ACADEMIE ROYALE DE BELGIQUE-COLLEGE BELGIQUE

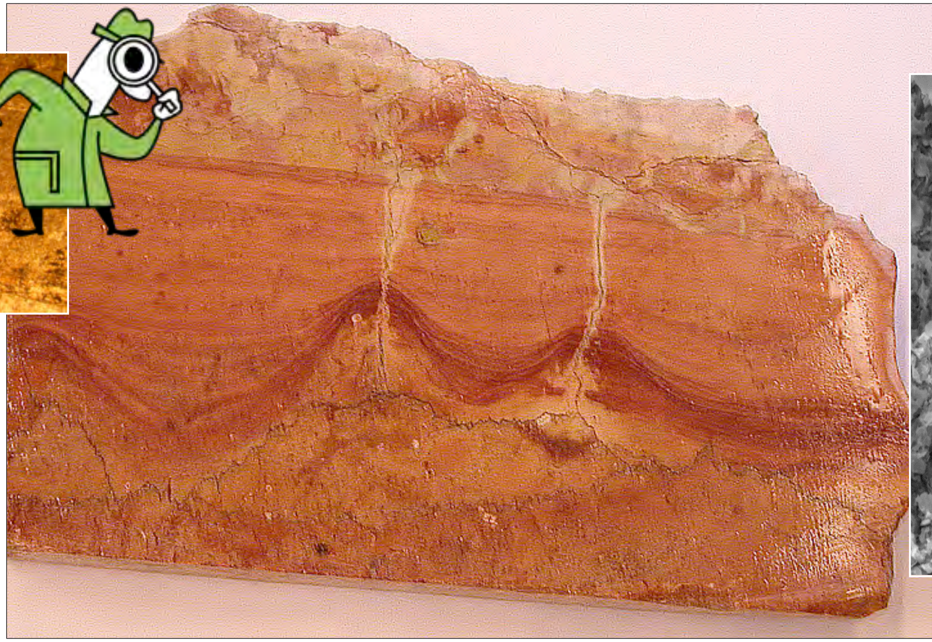
10 novembre 2016

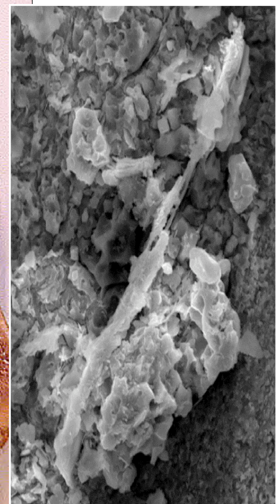
LES BIOMINERAUX MICROBIENS DES GISEMENTS TERRESTRES À L'EXOBIOLOGIE

PARTIE II
POURQUOI DONC LES MARBRES ROUGES SONT-ILS ROUGES?

Alain PREAT – ULB

David GILLAN – UMons





STROMATOLITHES ET TAPIS MICROBIENS PRECAMBRIENS (CONGO-BRAZZAVILLE)

A. Préat – D. Gillan 10 nov 2016 Acad Roy Belgique

WHY IS ‘RED MARBLE’ RED : COULD FE-ISOTOPES SHED LIGHT ON THIS QUESTION THROUGH THE STUDY OF THE ITALIAN AMMONITICO ROSSO AND RECENT ORGANISMS?

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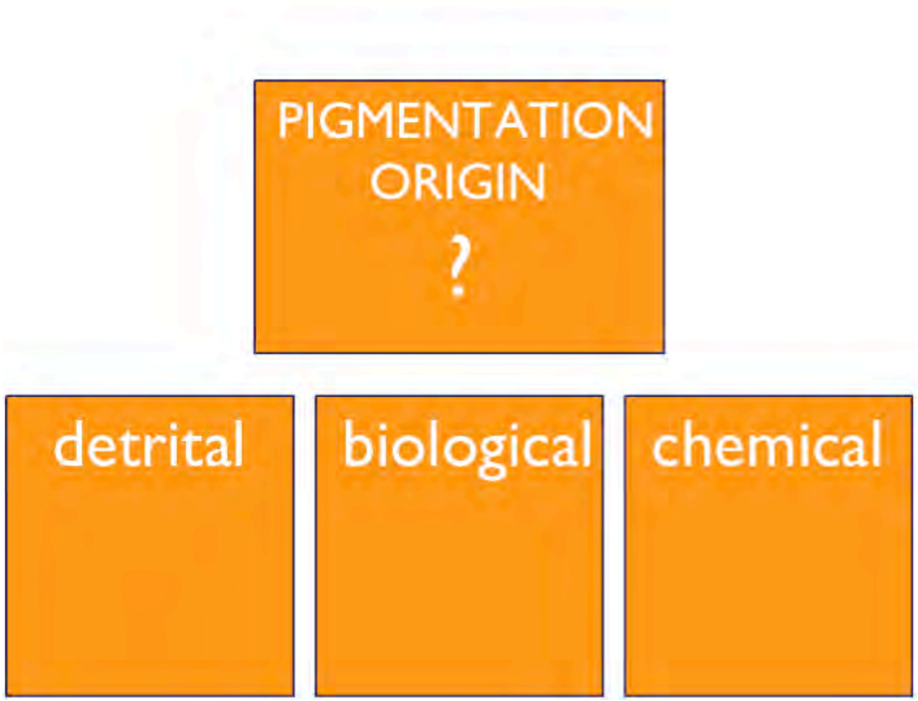
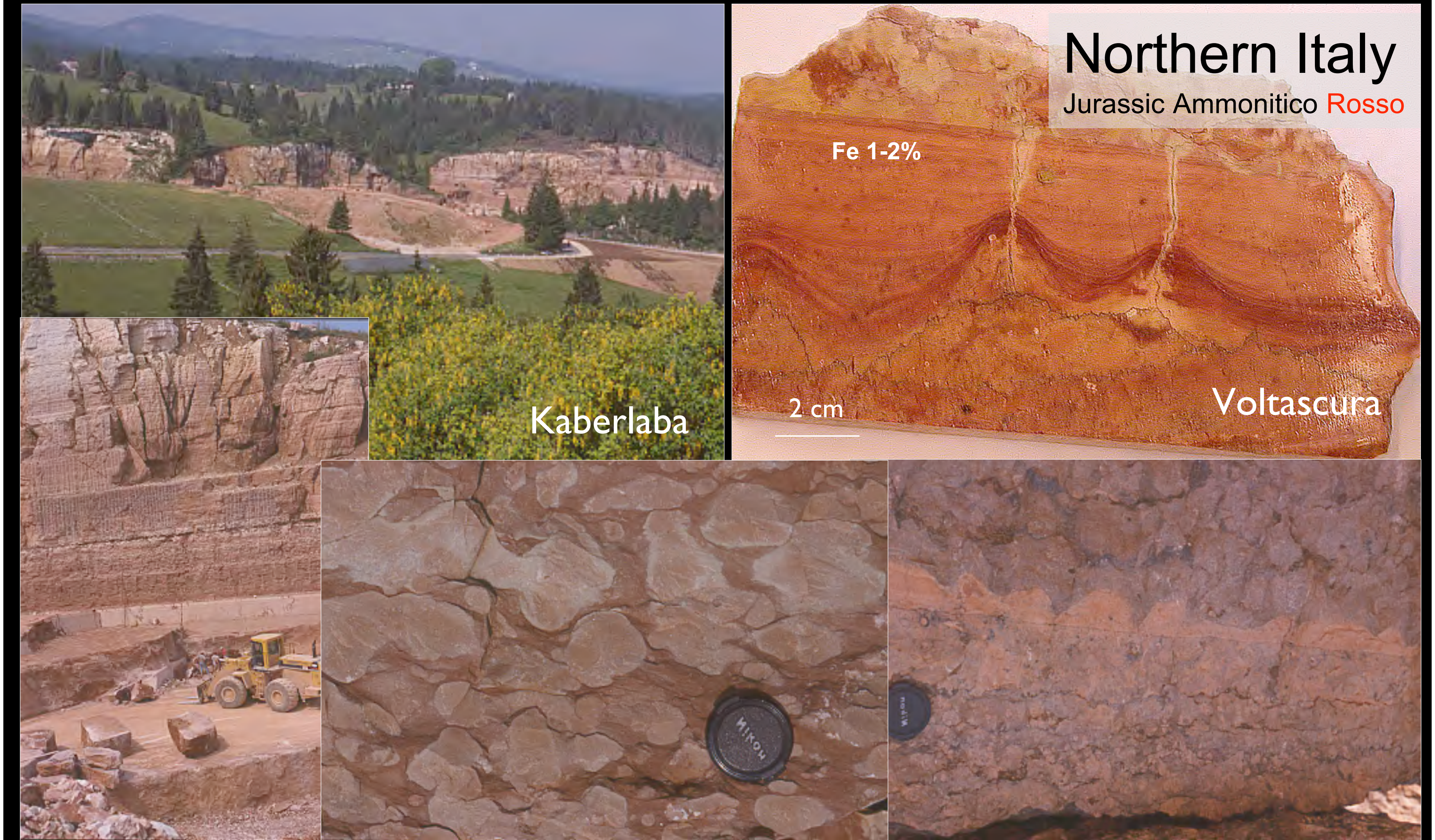
Red limestones are rare but precious …

THE PROBLEM is
their red pigmentation



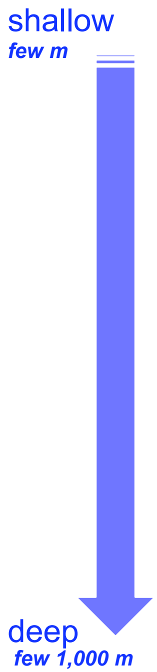
OF WHAT CONSISTS THE RED PIGMENTATION ?



Our studied Red limestones . . .

PALEOZOIC and MESOZOIC

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



OF WHAT CONSISTS THE RED PIGMENTATION ?

A simple solution is just to ignore the problem!

The Ammonitico Rosso Symposium (1991)
The thick abstract book with its appropriate SCARLET cover deals with sedimentology, palaeontology, diagenesis but nothing on the origin of the colour of the Ammonitico Rosso !

MUD MOUND = MONTICULE DE BOUE
= 'MARBRES ROUGES BELGES'

P A L E O Z O I C

F R A S N I A N

Diam 100-250'm X H 30-80m

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Only 30m (upper part) are visible on ±60m

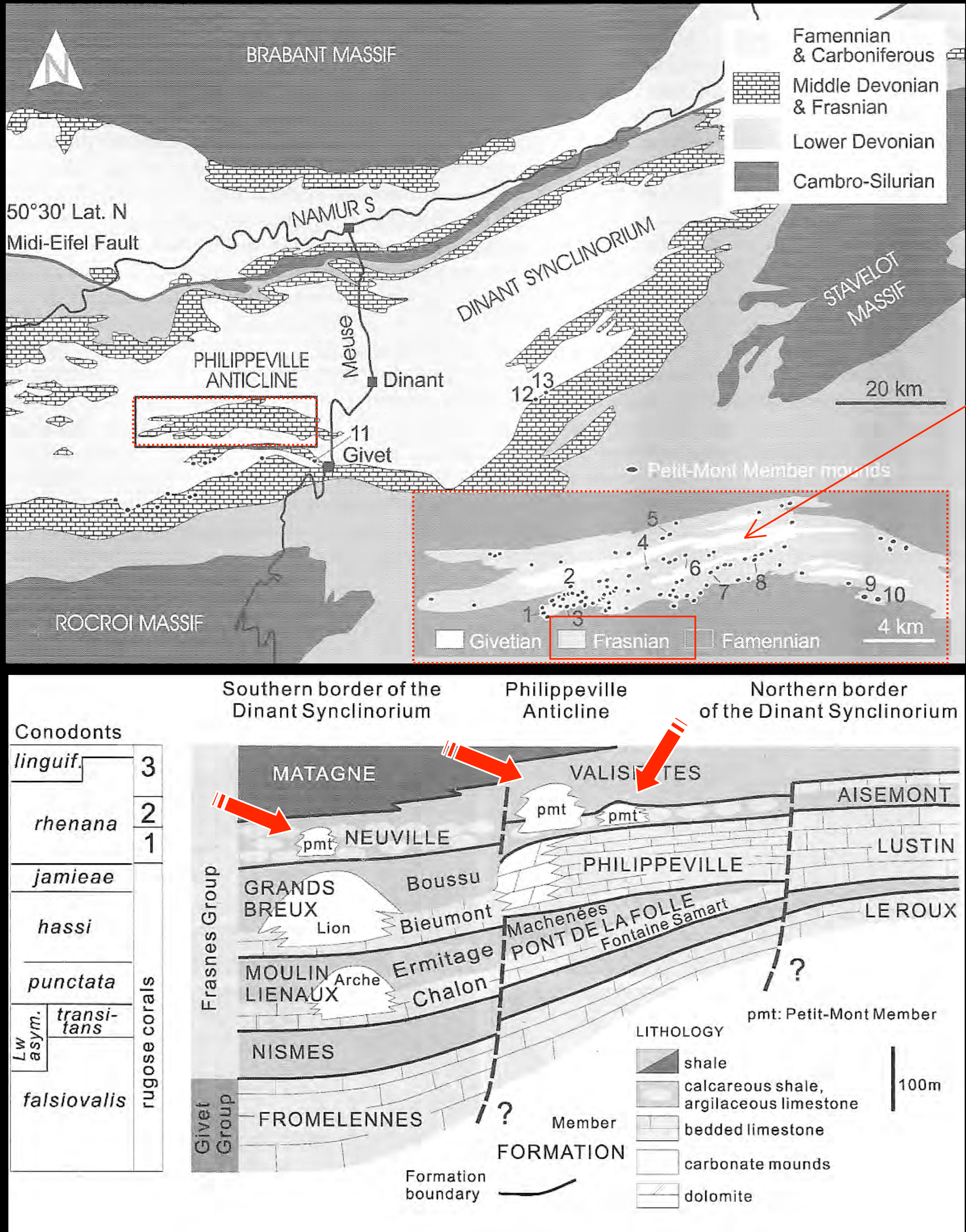
Researches in our laboratory, ULB/1989

… 'Frasnian mud mounds of the Dinant basin are bioconstructions 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' …

BEAUCHATEAU QUARRY

° The base of the bioconstructions is in very calm environments under the SWB, and then the mounds pass into the FWWB where sedimentation ends

° No signs of subaerial exposure as observed in modern reefs



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<u>69 reported 'red 'mud mounds</u>

Severe eustatic sea level rises

High vertical facies differenciation

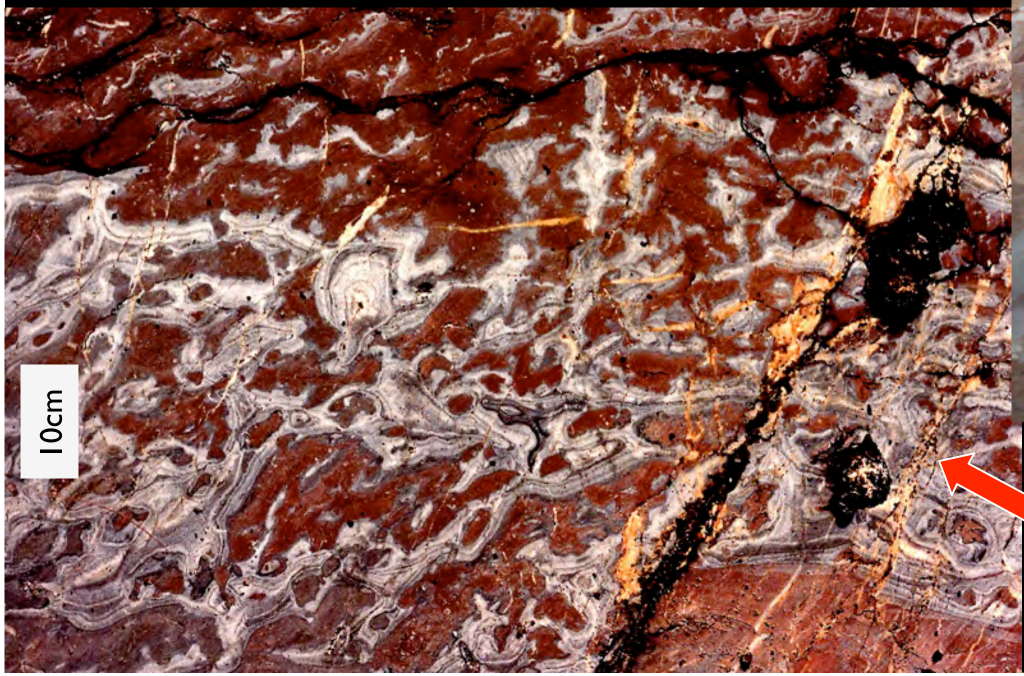
High content in microaerophilitic iron bacteria (in *stromatactis* cavities)

Submicronic hematite hexagonal plates dispersed in the matrix

Fe_2O_3 : average 2% (max 5%)

BEAUCHATEAU QUARRY
near Senzeilles
Philippeville Massif
BELGIUM

Frasnian 'F2j' mud mound



Griottes
+ 'stromatactis' (1880)

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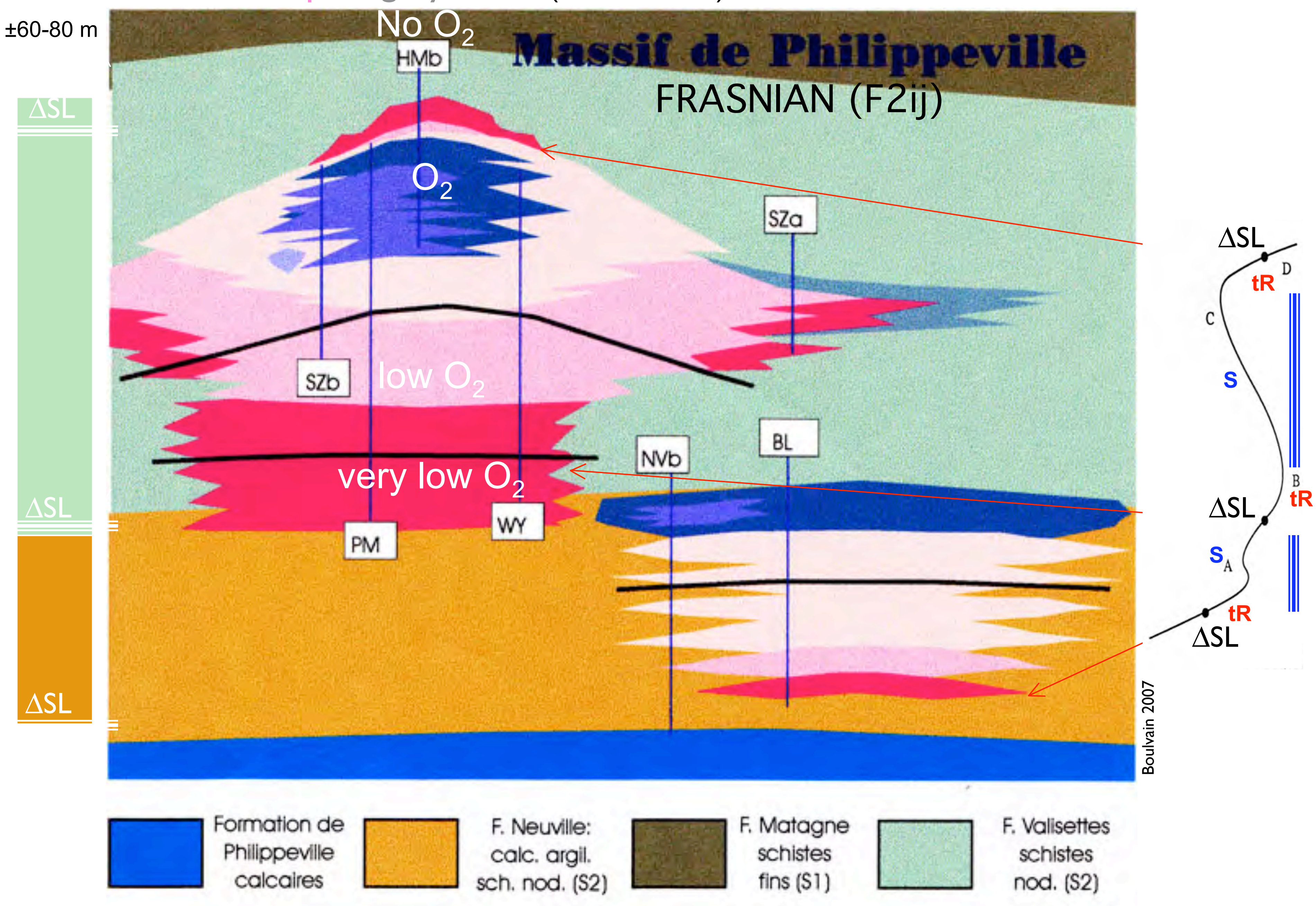
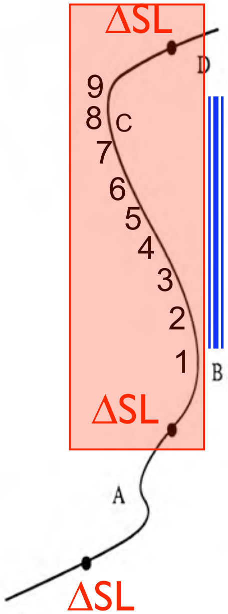
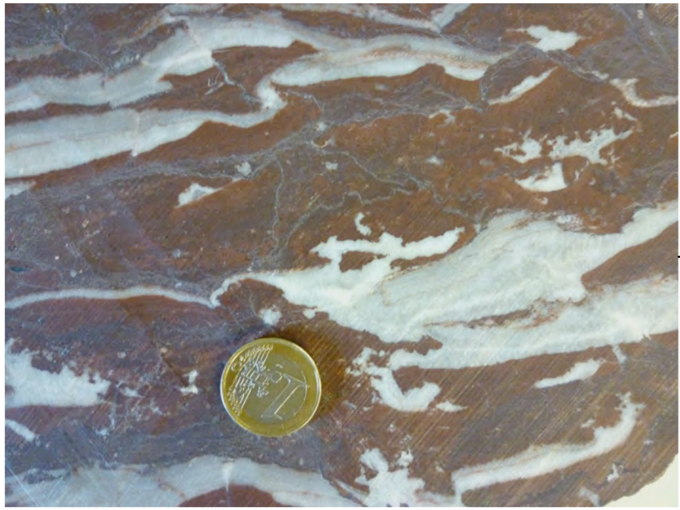
The red-pink-grey color (succession) is 'ECOLOGICAL'

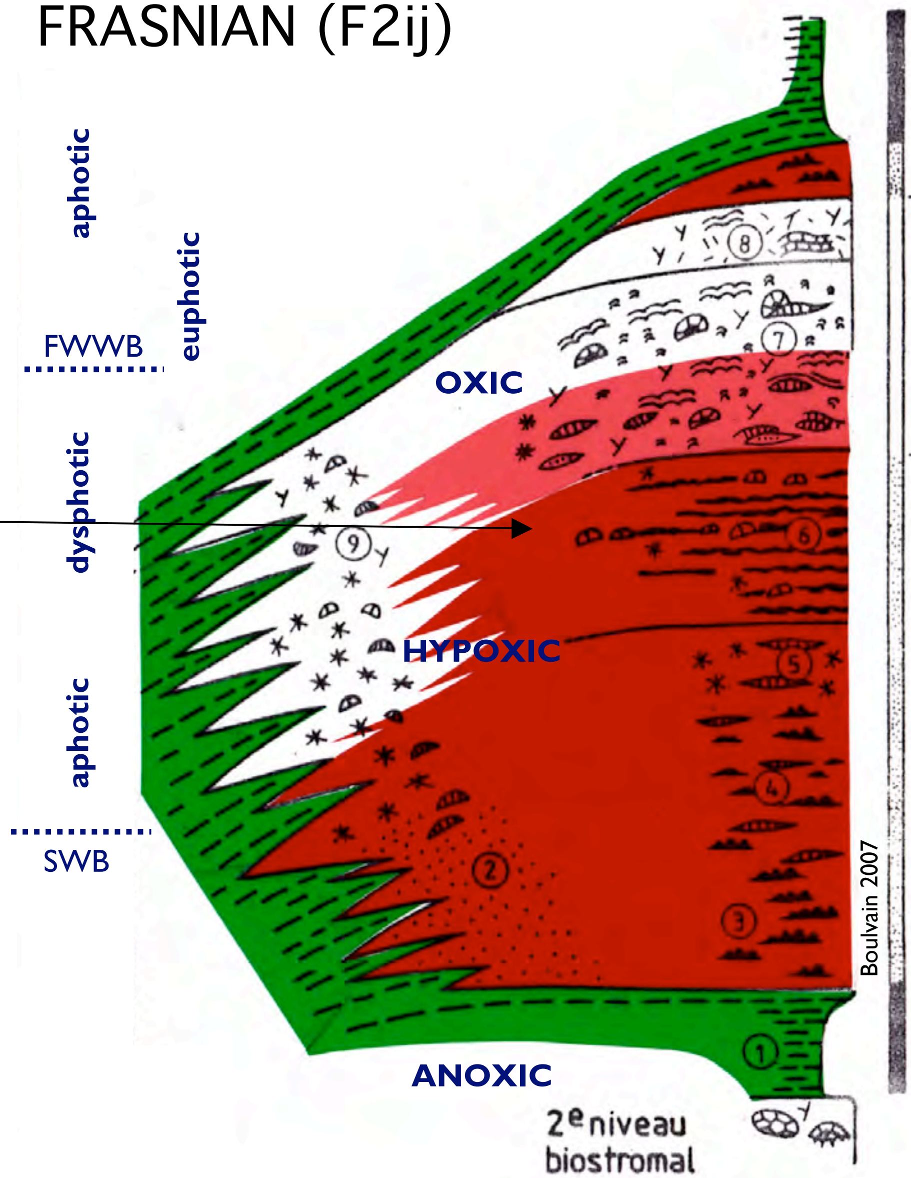


The red-pink-grey colour (succession) is 'ECOLOGICAL'

FRASNIAN (F2ij)







1 : **recurrence**

7-8-9 : FWWB, cyanobacterial, algal (<u>green algae</u>)-coral-peloid wackestones-packstones

5-6 : progressive biotic enrichment (<u>stromatoporoids</u>, corals...)

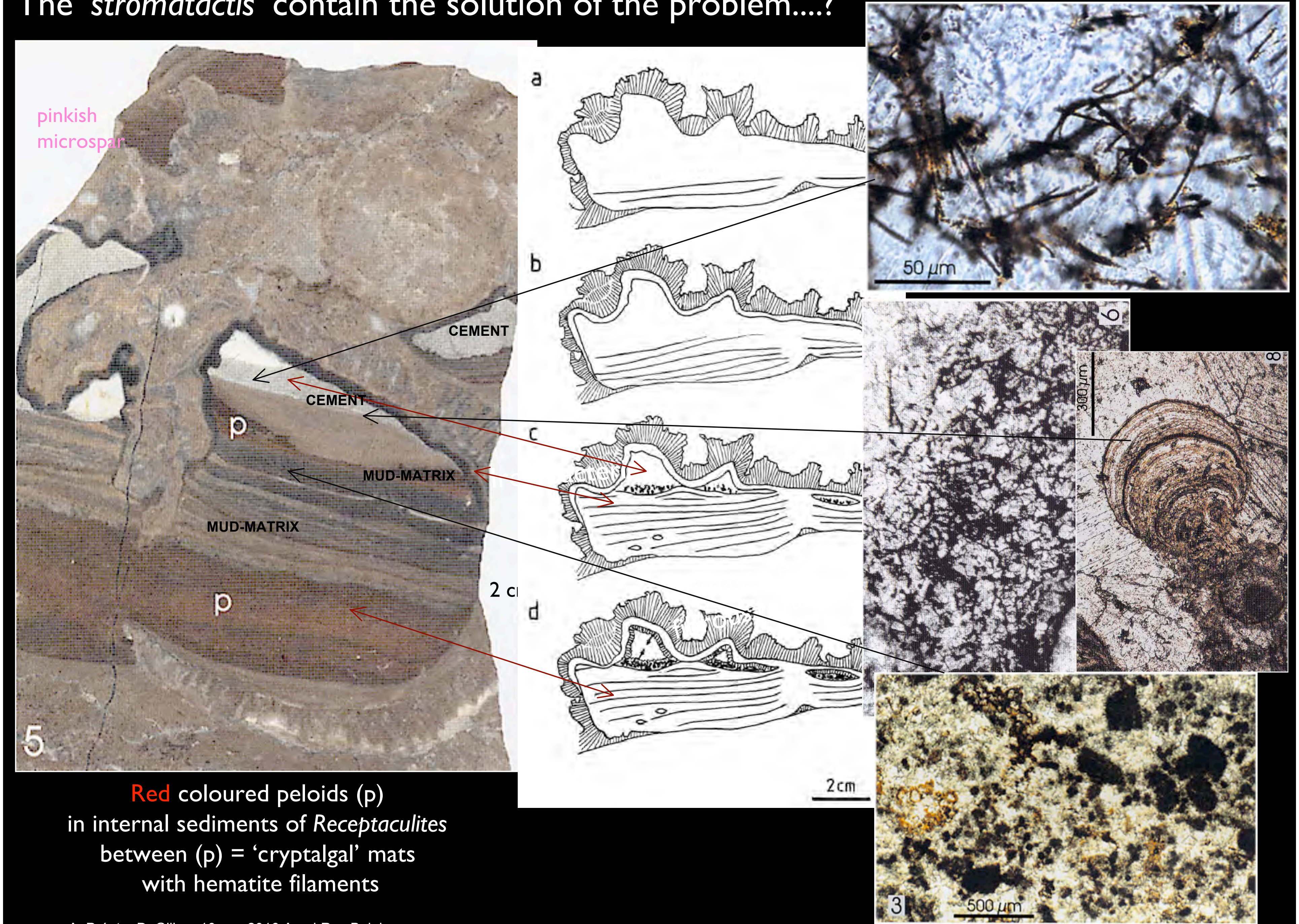
4 : SWB, oligophotic environment (corals, crinoids, *stromatactis*)

3 : <u>iron bacteria</u>-sponge in a quiet aphotic/hypoxic environment, *<u>stromatactis</u>*

2: shale and carbonates with <u>brachiopods, corals,</u> <u>crinoids,</u> sponges

1 : shale with poor fauna, mainly <u>sponges</u> (substrate)

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

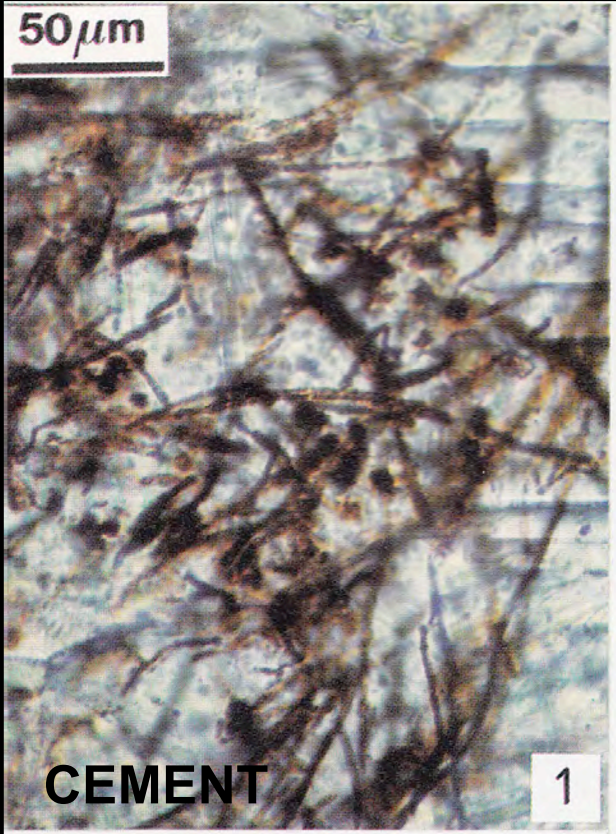


Red coloured peloids (p)
in internal sediments of *Receptaculites*
between (p) = 'cryptalgal' mats
with hematite filaments

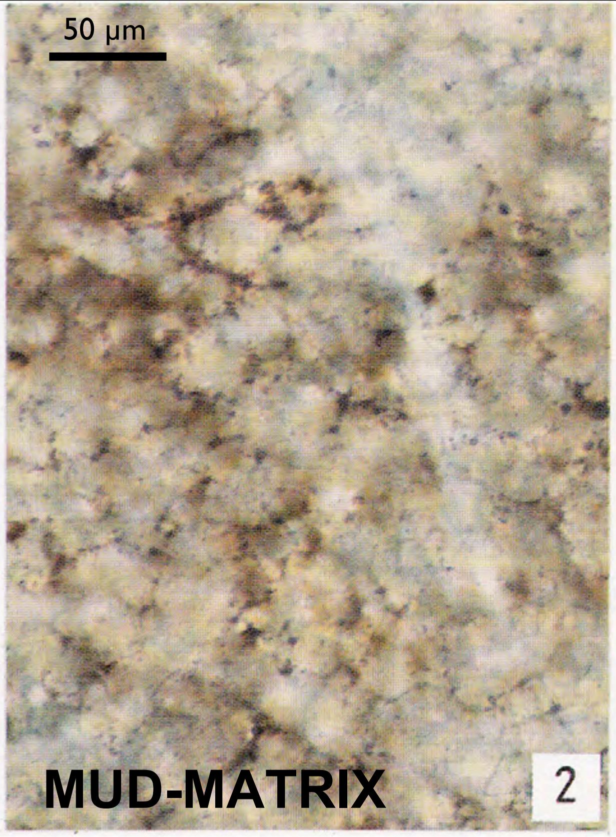
GEOLOGY

BIOLOGY

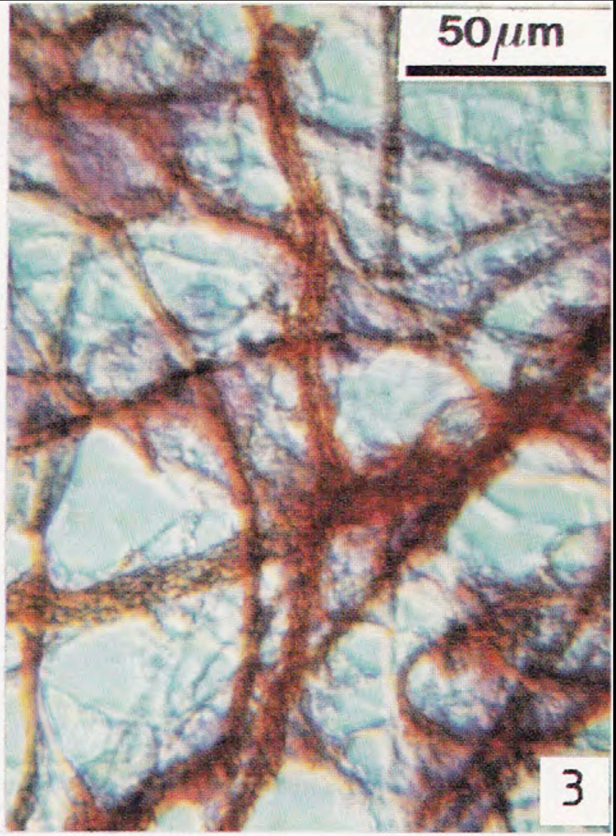
Iron bacteria and iron coccoids
(hematite in the sheaths)
Granular sparite, internal sediment



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



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



'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. (microaerobic)

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

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

BUT …

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

So what?

Our first basic observation

The Fe content of red limestones
of biotic origin is low

1 to 2 %, often < 1 %

... therefore this content is not responsible
of the coloration

Our second basic observation

Sedimentation is in a
NORMAL OPEN MARINE
facies

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

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

QUID ?

B
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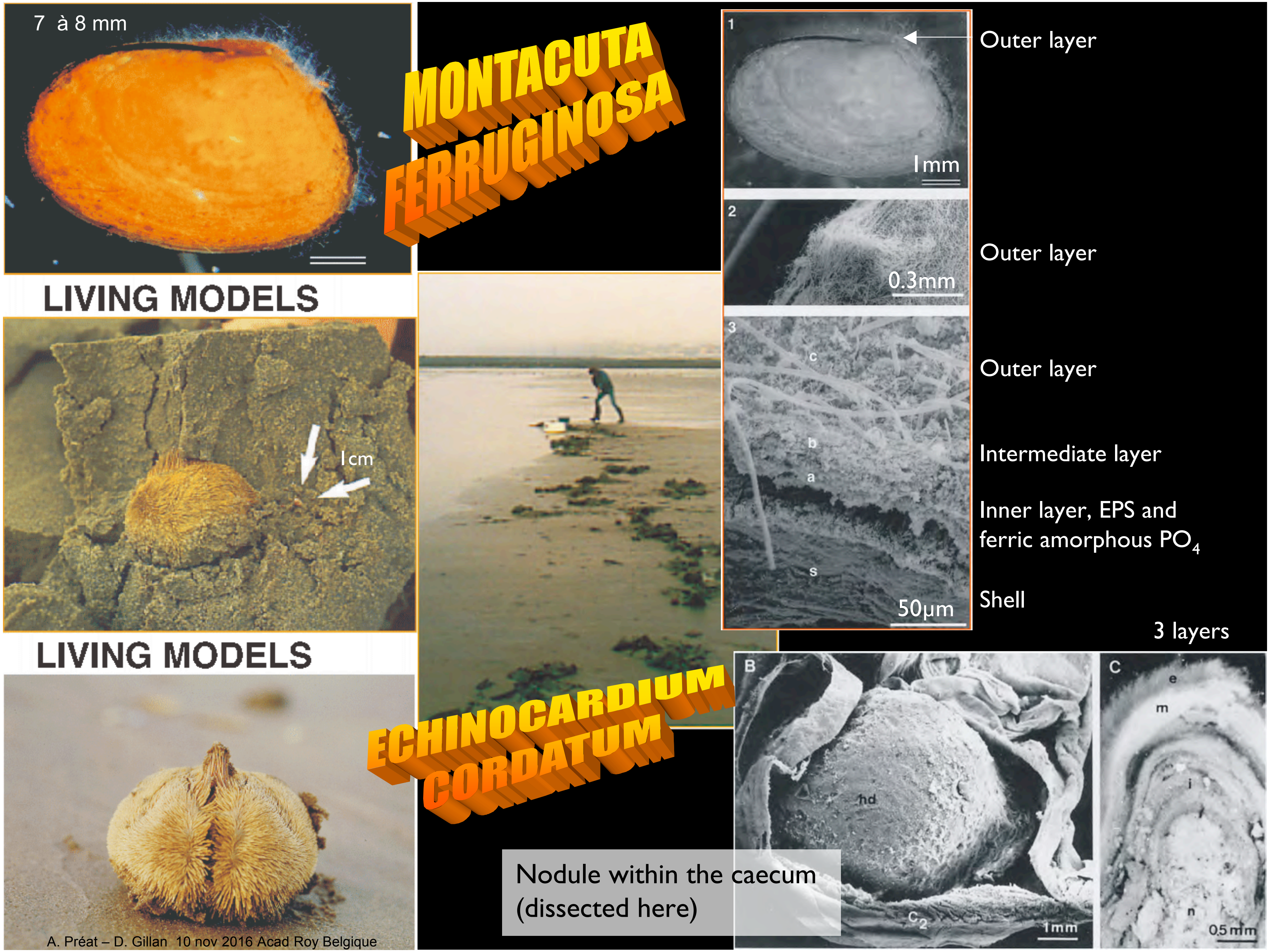
G
Y

Echinocardium cordatum

Burrowing echinoid that lives at 15 cm in the sediment (silty quartz sand)

and its biofilms…


7 à 8 mm
MONTACUTA
FERRUGINOSA
LIVING MODELS
1 cm
LIVING MODELS
ECHINOCARDIUM
CORDATUM
1
1mm
2
0.3mm
3
c
b
a
s
50µm
Outer layer
Outer layer
Outer layer
Intermediate layer
Inner layer, EPS and
ferric amorphous PO_4
Shell
3 layers
B
hd
C_2
1mm
C
e
m
i
n
0,5 mm
Nodule within the caecum
(dissected here)
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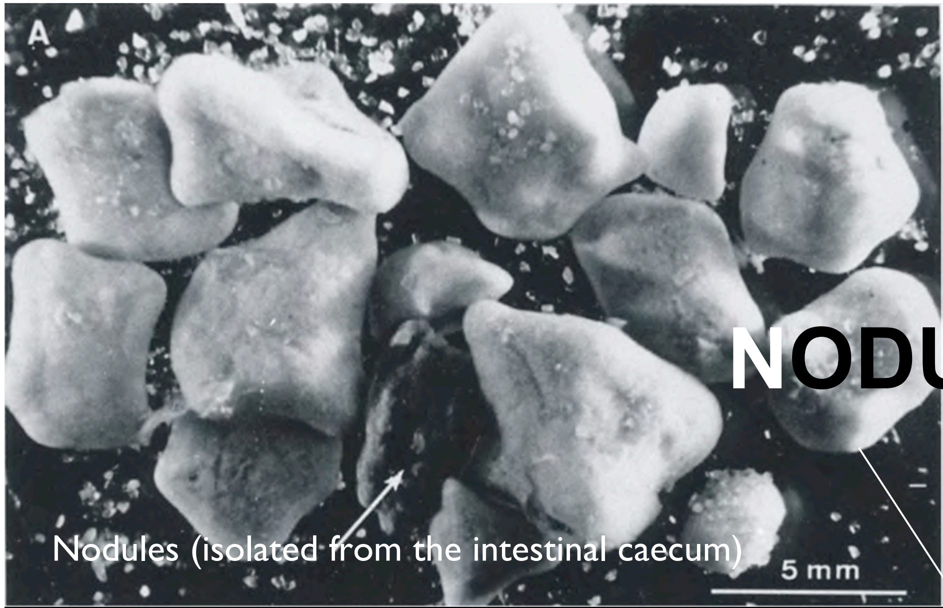
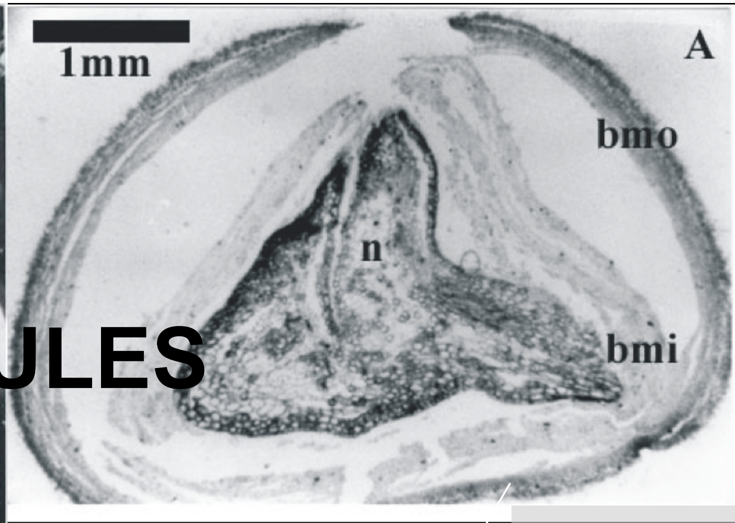
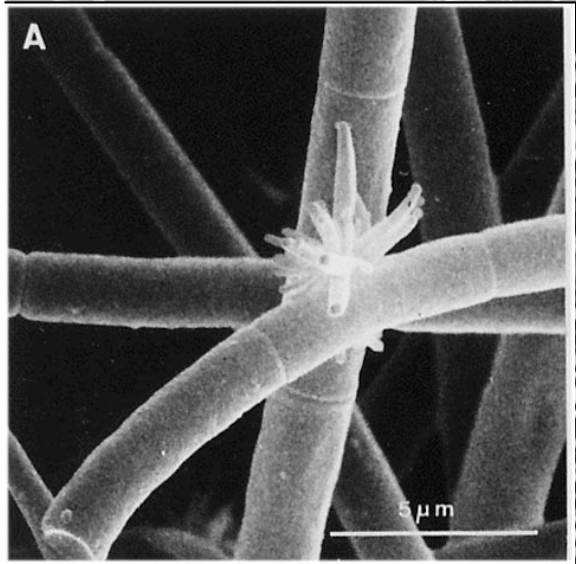
NODULES

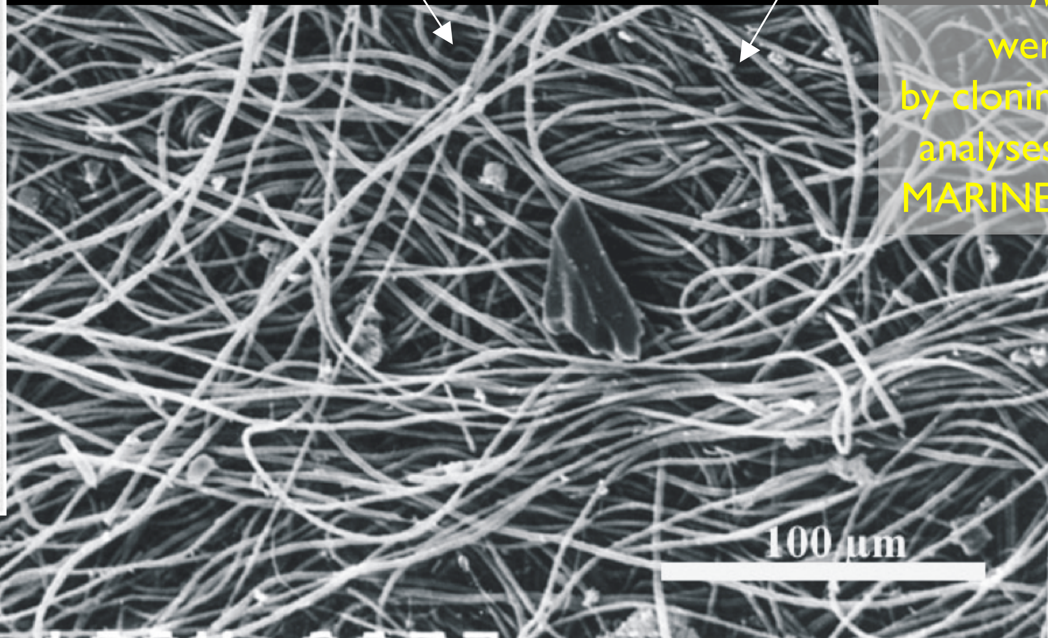




De Ridder 1986

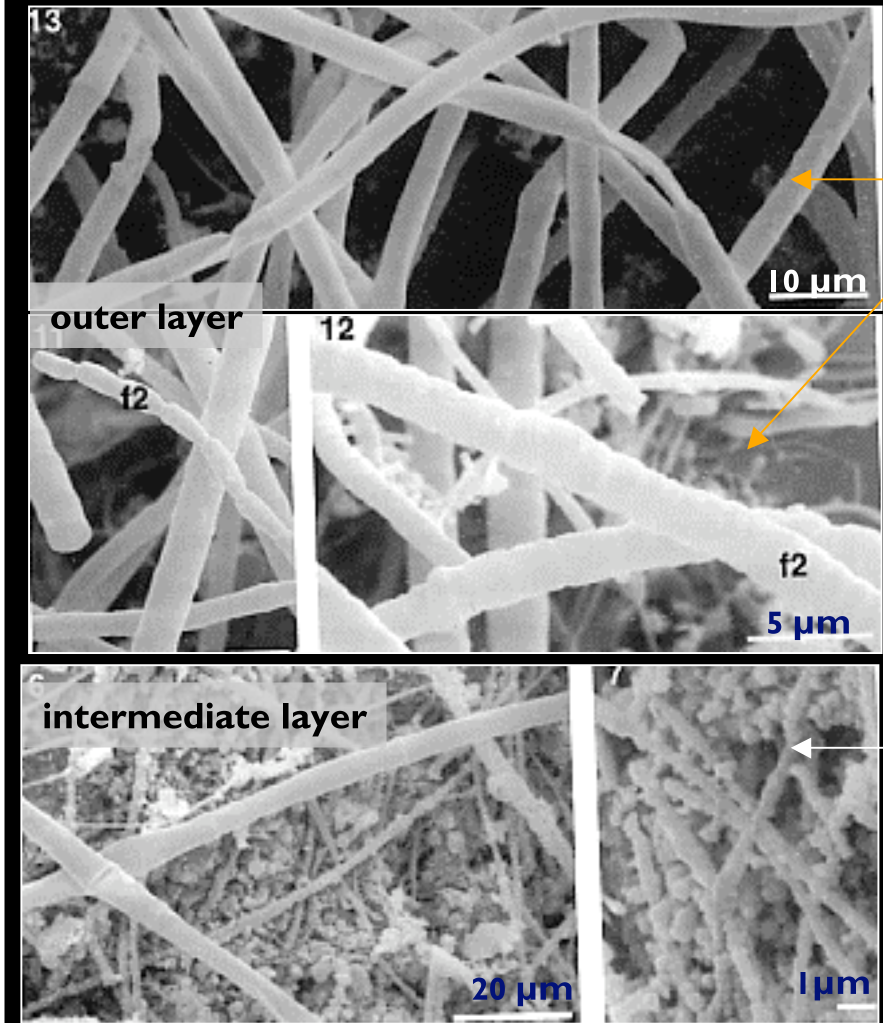
The bacteria of *Echinocardium* AND *Montacuta* were identified by cloning and sequences analyses (16S rRNA) ... MARINE BIOLOGY LAB

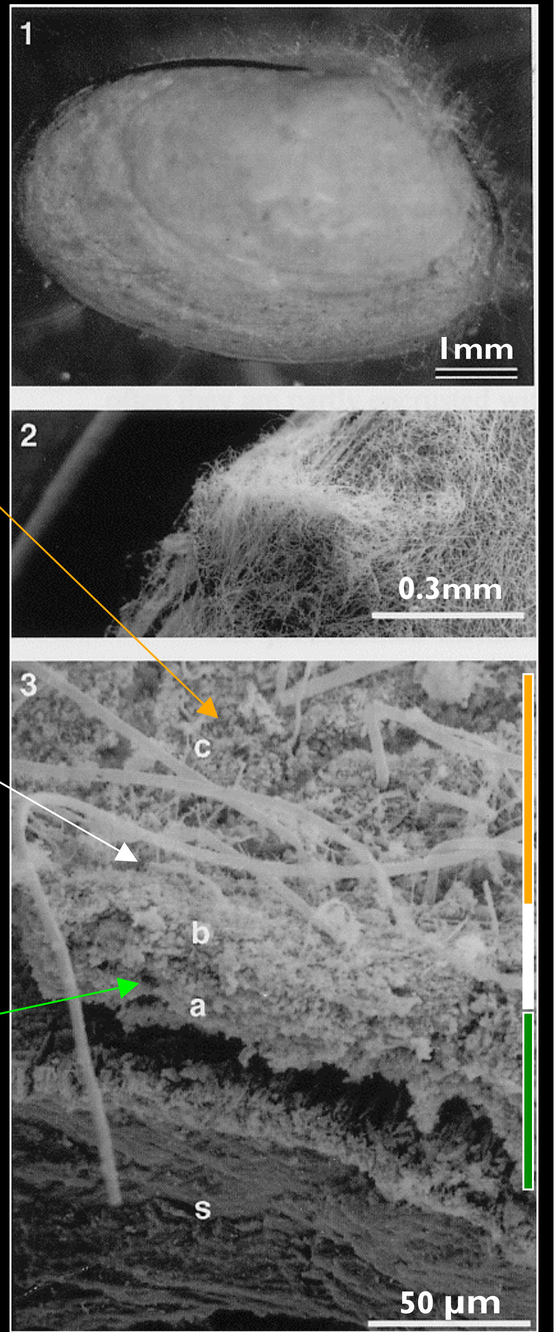




OUTER LAYER: BACTERIAL MAT (LIVING FILAMENTOUS BACTERIA MAINLY IN DYS /ANAEROBIC CONDITIONS)

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





Outer layer
= bacteria
non incrusted
or
with limited
Fe deposits

Intermediate
= bacteria
heavily incrusted
with
Fe deposits

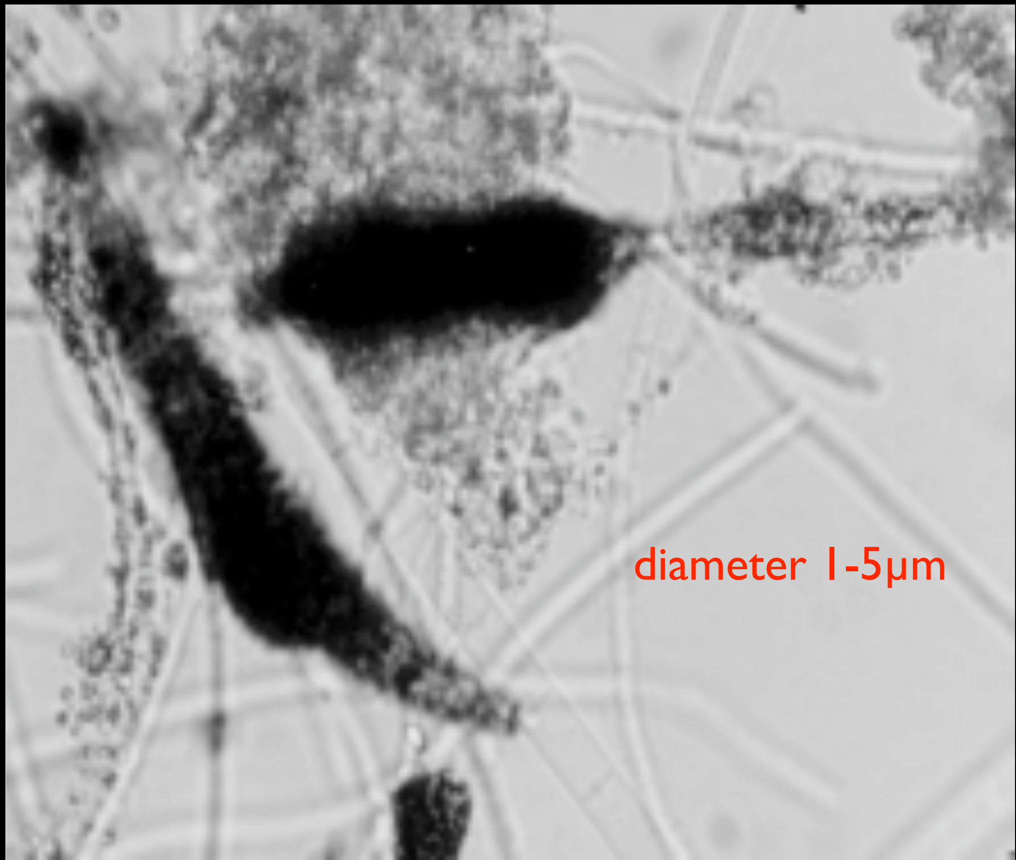
Inner
=
ferric iron deposits
+EPS accumulation

MONTACUTA FERRUGINOSA

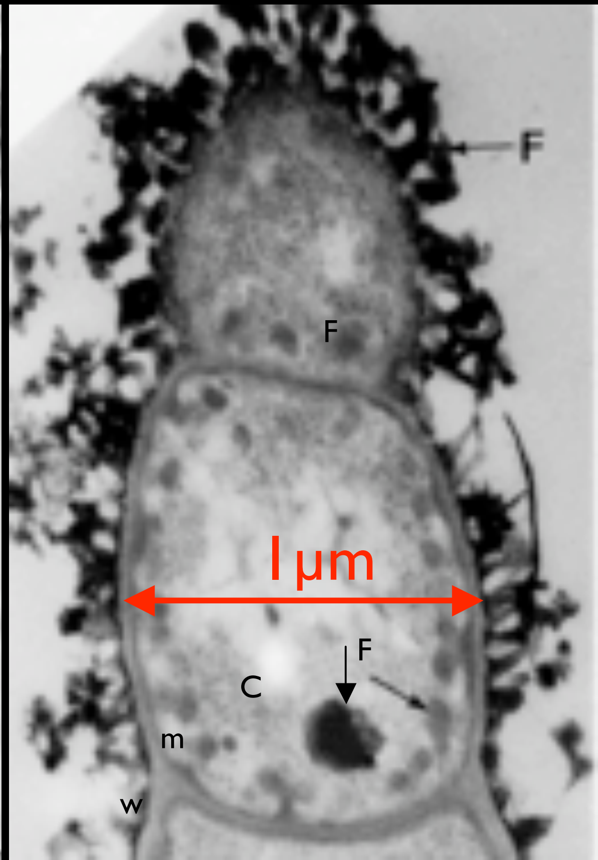
Gillan & De Ridder 2001. *Chemical Geology* 177:371–379

Filamentous iron bacteria from the shell of *M. ferruginosa*

(base of outer layer)

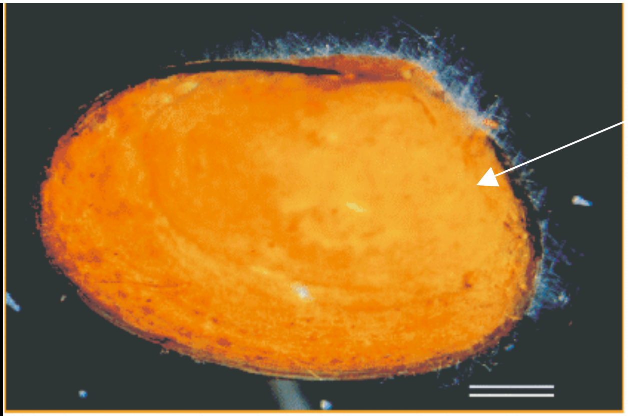


Bacterial filaments on the shell
(photonic microscopy)

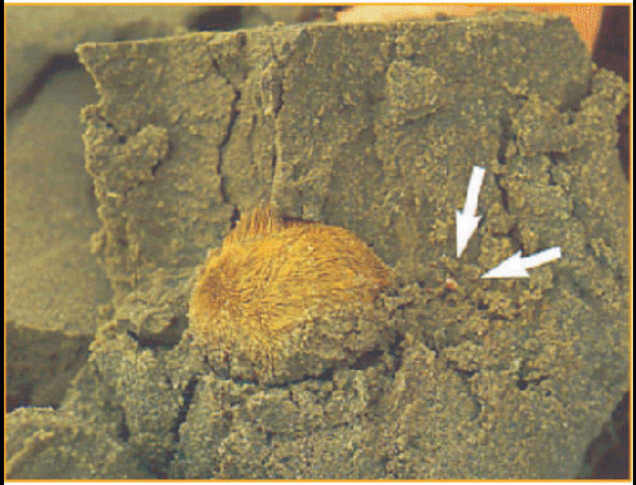


Bacterial filament - detail
TEM (F: Fe)

MONTACUTA FERRUGINOSA



LIVING MODELS



LIVING MODELS

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

MICROBIAL MAT WITH THREE DISTINCT LAYERS

1. *Outer layer* Filamentous and coccoid bacteria, also protozoa
2. *Intermediate layer* Microbial AND mineral (heavily ferric iron-encrusted filamentous bacteria and protozoa
3. *Inner layer* Essentially mineral (ferric iron deposits), no or rare living microorganisms

GENESIS OF THE MINERAL-MICROBIAL MAT

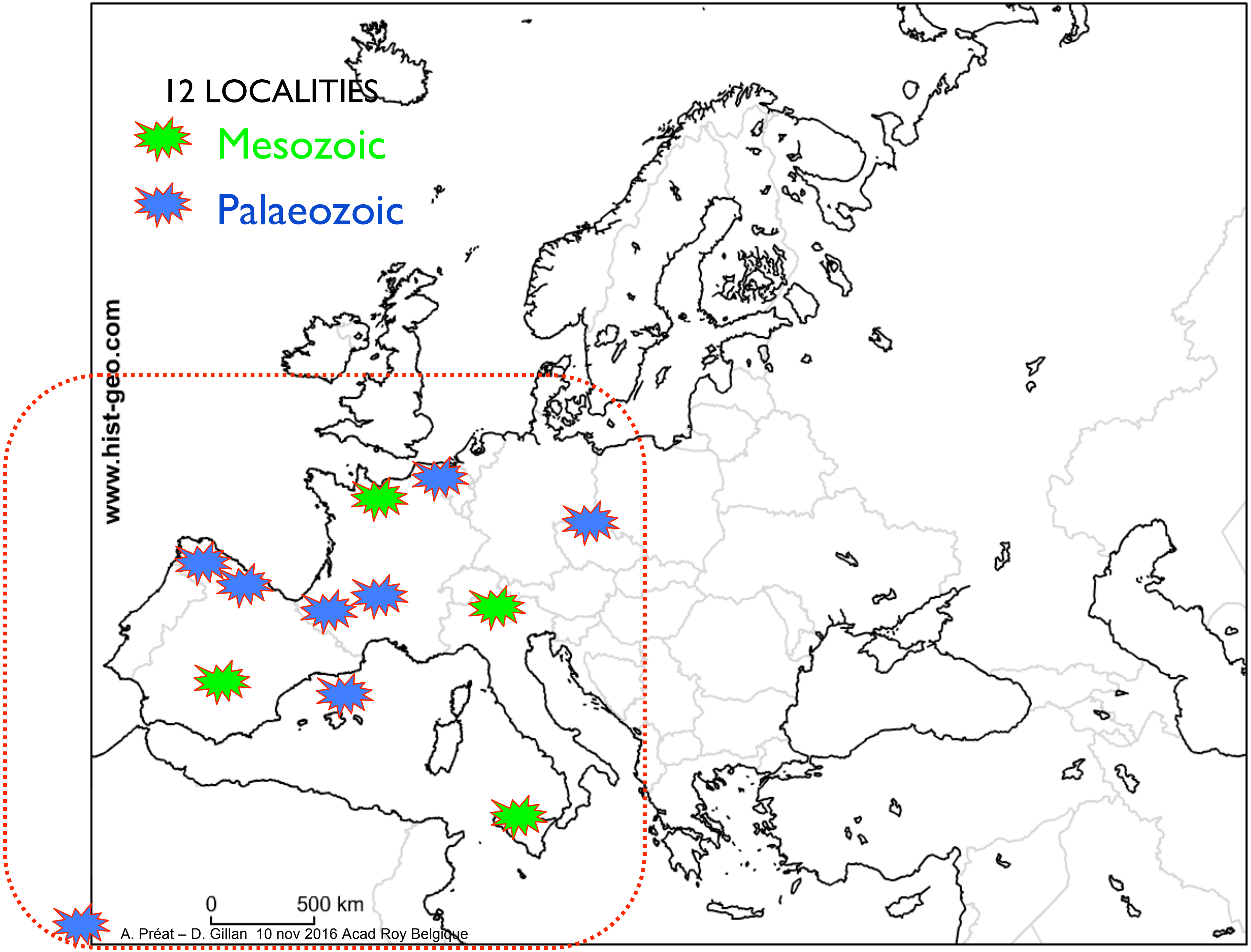
1. Ferric iron *deposition* within bacterial sheaths in the outer layer
2. *Release and accumulation* of heavily ferric iron-encrustated sheaths after lysis of the bacteria in the intermediary layer
3. *Degradation* of bacterial sheaths and *accumulation* of ferric iron minerals in the inner layer

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

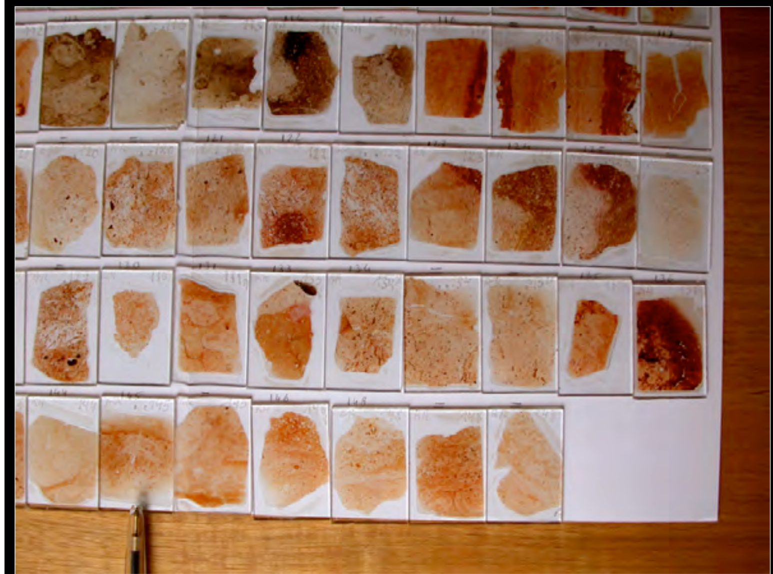
= PASSIVE PROCESS => BIOMINERALIZATION-INDUCED and BIOACCUMULATION (microbes dead or alive)

From PhD thesis C. DE RIDDER 1986 and D. GILLAN, 1999, Marine Biology Dept, ULB and several papers in Journals of Microbiology...)

… BACK TO GEOLOGY ➡ OBSERVED MICROFACIES OF DIFFERENT AGES AND LOCALITIES



OF WHAT CONSISTS THE RED PIGMENTATION?



° infillings of original fossil cavities

° calcite replacement of dissolved echinoderm plates

° infillings of bioperforations

° bacterial/fungal filaments

° ‘hedgehogs’ and ‘erythrospheres’

° massive hematite/goethite coating around microfossils

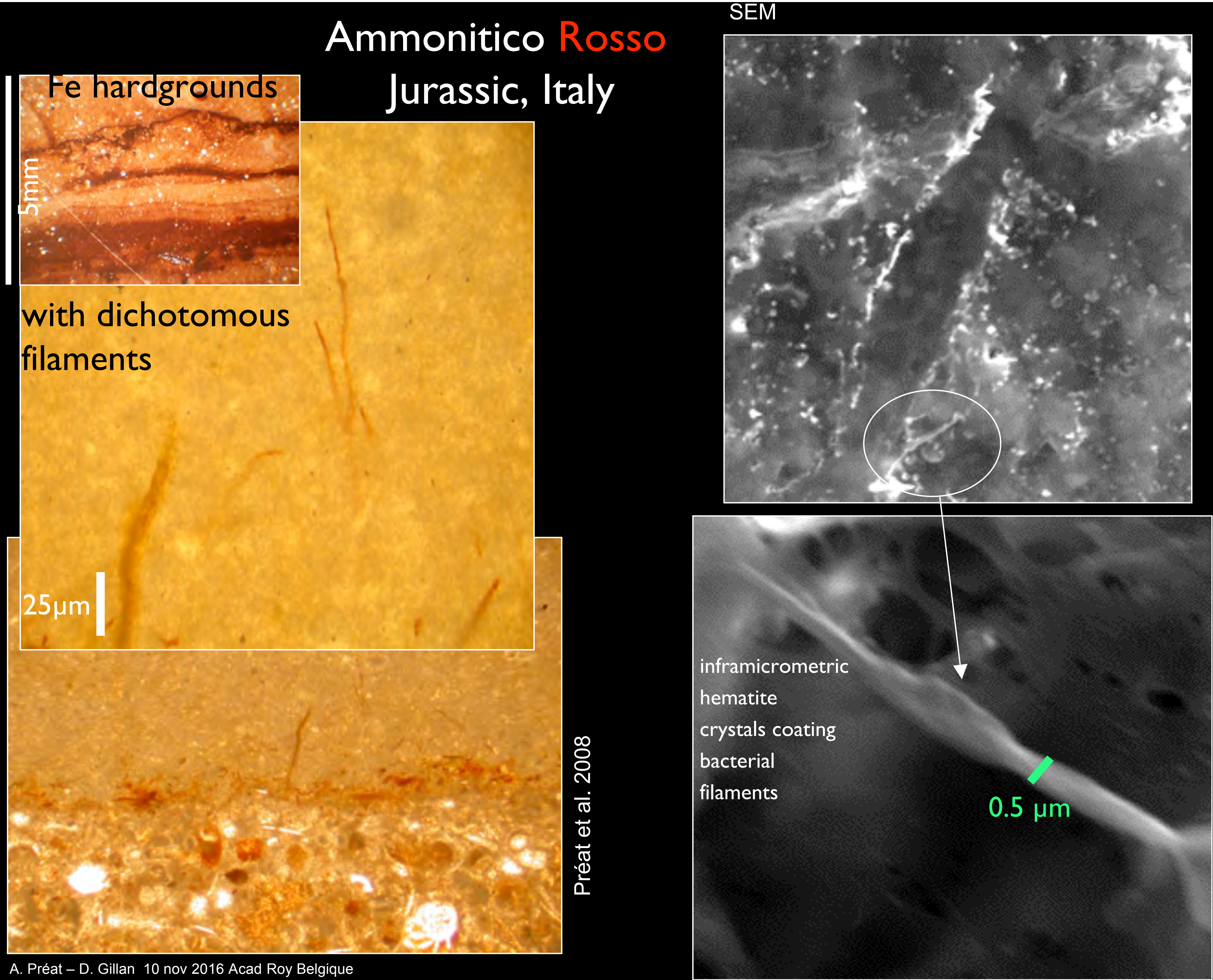
° simple or multiple biofilms

° microstromatolites (exogens ou endogens,
crenulated or not...)

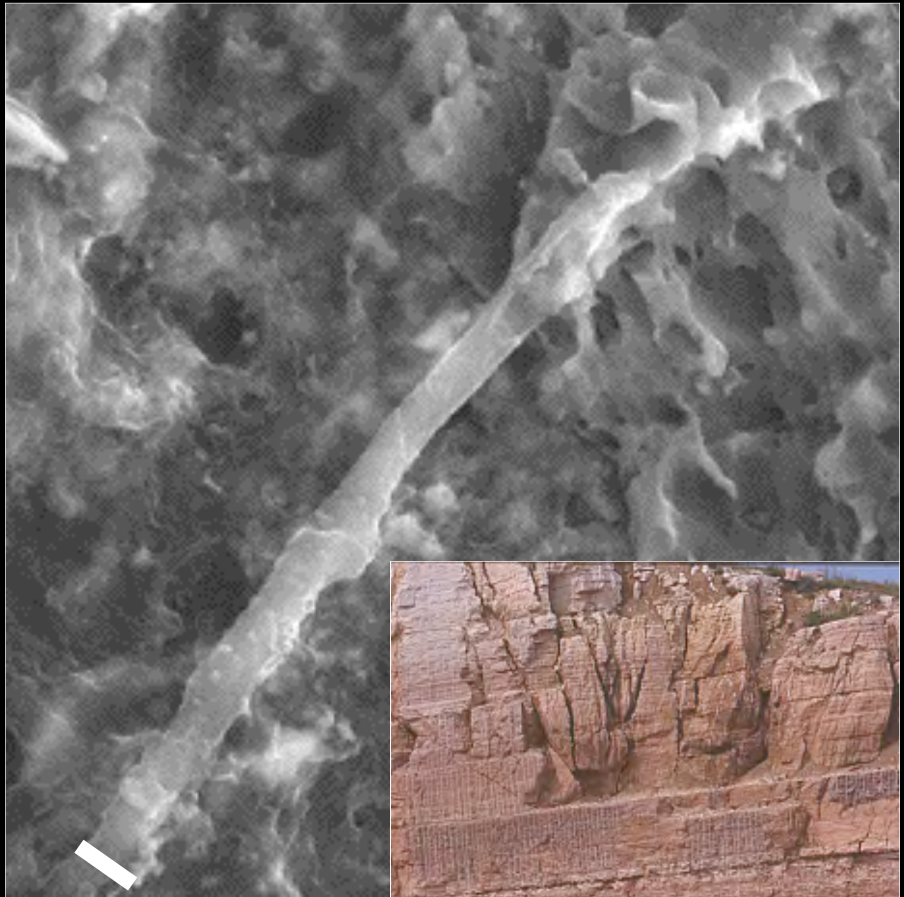
° oncolites

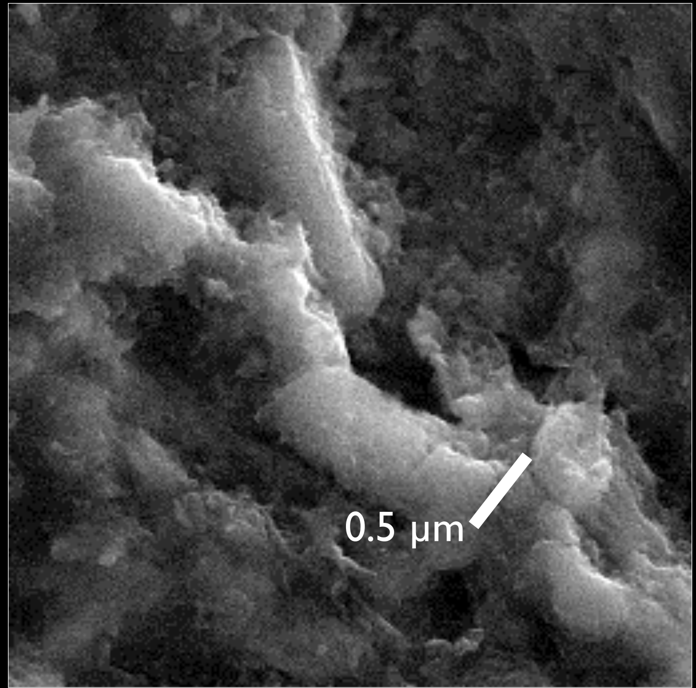
….. *non exhaustive* ….

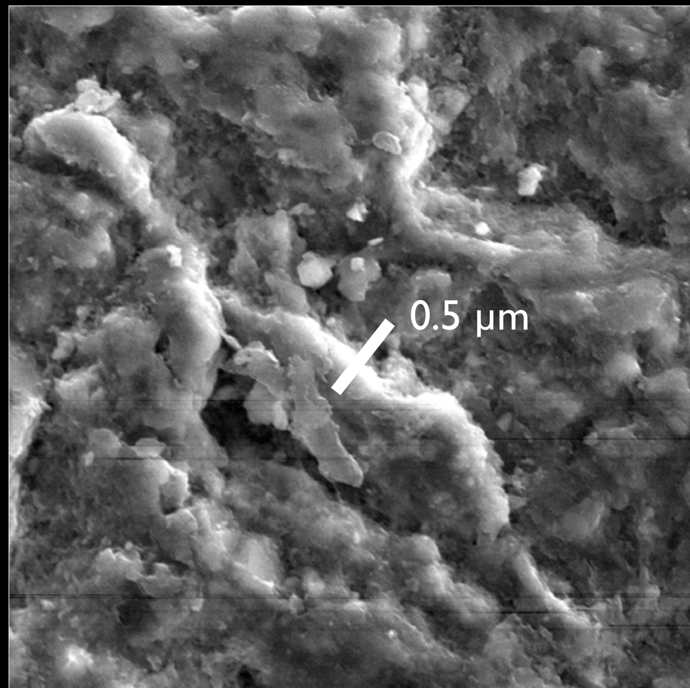
Ammonitico Rosso
Jurassic, Italy



SEM Ammonitico Rosso Jurassic, Italy







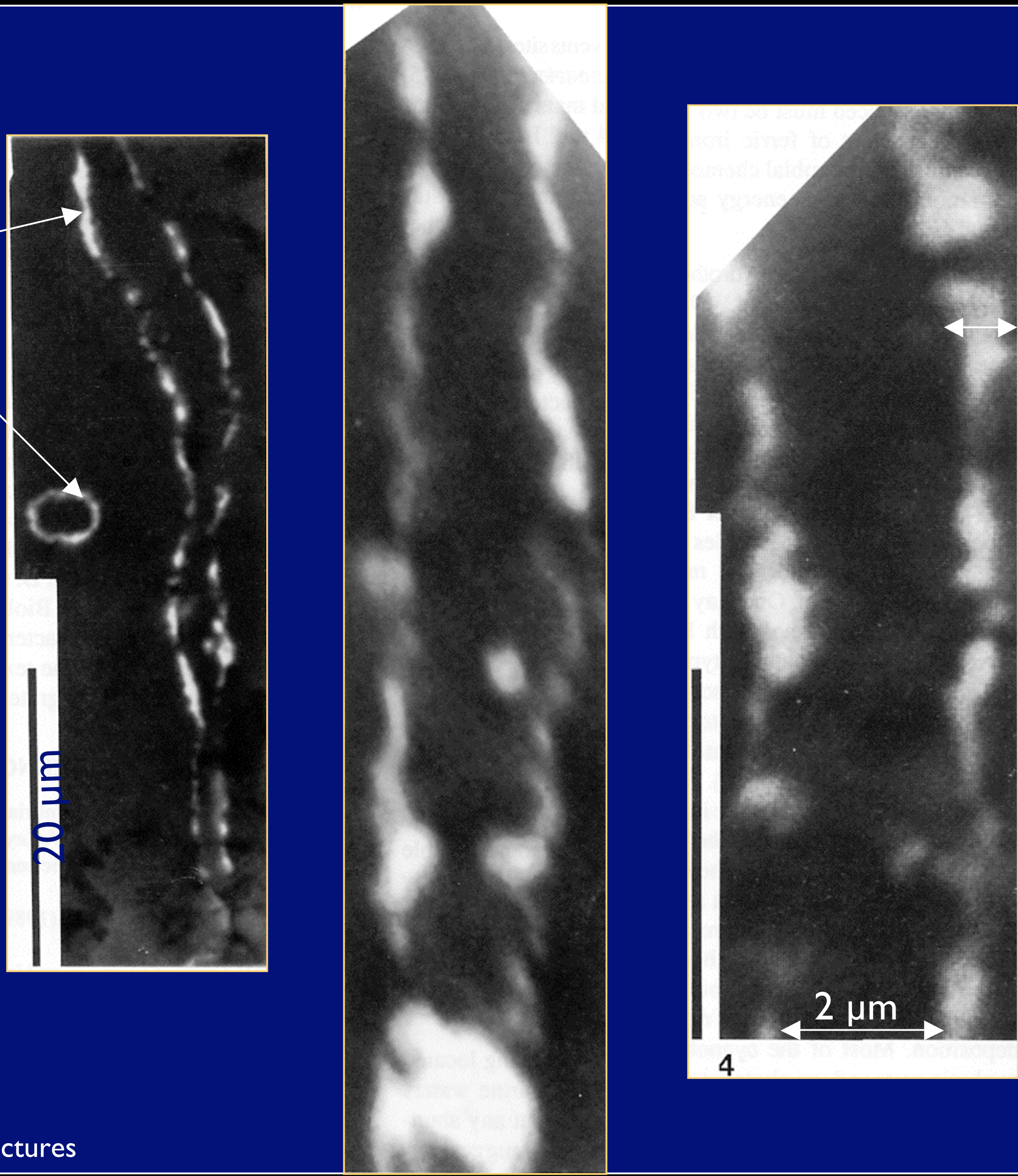
benthic
bacterial
mats
up to 20%

Préat et al. 2008

CZECH REPUBLIC, LOWER DEVONIAN

SEM

Fe

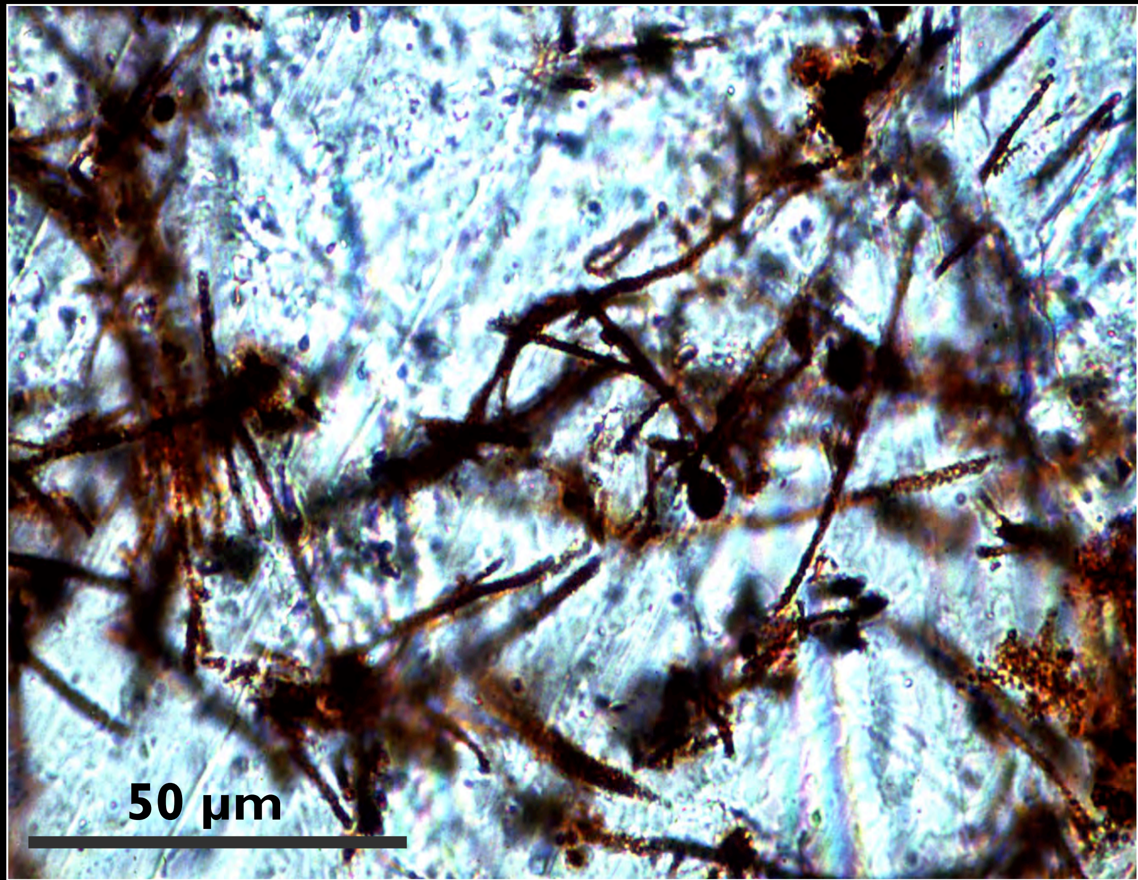


0.1-0.6 µm

Praguian, Czech R., Mamet et al 1997

SEM pictures

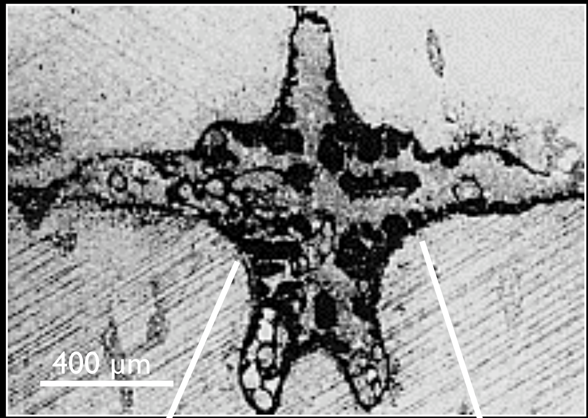
FRENCH-BELGIAN MUD MOUNDS, FRASNIAN

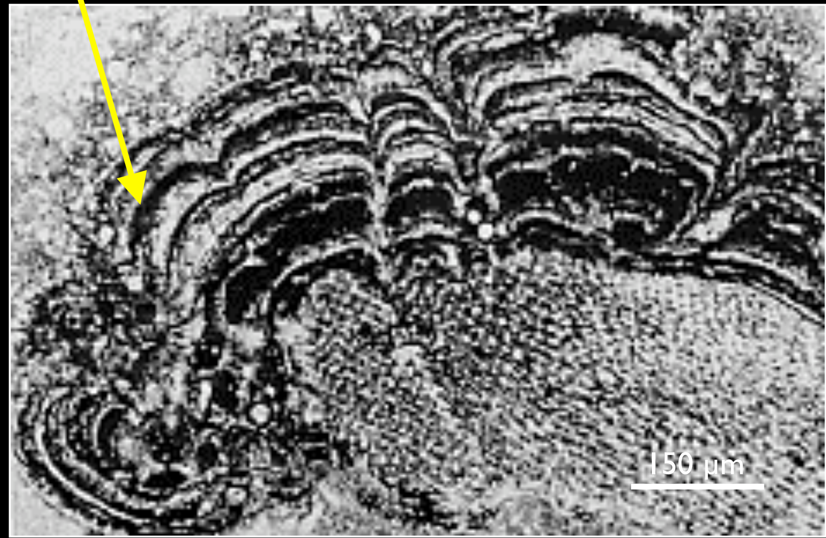


Boulvain et al. 2001

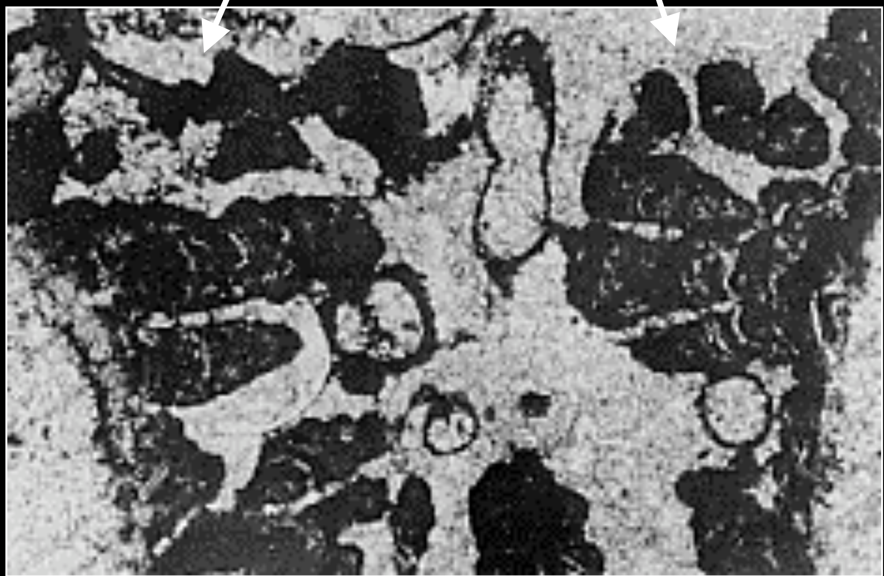
Iron-bacteria
(*Siderocapsa*-like, *Sphaerotilus-Leptothrix*-like
in the internal sediments (stromatactis) of *Receptaculites*
Rochefontaine quarry, Franchimont, Philippeville Massif

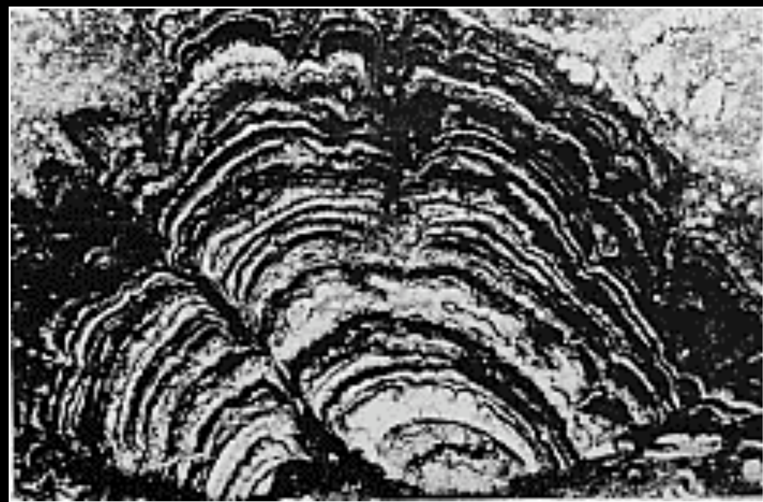
BALEAS GRIOTTES, SPAIN, CARBONIFEROUS





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





Mamet, Boulvain 1990

with endostromatolites … and microstromatolites

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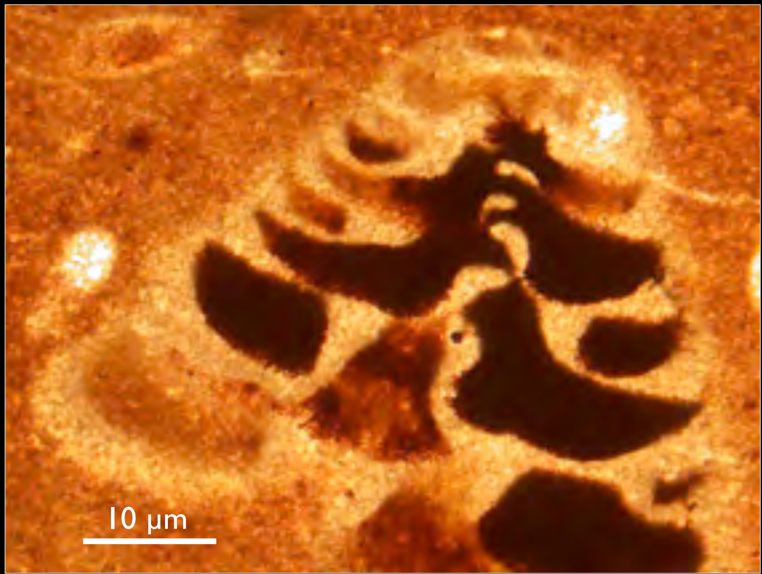
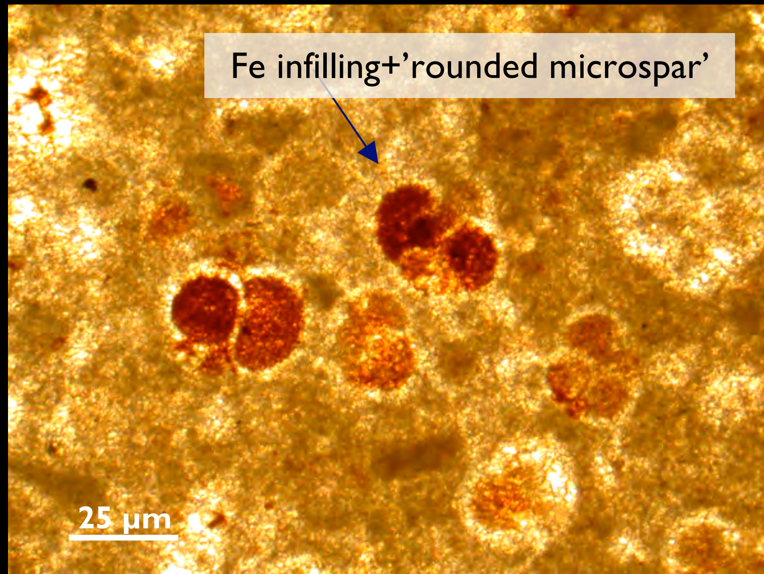
SIERRA DEL CUERA, SPAIN, CARBONIFEROUS - PLATEAU DI ASIAGO, ITALY, JURASSIC

Infillings of original fossil cavities (here, Foraminifer)



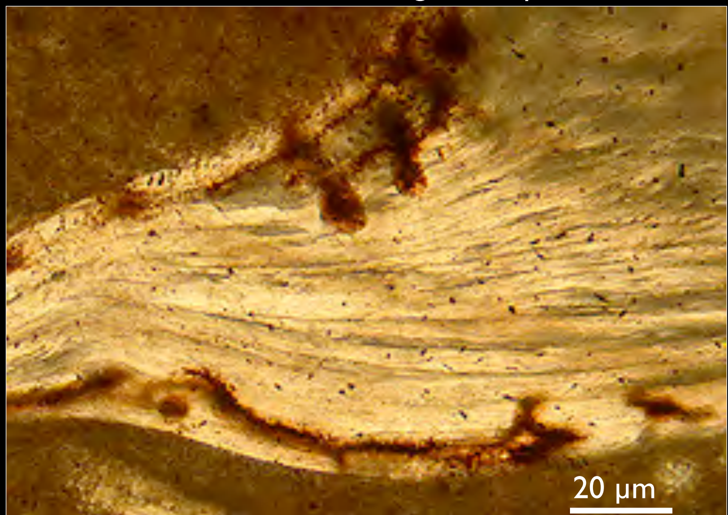
Also Bryozoan, Gastropods, Ostracods, Tentaculids, Protoglobogerinids…



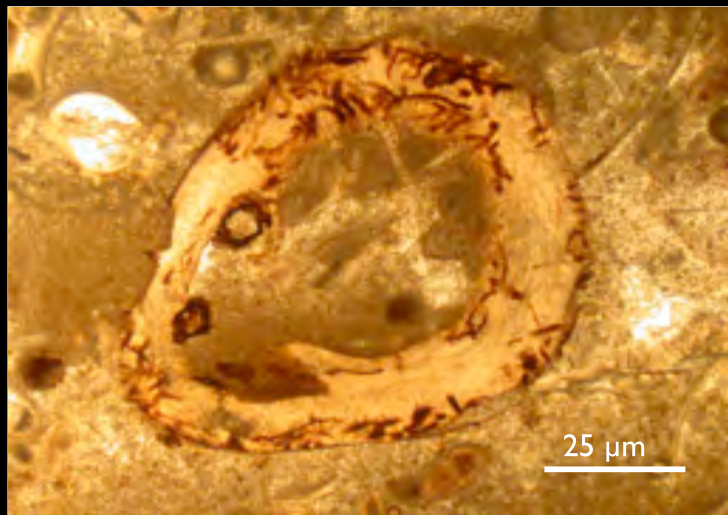
Mamet, Préat 2006

SIERRA DEL CUERA, SPAIN, CARBONIFEROUS

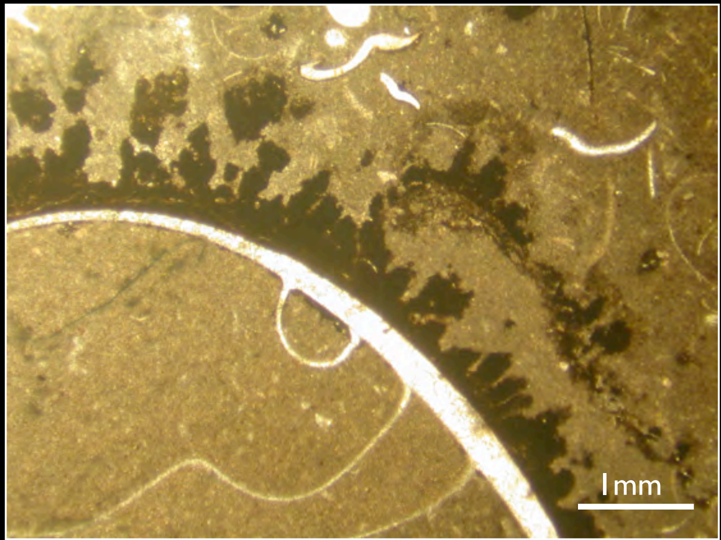
Infillings of bioperforations



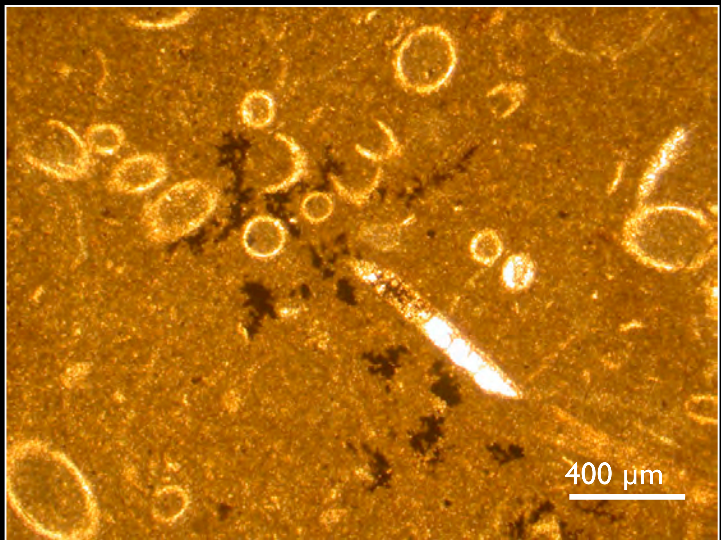
Brachiopods, Pelecypods, Bryozoans, Foraminifers



ANTI-ATLAS, MOROCCO LOWER-UPPER DEVONIAN



Mamet, Préat 2007

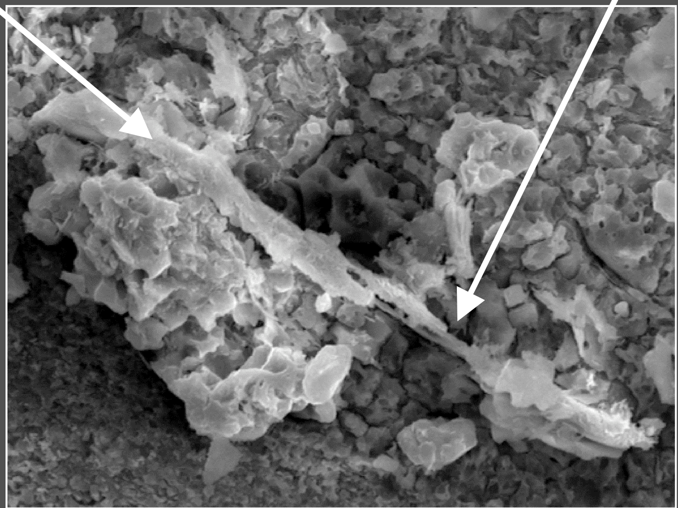


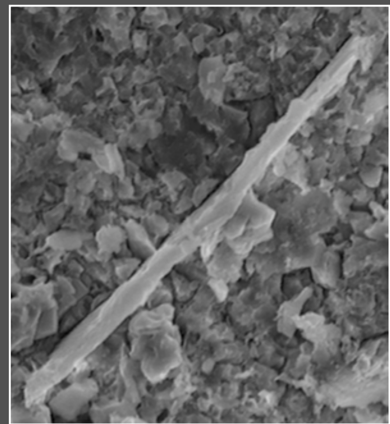
ANTI-ATLAS, MOROCCO LOWER-UPPER DEVONIAN

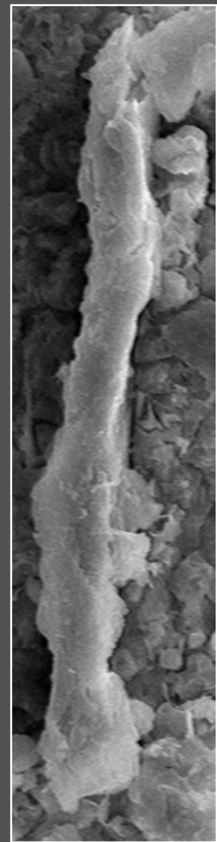
Filamentous iron bacteria

Iron encrustation
(25-50% Fe)

Sheath





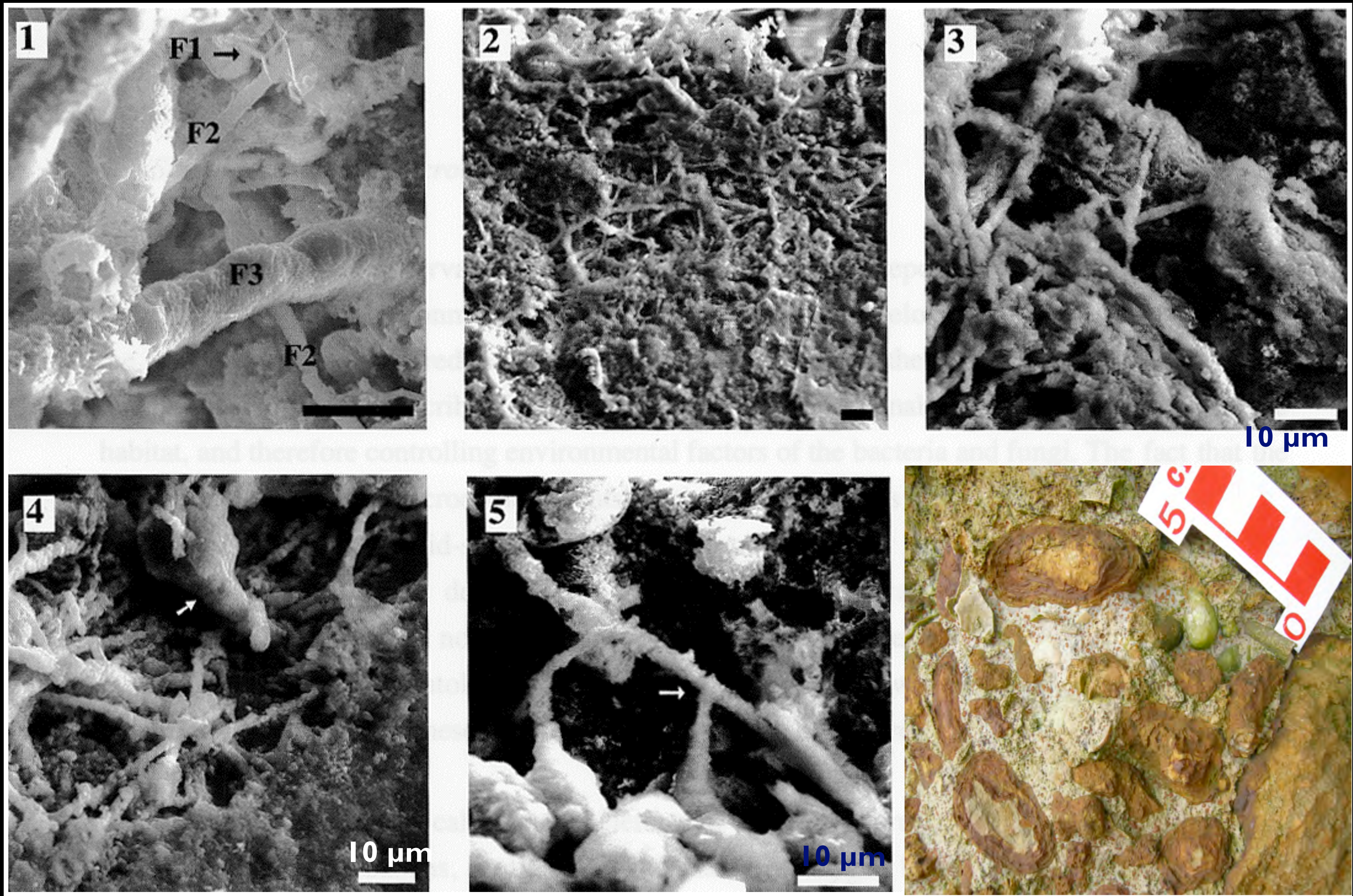


Diameters: 1.5-4 µm
[SEM]

Mamet, Préat 2007

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

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



Bajocian, SHP, France, Préat et al. 2000

SEM observations (x1,000 … x35,000…)

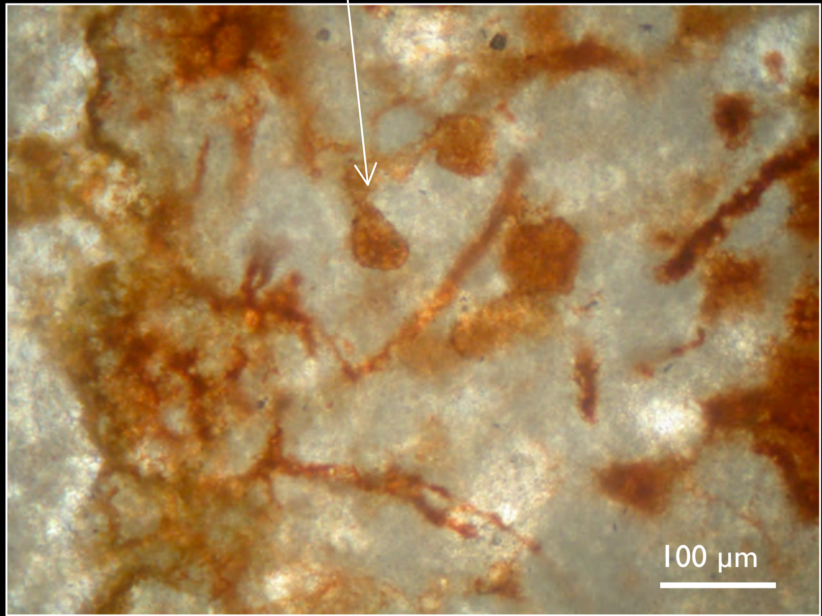
- Simple and regular filaments
- Simple filaments with regular constrictions
- Dichotomous filaments with constrictions
- Concentrations of regular sphaerules

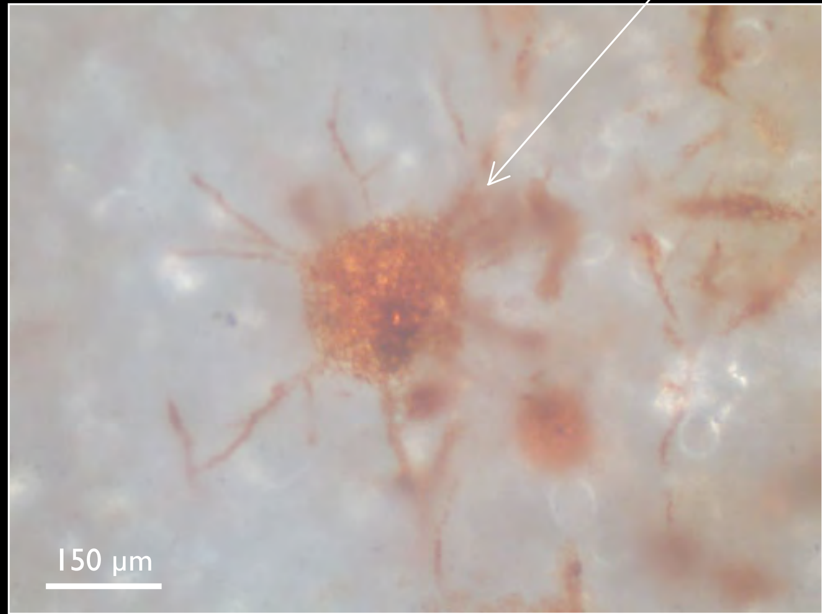
Diameters ⩽ 2 µm

with submicronic hematite $Fe_2 0_3$ or goethite $FeO.OH$ 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

First conclusion

Hematite/Goethite are not dispersed at random but follows regular patterns

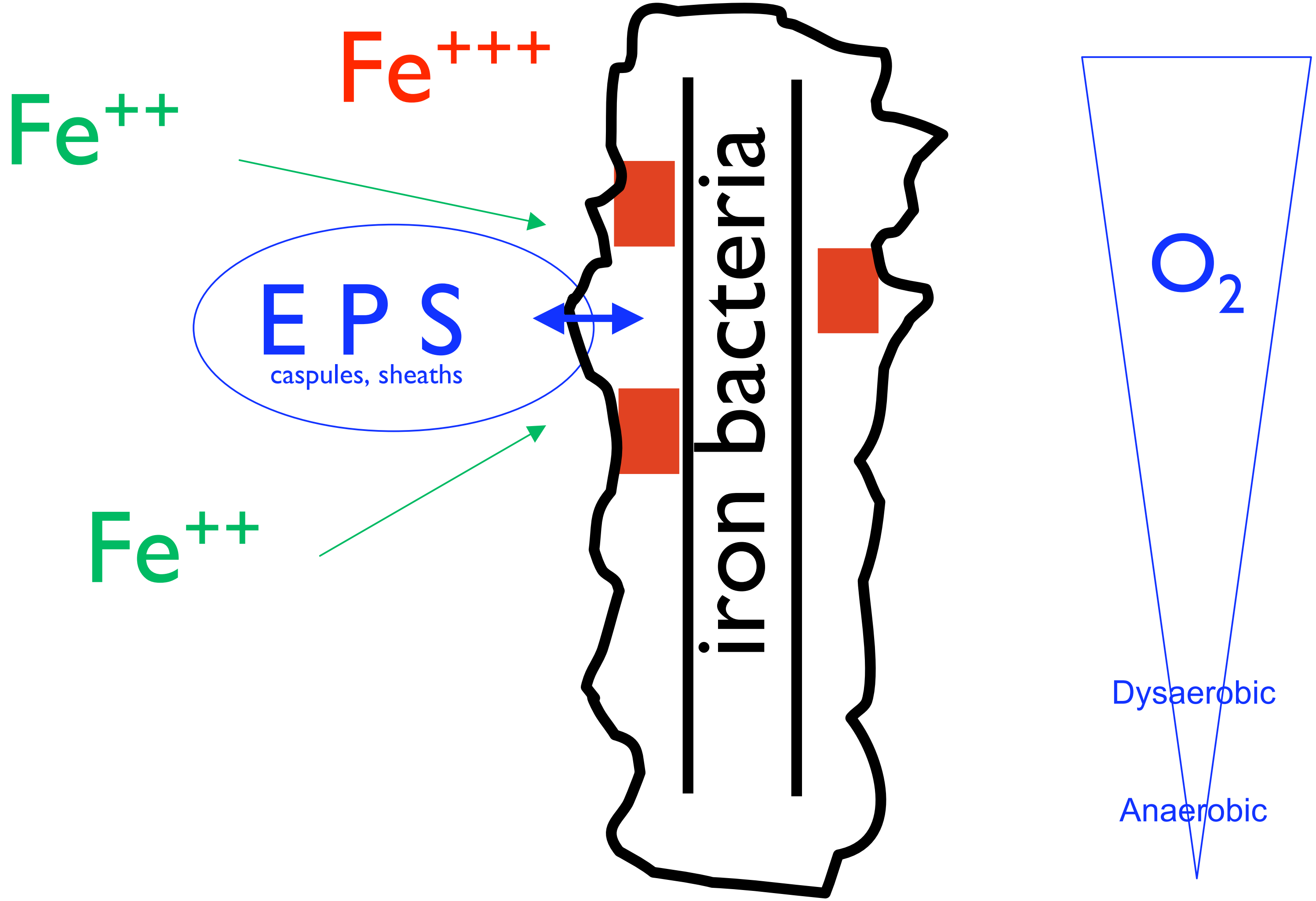
…

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* …

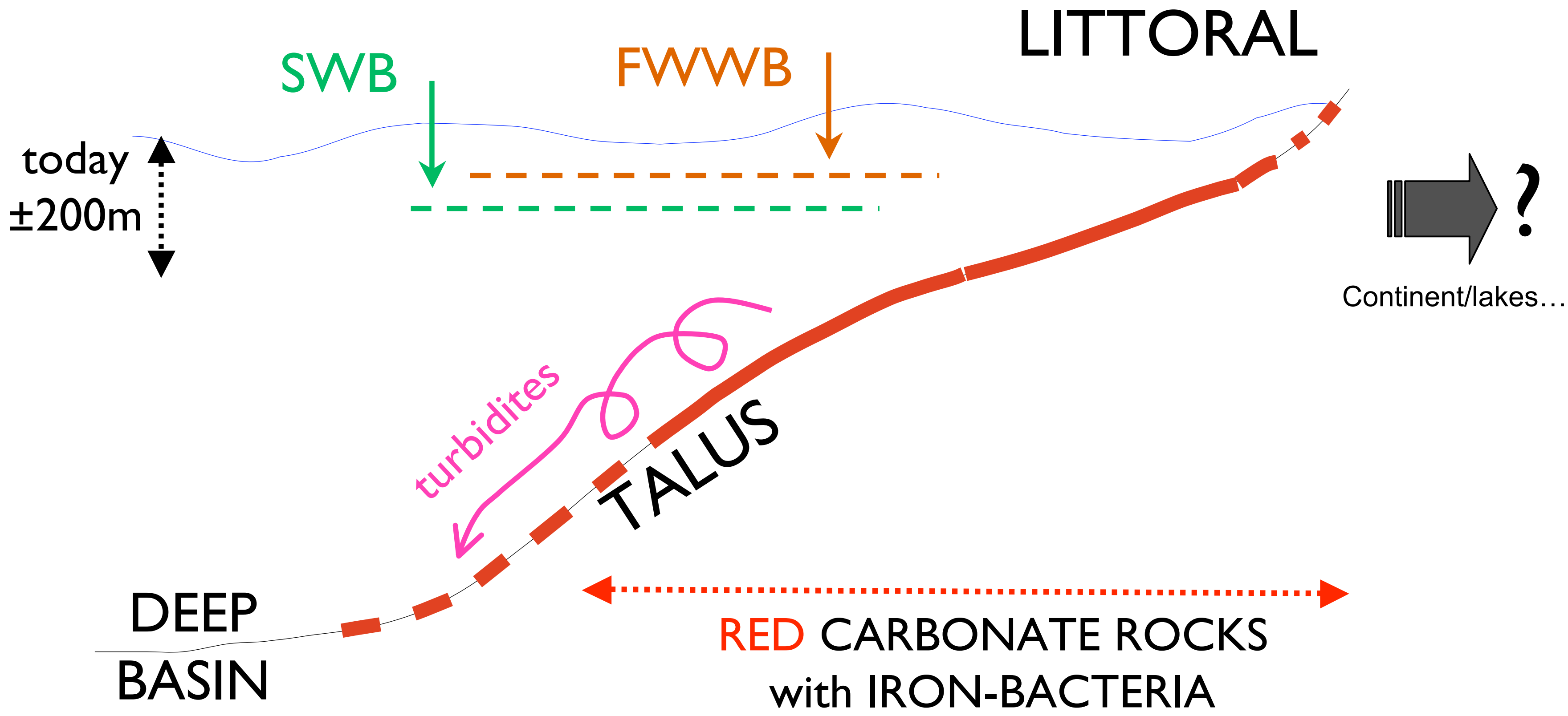
3. Iron biomineralization is linked to the production of EPS - exopolymeric substances = sheaths or capsules rich in polysaccharides forming the main part of the bacterial mats. The Fe^{3+} is passively precipitated in the EPS of the Recent bacterial films



Ferrihydrite: nanocrystals of hydrous ferric oxide, $5Fe_20_3.9H_2O$

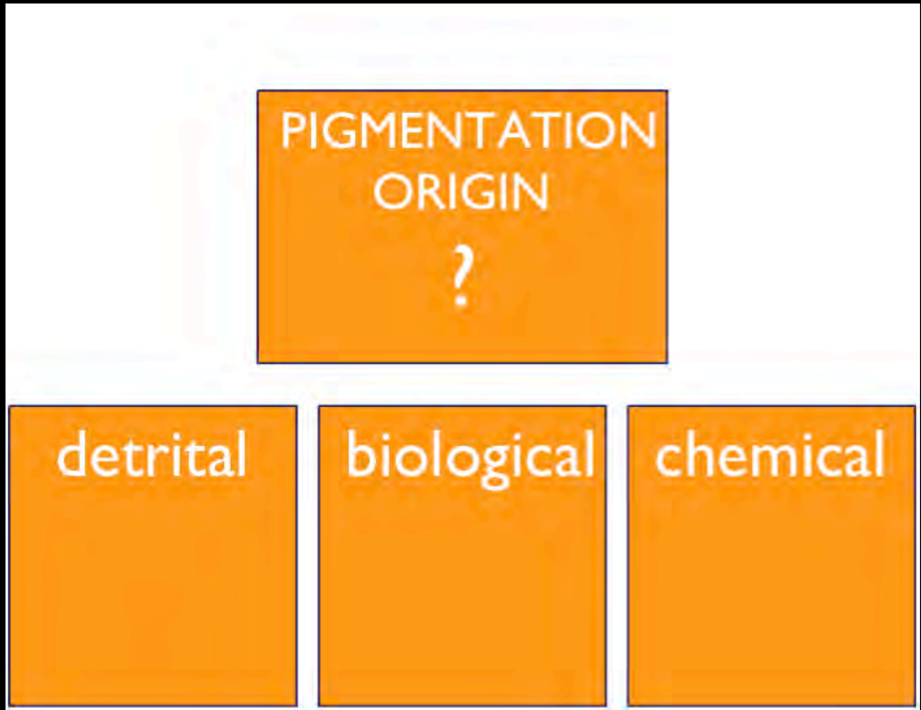
PASSIVE BIOACCUMULATION-BIOMINERALIZATION-PRECIPITATION OF FERRIC MINERALS

SECOND CONCLUSION



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

CONCLUSION OF THE FIRST PART



Red pigmentation = Fe microbial activity

Microenvironmental significance

and

No paleogeographical significance

Stable isotope geochemistry of iron

- griottes Devonian S-France, Viséan N-Spain
- 'red marbles' Devonian (Frasnian), Belgium
- Ammonitico Rosso Jurassic, N-Italy, S-Spain, Sicily
- 'red marble' Devonian, Czech Republic
- red condensed series Devonian, Morocco
- red lenses in slope Carboniferous, N-Spain
- 'Oolite Ferrugineuse de Bayeux' mid-Jurassic Normandy

GEOLOGY

Echinocardium cordatum
Montacuta ferruginosa

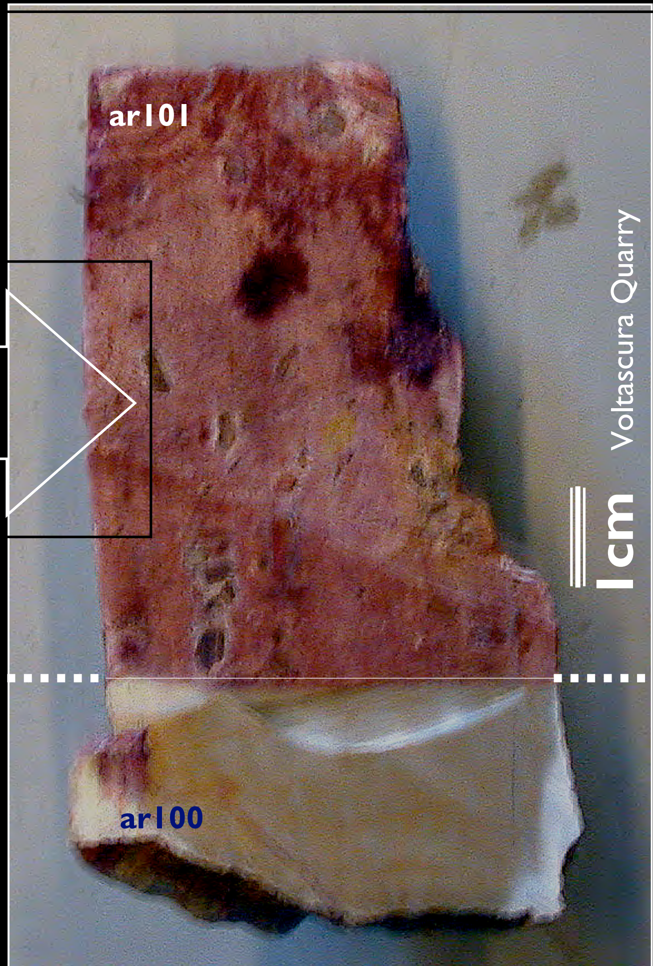
BIOLOGY

^{56}Fe 91.76%
^{54}Fe 5.84 %
^{57}Fe 2.12 %
^{58}Fe 0.28 %

What about Fe-isotopes?

4 outcrops (60 km)

Fe-hardgrounds
Filamentous Fe-microbes
Fe-microstromatolites
Fe-biofilms



RAI

hiatus

Calcari Grigi

U. Bajocian - L. Callovian

Hettangian - Domerian

$$\delta^{56}Fe = (^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM014} - 1) * 10^3 \quad (‰)$$
$$\delta^{57}Fe = (^{57}Fe/^{54}Fe_{sample}/^{57}Fe/^{54}Fe_{IRMM014} - 1) * 10^3$$

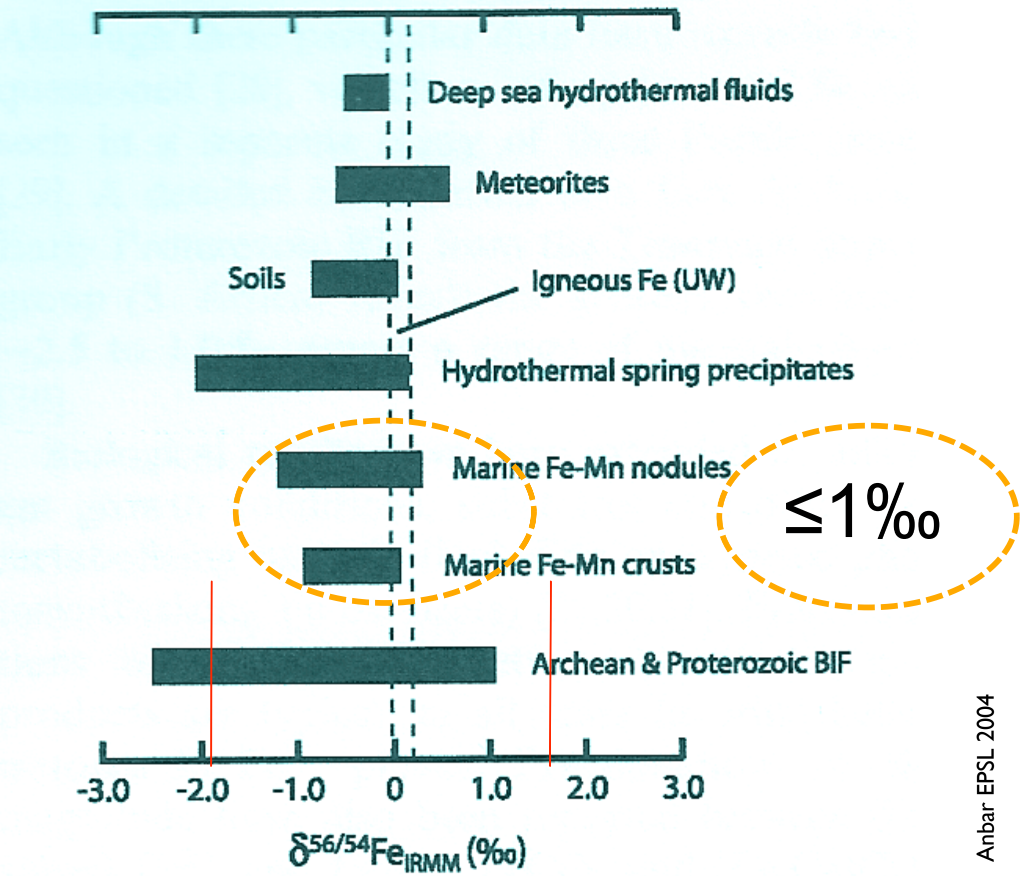
What about Fe-isotopes?

$\delta^{56}Fe = (^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM014} - 1) * 10^3$

Fe isotope variations in natural materials

<u>Fe isotope fractionation effects</u>

Natural mass-dependant variation in isotopic composition of Fe <u>are small</u>
+0,9 to -1.6‰ in sedimentary environments
0±0.3‰ igneous rocks Earth and Moon



Mass-dependent isotope variations of Fe in the rock record span a range of 4 ‰ in $^{56}Fe/^{54}Fe$ ratio.

^{56}Fe 91.76%
^{54}Fe 5.84 %
^{57}Fe 2.12 %
^{58}Fe 0.28

What about Fe-isotopes?

$$\delta^{56}Fe = (^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM014} - 1) * 10^3$$

Fe isotope fractionation effects

Natural mass-dependant variation in isotopic composition of Fe are small
+0,9 to -1.6‰ in sedimentary environments
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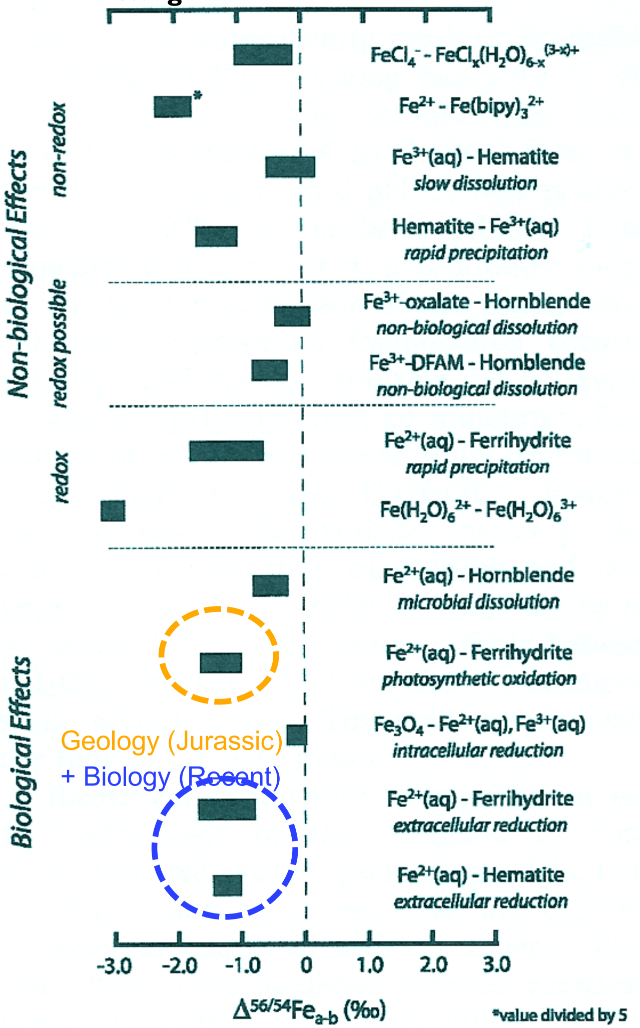


Anbar EPSL 2004

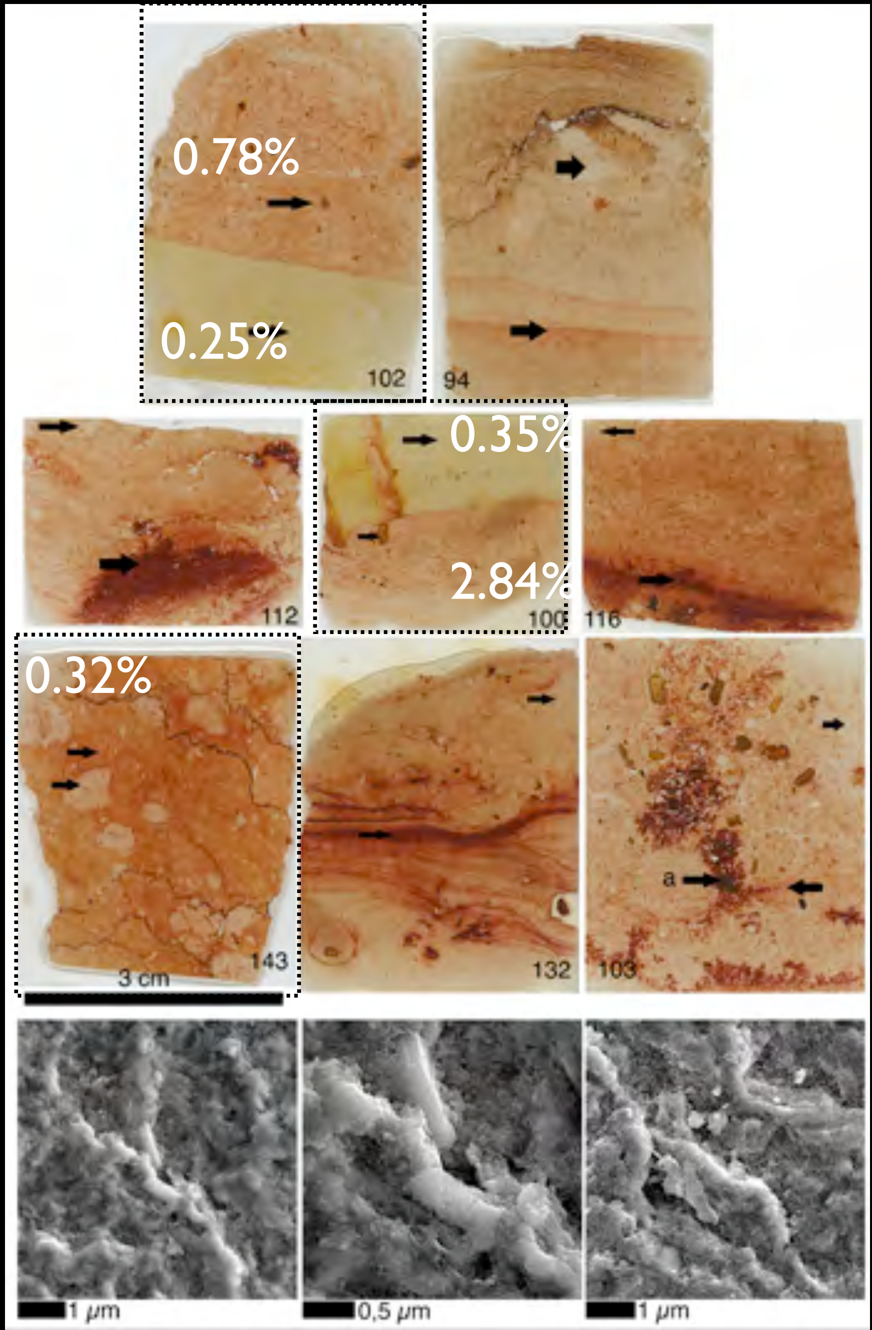
EXPERIMENTS IN BIOLOGICAL SYSTEMS

$^{56}Fe/^{54}Fe$ ratios of the (solid) ferrihydrite precipitate **with an 1.5‰ increase** relative to the aqueous Fe(II) source

AND

the net Fe isotope fractionation is remarkably similar (**1.3% more negative**) to that obtained for dissimilatory Fe(III) reducing bacteria

SO, WHAT IN NATURAL SYSTEMS (GEOLOGY AND BIOLOGY)?



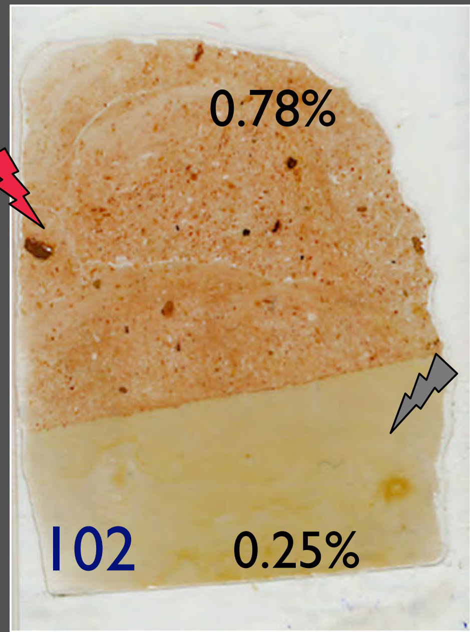
PREAT et al. 2008

total Fe_2O_3

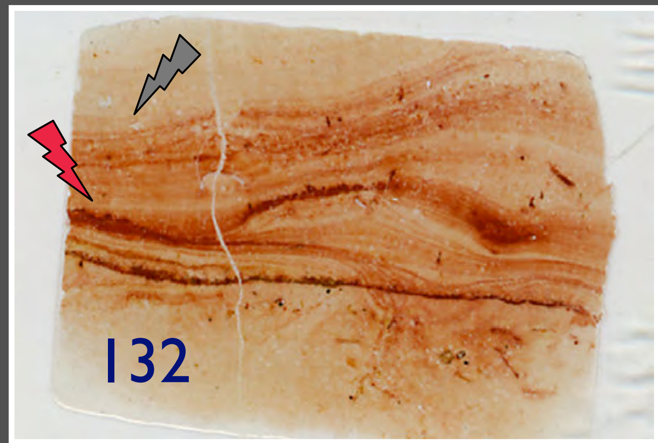
100G = 0.35%
100R = 2.84%

102G = 0.25%
102R = 0.78%

143R = 0.32%



3 cm



Sample preparation

A small electric drill with a titanium drill head was used to extract powder from individual grey and red layers
(25 mg for each sample)

Analytical Procedure

- Bulk sample dissolution
- Leaching (HCl 3M for 3h at 50°C) in order to remove the carbonate phases without dissolving the other phases (silicates, oxides)

Separation of Fe by one-step ion-exchange chromatography

Needs iron separation and purification...

Iron Isotopic Analyses by Nu Plasma MC-ICP-MS

Electrostatic Analyzer

Magnet

Cetac Aridus

Collector block (12 Faraday cups)

Dry plasma: Aridus desolvating sample introduction system

Minimalizing interferences ArOH: mass 57, ArO: mass 56,ArN: mass 54

... an analysis takes about 9 minutes, and consumes about 1ml of sample or 400 ng of Fe

Analytical conditions

- $\delta^{56}Fe = (^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM014} - 1) \times 10^3$
- Simultaneous external normalization (Cu-doping method in dynamic mode) and standard-sample bracketing with the IRMM014 reference material;
- Cr correction on mass 54;
- Every sample in duplicate;
- Long-term accuracy and reproducibility of 0.15 ± 0.06 ‰ for $\delta^{56}Fe$
- (1 sigma, n = 21) for a basalt relative to IRMM014.

Per sample: 10 days (dissolution, separation) + 2 days (ICP-MS)/3 samples
Optimal timing: 15 days -1 month for 2 or 3 samples

GEOCHEMICAL STUDY

Voltascura + Forte di Campo Luserna
RAI, 25 samples

- $CaCO_3$, Mg, Fe, Mn, Sr (whole rock and selective)
- $\delta^{18}O$-$\delta^{13}C$ (selective microdrillings)

+

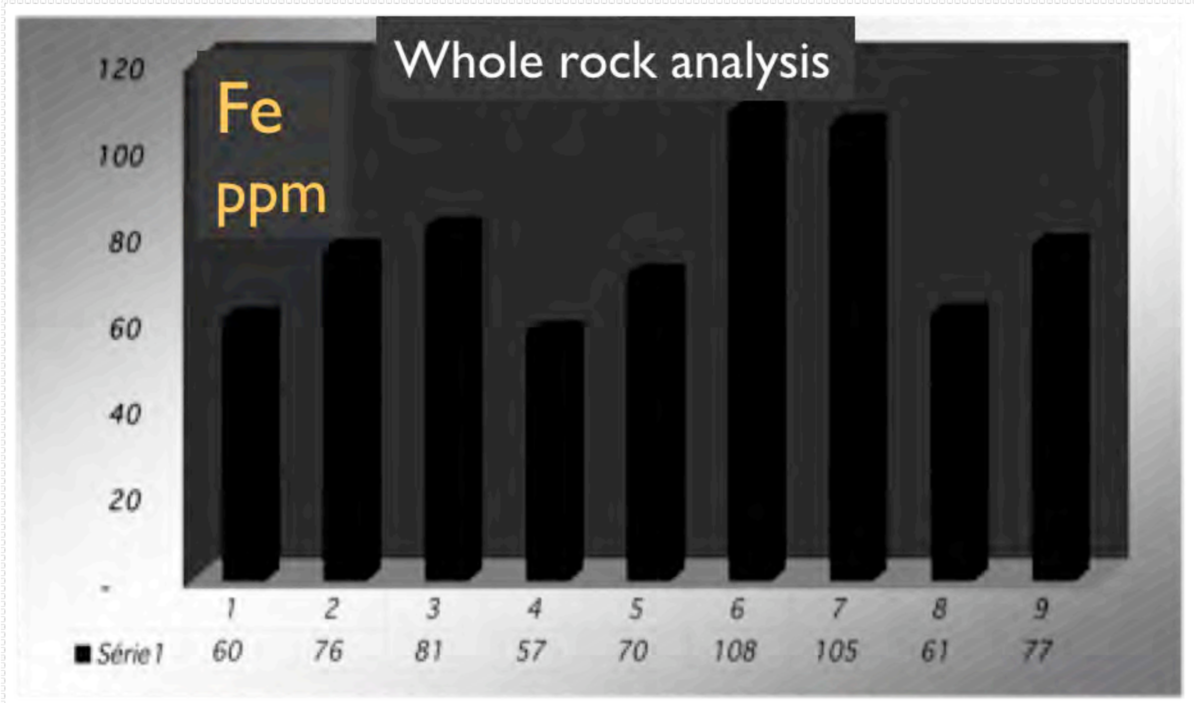
17 samples for iron isotopes
(non selective and selective)

+

cathodoluminescence

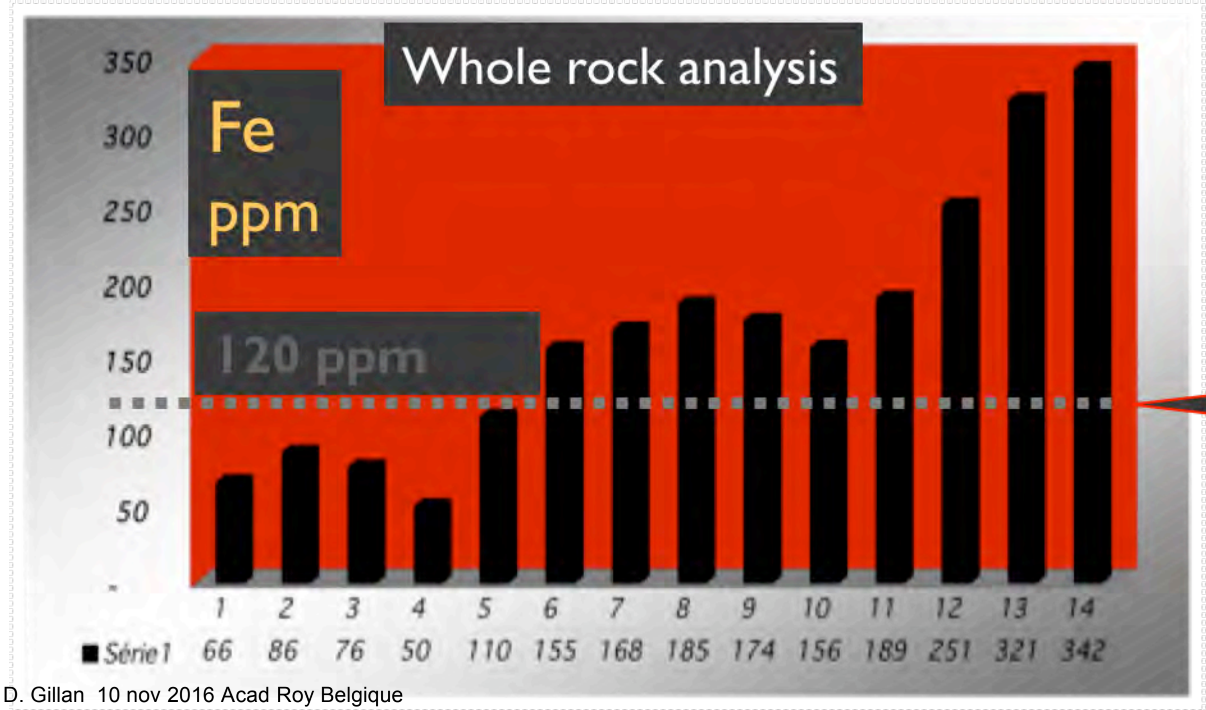
Red
Pink
Grey

The RED colour is NOT related to the iron content
but to its MINERALOGICAL PHASE



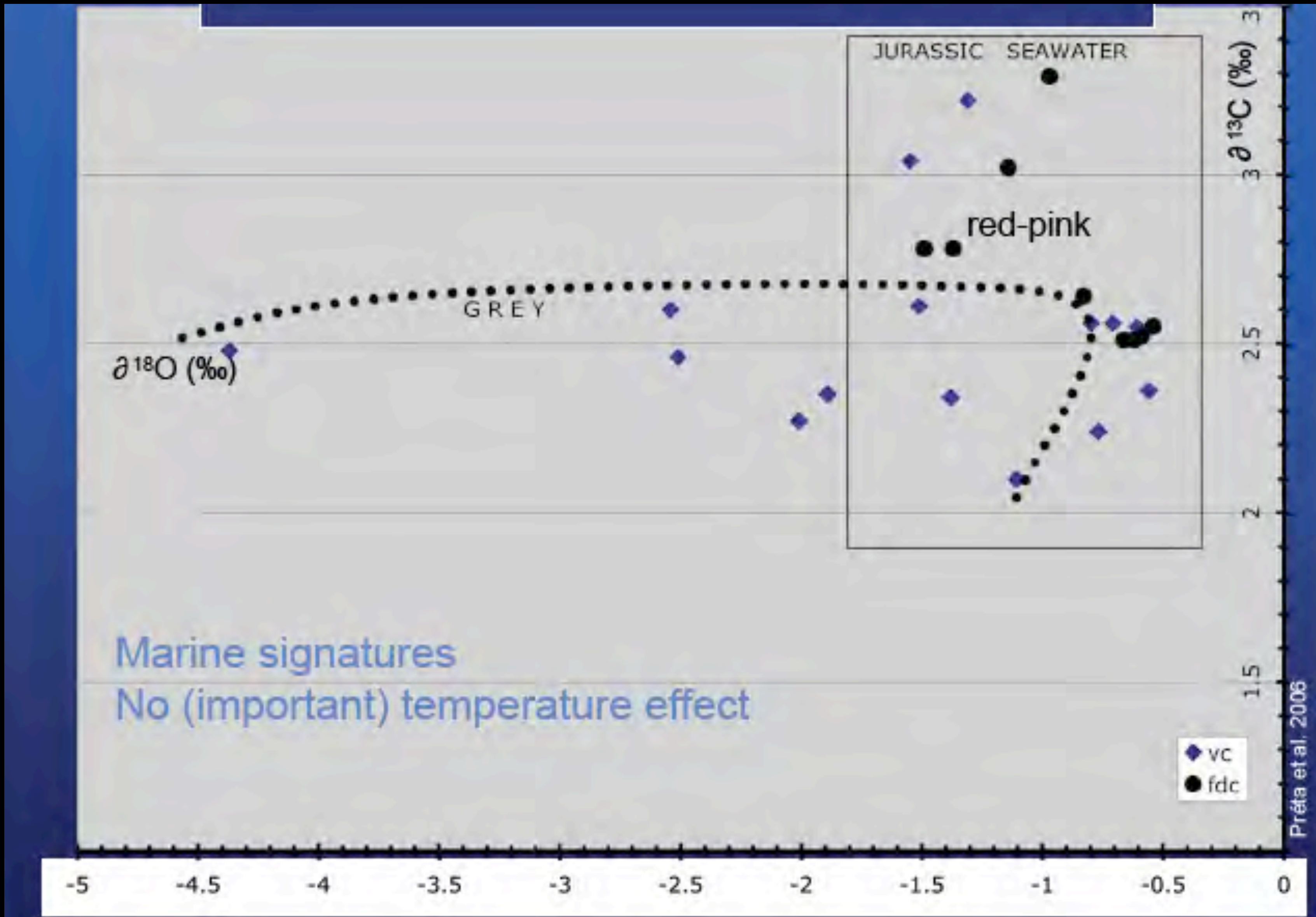
Grey
=
Crystal
Calcite
Lattice
+
Clays (...)

Fe^{2+} <300 ppm
[Miller, 1988]



Red
=
(Hydr)-
oxides

$\delta^{13}C$ vs $\delta^{18}O$ RAV



FIRST CONCLUSIONS

◊ The analyzed carbonates are pure: 88-98% [$CaCO_3$]

◊ No relation between Mn and Fe contents
===> early diagenetic mobility of Mn
confirmed by cathodoluminescence analysis
(not shown here) and SEM on Mn-oncoids (Sicily) (*id.*)

◊ Very low Sr contents (50-100 ppm)
===> no aragonitic precursor?

◊ No meteoric influence

First preliminary Results were discouraging!

WHOLE R-ROCK	$\delta\,^{56}Fe$ ‰	WHOLE G-ROCK	$\delta\,^{56}Fe$ ‰		Δ R-G ‰
#100/101R	-0.31	#100/101G	-0.28	=	-0.03
#102R	-0.06	#102G	-0.27	>	0.21
#160R	-0.39	#160G	-0.14	<	-0.25

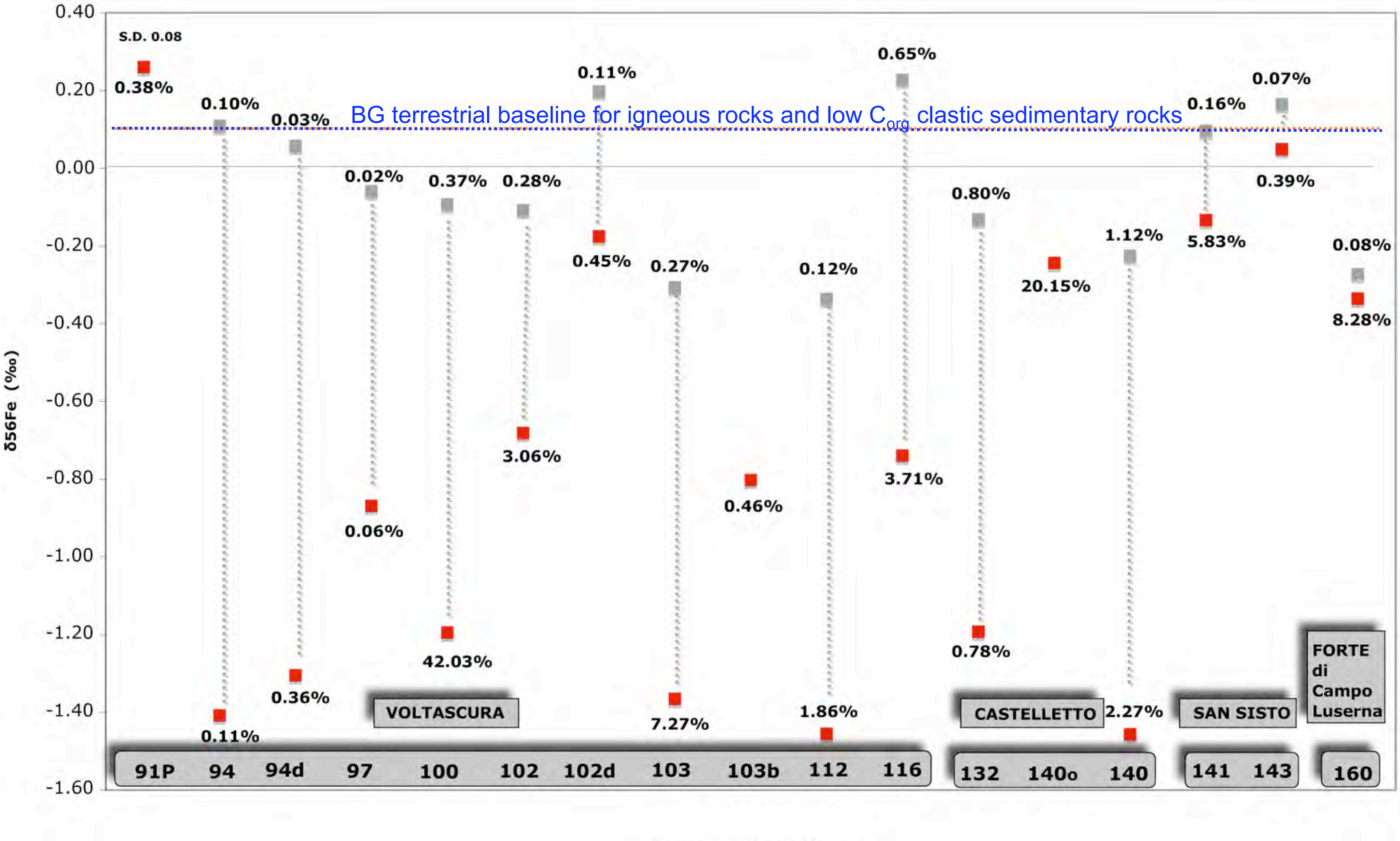
3M HCl/3h/50°C leach + total digestion residue

Hematite XRD

	$\delta^{56}Fe$ ‰	Δ LEACH-RES ‰		$\delta^{56}Fe$ ‰	Δ LEACH-RES ‰	Δ R-G ‰
#100/101R-LEACH	-1,11	0,08	#100/101G-LEACH	-0,21	-0,12	-0,90
#100/101R-RES	-1,19		#100/101G-RES	-0,09		-1,10
#102R-LEACH	-0,38	0,30	#102G-LEACH	-0,25	-0,14	-0,13
#102R-RES	-0,68		#102G-RES	-0,11		-0,57
#160R-LEACH	-0,02	0,32	#160G-LEACH	-0,39	-0,12	0,37
#160R-RES	-0,34		#160G-RES	-0,27		-0,07
Average Δ LEACH-RES		0,23			-0,13	
stdev		0,13			0,01	

+ 0.1M HCL/18h/25°C and 3M HCL/1h/50°C and 3M HCL/2h/25°C

VITAL EFFECT? or (BIO)FRACTIONATION FROM A MORE NEGATIVE SOURCE?



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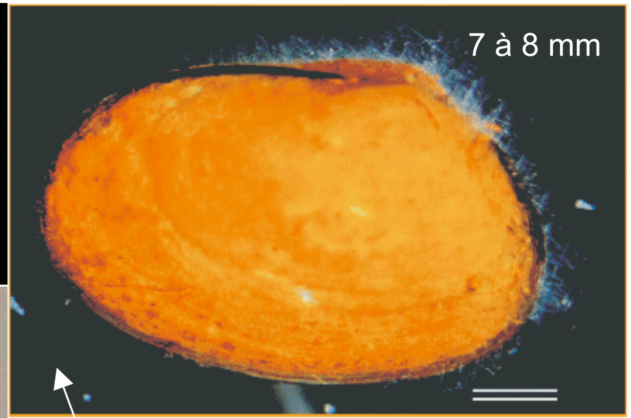
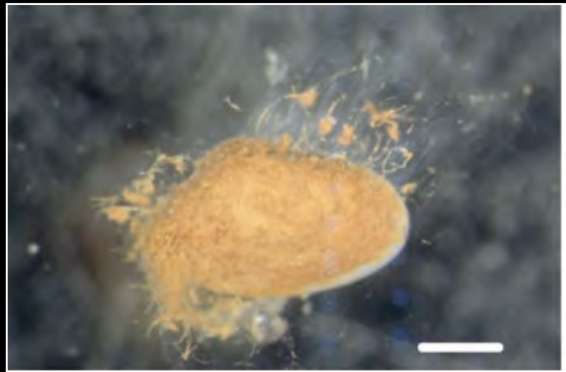
TRY TO SOLVE FROM THE RECENT?



LIVING MODELS

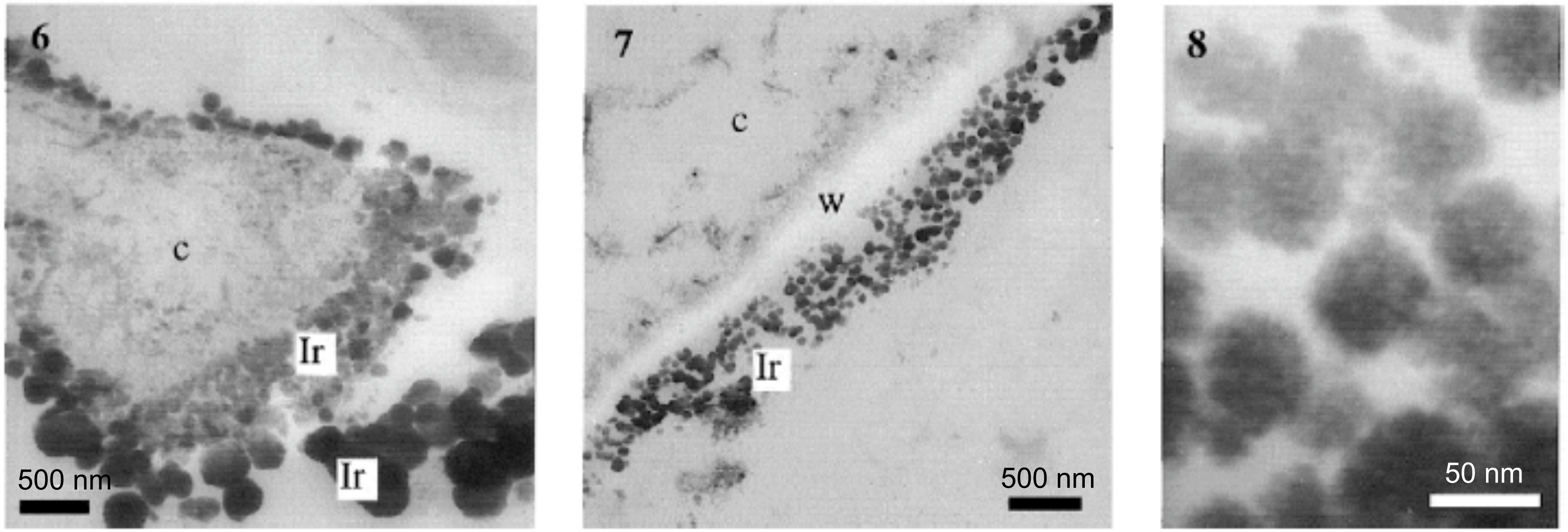
Going back again to biology…

IRON GRANULES IN THE BACTERIAL SHEATH
(*Montacuta ferruginosa*)



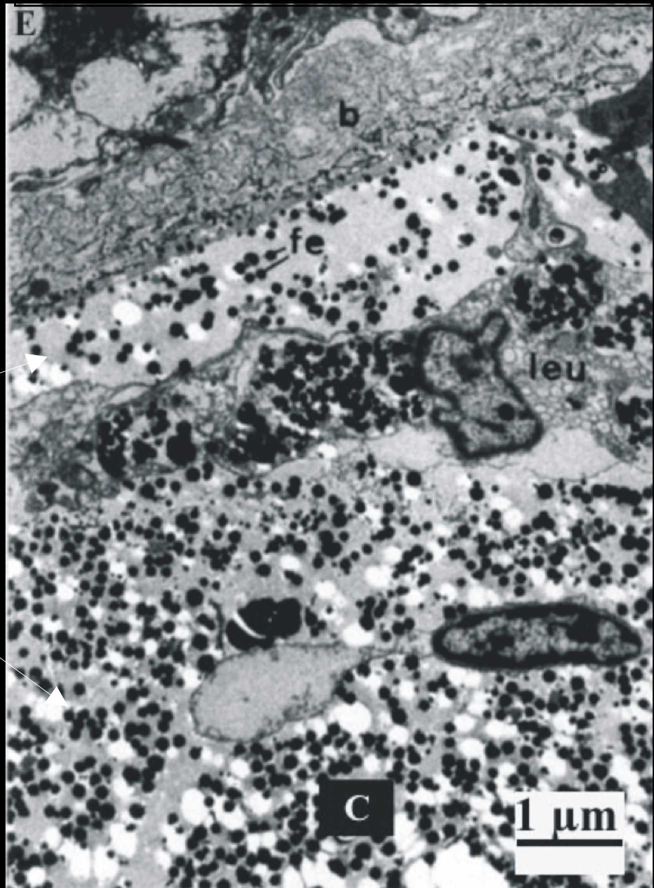
Transmission electron microscopy

Gillan & De Ridder 2001. *Chemical Geology* 177:371–379



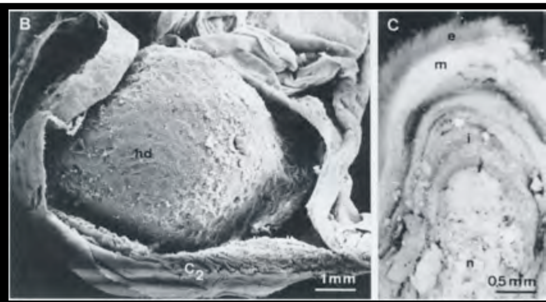
Nanoparticules

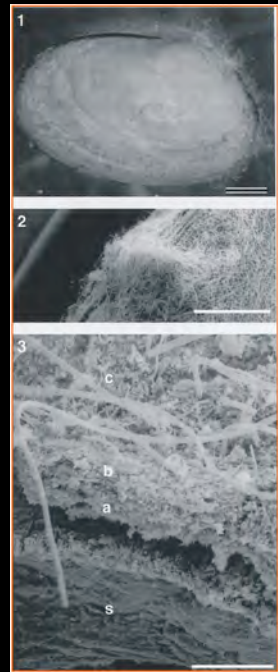
SECTION IN THE INTESTINAL WALL WITH IRON GRANULES IN THE CONNECTIVE TISSUE



INSOLUBLE
FERRIC
PHOSPHATE
(*E. cordatum*)

De Ridder 1994





OUTER LAYER WITH FERRIC IRON
(AMORPHOUS WITH Fe, P, Ca and TRACES of Si, Mg)
0.05-1µm (COLLOIDAL RANGE)
Infrared absorption spectra = amorphous iron oxyhydroxide gel with phoshate sorbed on the its surface rather than a pure ferric phosphate

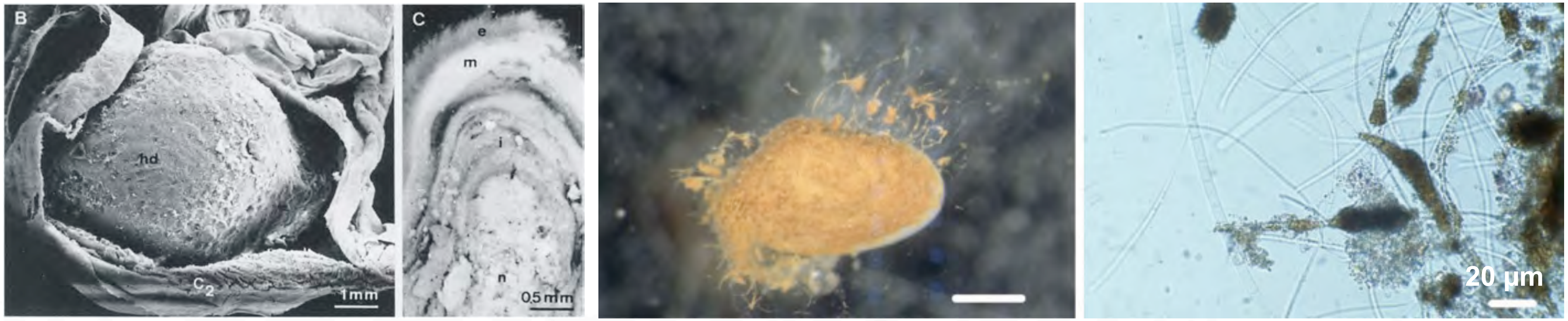


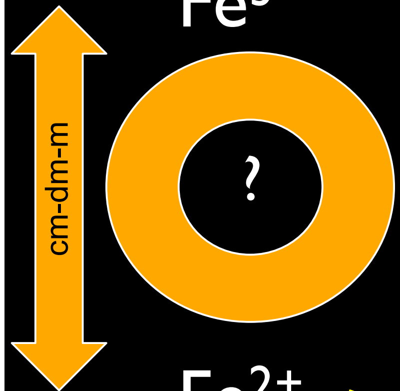
Table 2. Iron isotopic composition of iron-encrusted biofilms of *M. ferruginosa* (samples M1–M5) and iron-encrusted nodules and intestinal wall of *E. cordatum* (samples E1, E2, E3). First column gives the iron content (%) of the samples. Sample description in text. See Préat et al. (2008a, b) for comparison with iron isotopic composition of Rosso Ammonitico Veronese samples.

		δ^{56}Fe (‰)		δ^{57}Fe (‰)		
	% Fe	Avg	SD	Avg	SD	*n*
Bivalve M1	1.61	−0.84	0.04	−1.25	0.07	2
Bivalve M2	0.80	−0.74	0.01	−1.08	0.00	2
Bivalve M3	0.78	−1.66	0.04	−2.44	0.03	3
Bivalve M4	1.72	−1.14	0.04	−1.71	0.04	3
Bivalve M5	0.75	−1.15	0.01	−1.64	0.00	2
E1 nodule	2.73	−1.06	0.01	−1.54	0.01	2
E2 nodule	2.72	−0.76	0.06	−1.08	0.09	2
E3 wall	10.10	−1.78	0.02	−2.64	0.01	2

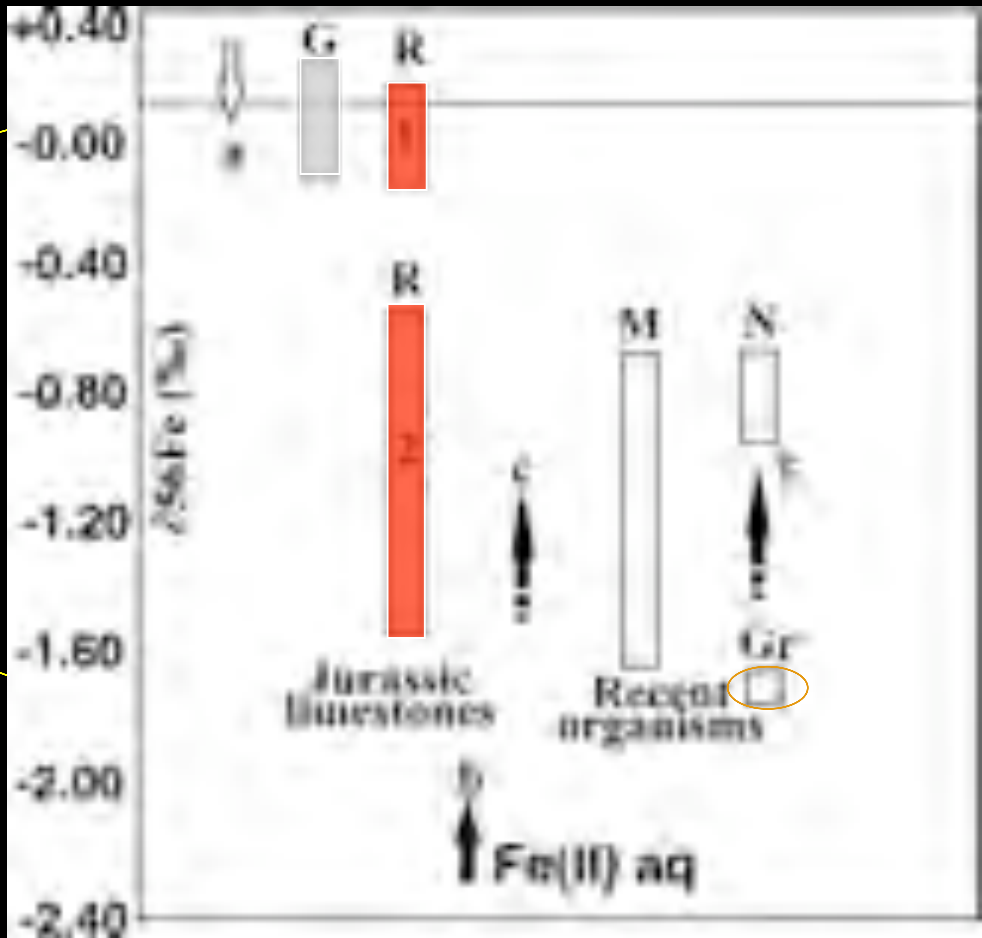
	%Fe	$\delta^{56}Fe$ (‰)		$\delta^{57}Fe$ (‰)		
		avg	sd	avg	sd	n
bivalve M1	1.61	-0.84	0.04	-1.25	0.07	2
bivalve M2	0.80	-0.74	0.01	-1.08	0.00	2
bivalve M3	0.78	-1.66	0.04	-2.44	0.03	3
bivalve M4	1.72	-1.14	0.04	-1.71	0.04	3
bivalve M5	0.75	-1.15	0.01	-1.64	0.00	2
E1 nodule	2.73	-1.06	0.01	-1.54	0.01	2
E2 nodule	2.72	-0.76	0.06	-1.08	0.09	2
E3 wall	10.10	-1.78	0.02	-2.64	0.01	2

Individual Fe atoms may undergo HUNDREDS of oxidation-reduction before ULTIMATE burial

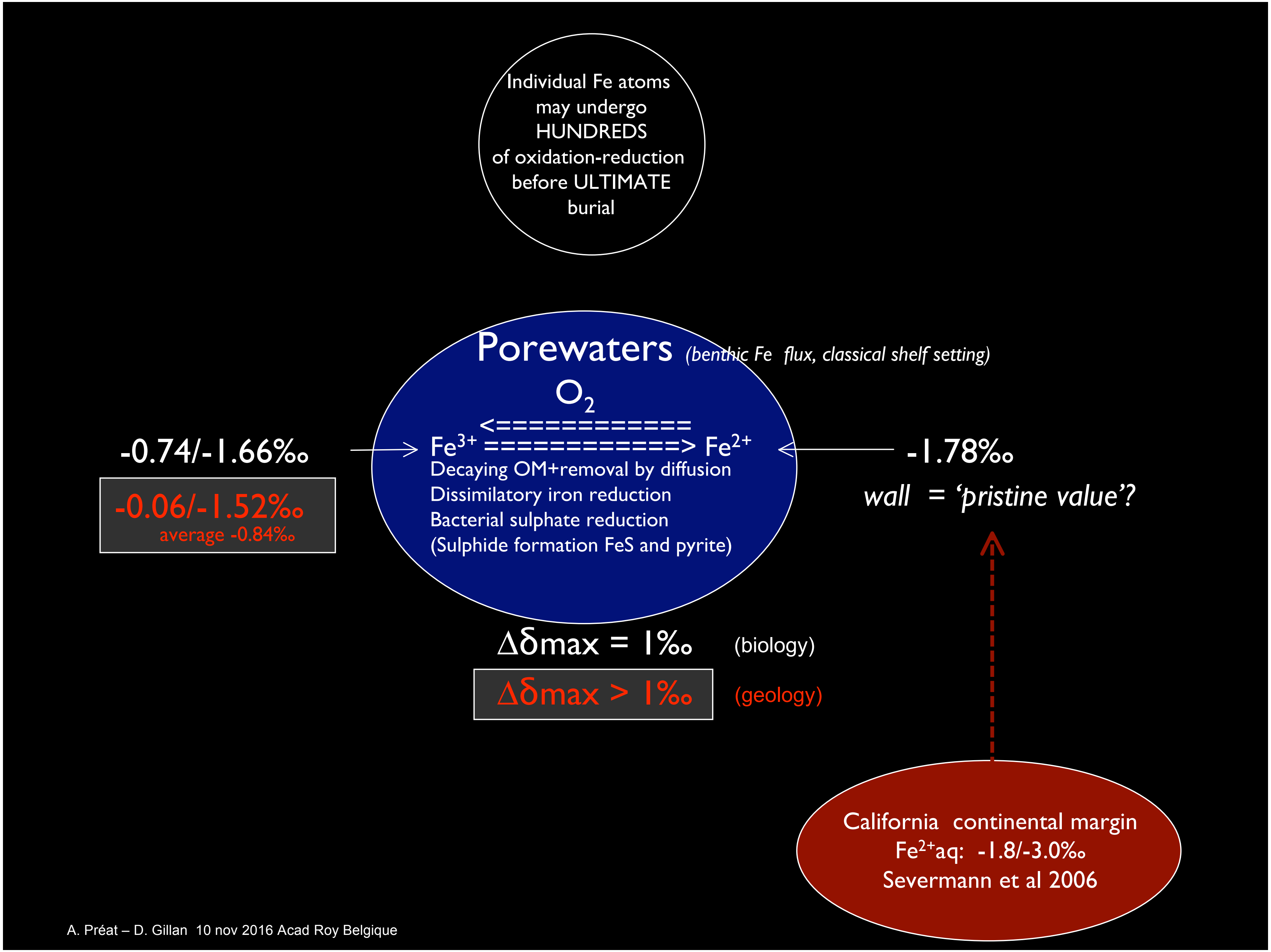
Fe^{3+}



Fe^{2+}



Decaying OM + removal by diffusion
Dissimilatory iron reduction
Bacterial sulphate reduction



Individual Fe atoms may undergo HUNDREDS of oxidation-reduction before ULTIMATE burial
Porewaters (benthic Fe flux, classical shelf setting)
O2
<=============
Fe3+ =============> Fe2+
Decaying OM+removal by diffusion
Dissimilatory iron reduction
Bacterial sulphate reduction
(Sulphide formation FeS and pyrite)
-0.74/-1.66‰
-0.06/-1.52‰
average -0.84‰
-1.78‰
wall = 'pristine value'?
Δδmax = 1‰ (biology)
Δδmax > 1‰ (geology)
California continental margin
Fe2+aq: -1.8/-3.0‰
Severmann et al 2006
A. Préat – D. Gillan 10 nov 2016 Acad Roy Belgique

CONCLUSIONS

1. The red color is related to the submicronic hematite/goethite dispersed in the matrix. The hematite is a result of the activity of iron bacteria and Fungi that precipitated Fe-Mn hydroxydes at dysoxic sediment-water interfaces

2. The iron contents are comparable in red, pink and grey facies

3. The iron bacteria have passively 'fractionated' the iron isotopes at an infra-millimetric scale

4. Comparison of the Fe isotopic compositions of the 'biominerals' in the Recent organisms and the red-grey Jurassic facies suggest an isotopic biofractionation of at least +0.7 ‰, and around 1‰ (or more in the Ammonitico Rosso)

5. The Recent sea-urchin and the bivalve thrive in similar microenvironmental conditions as the microorganisms of the Jurassic condensed red facies.

A biosignature is probably present….

THANK YOU

Future Research

Biosignature ?

$Fe^{2+}aq$