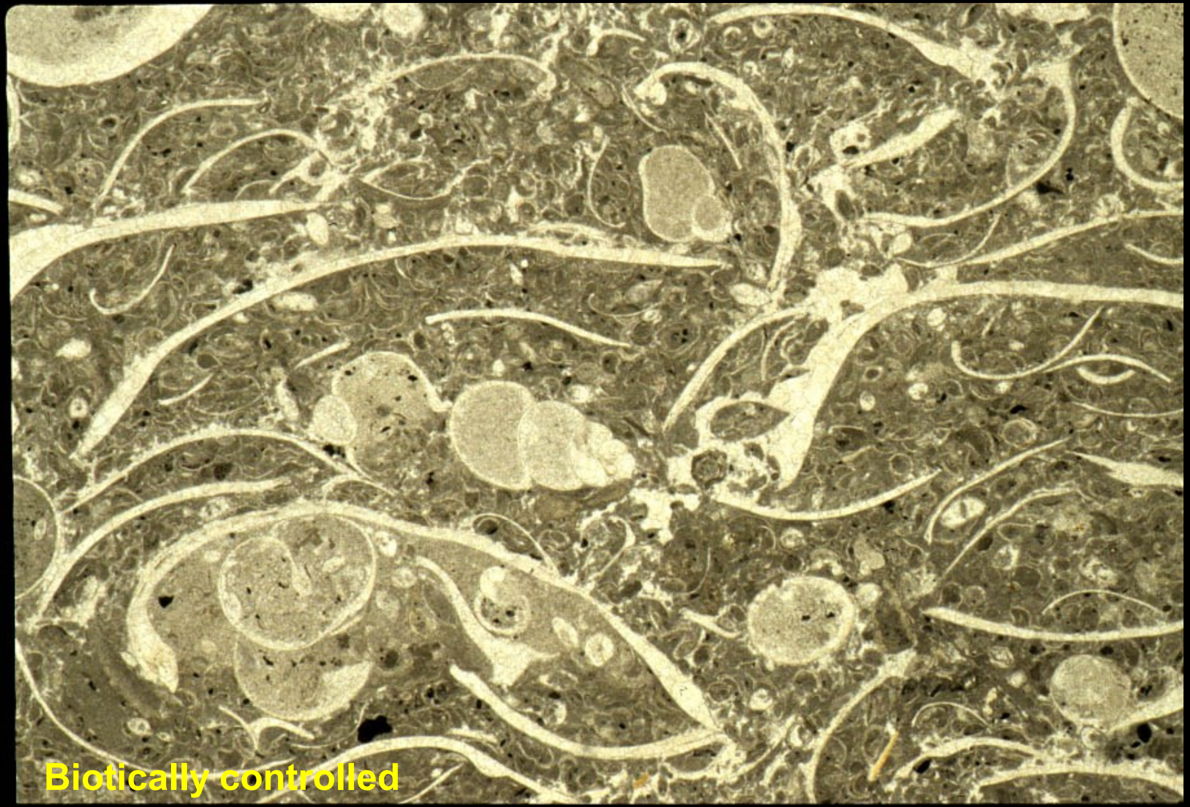


Biotically controlled precipitation

Some organisms precipitate carbonate and determine their mineralogy and structure (i.e., arrangement of crystals or crystallites in space), not only as a byproduct of their metabolism, but in a controlled and ordered way so that they produce an organized structure like a shell or skeleton.
This process, also known as biocalcification, is probably the most common mode of carbonate precipitation in Recent carbonate platforms. There are two sub-cases:

Biotically controlled precipitation is performed by:

autotrophic organisms
heterotrophic organisms.



Biotically controlled precipitation by autotrophs

These are the most common organisms in tropical carbonate platforms. Also calcareous plankton belongs to this category.

Corals are heterotrophic, but they are symbiontic with photosynthesizing zooxanthellae that are autotrophs.

Dasycladacean algae

middle Triassic, Latemar platform, Dolomites, Italy.

Calcareous nannoplankton

http://www.greenelectron-images.co.uk/sem/coccoliths/

Corals

https://commons.wikimedia.org/wiki/File:Coral_polyp_patterns,_Red_Sea_(38258546392).jpg

Biotically controlled precipitation by heterotrophs

The most common carbonate secreting organisms in Mediterranean-type carbonate platforms.

These include mollusks, echinoderms, solitary and deep-water corals, most foraminifers, bryozoans...

Foraminifera

Echinoderms

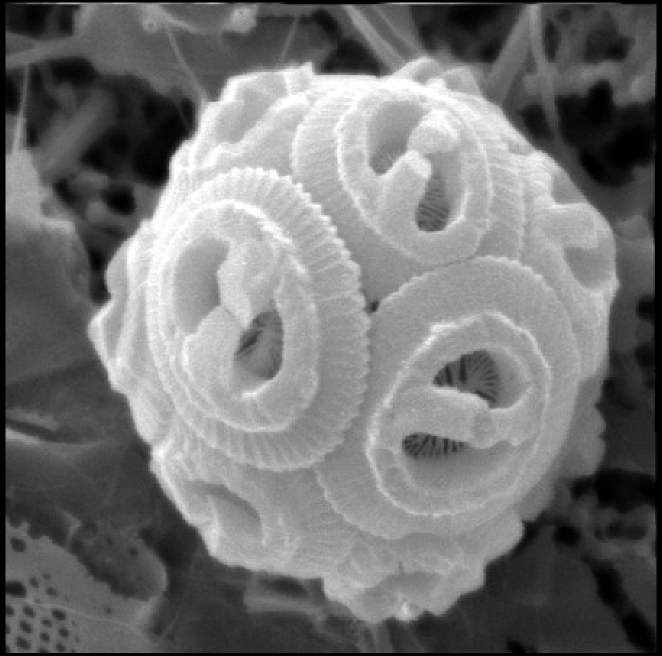
Bivalves, gastropods...

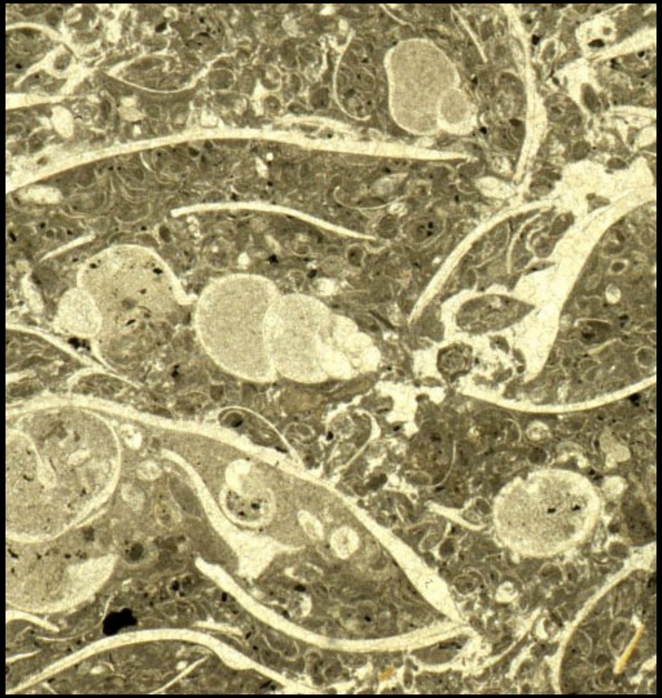
Biotically controlled precipitation

Biocalcification in marine calcifiers results in structures that are made either of calcite, aragonite or high-Mg calcite.
In modern organisms biotically controlled calcification can be an extracellular or intracellular process

Extracellular e.g. molluscs, corals organisms
Intracellular e.g. coccolitophores

Only hypotheses exist about the origin of biocalcification. Some authors have suggested that it may be a consequence of cytotoxicity of Ca^{2+} ion (e.g. Kemple and Kazmierczak, 1994).

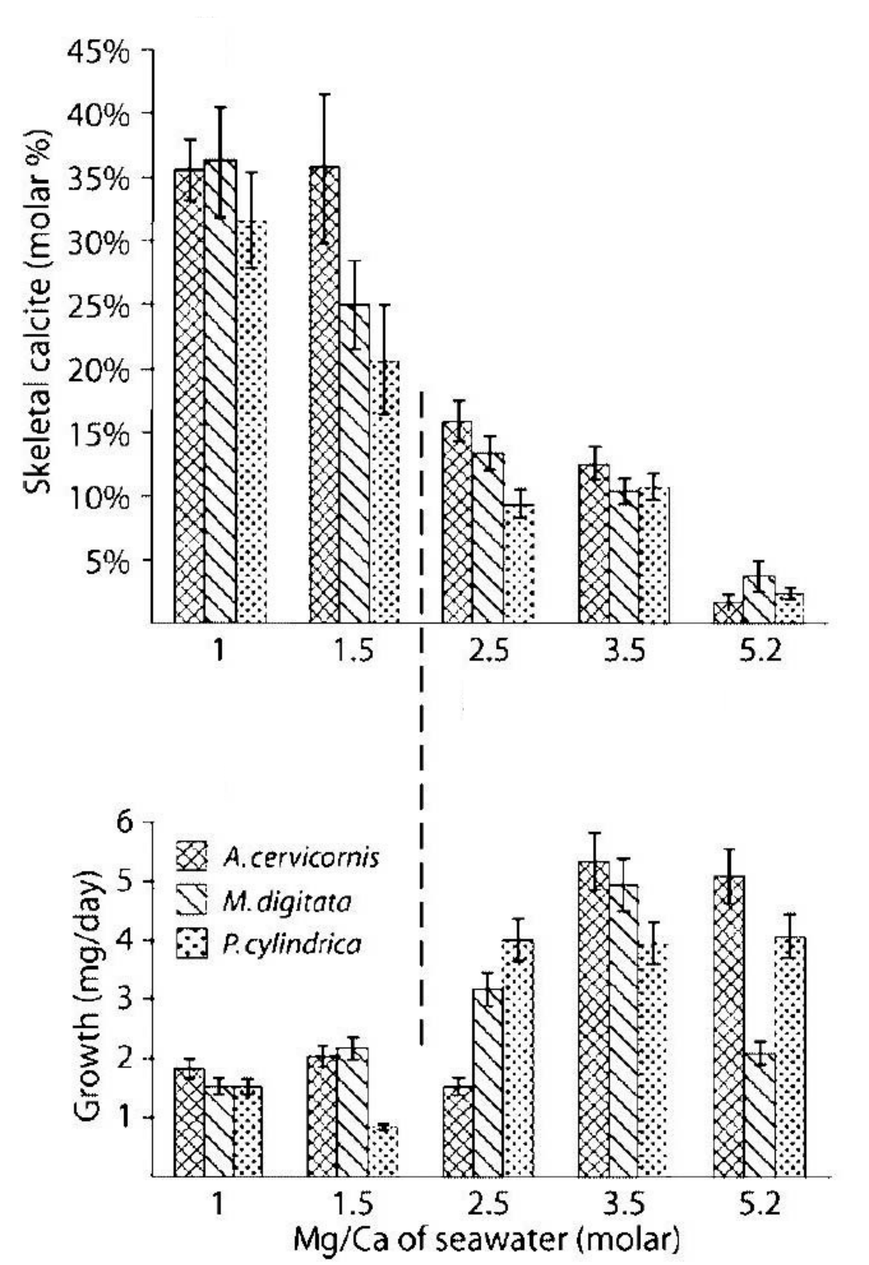




Influence of seawater chemistry on biotically controlled carbonate precipitation

Although carbonte-producing organisms can create the conditions favorable to carbonate precipitation through metabolic expenditure, biotically controlled precipitation is not independent from the external conditions.
Seawater chemistry can exert an important influence

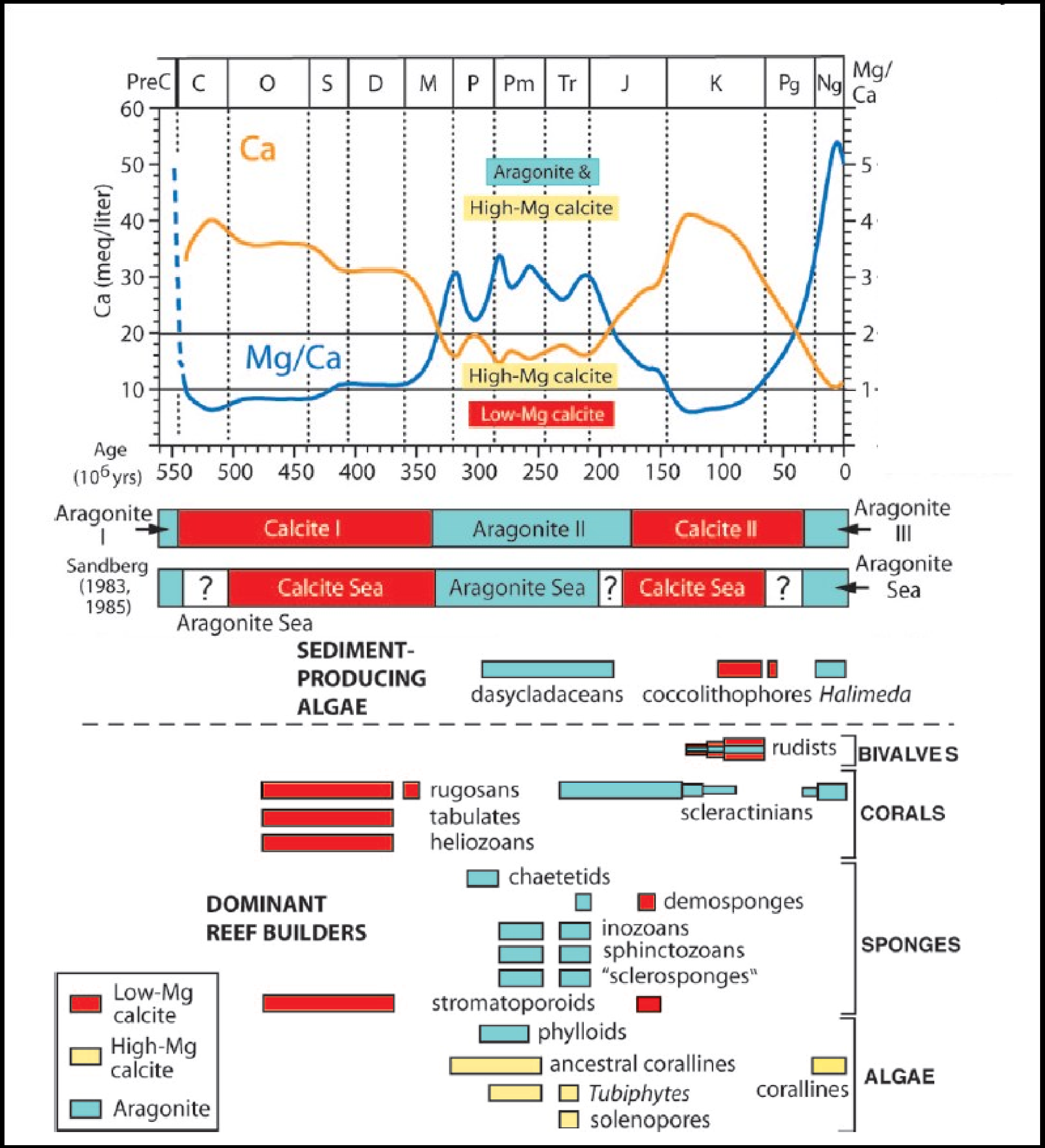
To the right you see results of an experiment on scleractinian corals. Three common species were grown in aquariums in artificial seawater having different Mg/Ca ratios.
Effects were observed both on the growth rate and on the amount of precipitated calcite.
At low Mg/Ca ratios corals grew more slowly and precipitated up to 35% less calcite.



From Stanley, 2008, slightly modified

Influence of seawater chemistry on biotically induced precipitation

Carbonate precipitated by organisms changed through time. It was observed that there were periods in which calcite was prevailing precipitated (**calcite seas**), and others in which aragonite was instead dominant (**aragonite seas**).
Modern ocean is an aragonite sea.
This phenomenon is thought to be linked to variations in the availability of **Mg** in seawaters possibly related to phases of more or lesser pronounced activity of mid atlantic ridges.



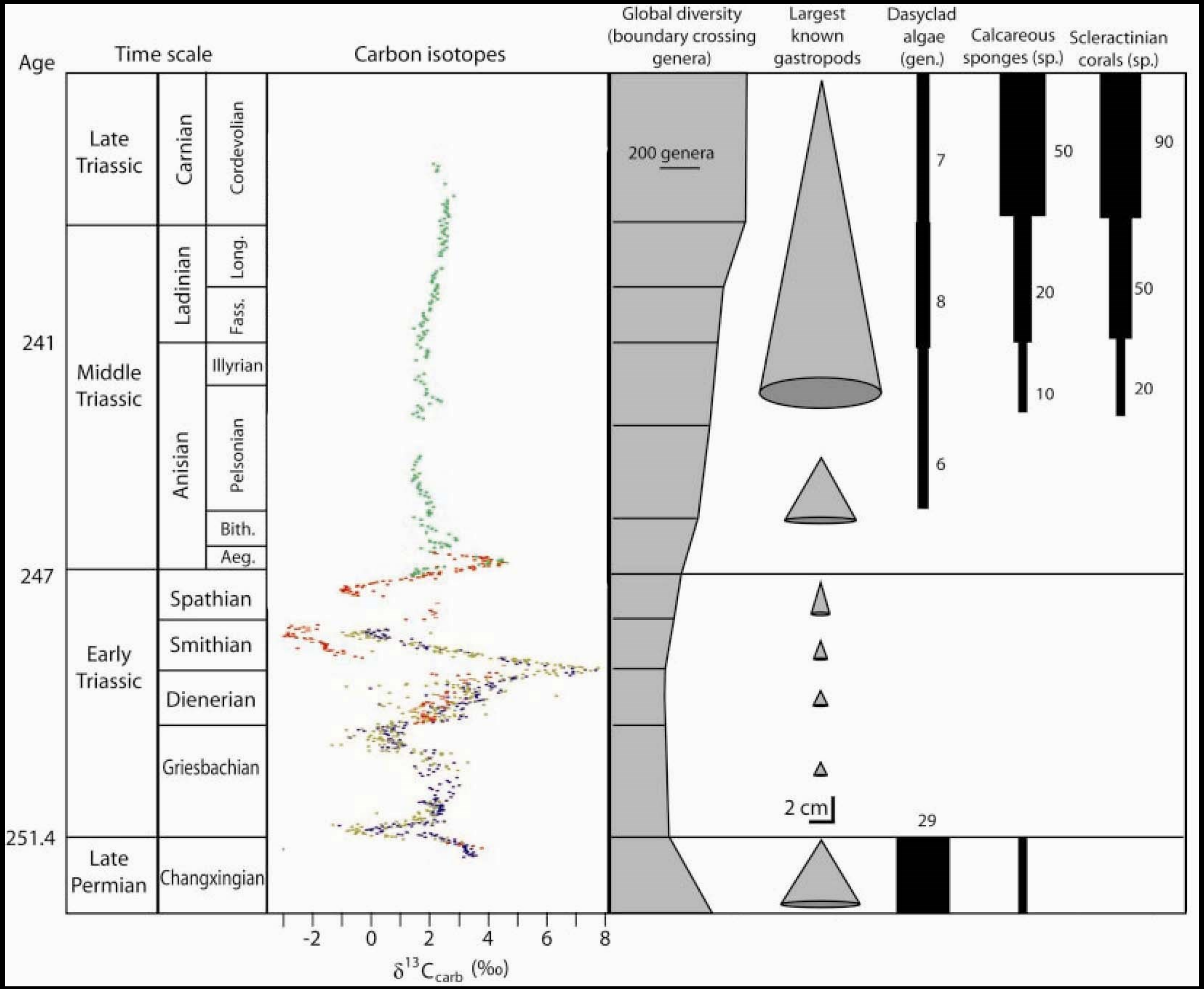
Stanley, 2004 modified

CARBONATE SEDIMENTOLOGY

Influence of seawater chemistry on biotically controlled precipitation

The example of early Triassic lazarus taxa.

Green algae disappeared at the P/T boundary, to “resurrect” in the middle Triassic. Clearly, they were there also in the early Triassic but couldn't form calcareous stems. They could not, apparently, “control” carbonate precipitation.

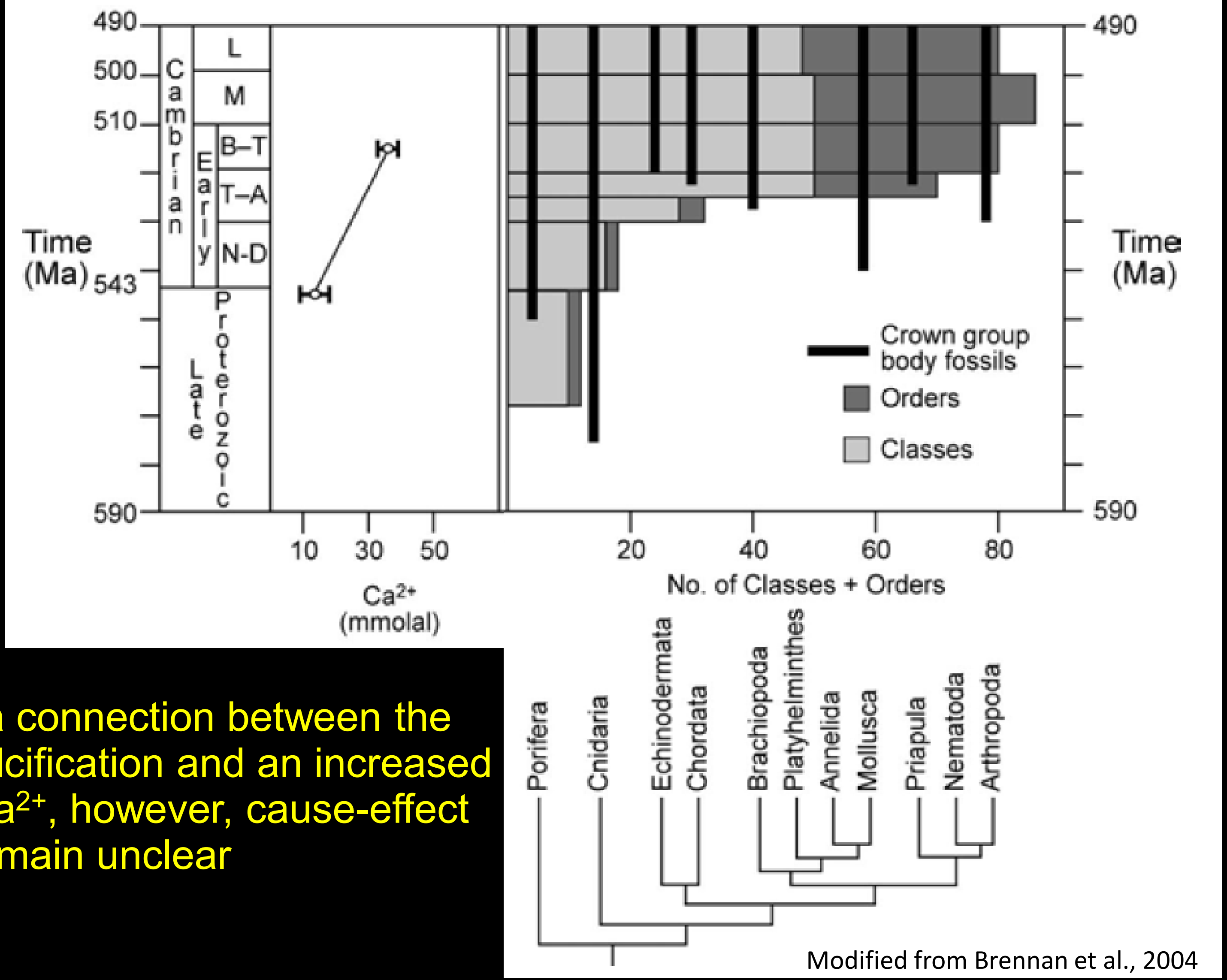


From Payne et al., 2004

Origin of biocalcification

Only hypotheses exist about the origin of biocalcification. Some authors have suggested that it may be a consequence of cytotoxicity of Ca^{2+} ion (e.g. Kemple and Kazmierczak, 1994).

The study of fluid inclusions in halites has revealed a sharp increase in Ca^{2+} concentration in ocean waters in the Early Cambrian. Approximately at that time a large increment in the number and diversity of calcifying organisms is observed



Modified from Brennan et al., 2004

This suggests a connection between the advent of biocalcification and an increased availability of Ca^{2+}, however, cause-effect relationships remain unclear

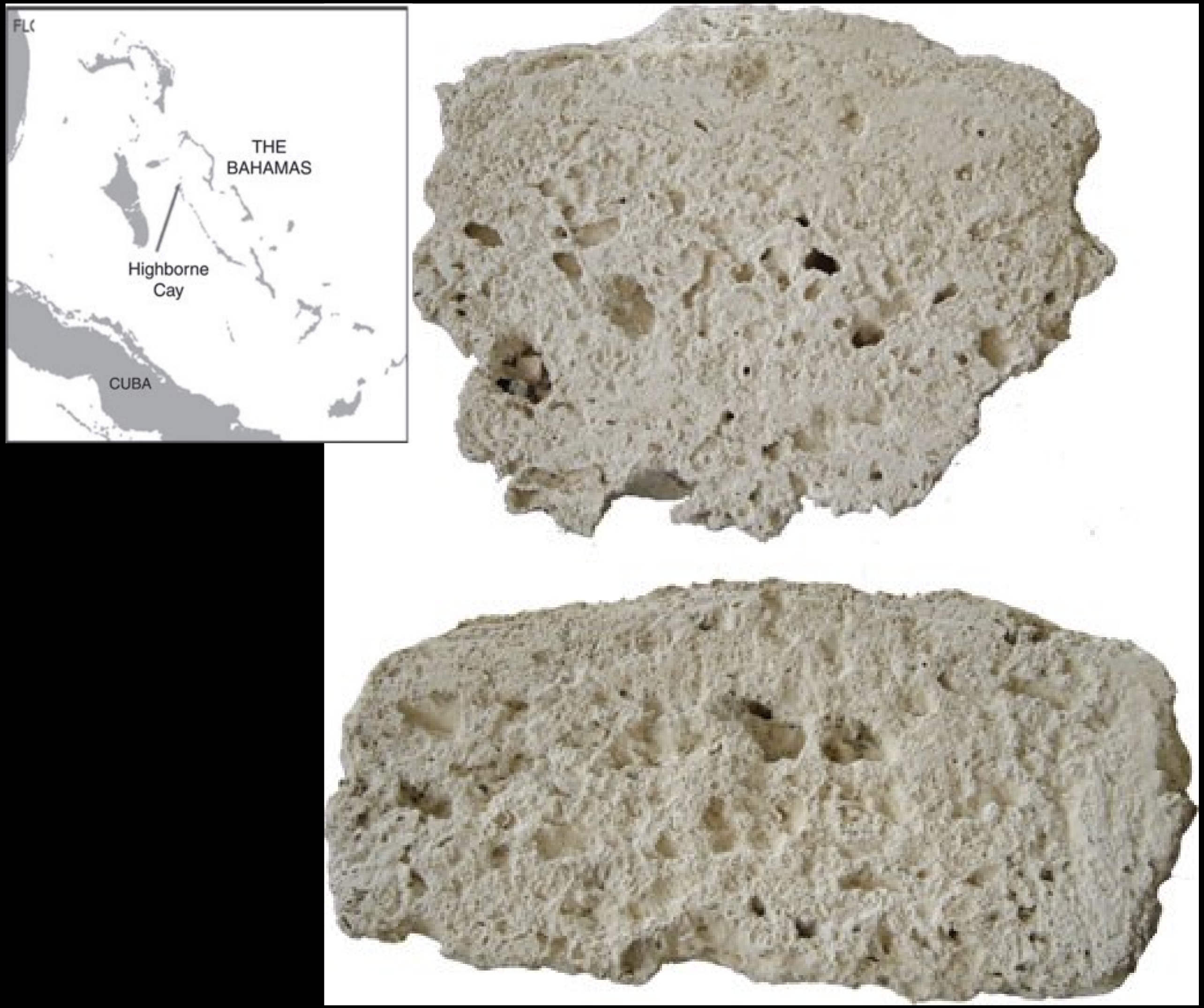
Biotically induced precipitation

In this mode, carbonate precipitates from seawater as a byproduct of biotic metabolism. Biotic activity can change seawater saturation state locally, or some organic compounds can act as a substrate for carbonate nucleation.

Although this is a complex group of processes, two examples of how metabolic activity has the potential of steering the precipitation-dissolution equilibrium reaction are photosynthesis and bacterial sulfate reduction:

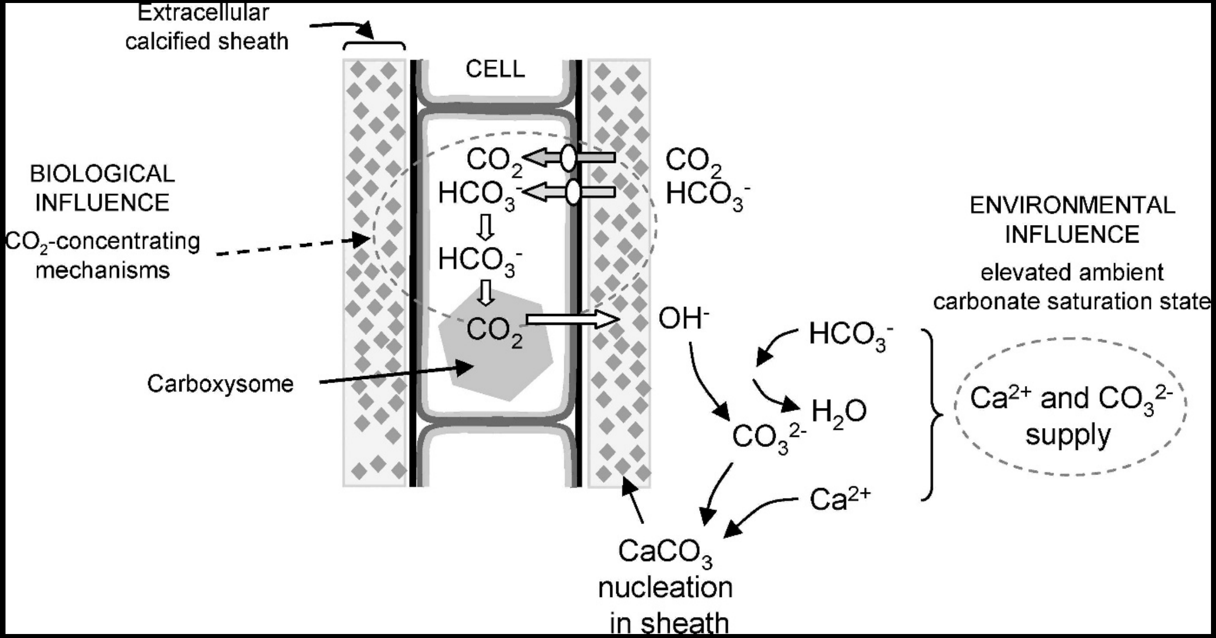
- Photosynthesis: $\mathbf{CO_2} + H_2O \rightarrow CH_2O + O_2$
- Bacterial sulfate reduction: $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2\mathbf{HCO_3^-}$

Biotically induced precipitation



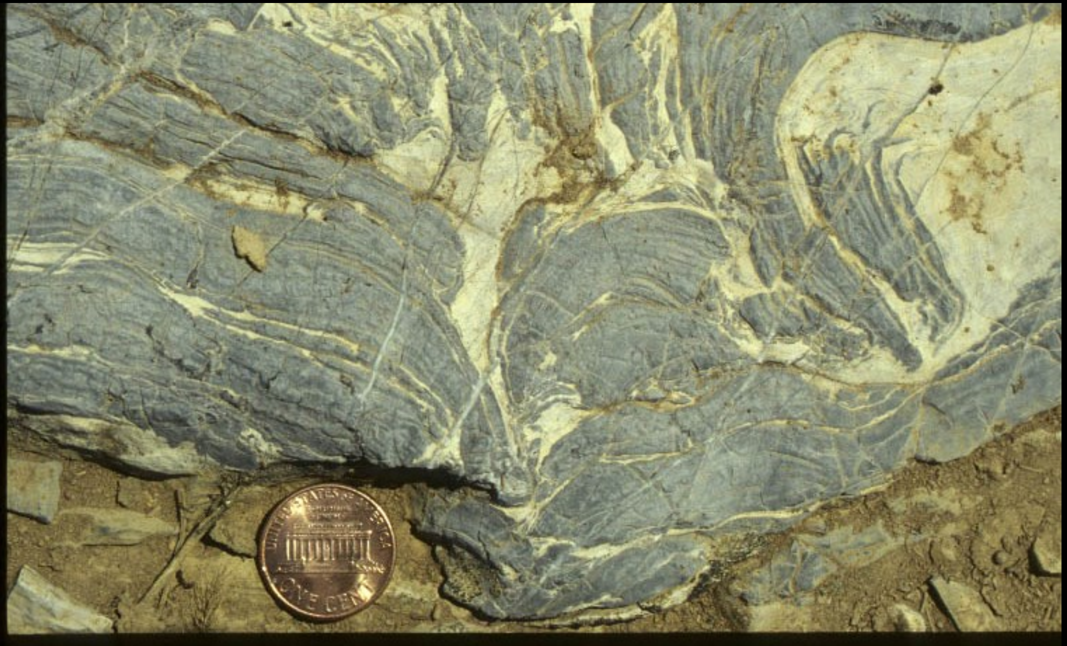
Thrombolitic microbialites from Bahamas.
Slab is ~ 1.5 m across

Calcified cyanobacterial filaments.
From Planavsky et al., 2009.



Inferred model of calcification in cyanobacteria
From Riding, 2009.

Biotically induced precipitation

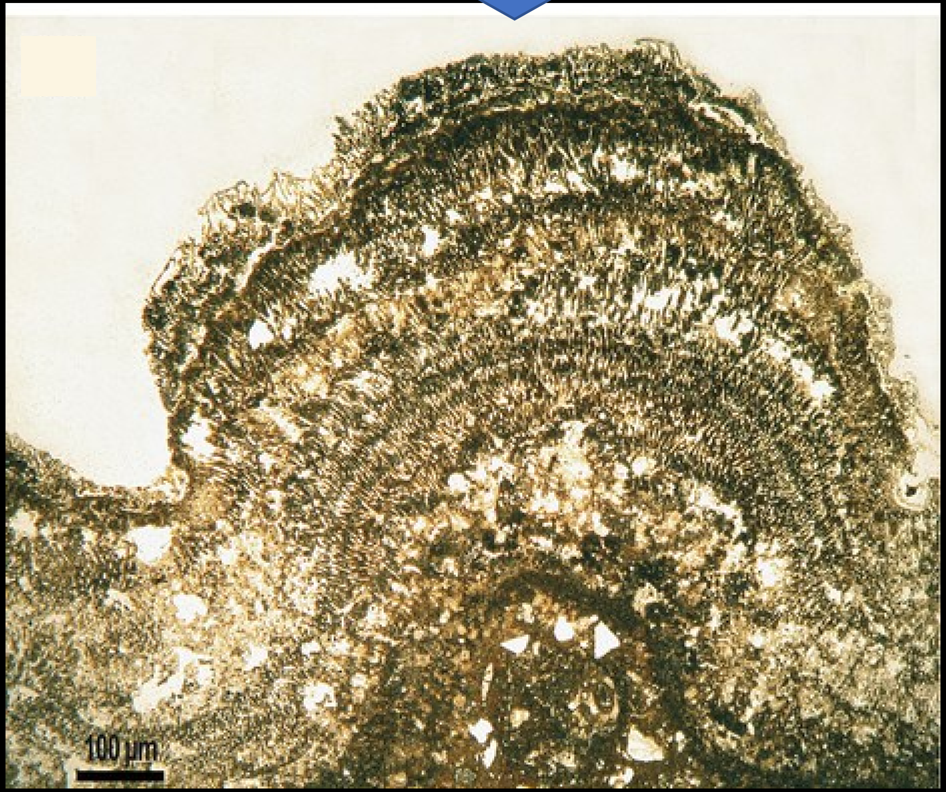


Stromatolites are a byproduct of microbial metabolism – in particular Recent stromatolites (left) are made of a consortium of cyanobacteria, performing photosynthesis, and sulfate reducing bacteria. The fossil example to the right is from the Ordovician of the Appalachians (Va)

Cayeuxia is a calcimicrobe, common in Paleozoic and Mesozoic carbonate platform rocks, which is interpreted as the rests of cyanobacterial tufts. Carbonate was supposedly precipitated from a seawater which Ω was enhanced by photosynthesis.

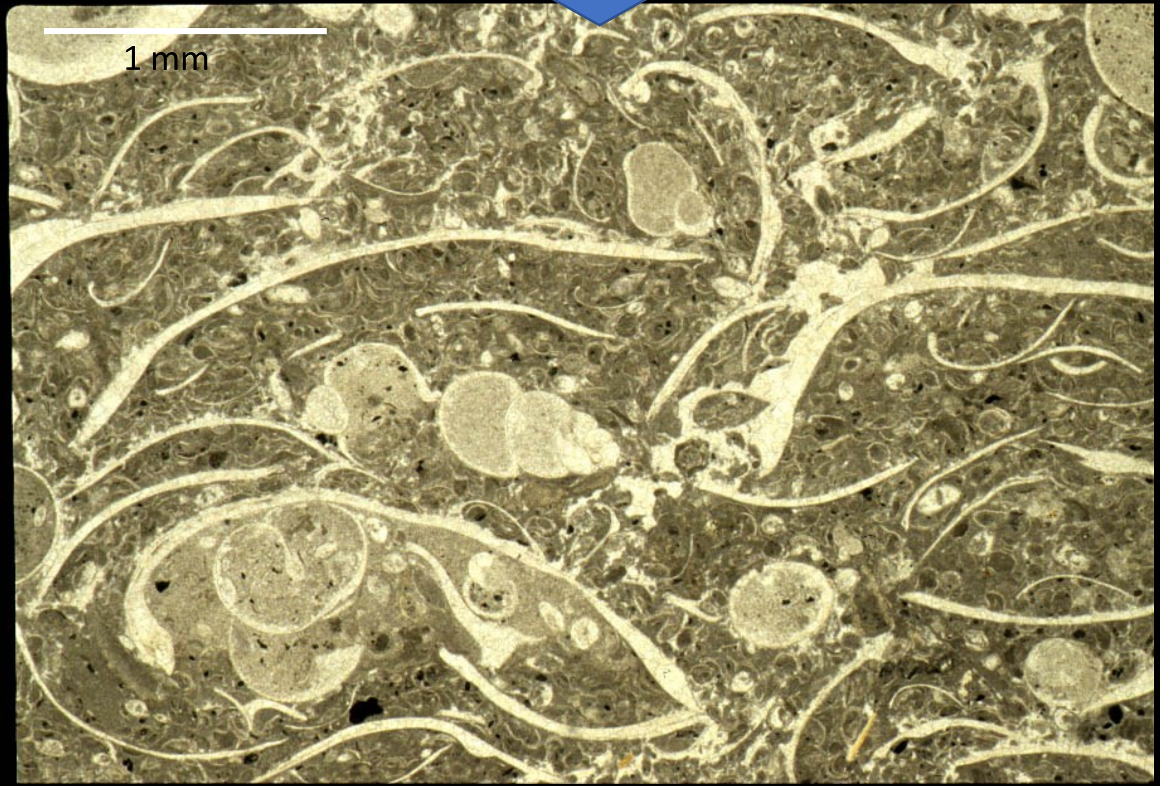
Biotically induced vs biotically controlled calcification

biotically induced



In biotically induced calcification, precipitation of carbonate is a by-product of the metabolism of microorganism

biotically controlled



In biotically controlled calcification, organism produce shells and other hard parts with a defined and ordered structure.

Abiotic precipitation

There is a kinetic barrier to abiotic precipitation from seawater. However, this barrier can be overcome...

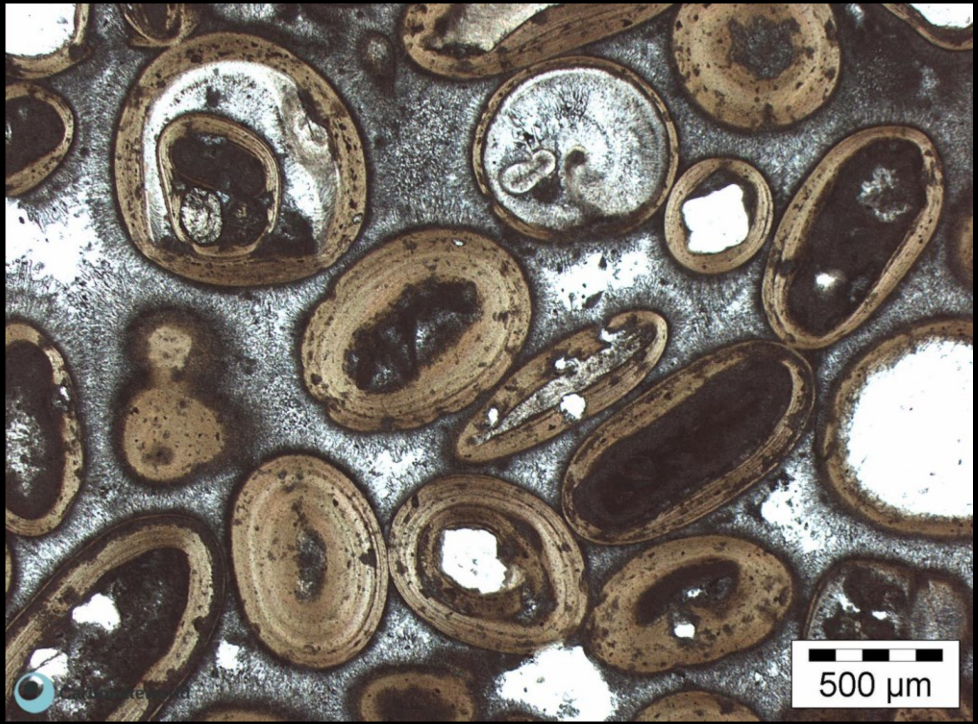
- By concentrating salts, including carbonates, with evaporation (e.g., precipitation of carbonates at the base of evaporite series)
- From Precambrian to the Mesozoic, because the composition of seawater was different (much higher TIC and Ω)*
- In the environment of formation of ooids

However, in the present oceans, the volume of carbonate precipitated abiotically is nearly negligible.

* Despite those different chemical compositions, precipitating from Mesozoic seawater could have been still not so easy after all. Lee and Morse (2010, Geology, 38:115-118) were not able to precipitate calcite from an artificial seawater of Cretaceous composition until they brought it to a **Ω of 28 or higher**

Abiotic precipitation

Two recent examples from the Bahamas: whitings and ooids.



Ooids today form in seawater in a few places of the World, including the Bahamas. Ooids are abiotic carbonate grains. However, recent works demonstrate that microbes (e.g., bacteria) are always associated to ooids. The role of these microbes in the formation of the ooids is still unclear.

Scanning electron microscope image of aragonite needles of a whiting

Whitings on the Great Bahama Bank. Whitings are areas of shallow water with light color which are dusty with carbonate mud. Hypotheses exist that whitings are a case of abiotic precipitation. Others believe it is carbonate mud reworked from the sea floor, or that its precipitation is triggered by microbial activity. From http://strata.geol.sc.edu

Which of these definitions of sedimentary rocks is more accurate?

Sedimentary rocks are produced by the weathering of preexisting rocks and the subsequent transportation and deposition of the weathering products.

Encyclopaedia Britannica

Sedimentary rocks are formed from pre-existing rocks or pieces of once-living organisms. They form from deposits that accumulate on the Earth's surface.

US Geological Survey

Rock [...] formed by the deposition of either the weathered remains of other rocks, the results of biological activity, or precipitation from solution.

Wicktionary

Take home messages from this class

- Carbonate precipitation today occurs in two main settings: deep water and shallow water
- Carbonate not only precipitates, but also dissolves in seawater. Dissolution in seawater is mainly linked to the saturation conditions. Dissolution processes also occur within the sediments, after deposition
- Carbonate precipitation occurs in three pathways (or modes): biotically controlled, biotically induced, abiotic
- Even biotically controlled precipitation is strongly controlled by the chemistry of seawater