Diagenesis of carbonates

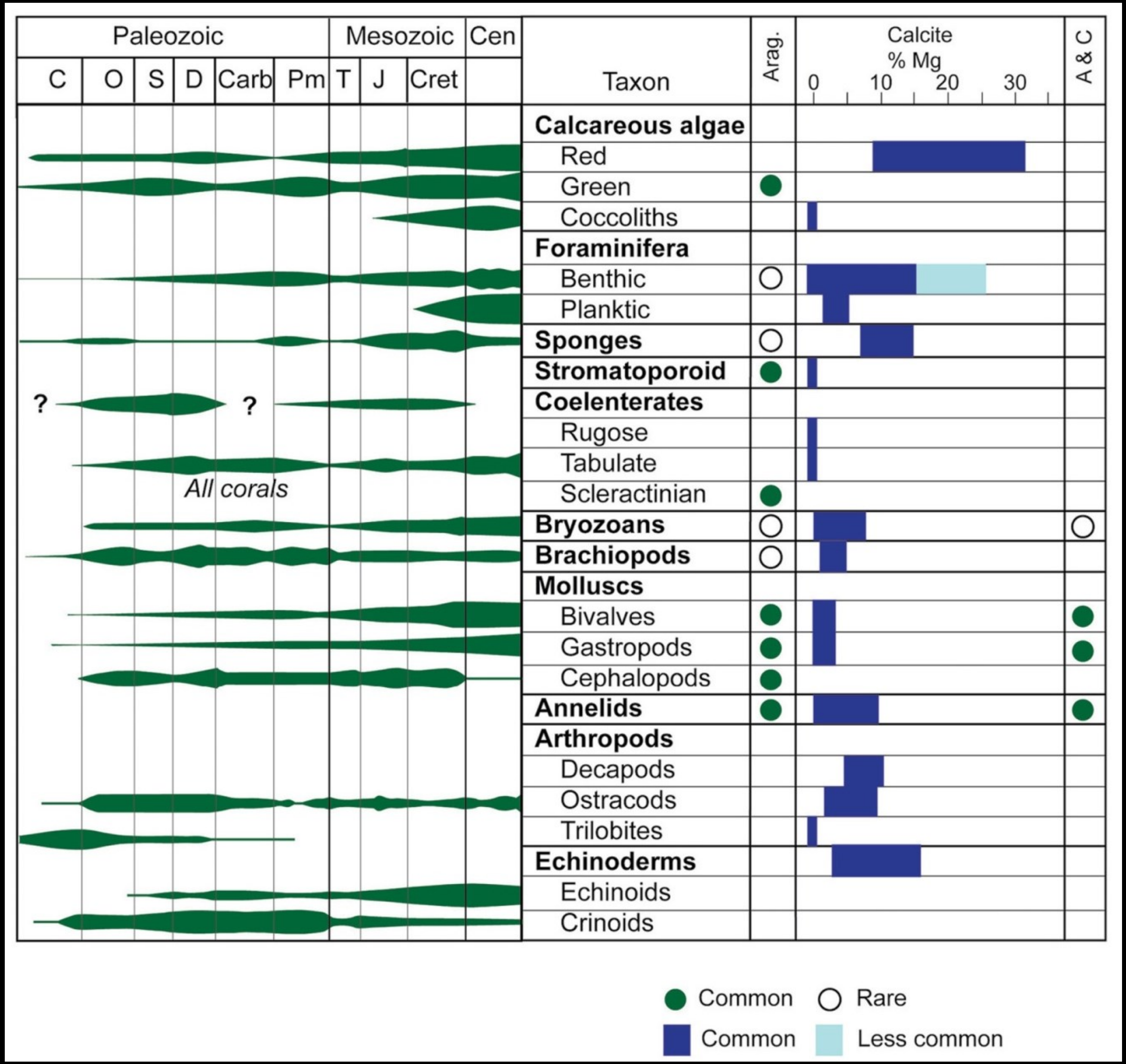
Once the sediment is deposited, **diagenesis** and burial start.
With the term diagenesis we refer to a complex set of processes that turn a sediment into a rock. Typically, diagenesis includes:

- 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

Diagenesis of carbonates

Carbonate of skeletal organisms may have different mineralogical composition.

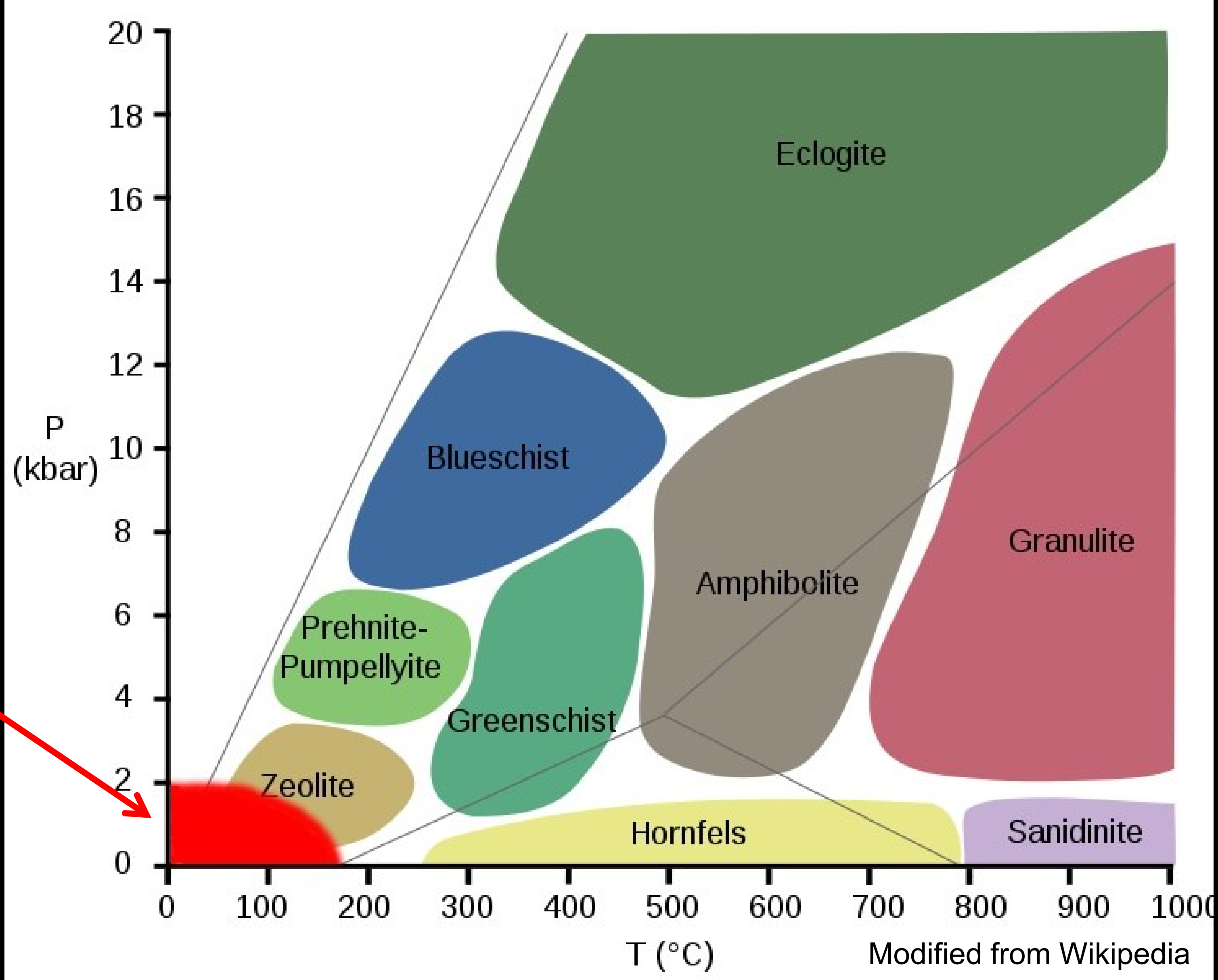
Normally, a diagenized limestone is **only made of low magnesium calcite**. High magnesium calcite and aragonite are present in limestones only in cases of exceptional preservation.



Geological ranges and mineralogical compostion of skeletal organisms. From James and Jones, 2015.

Diagenesis of carbonates

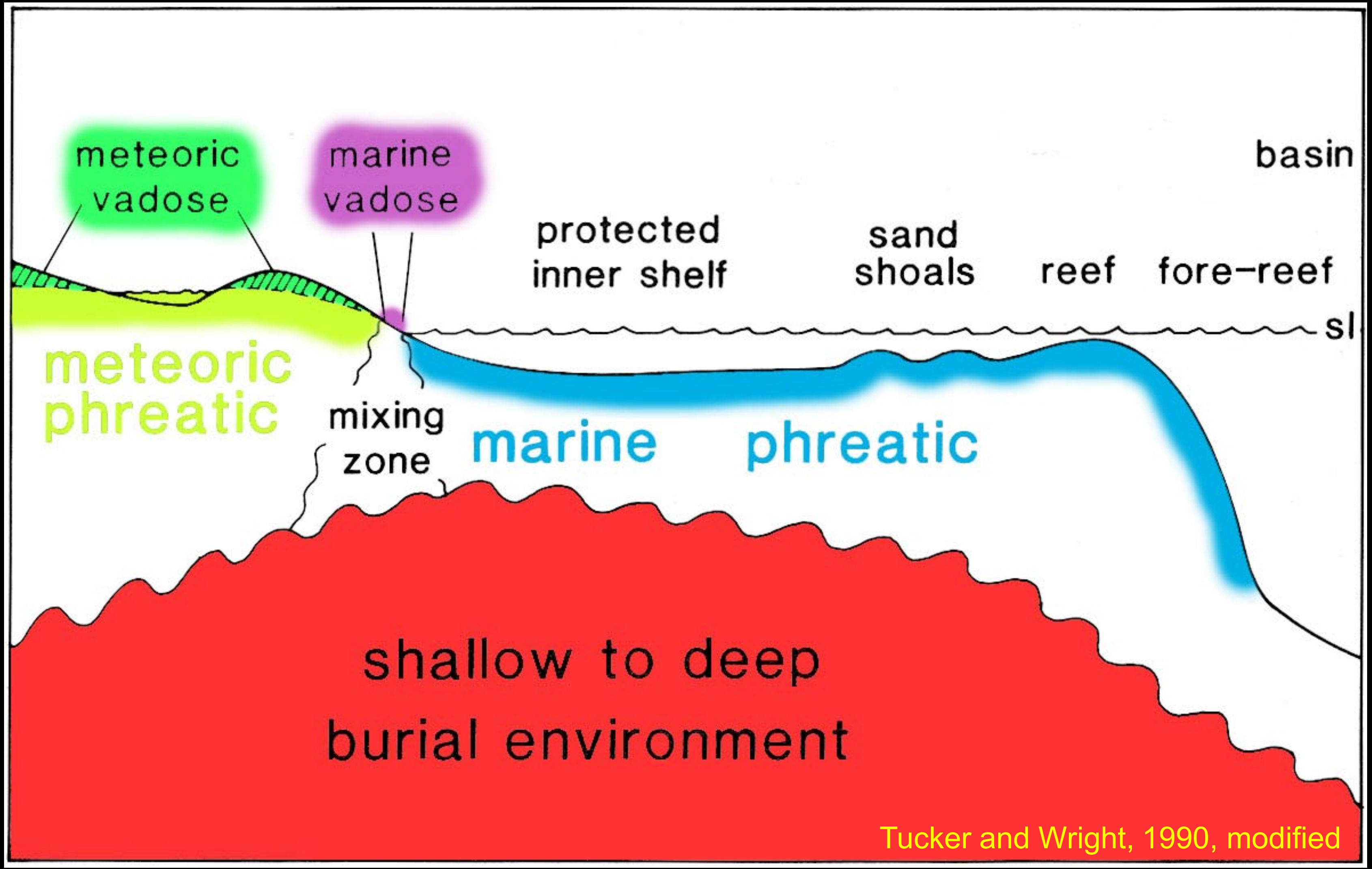
The realm of **diagenesis**: between deposition and metamorphism



Modified from Wikipedia

Diagenesis of carbonates – diagenetic environments

The products of diagenesis (including cements) are formed in specific environments within the lithosphere.



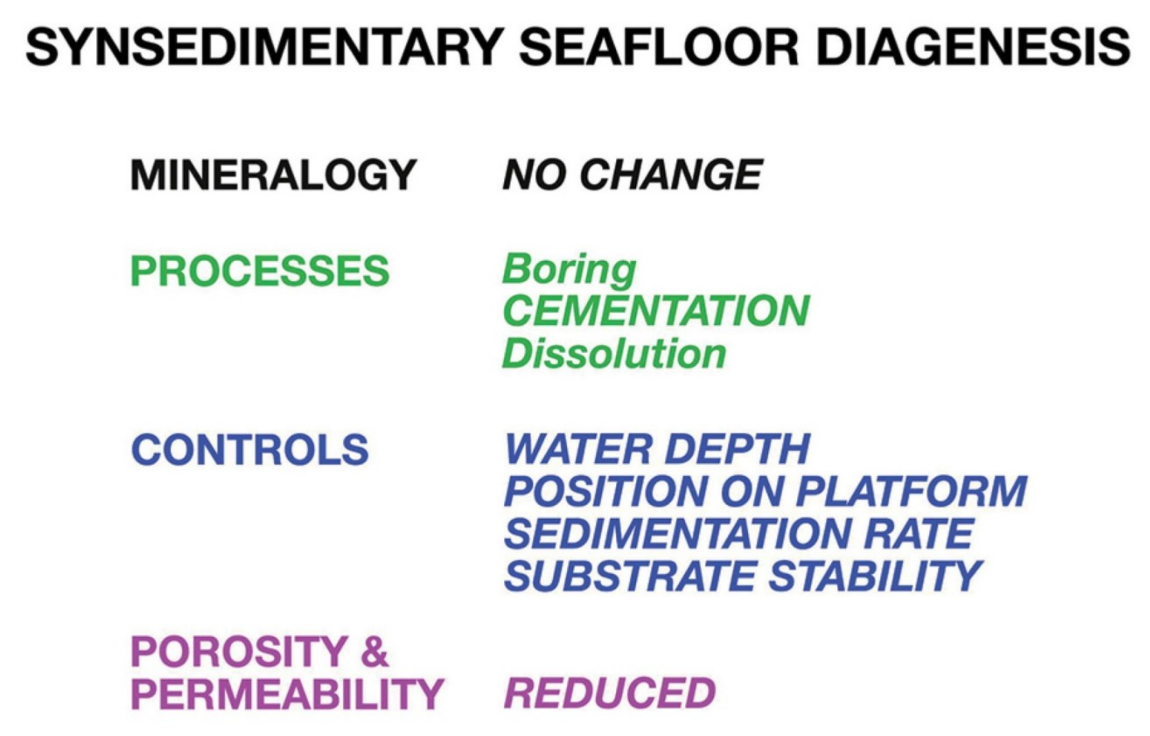
Tucker and Wright, 1990, modified

Diagenesis of carbonates – synsedimentary marine environment

Two main diagenetic environments can be distinguished in marine realm:

Neritic, where seawater (today) is normally supersaturated with respect to carbonate.
Here little or no dissolution occurs in the water, but instead happens within the sediments because of reduction of organic matter that reduces alkalinity in pore-waters

Slope and basin, where seafloor can intersect lysocline or CCD.
Dissolution is largely water-driven and depends on the undersaturation conditions in the water column



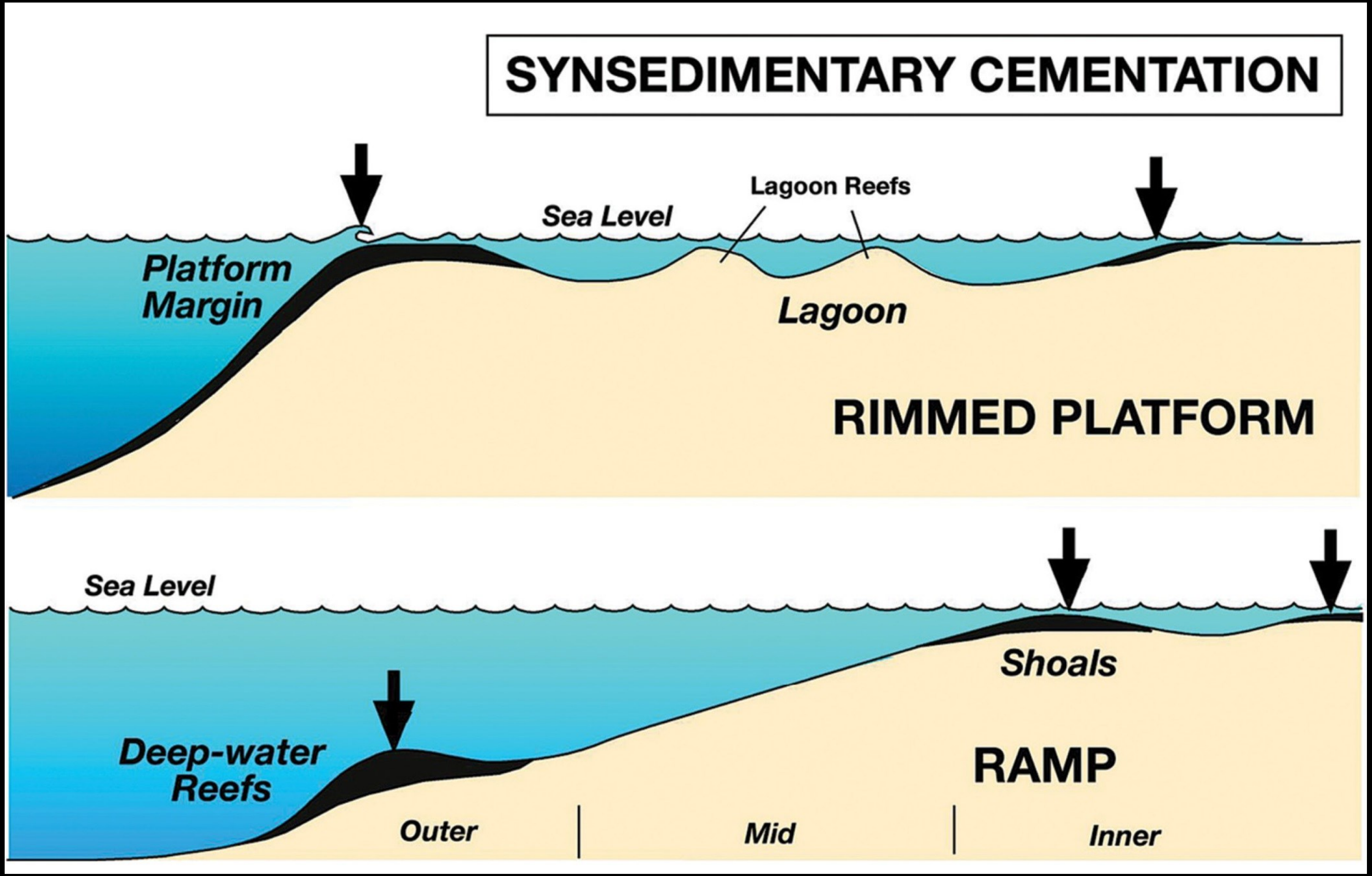
SYNSEDIMENTARY SEAFLOOR DIAGENESIS

MINERALOGY	***NO CHANGE***
PROCESSES	***Boring*** ***CEMENTATION*** ***Dissolution***
CONTROLS	***WATER DEPTH*** ***POSITION ON PLATFORM*** ***SEDIMENTATION RATE*** ***SUBSTRATE STABILITY***
POROSITY & PERMEABILITY	***REDUCED***

From James and Jones, 2015.

Diagenesis of carbonates – synsedimentary marine cementation

Carbonate synsedimentary systems can be characterized by synsedimentary cementation



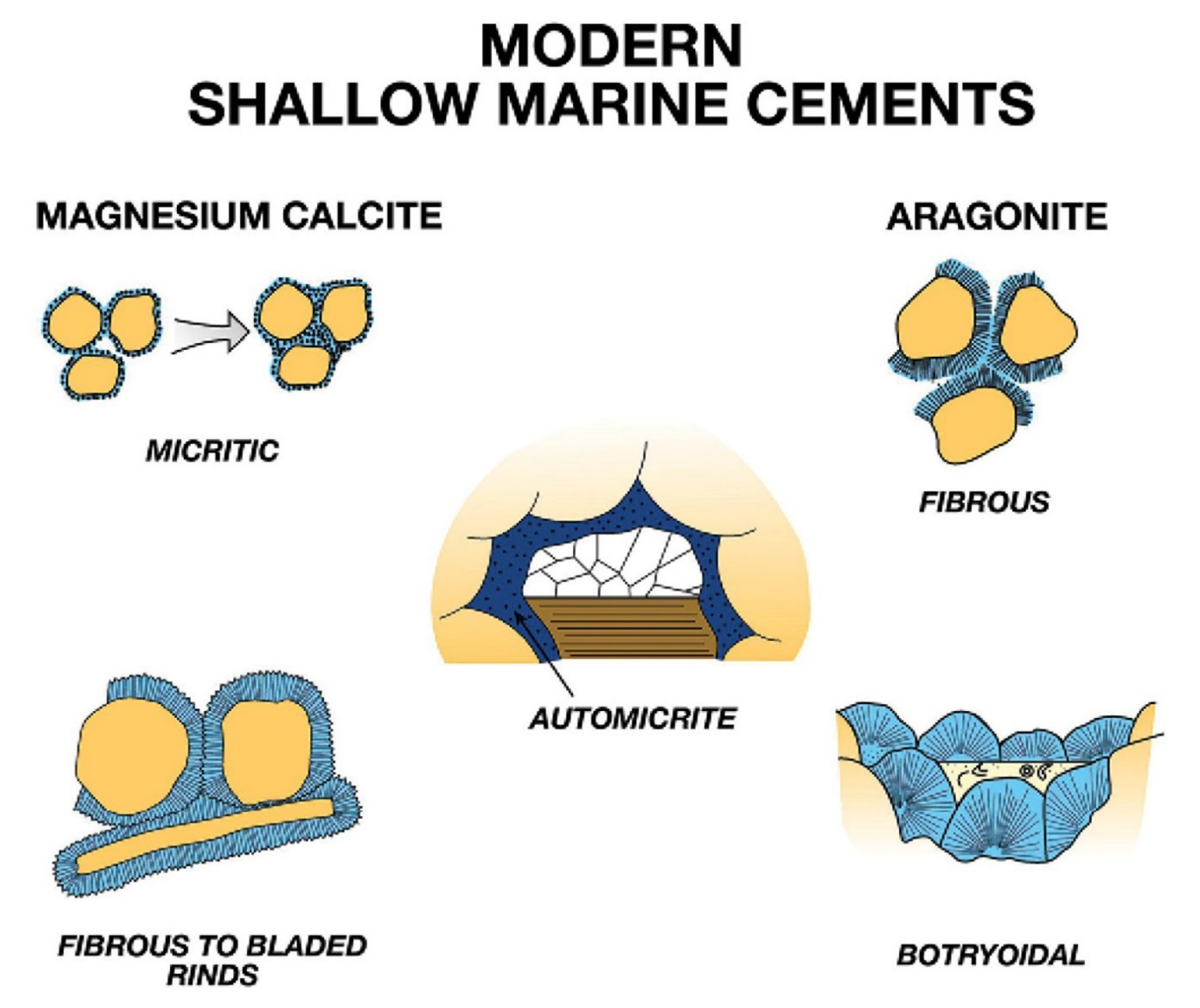
From James and Jones, 2015.

Diagenesis of carbonates – synsedimentary marine cementation

A product of marine synsedimentary diagenesis are marine cements that contribute to the lithification process:

Synsedimentary carbonate precipitation occurs in marine phreatic environments and today is largely restricted to the neritic zone.

Precipitated cements are aragonite or Mg-calcite, are normally peloidal, micritic of fibrous and typically isopachous.

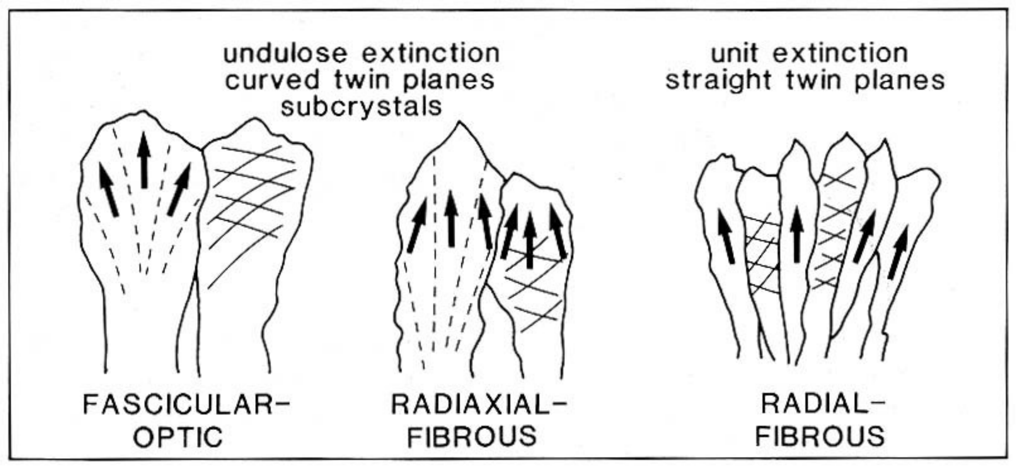


From James and Jones, 2015.

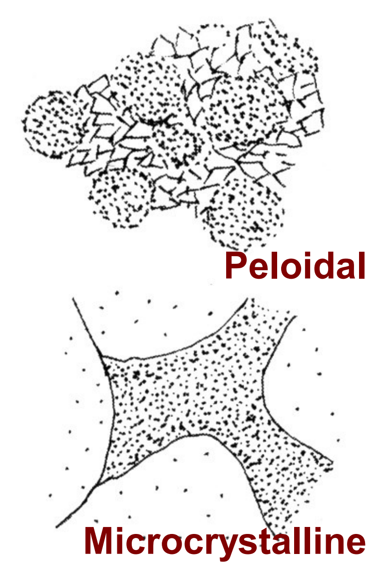
Diagenesis of carbonates – synsedimentary marine environment

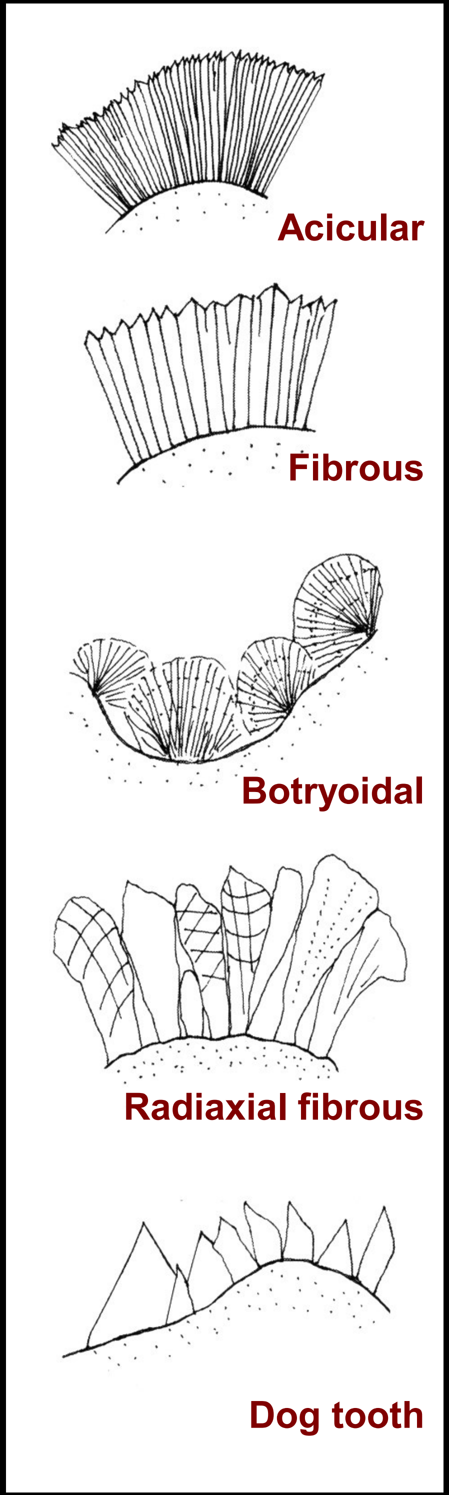
Cements are first of all described by the shape of their crystals and crystal aggregates.

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



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

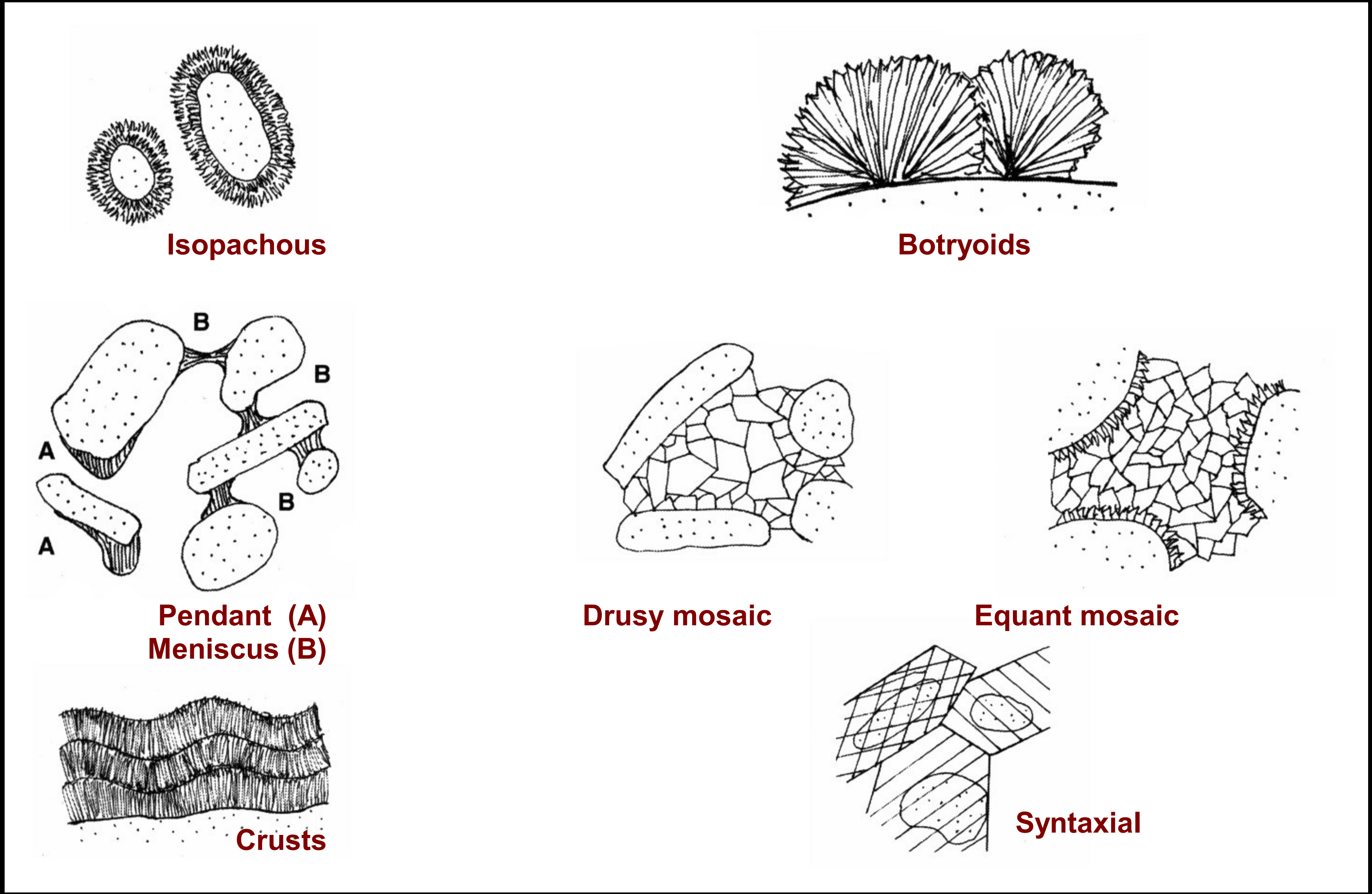




Flügel, 2004

Diagenesis of carbonates – synsedimentary marine environment

Secondly, the relation between cement and grains should be described.



Flügel, 2004

Diagenesis of carbonates – marine phreatic cements

Typical marine phreatic cements

- aragonitic crusts and **botryoidal cements**
- crusts of **radiaxial fibrous** cements
- **peloidal cement** made of high magnesium calcite

These cements often form in semi-closed cavities as intrareef spaces, or the internal cavity of tepee structures.

Peloidal cements are typical of **geopetal cavities** within bioclasts (e.g., gastropods). They are interpreted as the result of the activity of heterotrophic bacteria feeding on the soft parts of the organism that made the bioclast.

Hardgrounds are a product of cementation in the marine phreatic diagenetic environment.

Diagenesis of carbonates – marine phreatic cements

Modern marine cements precipitated from seawater with high Mg/Ca ratio are mostly Mg-calcite or aragonite

Mg-calcite cement types

- micrite-size cement crystals
- fibrous cements
- blocky or equant crystals

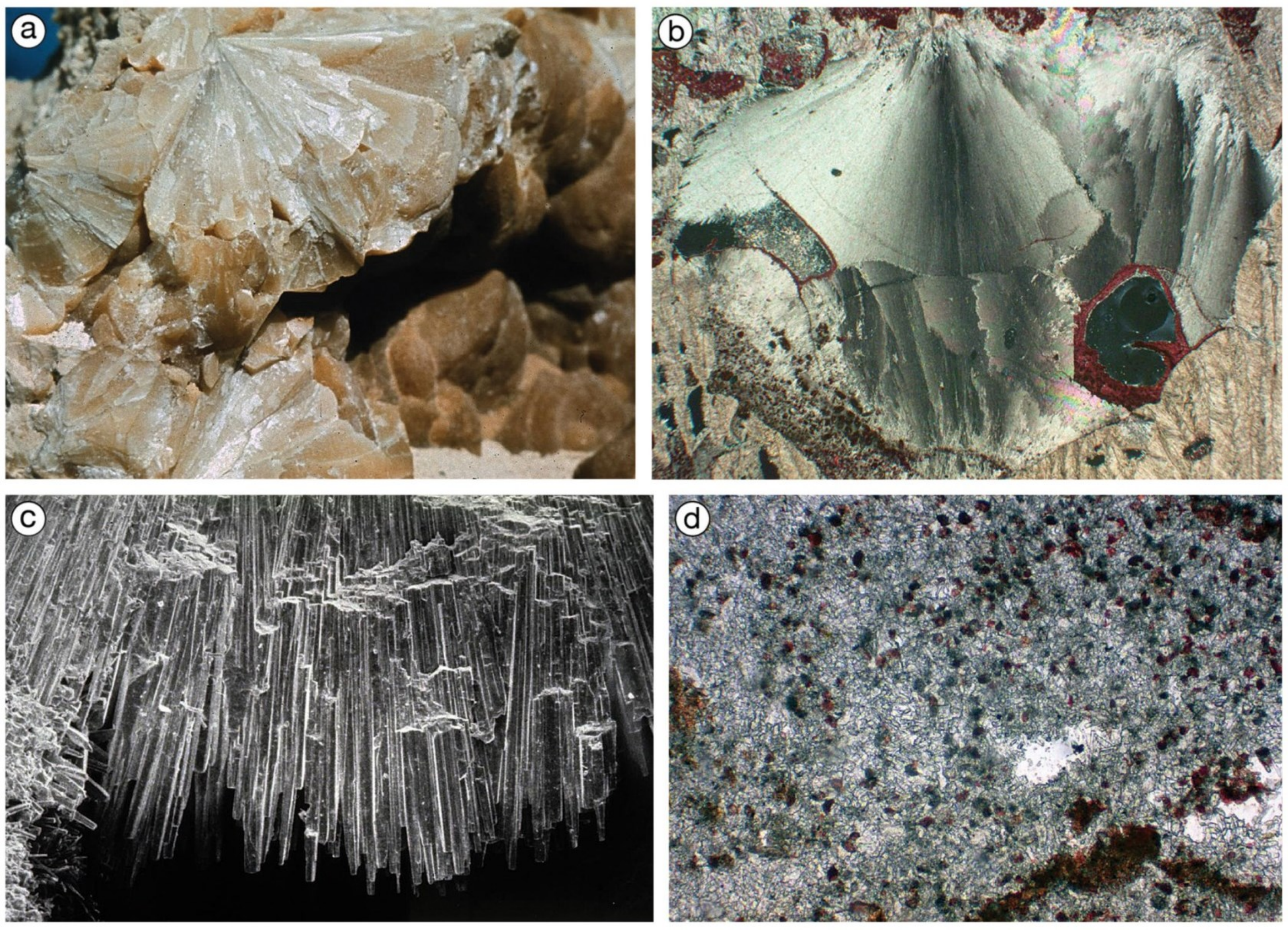
Aragonite cement types

- Botryoidal cements

Diagenesis of carbonates – marine phreatic cements

One of few Recent marine phreatic cements, from the deep-reef cavities of Belize

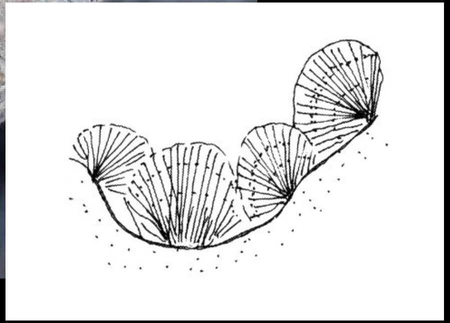
Aragonite botryoidal cement precipitates today in Belize. These marine phreatic cements are peculiar for their cm scale dimensions and their formation is probably related to local supersaturation of seawater in semiclosed microenvironments as intrareef cavities. a) Aragonite botryoids partially filling a sedimentary void, 6 cm; b) thin section image of an aragonite botryoid, 9 mm c) SEM image of aragonite crystals of a botryoidal cement, 1 mm; d) microctristalline aragonite cement (clear) and high-magnesium calcite peloids (red), 1.5 mm.



From James and Jones, 2015.

Diagenesis of carbonates – marine phreatic cements

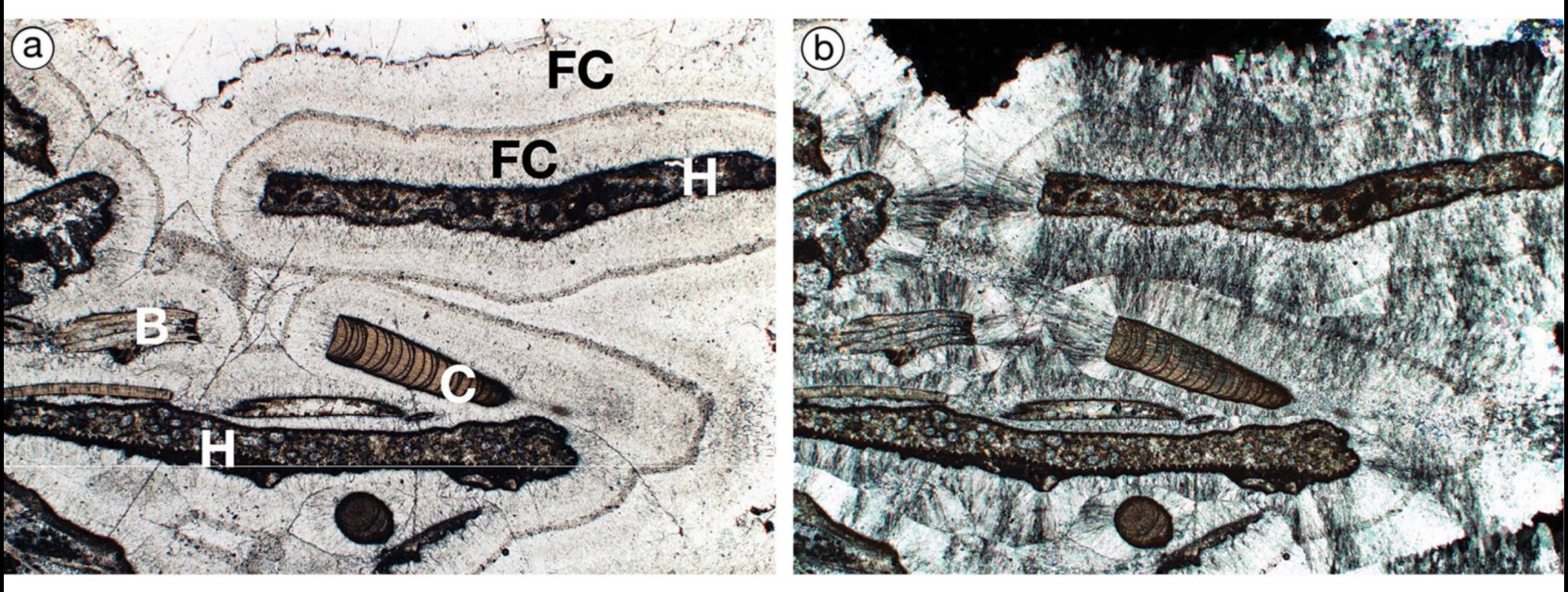
Ancient (Triassic) botryoidal and fibrous cements. Aragonite is recrystallized.



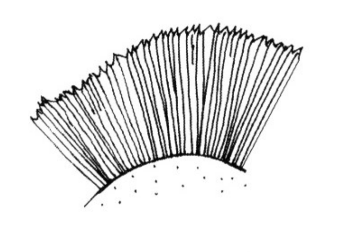
Latemar platform, Anisian, Dolomites, Italy

Diagenesis of carbonates – marine phreatic cements

Fibrous isopachous synsedimentary cement



Pliocene fibrous isopachous marine cement. a) bioclastic grainstone with Halimeda (H), coralline algae (C) and bryozoans (B). Note the two rims of fibrous calcite surrounding the fossil fragments. b) under polarized light the fibrous nature of the cements is highlighted. From James and Jones, 2015.



Diagenesis of carbonates – marine phreatic cements

Radiaxial fibrous cement in hand sample and under the optical microscope

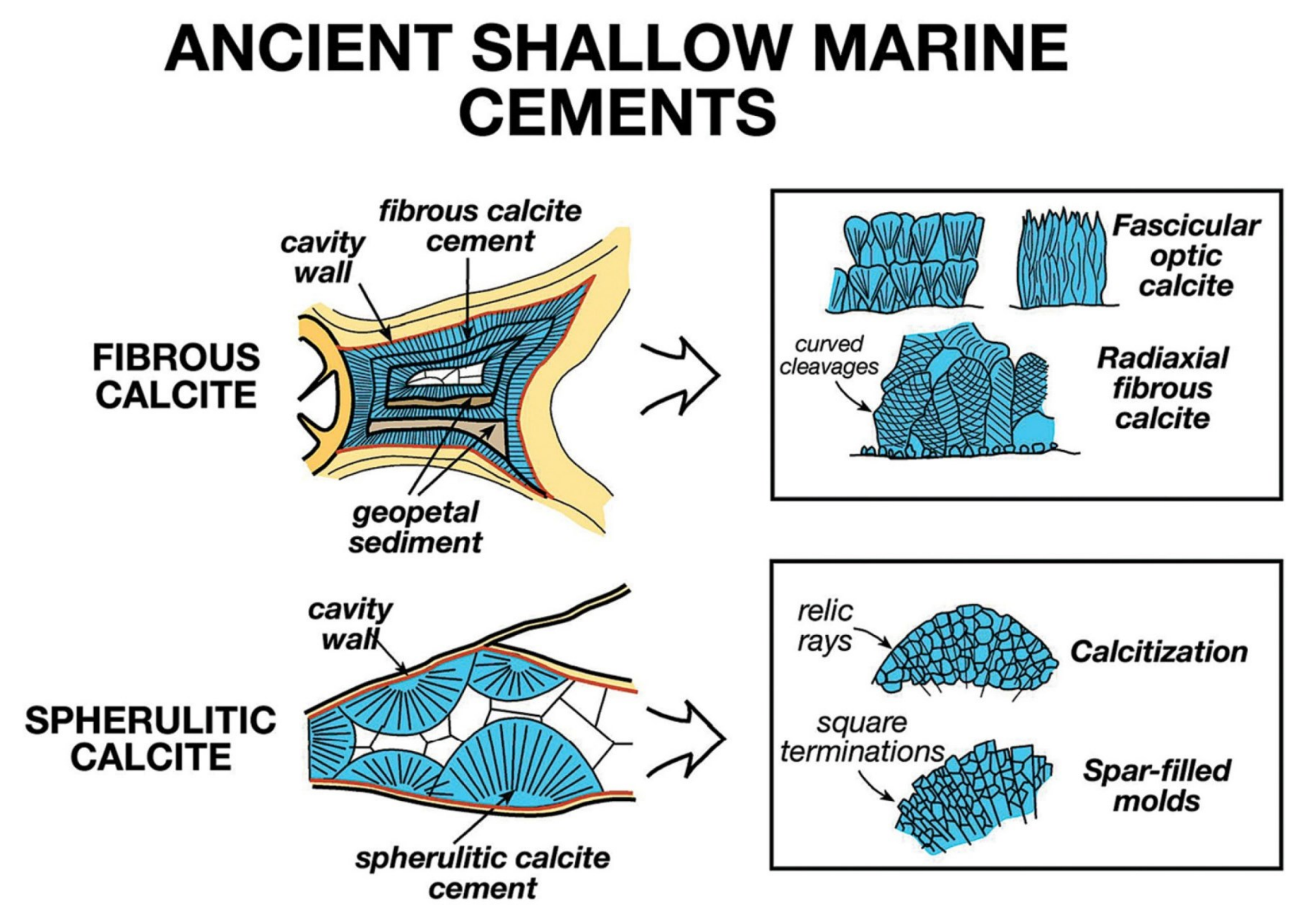
Latemar platform, Anisian, Dolomites, Italy

Carnian, Cortina d'Ampezzo, Dolomites, Italy, crossed polarizers. Note undulated extinction and sediment sitting on top of the cement. The bioclast is a brachiopod shell.

Diagenesis of carbonates – marine phreatic cements

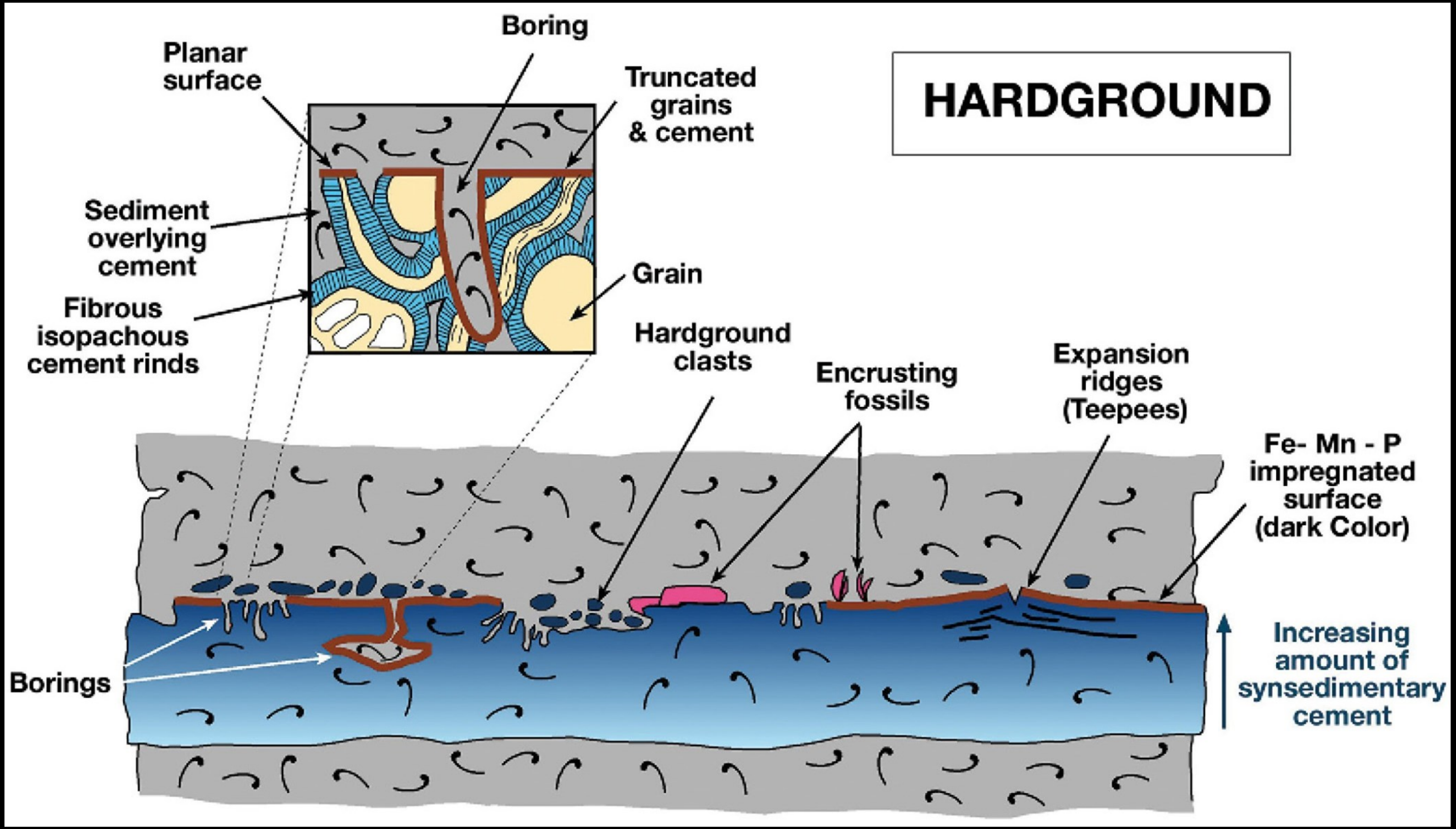
N.B. Always remember that most of ancient carbonates, regardless their original mineralogy are now low-Mg calcite

Ascertain the original mineralogy of ancient sediments is a major problem.
Note also that water composition (e.g. Mg/Ca ratio) changed through time.
For instance, radiaxial fibrous cements (rare today) were common in the Cretaceous when Mg/Ca ratio is thought to have been very low. It is therefore possible that they were originally low-Mg Calcite

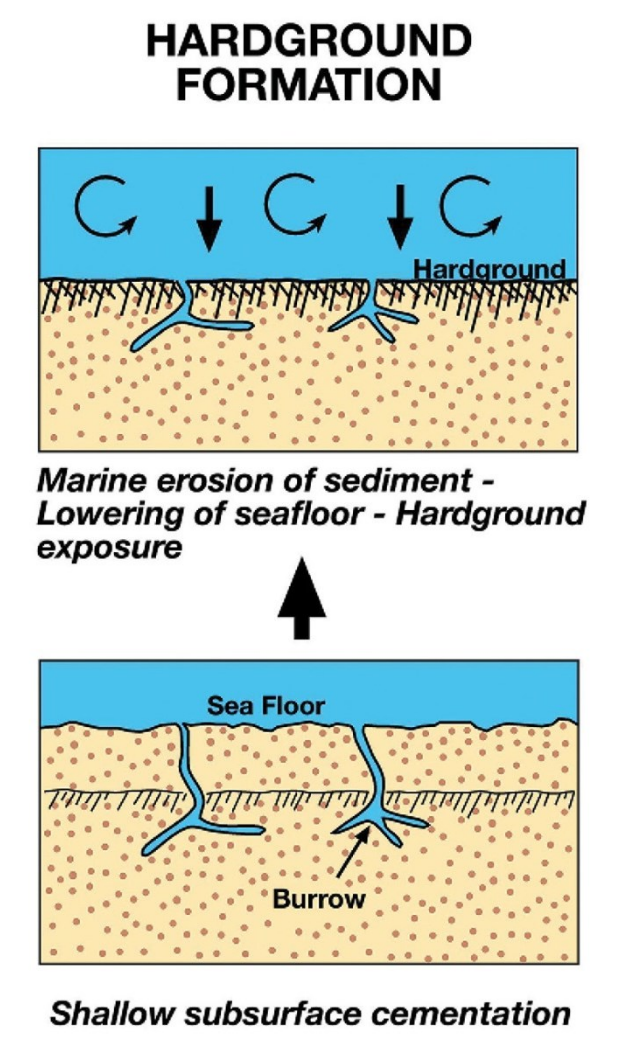


Diagenesis of carbonates – synsedimentary cementation

Hardgrounds can be a product of diagenetic synsedimentary cementation



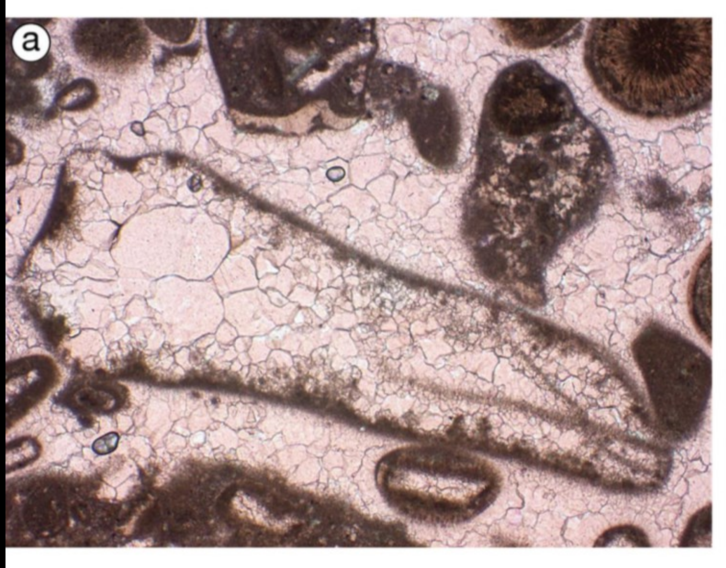
Main macroscale and petrographic attributes of hardgrounds. From James and Jones, 2015.

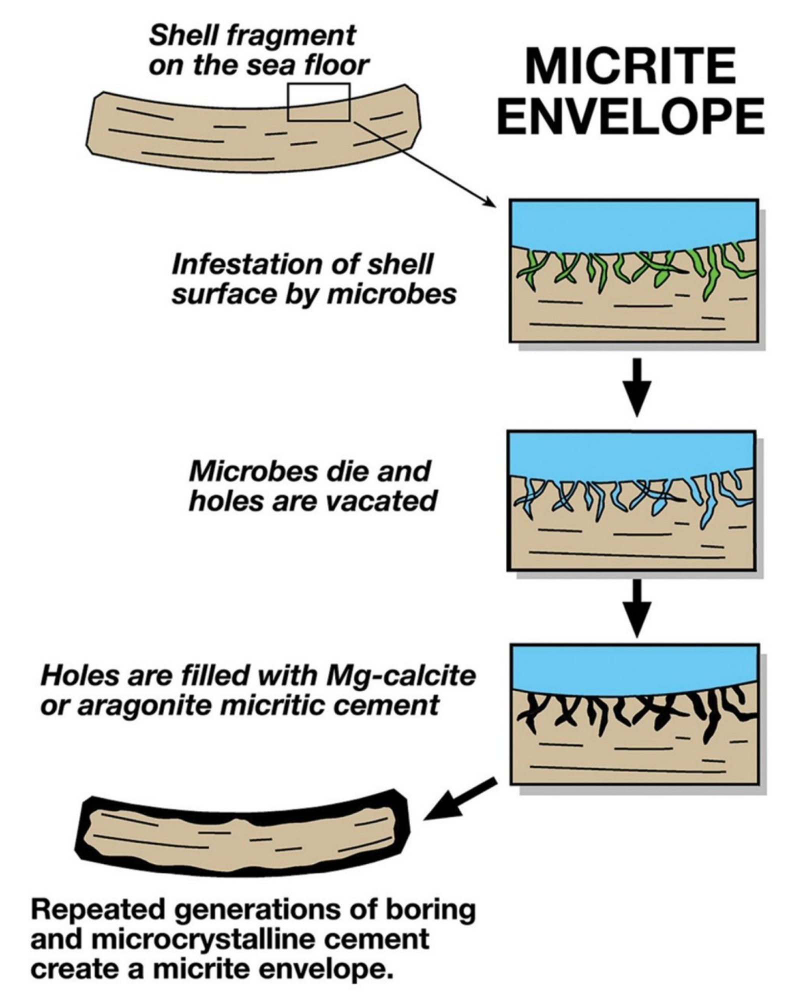


From James and Jones, 2015.

Diagenesis of carbonates – synsedimentary alteration

Carbonates can undergo alterations right after precipitation because of the action on endolith organisms (algae, fungi, bacteria). This phenomenon can be recognized from the presence of a micritie envelope surrounding carbonate grains. If the phenomenon is particulary intense, a grain can be completely altered and became a diagenetic peloid.





MICRITE ENVELOPE

Shell fragment on the sea floor

Infestation of shell surface by microbes

Microbes die and holes are vacated

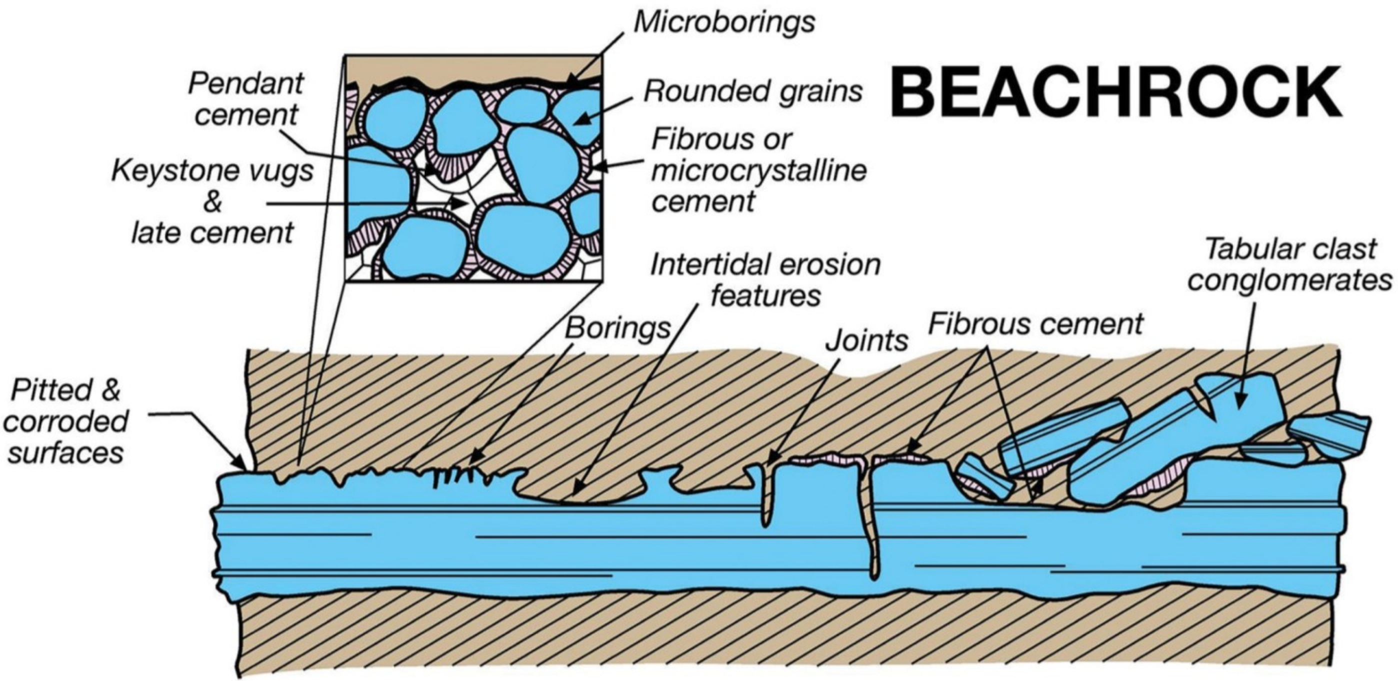
Holes are filled with Mg-calcite or aragonite micritic cement

Repeated generations of boring and microcrystalline cement create a micrite envelope.

Diagenesis of carbonates – marine vadose cements

Marine vadose cements are pendant and meniscus cements, aragonitic or micritic (derived from high magnesium calcite). It is a form of early lithification.

Beach rock: sea water promotes cementation of shoreface sands, later exposed by, e.g., storms.




Anna Breda

Diagenesis of carbonates – marine vadose cements

Tepee structures are usually a product of supratidal diagenesis

Diagenesis of carbonates – marine vadose cements

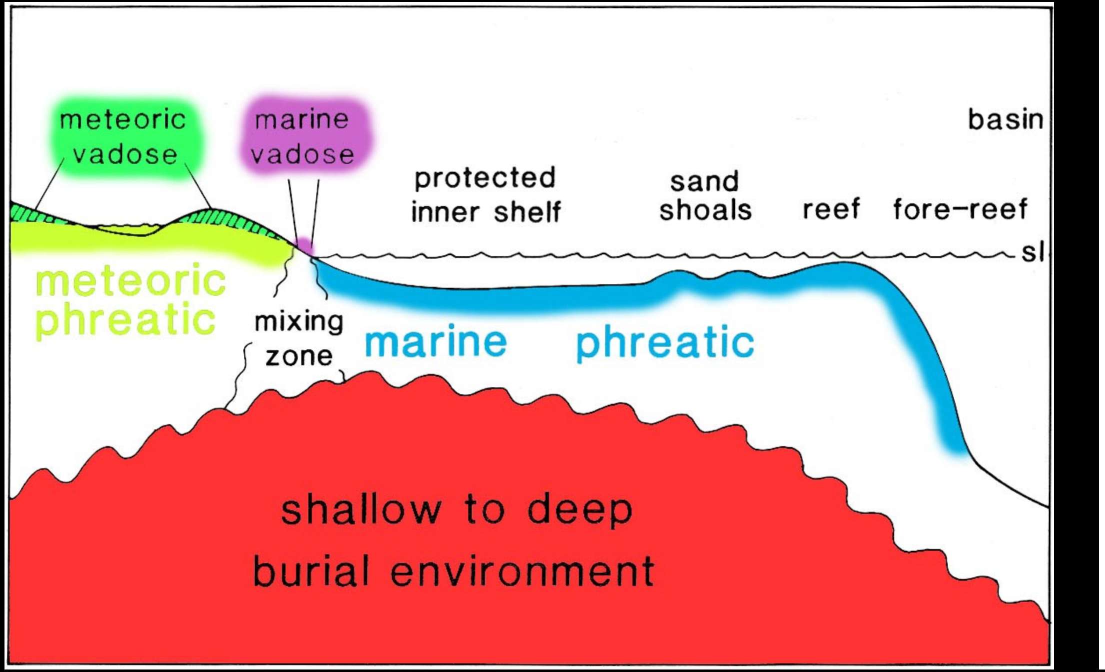
Aragonitic dripstone and meniscus cements, recrystallized into a mosaic of low magnesium calcite.

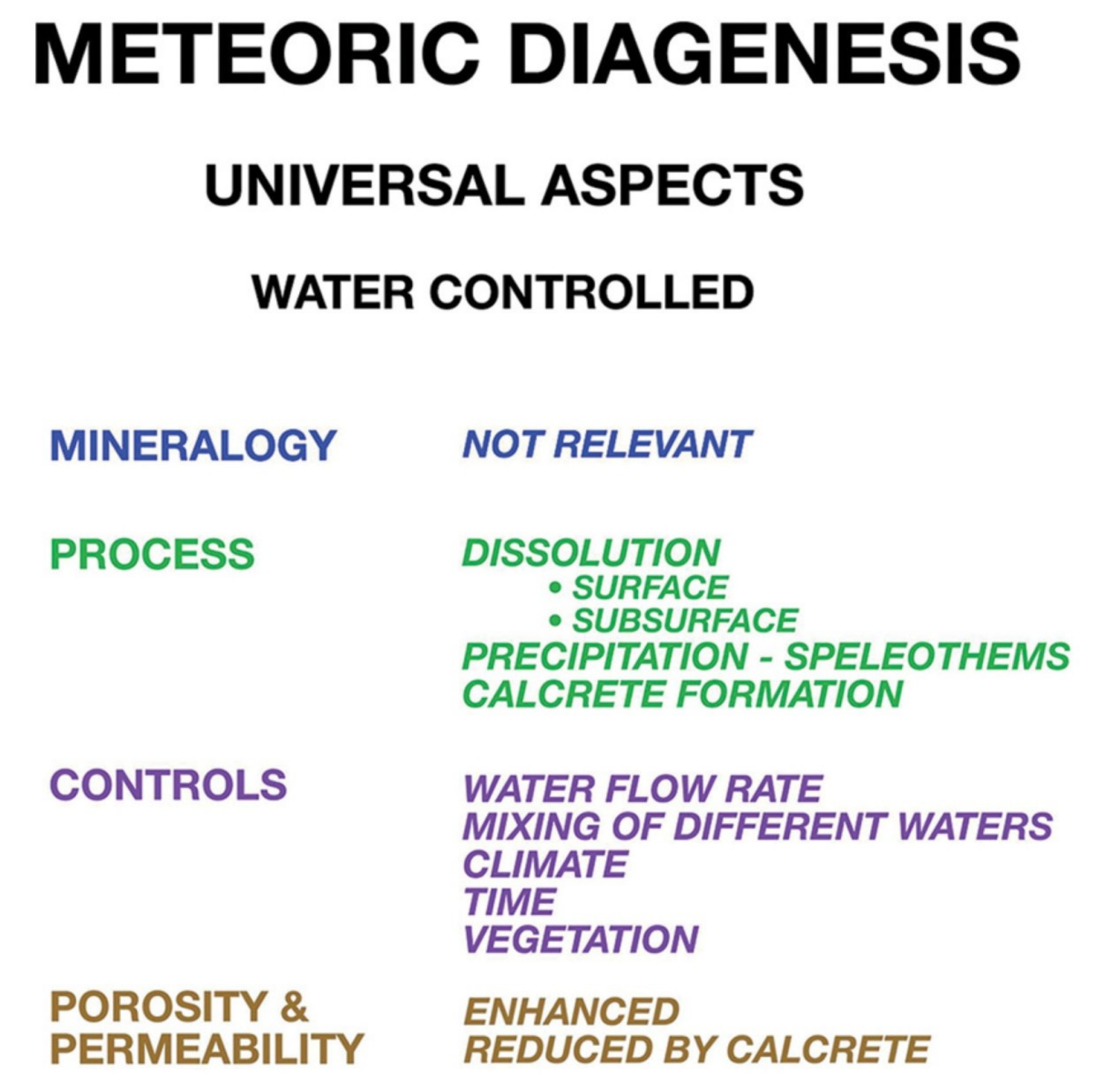
Diagenesis of carbonates – meteoric diagenesis

Meteoric diagenesis occurs when carbonate sediments or limestone interact with freshwater.

Two main types of meteoric diagenesis:

- **Mineral-driven**
- Water-driven





METEORIC DIAGENESIS

UNIVERSAL ASPECTS

WATER CONTROLLED

MINERALOGY	*NOT RELEVANT*
PROCESS	*DISSOLUTION* *• SURFACE* *• SUBSURFACE* *PRECIPITATION - SPELEOTHEMS* *CALCRETE FORMATION*
CONTROLS	*WATER FLOW RATE* *MIXING OF DIFFERENT WATERS* *CLIMATE* *TIME* *VEGETATION*
POROSITY & PERMEABILITY	*ENHANCED* *REDUCED BY CALCRETE*

Diagenesis of carbonates –water controlled meteoric diagenesis

- When they precipitate, meteoric waters are undersaturated.
- they have a low Mg/Ca ratio.

Therefore:

- **Dissolution and karst** are common processes, especially for high-Mg calcite and aragonite
- Meteoric waters can become supersaturated percolating through soils, rocks and sediments
- Once supersaturated **low magnesium calcite can precipitate**.

Diagenesis of carbonates – meteoric diagenesis

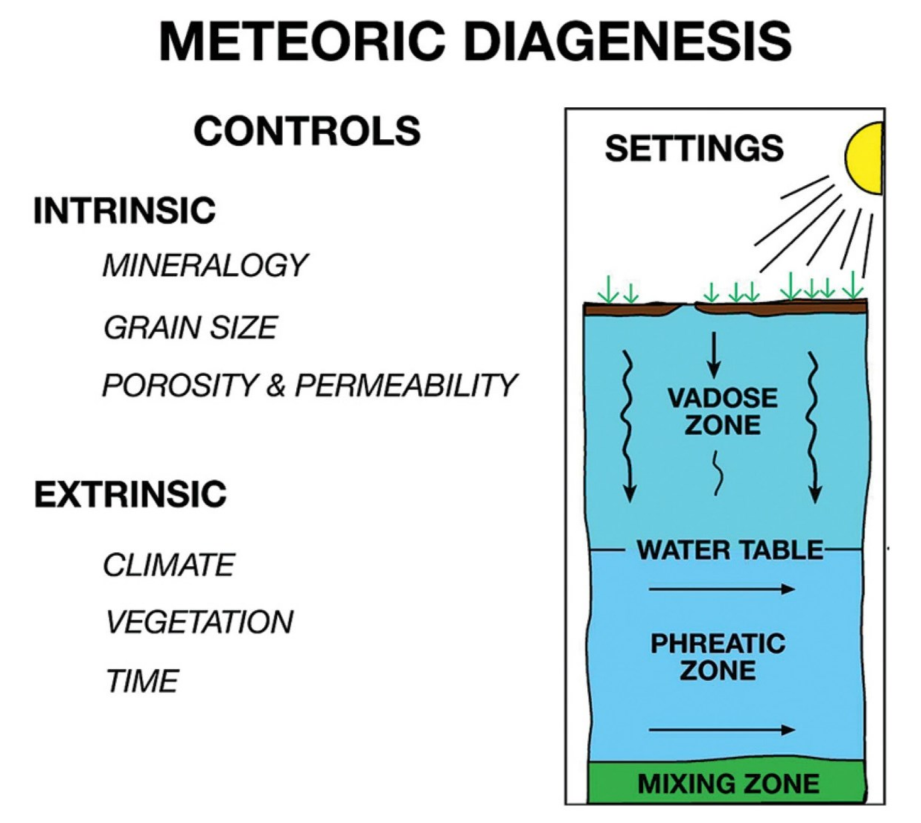
Above the water table, pores are filled with water only episodically. This is the **meteoric vadose environment**.

- Pendant and meniscus cements, calcitic

Below the water table, **meteoric phreatic environment**.

- Isopachous calcitic cements
- Usually they form a rim on grains but do not fill completely the pores.

“Meteoric diagenesis may set the stage for subsequent porosity evolution, but the most significant porosity loss still occurs during burial diagenesis” *Schmoker and Hester, 1986.*



From James and Jones, 2015.

Diagenesis of carbonates – meteoric diagenesis

Rain water*

Total dissolved salts (salinity):
- 4.7 ppm

pH:
- 5.7

Mg/Ca:
- Ca. 0.4

*) A typical meteoric water is that of rivers, which is of course much more saline than rain water. Rhine river as it exits the Alps has:

Total dissolved salts:
- 207 ppm

pH:
- Ca. 7 – 7.8

Mg/Ca:
- 0.18

Seawater

Total dissolved salts (salinity):
- 35000 ppm (35 ‰)

pH:
- 8.1

Mg/Ca:
- 5.2

http://www.tate.org.uk/art/artworks/gursky-the-rhine-ii-p78372

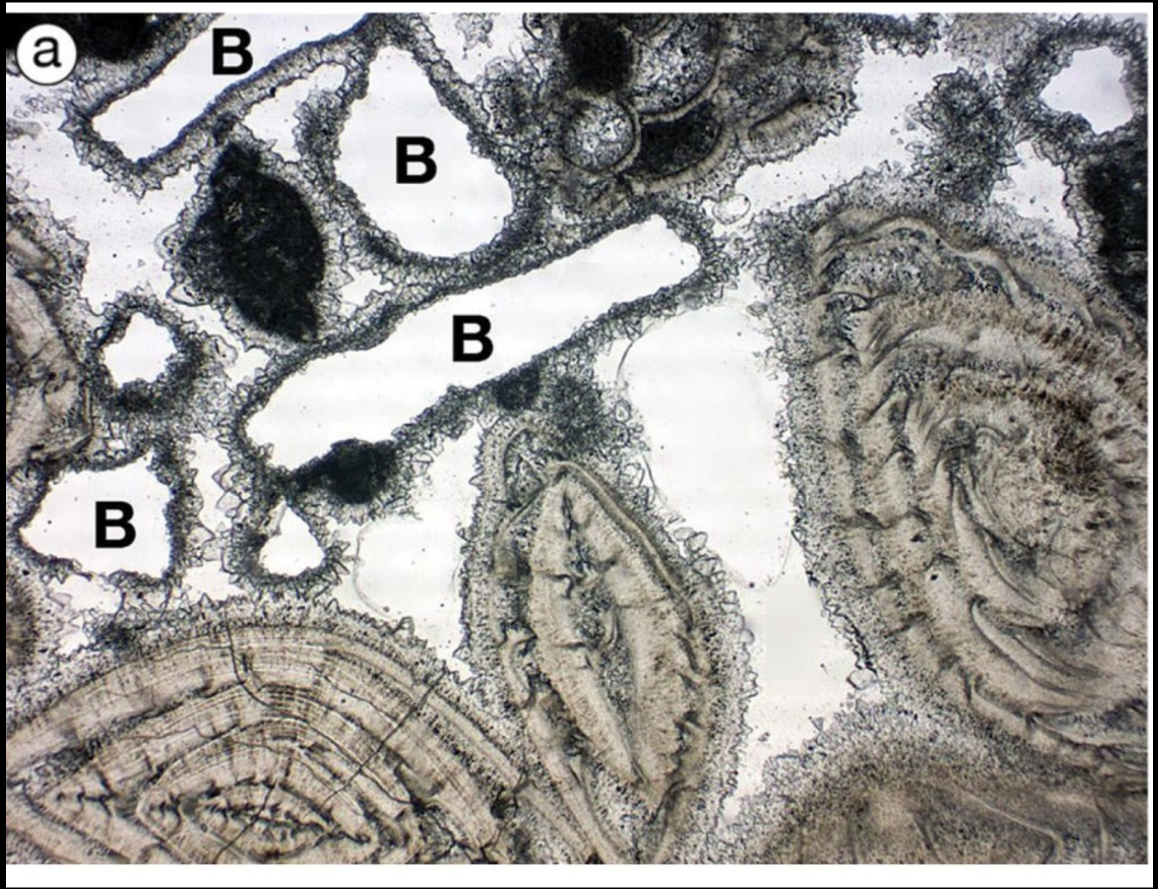
Diagenesis of carbonates – mineral specific meteoric diagenesis

Mineral-driven diagenesis includes dissolution, cementation and porosity formation occurring while metastable minerals are transformed in diagenetic low-Mg Calcite.

In this type of diagenesis:

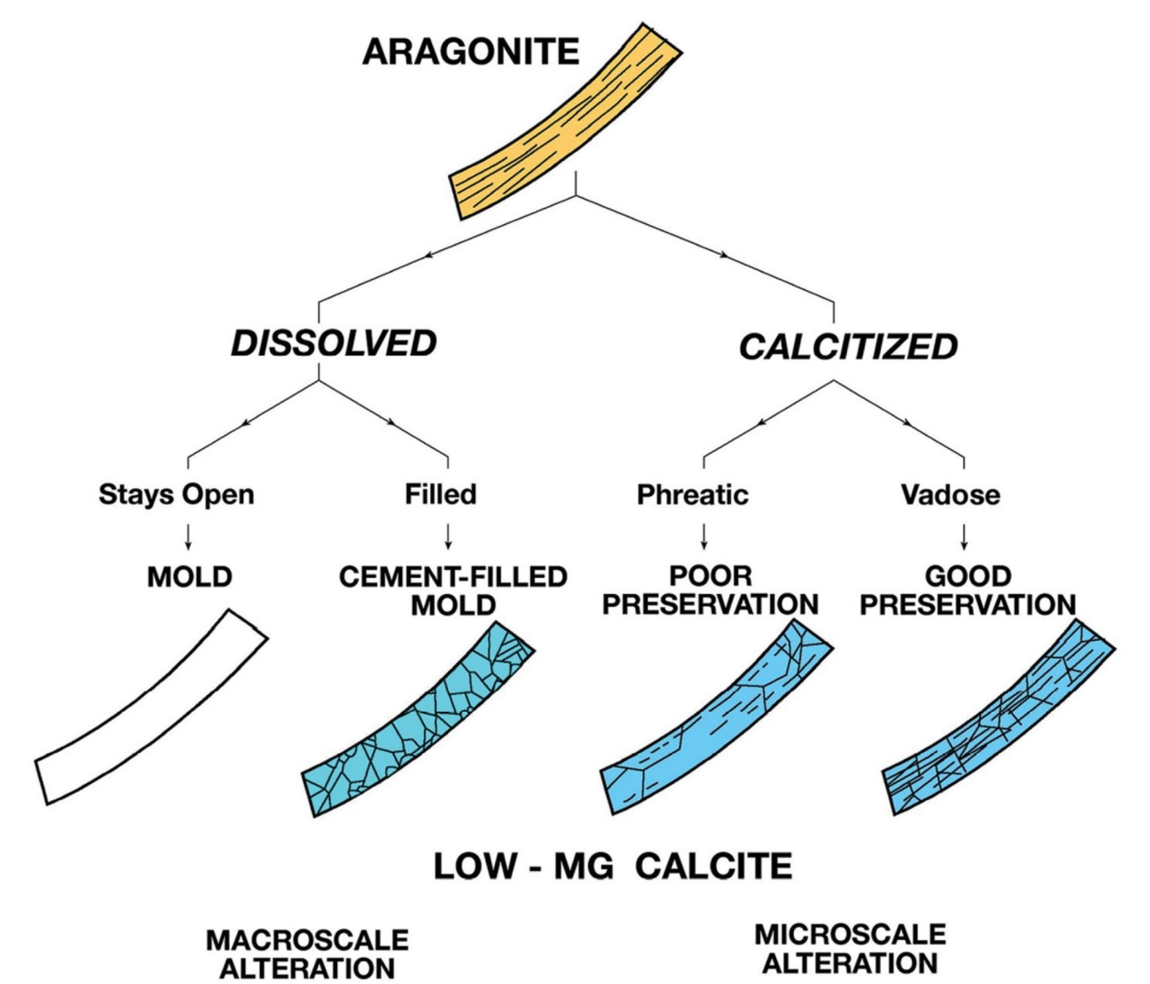
Original Mg-Calcite becomes low-Mg Calcite, but microstructure is preserved and is distinguishable only with SEM

Aragonite components are
- completely dissolved forming a pore that can remain open or be filled.
- Calcitization occurs with the formation of a mosaic of calcite crystals cross-cutting origina fabric.



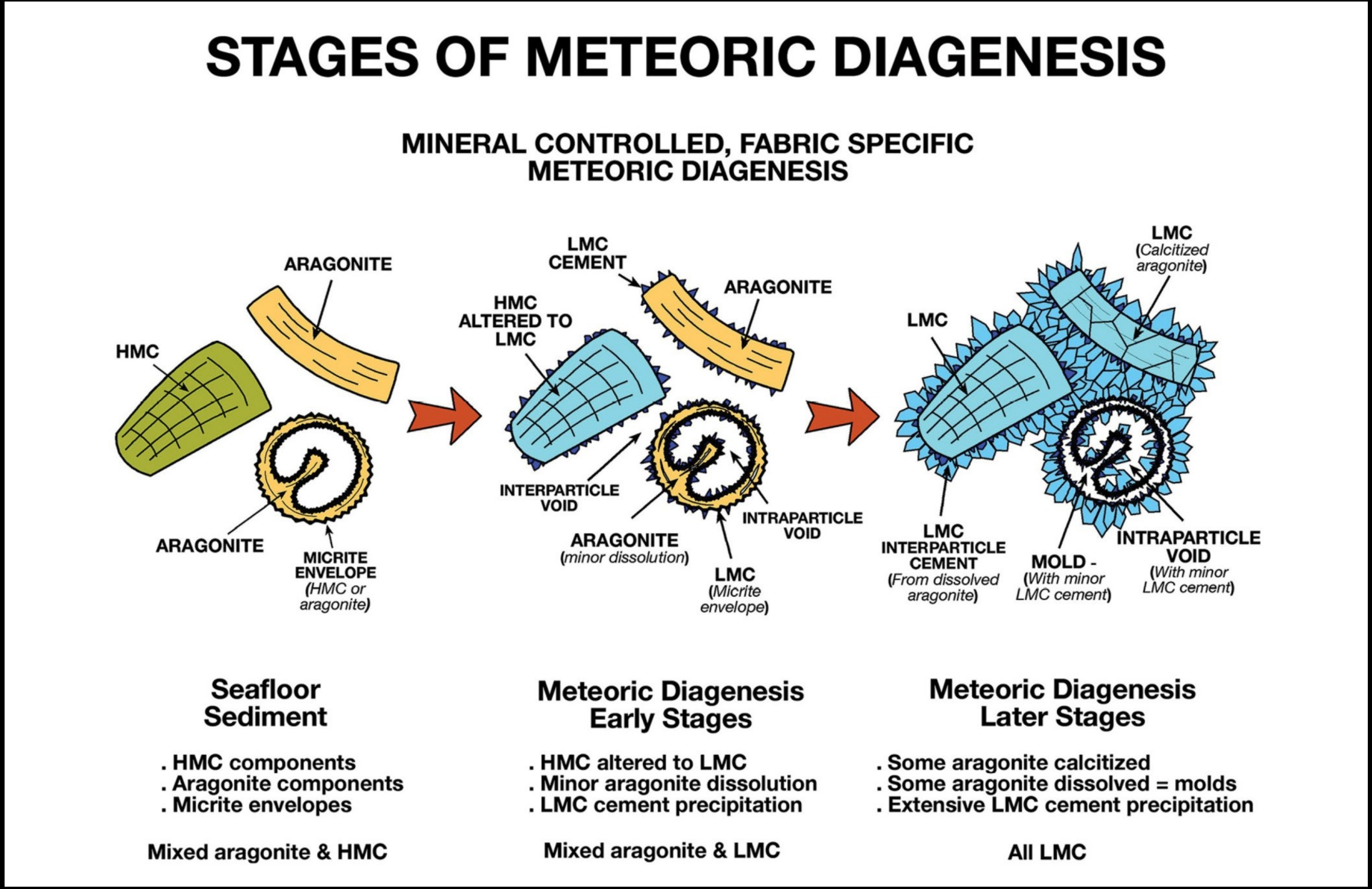
Pliocene benthic forams that were originally Mg-Calcite are well preserved and now are made of low-Mg Calcite. Aragonitic bivalves (B) are completely dissolved.
From James and Jones, 2015.

Diagenesis of carbonates – mineral specific meteoric diagenesis



From James and Jones, 2015.

Diagenesis of carbonates – mineral specific meteoric diagenesis



STAGES OF METEORIC DIAGENESIS

MINERAL CONTROLLED, FABRIC SPECIFIC METEORIC DIAGENESIS

Seafloor Sediment

- HMC components
- Aragonite components
- Micrite envelopes

Mixed aragonite & HMC

Meteoric Diagenesis Early Stages

- HMC altered to LMC
- Minor aragonite dissolution
- LMC cement precipitation

Mixed aragonite & LMC

Meteoric Diagenesis Later Stages

- Some aragonite calcitized
- Some aragonite dissolved = molds
- Extensive LMC cement precipitation

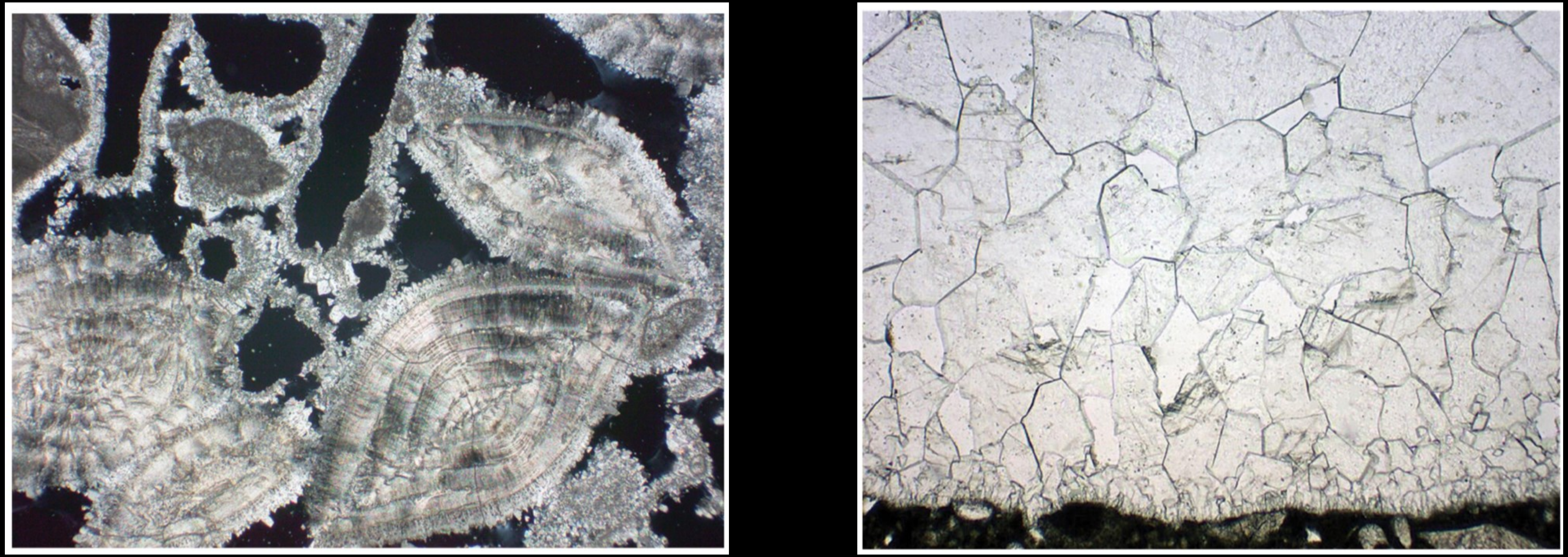
All LMC

From James and Jones, 2015.

Diagenesis of carbonates – mineral specific meteoric diagenesis

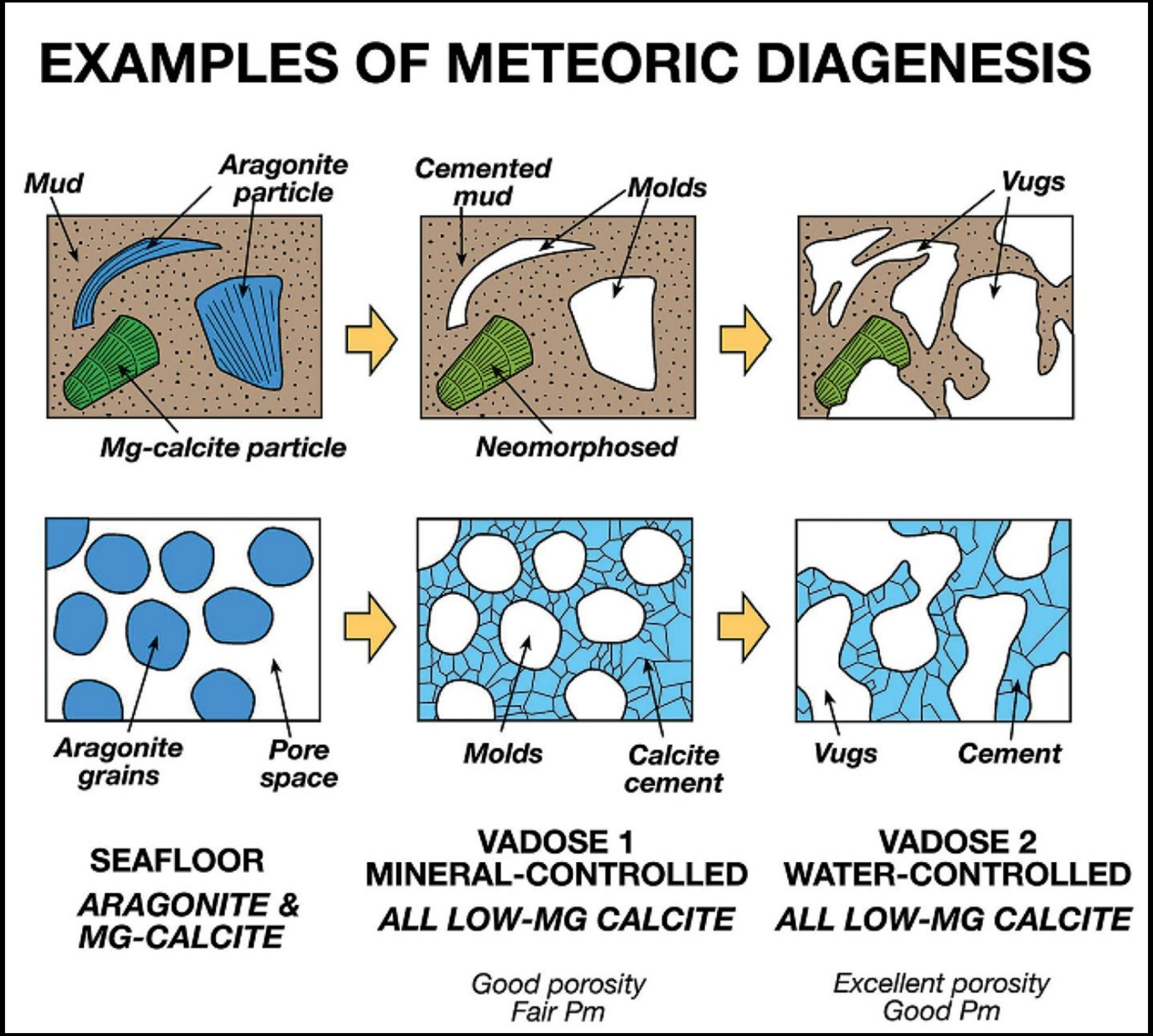
If meteoric waters become supersaturated, cements can precipitate. These cements can be:

- Drusy
- Epitaxial (syntaxial)
- Blocky



Left, syntaxial cements growing on benthic foraminifera. Right, drusy cement growing on a carbonate substrate. Note that the syze of crystals increases upwards. From James and Jones, 2015.

Diagenesis of carbonates – mineral specific meteoric diagenesis



From James and Jones, 2015.

Diagenesis of carbonates – burial diagenesis

What happens to sediment once it is buried?

The first process is the **aerobic respiration of organic matter**. OM is thus consumed by heterotrophic organisms (mostly bacteria) until either OM or O_2 is exhausted.

if OM is exhausted:

- we go on with the inorganic diagenesis of carbonates;

If O_2 is exhausted instead:

- **anaerobic respiration processes** take over.

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

Carbon of organic matter compounds is the **electron donor** in all respiration processes.

Oxygen is the **electron acceptor** in the metabolic reaction of aerobic respiration.

All respiration reactions are performed by living organisms in order to produce energy. Aerobic respiration is the most efficient of these reactions.

Diagenesis of carbonates – burial diagenesis

We can subdivide the burial diagenetic environment in three parts

Shallow burial

(from surface to ca. 600-1000 m under continental settings)

- overall oxydizing conditions
- fresh water groundwaters

Intermediate burial

(down to ca. 2000-3000 m under continental settings)

- reducing conditions
- salty groundwaters and brines

Deep burial

- entering the «oil window»

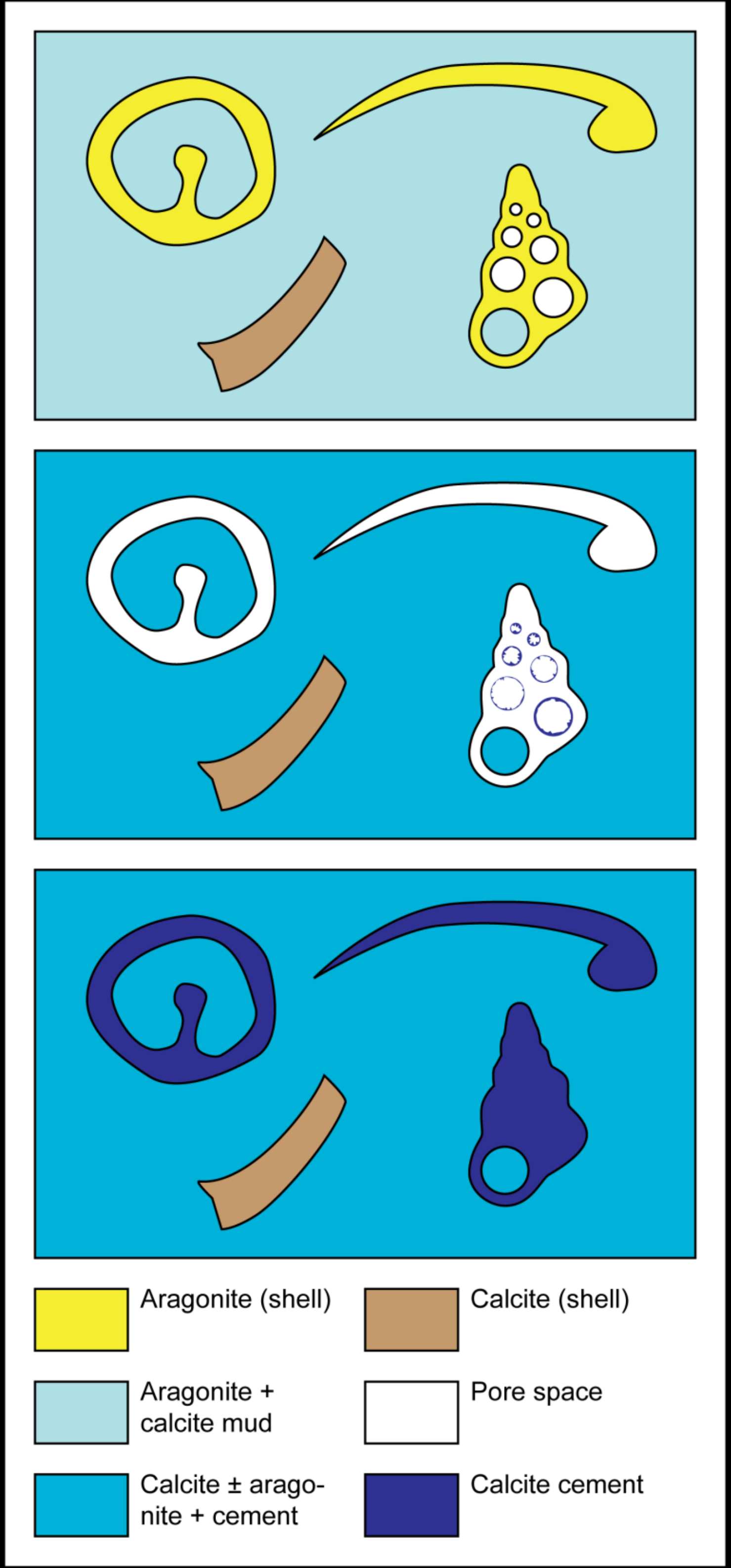
Diagenesis of carbonates – burial diagenesis

dissolution of aragonite and lithification

A significant proportion of marine carbonate is made of aragonite, which is a metastable carbonate mineral during burial.

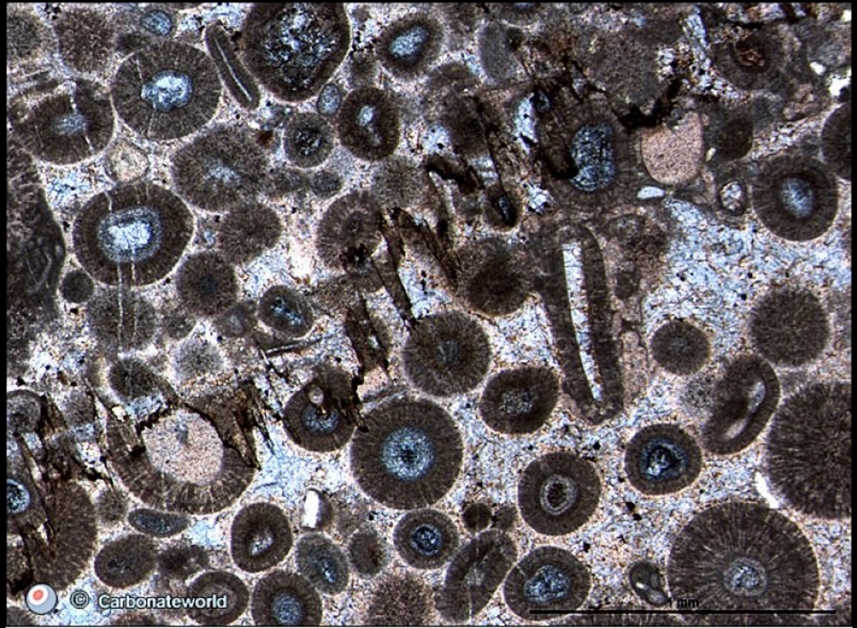
Soon, aragonite starts to dissolve, and a stage exists when new (moldic) porosity is generated by aragonite dissolution.

As burial proceeds, all aragonite dissolves and all pores end up being filled by low-magnesium calcite cement. Aragonite is replaced by a dissolution-precipitation process and not substituted.

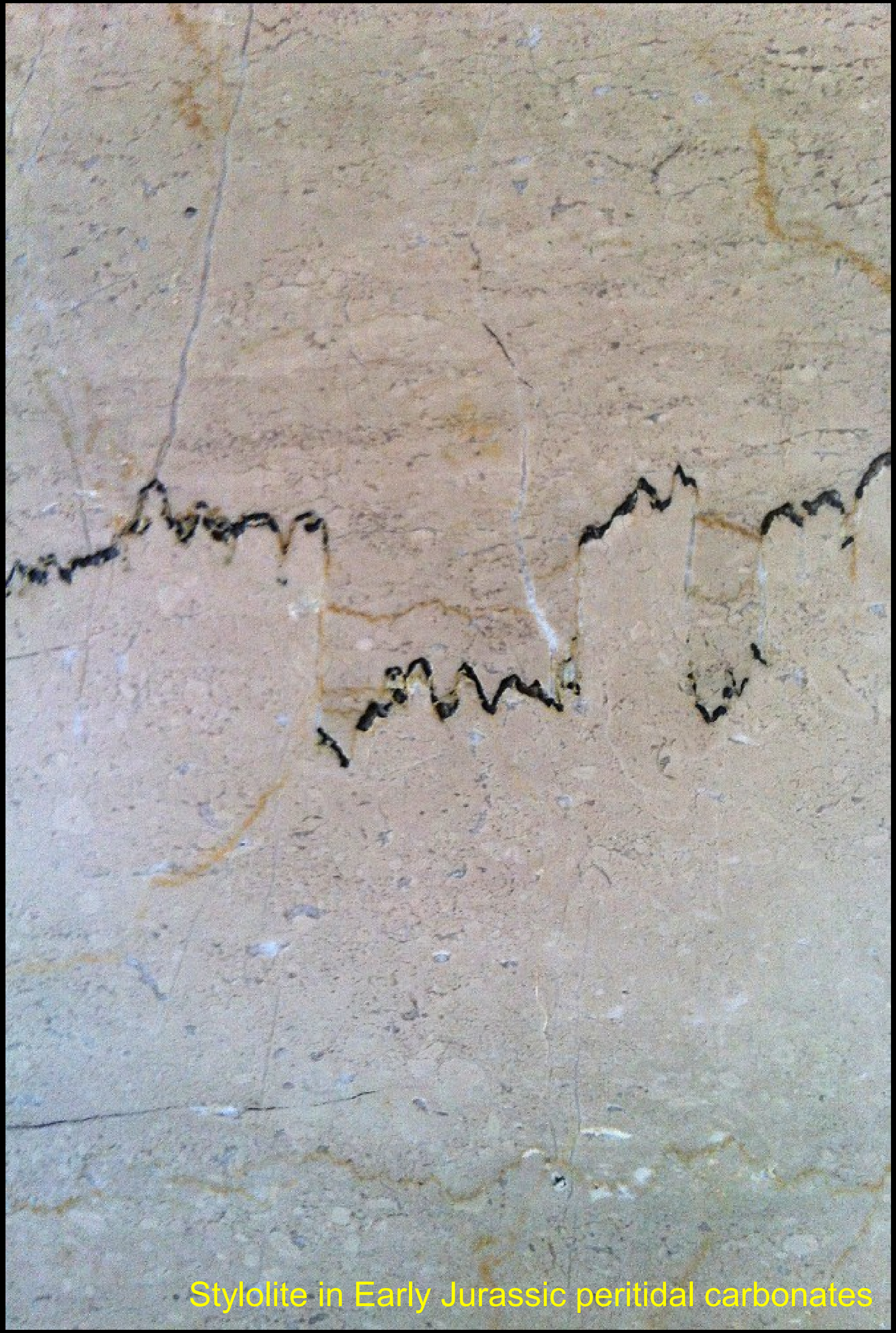


Diagenesis of carbonates – burial diagenesis

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

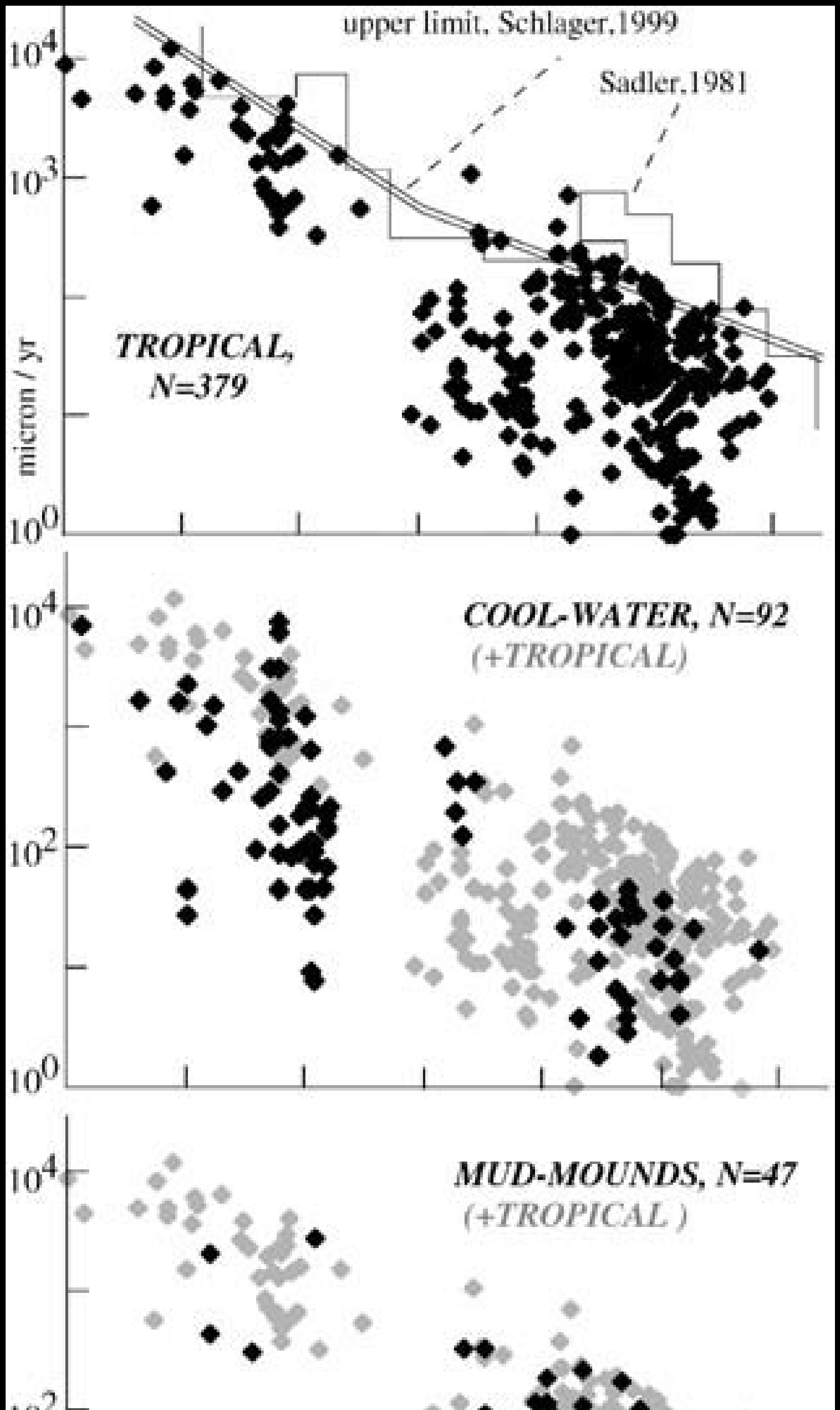


Stylolite in Early Jurassic peritidal carbonates

Diagenesis of carbonates – burial diagenesis

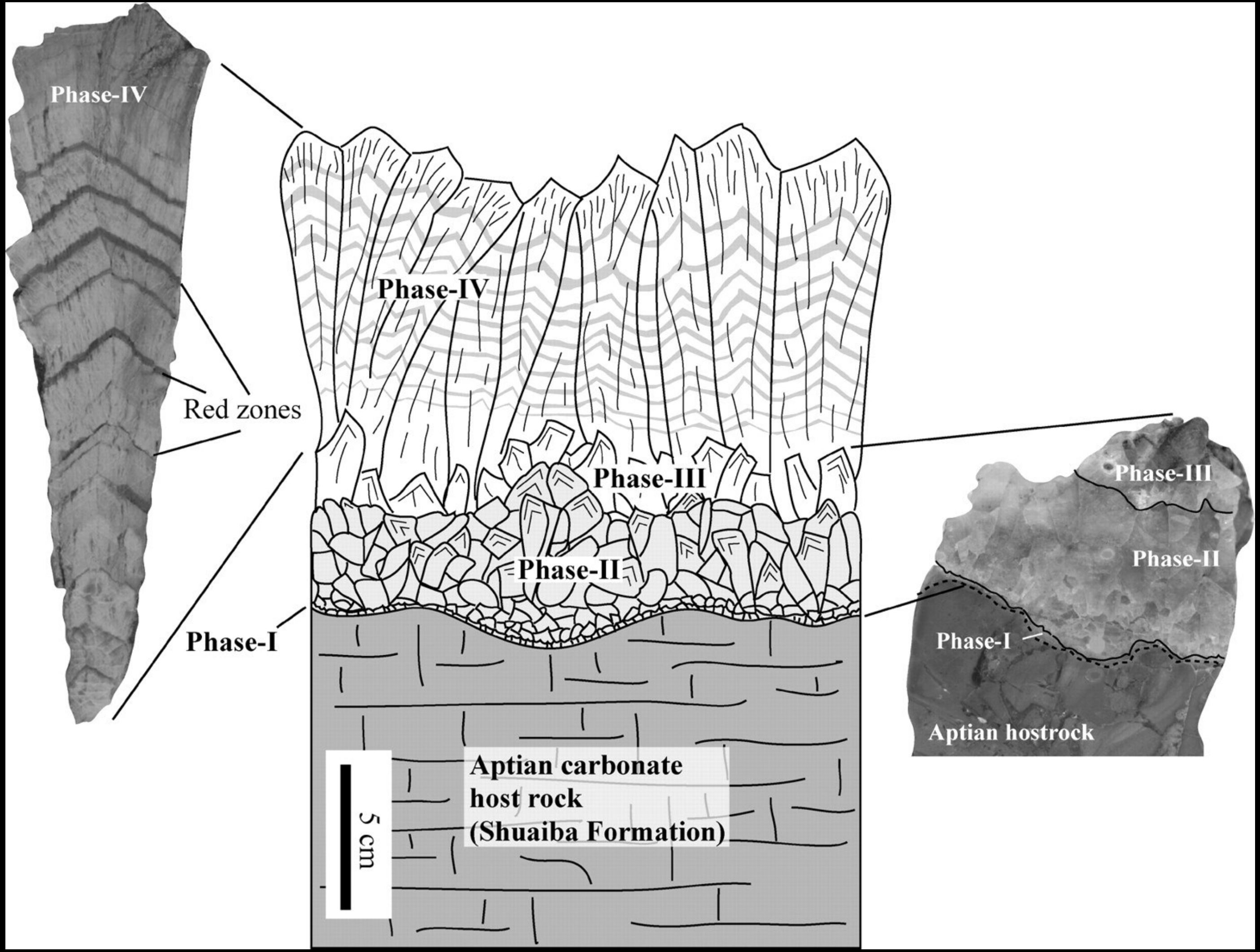
The amplitude of stylolites gives a minimum estimate of sediment loss by chemical (pressure) compaction.

Stylolite from a step on a stair. Most probably from Botticino (Jurassic peritidal carbonates).


upper limit, Schlager,1999
Sadler,1981
TROPICAL, N=379
micron / yr
10^4
10^3
10^0
COOL-WATER, N=92
(+TROPICAL)
10^4
10^2
10^0
MUD-MOUNDS, N=47
(+TROPICAL)
10^4
10^2

Diagenesis of carbonates – reconstruction of diagenetic history

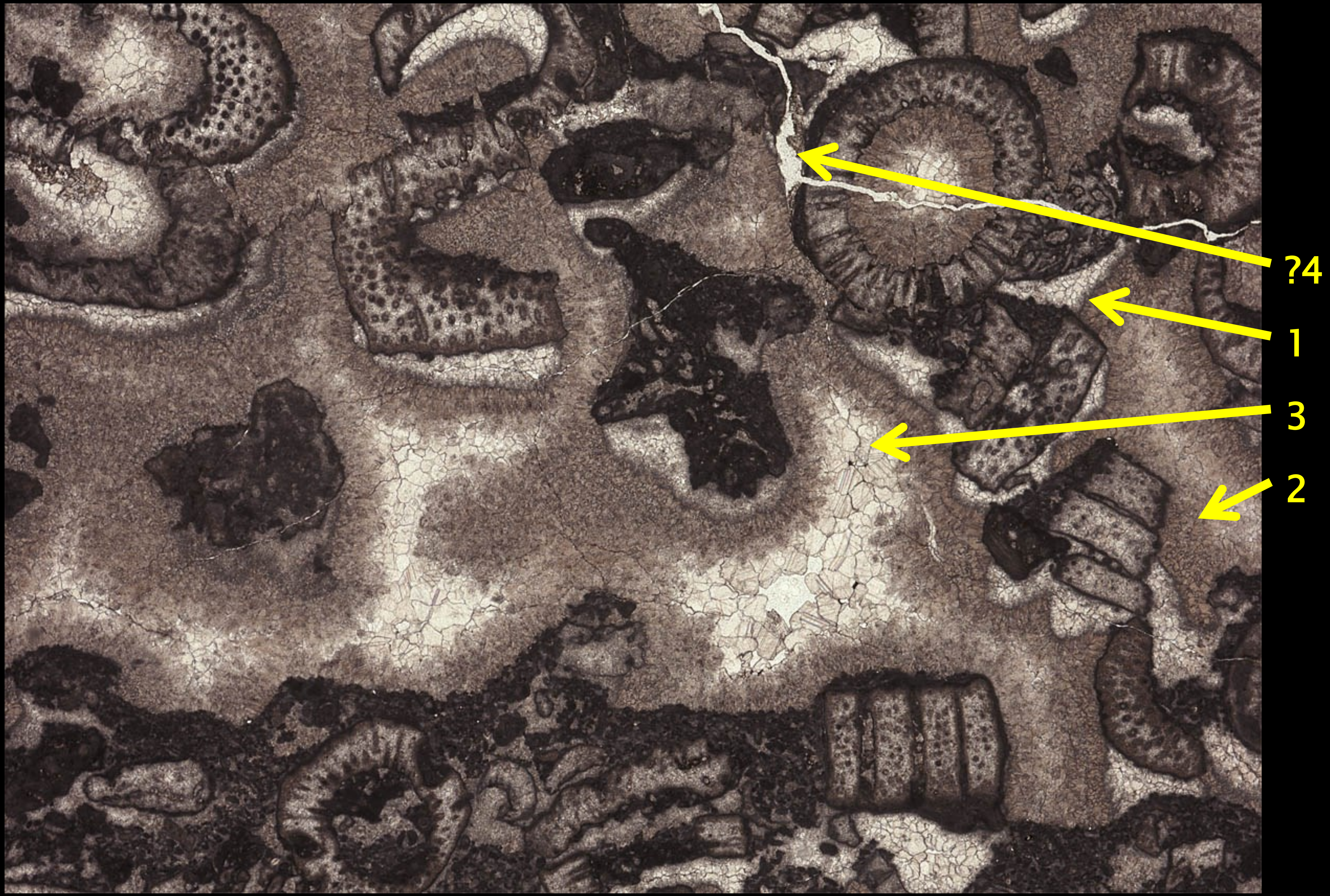
In the common petrographic practice, (1) Identify different **cement phases**; (2) Identify **other diagenetic events** (dissolution, fracturing...); (3) **put them in the right order**.



http://jsedres.sepmonline.org/content/vol77/issue2/images/large/gsjsedres770068-fg5.jpeg

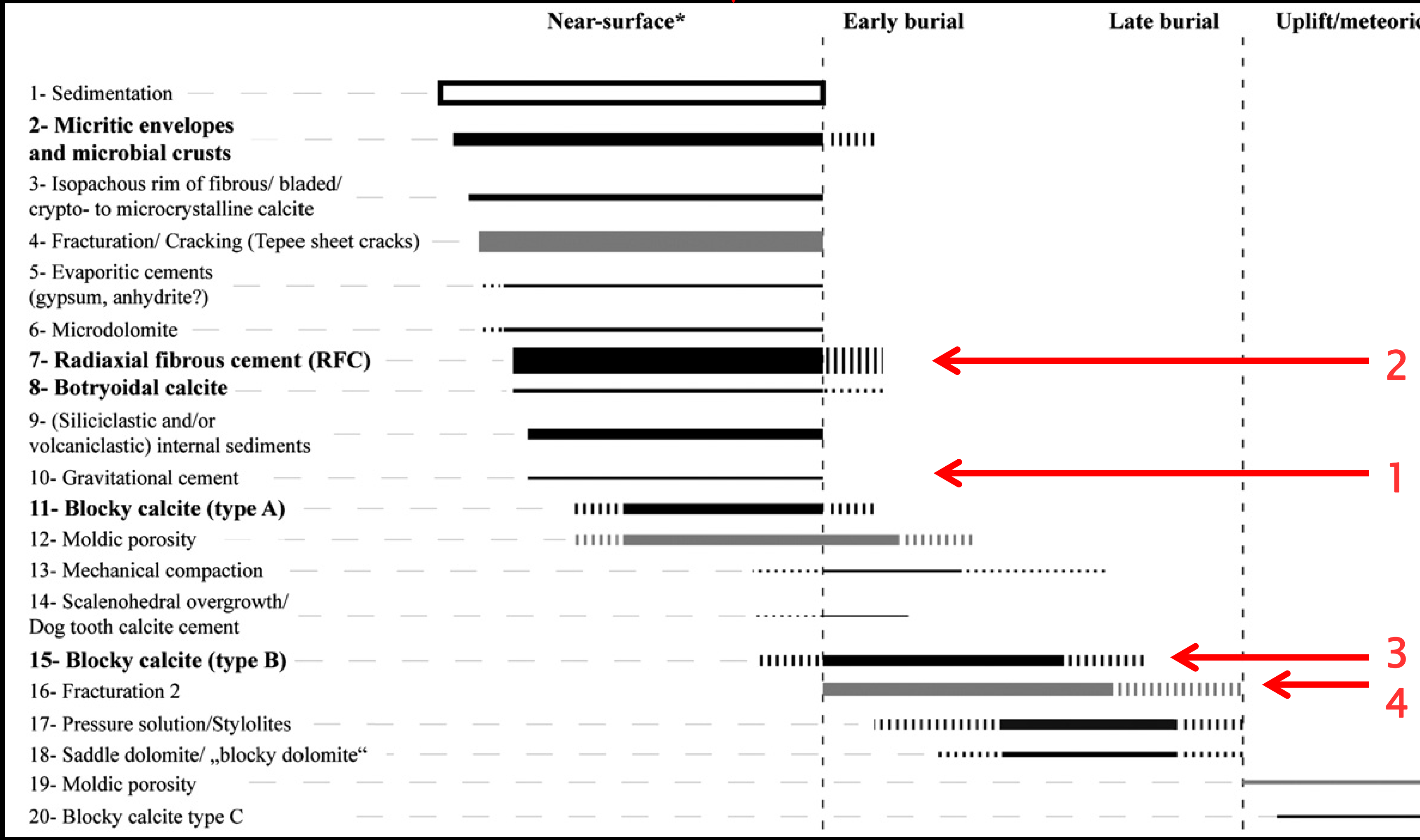
Diagenesis of carbonates – reconstruction of diagenetic history

Diagenesis of carbonates – reconstruction of diagenetic history



Diagenesis of carbonates – reconstruction of diagenetic history

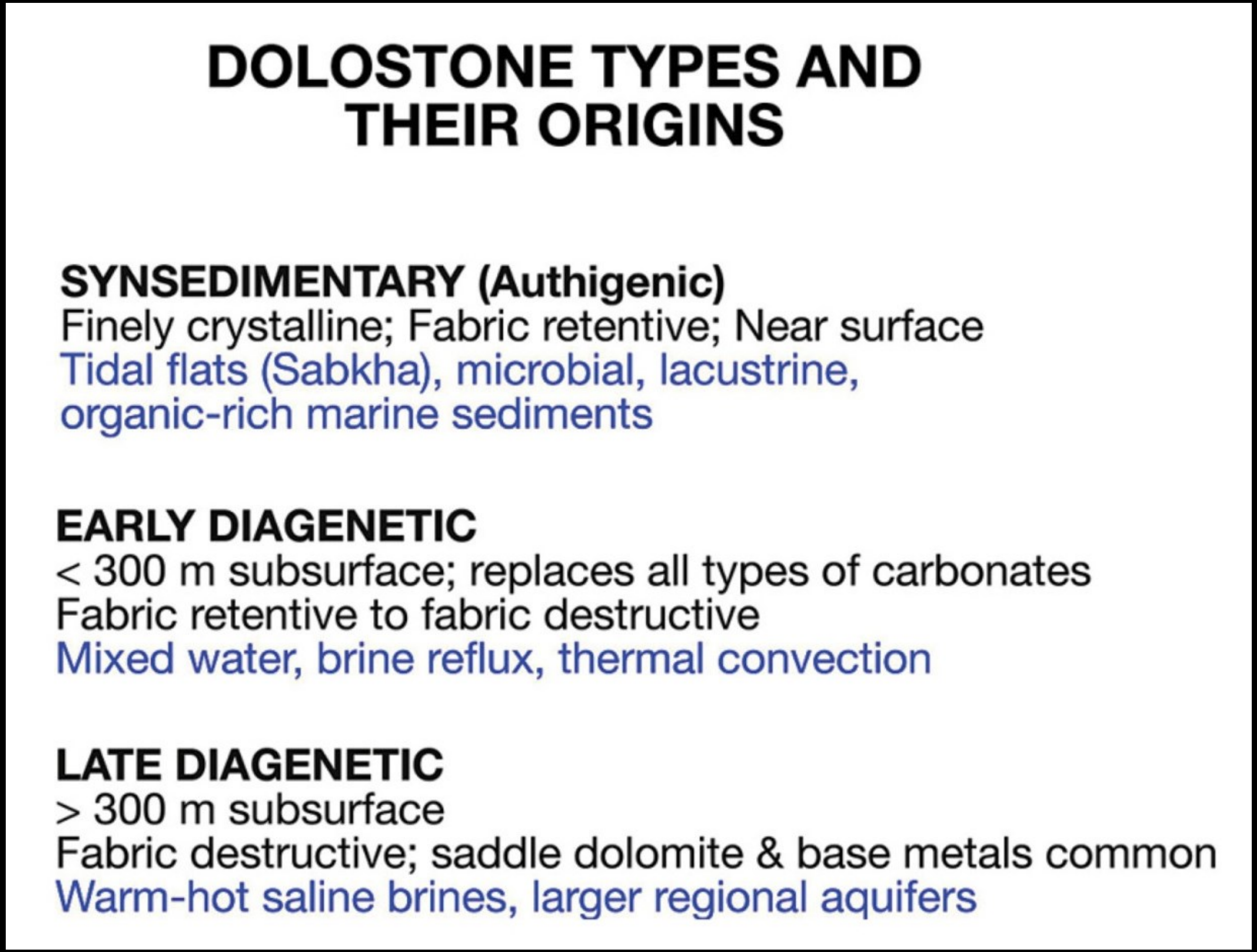
Paragenetic sequence of the Latemar limestone (Christ et al., 2012) with indication of cement phases but also of other diagentic processes (dissolution, fracturation, micritization...). Grey bars represent processes that create porosity; black bars are porosity-destructive processes.



Diagenesis of carbonates – dolomitization

The occurrence of large volumes of dolostones in the geologic record represents a conondrum, because, although seawater is supersaturated with respect to dolomite, this mineral rarely precipitates in modern seawaters.

At present, there is consensus that dolomite can form in synsedimentary sistuations and during early or late diagenesis.



DOLOSTONE TYPES AND THEIR ORIGINS

SYNSEDIMENTARY (Authigenic)
Finely crystalline; Fabric retentive; Near surface
Tidal flats (Sabkha), microbial, lacustrine, organic-rich marine sediments

EARLY DIAGENETIC
< 300 m subsurface; replaces all types of carbonates
Fabric retentive to fabric destructive
Mixed water, brine reflux, thermal convection

LATE DIAGENETIC
> 300 m subsurface
Fabric destructive; saddle dolomite & base metals common
Warm-hot saline brines, larger regional aquifers

Diagenesis of carbonates – dolomitization

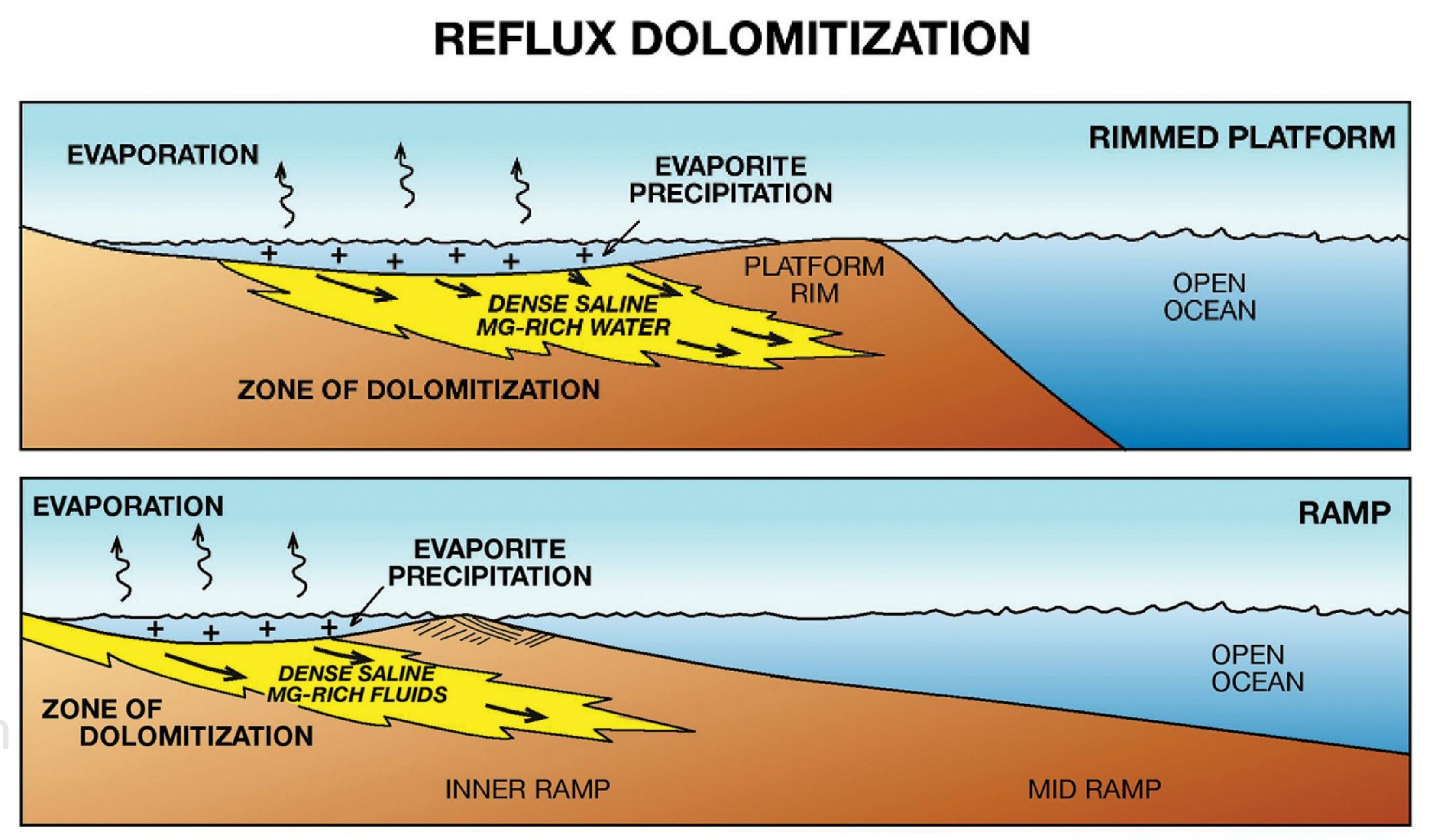
Synsedimentary dolomite can form in saline waters and the process normally involves microbial activity. Today dolomite can be found in tidal flats both in humid and arid settings. In some cases synsedimentary dolomite can form in lakes or lagoons.

Dolomite (the brown sediment) precipitated in a modern supratidal sabkha environment. From James and Jones, 2015

Diagenesis of carbonates – dolomitization

Research has shown that most of dolomite in the geologic record was originated by subsurface diagenesis. Dolomitization can be induced by:

Bryne reflux.
High salinity waters concentrated by evaporation in shallow water marine environment flow downward and become enriched in Mg. Mix with marine with underlying marine fluids induces dolomitization.
N.B. No modern analogs exist. This phenomenon is deduced from the observation of the geologic record



Diagenesis of carbonates – dolomitization

Hydrothermal circulation.

Hydrothermal circulation can promote circulation of Mg-rich fluids into limestone, thus causing dolomitization. Dolostones are also often associated with faults whose presence can favor circulation of Mg-rich hydrothermal waters..

Dolosone bodies within the Early Jurassic limestone of the Calcari Grigi Group nearby Tonezza del Cimone. In this case dolomitizing fluids have flown along Jurassic synsedimentary faults during alpine orogenesis. From Di Cuia et al., 2011

Carbonate Porosity

Limestones and dolostones host some of the largest hydrocarbon reservoirs and metallic ore deposits

This is due to the fact that carbonate rocks can be characterized by relevant porosity and a great part in determining porosity is played by diagenesis. Diagenesis can create or destroy porosity.

Always remember that, besides porosity, permeability (K) is crucial as it determines how easily fluids can flow into a rock.

Moldic porosity in a Pleistocene coral limestone.
From James and Jones, 2016

Carbonate Porosity

Unlike clastic rocks, which typically are single-porosity systems (i.e., interparticle pores) of relative uniform (homogeneous) nature, reservoirs in carbonate rocks commonly are multiple-porosity systems.
This imparts petrophysical heterogeneity to carbonate reservoirs.

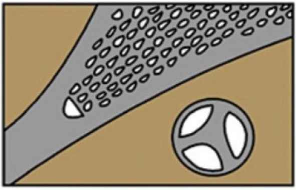
Porosity in carbontes can be of two main types:

- Primary (or depositional).
  Deriving from the sedimentation process of the carbonate sediment

- Secondary.
  Acquired after deposition following a number of modification during burial and diagenesis.

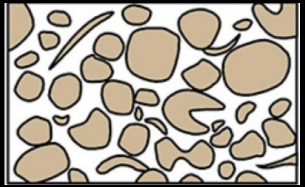
Carbonate Porosity – fabric selective

- Intraparticle pores



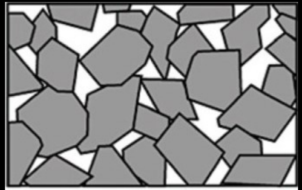
This porosity is inside the grains. Size, sahpe and volume of pores depends on the architecture of the carbonate particles

- Interparticle pores



Refers to the space within the grains

- Intercrystalline and intracrystalline porosity

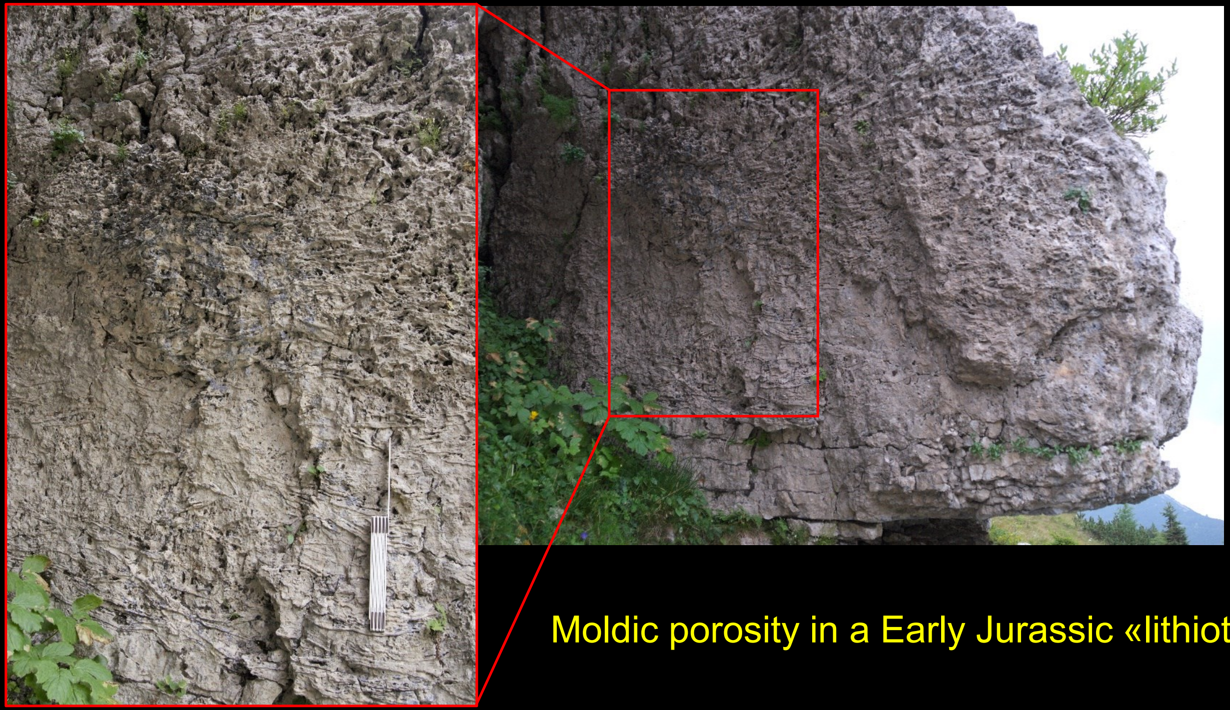


This porosity is common in dolostone and is given by the spaces between or inside crystals. Depends on the size, shape and arrangement of the crystals

Carbonate Porosity – fabric selective

- Moldic porosity

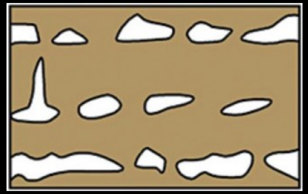
Develops following selctive dissolution of some of the components of a carbonate rock/sediment. A typical example of moldic porosity is that that forms because of the dissolution of aragonitic skeletons (corals) and shells (bivalves)



Moldic porosity in a Early Jurassic «lithiotid» limestone. Pasubio area, Italy.

Carbonate Porosity – fabric selective

- Fenestral porosity

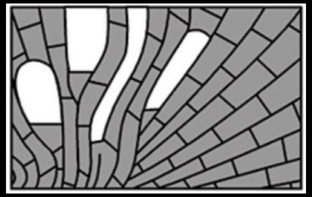


This is due to the presence of open cavities such as fenestrae and birds-eyes. In some cases can be up to 45%.

- Shelter porosity

Porosity that may develop when shells are deposited in convex-up position. This type of porosity contributes little to the overall porosity of a carbonate rock

- Growth framework porosity



This is typical of reefs and related structures formed by colonial organisms such as corals and stromatoporoids and depends on their growth pattern

Carbonate Porosity – non fabric-selective

- Fractures

Fractures can create excellent porosity, but fructures play a prmominent role in determining permeability

- Channels, vug and caverns

Porosity usually associated with dissolution phenomena such as subsurface karst.

- Shrinkage

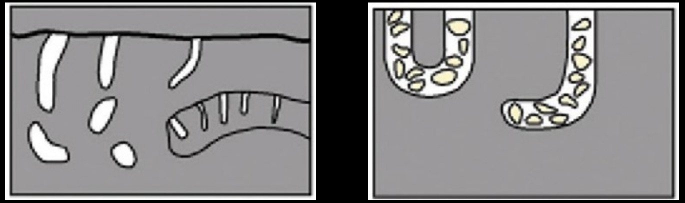
Processes such as formation of mud cracks can form porosity, but shrinkage porosity represents a minor part of the overall porosity in a carbonate rock.

Carbonate Porosity – other types

- Breccias

Breccia facies can be associated with high porosity. Some processes that can produce breccias are collapse breccias (karst), and hydrofracturing due to hydrothermal circulation.
Breccias and mega-breccias can be also typical of some of the main depositional environments of carbonate systems (e.g. slopes)

- Borings and burrows



Porosity can be due boring and burrowing processes and can range from the sub-mircron to cm size.

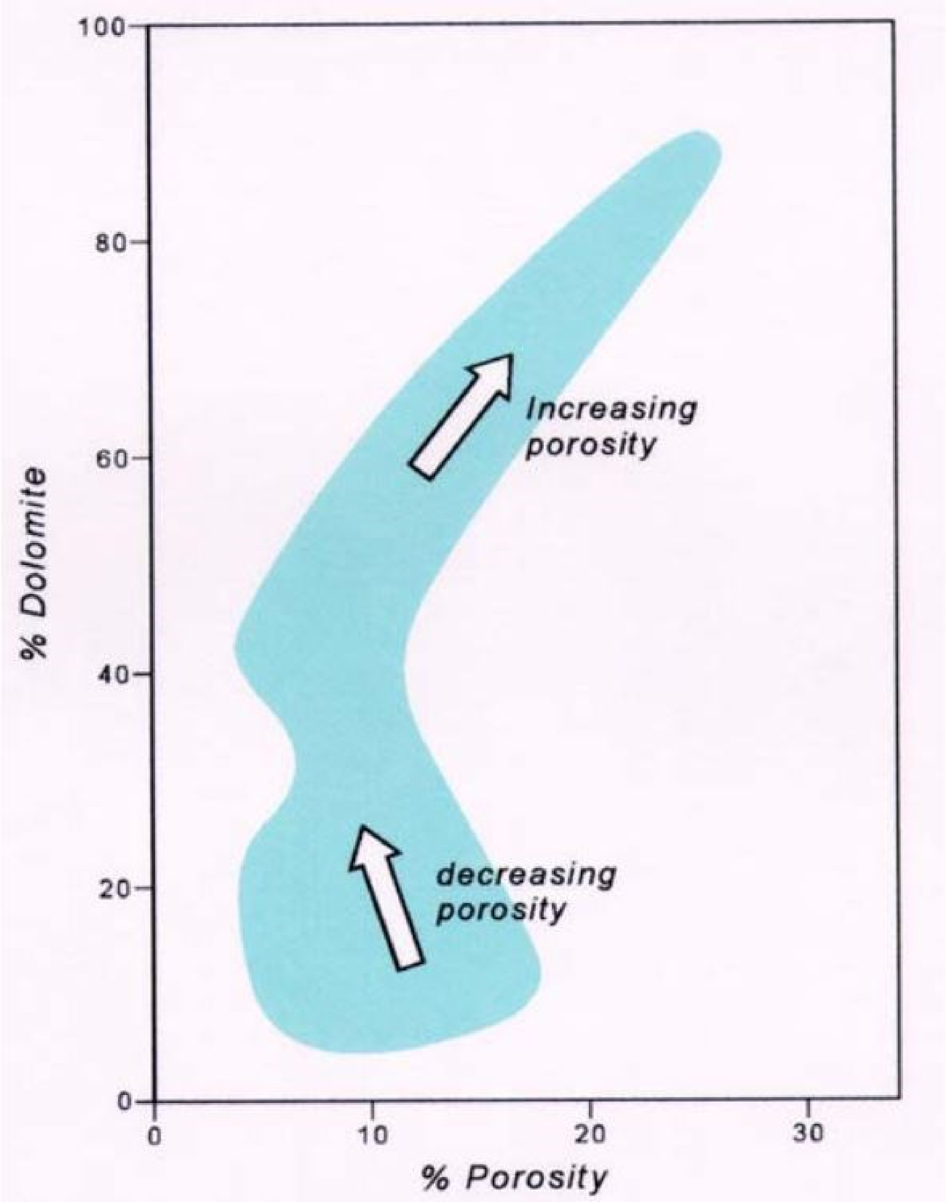
Carbonate Porosity

In general, the natural tendency in most carbonate sediments is that primary porosity is substantially reduced by cementation and compaction during post-depositional burial.

Precipitation processes (such as precipitation of marine cements or saddle dolomite) tend to reduce porosity, whille dissolution process tend to enhance it.

A process that can stop the natural tendency of decrease in the porosity of carbonate rocks by cementation and compaction is the early inflow of hydrocarbons or other fluids in the rock. The fluids, occupying the pore-space, preserve the porosity.

Carbonate Porosity



From Murray, 1960

Dolomitization is a process tends to increase porosity.
This happens because partly dolomitized carbonates exposed to telogenetic fluids tend to become more porous when relict limestone is quickly dissolved leaving open pore-space in the form of vugs or intercystalline porosity.

Take home messages for this part

- Diagenesis encompasses processes that turn a sediment into a rock. It precedes metamorphism in a P/T diagram.
- Most information on diagenesis is stored in cements
- Cements are described with their mineralogy, crystal shapes and relationships with their substrate (grains)
- Cements can be used to identify different diagenetic environments: meteoric (phreatic or vadose), marine vadose, marine phreatic, burial
- Aragonite dissolves, and the resulting carbonate re-precipitates as low-Mg calcite, during burial
- The stratigraphy of cements (and other diagenetic features) is the first step to reconstruct a rock paragenesis
- Porosity in carbonates is an important feature that has relevant applicative consequences.
- Porosity can be primary or secondary and of several types. The evolution of porosity is intimately linked to diagenetic processes that impact carbonates after.