BACTERIAL ORIGIN OF SELECTED PHANEROZOIC RED CARBONATE ROCKS (1/2)

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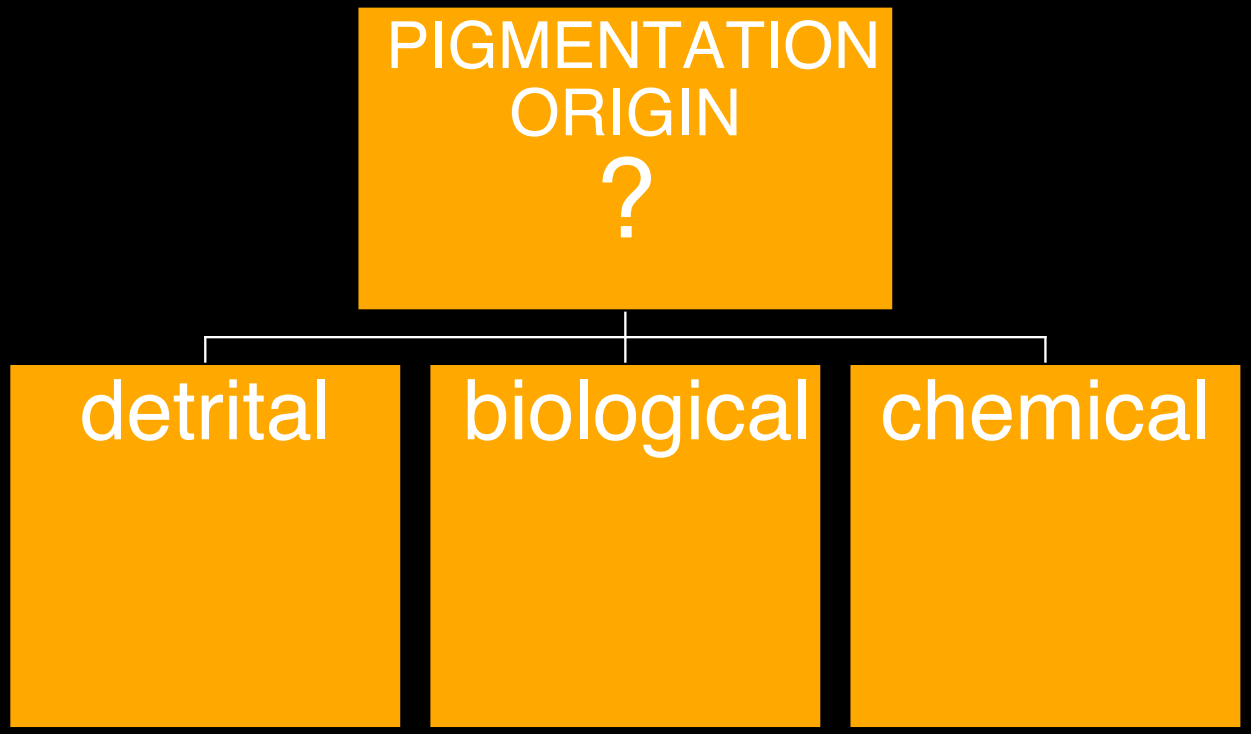
Torino, Nov 2009

THE PROBLEM…

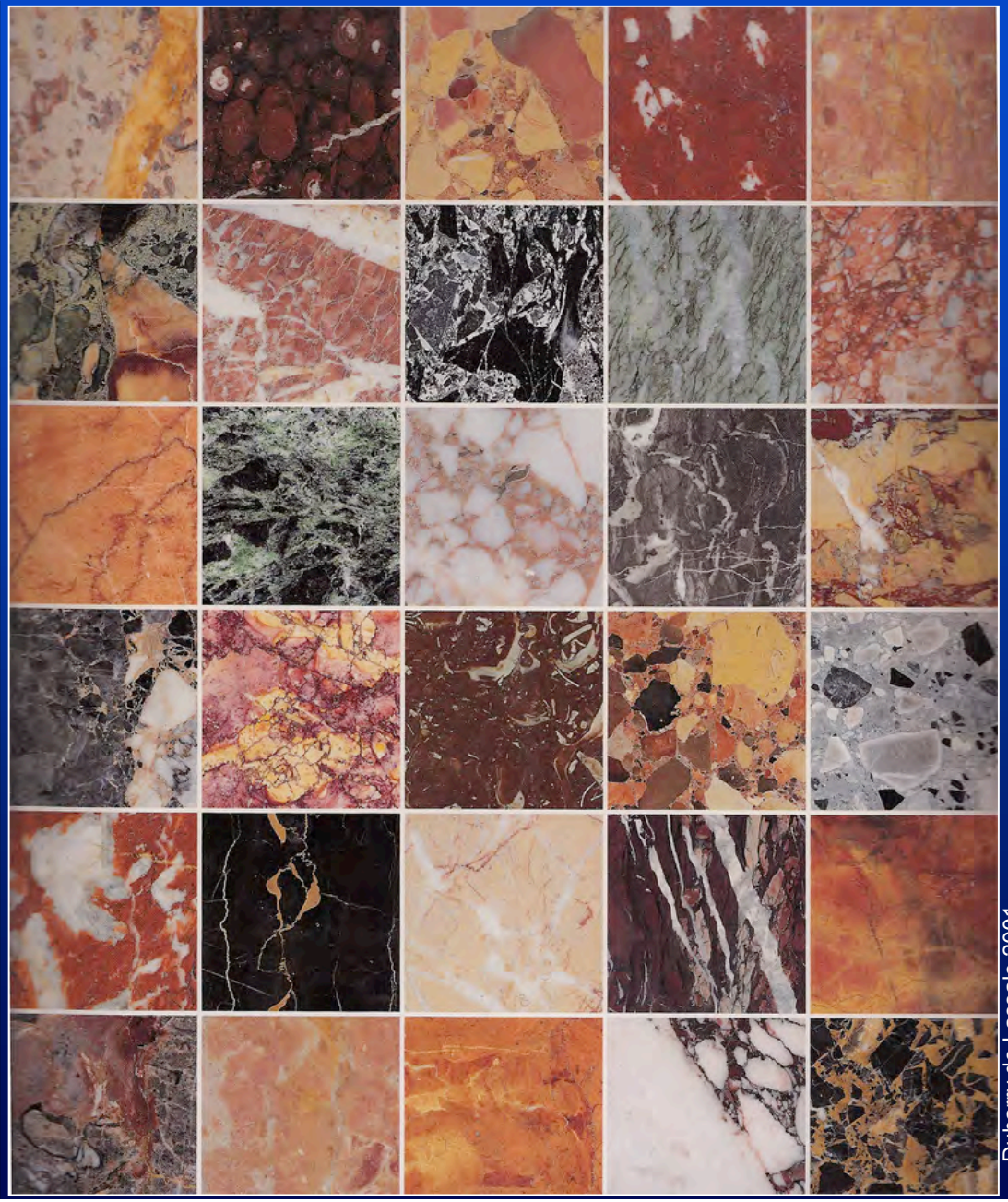


Red limestones are rare but precious …

- griottes Devonian S-France, Viséan N-Spain = OUTER RAMP + SHALLOW PF
- 'red marbles' Devonian (Frasnian), Belgium = OUTER RAMP
- Ammonitico Rosso Jurassic, N-Italy, S-Spain, Sicily = (HEMI)-PELAGIC
- 'red marbles' Devonian (Praguian), Czech Republic = INNER RAMP
- red condensed series Devonian (F/F), Morocco = PELAGIC
- red lenses in slope Carboniferous (Bashkirian), N-Spain = SLOPE
- 'Oolite Ferrugineuse de Bayeux' mid-Jurassic Normandy = 'LITTORAL'

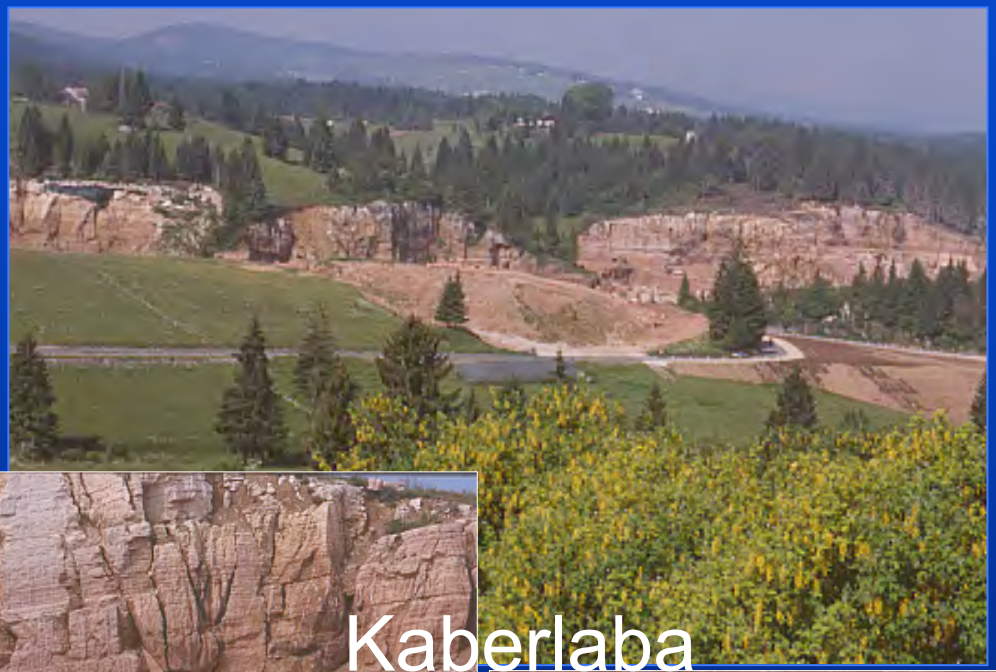
Red limestones are rare but precious …

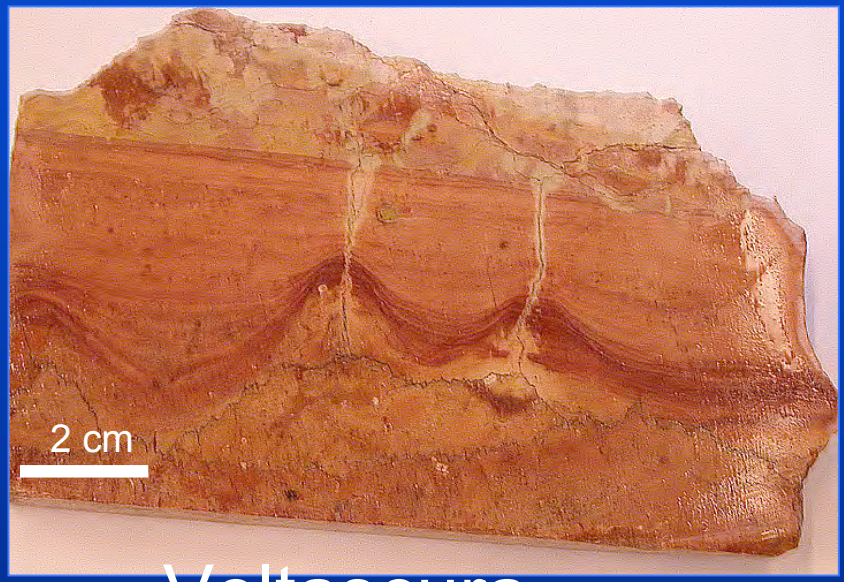
cathedrals, castles, Versailles, Trianon…



Dubarry de Lassale 2001

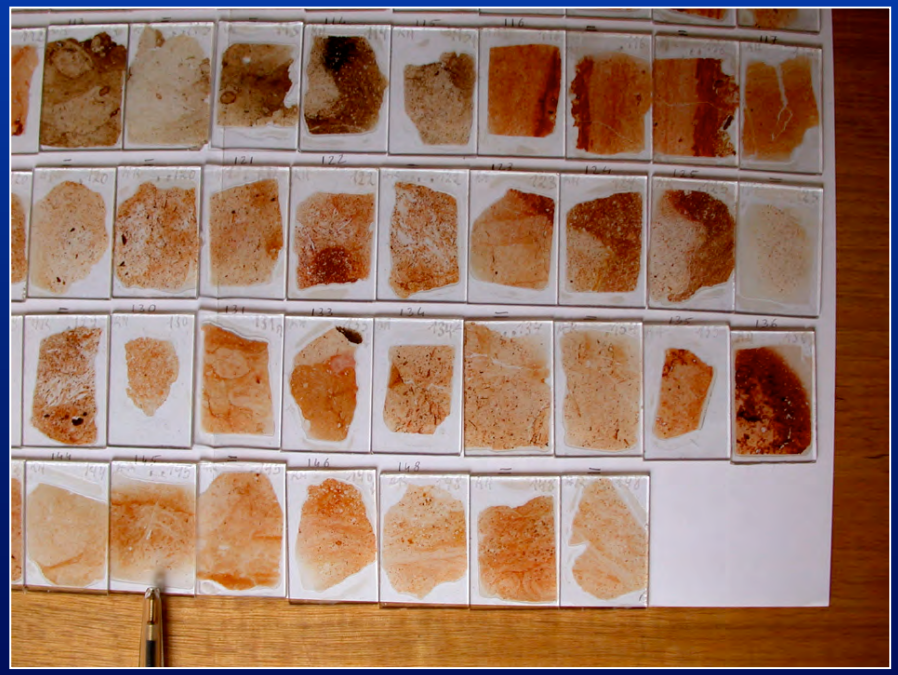
OF WHAT CONSIST THE RED PIGMENTATION?





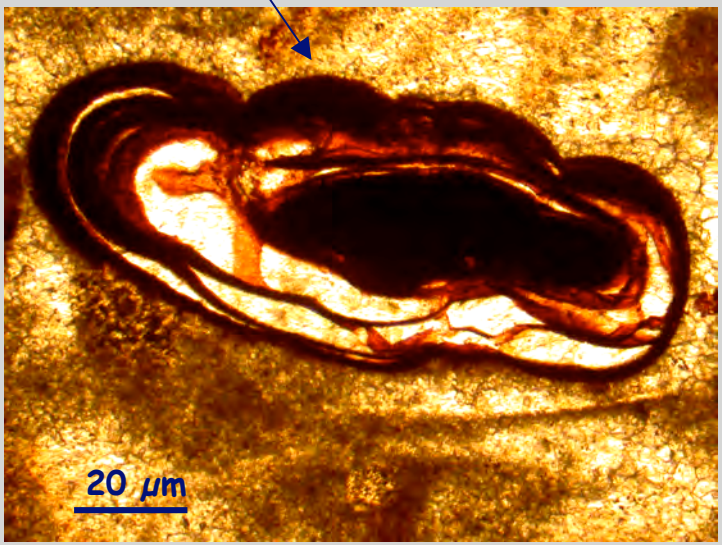
Voltascura

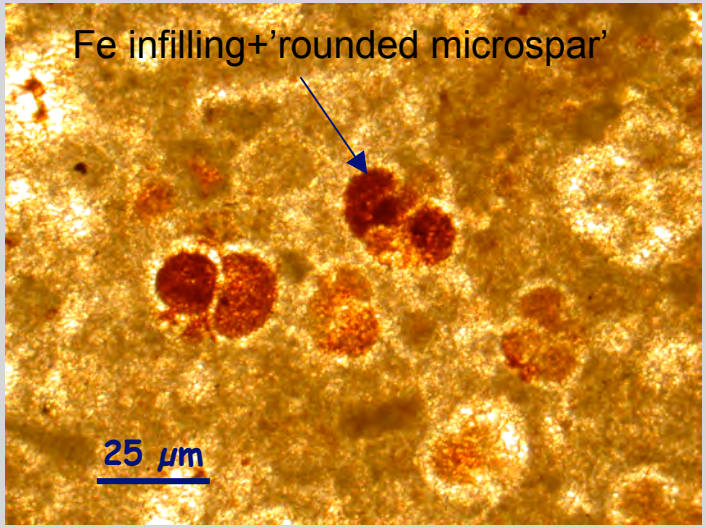
Kaberlaba



OF WHAT CONSIST THE RED PIGMENTATION?

Fe-Mn microstromatolites biofilms





… low Fe (Mn) content and pronounced reddish color

Mamet, Préat 2003

OF WHAT CONSIST THE RED PIGMENTATION?

A simple solution is just to ignore the problem!

Ex: the thick Ammonitico Rosso Symposium (1991) with its approriate SCARLET cover deals with sedimentology, palaeontology, diagenesis ... but not a single word on the origin of the colour of the Ammonitico Rosso...

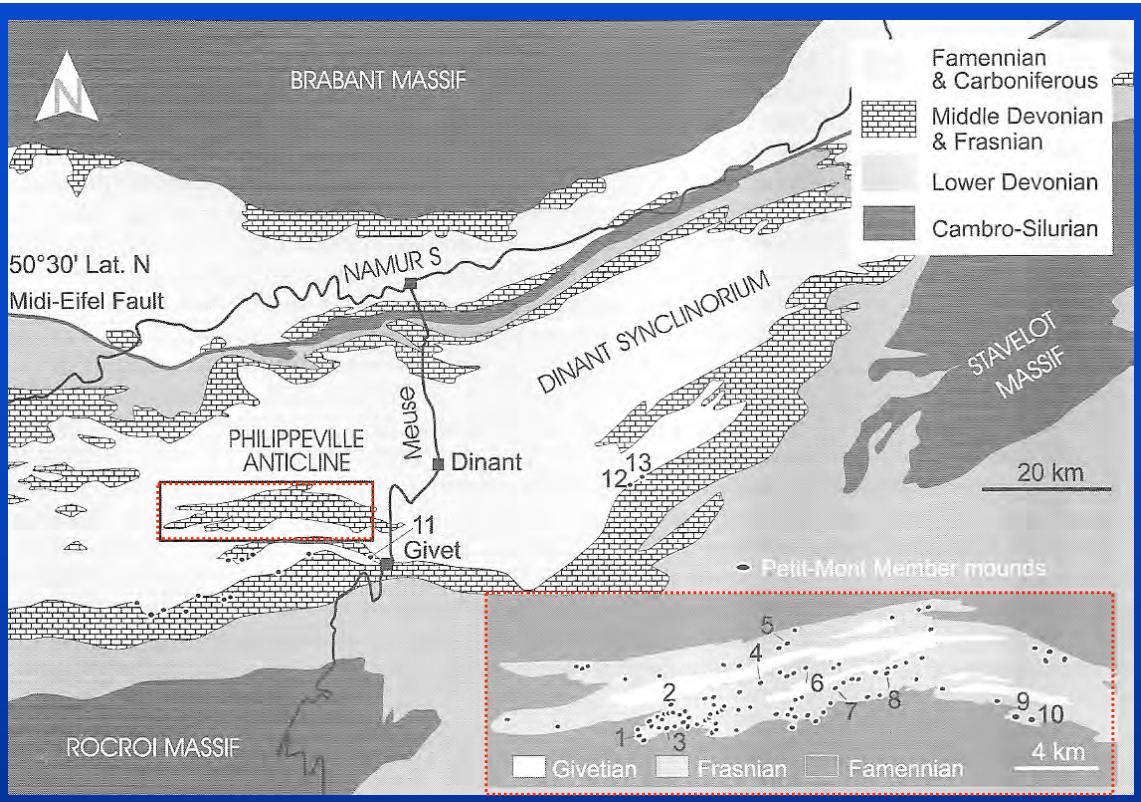
another avenue... ...

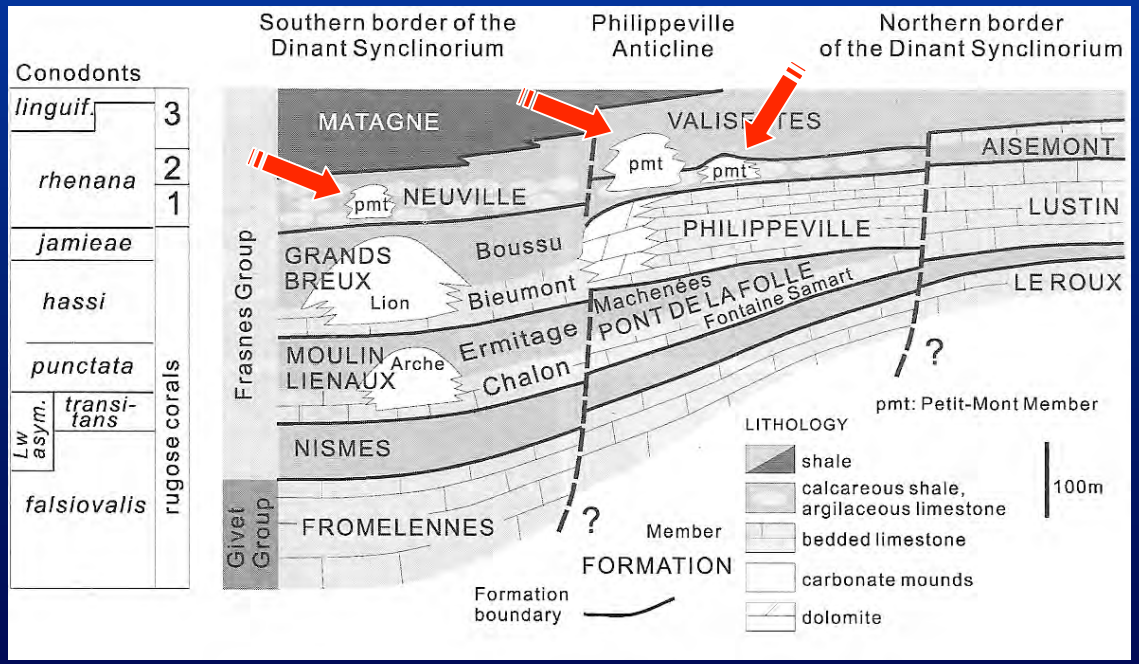
Frédéric BOULVAIN PhD, ULB/1989

... 'Frasnian mud mounds of the Dinant basin are bioconstructions that are built during a regressive phase that passes from an aphotic to an euphotic zone, and through the dysphotic level where the red marbles are concentrated' ...

- the base of the bioconstructions is in very calm environments under the SWB, and then, the mound passes into the FWWB where sedimentation ends

- no signs of subaerial exposure as observed in modern reefs





Boulvain et al 2001

69 reported 'red' mud mounds

Severe eustatic sea level rise

High vertical facies differenciation

High content in microaerophilitic iron bacteria (*stromatactis*)

Submicronic hematite hexagonal plates dispersed in the matrix

Fe_2O_3 : average 2% (max 5%)

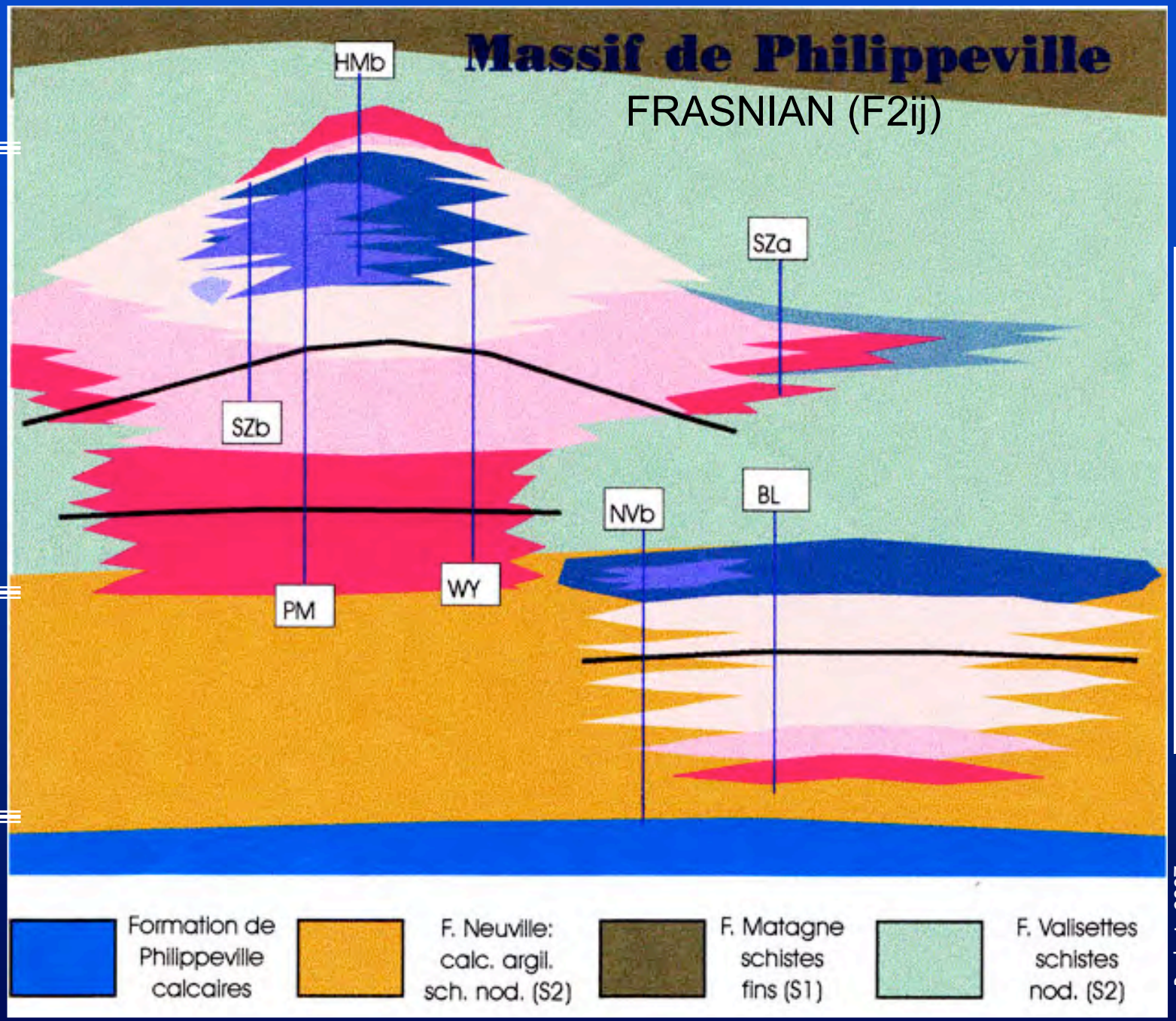
BEAUCHATEAU QUARRY
near Senzeilles
Philippeville Massif
BELGIUM

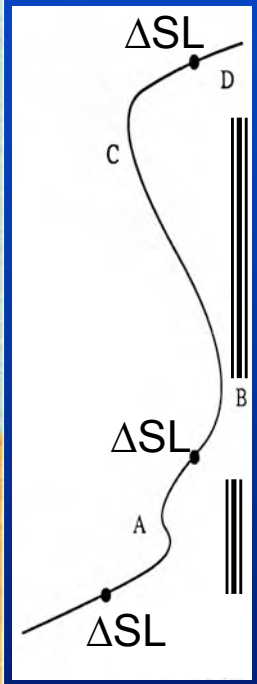
'F2j'
mud mound

griottes
+'stromatactis'
(1880)

Fe_2O_3 : average 1,8% (XRD)
// Mg, Si, Al i.e. // clay content ⟸ *as already mentioned by Delhaye, 1908*

The red-pink-grey color (succession) is ‘ECOLOGICAL’





Boulvain 2007

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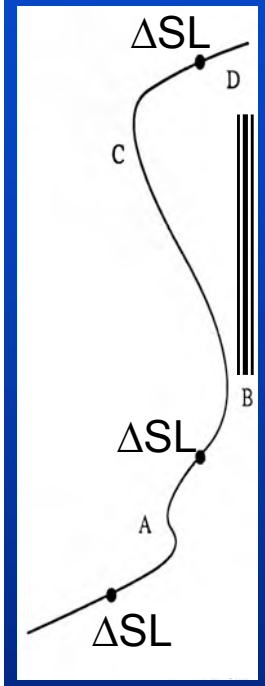
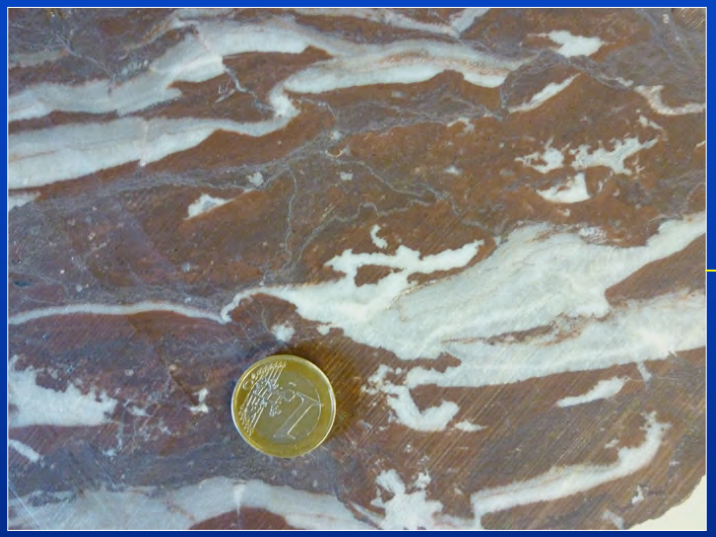
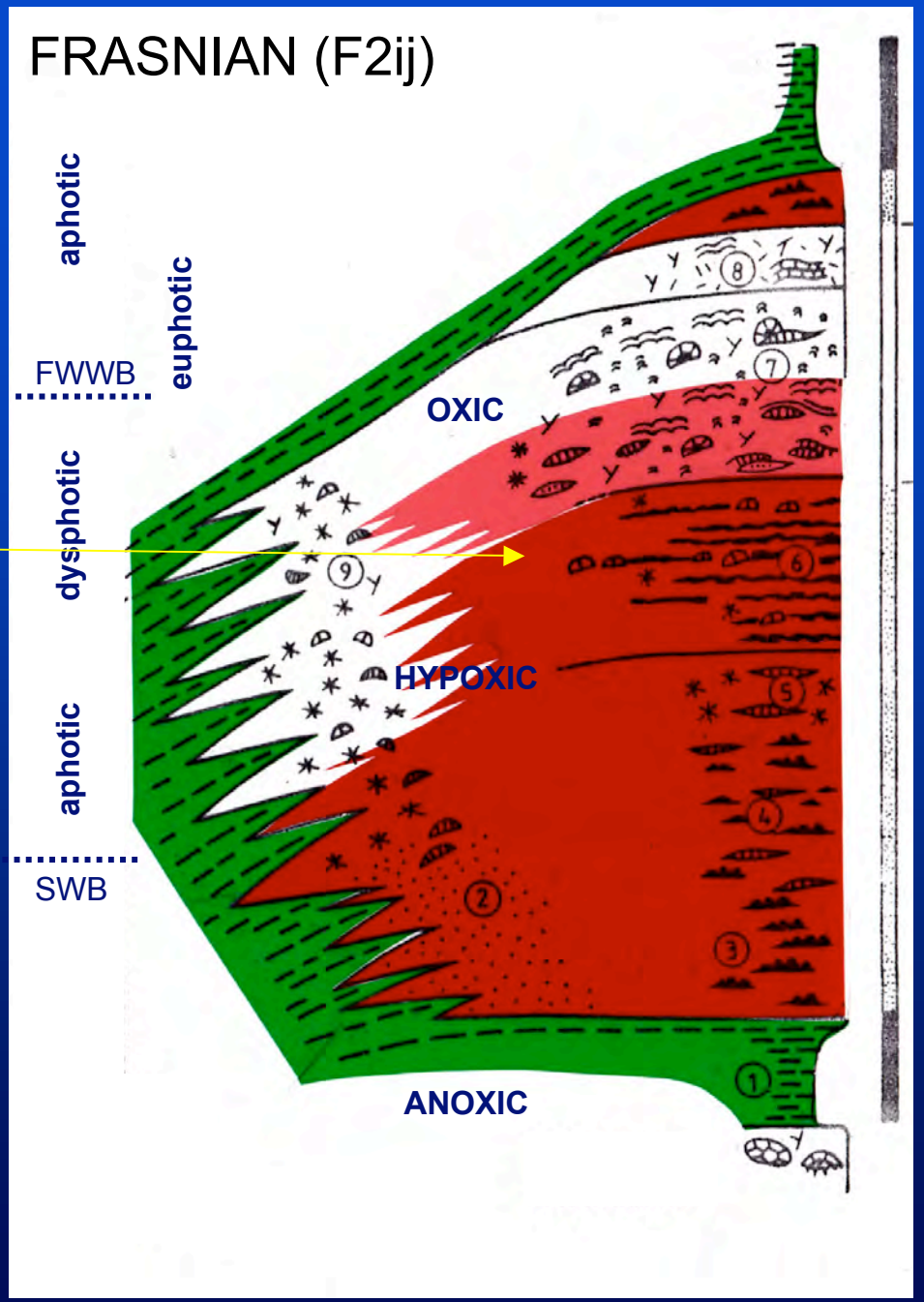
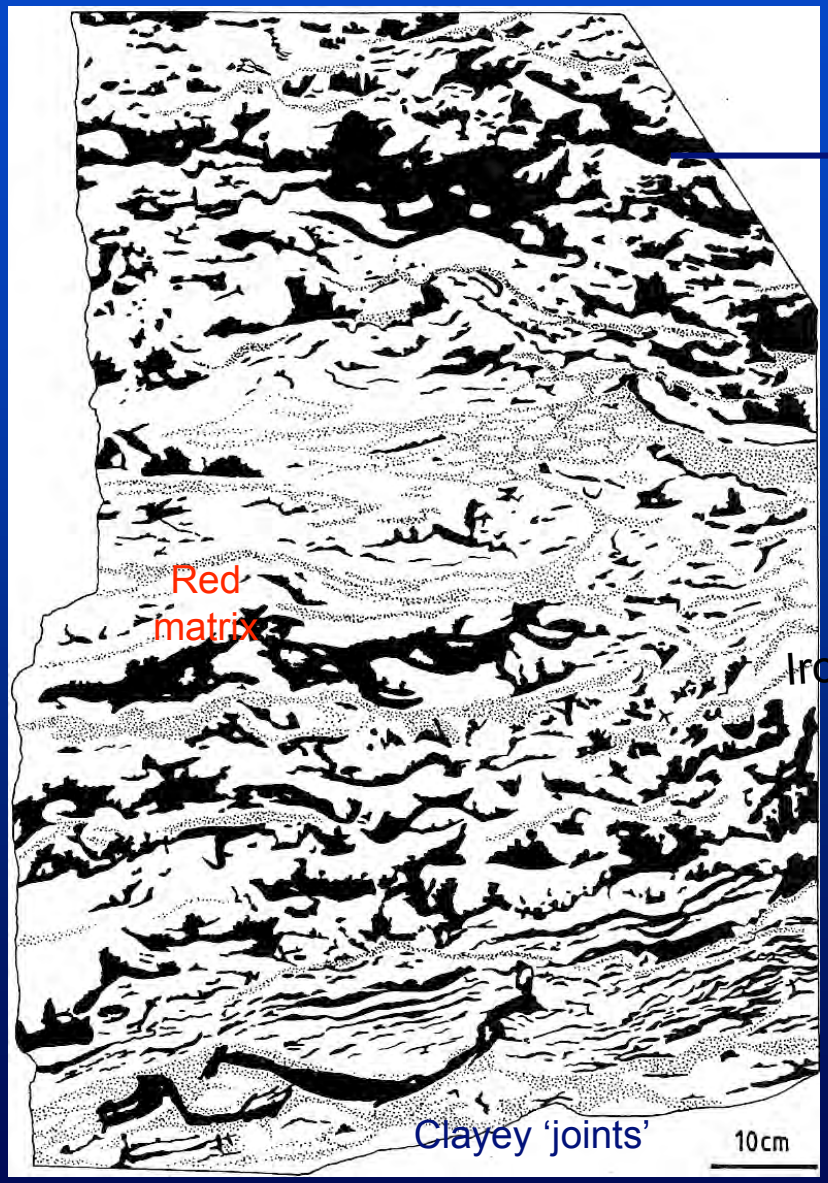


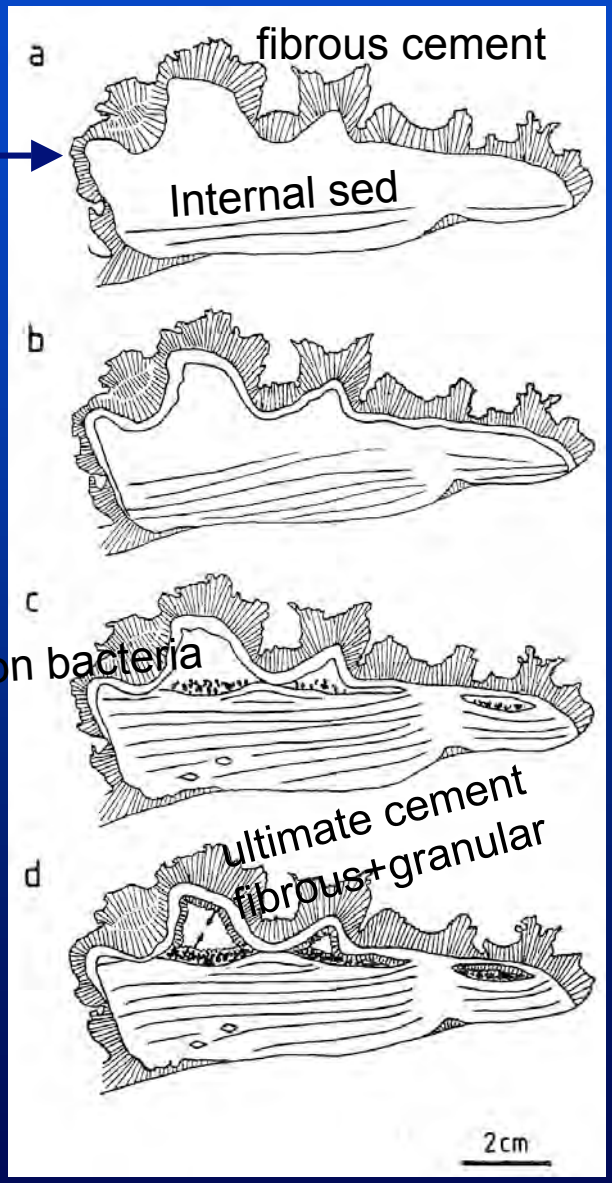


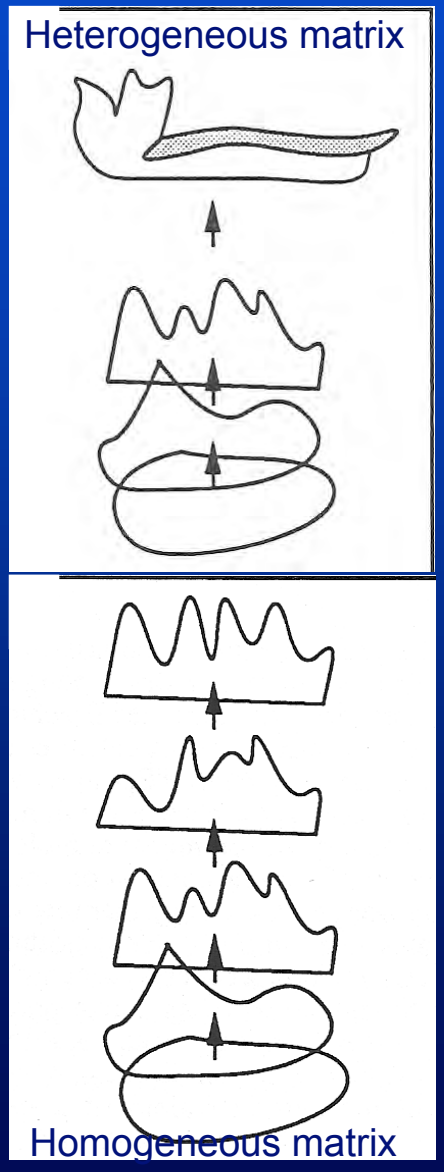


1 : recurrence
7-8-9 : FWWB, cyanobacteria, algal (green algae)-coral-peloid wackestones-packstones
5-6 : progressive biotic enrichment (stromatoporoids, corals...)
4 : SWB, oligophotic environment (corals, crinoids, *stromatactis)*
3 : iron bacteria-sponge in a quiet aphotic/hypoxic environment, *stromatactis*
2: shale and carbonates with brachiopods, corals, crinoids _sponges
1 : shale with poor fauna, mainly sponges (substrate)

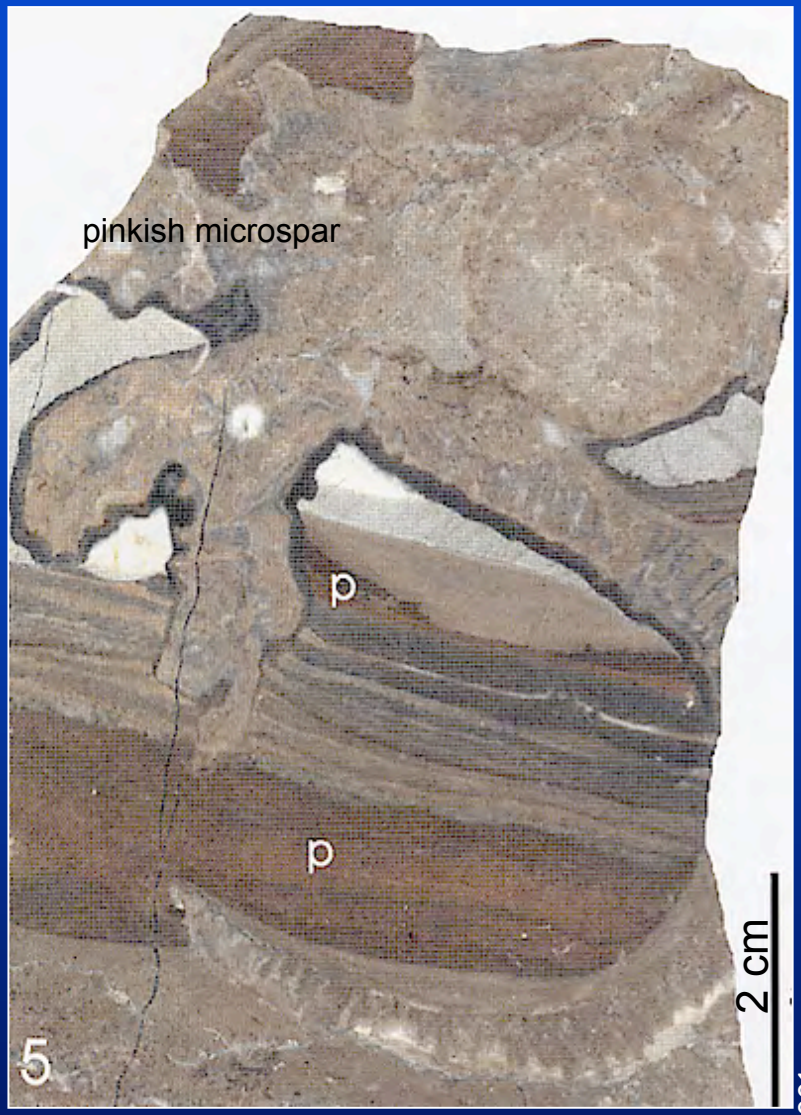
The '*stromatactis*' contain the solution of the problem....?



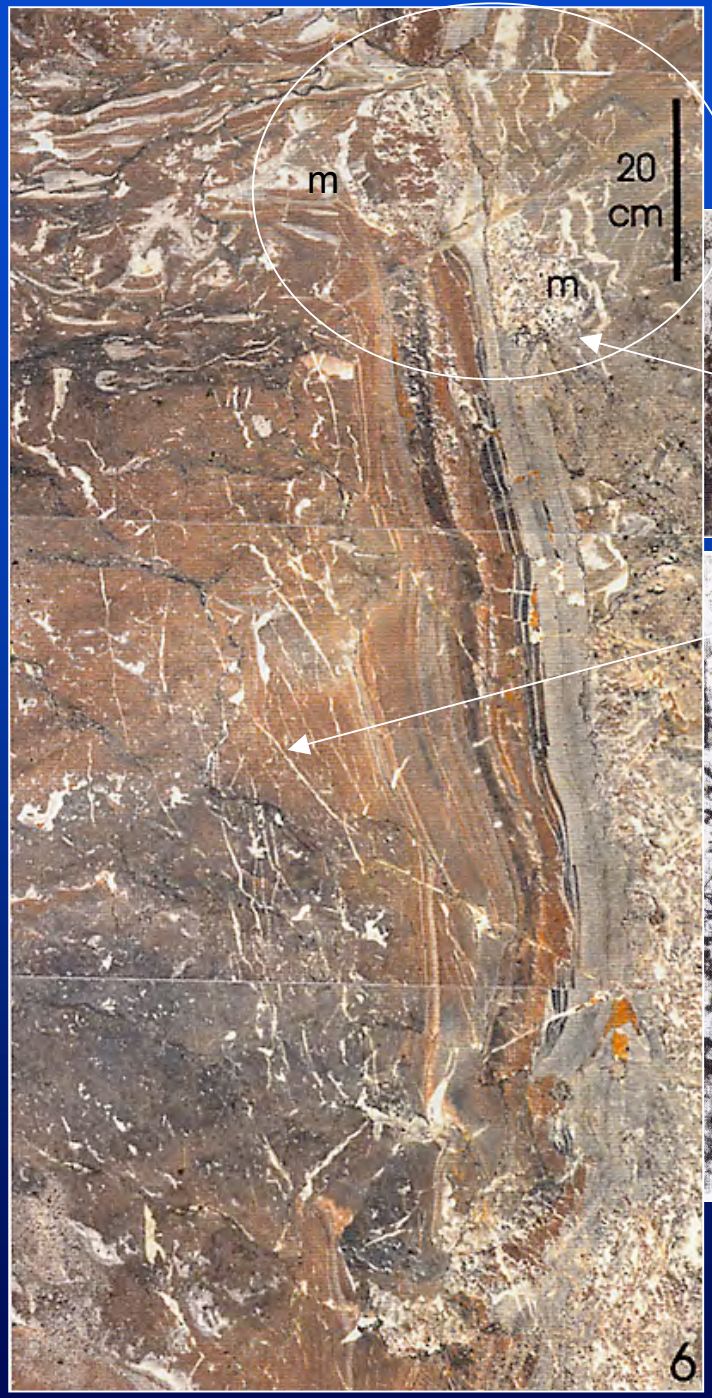




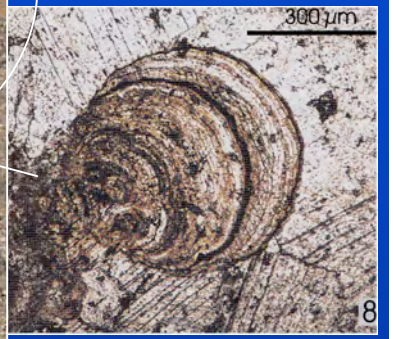
NEPTUNIAN DYKE with microstromatolites (m)

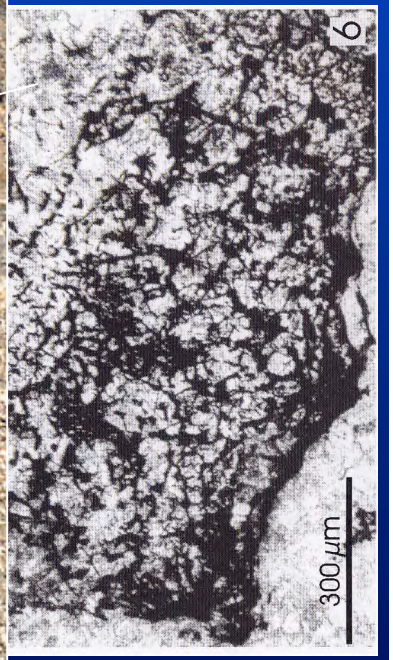


Red coloured peloids (p)
in internal sediments of *Receptaculites*
Between (p) = 'cryptalgal' mats with hematite filaments



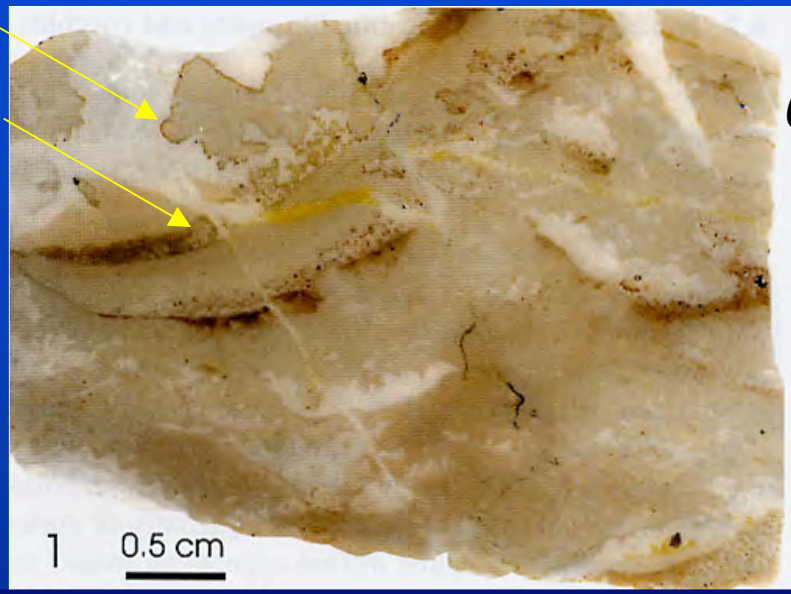
Boulvain et al. 2001



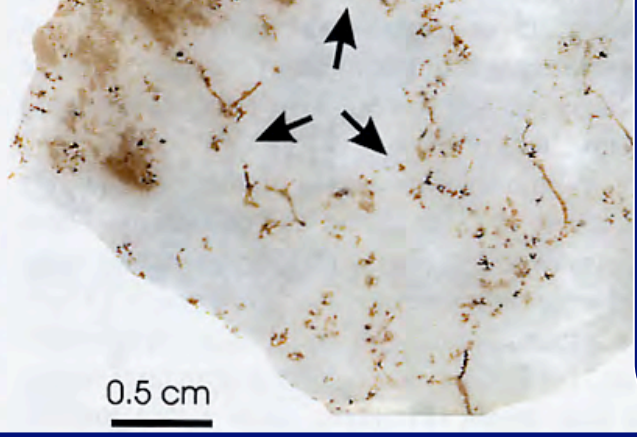


IRON MICROBIAL COMMUNITIES IN FRASNIAN MOUNDS (IN BELGIUM)

Red internal sediments in red limestone with stromatactis *and fenestrae*

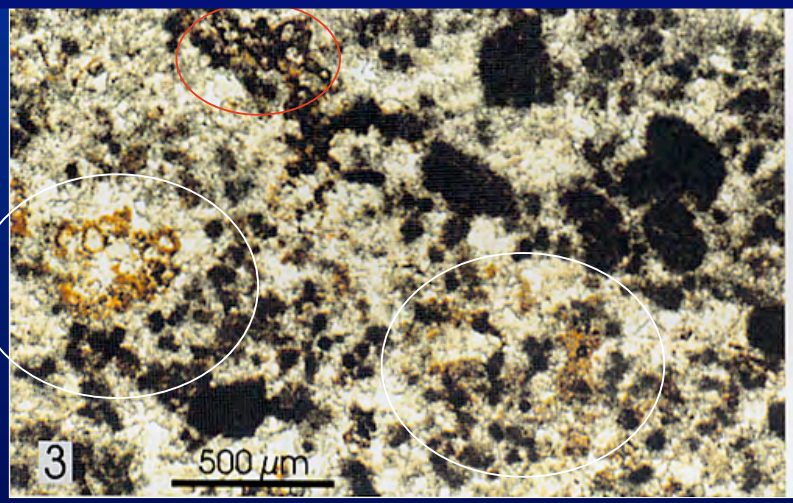


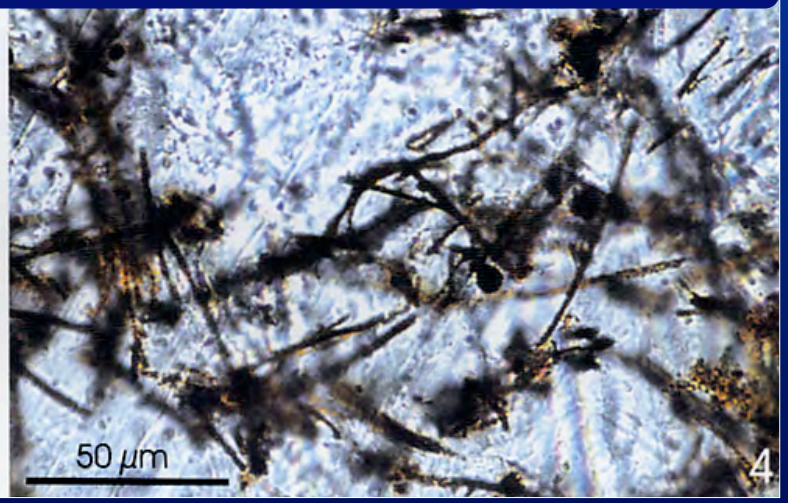
Veils, blisters and microstromatolites (in neptunian dykes)



Veils cm-extension 100 µm thick cross the cavity delimite cm-spheric 'voids' centripete (cathodo-luminescence)

Red-coloured peloids and aggregates in internal sediments of Receptaculites





*Iron-coccoids and bacteria (*Siderocapsa*-like and* Sphaerotilus-Leptothrix*-like) in the internal sediments-cavities of* Receptaculites

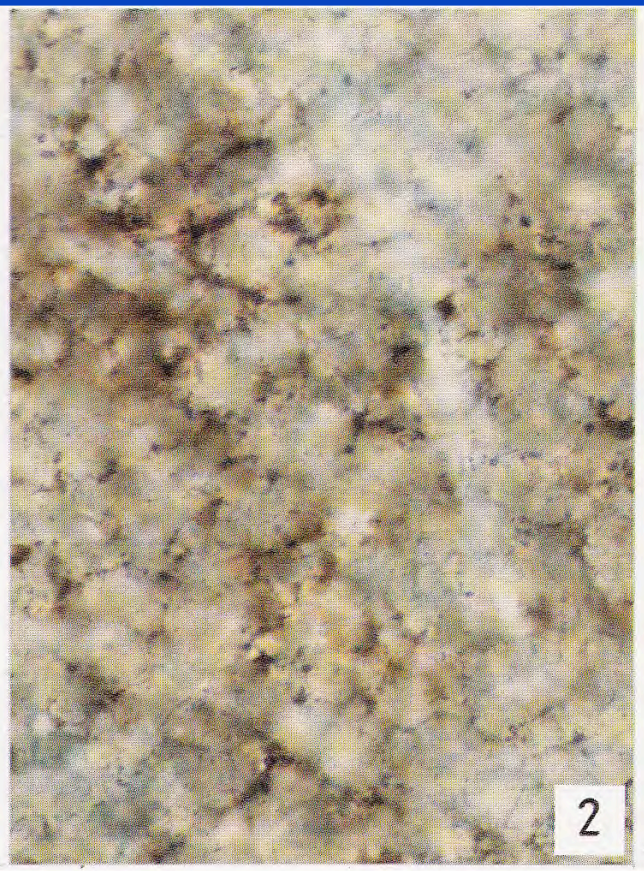
Boulvain et al. 2001

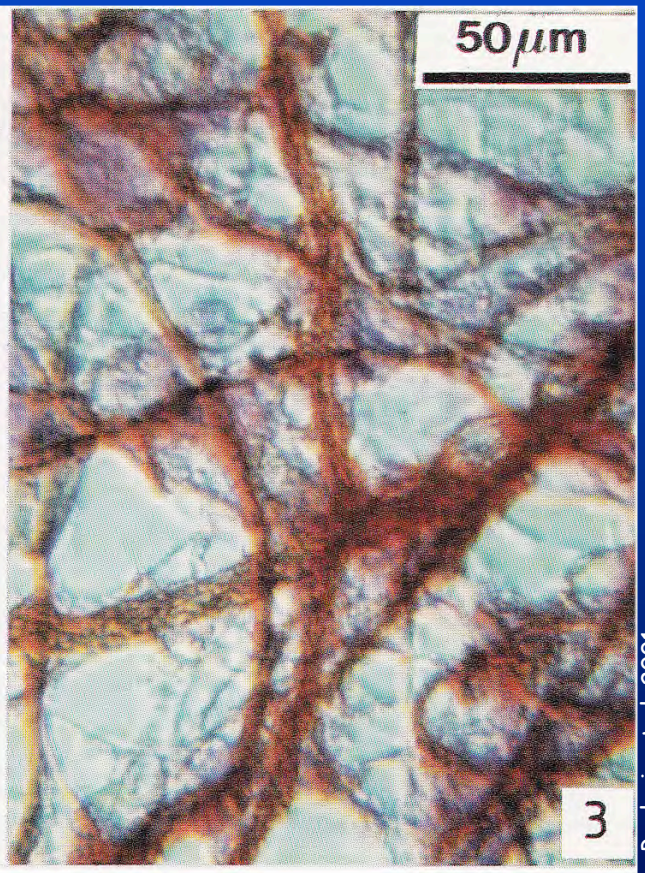
G E O L O G Y | BIOLOGY

Iron bacteria and iron coccoids (hematite in the sheaths) Granular sparite, internal sediment

Relicts of iron bacteria in a slitghtly microsparitized matrix (griotte)

Present day iron bacteria (*Sphaerotilus-Leptothrix* group) Small stream in Brussels





Boulvain et al. 2001

'Perfectly' fossilized during cementation of the cavity (*stromatactis*)

Strongly altered-broken during 'recrystallization' (microsparitization) of the micrite matrix

Red color due to ruthenium (interferential contrast) *Beggiatoa* sp.

… how can we explain the red colour that made the stone so scarce?

XVIIIth-XIXth centuries : red = iron (Delhaye, 1908)

- the iron is detrital (Reijers, 1985), transported from the continent, then mixed with the carbonate matrix during sedimentation …
- its concentration and degree of oxidation produce colour variations (reddish)

LATER ON (1964-1988)

a relation between ferruginization/palaeogeography/climate is the fashion : washed equatorial laterite soils provide great quantities of iron oxides… thus the red limestones are used as palaeoclimatic indicators!

oxygenation degree ?
(in non clastic rocks)

- red limestones are found in oxidized facies
- green limestones indicate reducing conditions

both indicate shallow waters

red silicified limestones (lydites)
indicate deep environments
with minimum amounts of iron and oxygen !
… but they are not reduced…

basic observations …

the Fe content of red limestones
of biotic origin is comparatively low

1 to 2 %, often < 1 %

…therefore this content is not responsible
of the coloration

There is no direct relation between oxygen content and overall iron oxidation...

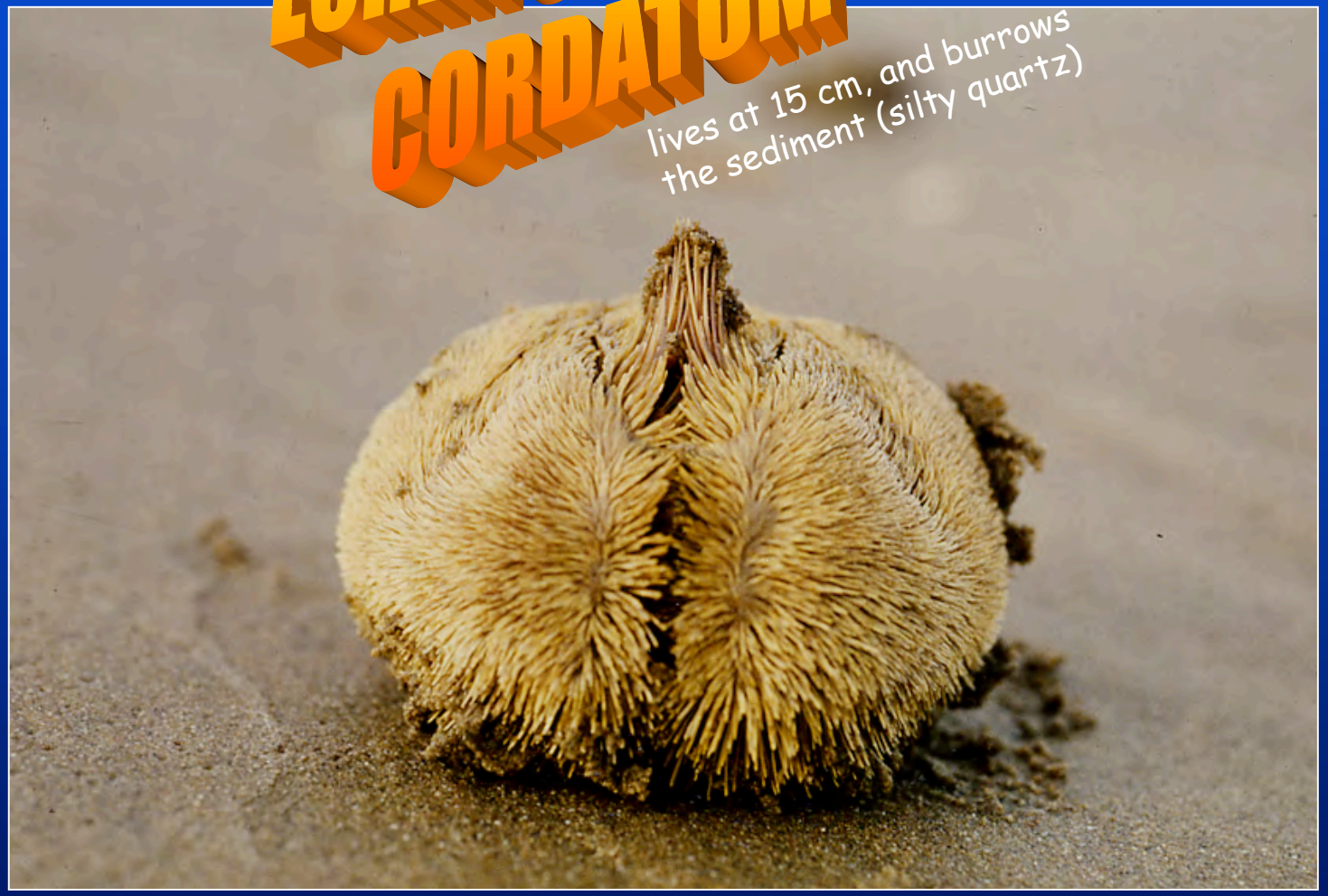
Thus the colour is not necessarily linked to shallow water marine environments where oxygen is abundant

sedimentation is in a NORMAL OPEN MARINE facies

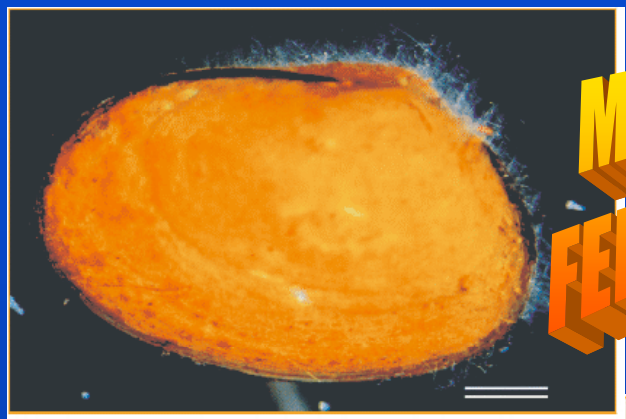
red limestones are formed in calm environments, with low levels of oxygen

B I O L O G Y

ECHINOCARDIUM CORDATUM



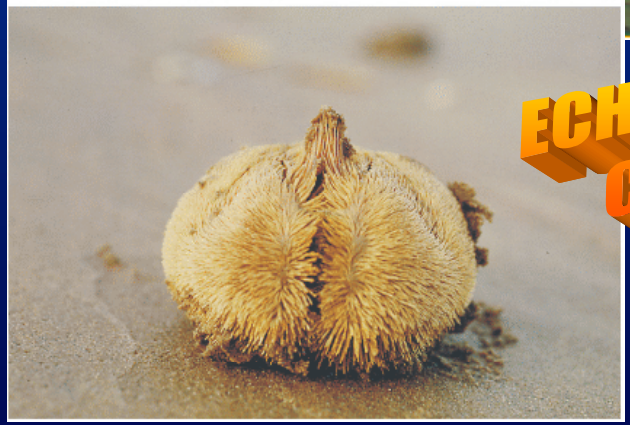
and its biofilms…



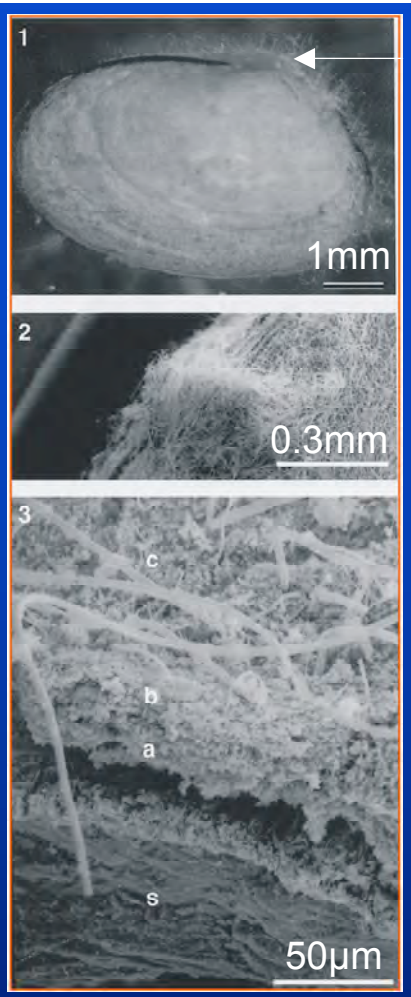
MONTACUTA FERRUGINOSA

LIVING MODELS

LIVING MODELS



ECHINOCARDIUM CORDATUM



Outer layer

Outer layer

Outer layer

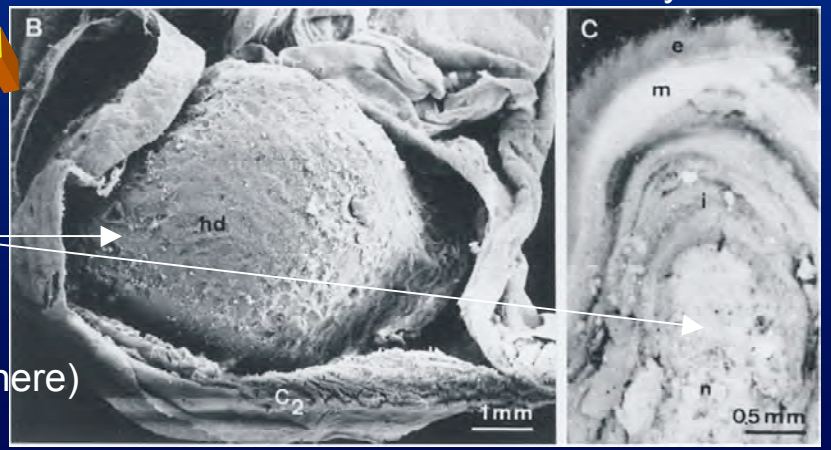
Intermediate layer

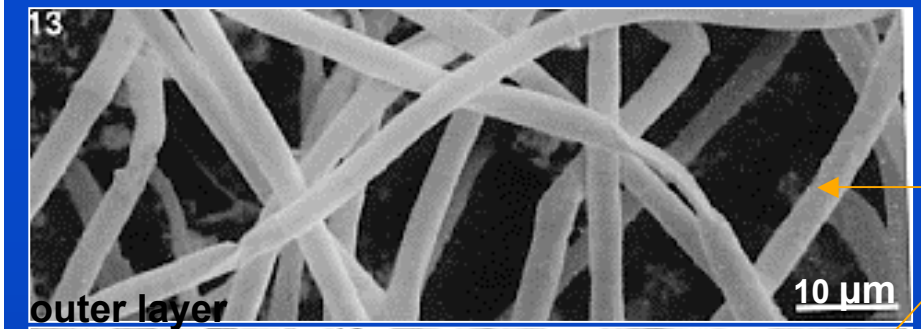
Inner layer, EPS and ferric amorphous PO_4

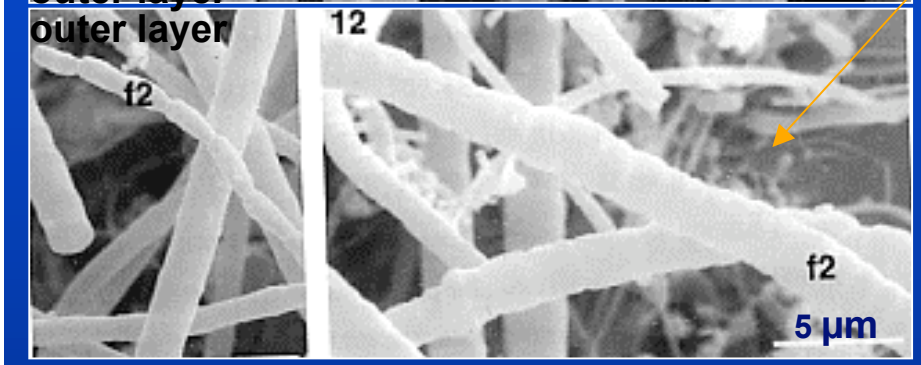
Shell

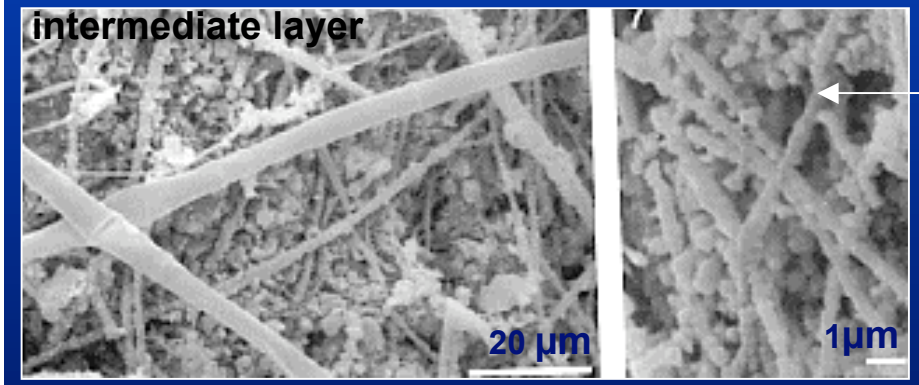
3 layers

Nodule in the caecum (dissected here)





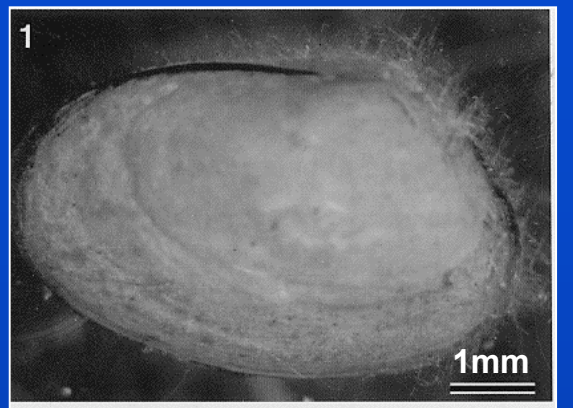


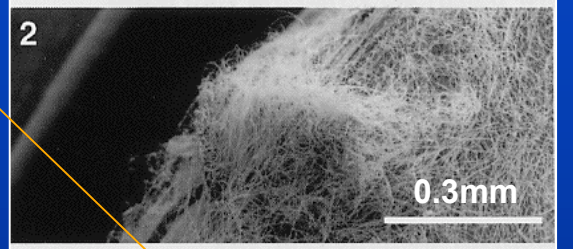


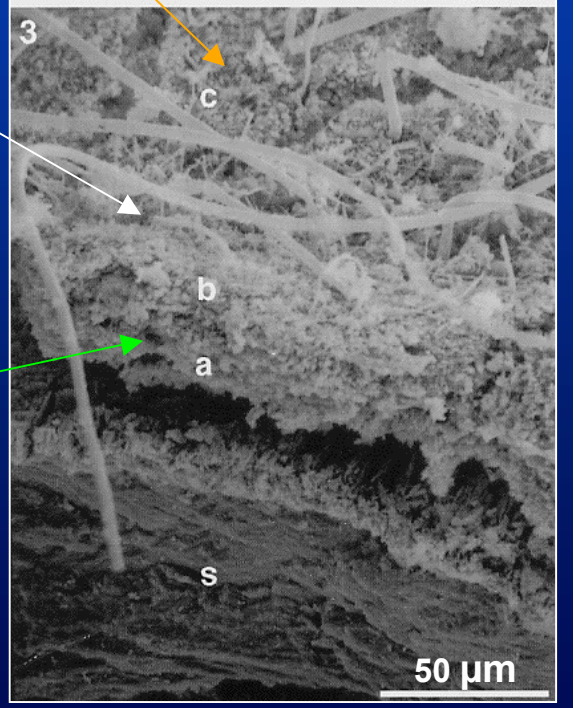
Outer layer
= bacteria
non incrusted
or
with limited
Fe deposits

Intermediate
= bacteria
heavily incrusted
with
Fe deposits

Inner
=
ferric iron deposits
+EPS accumulation

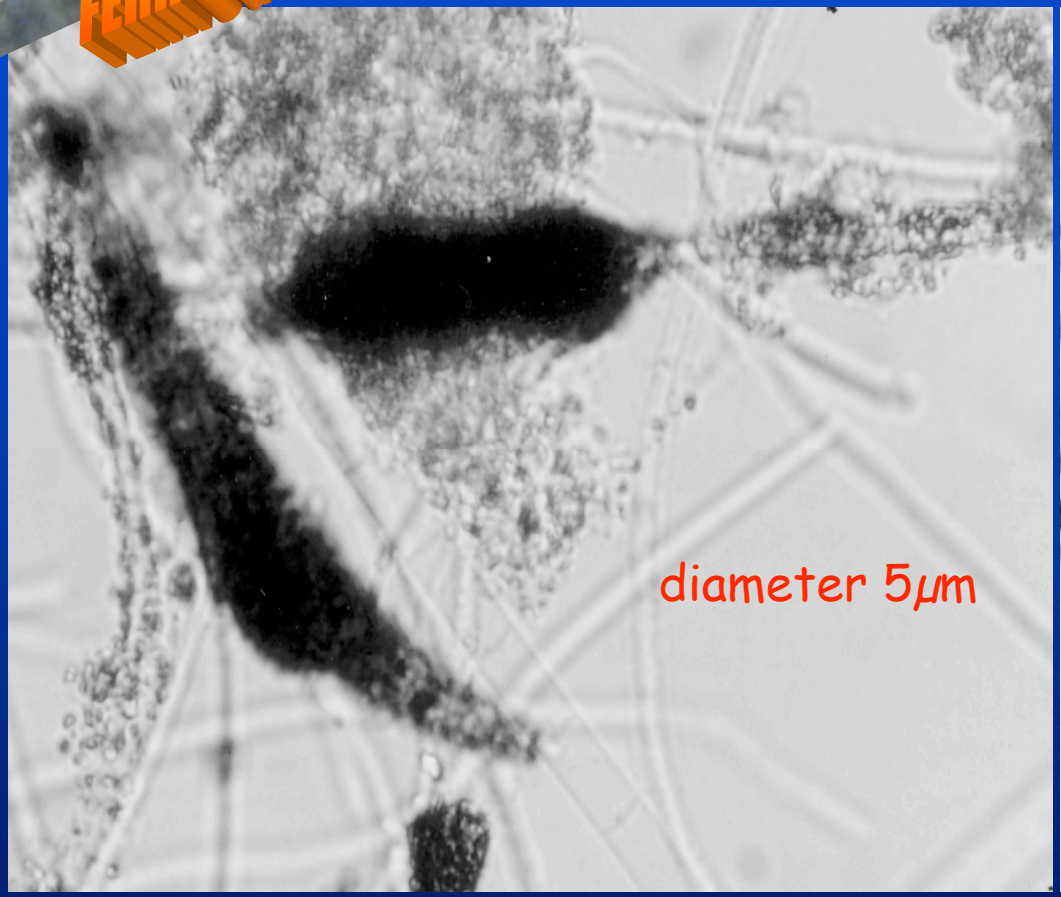




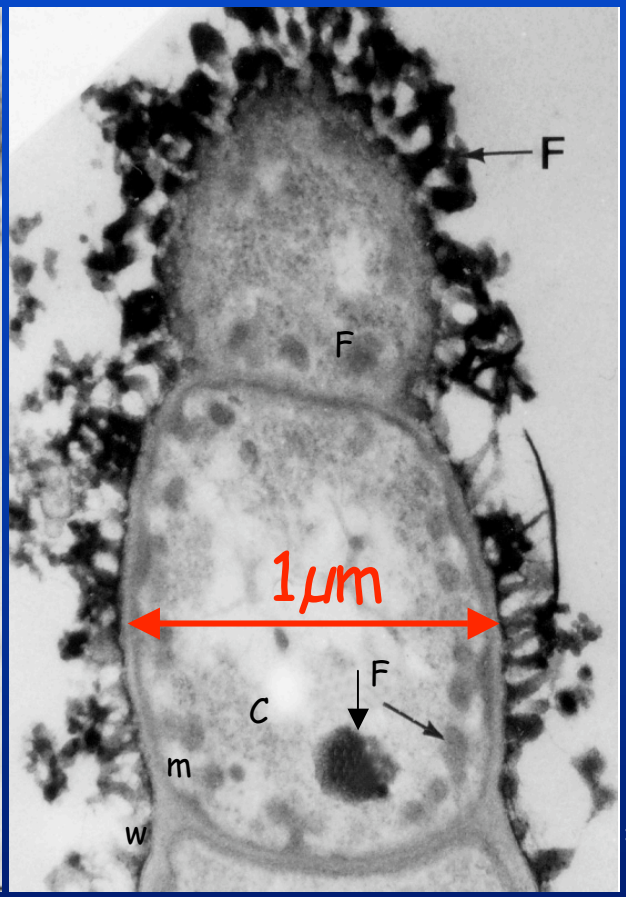


Gillan 2001

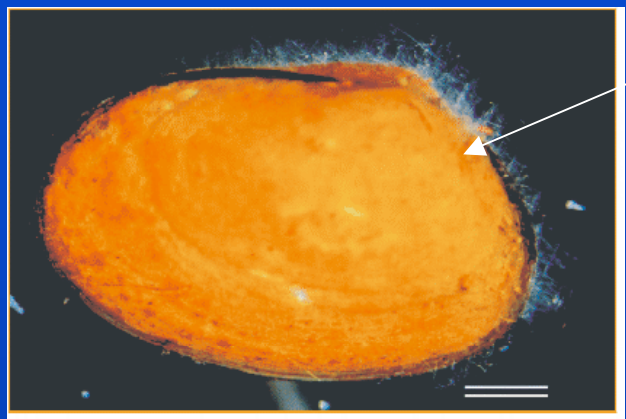
MONTACUTA FERRUGINOSA



Iron bacterial filaments
on a shell
(photonic microscopy)



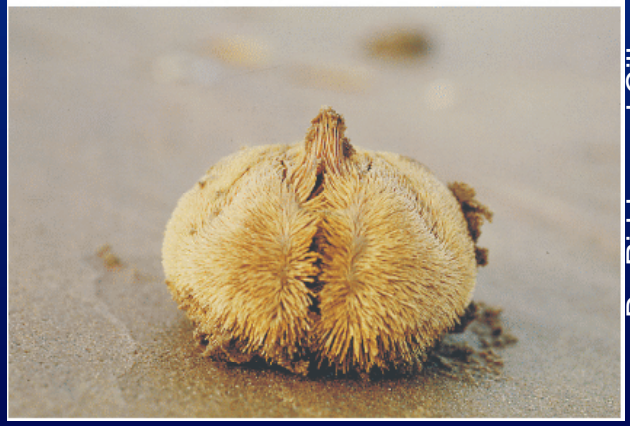
Filamentous iron bacteria
(TEM)
F = Fe



Rust-coloured and ferric iron encrusted biofilm (3mm thick)

LIVING MODELS

LIVING MODELS



De Ridder and Gillan 2003

MICROBIAL MAT WITH THREE SEPARATE LAYERS

Outer layer filamentous and coccoid bacteria, also protozoa

Intermediate layer microbial AND mineral (heavily ferric iron-encrusted filamentous bacteria and protozoa

Inner layer essentially mineral (ferric iron deposits), no or rare living microorganisms

GENESIS OF THE MINERAL-MICROBIAL MAT

1. Ferric iron *deposition* within bacterial sheaths in the outer layer
2. *Release and accumulation* of heavily ferric iron-encrustated sheaths after lysis of the bacteria in the intermediary layer
3. *Degradation* of bacterial sheaths and *accumulation* of ferric iron minerals in the inner layer

ferric iron deposits = 0.05-1µm (granules, amorphous oxyhydroxide 'gel' with phosphate)

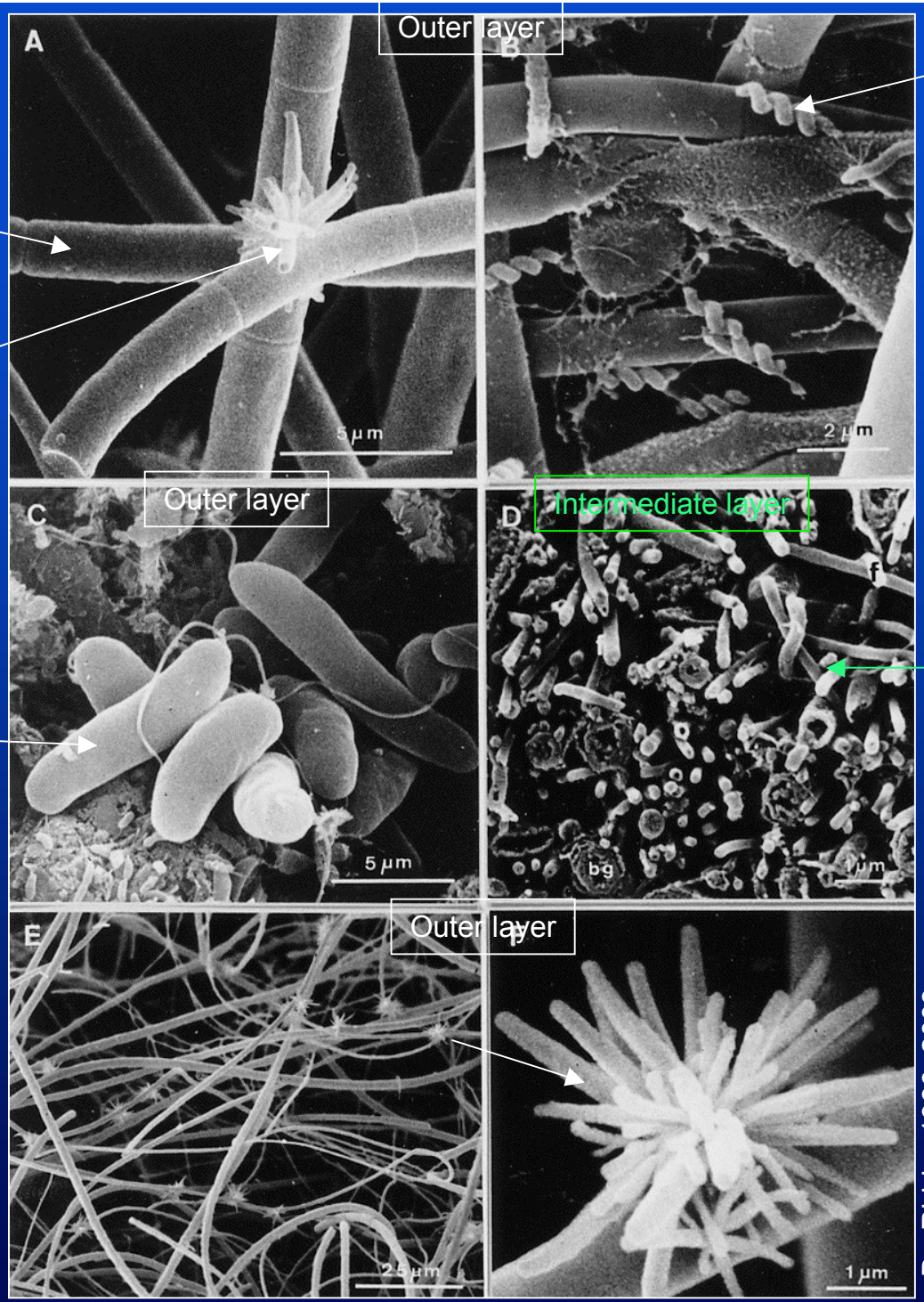
= PASSIVE PROCESS => BIOMINERALIZATION-INDUCED and BIOACCUMULATION (microbes dead or alive)

From PhD thesis David GILLAN, 1999, Marine Biology Dept, ULB (and numerous papers in Journals of Microbiology...)

Large bacteria (chains)

Small bacteria (rosette-like)

Large bacteria (rods)



Spiral-bacteria

The bacterial sp. of *Echinocardium* AND *Montacuta* have been determined by cloning and sequence analyses (16S rRNA) ... MARINE BIOLOGY LAB ...

Small-rods forming chains

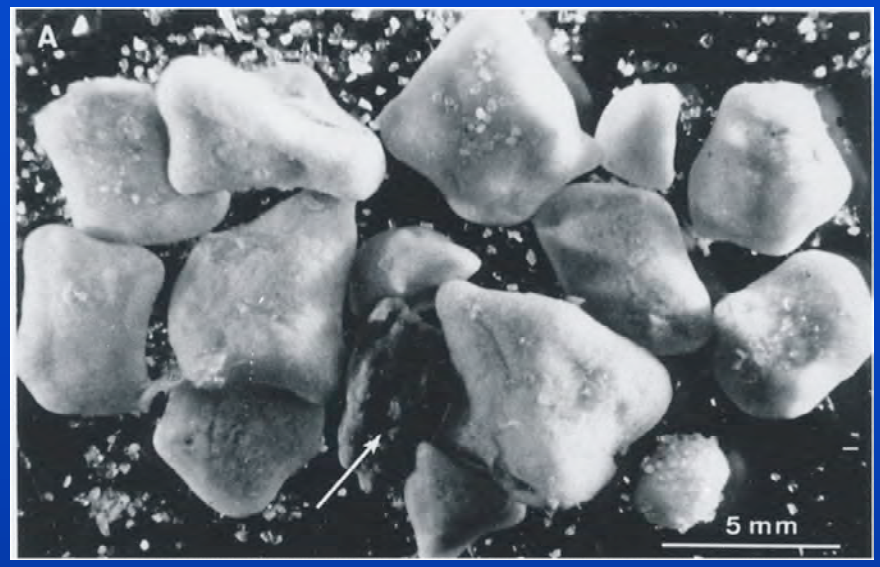
MARINE BIOLOGY LAB ...

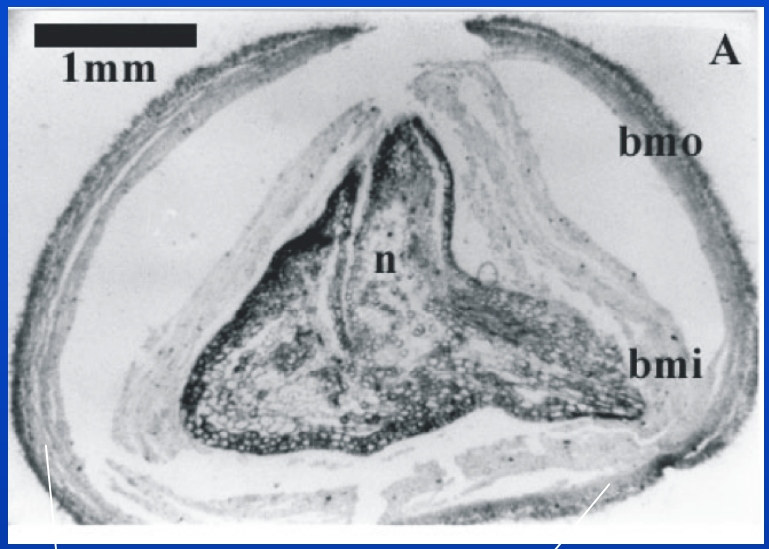
+ burrowing amphipod *Urothoe poseidonis*

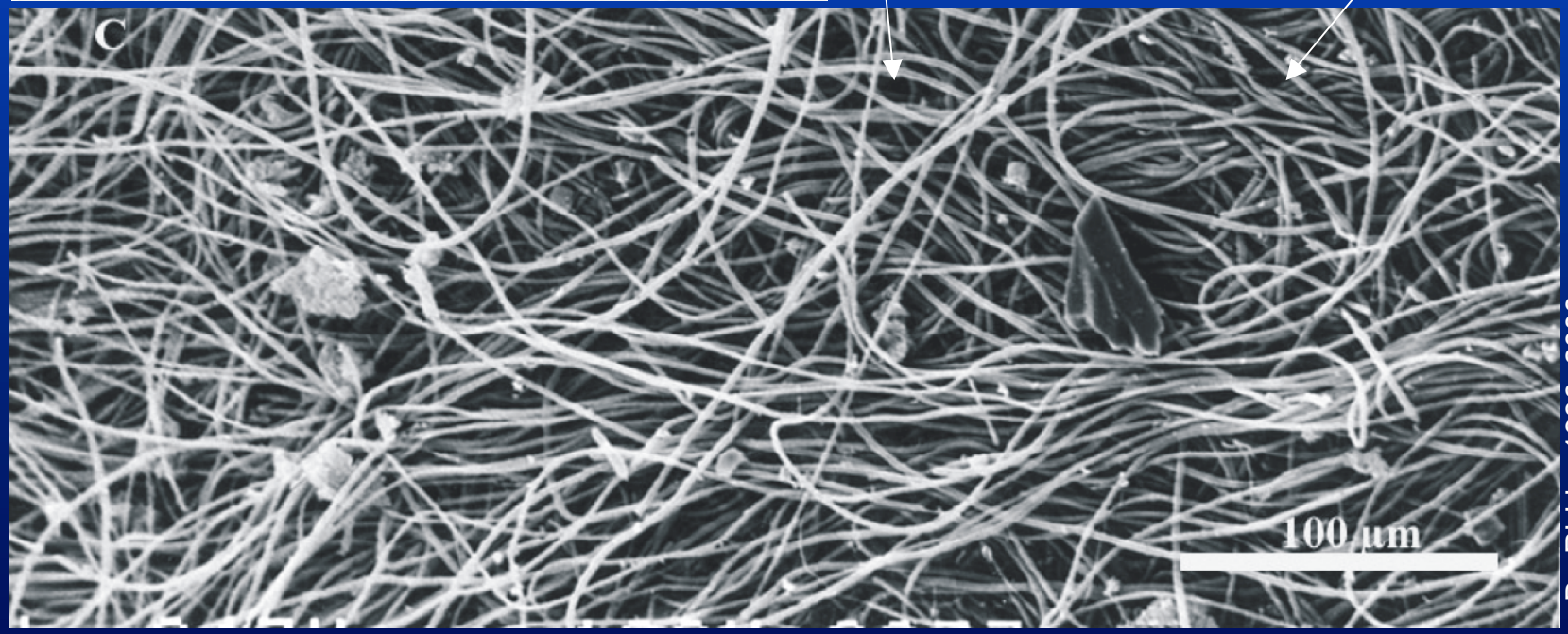
+ mudsnail (gastropod) *Hydrobia ulvae*

De Ridder 1986, 2003

Nodules (after dissection of the intestinal caecum))



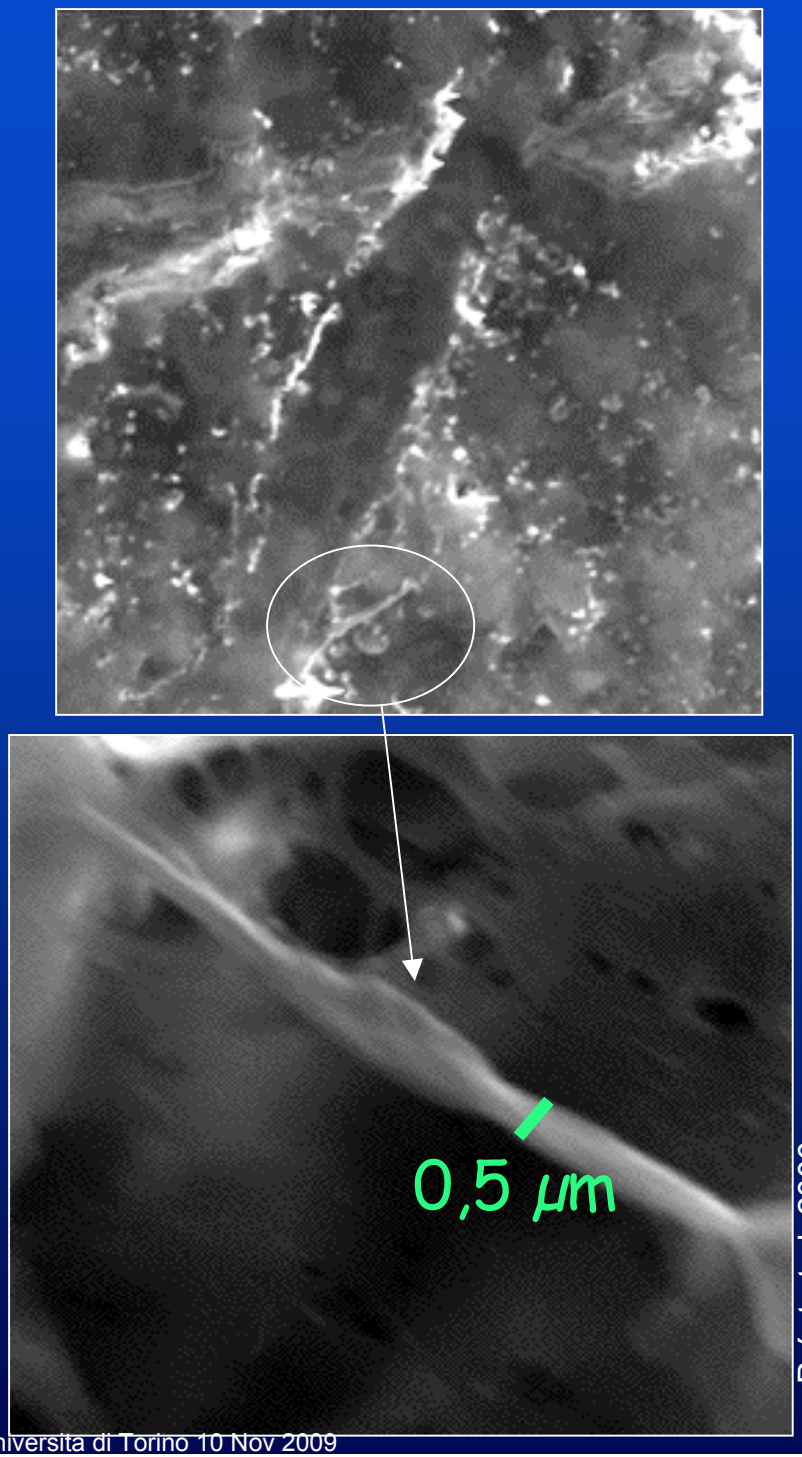




De Ridder 1986, 2003

OUTER LAYER: BACTERIAL MAT (LIVING FILAMENTOUS BACTERIA MAINLY IN ANAEROBIC CONDITIONS)

∂-Proteobacteria (Desulfonema G.), *Bacteroidetes*, *Firmicutes* + *Thiothrix?*

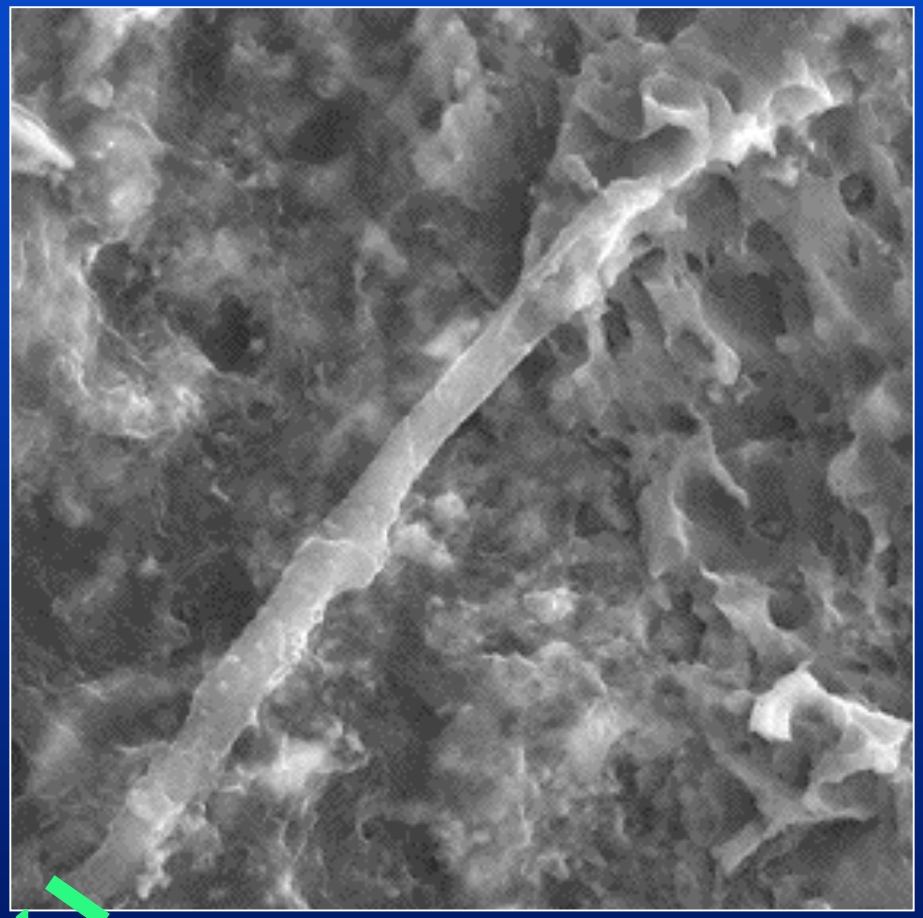


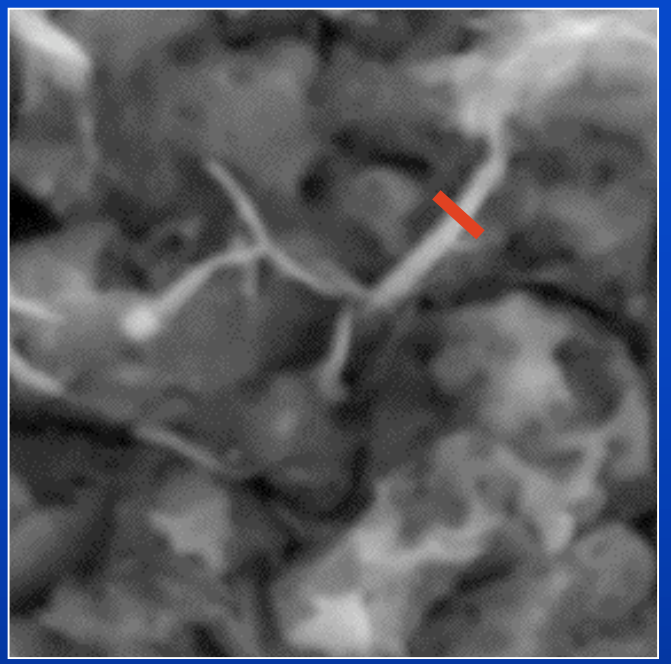
In the Phanerozoic

inframicrometric
hematite
crystals coating
bacterial
filaments

Préat et al. 2006

Italian
Ammonitico Rosso
Jurassic

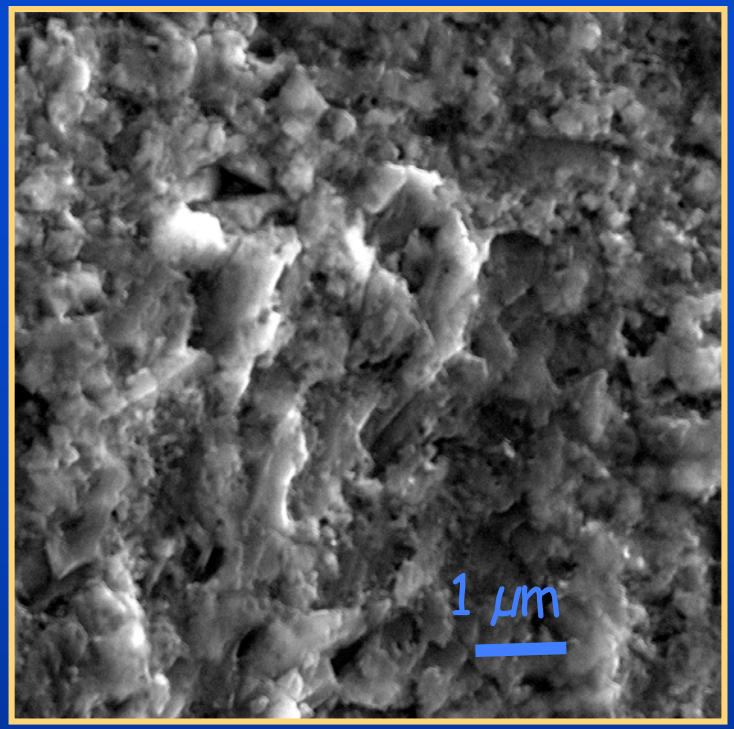


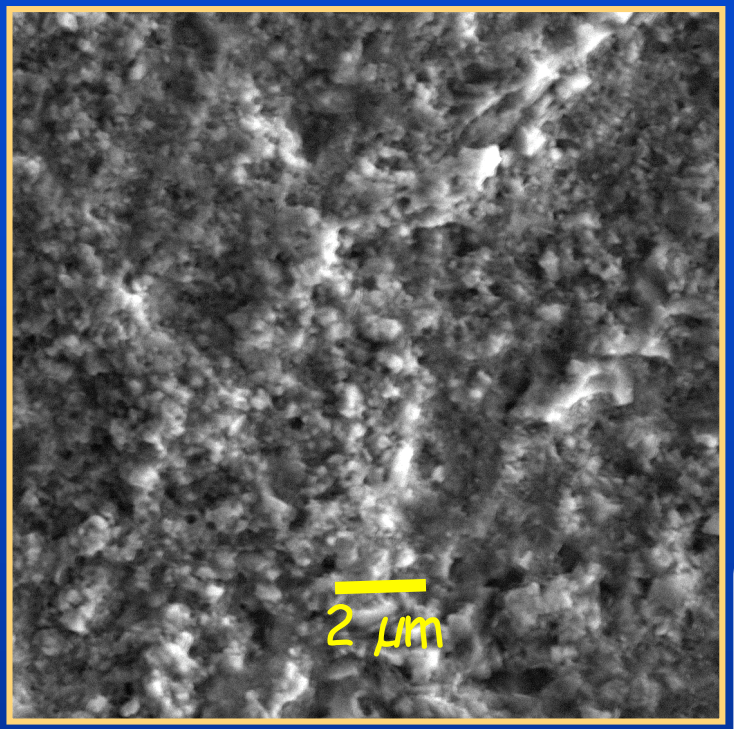


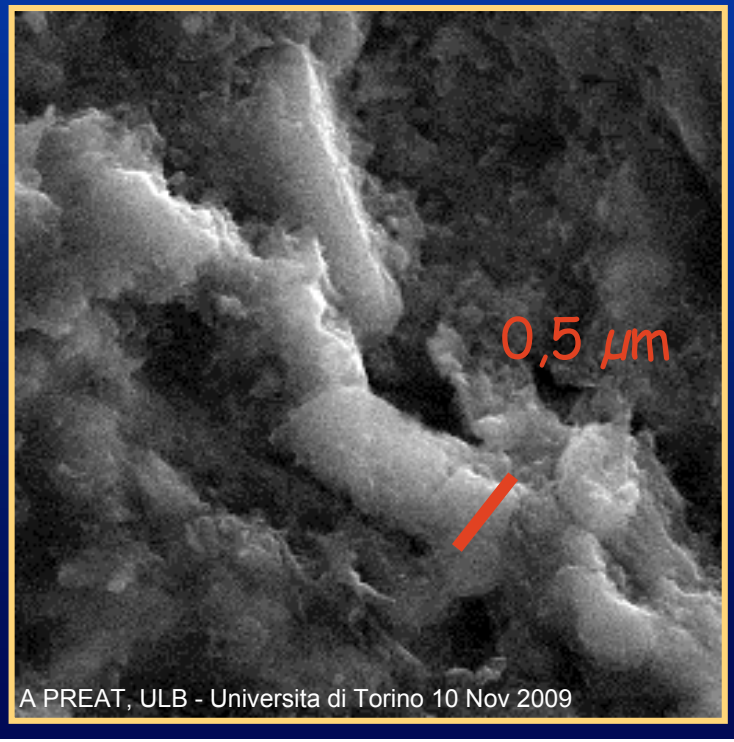
0,5 µm

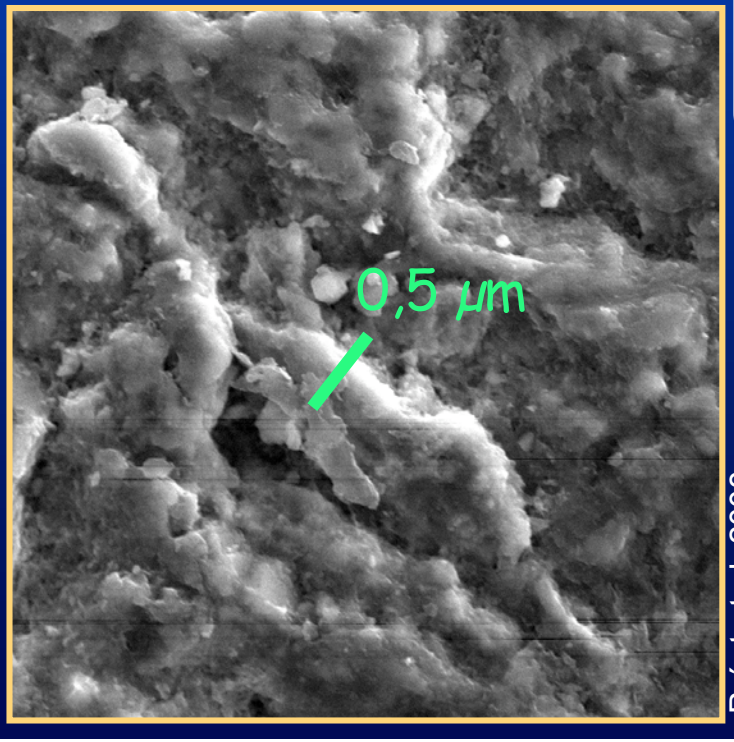
Préat et al. 2006

Italian Ammonitico Rosso Jurassic







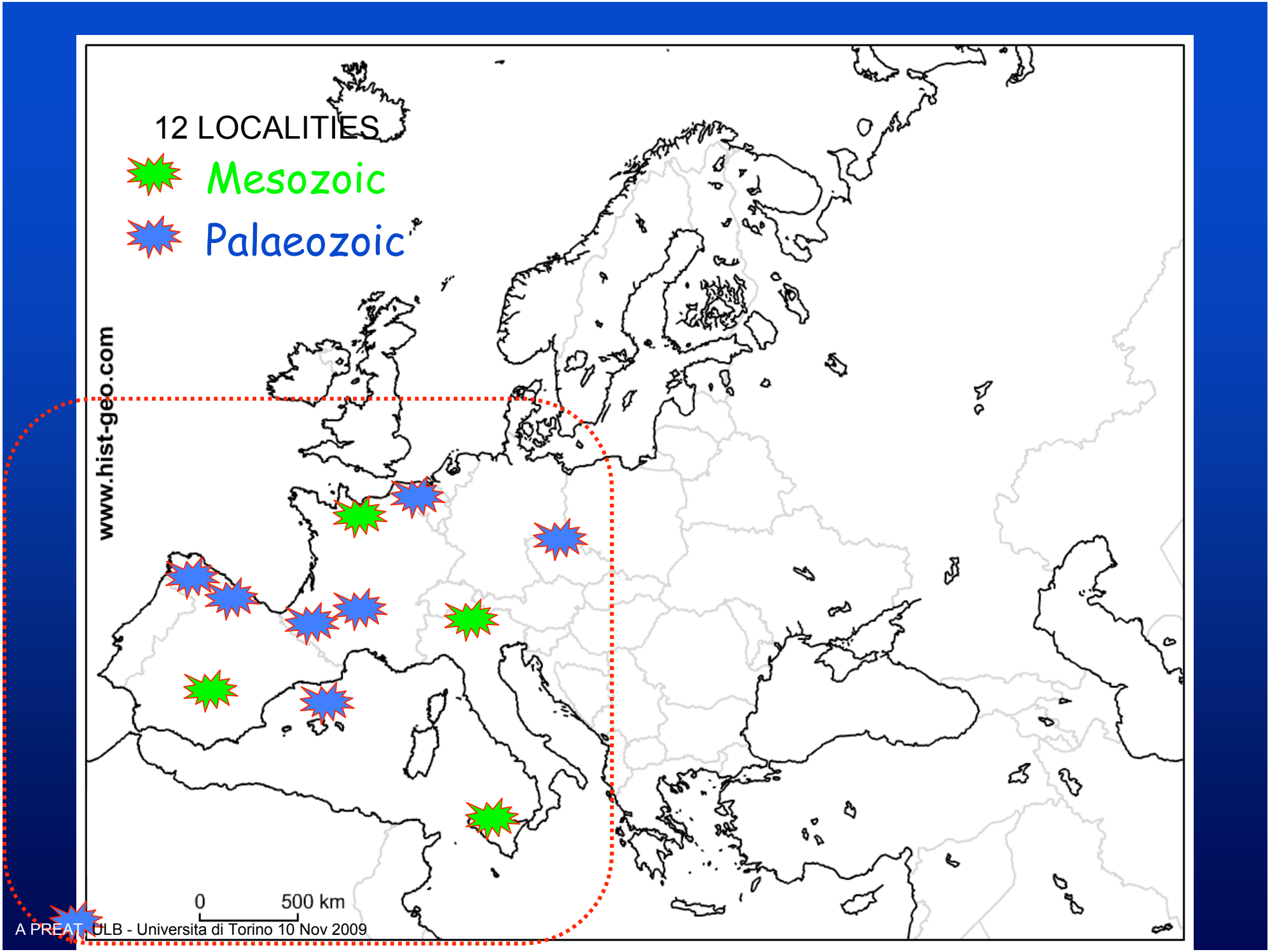


Italian Ammonitico Rosso Jurassic

benthic bacterial mats up to 20%

Préat et al. 2008

OBSERVED MICROFACIES OF DIFFERENT AGES AND LOCALITIES


12 LOCALITIES
Mesozoic
Palaeozoic
www.hist-geo.com
0
500 km

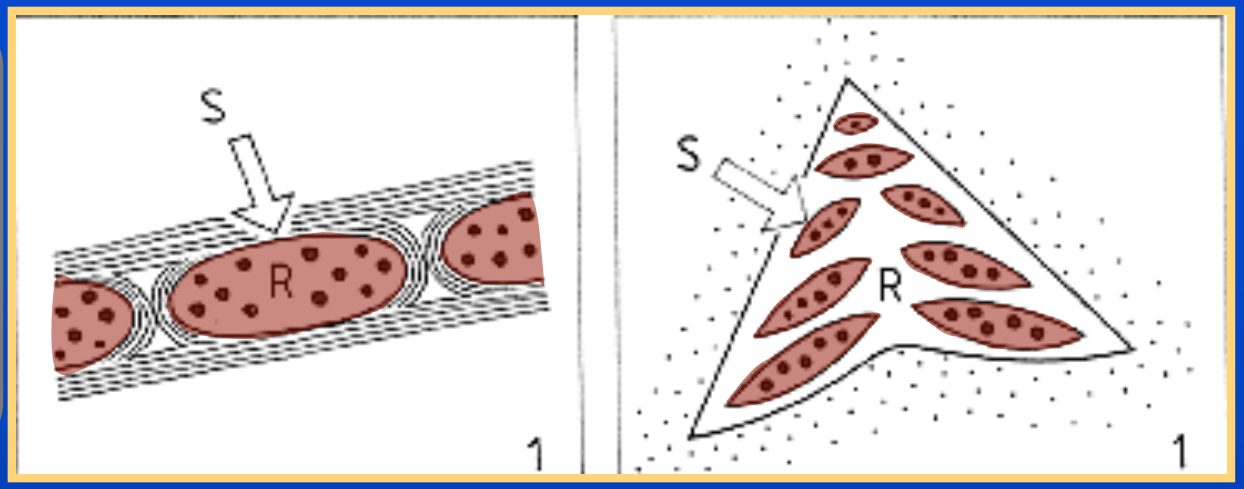
Microscopic morphologies of the iron constructions

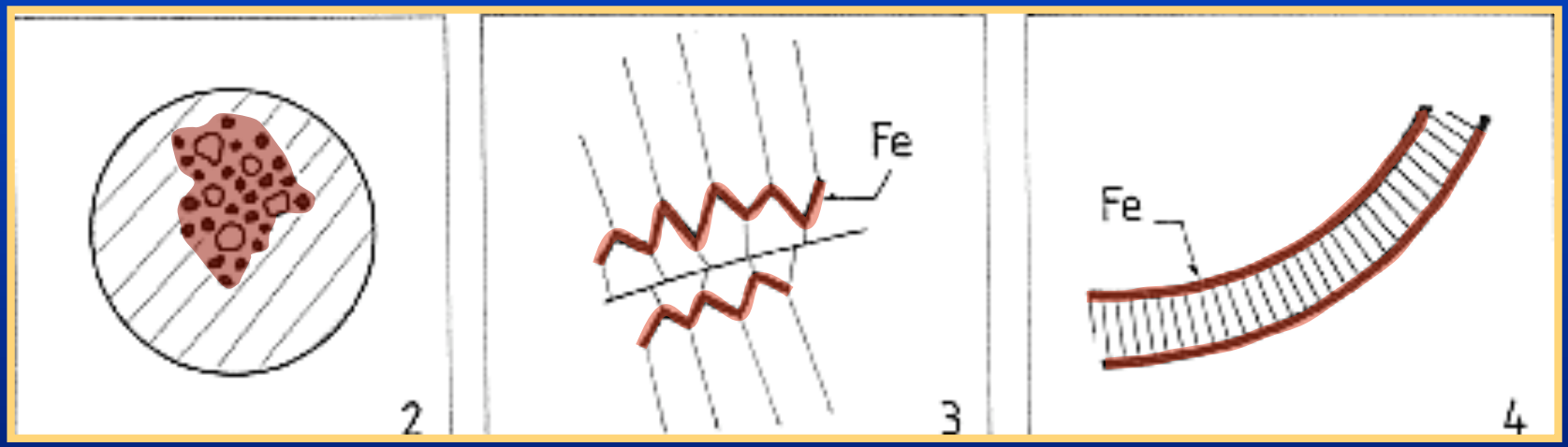
- infillings of original fossil cavities
- calcite replacement of dissolved echinoderm plates
- infillings of bioperforations
- bacterial/fungal filaments
- ‘hedgehogs’ and ‘erythrospheres’
- massive hematite coating around microfossils
- simple or multiple biofilms
- microstromatolites (exogens ou endogens, crenulated or not...)
- oncolites

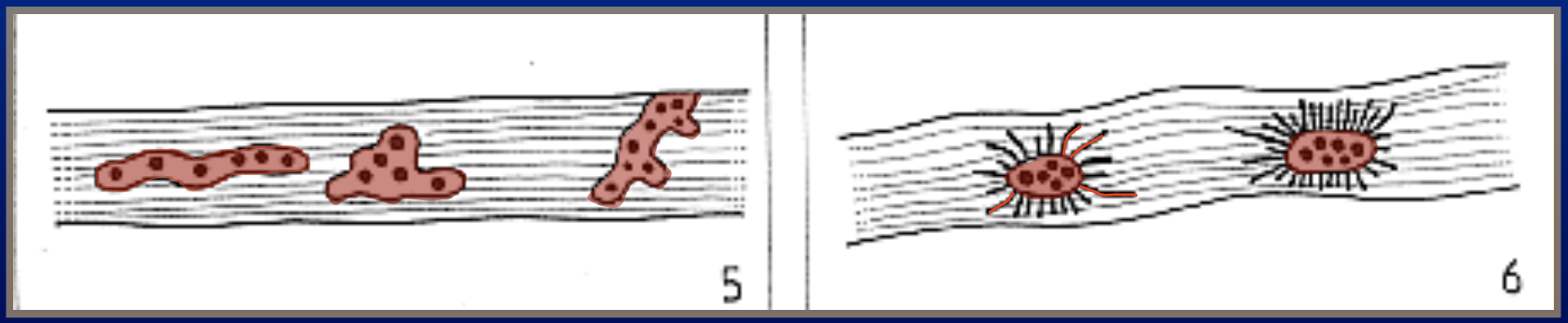
..... non exhaustive ....

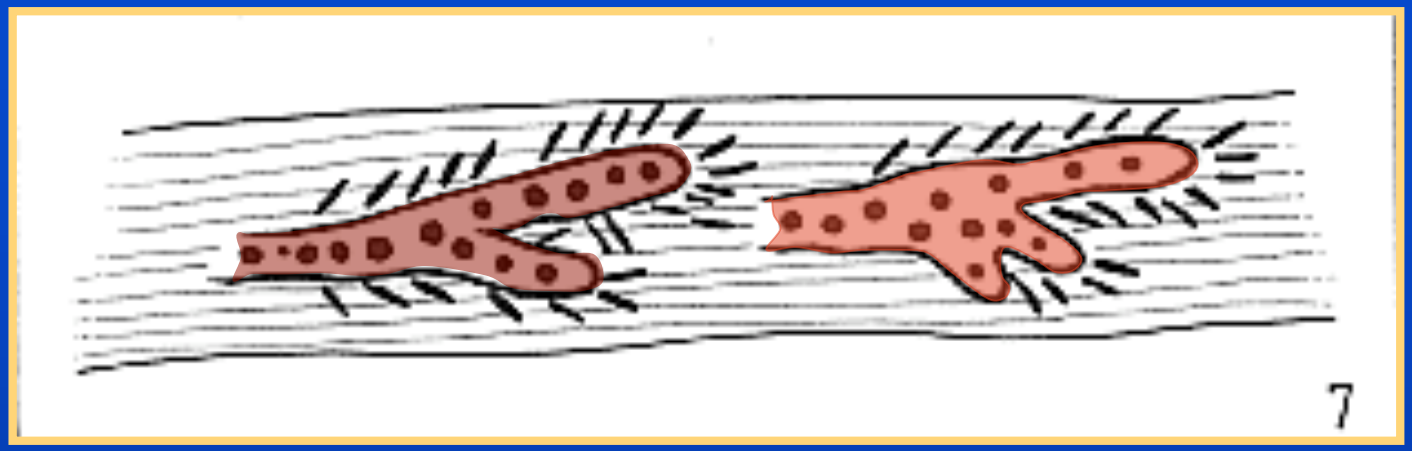
S= sediment

R= red





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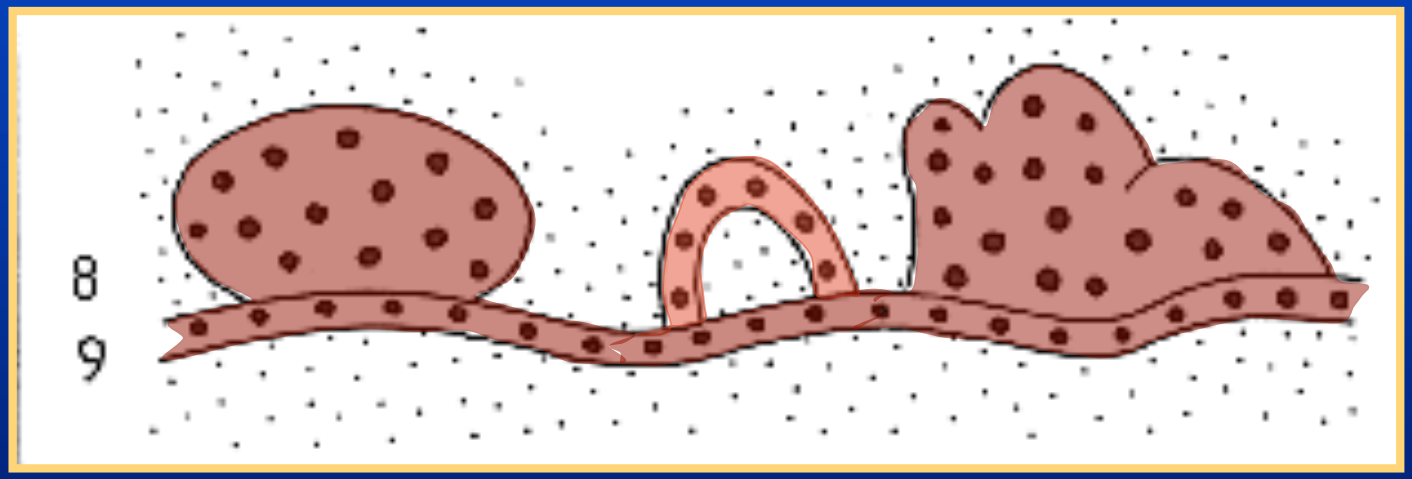
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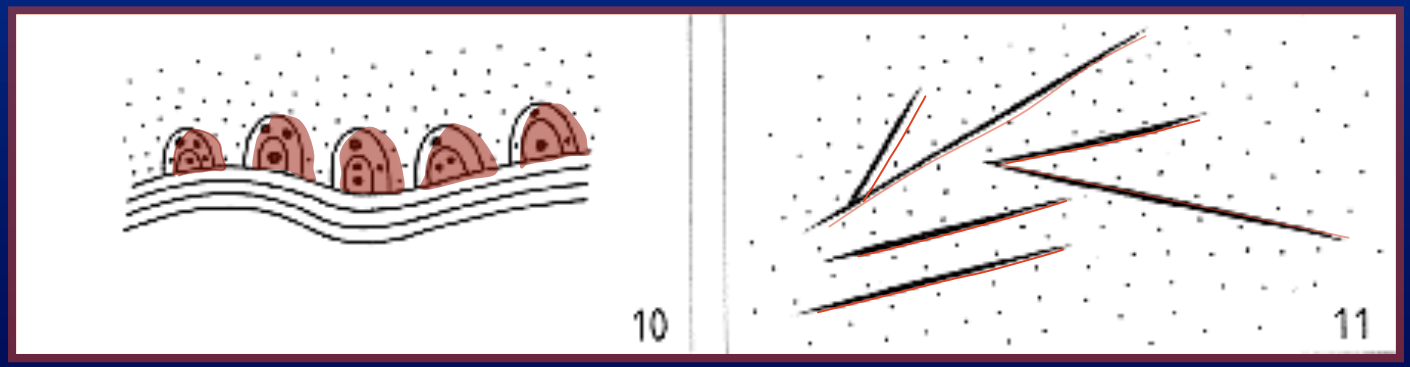
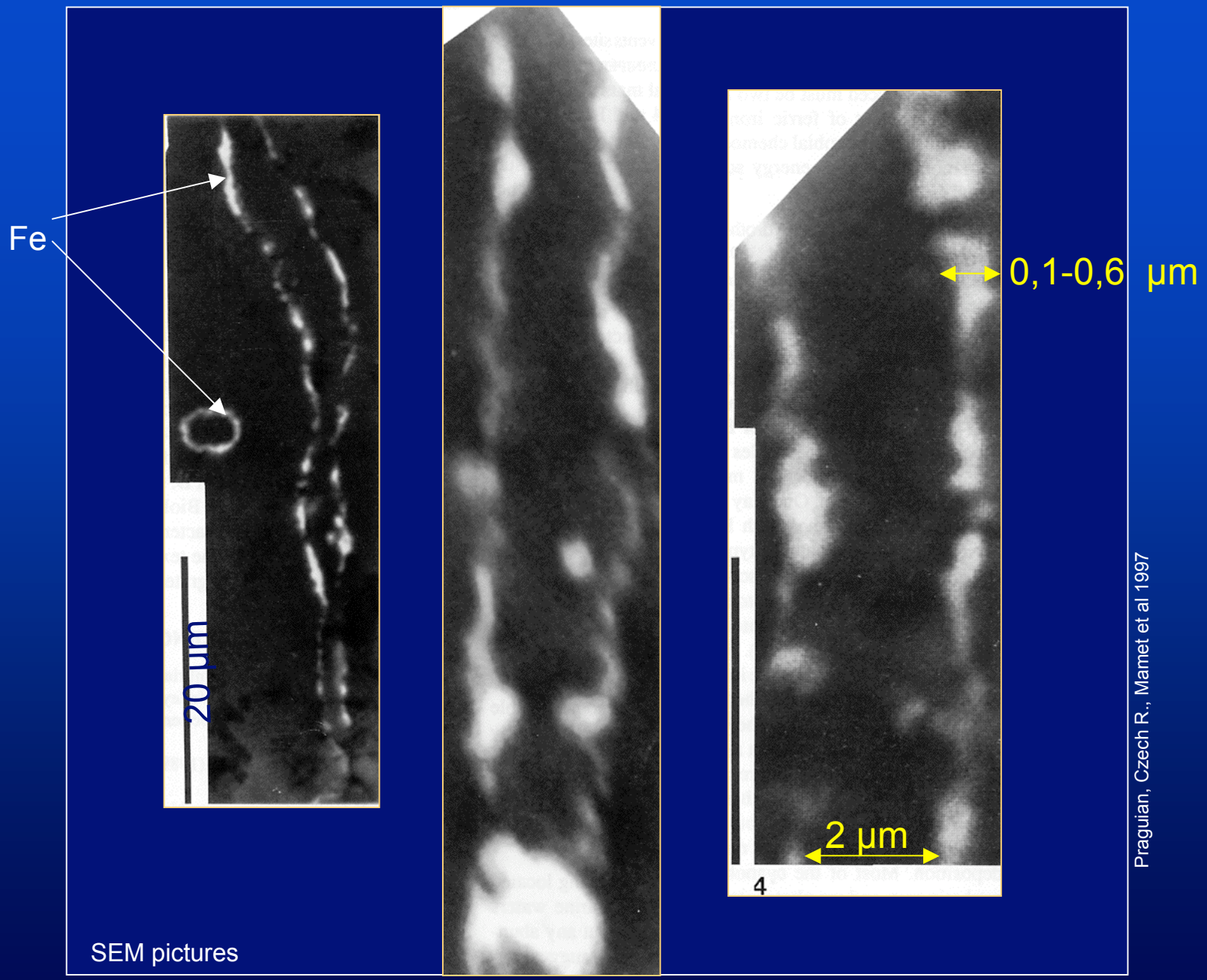
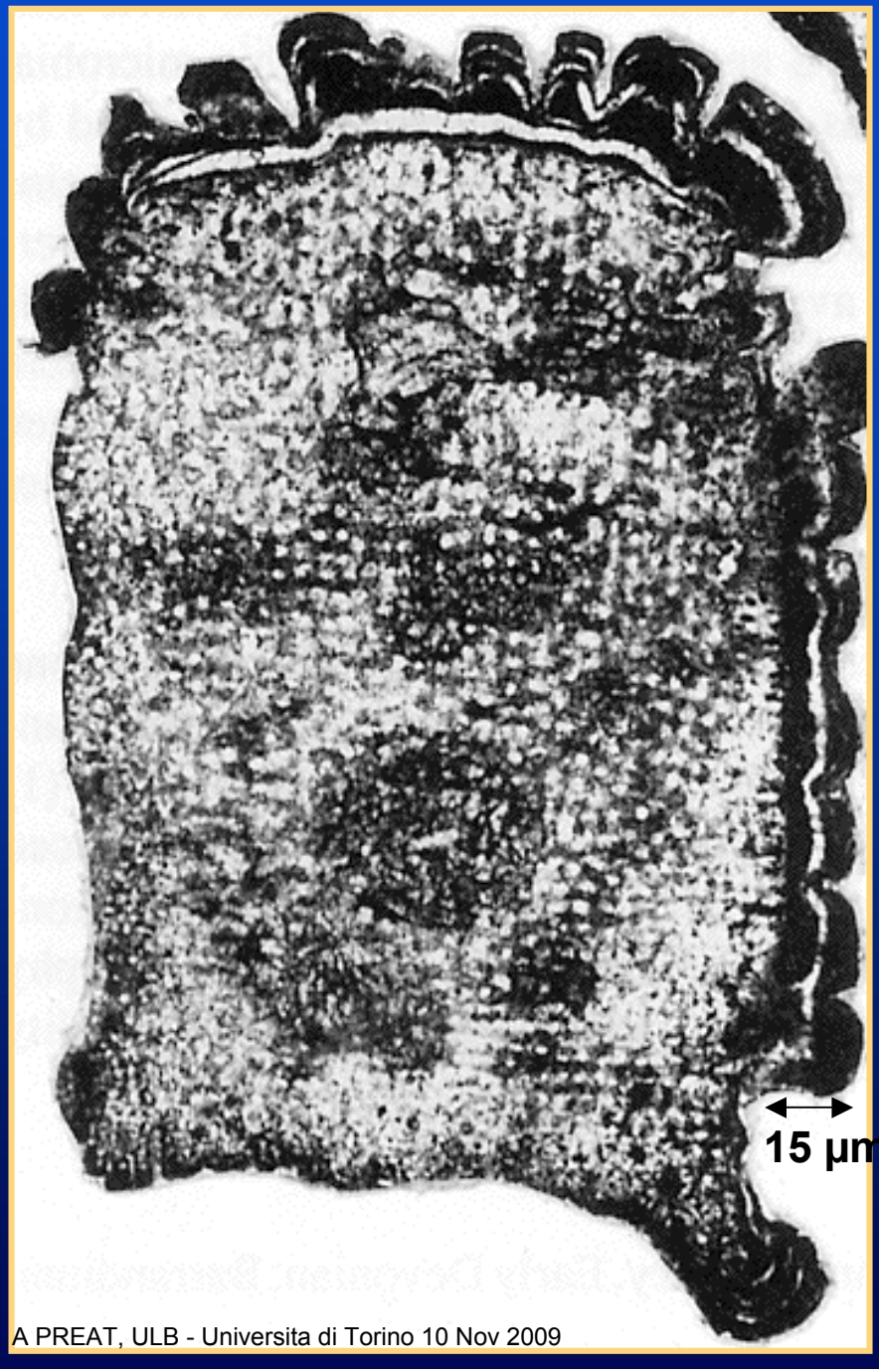
9


10
11

CZECH REPUBLIC, LOWER DEVONIAN



CZECH REPUBLIC, LOWER DEVONIAN

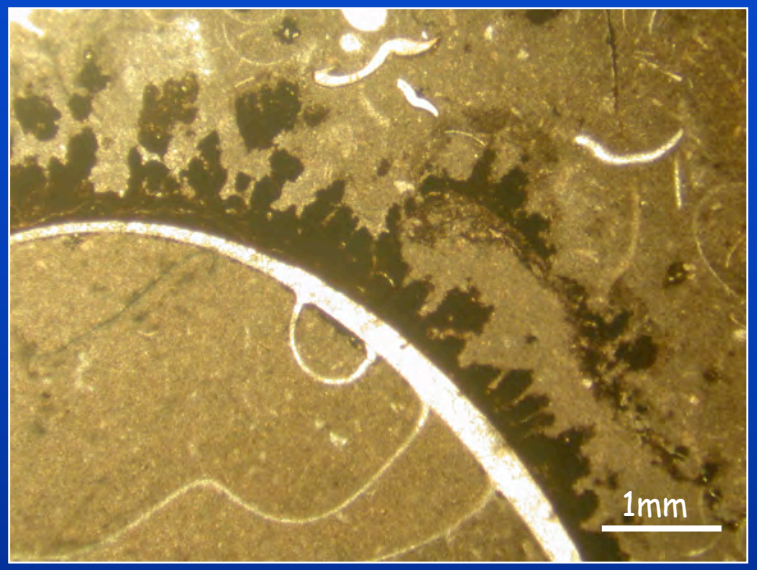


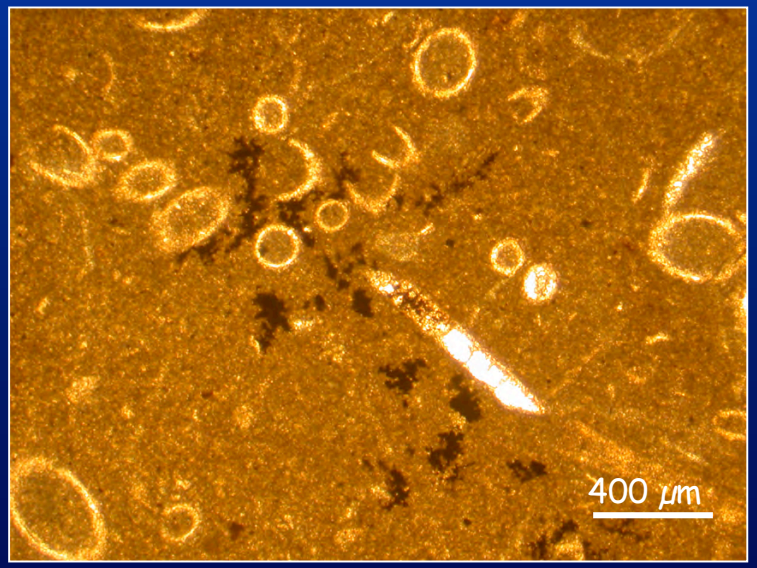
Praguian, Czech R,Mamet et al 1997

Asymmetrical growth of Fe-stromatolites on two sides of an altered echinodermal plate

The two other sides are devoid of coating

ANTI-ATLAS, MOROCCO LOWER-UPPER DEVONIAN





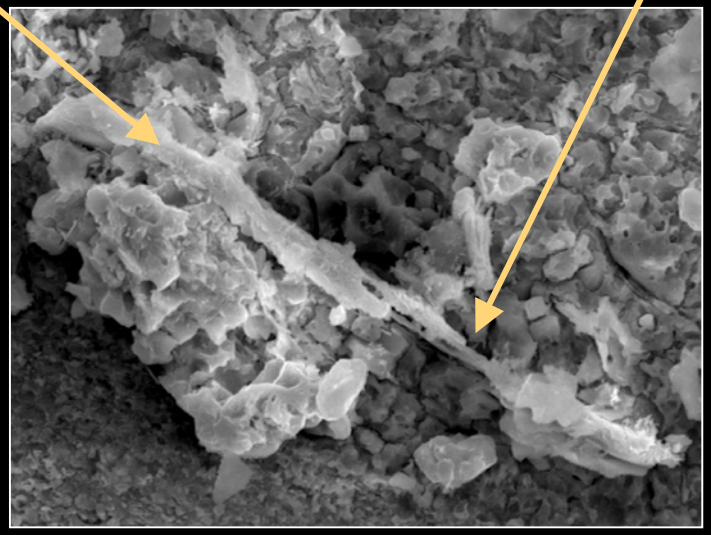
Mamet, Préat 2007

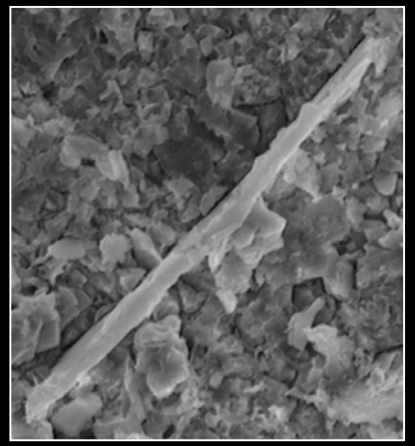
ANTI-ATLAS, MOROCCO LOWER-UPPER DEVONIAN

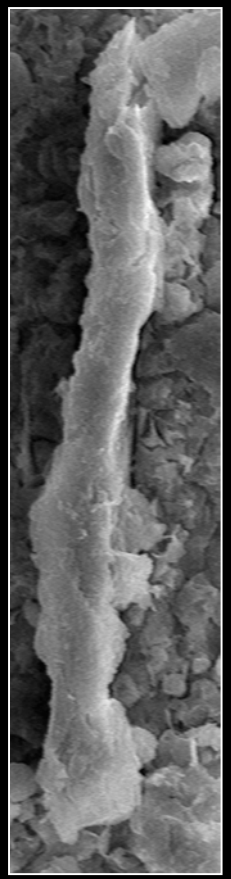
Filamentous iron bacteria

Iron encrustation
(25-50% Fe)

Sheath



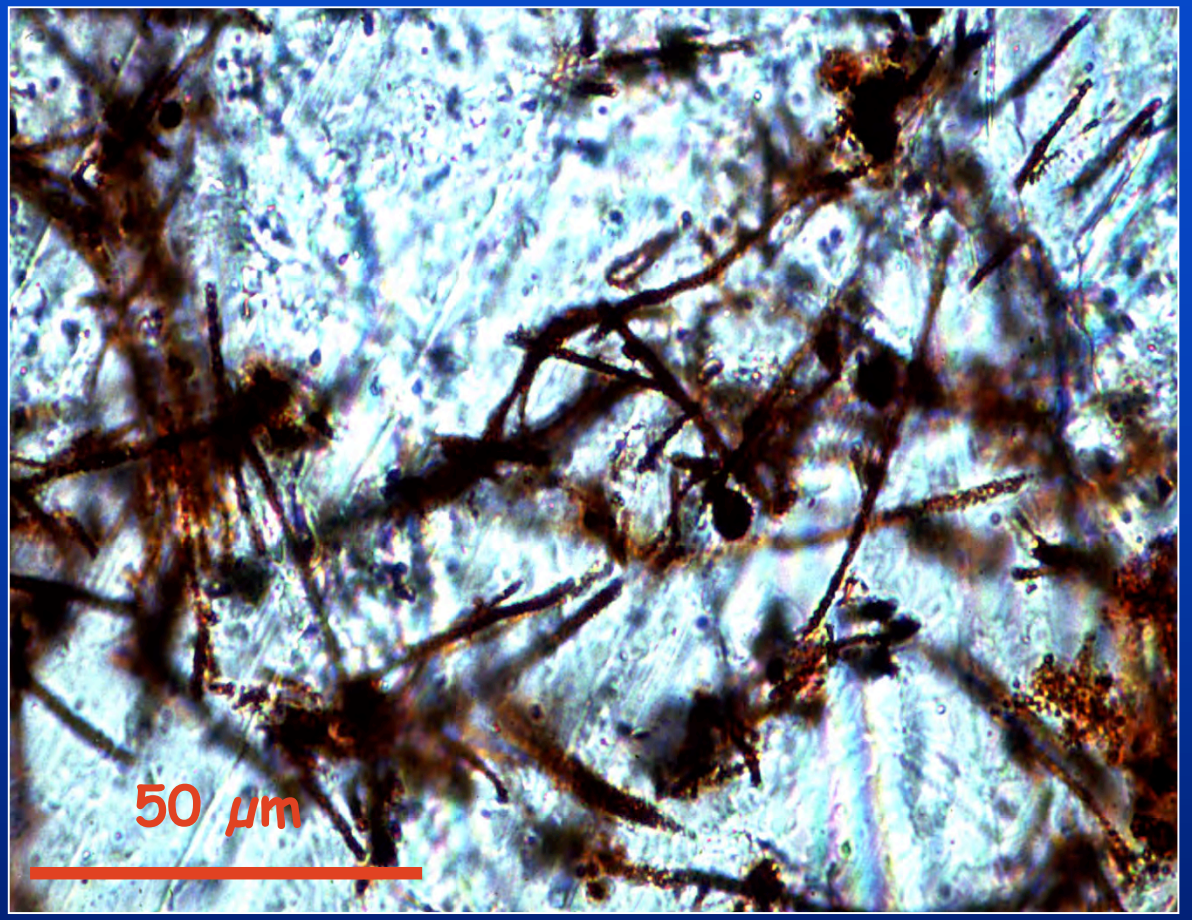




Diameters: 1,5-4 µm
[SEM]

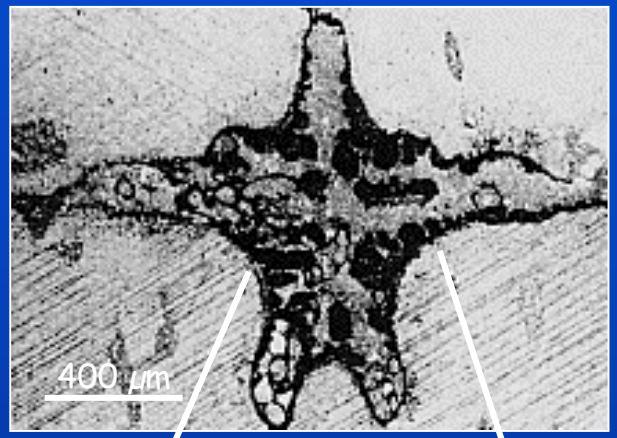
Mamet, Préat 2007

FRENCH-BELGIAN MUD MOUNDS, FRASNIAN

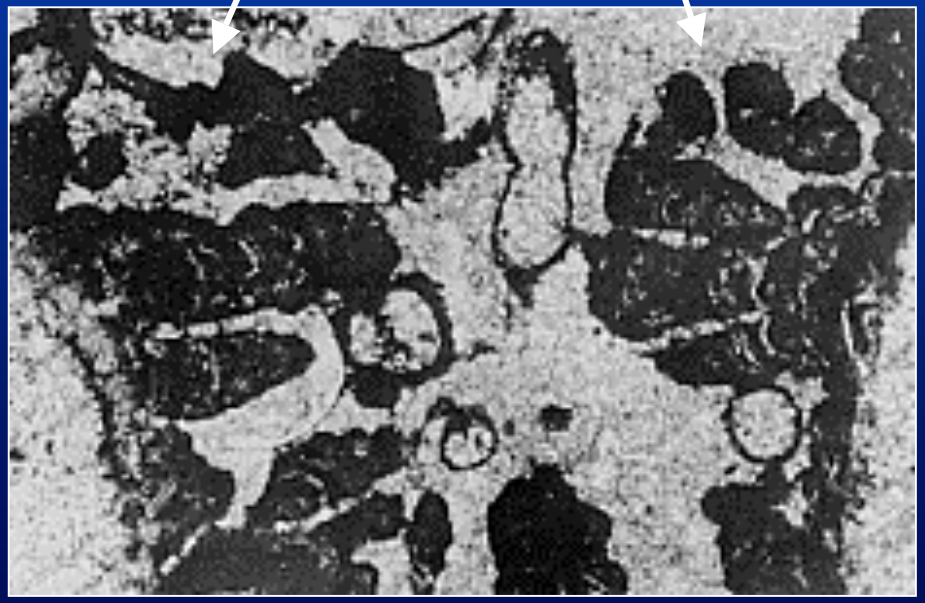


Iron-bacteria
(*Siderocapsa*-like, *Sphaerotilus-Leptothrix*-like
in the internal sediments of *Receptaculites*
Rochefontaine quarry, Franchimont, Philippeville
Massif (Boulvain et al. 2001)

BALEAS GRIOTTES, SPAIN, CARBONIFEROUS



Centripetal growth of microstromatolitic columns
(blisters and small tubes hematitized)



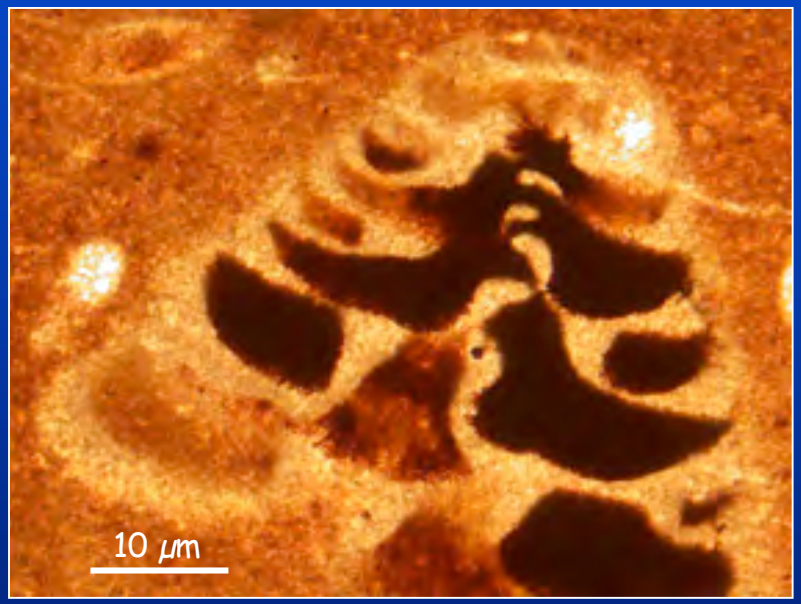
with endostromatolites

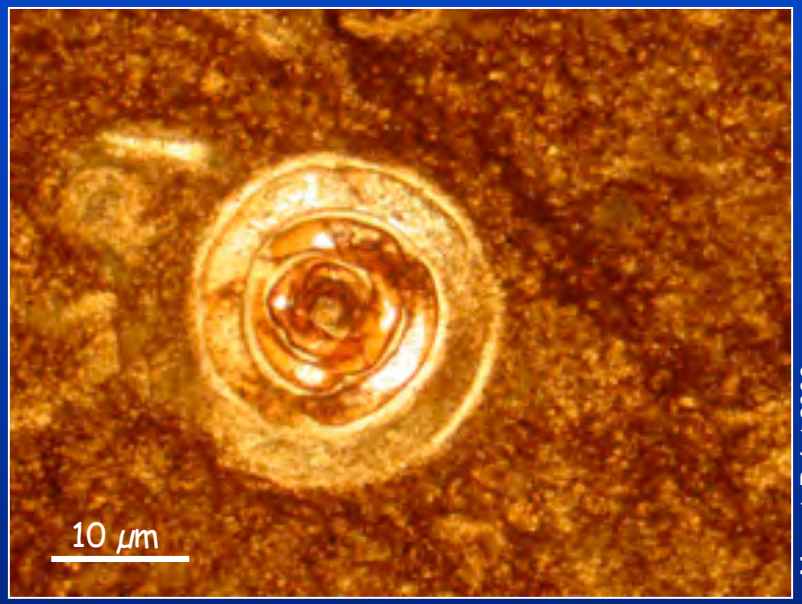
and microstromatolites

Mamet, Boulvain 1990

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

Infillings of original fossil cavities, biofilms



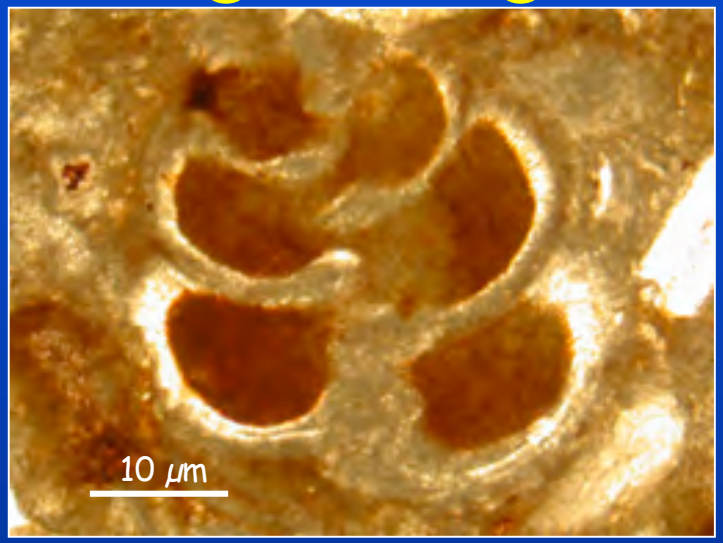


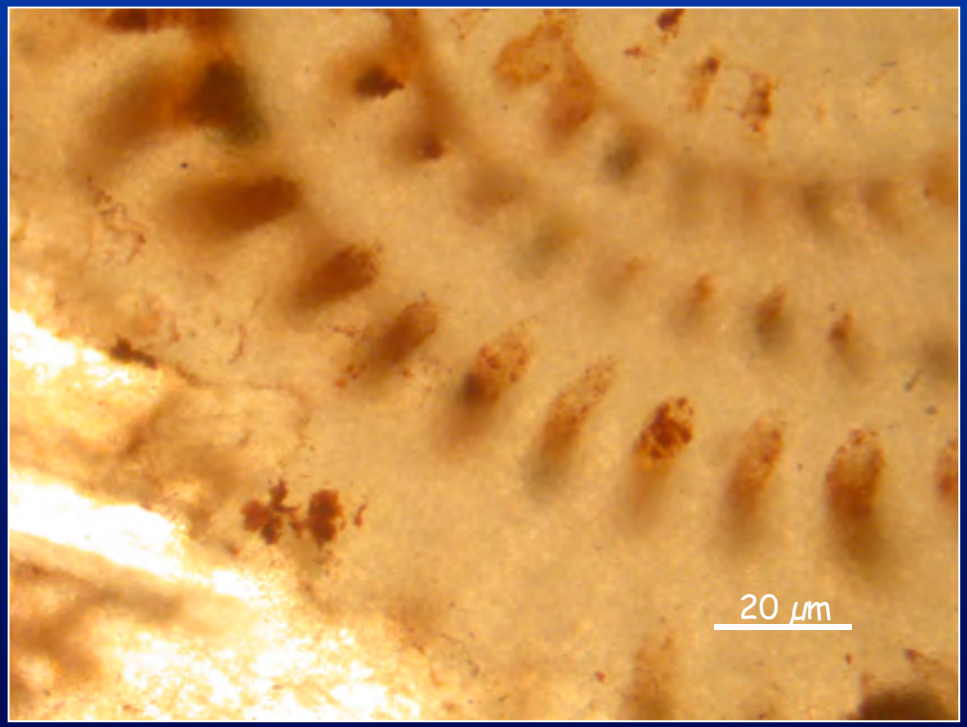
Mamet, Préat 2006

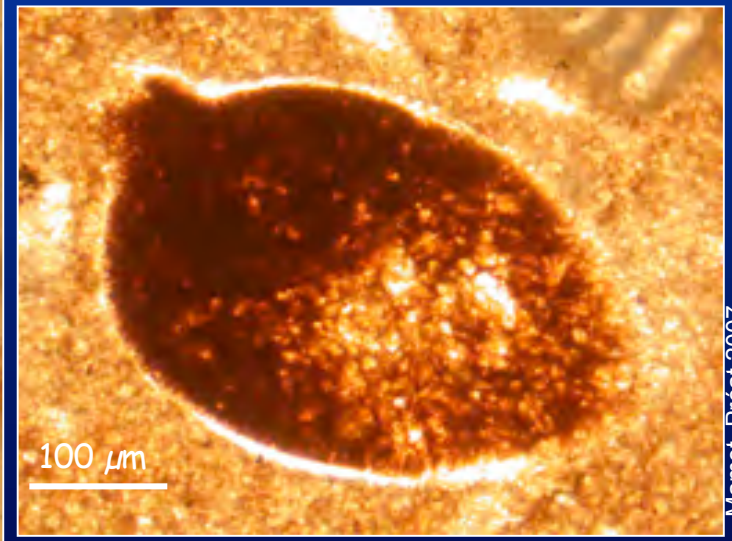
also bryozoans, gastropods, ostracods, tentaculids ...

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

Infillings of original fossil cavities, biofilms



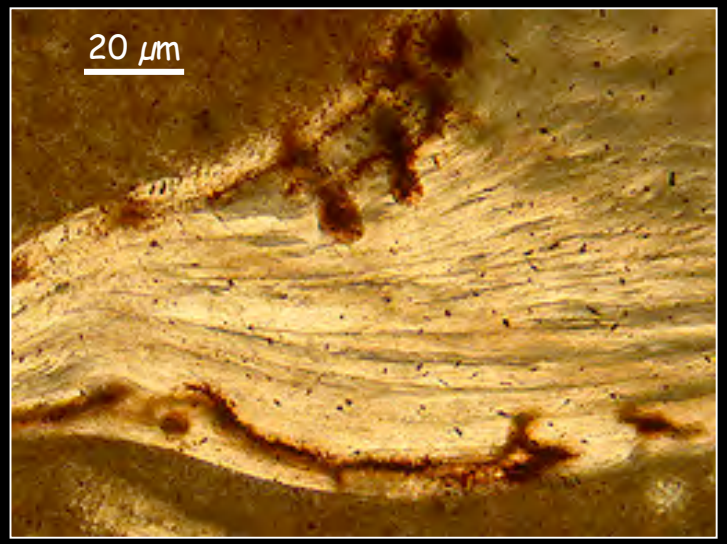


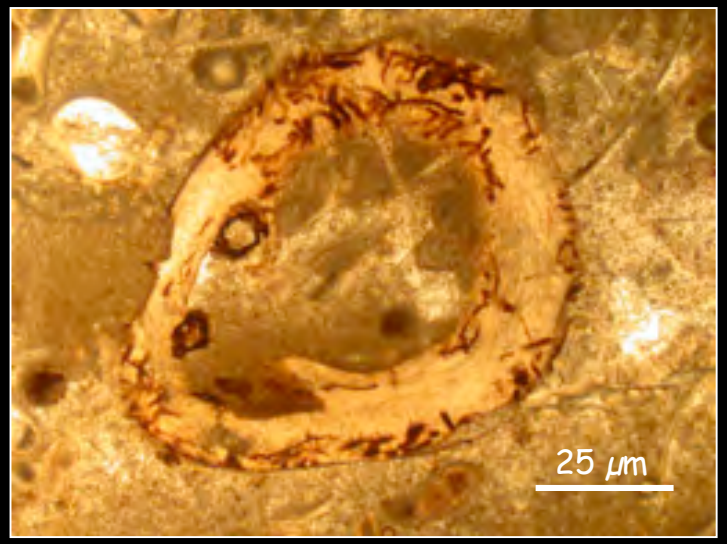


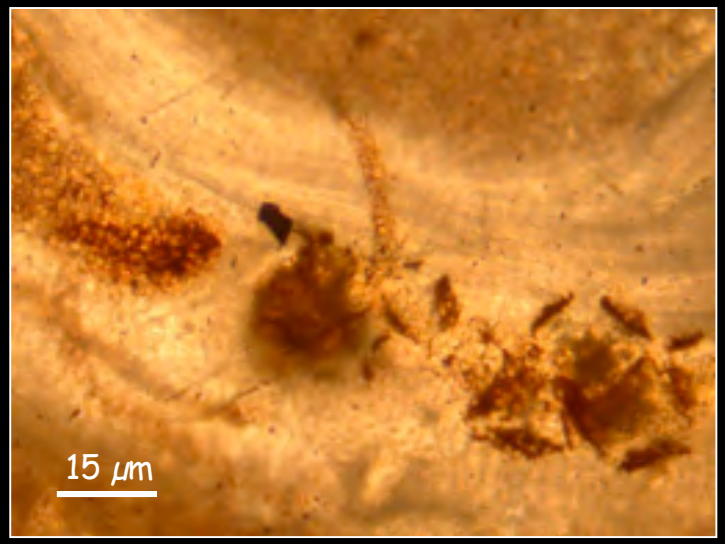
Mamet, Préat 2007

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

Infillings of bioperforations





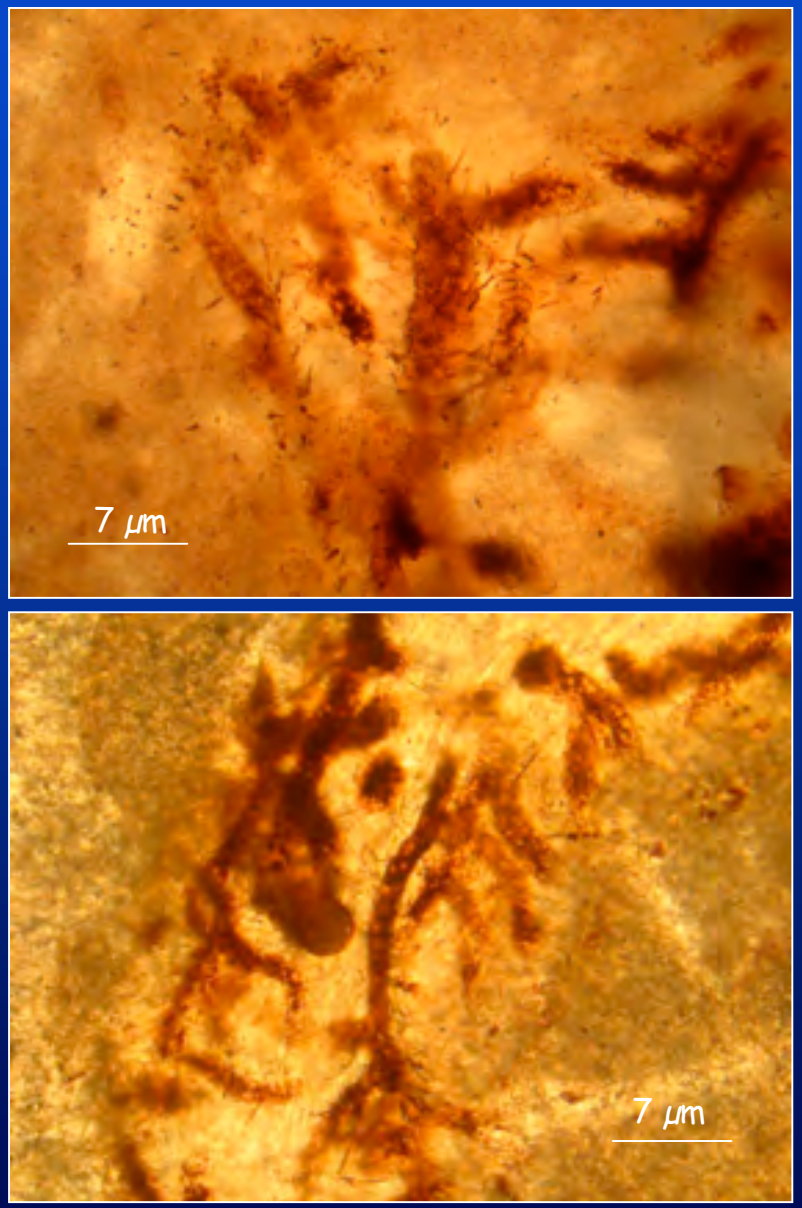


Brachiopods, Pelecypods, Bryozoans, Foraminifers

Dellaporta et al 2003

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

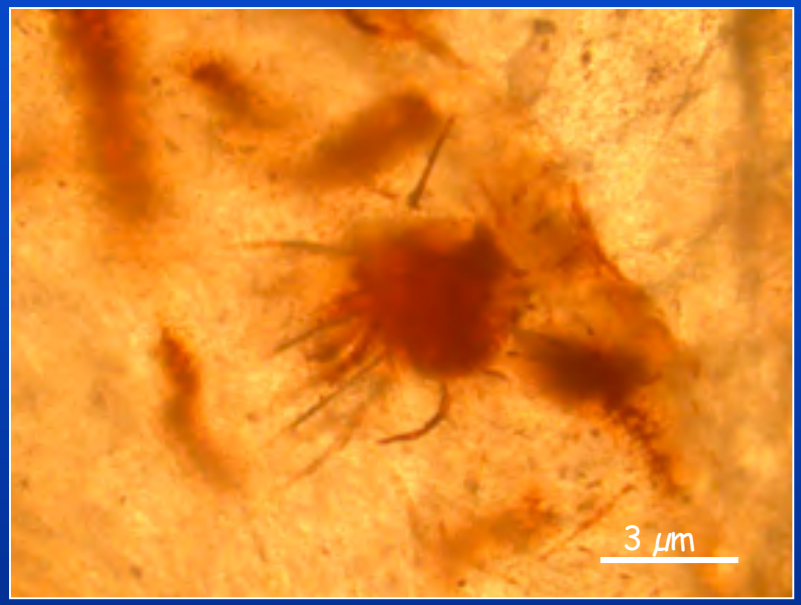
Infillings of bioperforations and filaments (‘cactus’)

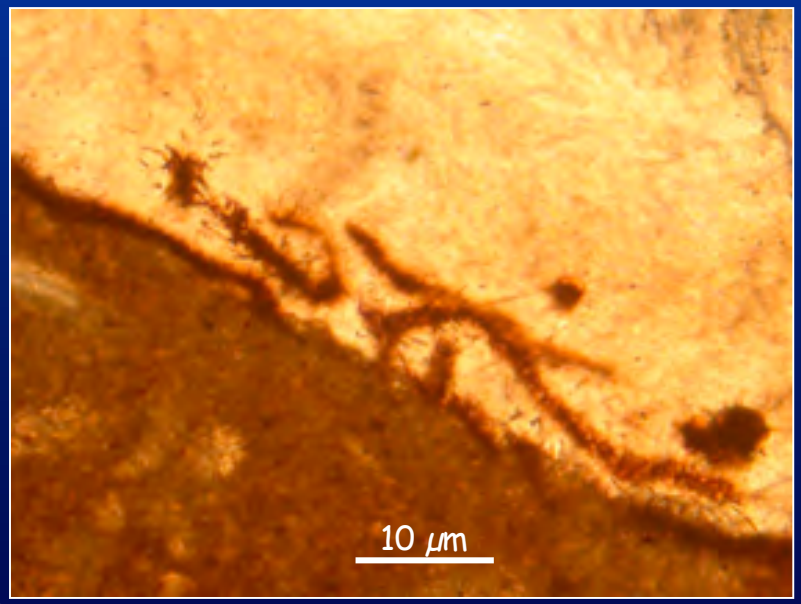


Dellaporta et al 2003

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

'Erythrospheres'

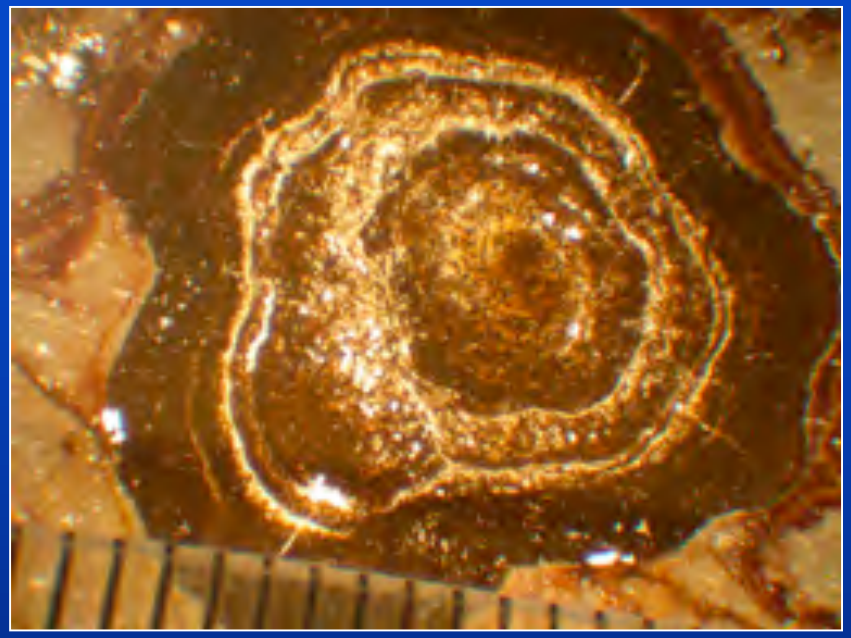


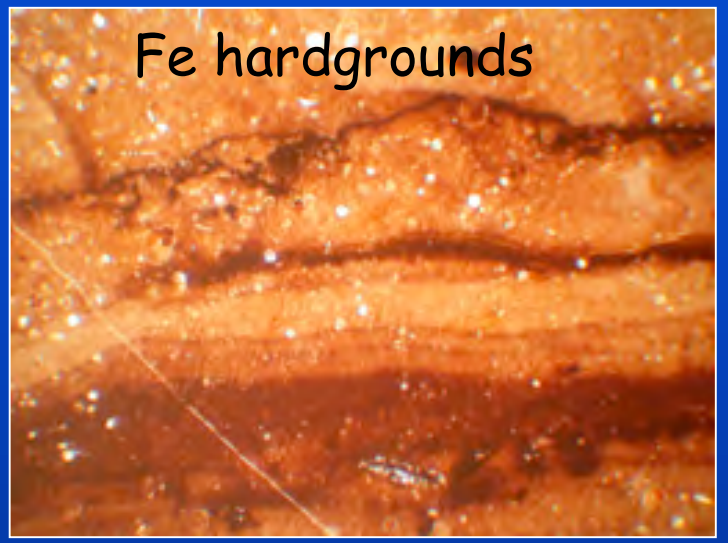


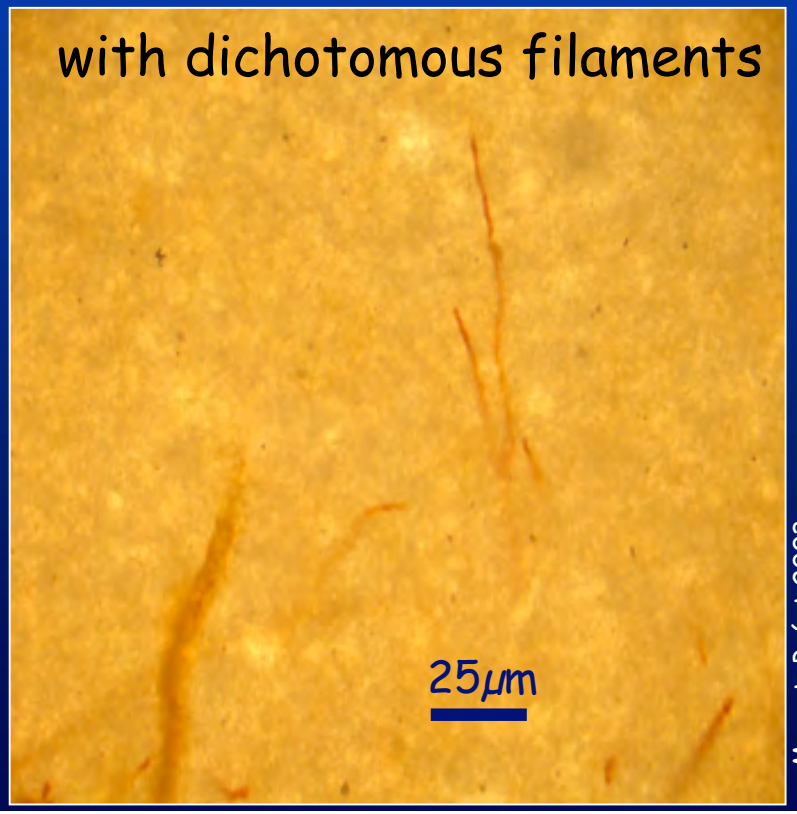
Dellaporta et al 2003

ROSSO AMMONITICO, ITALY, JURASSIC

Microstromatolites-Oncolites





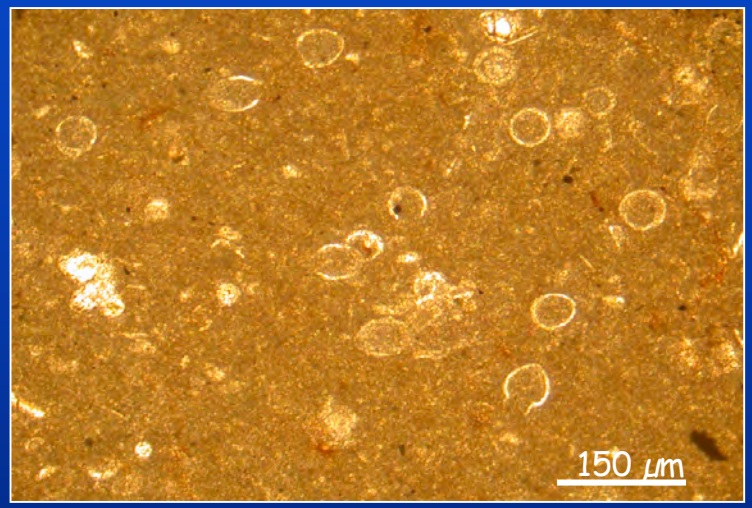


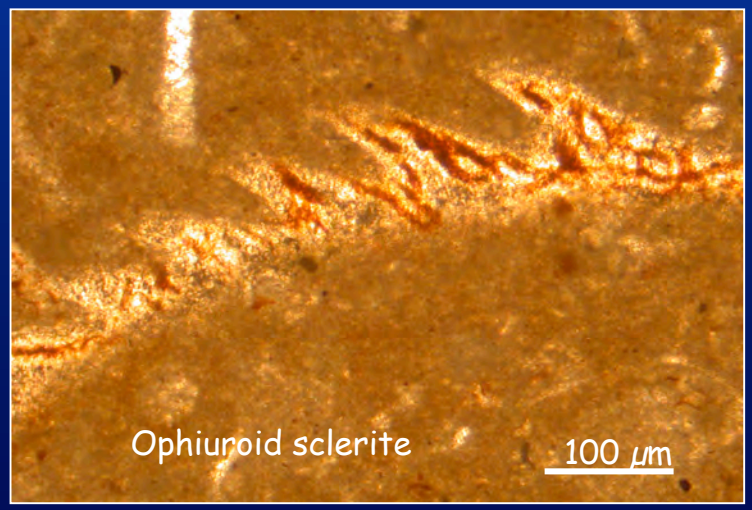
A PREAT, ULB - Universita di Torino 10 Nov 2009

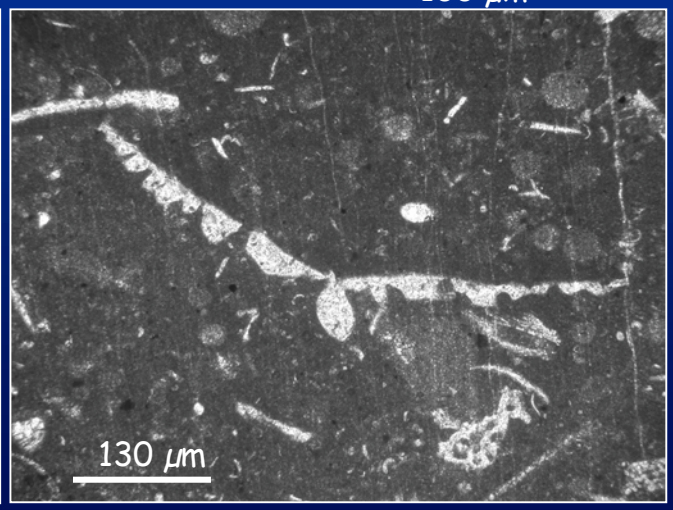
Mamet, Préat 2003

ROSSO AMMONITICO, SPAIN, JURASSIC

Calpionellid-Holothuroid-Ophiuroid packstone







Mamet, Préat 2006

first conclusion

hematite is not dispersed at random
but follows regular patterns

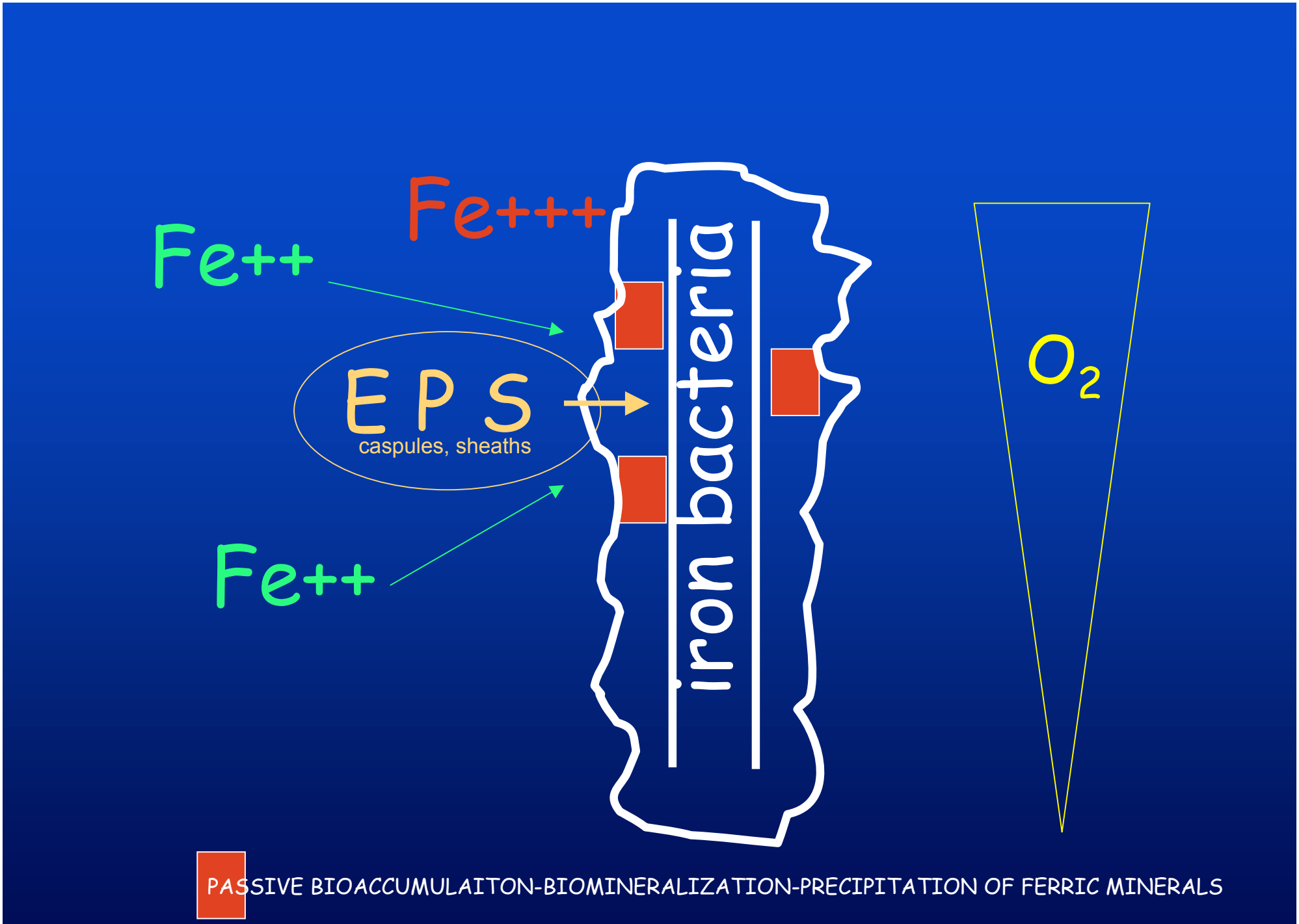
...

BIOsedimentary pathway?

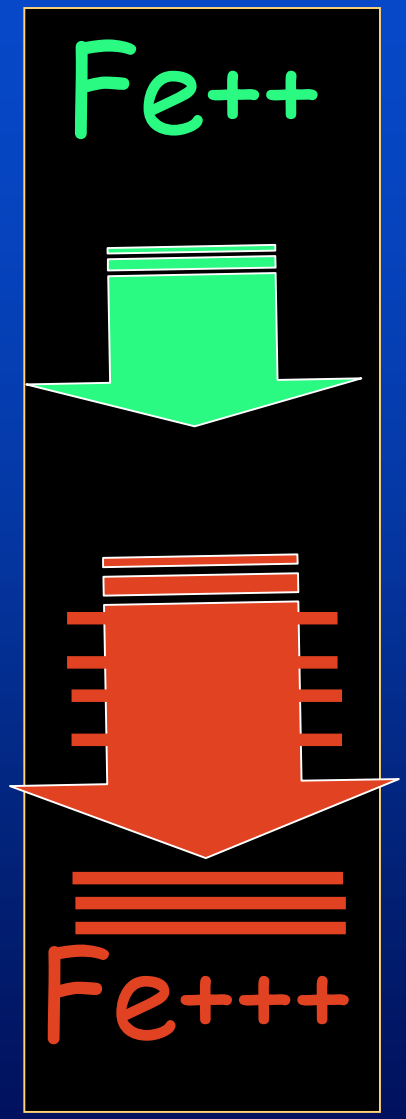
1. Today they are associated with Fe and/or Mn deposits. O_2 and pH values determine the iron solubility in aqueous solutions.

2. The neutrophile iron bacteria are associated with the oxic/anoxic interface
-*Sphaerotilus, Leptothrix, Gallionella, Beggiatoa …*

3. Iron biomineralization is linked to the production of EPS - exopolymeric substances = sheaths or capsules rich in polysaccharides forming the main part of the bacterial mats. The Fe^{3+} is passively precipitated in the EPS of the Recent bacterial films


Fe+++
Fe++
E P S
caspules, sheaths
Fe++
iron bacteria
O_2
PASSIVE BIOACCUMULAITON-BIOMINERALIZATION-PRECIPITATION OF FERRIC MINERALS

in the past,
coccoid and bacillar bacteria associated with other micro-fossils formed mineralized biofilms



SEM observations

X1000, x35000…

- simple and regular filaments
- simple filaments with regular constrictions
- dichotomic filaments with constrictions
- concentrations of regular sphaerules

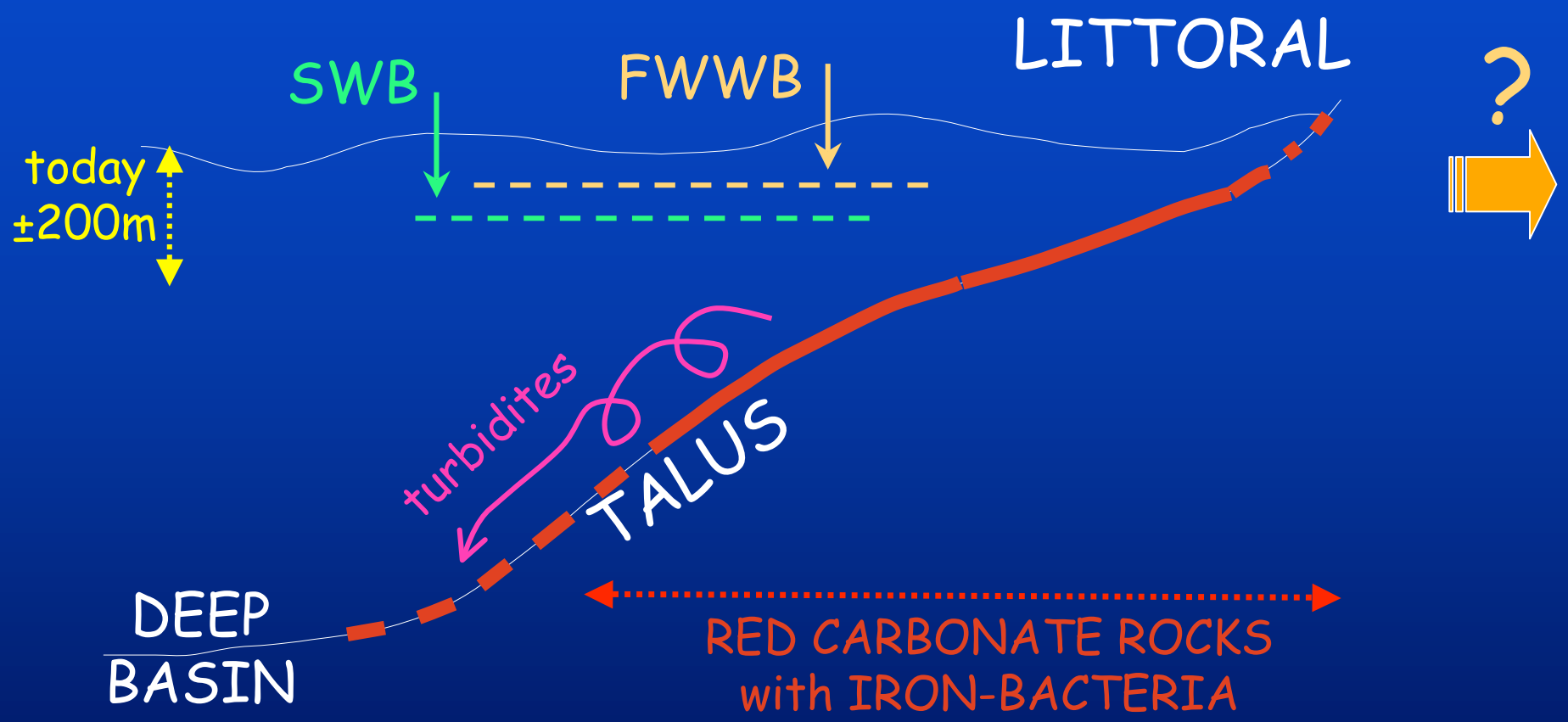
diameter: <= 2 µm
with submicronic hematite in the sheath

These morphologies are suggestive of iron bacteria

Irregular filamentous forms (10'µm), sometimes forming a network and associated with spores

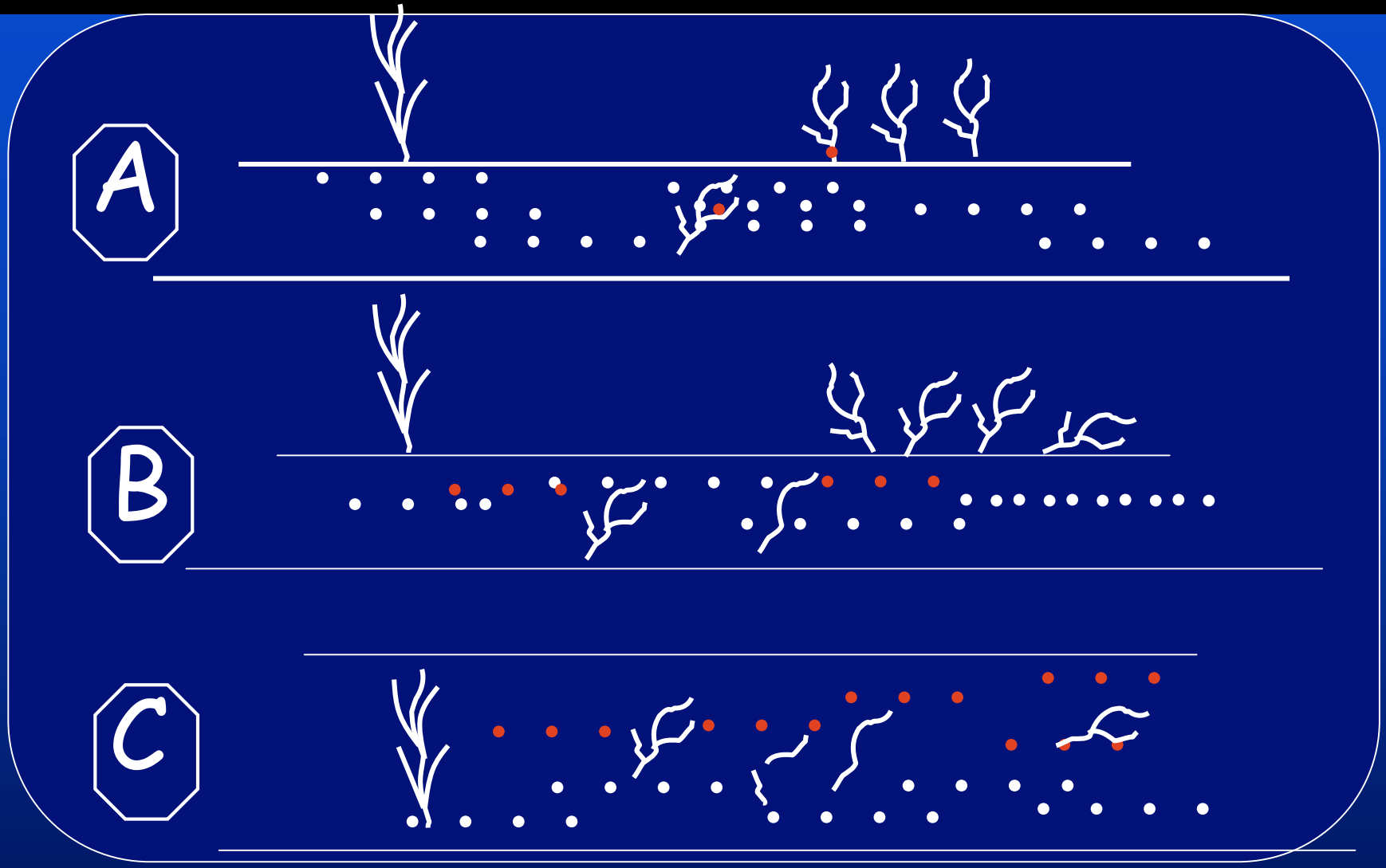
These morphs suggest the presence of FUNGI IMPERFECTI

SECOND CONCLUSION



... if iron bacteria are present, iron hydroxides are linked to an oxic/anoxic gradients in poorly oxygenated waters and independent of light

ORIGIN OF PIGMENTATION



Further diagenesis will transform the micrite into a porous microspar.
Iron hydroxides are now goethite or hematite.

Before concluding the first part ...

WHAT TO REMEMBER?
not a curiosity

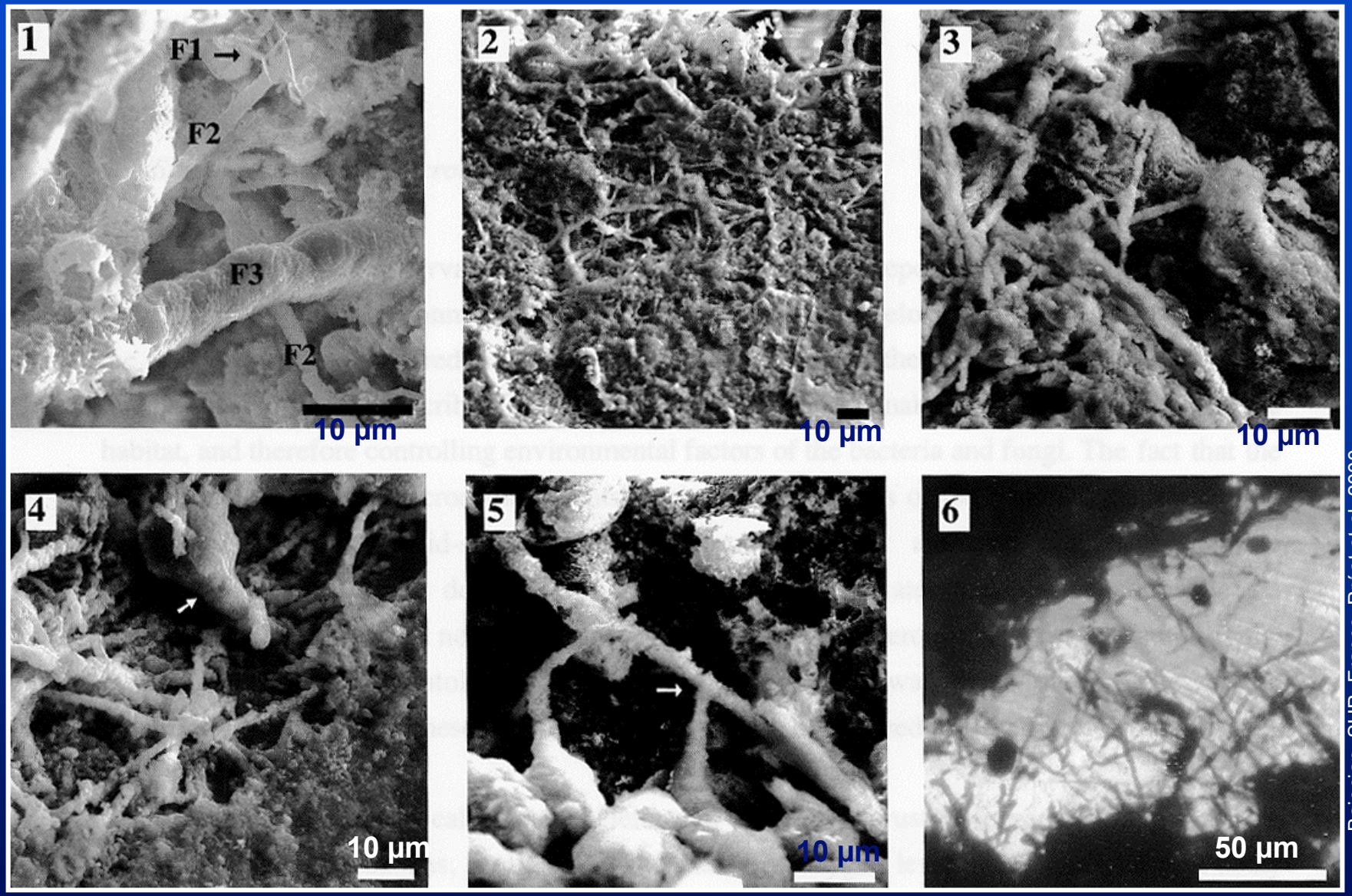
BACTERIAL FILAMENTS
ARE WIDESPREAD

BAJOCIAN GSSP, SAINTE-HONORINE-DES-PERTES, FRANCE
‘Oolite Ferrugineuse de Bayeux’, condensed series 2.5Myrs/50cm

Bajocian, SHP, France, Préat et al. 2000

BAJOCIAN GSSP, SAINTE-HONORINE-DES-PERTES, FRANCE

Inside a Fe-oncoid... (nucleus is a small ammonite)



Bajocian, SHP, France, Préat et al. 2000