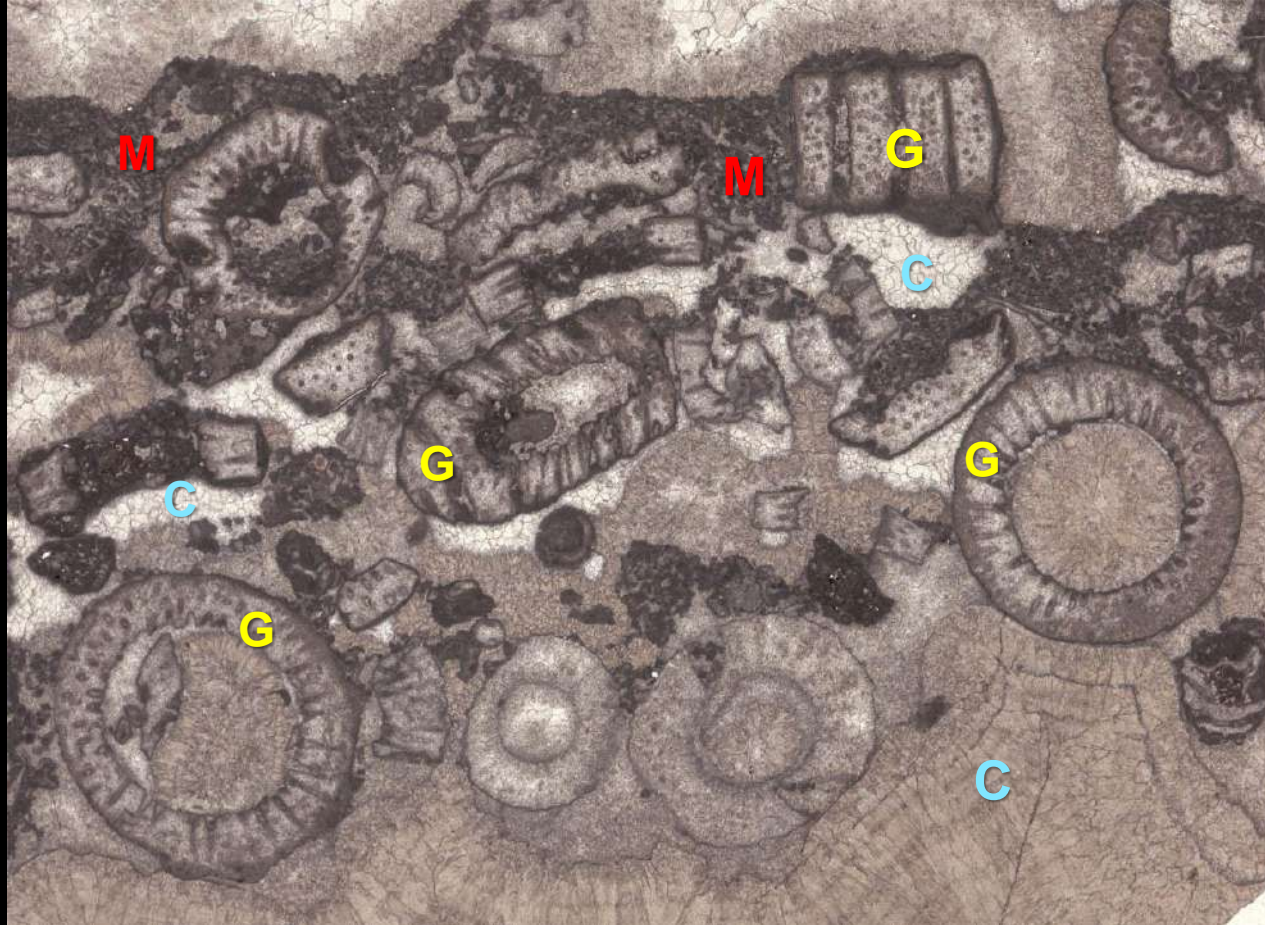


Carbonate rocks.
How do we look at them and what may
we see in them?
(continued)



What is left? Micrite and Cements



What is not grains in a carbonate rock, i.e. the matrix, can be made of two elements

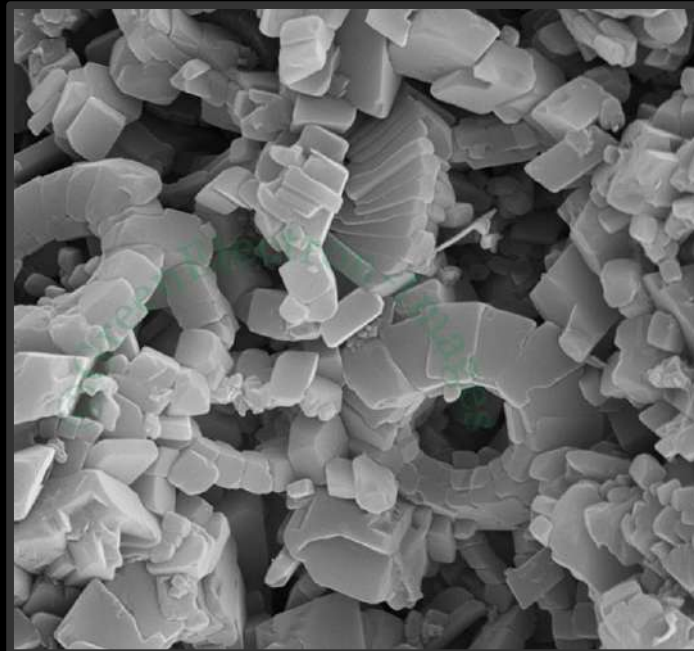
Micrite: fine grained carbonate mud that it indistinguishable observing hand samples and even at the optical microscope is difficult to characterize

Cements: Cements are the result of the diagenetic history of the carbonate rock

The origin of micrite

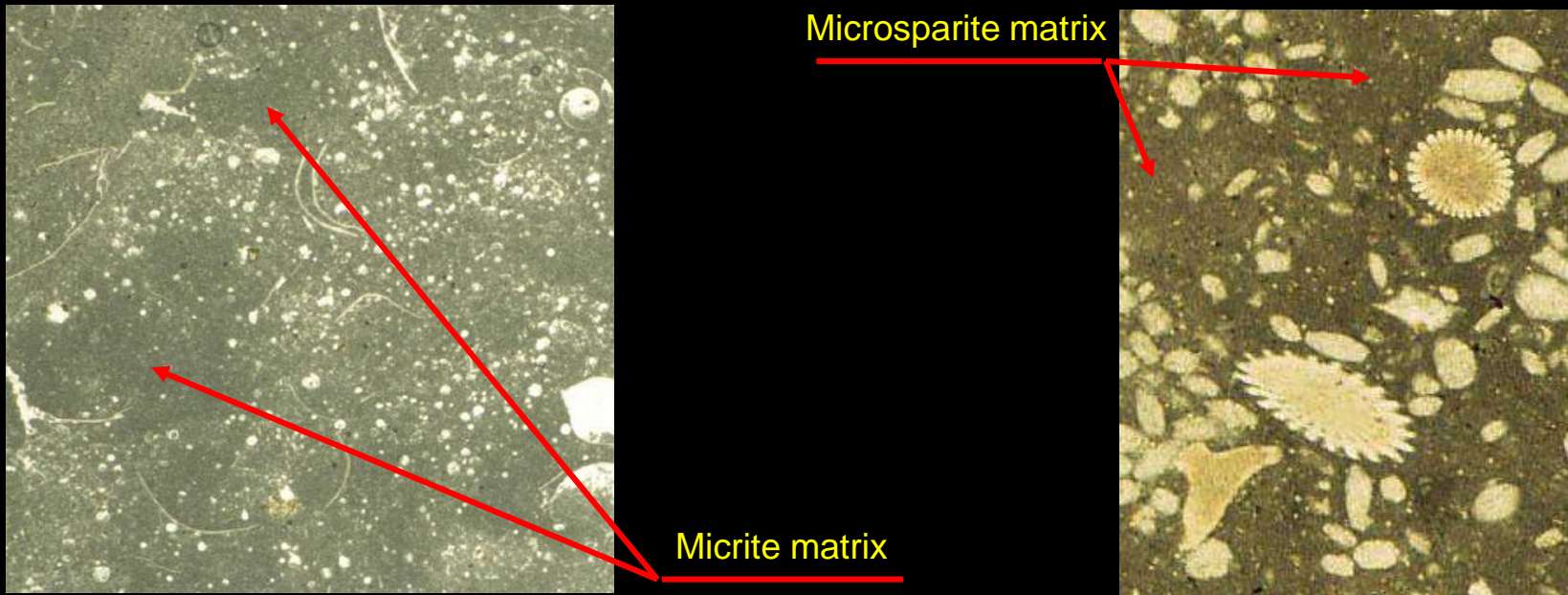
Carbonate mud may originate through several processes, including:

- **Abiotic** precipitation from highly supersaturated seawater (whittings)
- Precipitation **induced by microbial activity**
- Frantumation of **calcareous algae** (e.g., *Halimeda*, *Penicillus*)
- **Bioerosion**: the activity of borers, as fungi or sponge, on carbonate substrates
- **Mechanical erosion**, or abrasion, of carbonate grains or rocks by waves and currents
- Accumulation of **calcareous nannofossils**



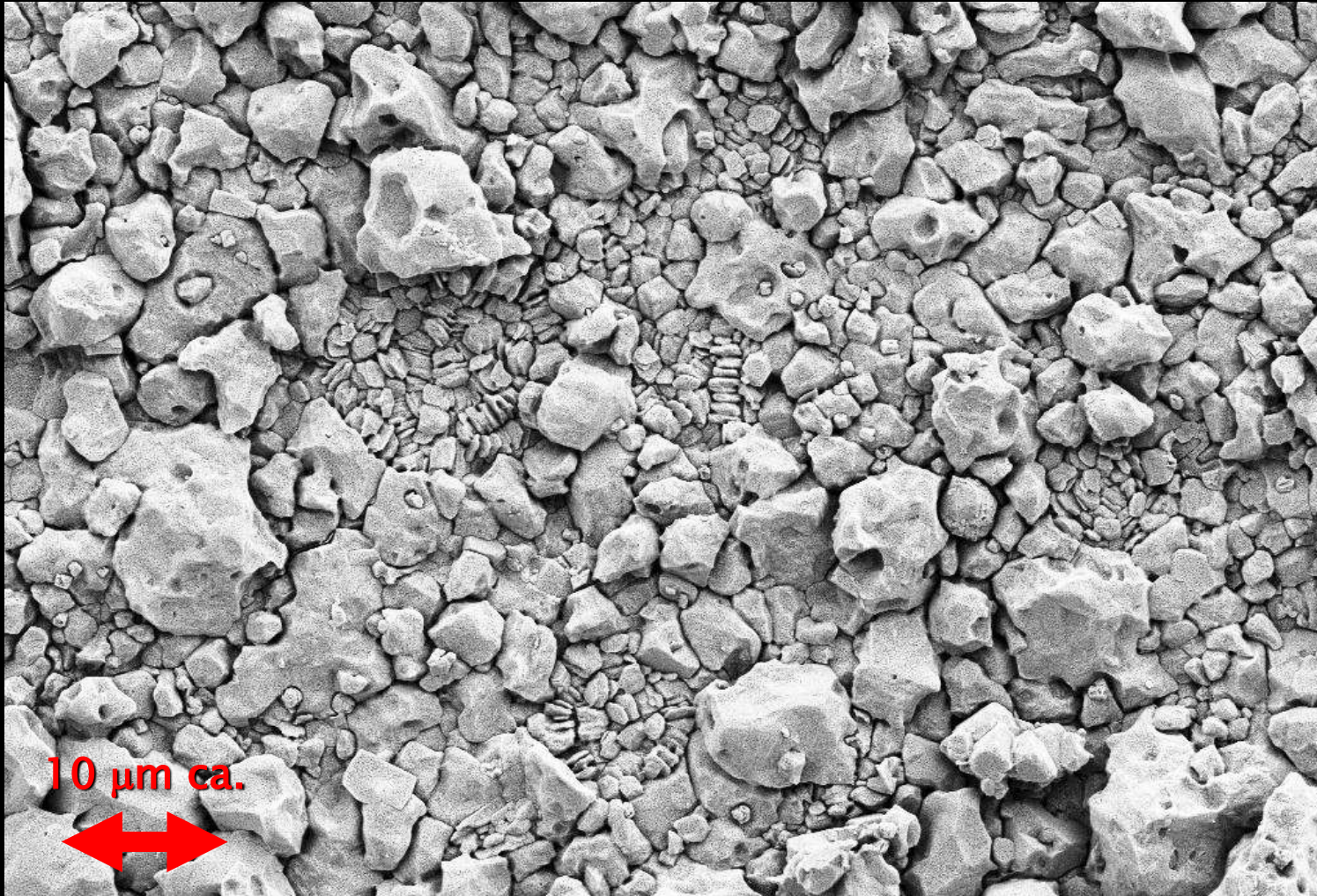
Definitions:

- **Micrite:** As in Microcrystalline calcite, refers to fine carbonate which crystals are less than 4 μm on average. This is a strictly descriptive term, and the 4 μm threshold (Folk, 1959) is arbitrary. Other authors go for 5 microns.
- **Microsparite:** interstitial carbonate with average diameters within 5 - 30 μm . Often identical to micrite under a microscope, the term is strictly descriptive, however, micrite and microsparite are often formed by distinct diagenetic processes.



Micrite and microsparite are hard to distinguish at the optical microscope. They are normally observed using a Scanning Electron Microscope

Micrite under the scanning electron microscope

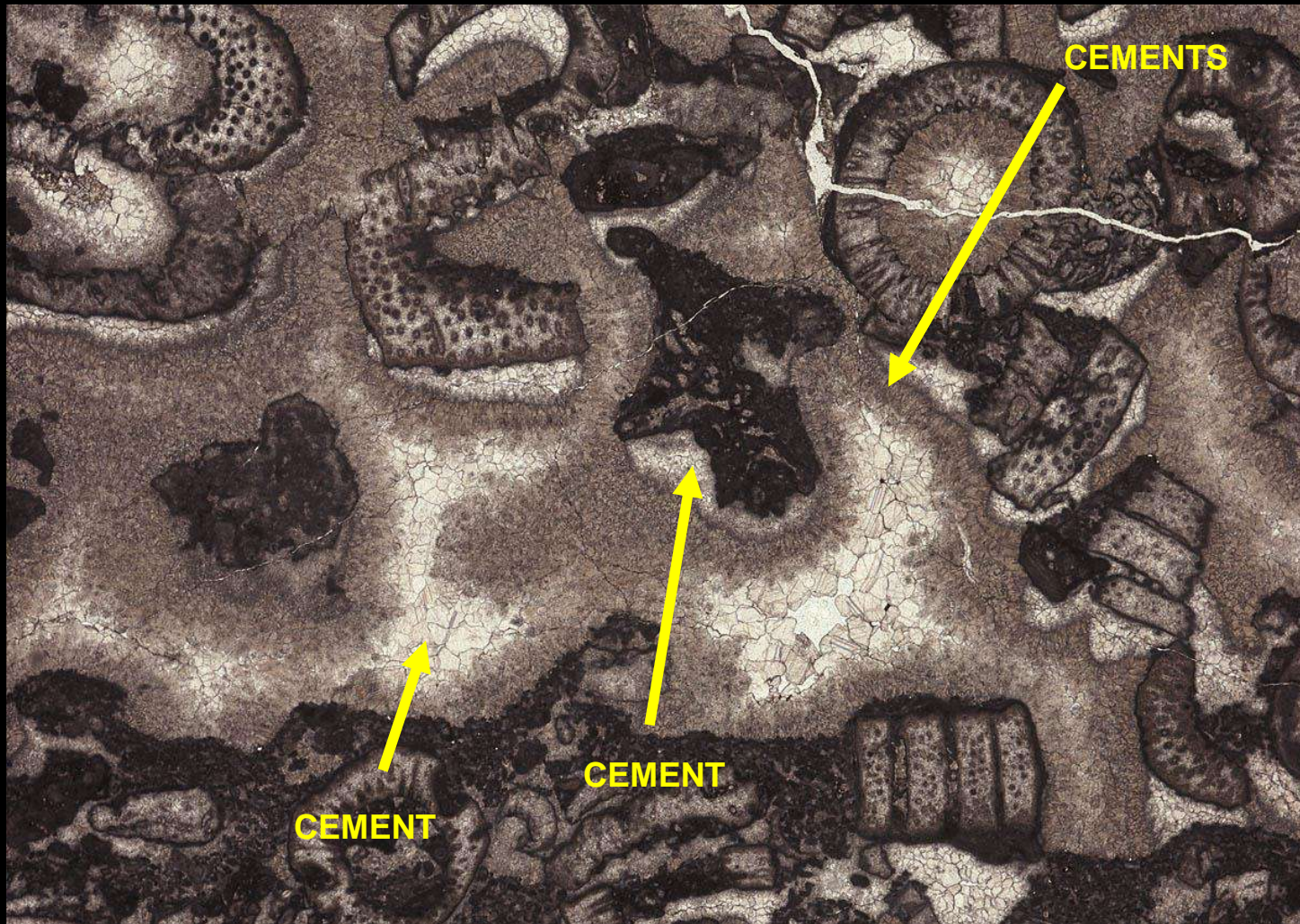


In this late Norian hemipelagic limestone of the Lagonegro Basin (Southern Apennines) the micrite component is nanofossils (*Prinsiosphaera* sp.). The rest is microsparite.

Cements

Cements in carbonate rocks are mainly a product of **diagenesis**. Keep in mind that diagenesis is a very important phenomenon for carbonate rocks.

Diagenesis starts immediately after carbonate precipitated. Virtually **all carbonate rocks show signs of diagenesis at various degrees.**



Diagenesis

Diagenesis is a process that involves physical and chemical changes in sediments that start once it is deposited.

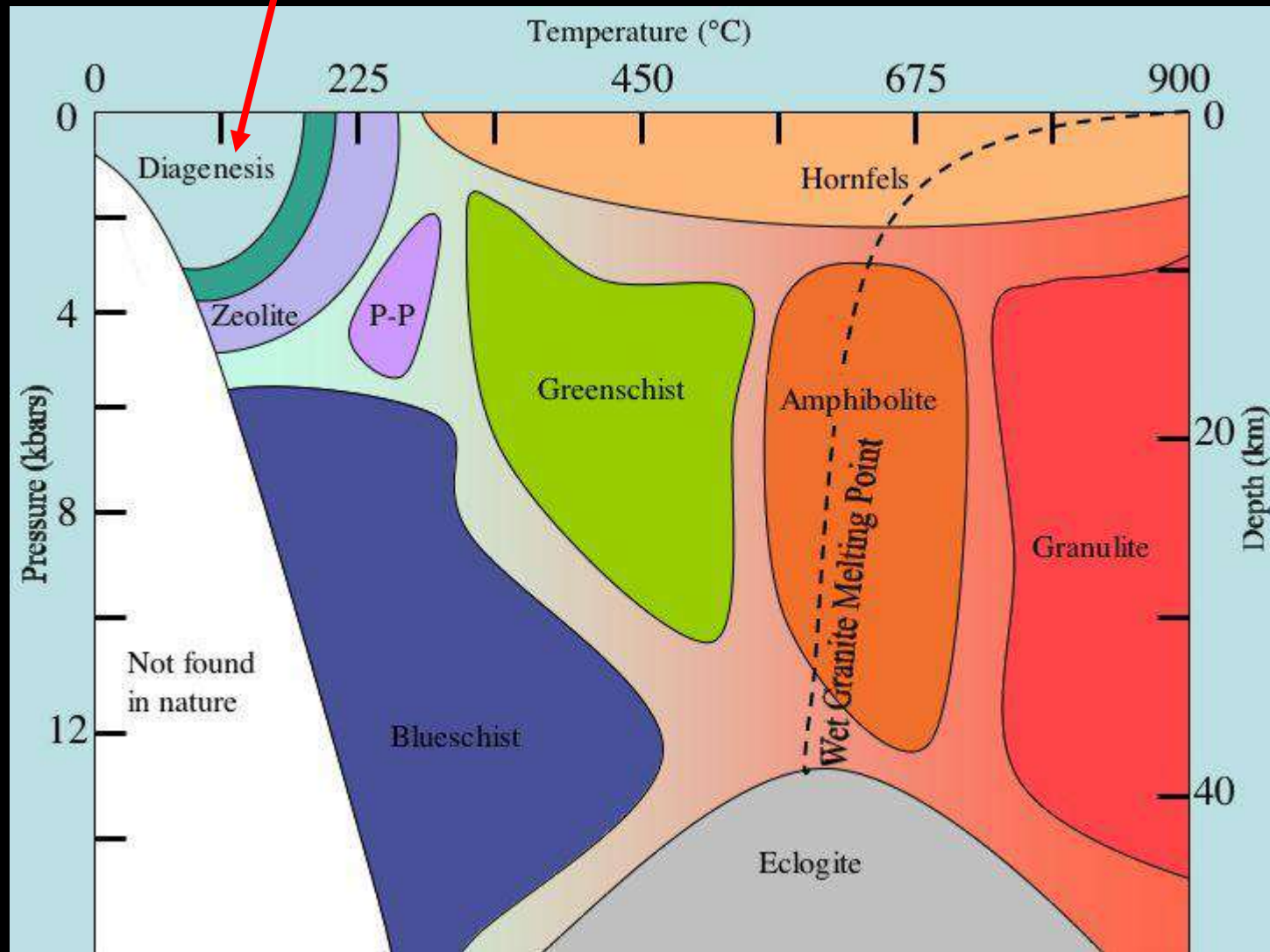
These changes are induced by increasing temperature and pressure during burial and may involve the circulation of fluids.

Carbonate sediments are particularly prone to diagenesis.

- compaction (under the load of overlying sediment)
- progressive pore occlusion
- **dissolution**
- **cementation**
- transformation of metastable carbonates (aragonite and high-Mg calcite) into low magnesium calcite (and dolomite)
- dolomitization*

Normally, a diagenized limestone is **only made of low magnesium calcite**. High magnesium calcite and aragonite are present in limestones only in cases of exceptional preservation.

The realm of **diagenesis**: between deposition and metamorphism

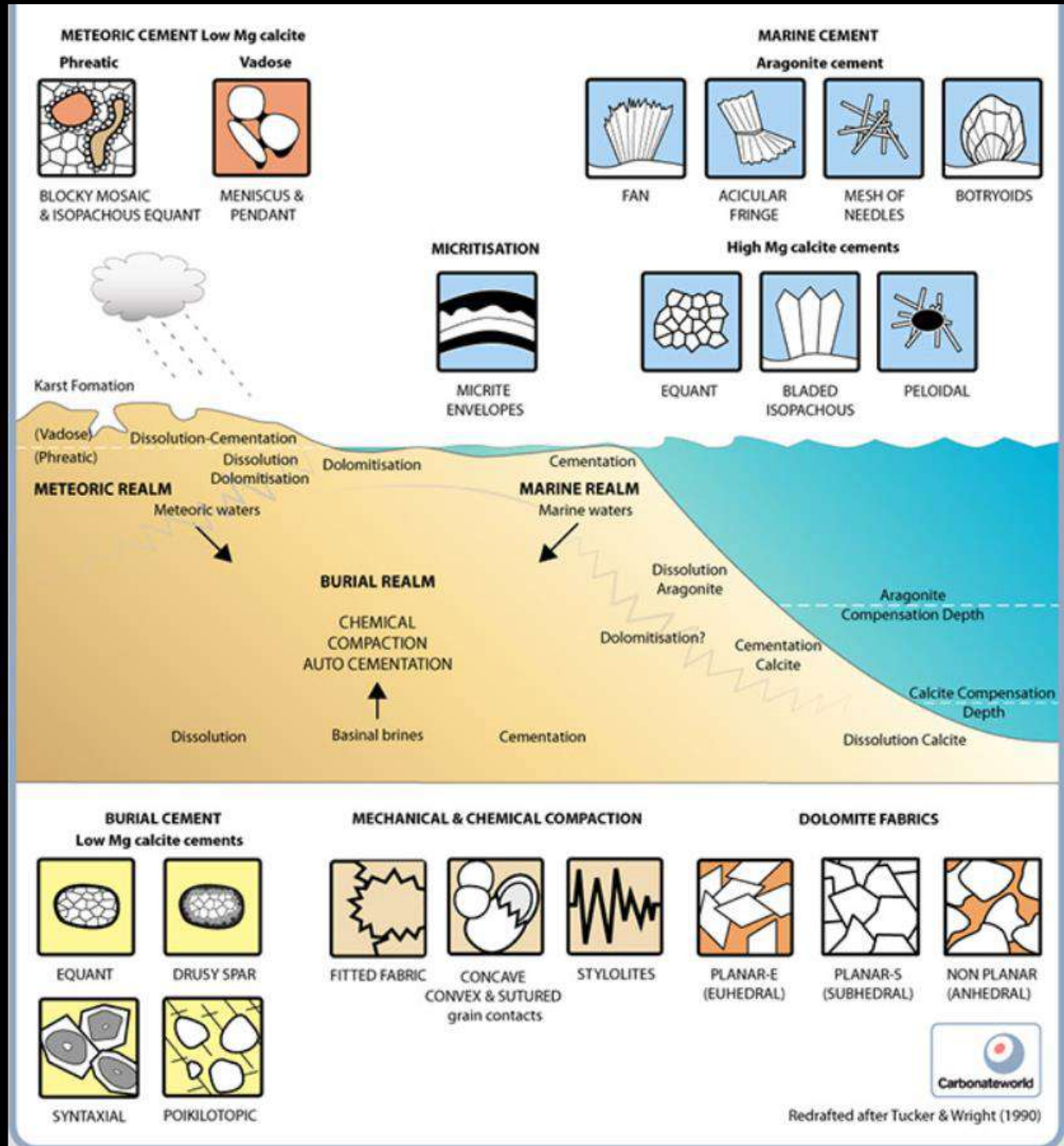


from Wikipedia

Diagenetic processes and environments and diagenetic products products in a carbonate platform

Carbonate platform are subject to a number of **diagenetic processes**.

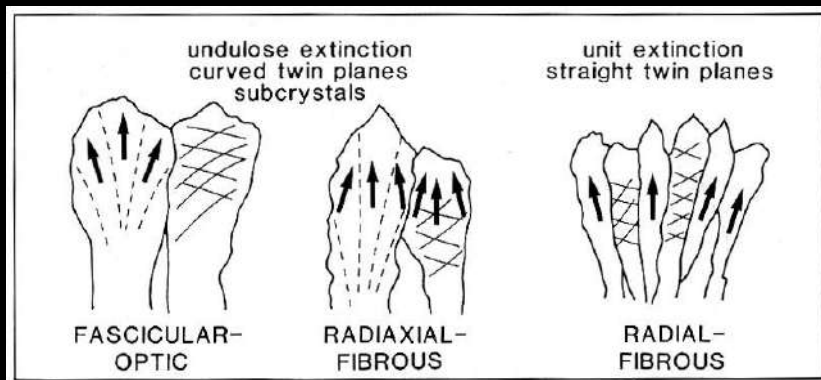
Besides processes that occur in deep waters, such as **dissolution** below the ACD and CCD, and processes linked to the burial (e.g. **cement formation** and **stylolitization**), their being close to the ocean/atmosphere interface, implies a series of diagenetic phenomena linked to the interaction with meteoric waters (a notable example is **karst formation**) and the mixing of these latter with seawater.



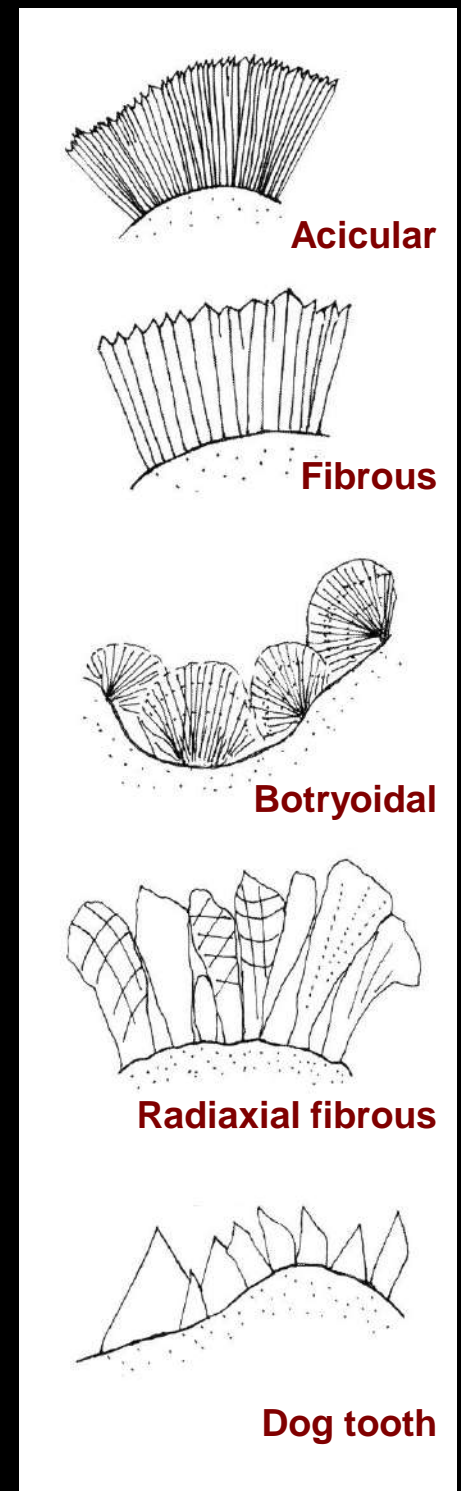
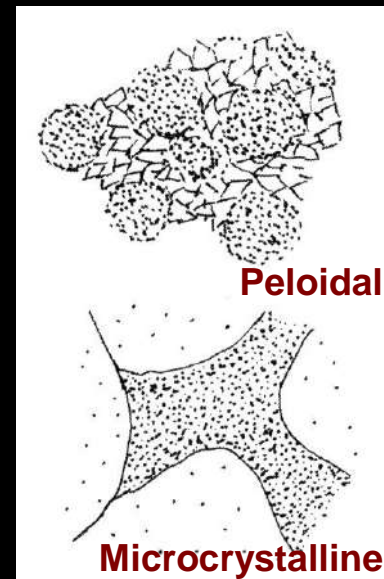
Morphology of cements

Cements are first of all described by the shape of their crystals and crystal aggregates.

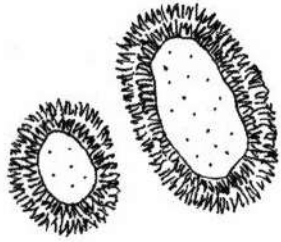
- **Aragonite** forms needles with square terminations
- **Calcite** forms scalenohedrons with pointy terminations, but it is rarely idiomorphic.



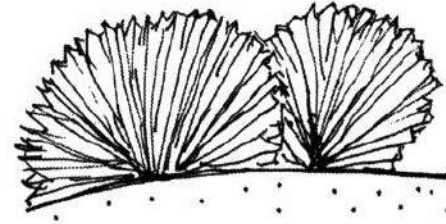
Radiaxial fibrous cement, and its variations, are calcite cements normally characterized by turbid appearance due to abundant inclusions. In the most common varieties, extinction is undulated.
From Tucker and Wright, 1990



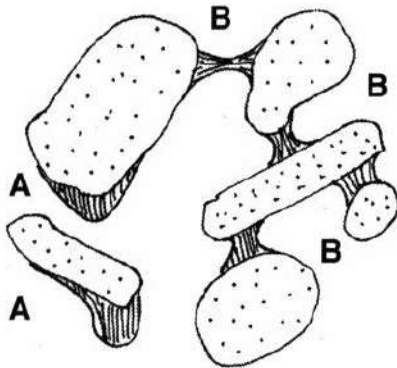
Cements in function of their relationships with grains



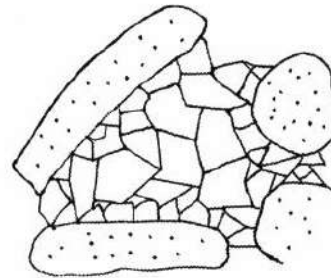
Isopachous



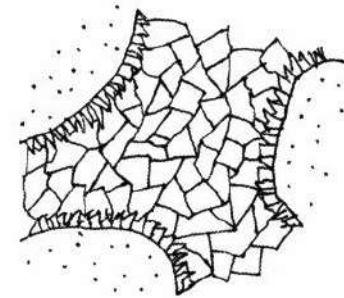
Botryoids



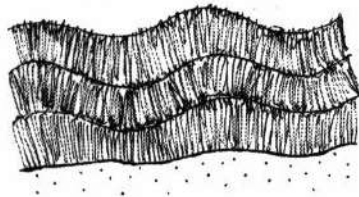
**Pendant (A)
Meniscus (B)**



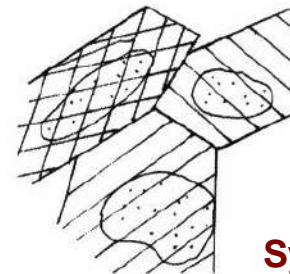
Drusy mosaic



Equant mosaic



Crusts

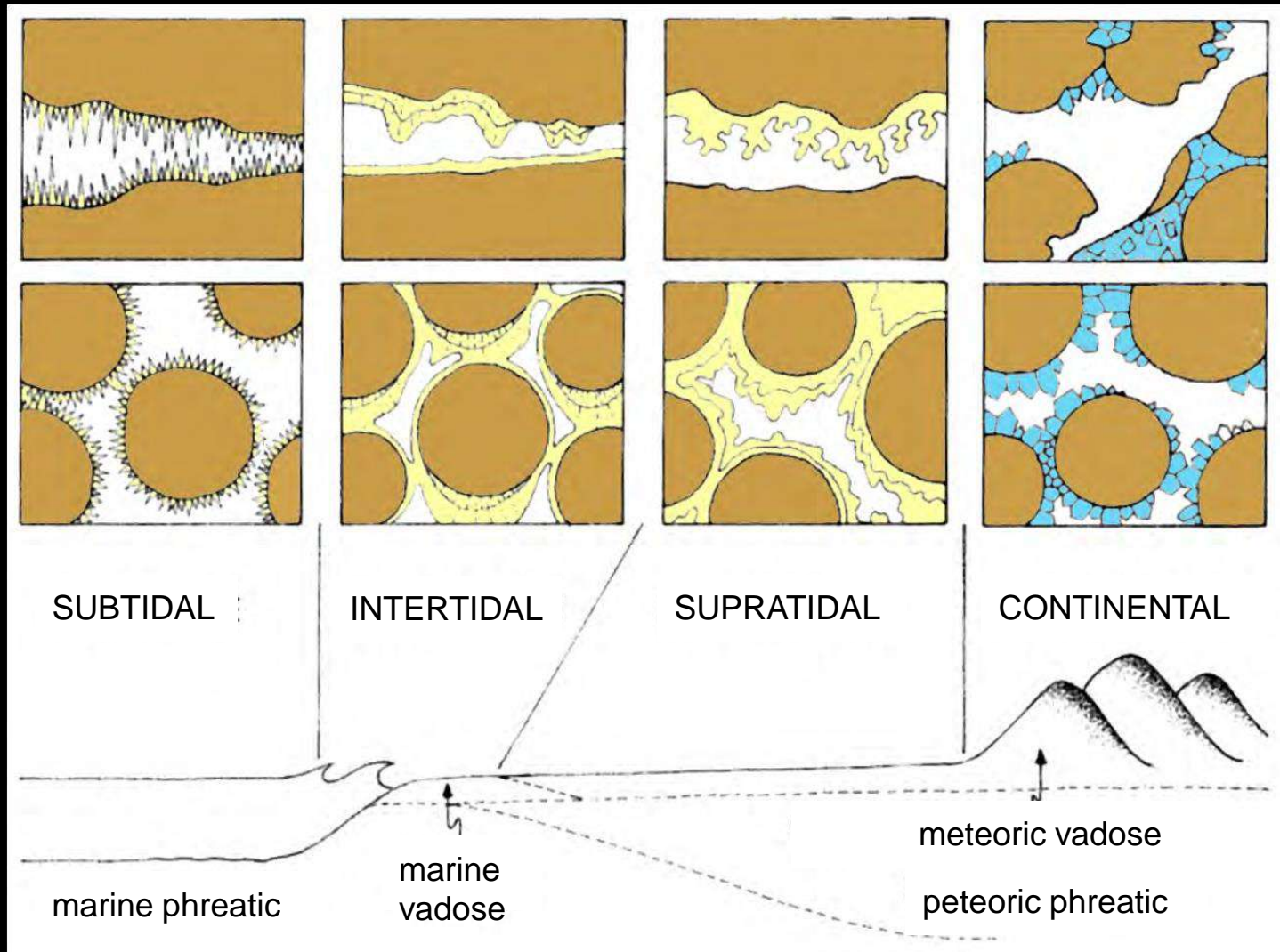


Syntaxial

ISOPACHOUS

MENISCUS/PENDANT

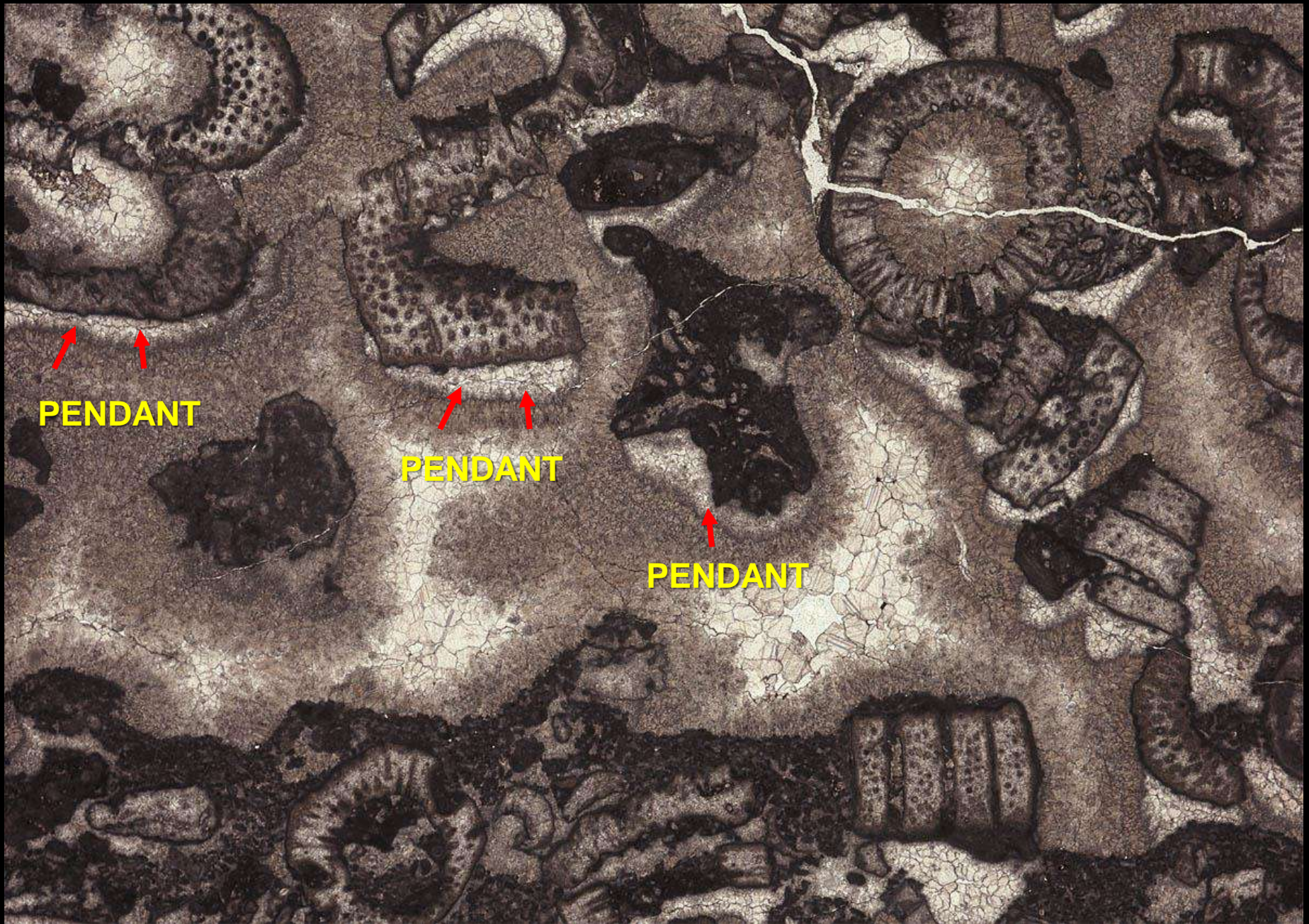
MOSAIC



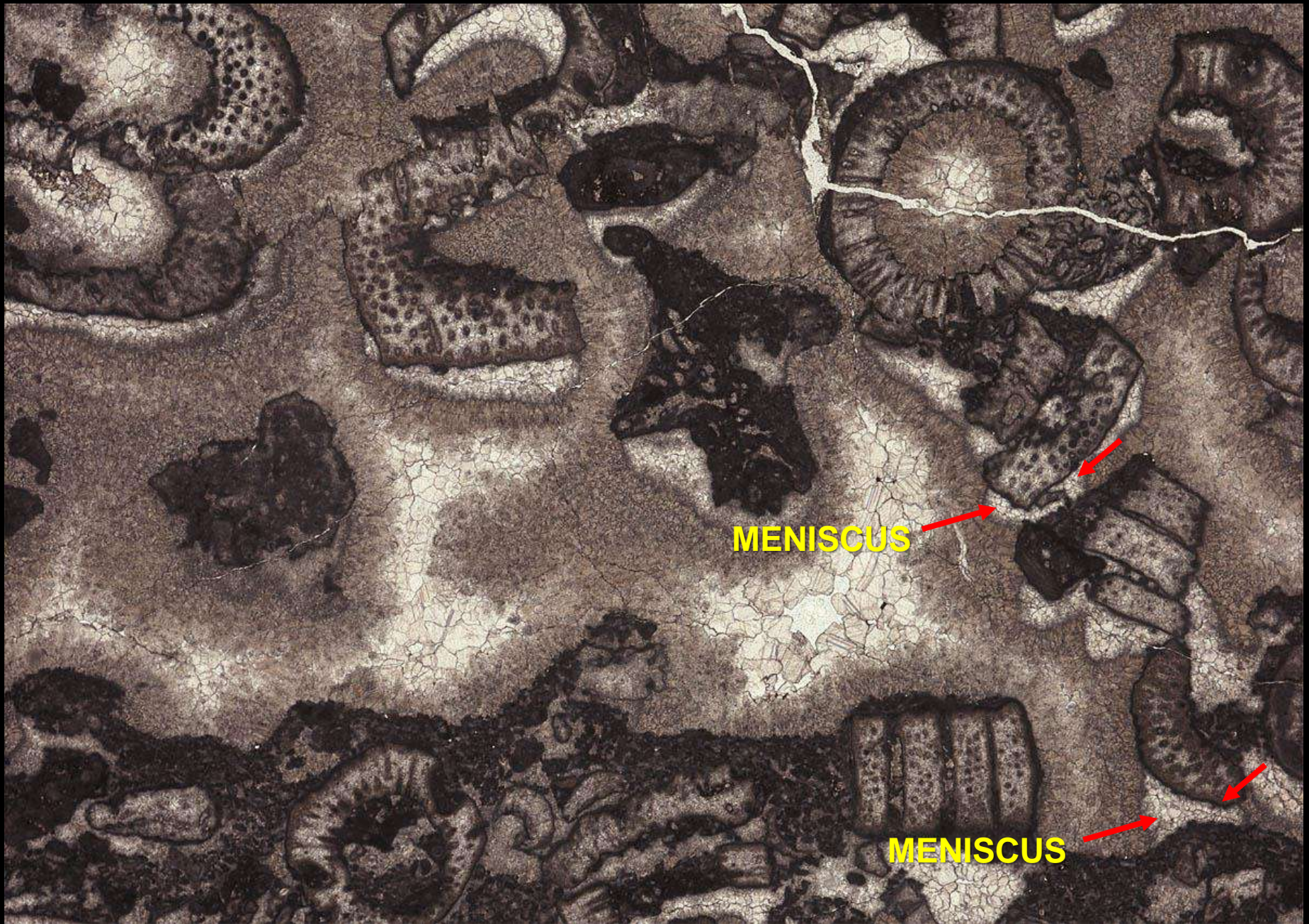
Different types of cement form in specific diagenetic environments. Characterizing the cements of a carbonate rock can help reconstructing its **diagenetic history**.



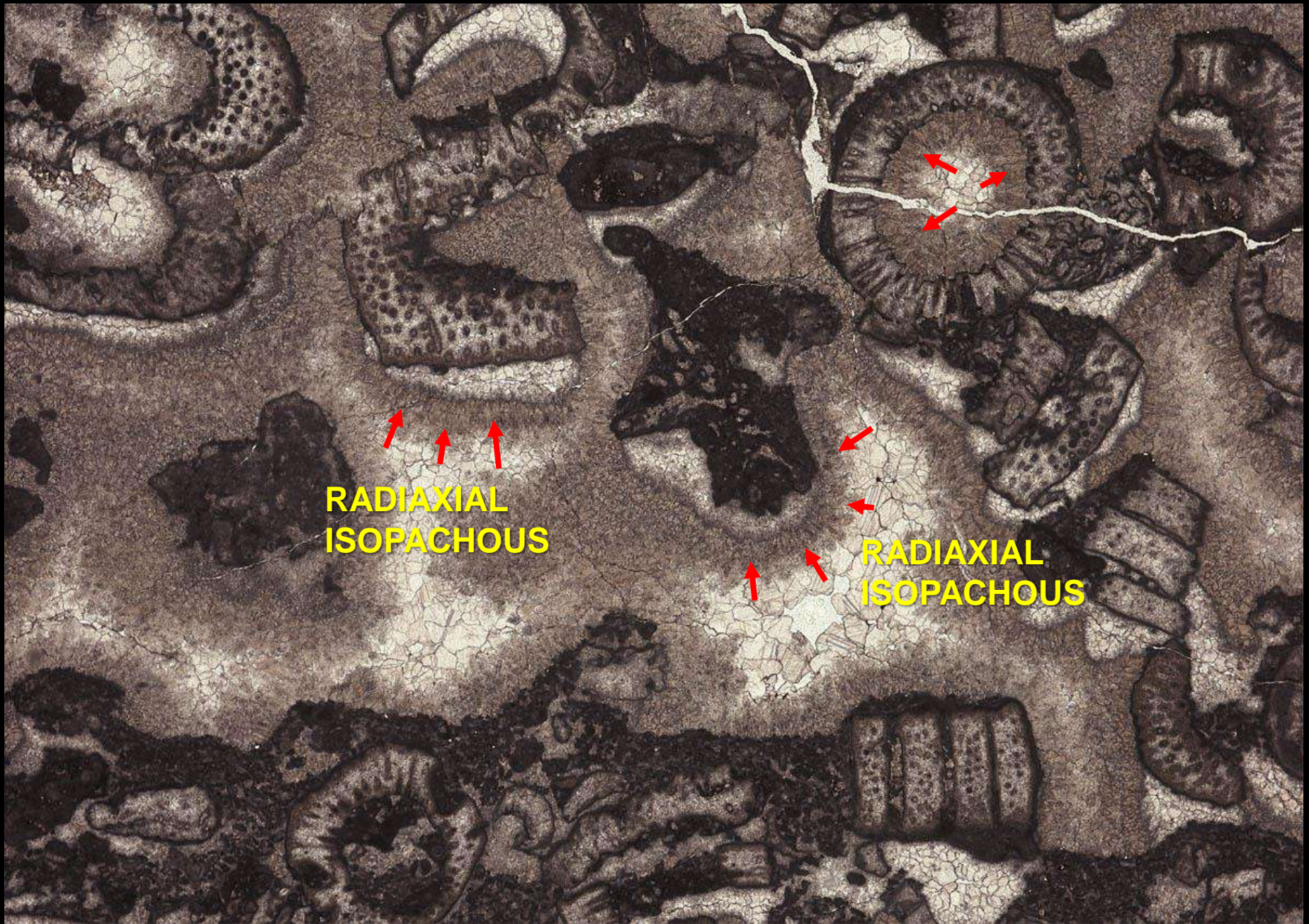
Some types of cements under the optical microscope



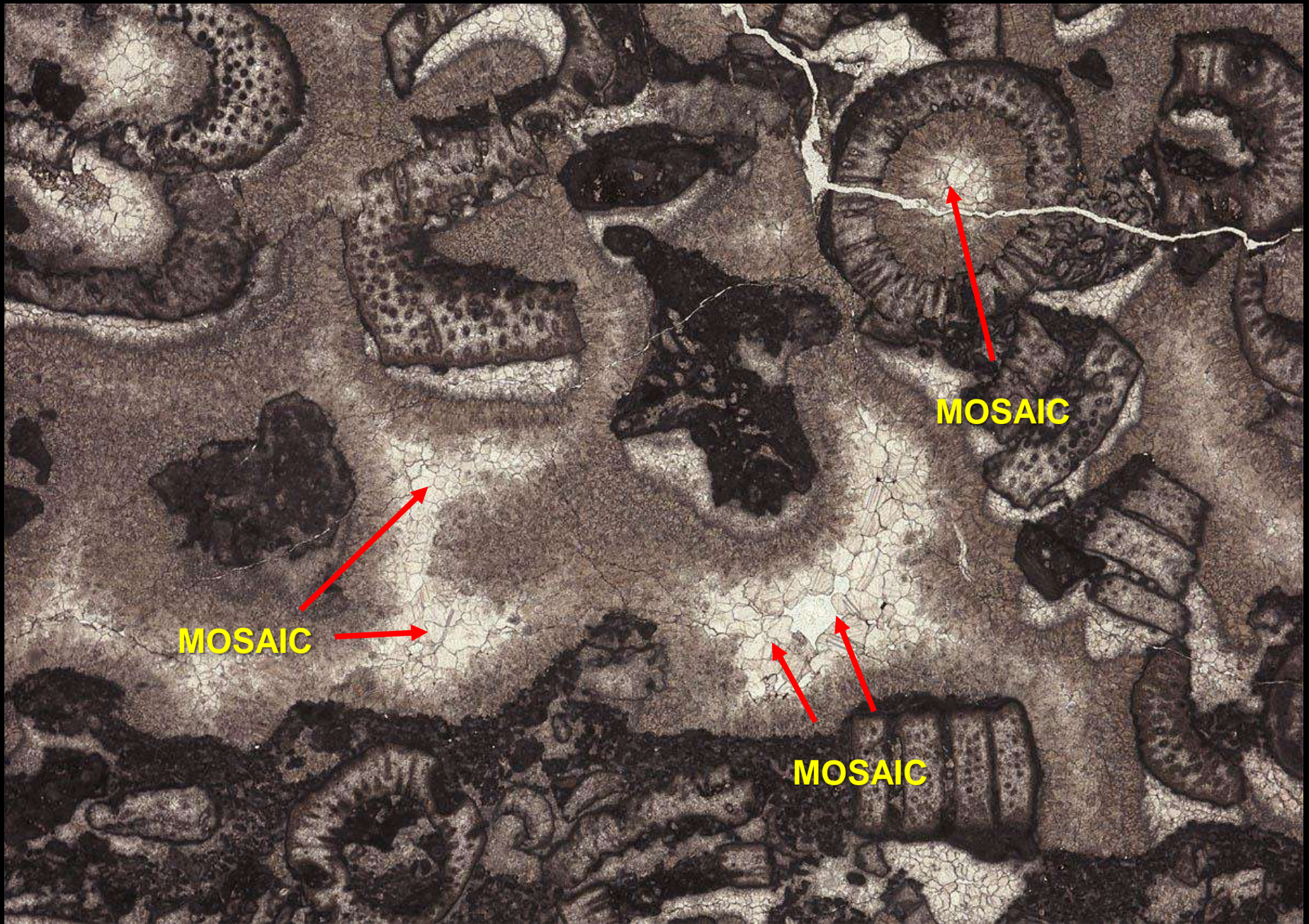
Some types of cements under the optical microscope



Some types of cements under the optical microscope



Some types of cements under the optical microscope

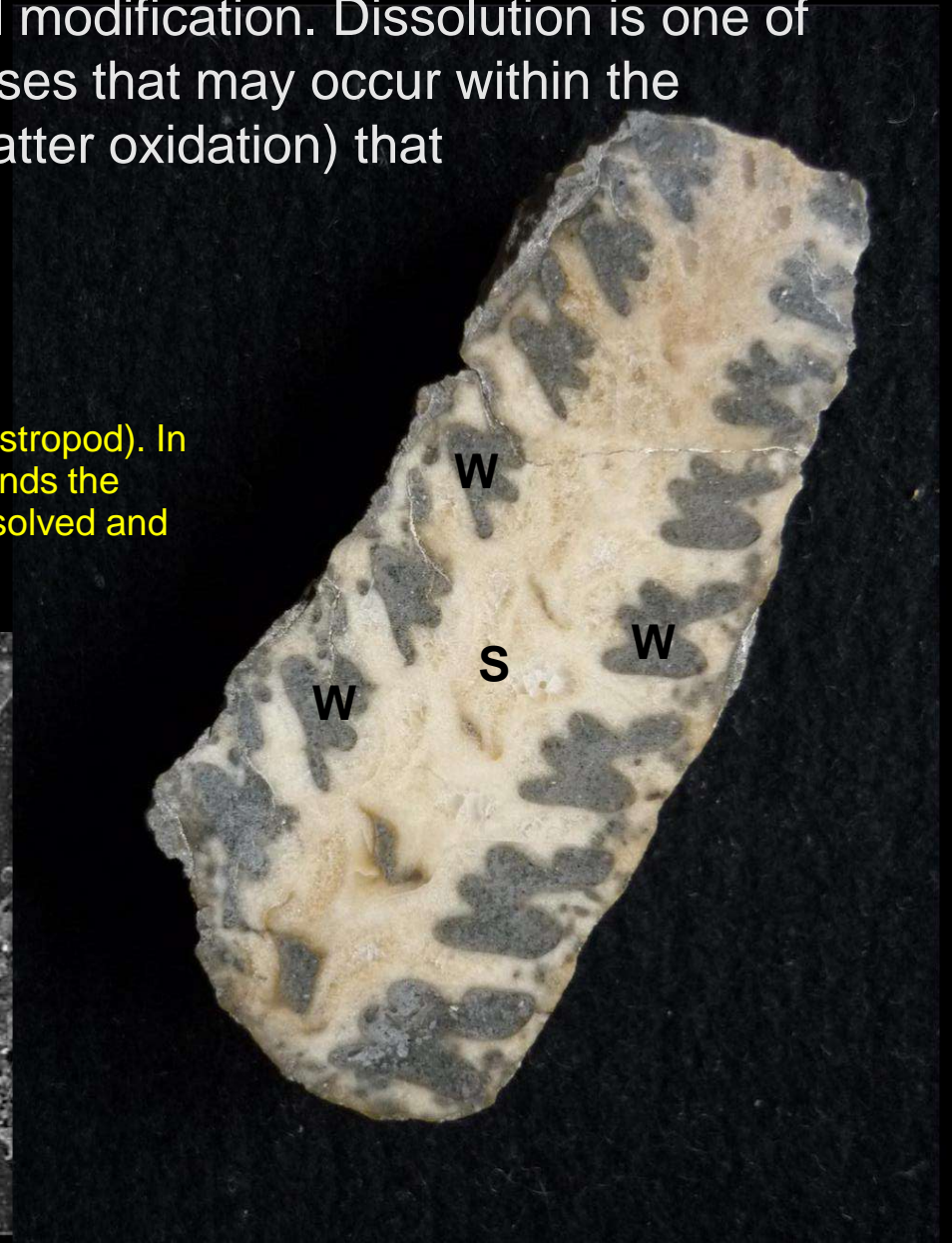
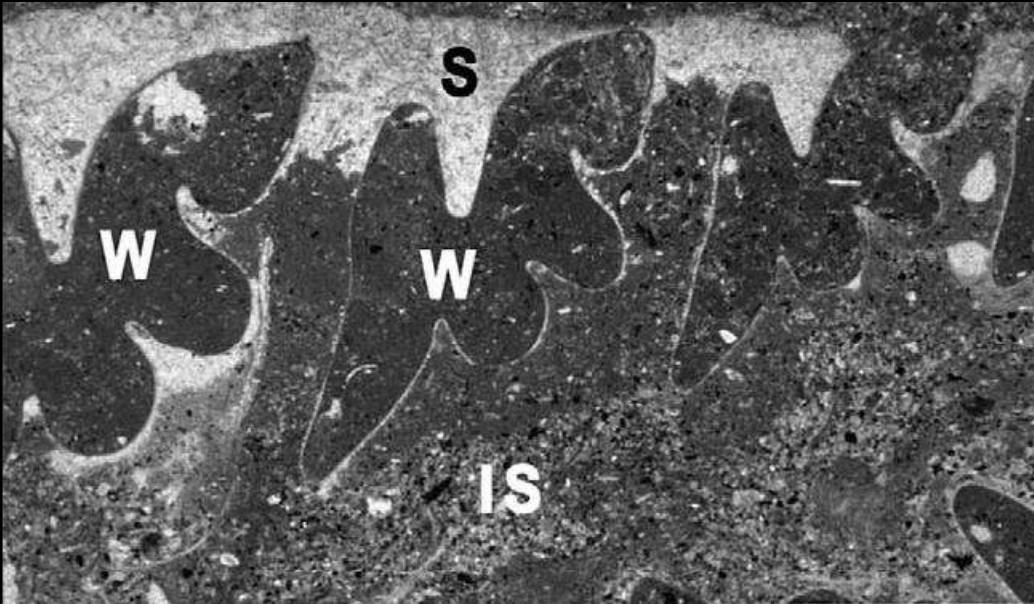


Some types of cements under the optical microscope

Syn depositional dissolution

Carbonates can undergo syn-depositional modification. Dissolution is one of these processes and is caused by processes that may occur within the sediment right after burial (e.g. organic matter oxidation) that cause a local CaCO_3 undersaturation.

Shallow water dissolution of a *Nerinea* shell (shallow water gastropod). In the preserved specimen (right) the shell (S) completely surrounds the wohrls (W). In the dissolved one (below) the shell is partly dissolved and partially substituted by sediment (IS). From Sanders, 2003.

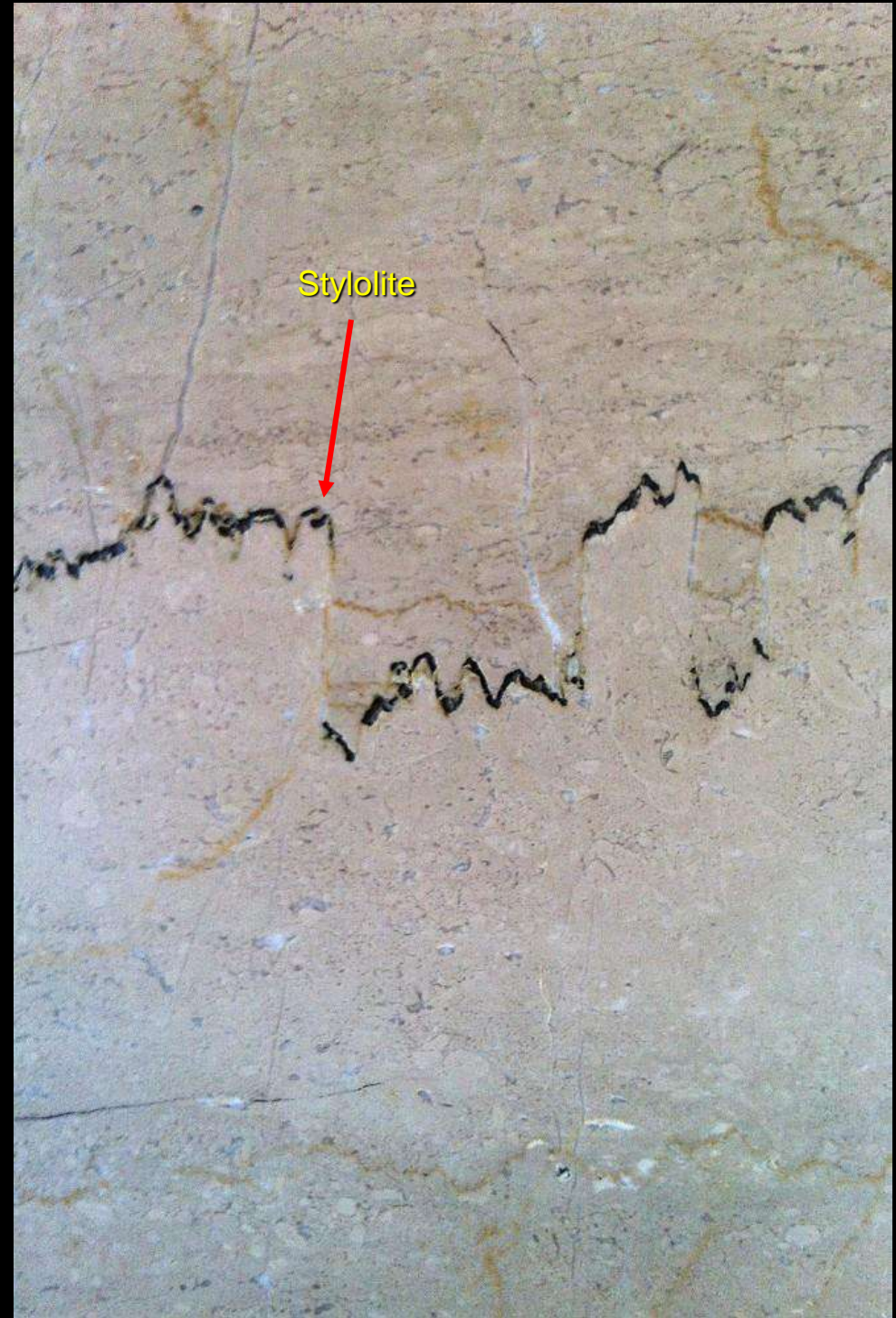


Burial diagenesis

A typical process of burial diagenesis is also **pressure solution**, and the consequent formation of **stylolites**. The amplitude of stylolites gives a minimum estimate of sediment loss by chemical (pressure) compaction.



Stylolite in thin section (Carboniferous of Asturias). From www.carbonateworld.com



Burial diagenesis: pressure solution and the stylolites

The amplitude of stylolites gives a minimum estimate of sediment loss by pressure solution.



Stylolite visible on a step on a stair.

Carbonate is seawater today



The carbon cycle – a quick overview

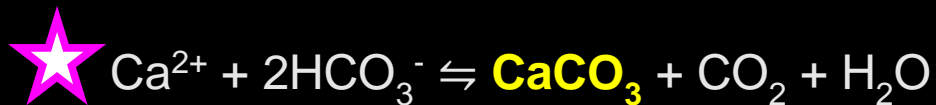
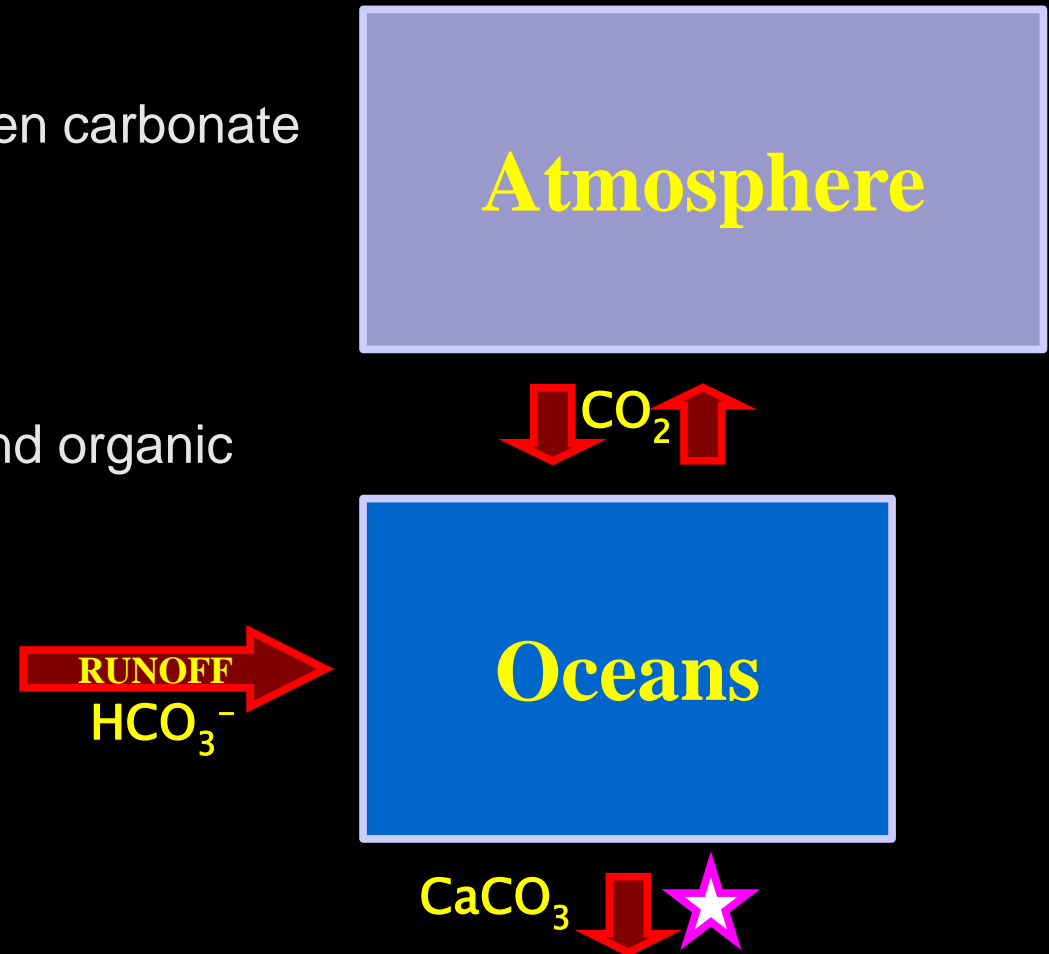
The carbon cycle is the biogeochemical cycle through which carbon is exchanged among the biotic (biosphere) and abiotic (lithosphere, atmosphere and hydrosphere) compartments of Earth.

Carbon **enters** sea water in ways:

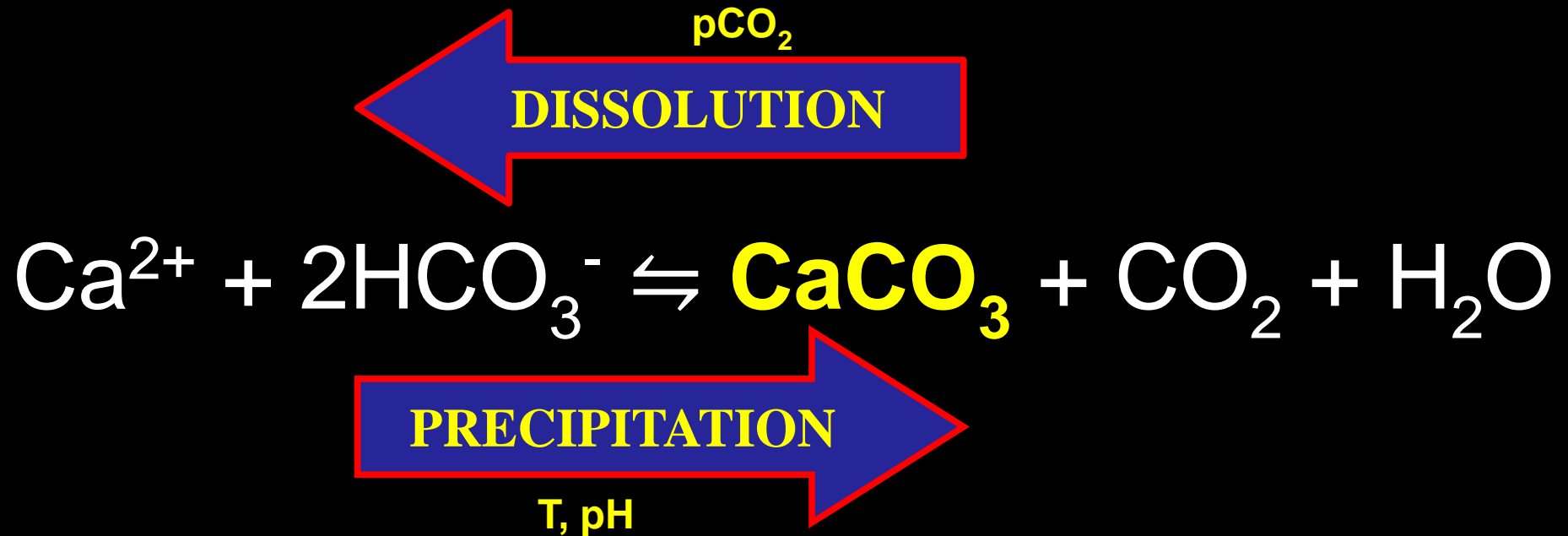
- As CO_2 , from the atmosphere
- As carbonate (CO_3^{2-}) and hydrogen carbonate (HCO_3^-) ions with runoff (e.g., rivers).

It **leaves** sea water:

- As CO_2 to the atmosphere
- As calcium carbonate (CaCO_3) and organic carbon in sediments.



How does carbonate precipitation work?



pCO₂, T and pH influence the reaction.

Furthermore, a major controller is seawater saturation state with respect to carbonate (Ω)

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

How does carbonate precipitation work?



$p\text{CO}_2$, T and pH influence the reaction.

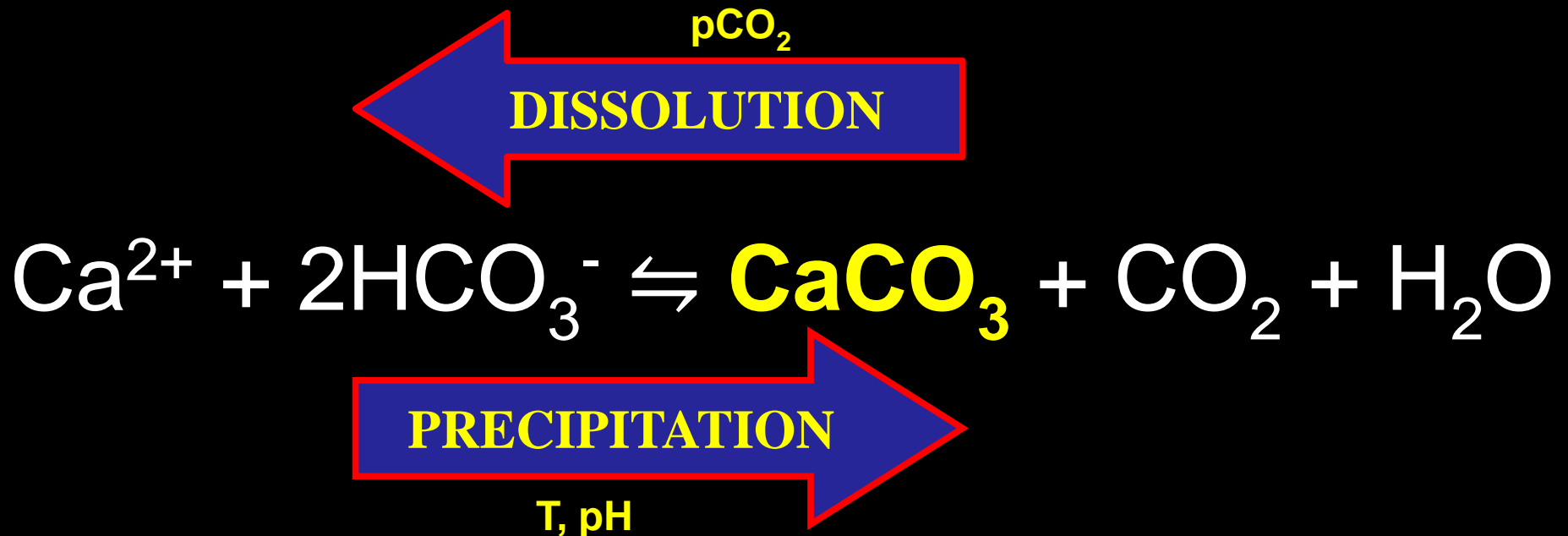
Furthermore, a major controller is **seawater saturation state with respect to carbonate (Ω)**

ION CONCENTRATIONS

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

REACTION CONSTANT

How does carbonate precipitation work?

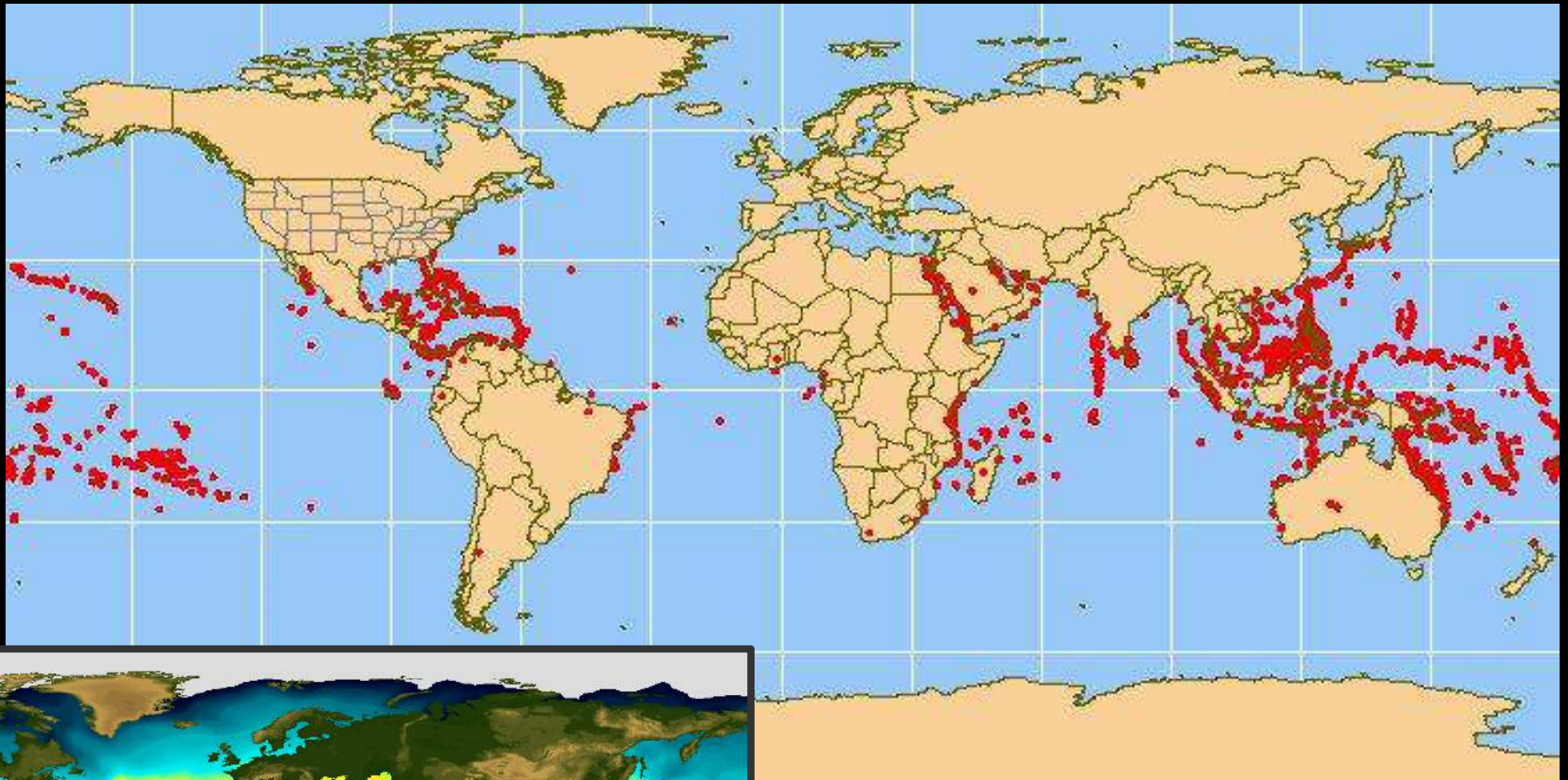


pCO₂, T and pH influence the reaction.

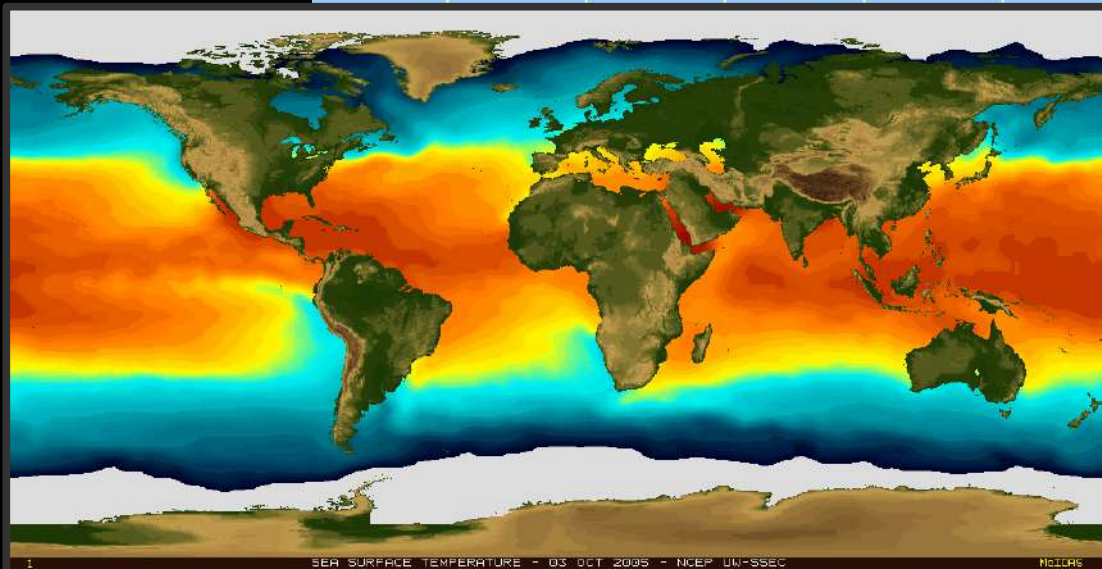
Furthermore, a major controller is **seawater saturation state with respect to carbonate (Ω)**

The **saturation state** of seawater with respect to carbonate, Ω , indicates whether sea water tends to precipitate CaCO₃ ($\Omega > 1$; **supersaturation**) or to dissolve CaCO₃ ($\Omega < 1$; **undersaturation**).

Example: temperature controls carbonate sedimentation



World distribution of coral reefs
(<http://www.coralreef.noaa.gov/>)

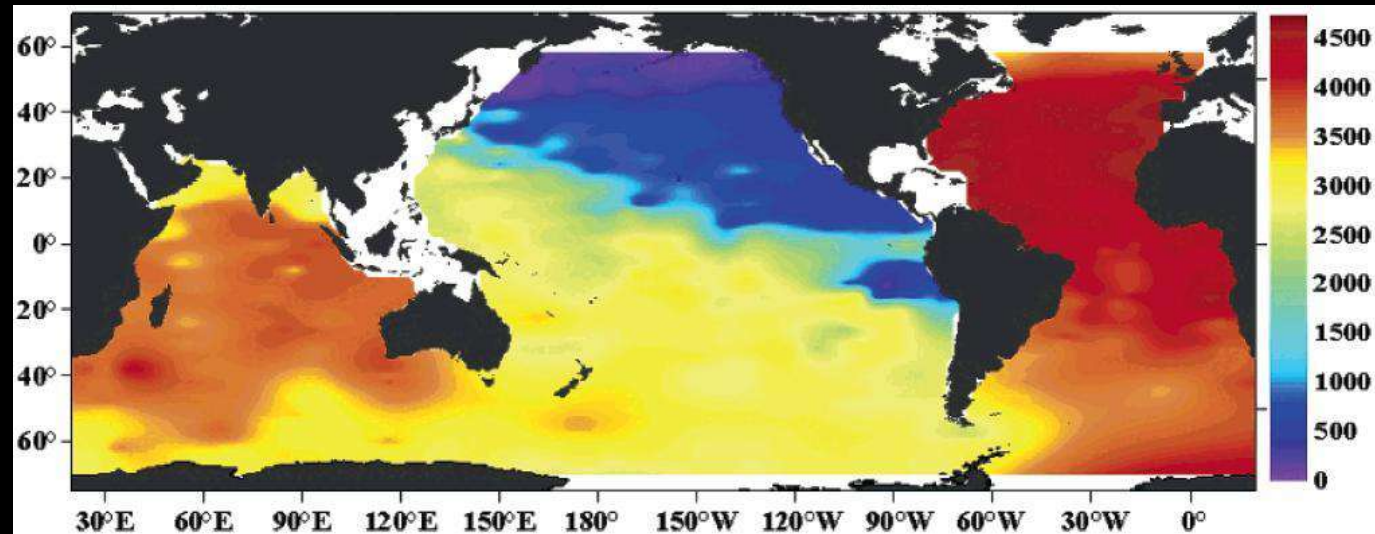
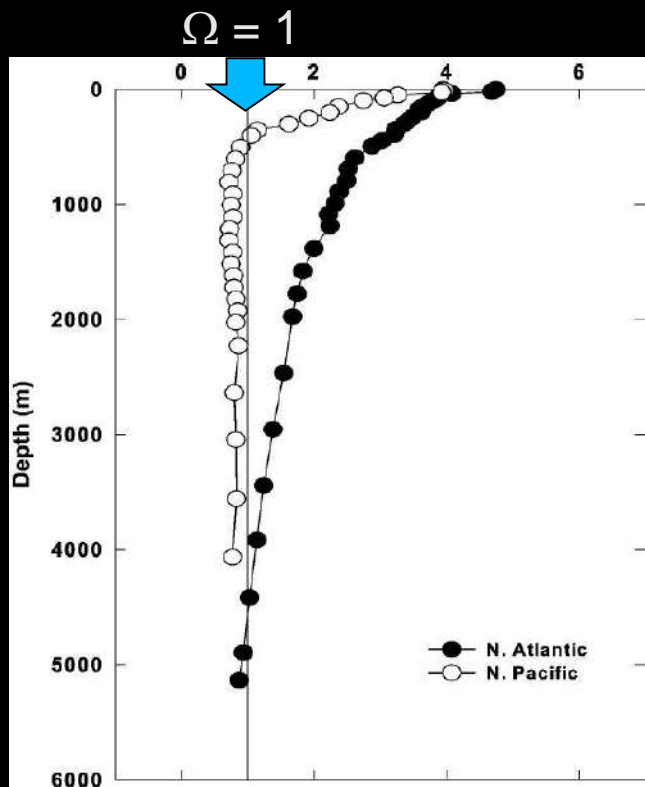


Global ocean surface temperature
(<http://www.ssec.wisc.edu/data/sst/>)

Structure of the water column and carbonate saturation:

Ω lowers with depth, mostly because carbonates are more soluble at high pressures. $\Omega = 1$ 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.

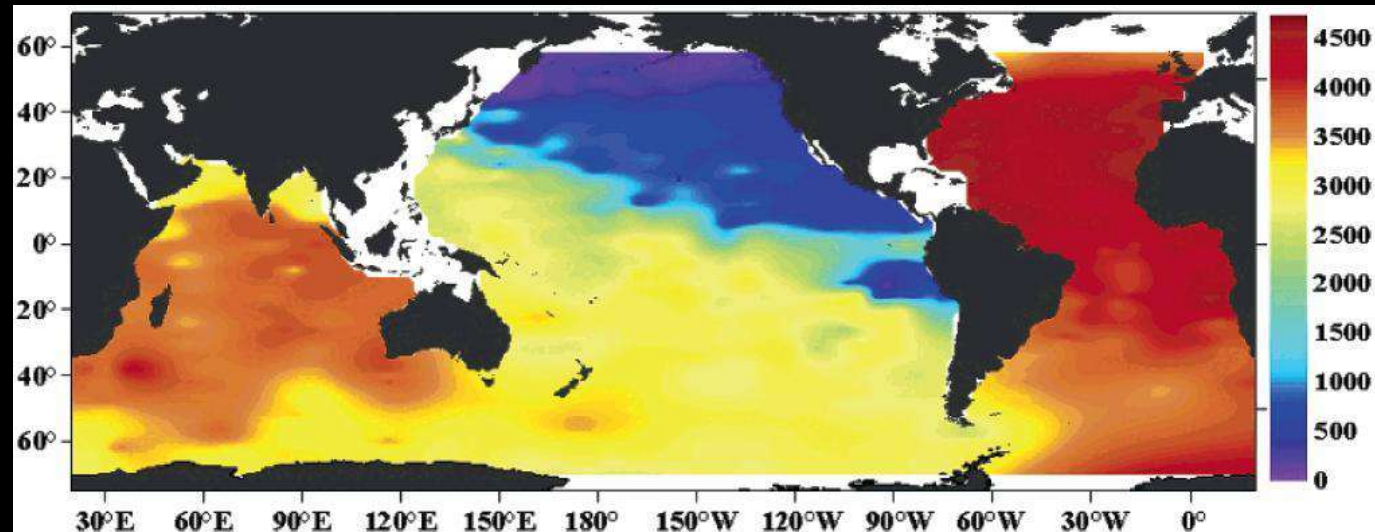
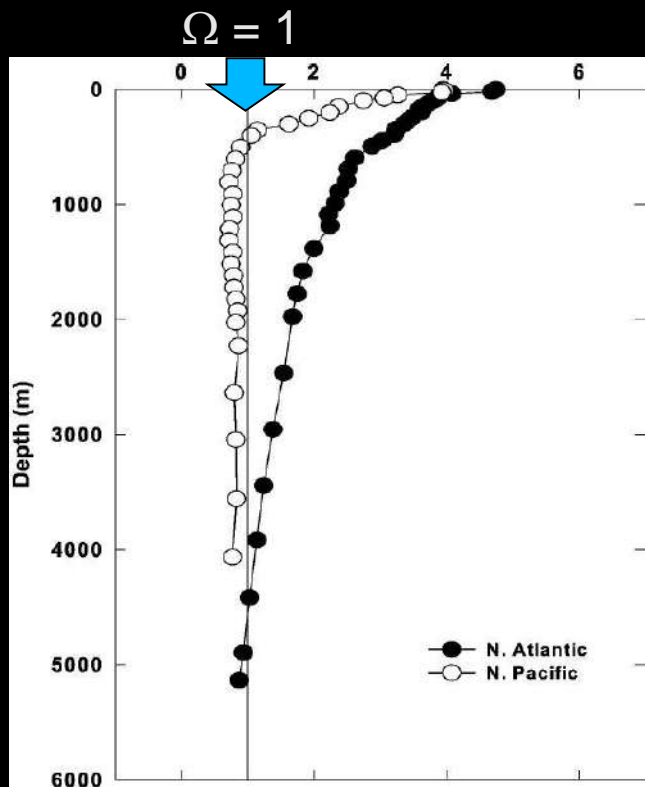


Profiles of Ω (calcite) versus depth, and a map of the saturation depth.

Structure of the water column and carbonate saturation:

Ω lowers with depth, mostly because carbonates are more soluble at high pressures. $\Omega = 1$ 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.

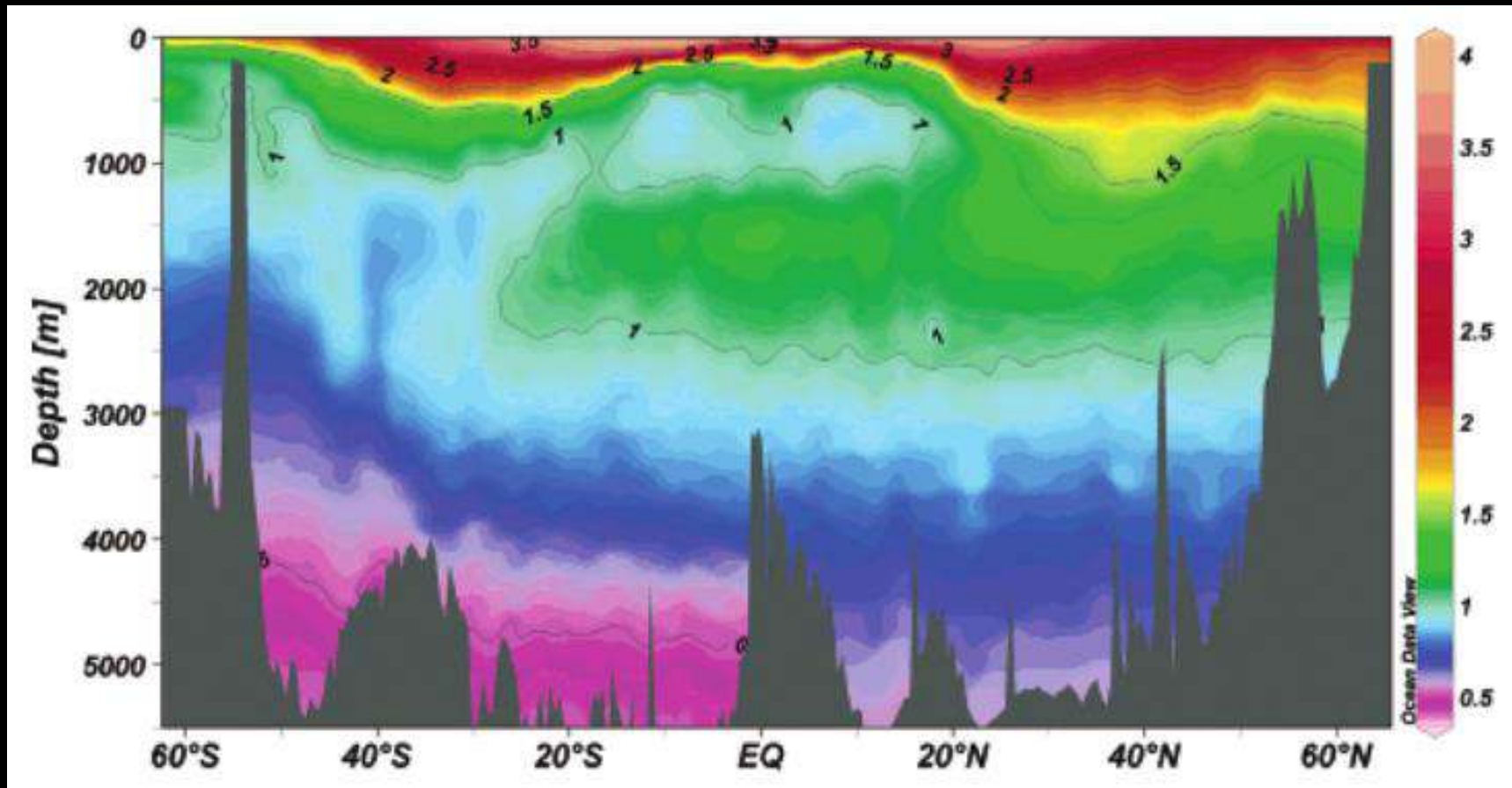


Profiles of Ω (calcite) versus depth, and a map of the saturation depth.

Note how the Atlantic is more supersaturated than the Pacific at most depths. From Millero, 2007.

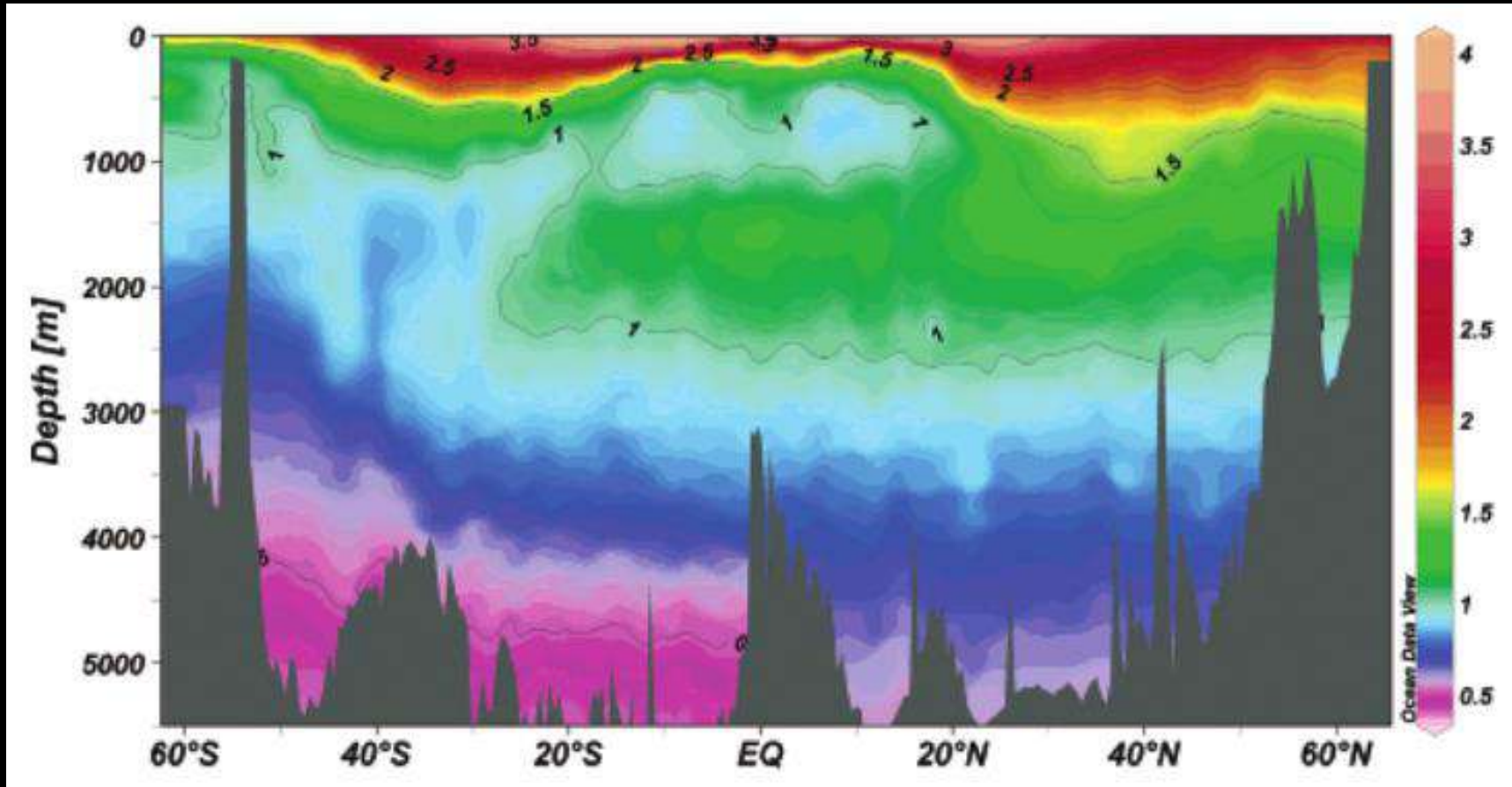
Structure of the water column and carbonate saturation

Ω versus depth in a latitudinal cross section of the Atlantic



Structure of the water column and carbonate saturation

Ω versus depth in a latitudinal cross section of the Atlantic

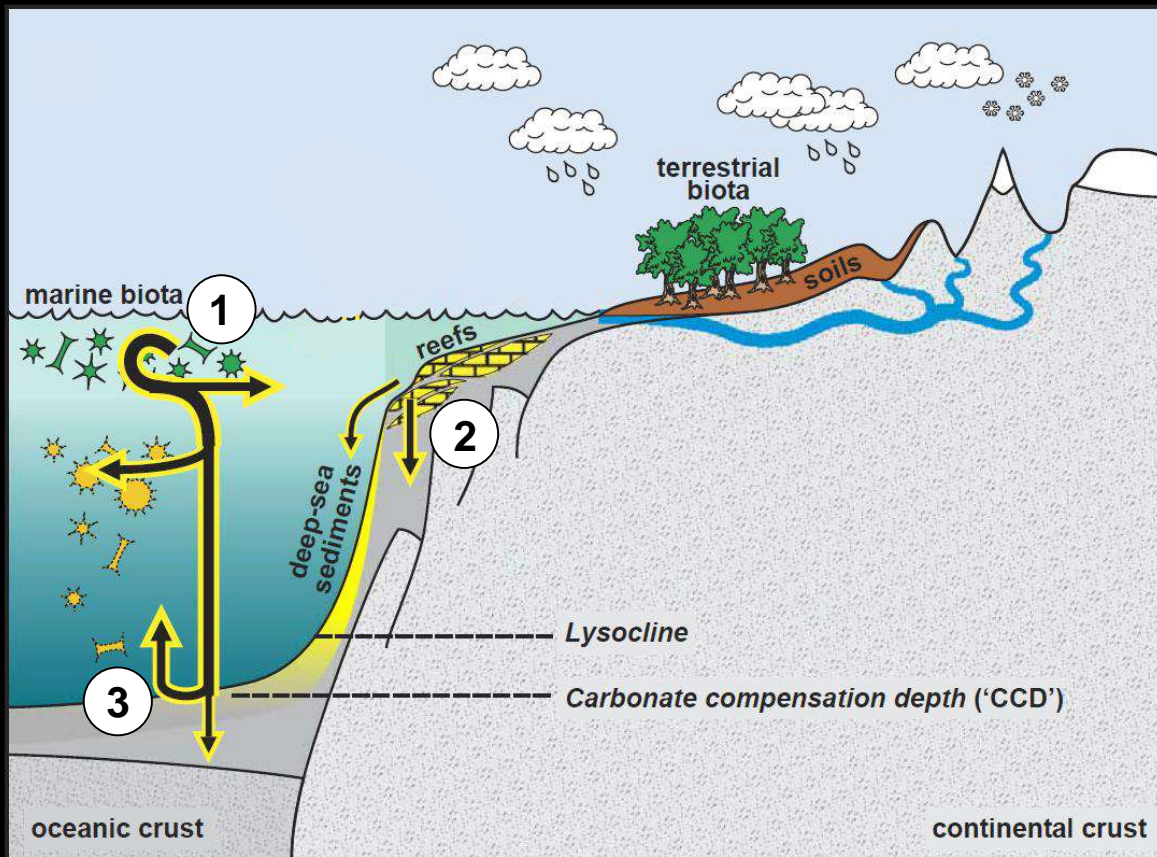


Millero, 2007

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.

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.

Precipitation of carbonate in seawater (today)



Modified from Ridgwell and Zeebe, 2015

- ③ Dissolution of carbonate in deep waters

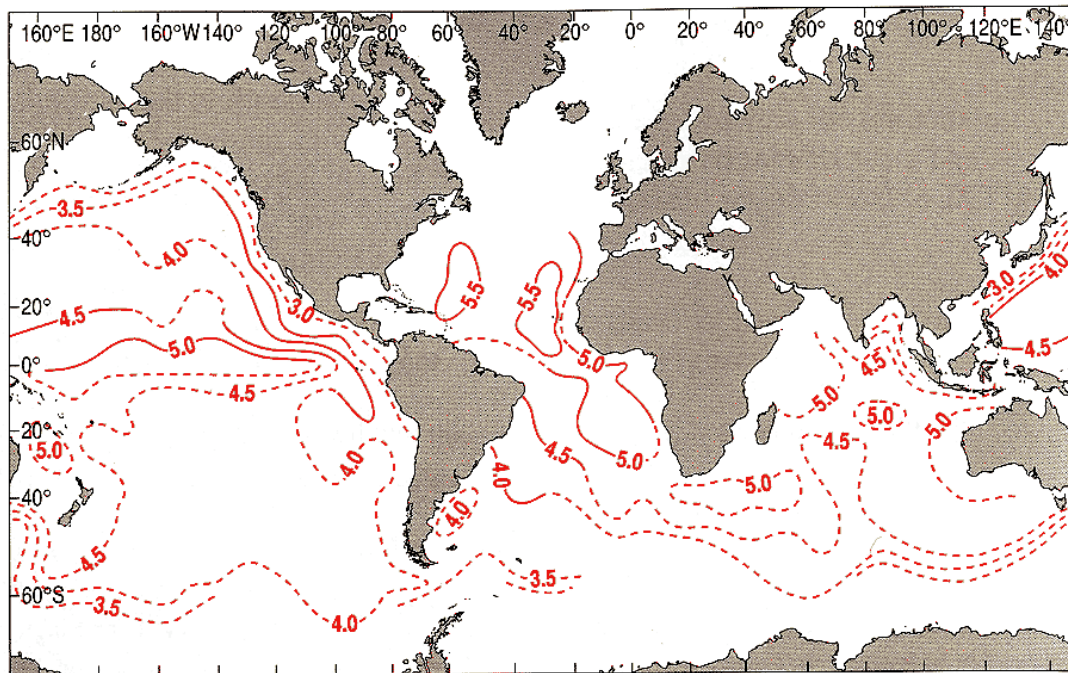
Coccolithofores and **foraminifera** live in the upper part of the water column. When they die, their shells fall to the bottom of ocean. When they fall below the saturation depth, they start dissolving.

Shallow water carbonates deposit above the saturation depth, in waters that are normally supersaturated in carbonate, therefore there is no significant dissolution there.

Structure of the water column and carbonate saturation:

Three surfaces can thus be defined.

- **Saturation depth:** surface at which $\Omega = 1$;
- **Lysocline:** depth at which carbonate dissolution becomes recognizable in sediments. Sometimes, it is conventionally considered as the surface at which $\Omega = 0.8$;
- **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.



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

CCD

There are actually two Compensation Depths, one for Aragonite (ACD) and one for Calcite (CCD). The ACD is shallower than the CCD because Aragonite is less stable than Calcite.

Below the CCD, carbonate is completely dissolved and therefore non-carbonate deposit such jaspers may form

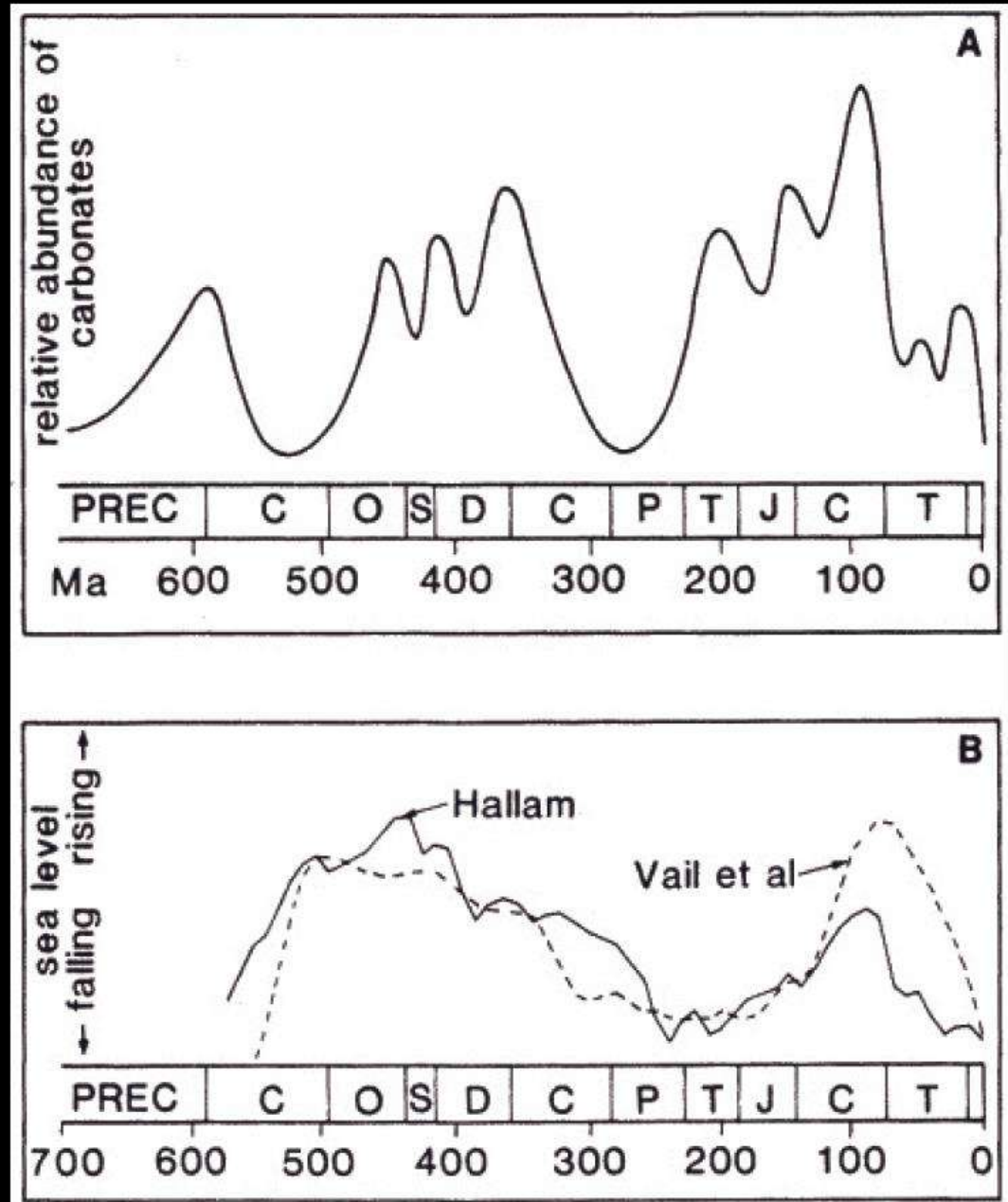


Carbonates through geological time

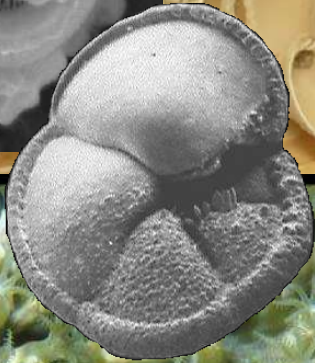
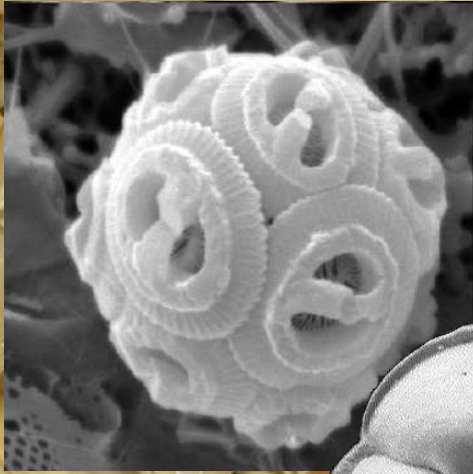


Carbonates abundance fluctuated through geological times and a broad correspondence is seen with large scale **oscillation of sea level**.

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



Remember that carbonates are formed with the **mediation of living organisms** (up to 90-95% grains are biogenic in origin)

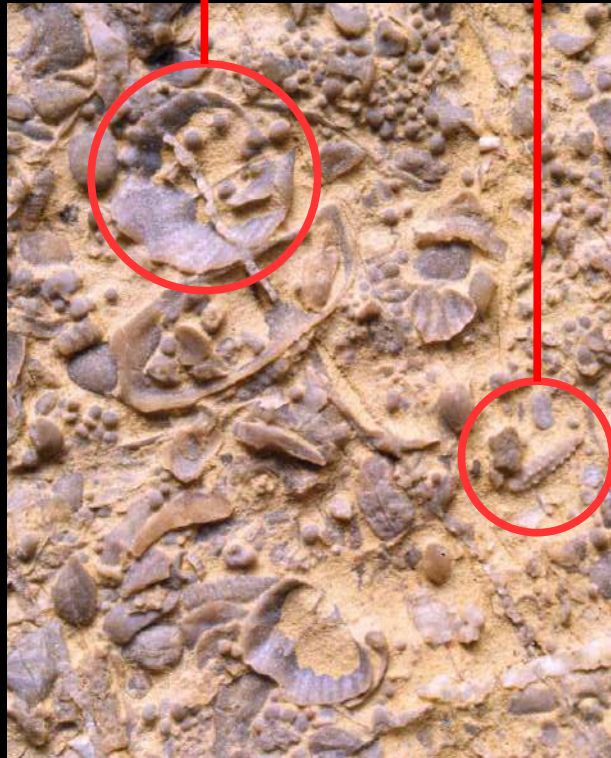


Carbonates: the biological factor

Reef-building organisms with carbonate shells or skeletons were there since the Precambrian. Each may have had **specific ecological preferences.**

Brachiopods

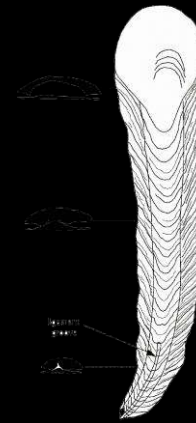
Echinoderms



Carbonate rocks may contain skeletal grains



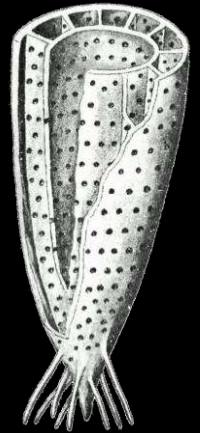
Mid Cambrian
to present



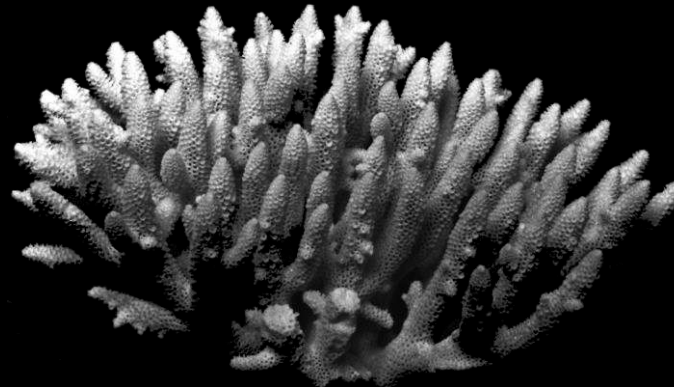
Lithiotis sp.
Early Jurassic



Rudist
Cretaceous



Archaeocyatha
Cambrian

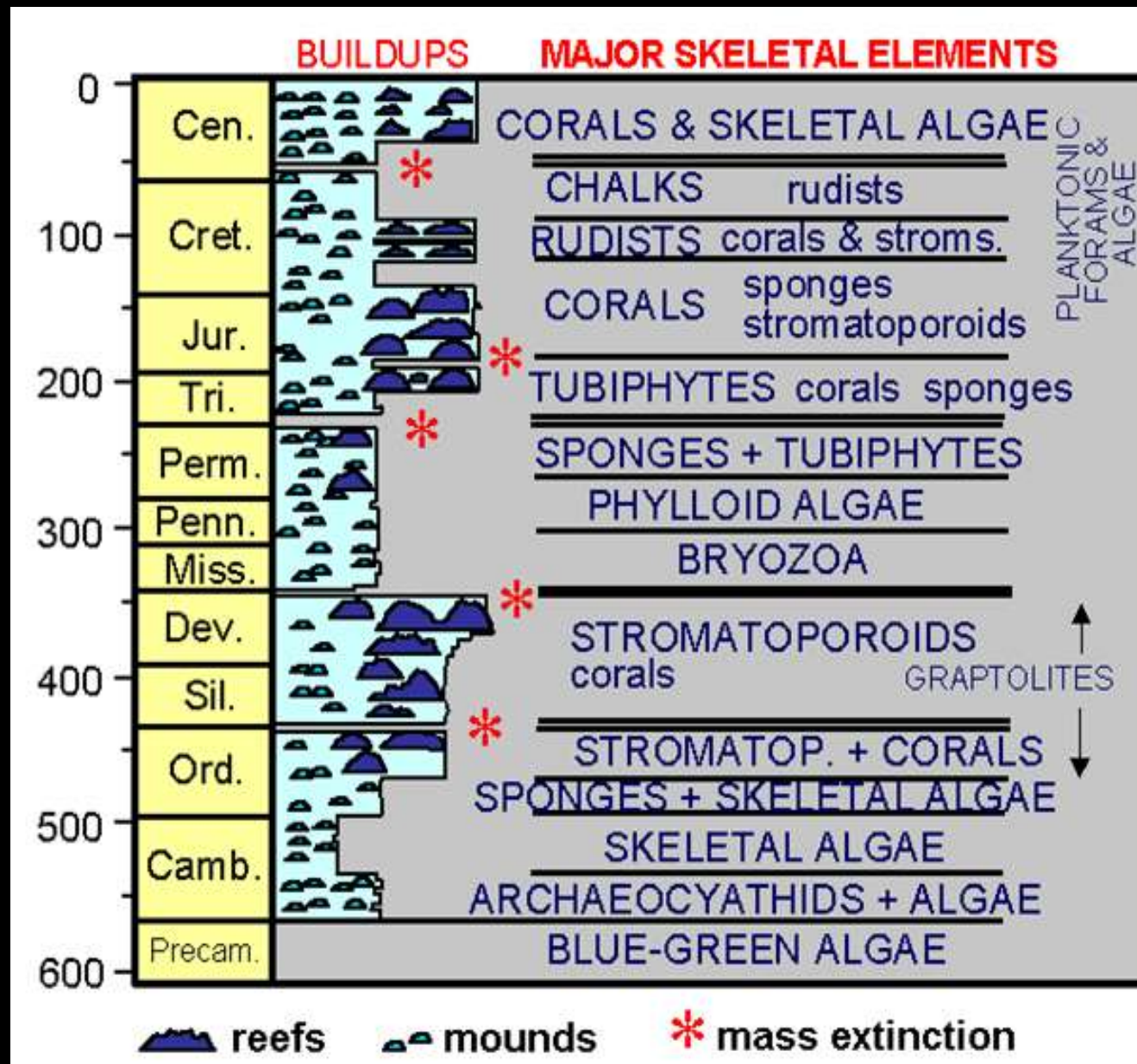


Scleractinian coral
Cenozoic to present



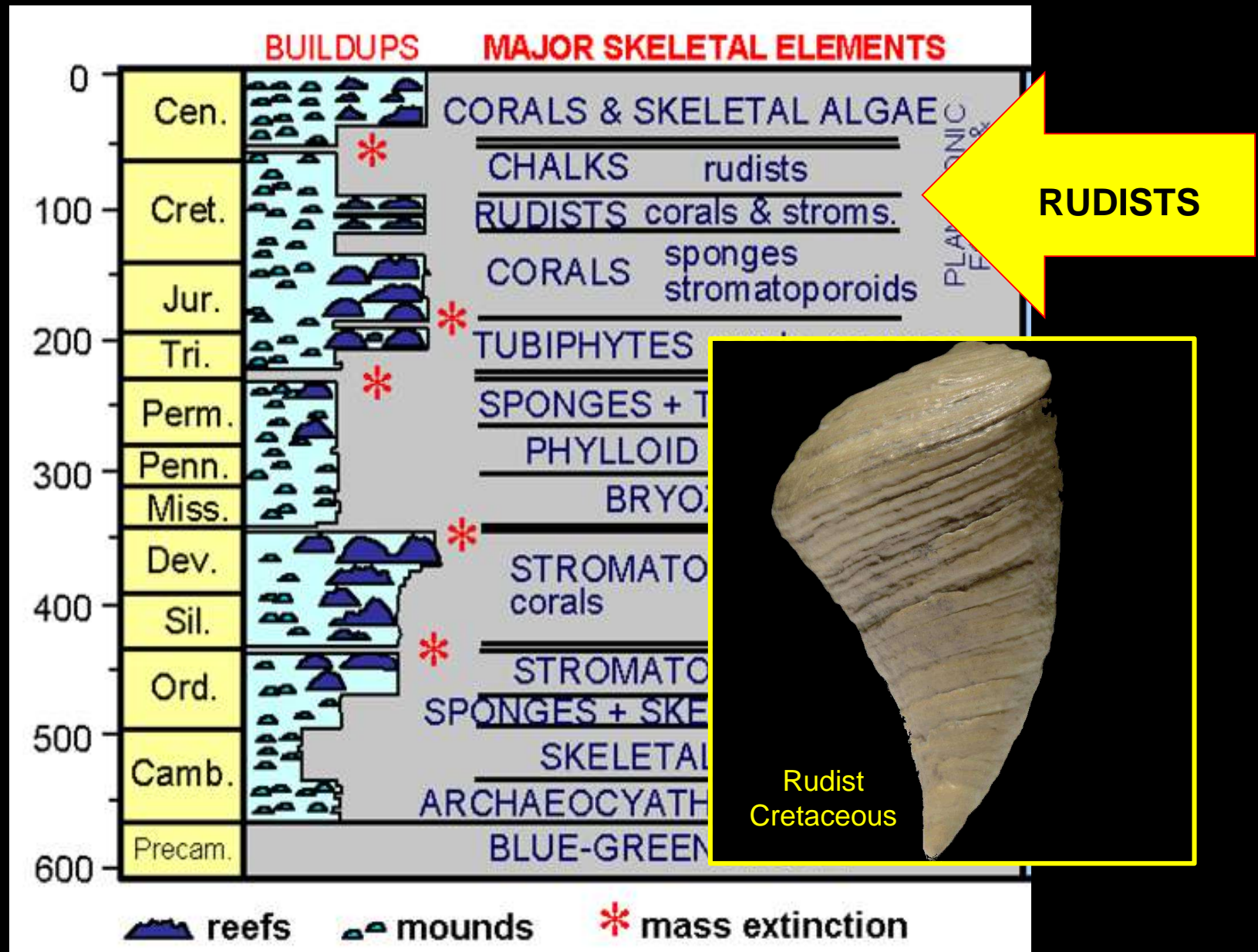
Stromatolite
Precambrian

Reef building organisms changed through geological times



Redrawn from James, 1983.

Reef building organisms changed through geological times



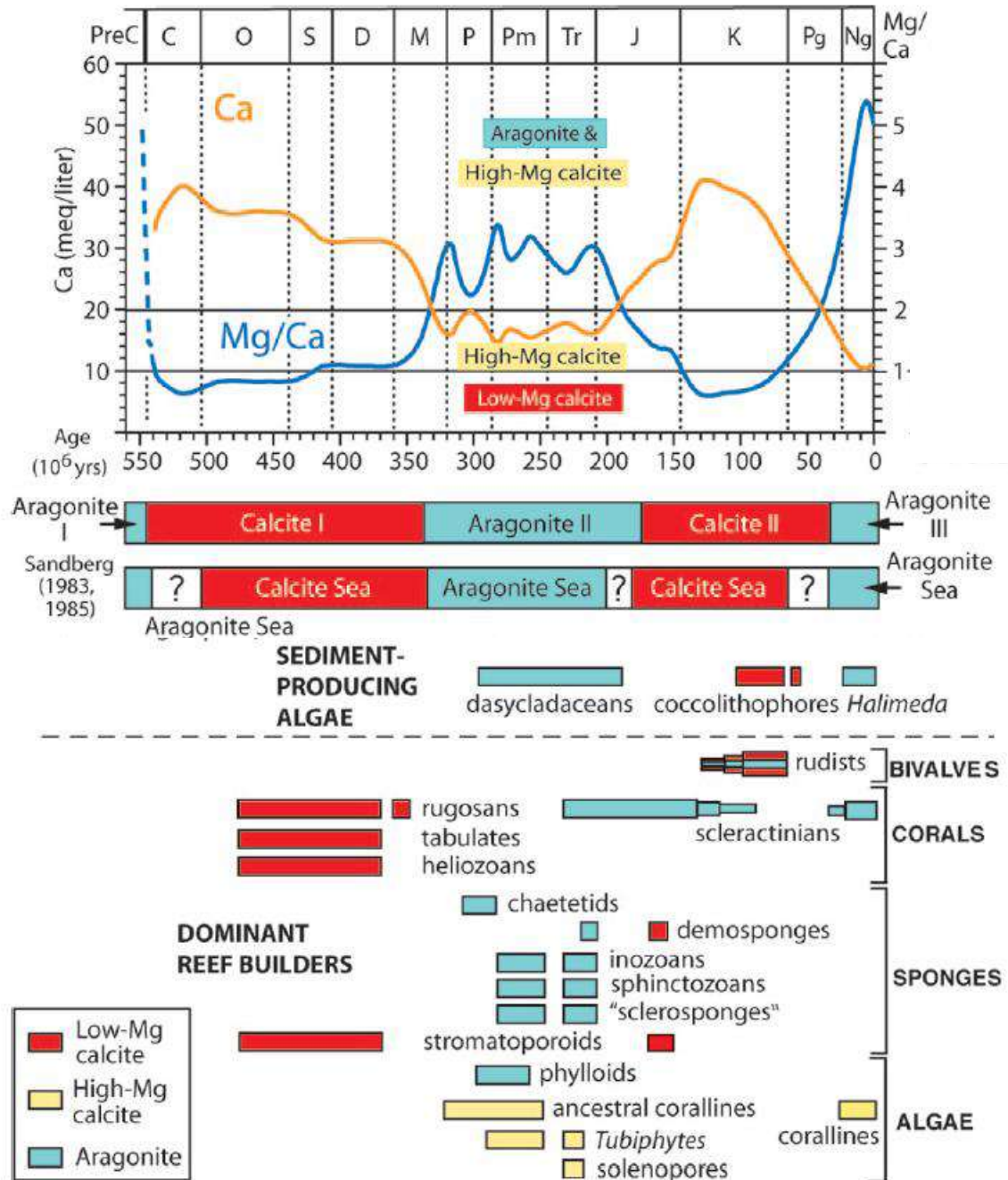
Redrawn from James, 1983.

Aragonite seas and Calcite seas

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.

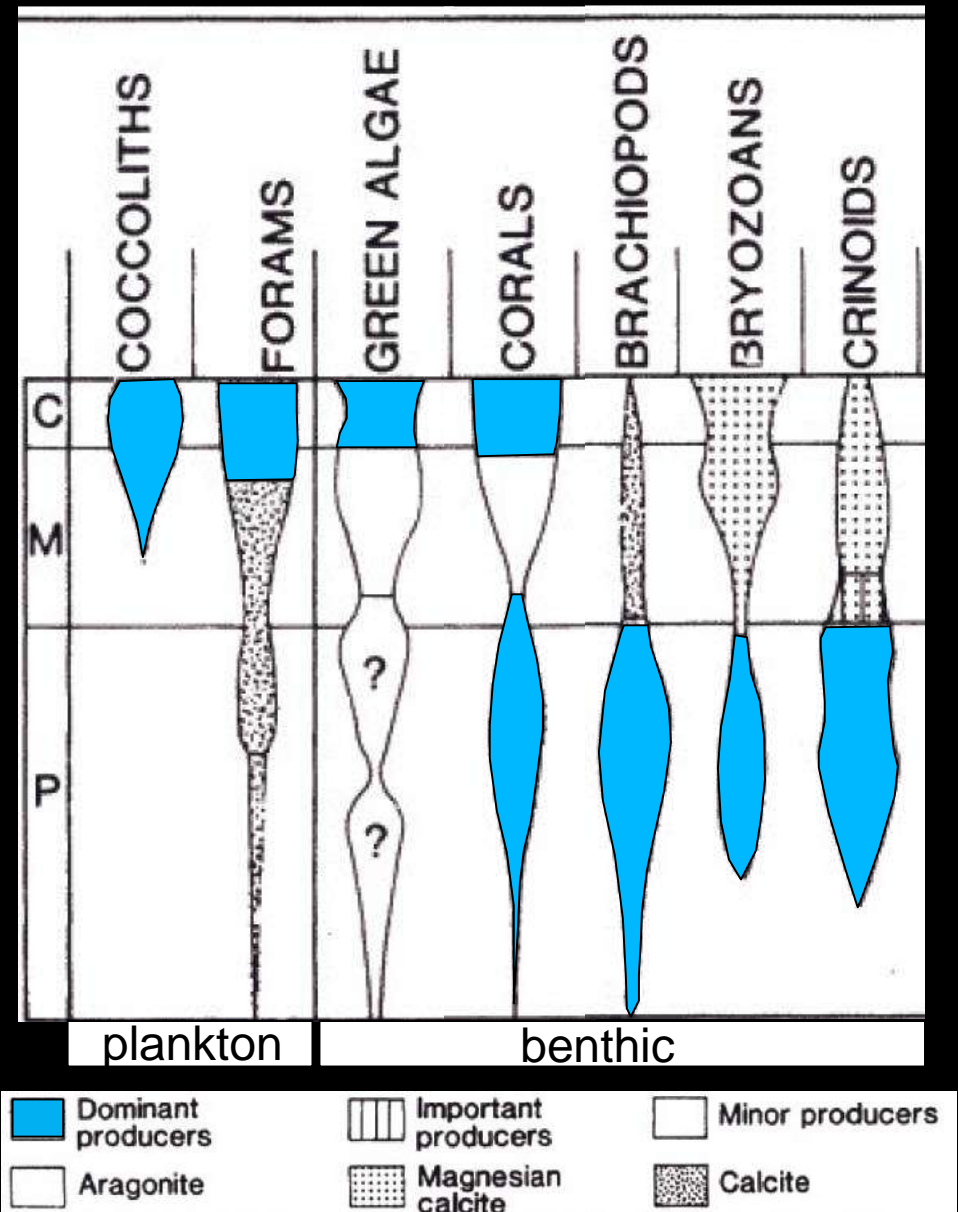
This phenomenon is thought to be linked to variations in the availability of **Mg** in seawaters possibly related to phases of more pronounced or lesser activity of mid atlantic ridges.



Major carbonate producers through time

Life evolved and so did carbonate producers

The importance of organisms that were main producers in some periods subsided and new ones appeared and became dominant

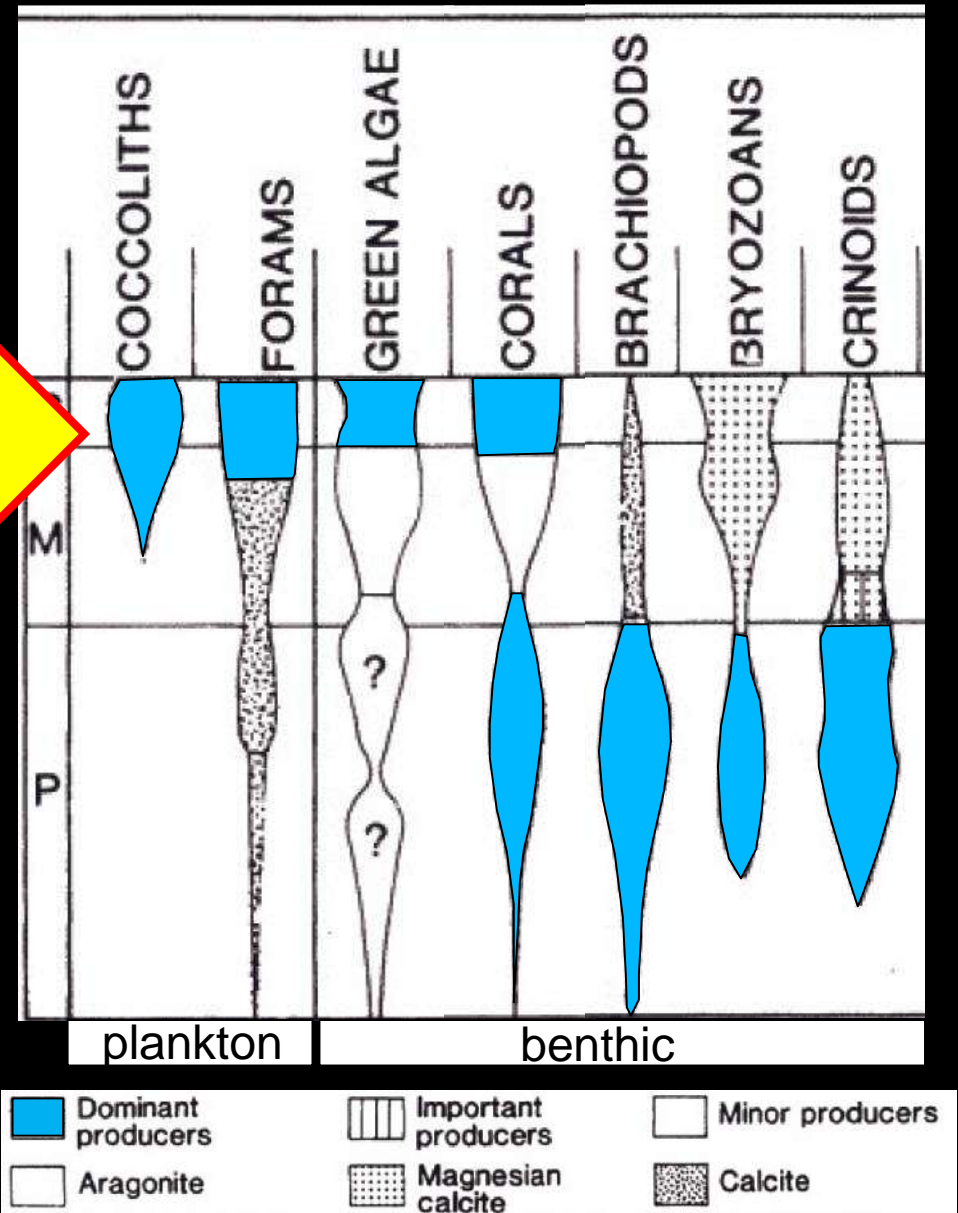
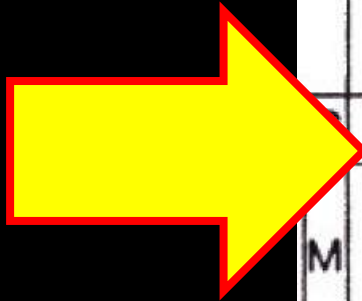


Tucker and Wright, 1990 modified

Major carbonate producers through time

Coccolithophores and forams became dominant only from the mid Mesozoic

Deep-water carbonate precipitation prior to mid Mesozoic was minor



Carbonate production through time

When did carbonate appear in the geological record?

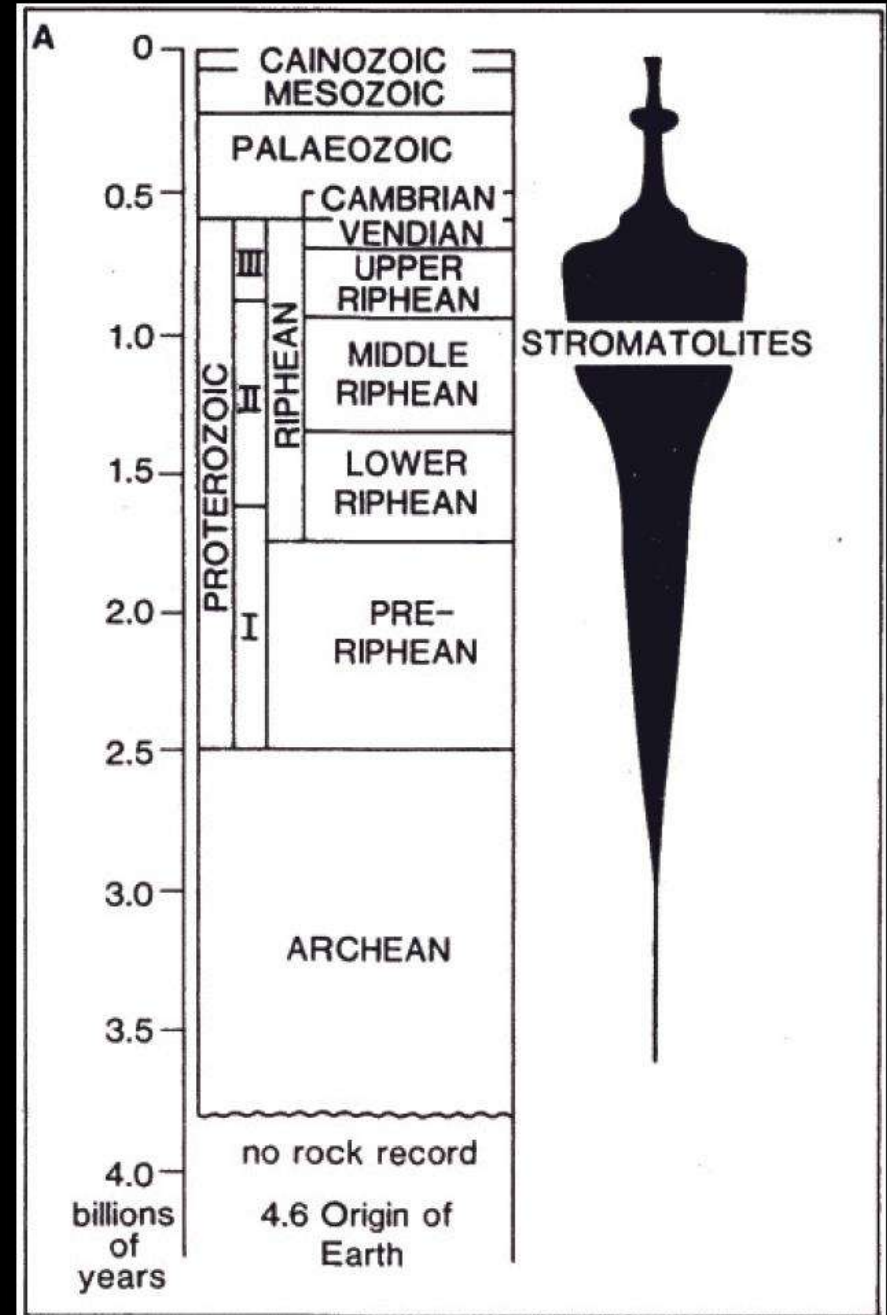
Oldest carbonates date back to the Archean and one important type are **stromatolites**

Stromatolites are carbonate sedimentary structures that are interpreted as originated by the activity of bacteria.

They belong to an important family of carbonates: **microbial carbonates**



Precambrian of Mauritania (Photo A. Riva)



Tucker and Wright, 1990 modified

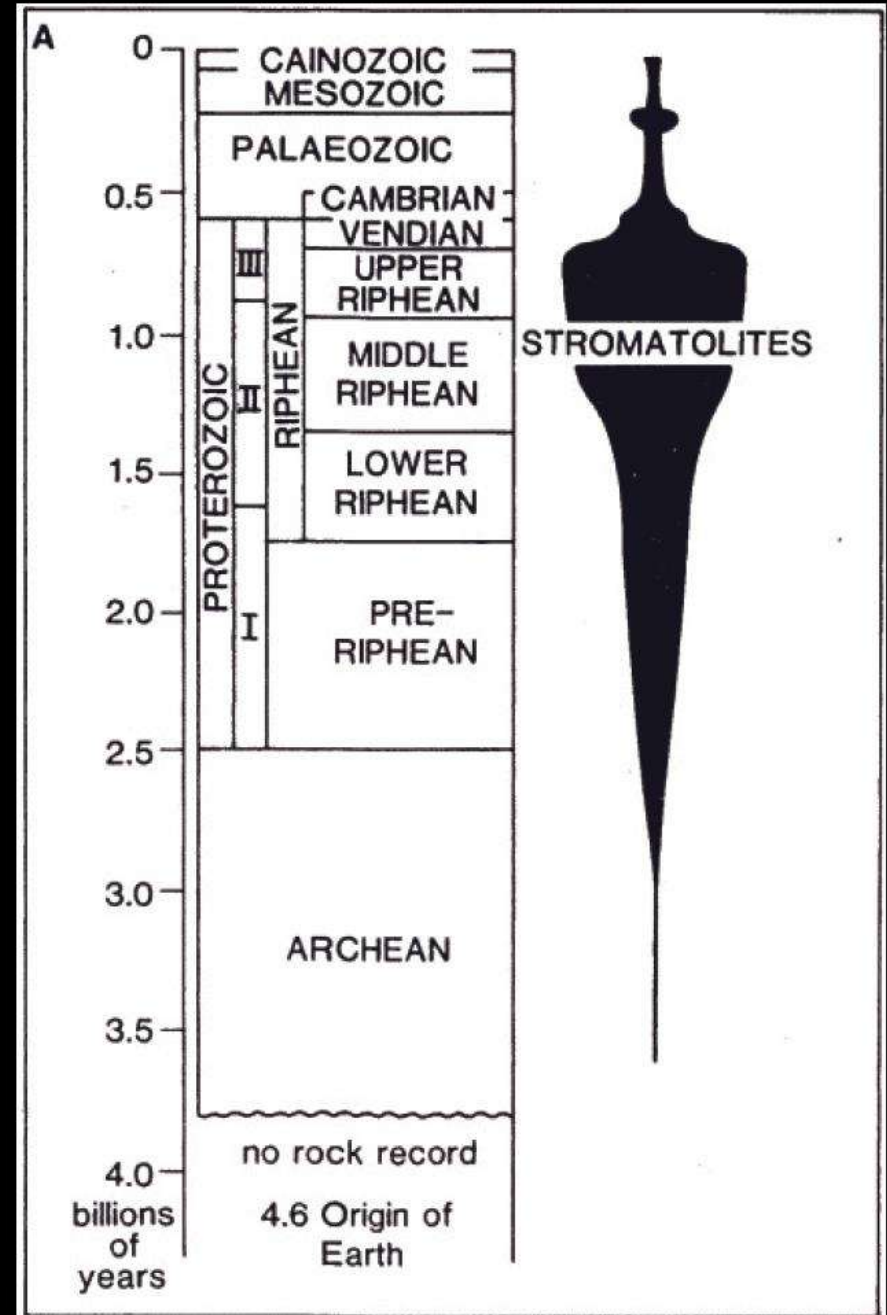
Carbonate production through time



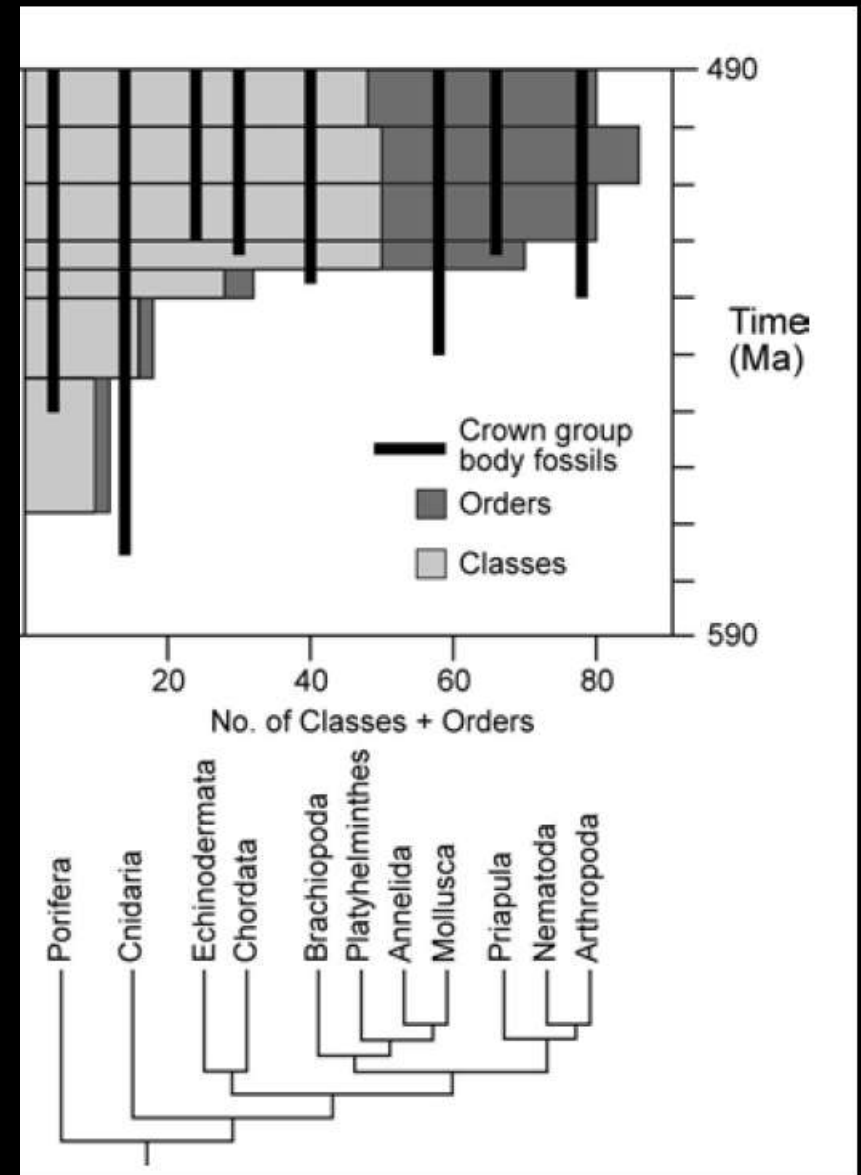
Modern stromatolites in Shark Bay, Australia



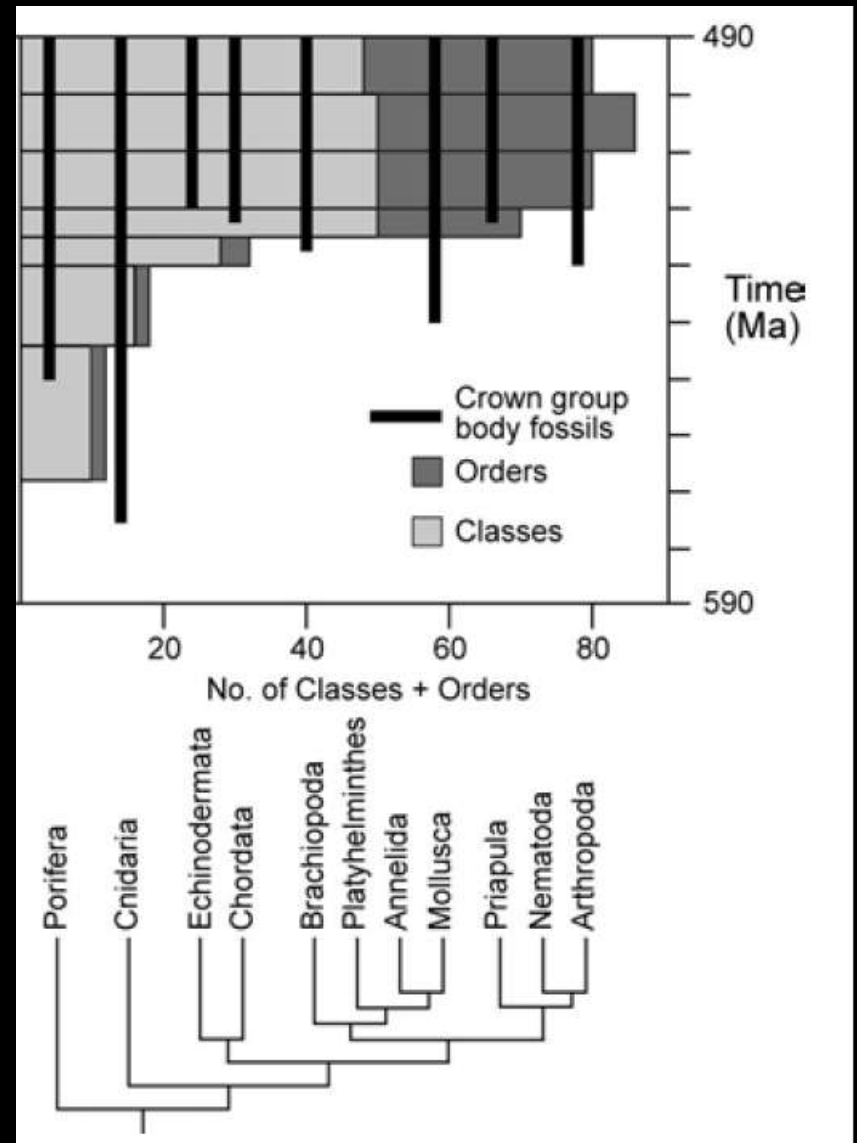
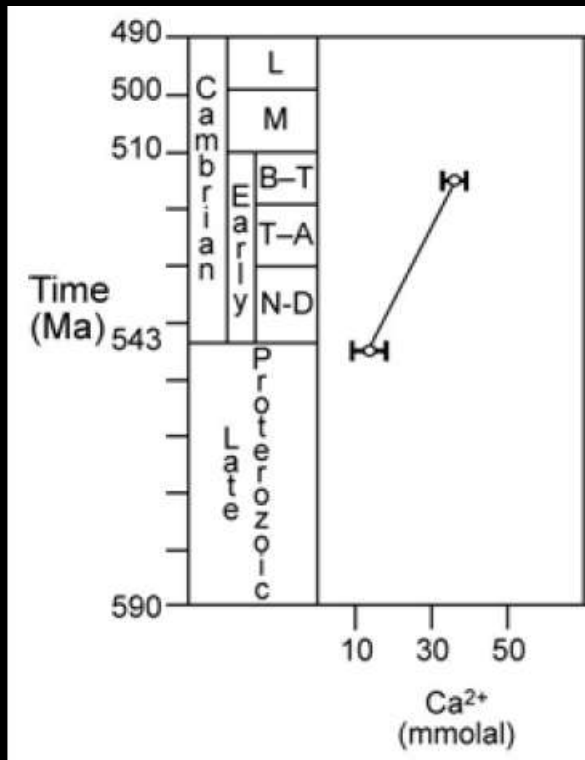
Cambrian stromatolites, USA



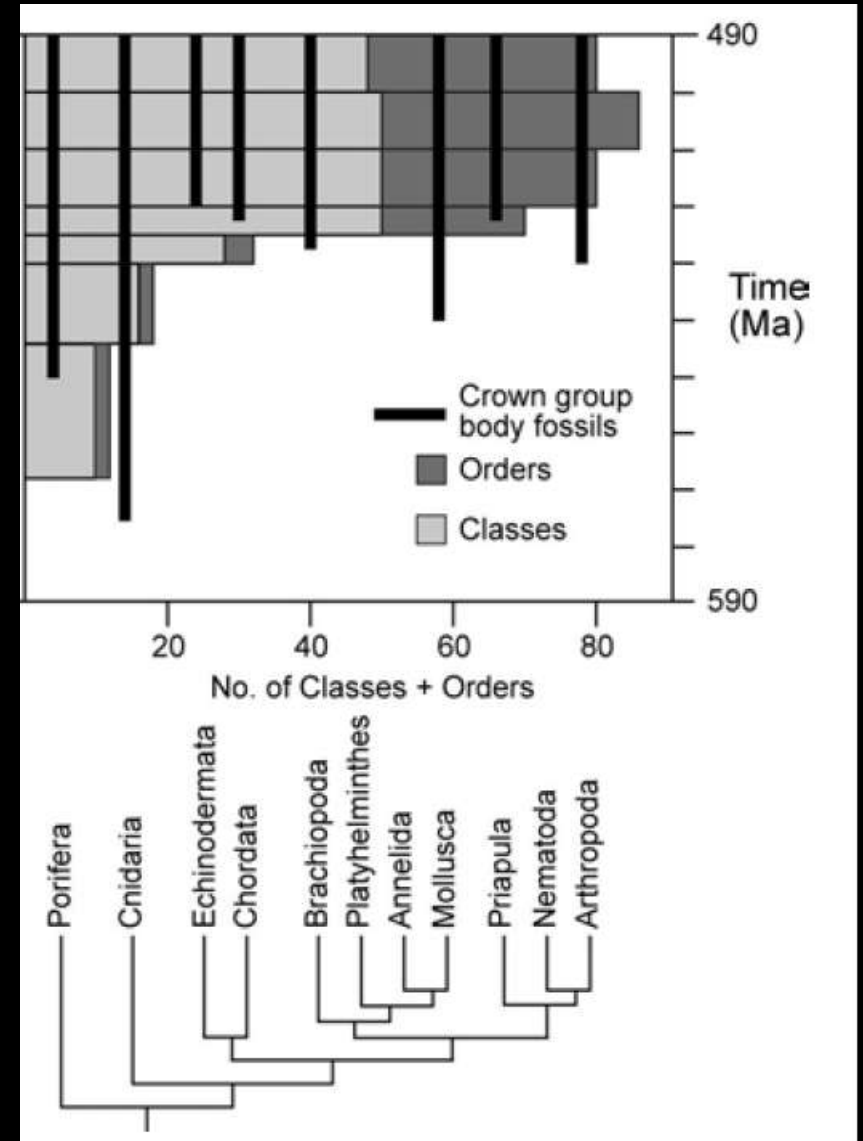
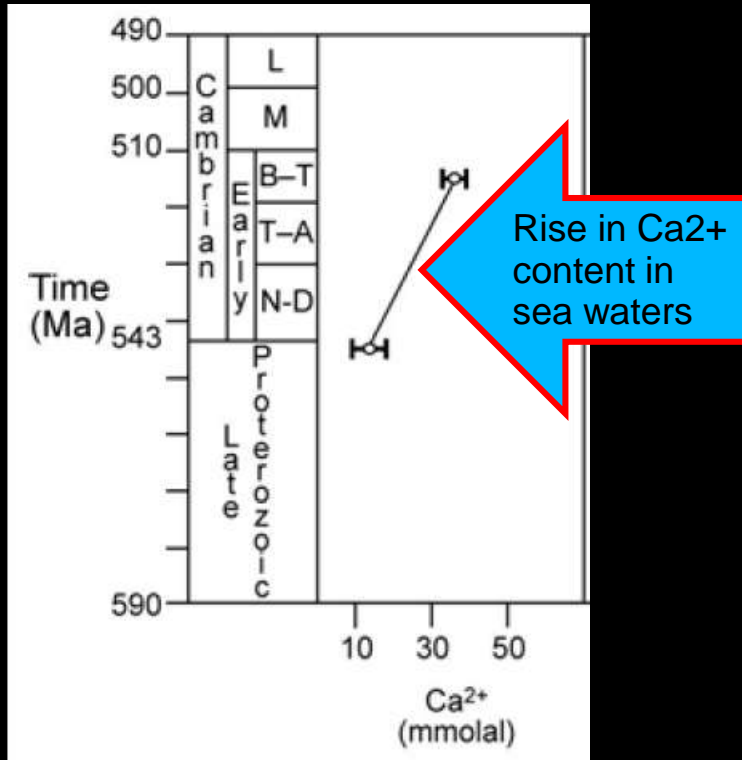
The **abundance of calcifying organisms** started to rise in the Precambrian and all major classes and orders appeared in the Cambrian



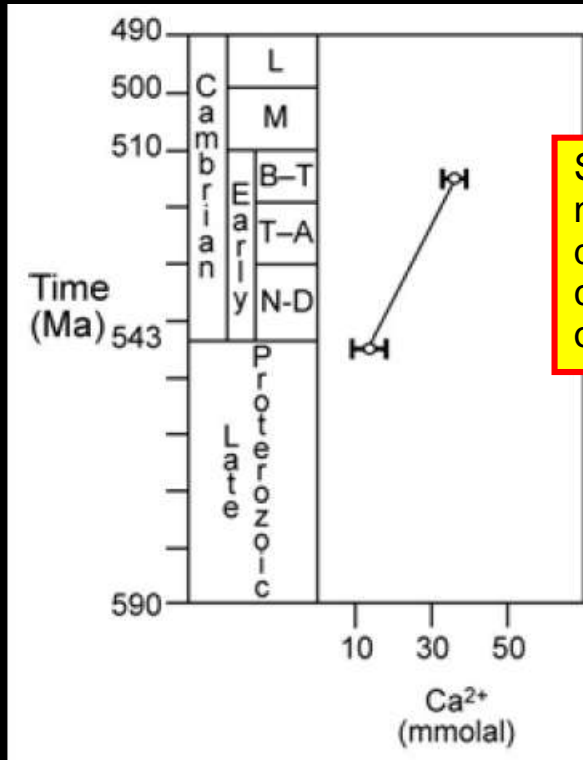
The study of fluid inclusions in halites has revealed a **sharp increase in Ca^{2+} concentration in ocean waters in the Early Cambrian**. Approximately at that time a large increment in the number and diversity of calcifying organisms is observed



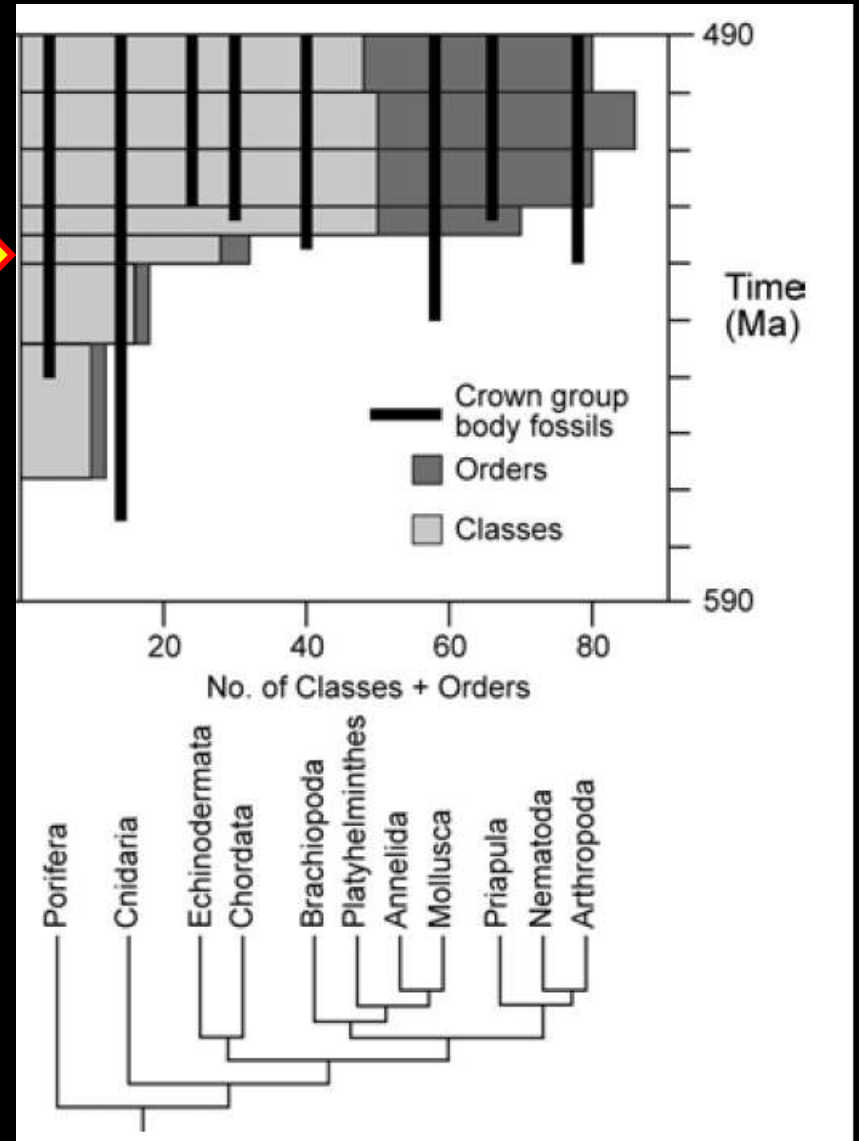
The study of fluid inclusions in halites has revealed a **sharp increase in Ca^{2+} concentration in ocean waters in the Early Cambrian**. Approximately at that time a large increment in the number and diversity of calcifying organisms is observed



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



Sharp rise in number and diversity of calcifying organisms



This suggests a connection between the advent of biocalcification and an increased availability of Ca^{2+} , however, what this connection might be still remains unclear

Uniformitarianism

assumption that the same natural laws and processes that operate in our present-day scientific observations have always operated in the universe in the past and apply everywhere in the universe

In Geology this assumption is often expressed as «**The present is a key for the past**»

In these lessons, however, you have learned that carbonates are intimately linked to life and life changed through time. Carbonate producers changed, ecological characteristics of organisms may have changed...so:



In the study of carbonates, present is the key for...the Pleistocene



Take home messages for today

- Besides grains, a carbonate rock is also made of micrite and cements
- Diagenesis is a phenomenon that virtually interests carbonates since their formation and beyond their burial
- There are various types of cements that form in different diagenetic environments
- Carbonate precipitation in the oceans is a fundamental part of the global carbon cycle
- The deposition of carbonates occurred since the early phases of Earth history. Through time, calcifying organisms changed so for carbonates the present is not necessarily the key to the past
- Carbonate precipitation in the ocean is a complex phenomenon that, in ways that are not yet completely understood, is influenced by sea level fluctuations, ocean chemistry and the “biological factor”