BACTERIAL ORIGIN OF SELECTED PHANEROZOIC RED CARBONATE ROCKS

(2/2)

Alain PREAT, University of Brussels
apreat@ulb.ac.be

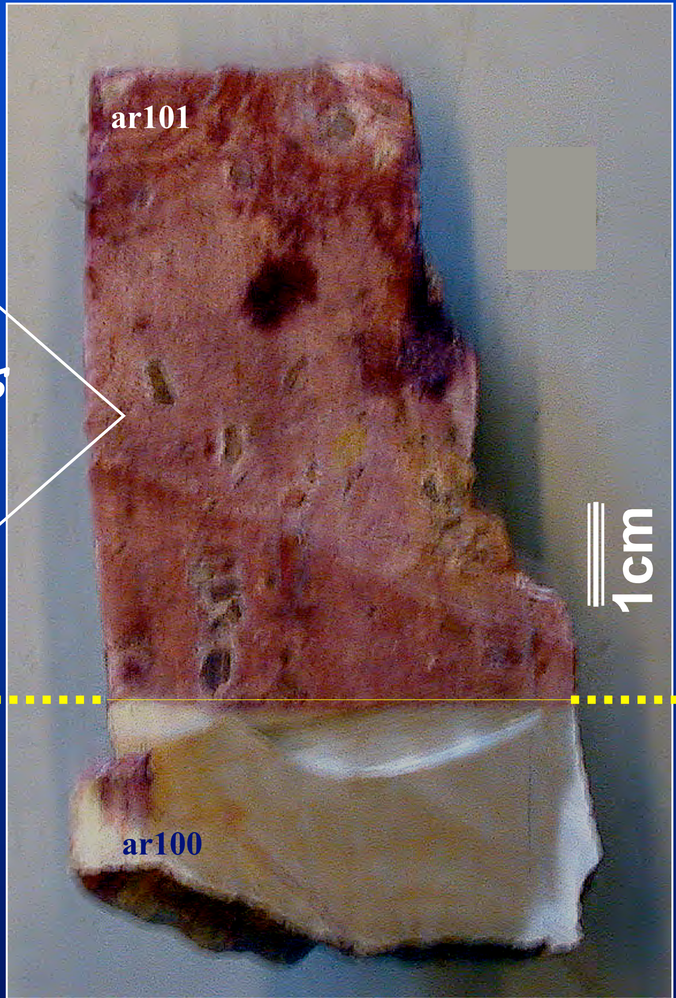
Torino, Nov 2009

- 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

^{56}Fe 91,76%
^{54}Fe 5,84 %
^{57}Fe 2,12 %
^{58}Fe 0,28 %

What about Fe-isotopes?

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



Voltascura Quarry

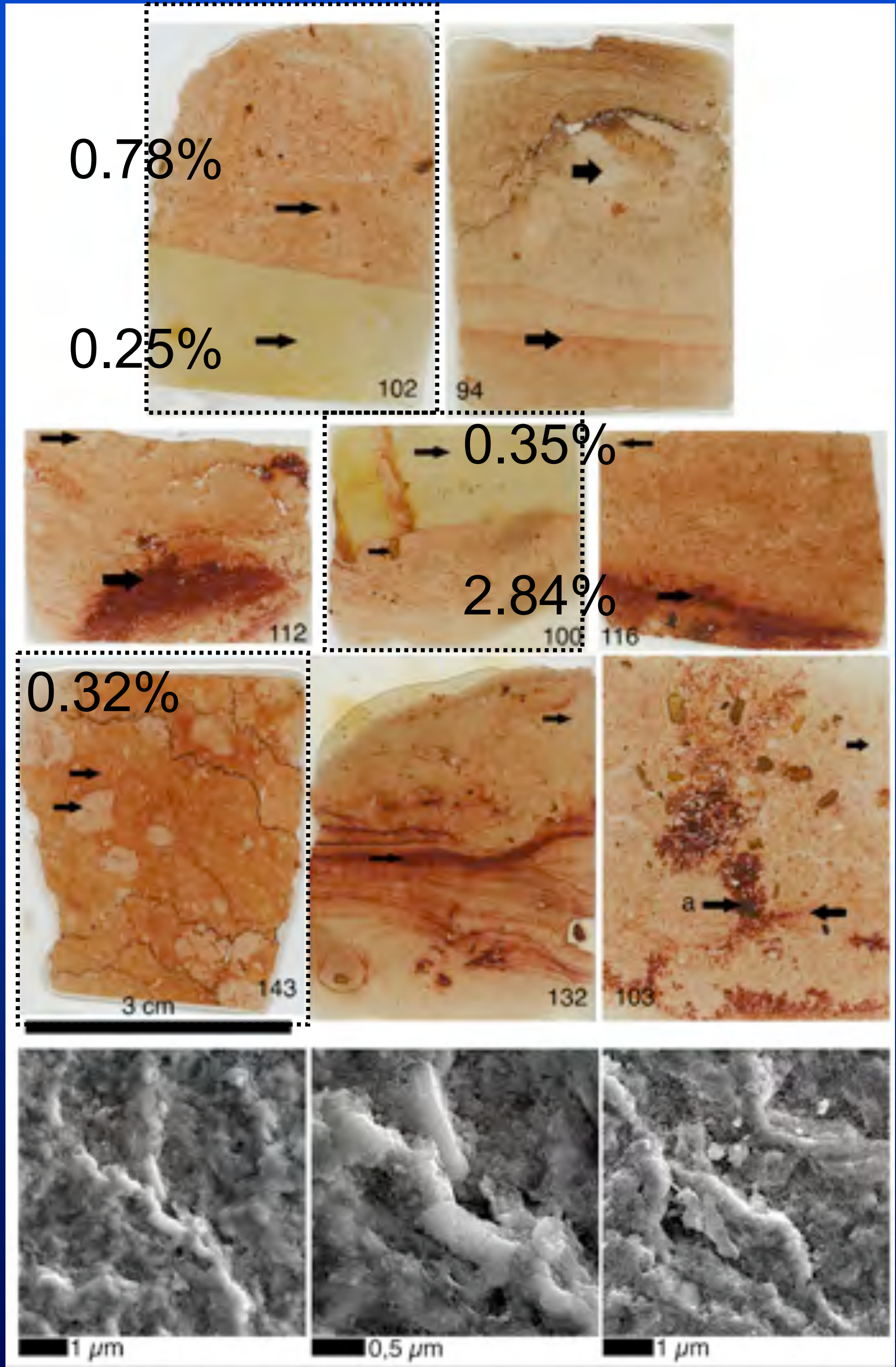
RAI

hiatus

Calcari Grigi

U. Bajocian - L. Callovian

Hettangian - Domerian



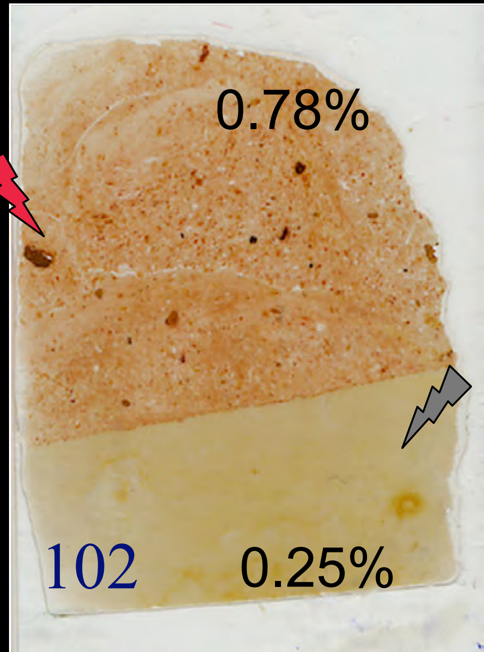
PREAT et al. 2008

total Fe_2O_3

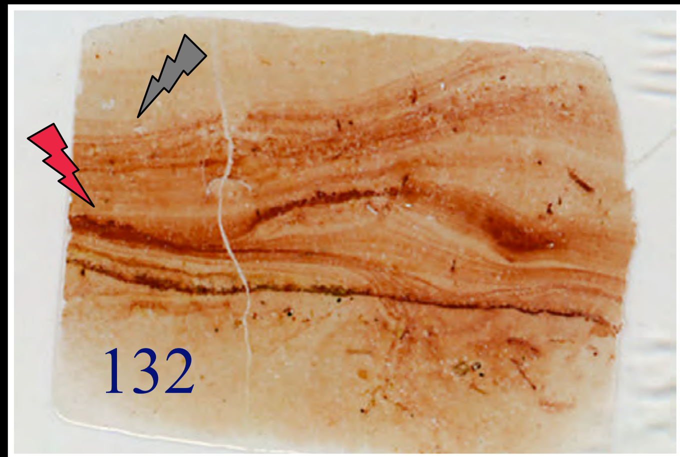
100G = 0.35%
100R = 2.84%

102G = 0.25%
102R = 0.78%

143R = 0.32%



3 cm

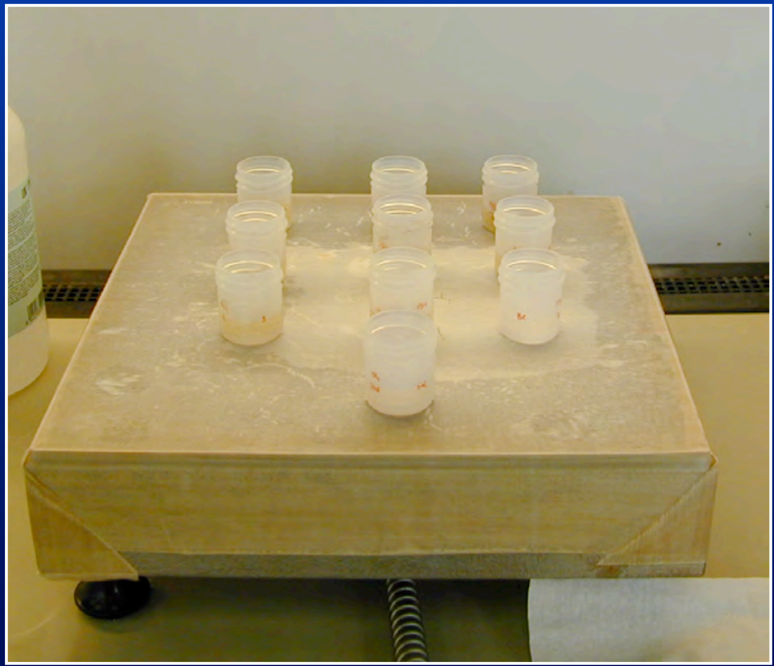


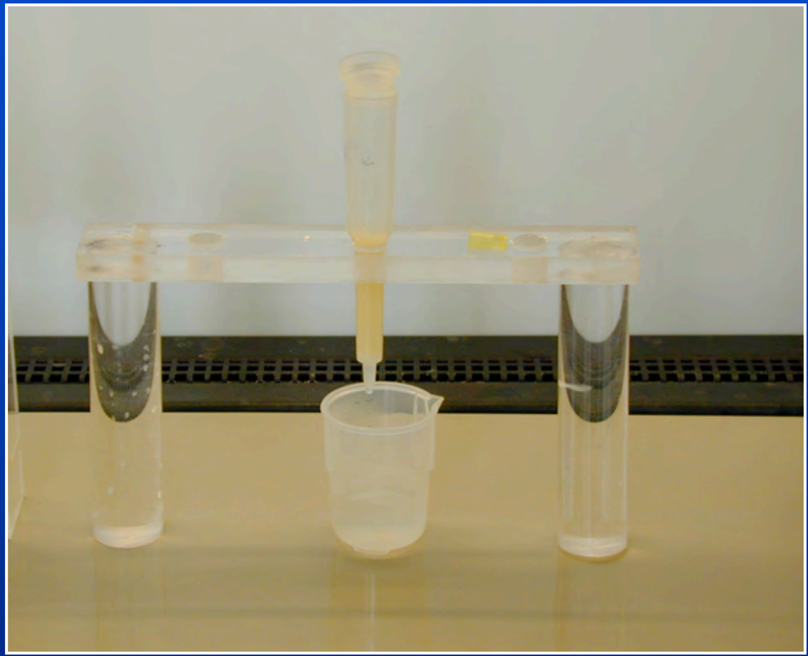
Sample preparation

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

- $\partial\ ^{56}Fe = (^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM014} - 1) \times 10^3$
- 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 $\partial\ ^{56}Fe$ (1 sigma; n =21) for a basalt relative to IRMM014.

Analysis : 160 €/sample
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)
- $\partial\,^{18}O$- $\partial\,^{13}C$ (selective microdrillings)

+

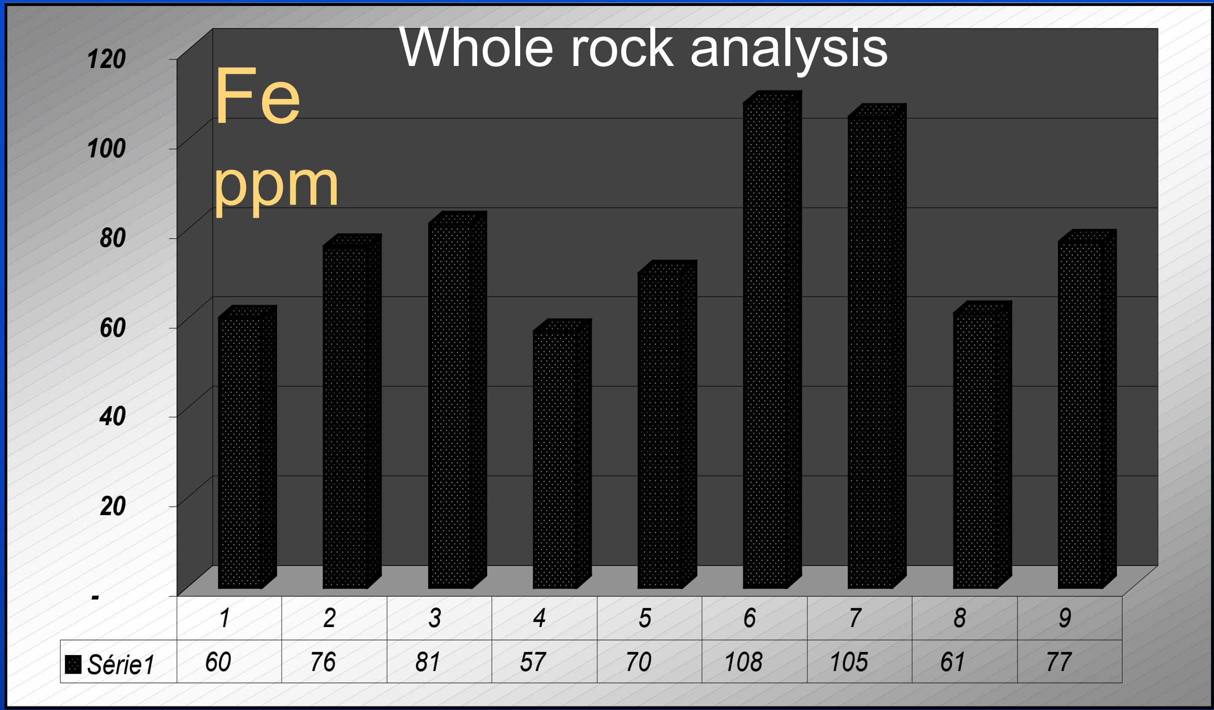
17 samples for iron isotopes
(non selective and selective)

+

cathodoluminescence

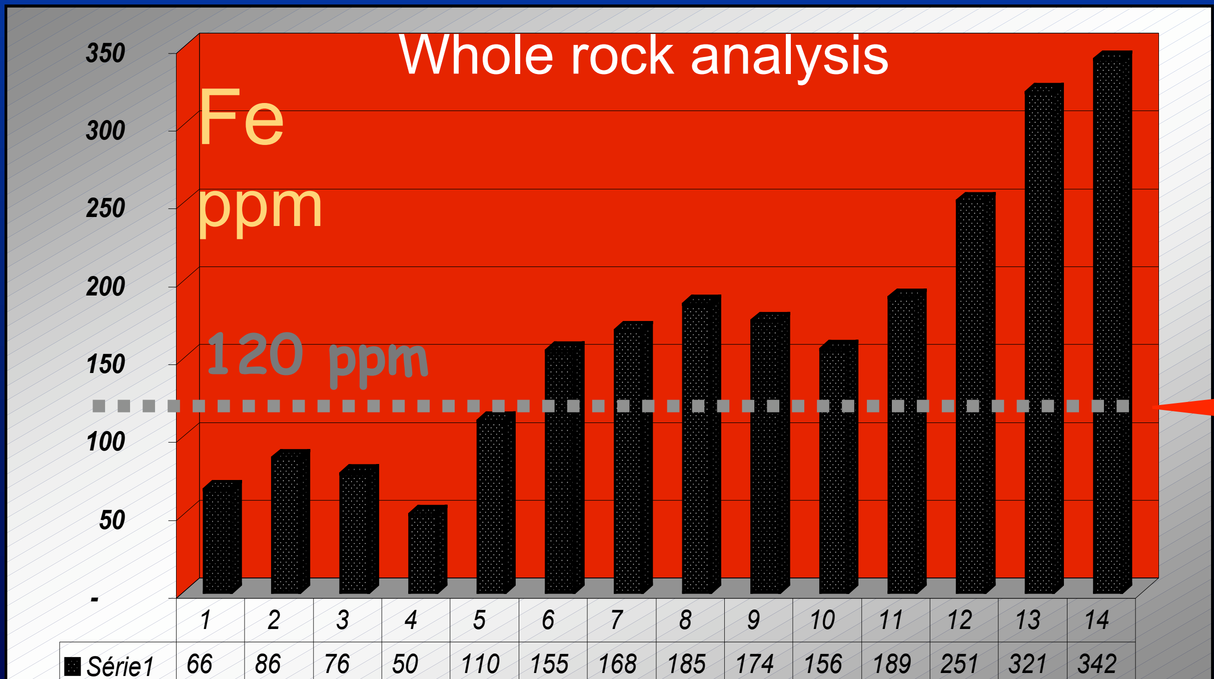
Red
Pink
Grey

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



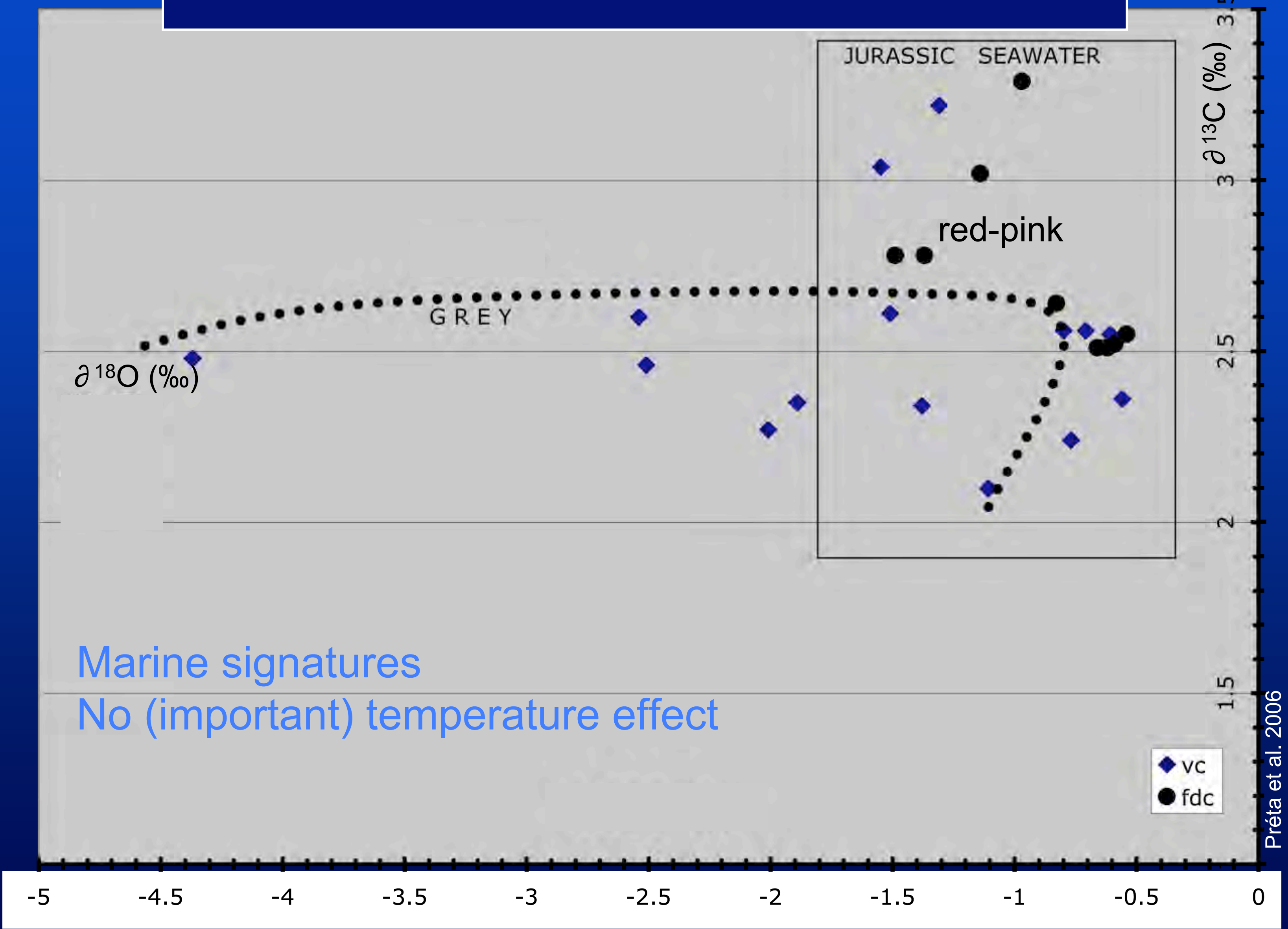
Grey
=
Crystal
Calcite
Lattice
+
Clays (...)

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



Red
=
(Hydr)-
oxides

∂ ^{13}C vs ∂ ^{18}O RAV



Marine signatures
No (important) temperature effect

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

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

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

	δ56Fe ‰	Δ LEACH-RES ‰		δ56Fe ‰	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?

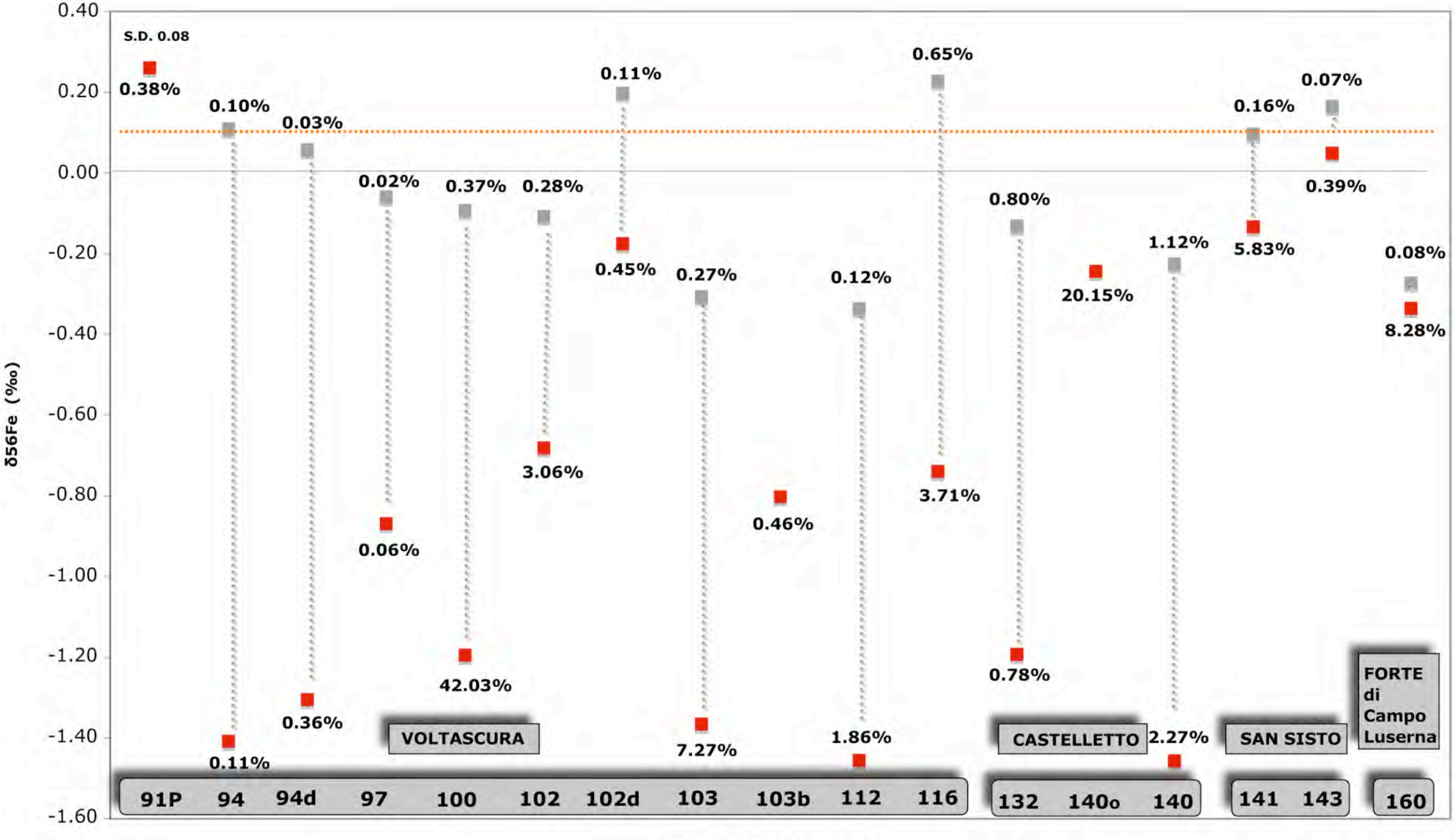
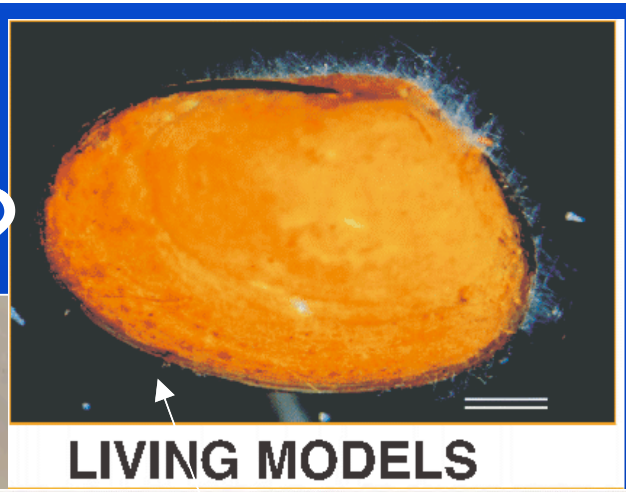


Fig. 4. RAV samples

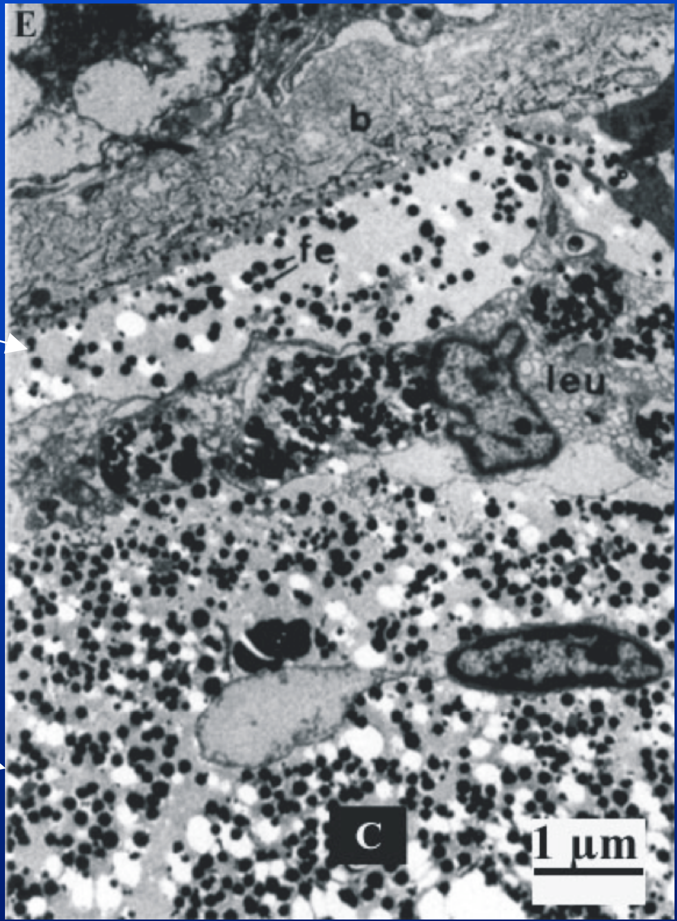
Préat et al. 2008

TRY TO SOLVE FROM THE RECENT?

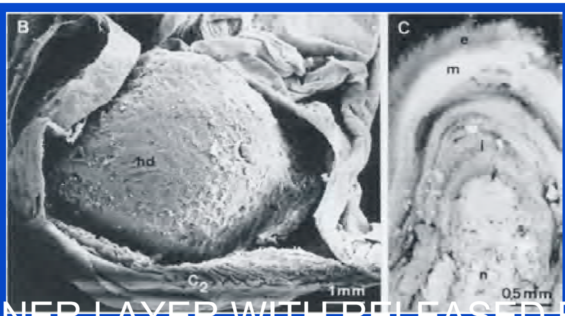


SECTION IN THE INTESTINAL WALL WITH IRON GRANULES IN THE CONNECTIVE TISSUE

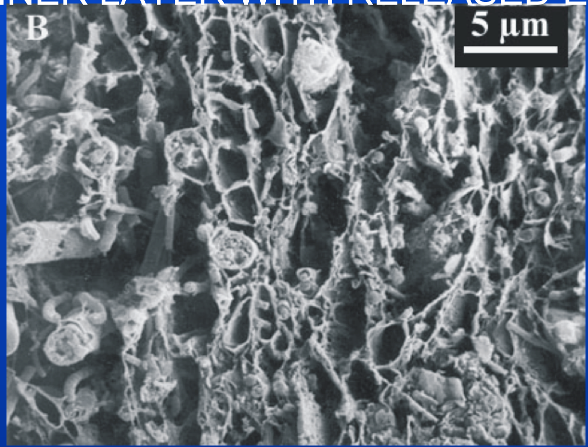
INSOLUBLE FERRIC PHOSPHATE

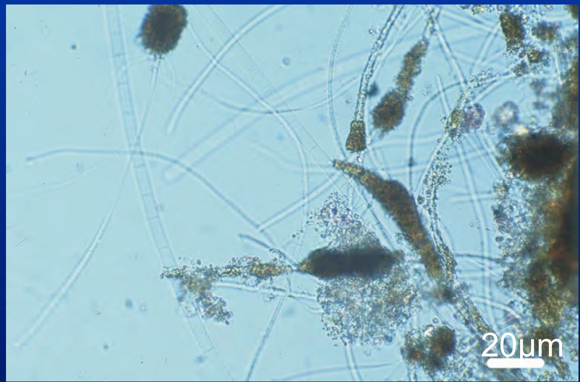


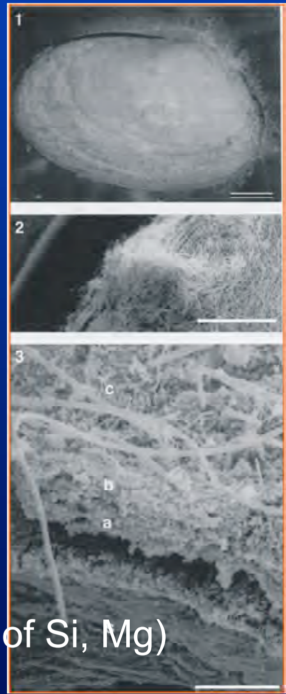
De Ridder 1994



INNER LAYER WITH RELEASED EPS







De Ridder and Gillan 2003

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

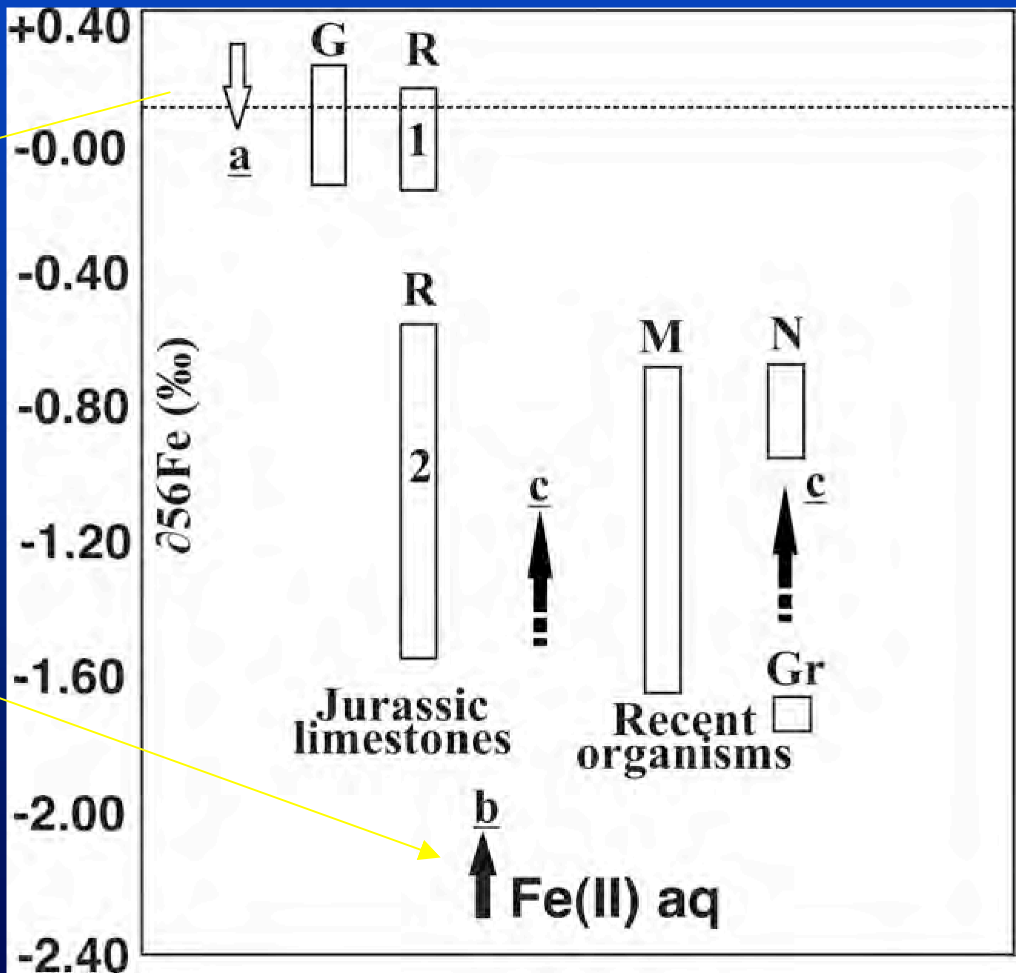
	%Fe	$\delta^{56}Fe$ (‰)		$\delta^{57}Fe$ (‰)		
		avg	sd	avg	sd	n
bivalve M1	1.61	-0.84	0.04	-1.25	0.07	2
bivalve M2	0.80	-0.74	0.01	-1.08	0.00	2
bivalve M3	0.78	-1.66	0.04	-2.44	0.03	3
bivalve M4	1.72	-1.14	0.04	-1.71	0.04	3
bivalve M5	0.75	-1.15	0.01	-1.64	0.00	2
E1 nodule	2.73	-1.06	0.01	-1.54	0.01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

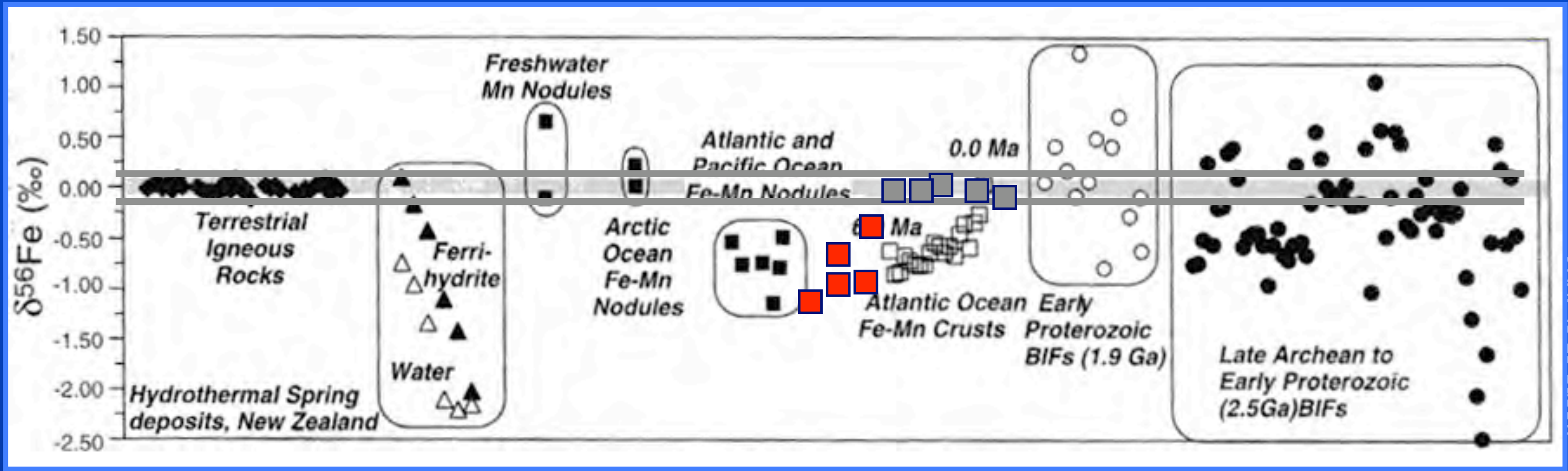
Fe^{3+}

Fe^{2+}

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



Préat et al. in press



∂ ^{56}Fe 'BIO'-FRACTIONATION

Microenvironmental significance
and
No paleogeographical significance

CONCLUSIONS (PRELIMINARY CONCLUSIONS)

1. The red color is related to the submicronic hematite 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 the red, pink and grey facies

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

4. The Fe isotope signature of the 180 Ma red RAV is similar to the Fe isotope compositions of the Recent (Atlantic and Pacific) Fe-Mn nodules and crusts

5. 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 ‰

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

Intertidal

Recent, Roscoff (France)

terrier

chemical oxidation

ORIGIN OF IRON?

Bensing et al. 2005 (JSR)
Importance of clay in iron transport and sediment reddening: evidence from reduction features of the clastic Permian Abo Fm, New Mexico, USA.

'... the detrital iron-bearing clay-size material (kaolinite an illite with 8.4% FeO total) is the primary source of iron in Abo Fm. The chemical and mineralogical data from those clays indicate that the ferric oxyhydroxides (10-20 µm) associated with the clays are a more important source than the iron from the clay crystal structure...'

... Kaolinite does not contain iron in the crystal structure, yet it is effective in transporting on the surfaces of clay particles as oxides and hydroxides....'

HOFSTETTER et al. 2003 (EST)
... Clays transport Fe^{3+} (ferric oxyhydroxides) AND Fe^{2+} ...

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

Porewaters *(benthic Fe flux, classical shelf setting)*

O_2

<============

-0.74/-1.66‰ → Fe^{3+} ============> Fe^{2+} ← -1.78‰

Decaying OM+ removal by diffusion
Dissimilatory iron reduction
Bacterial sulphate reduction
(Sulphide formation FeS and pyrite

-0.06/-1.52‰
average -0.84‰

wall = 'pristine value'?

$\Delta\,\partial$ max = 1‰

$\Delta\,\partial$ max > 1‰

Arabian Sea
Fe^{3+} and Fe^{2+}: -0.19/-0.77‰
Staubwasser et al 2006

California continental margin
Fe^{2+}aq: -1.8/-3.0‰
Severmann et al 2006

ANCIENT RESEARCH ...

Delhaye 1908 .... Fe//clays! (//red)

FUTURE RESEARCH ...

$Fe^{2+}aq$

BEAR IN MIND…

to continue…?

1. **Mineralogical fractionation?**

   Ferrihydrite ($FeOH_3$ reddish-brown, amorphous 'crystals), from (a)biotic oxidation, yields well-ordered, strongly crystalline, stable minerals such as hematite (Fe_2O_3) and goethite (FeOOH) over a period of weeks to months (Cornell & Schetmann 1996)

2. **(Mineralogical)-T° fractionation?**

   a. Equilibrium isotope fractionation between Fe^{II}-Fe^{III} (∂ ^{56}Fe) at 22°C is +2,75‰ and there is no fractionation at 98°C between Fe^{III} and hematite (Beard et al 2003).
   b. Isotope fractionations should decrease with increasing T° (Cu, high hydrothermal activity >300°C, Larson et al 2003)

3. **Leaching (complex!) interpretation**

   Fe^{III} reducing bacteria are able to remove 20-50% of the total clay-bound iron and therefore alter the physical and chemical characteristics of the clays (smectite) (Kostka et al 1999, 2002)