

Mardi 28 novembre 2006

**Micro analyse quantitative des éléments traces  
dans la calcite de la coquille Saint Jacques  
(*Pecten maximus*) par Ablation Laser ICP-MS:  
une archive journalière de la biogéochimie des  
environnements côtiers tempérés**

**Quantitative trace element micro analysis in  
calcite shell of the Great Scallop (*Pecten  
maximus*) by Laser Ablation ICP-MS: a daily  
archive of the biogeochemistry in temperate  
coastal environments**

Aurélie BARATS

# Outlines

## 1. Introduction

## 2. Methodological approach

2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

2.2. Application to the Great Scallop shell

## 3. Significance of trace element shell profiles

3.1. Background shell concentrations

3.2. Episodic shell enrichments of Ba, Mo and Mn

## 4. Conclusion







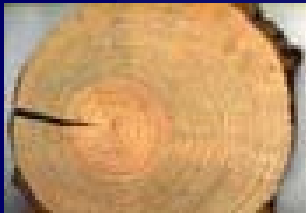
# 1. Introduction

# 1. Introduction

## Scientific context

Need for historical, archeological or paleo ecological archives for the study of environmental changes (climatic, biological, and anthropogenic)

### Continental ecosystem



Tree rings



Ice cores



Peat bogs



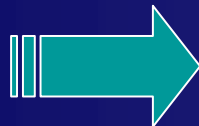
### Marine ecosystem



Cores of sediment



Corals



Need for archives of coastal environment



### Bivalve shells:

- Marine coastal environment for all latitudes;
- Incremental  $\text{CaCO}_3$  growth layers on their skeletal structure.

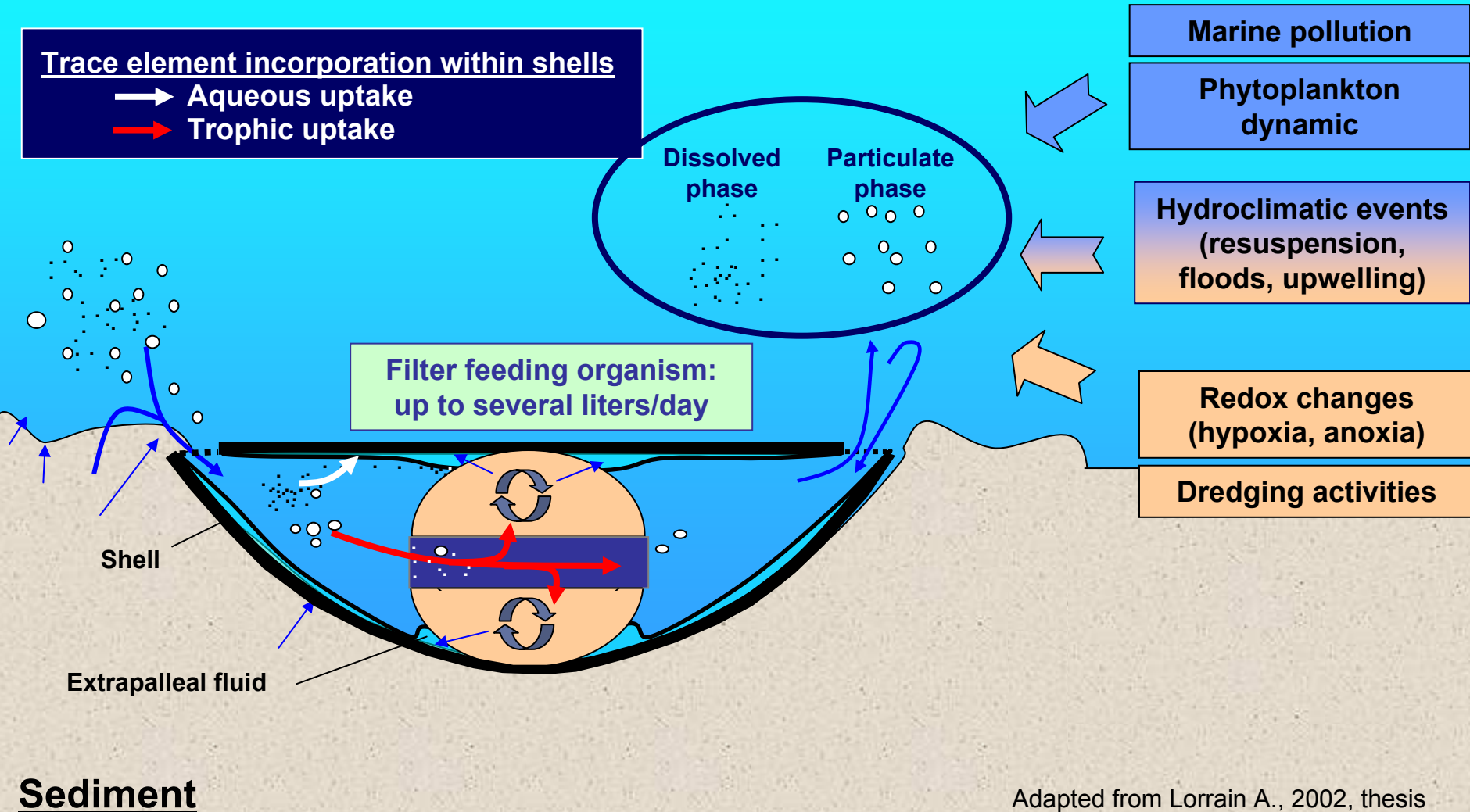
# 1. Introduction

Water column

Trace element enrichment in bivalve shells

Trace element incorporation within shells

- Aqueous uptake
- Trophic uptake



# 1. Introduction

## Pioneering studies

### Bivalves

#### Mussels

(Vander Putten et al. 2000)



*Mytilus edulis*

#### Clams

(Stetcher et al. 1996)



*Spisula solidissima*



*Mercenaria mercenaria*

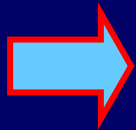
Scheldt estuary  
(Netherland)



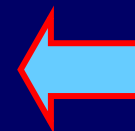
Temperate coastal  
environment



Chesapeake bay  
(USA)



Mg and Sr: tracer of seawater temperature

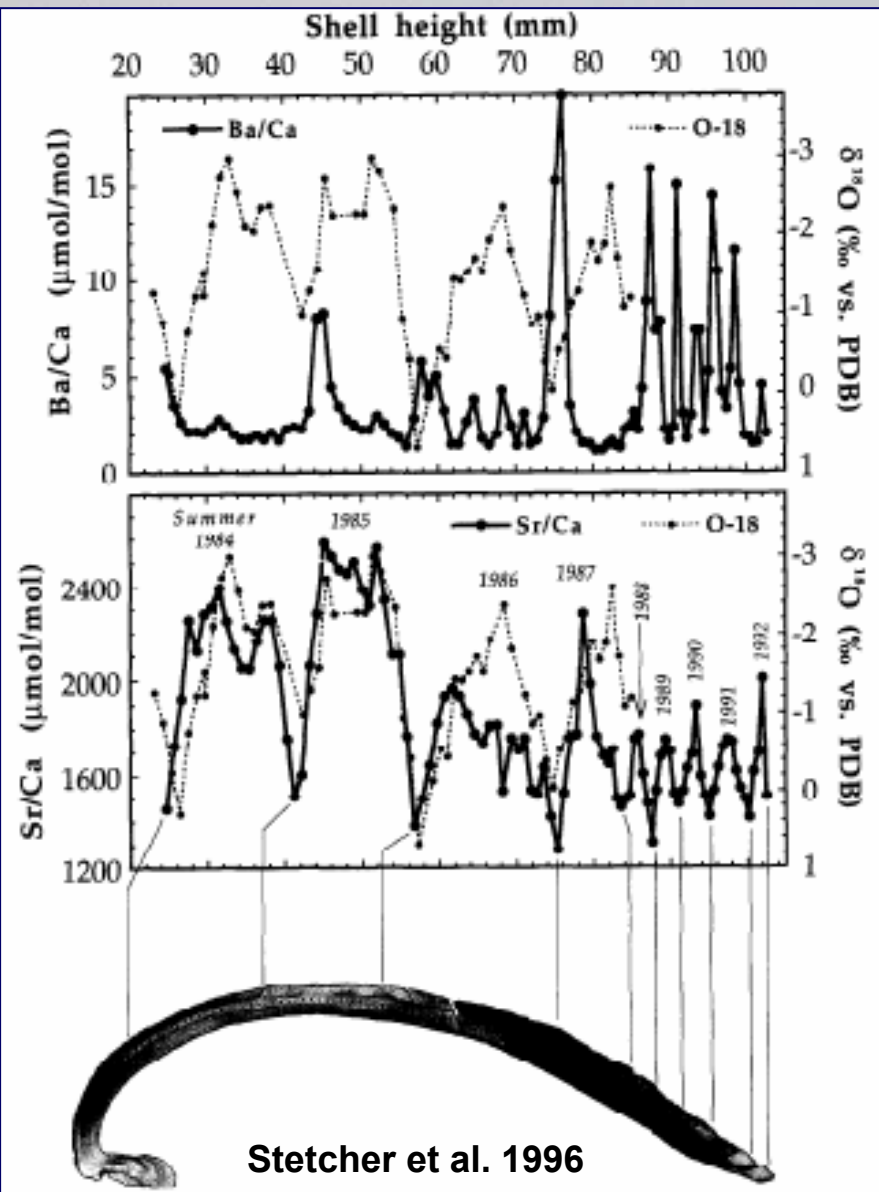


Ba and Mn: tracer of phytoplankton blooms



# 1. Introduction

## Pioneering studies



### Advances:

- Micro analyses by LA-ICP-MS of bivalves
- Potential tracers of environmental changes

### Limitations:

- Semi-quantitative analyses (No matrix-matched standards)
- Seasonal variations with an approximate datation

# 1. Introduction

## The Great Scallop shell *Pecten maximus*

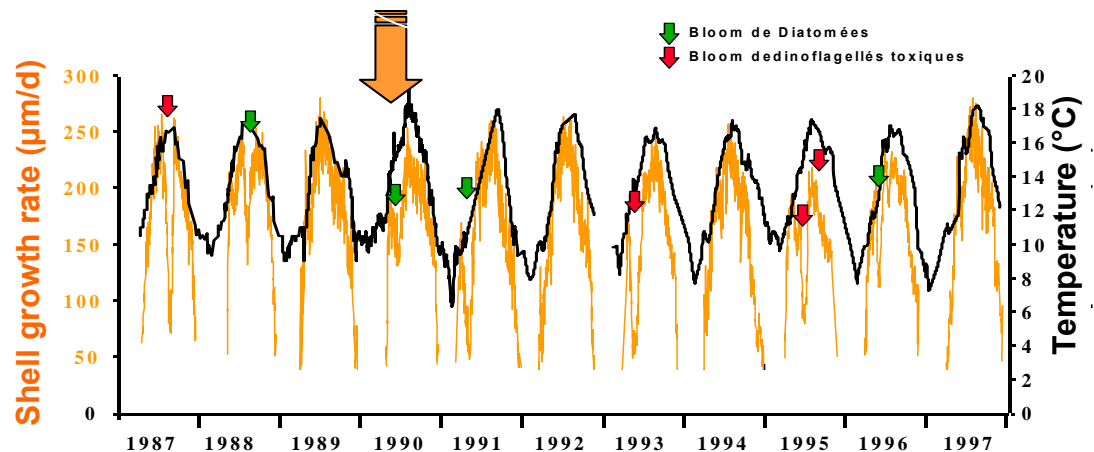
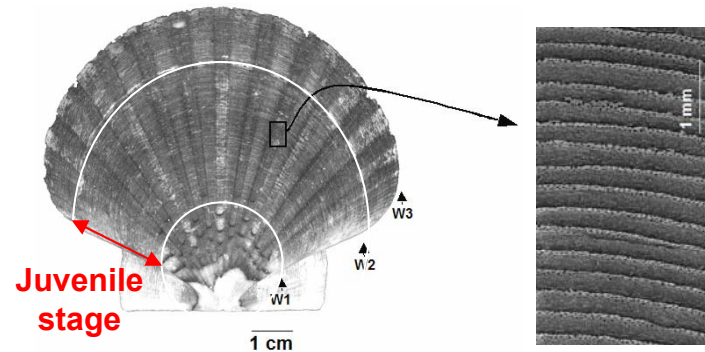
### Geographical distribution

- Coastal environment with low anthropogenic impact
- Latitude: 30-60 °N
- Bathymetry: 1-500 m



### Shell growth rate:

- Daily striae (50-300µm)
- Proxy of seawater temperature
- Influenced by the trophic uptake
- 9 months/year (47°N)





# 1. Introduction

## Objectives

Analytical tool:  
Laser Ablation ICP-MS  
(LCABIE)

Biological tool:  
The Great Scallop *Pecten maximus* (L.)  
(LEMAR, IUEM)

Bioanalytical tool:  
Definition of trace element  
shell profiles

Frequent monitoring of coastal  
ecosystem  
(IFREMER, SOMLIT, MAREL)

Environmental significance of these trace element shell profiles

Trace element shell profiles: tracer/proxy of environmental conditions?

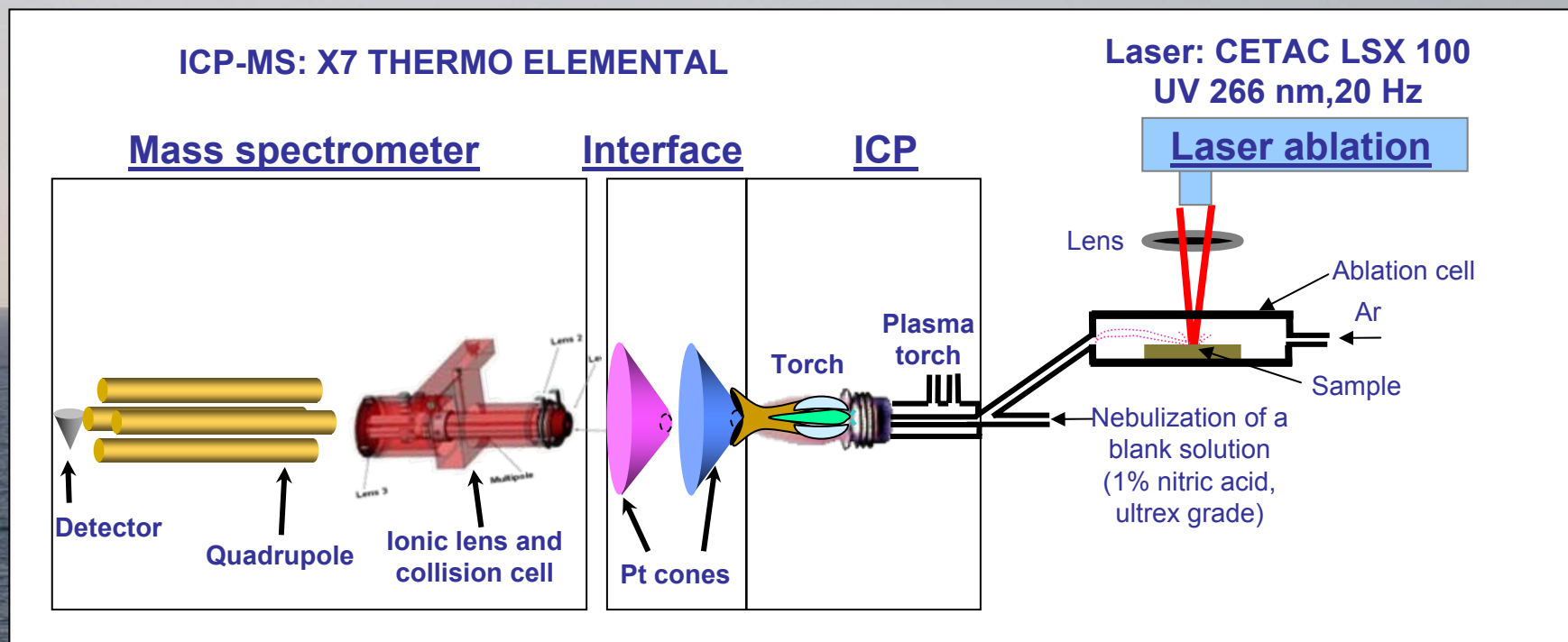
## **2. Methodological approach**

### **2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix**

# 2. Methodological approach

## 2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

### Analytical methods



### Advantages of this analytical technique:

- ✓ Multi elemental analysis (Mo, Ba, Pb, Mn,...)
- ✓ Micro analyse (20-100  $\mu\text{m}$ )  $\rightarrow$  1 day
- ✓ Sensitive: detection limits in the 10ng/g range



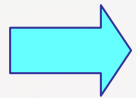
# 2. Methodological approach

## 2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

### Problems and issues of this method

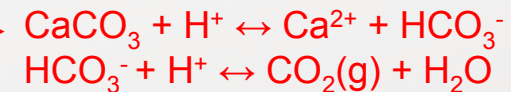
**Calibration:** No CaCO<sub>3</sub> certified standards

Macs 1 (USGS; ≈100 µg.g<sup>-1</sup>; certification in progress)



### Preparation of CaCO<sub>3</sub> standard pellets

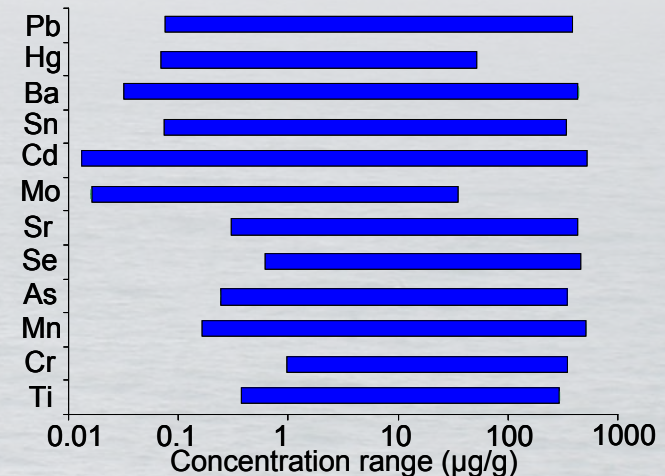
1- Dissolution of pure CaCO<sub>3</sub> powders with HNO<sub>3</sub> (ultra grade)



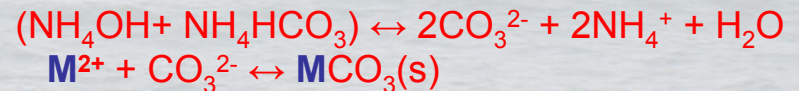
2- Spike with a multi elemental solution (25 elements) → 13 concentrations

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Db	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cs	Es	Fm	Md	No



3- Co-precipitation



4- Drying of the precipitates

5- Certification in lab

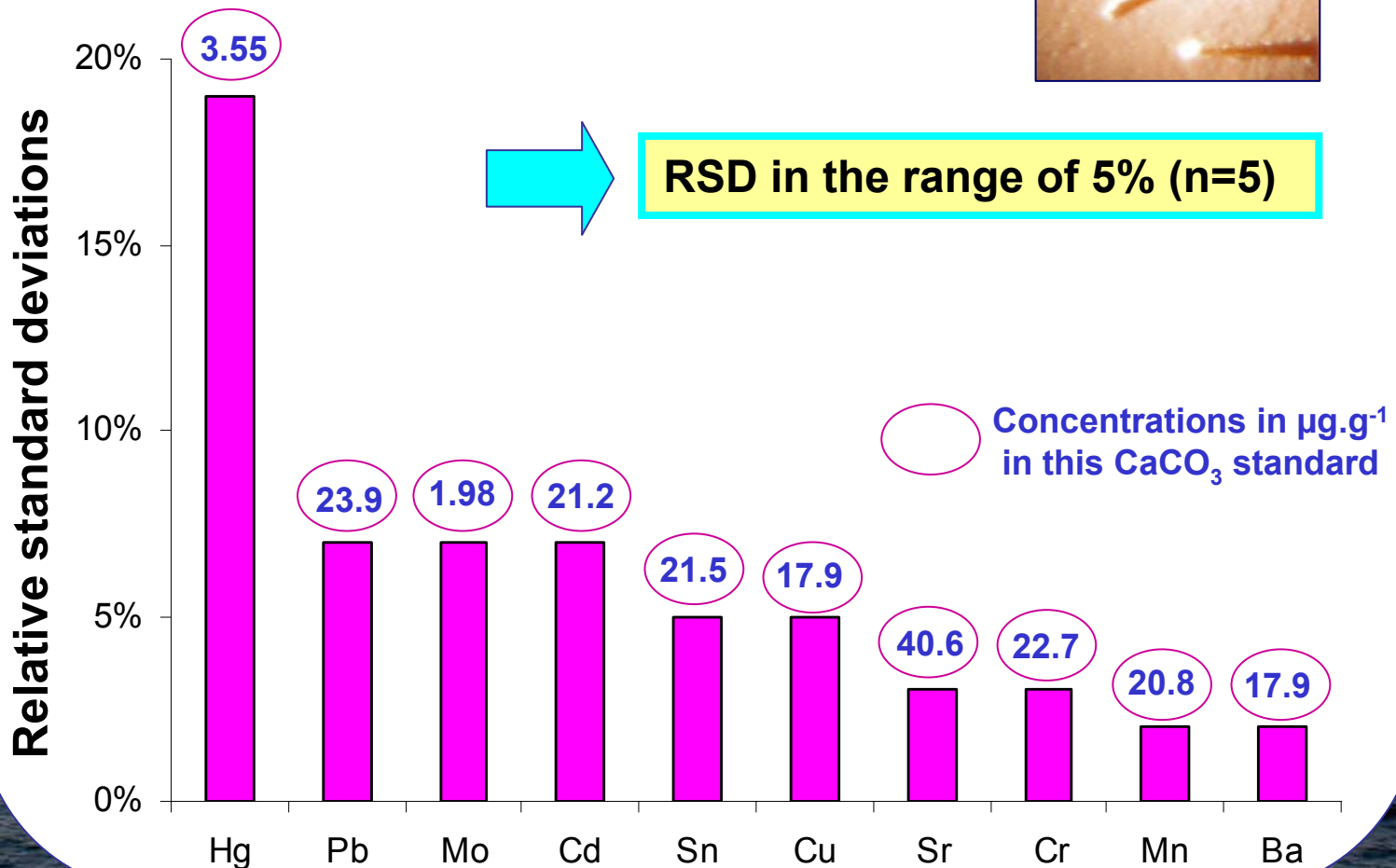
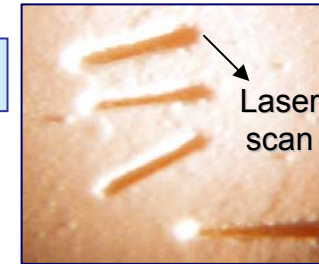
6- Pressing into pellets (7t, Ø1.3 cm, 2 min)

# 2. Methodological approach

## 2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

### Repeatability of CaCO<sub>3</sub> standard analyses

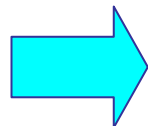
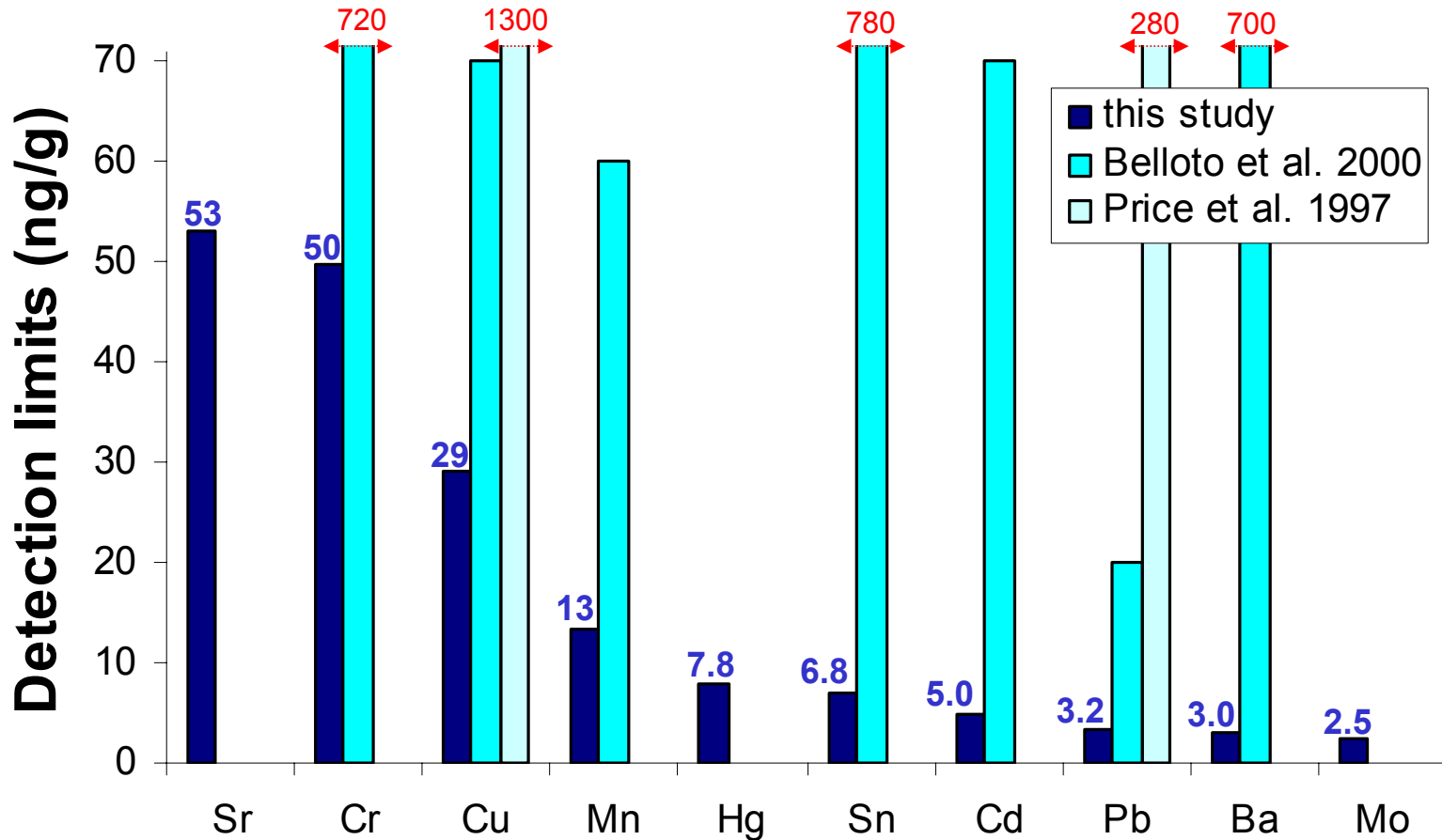
➤ Normalization against <sup>43</sup>Ca (40% in the matrix)



# 2. Methodological approach

## 2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

### Detection limits



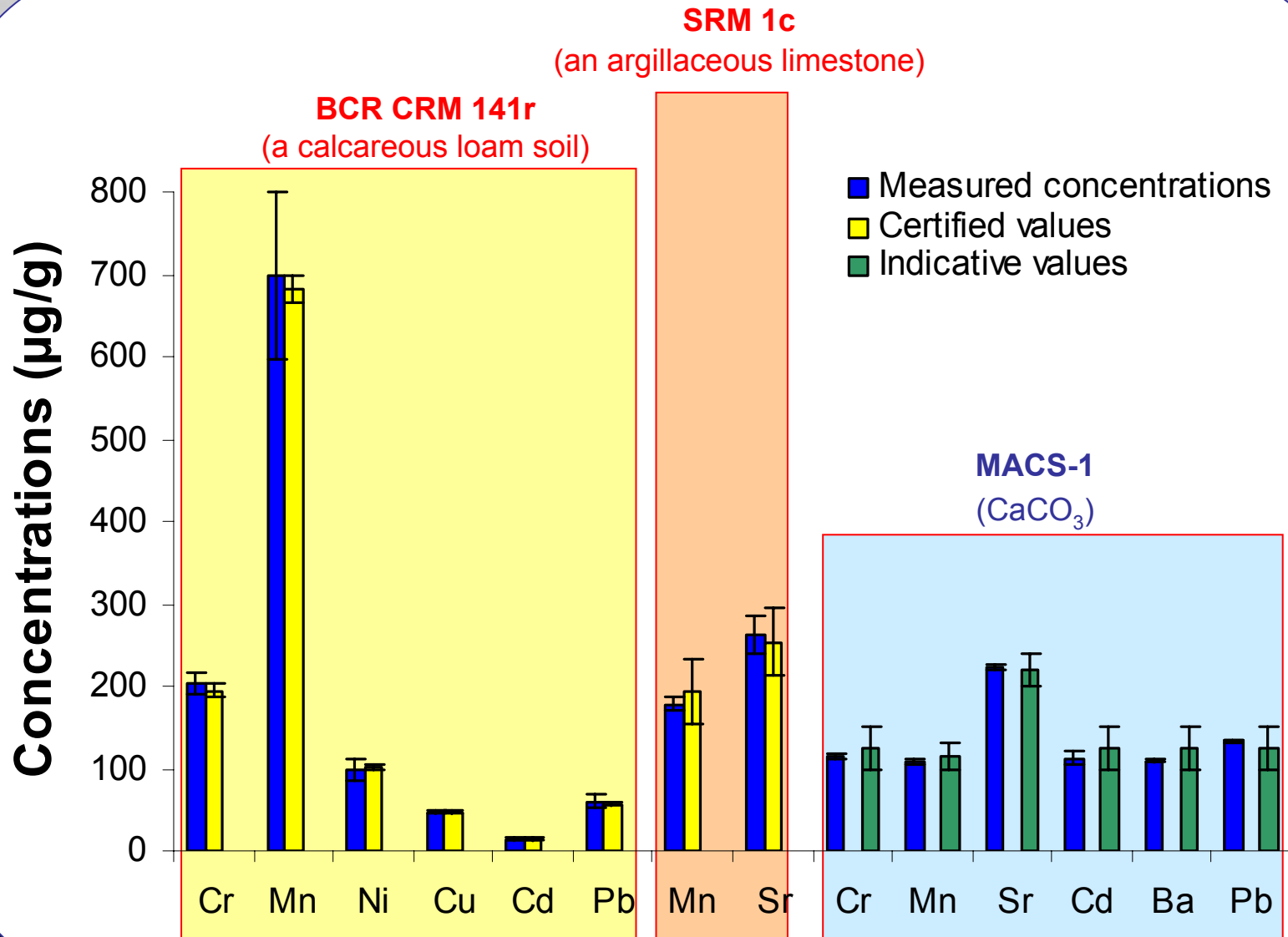
DL in the 10ng.g<sup>-1</sup> range



# 2. Methodological approach

## 2.1. Matrix-matched LA-ICP-MS analyses for CaCO<sub>3</sub> matrix

### Validation with reference materials





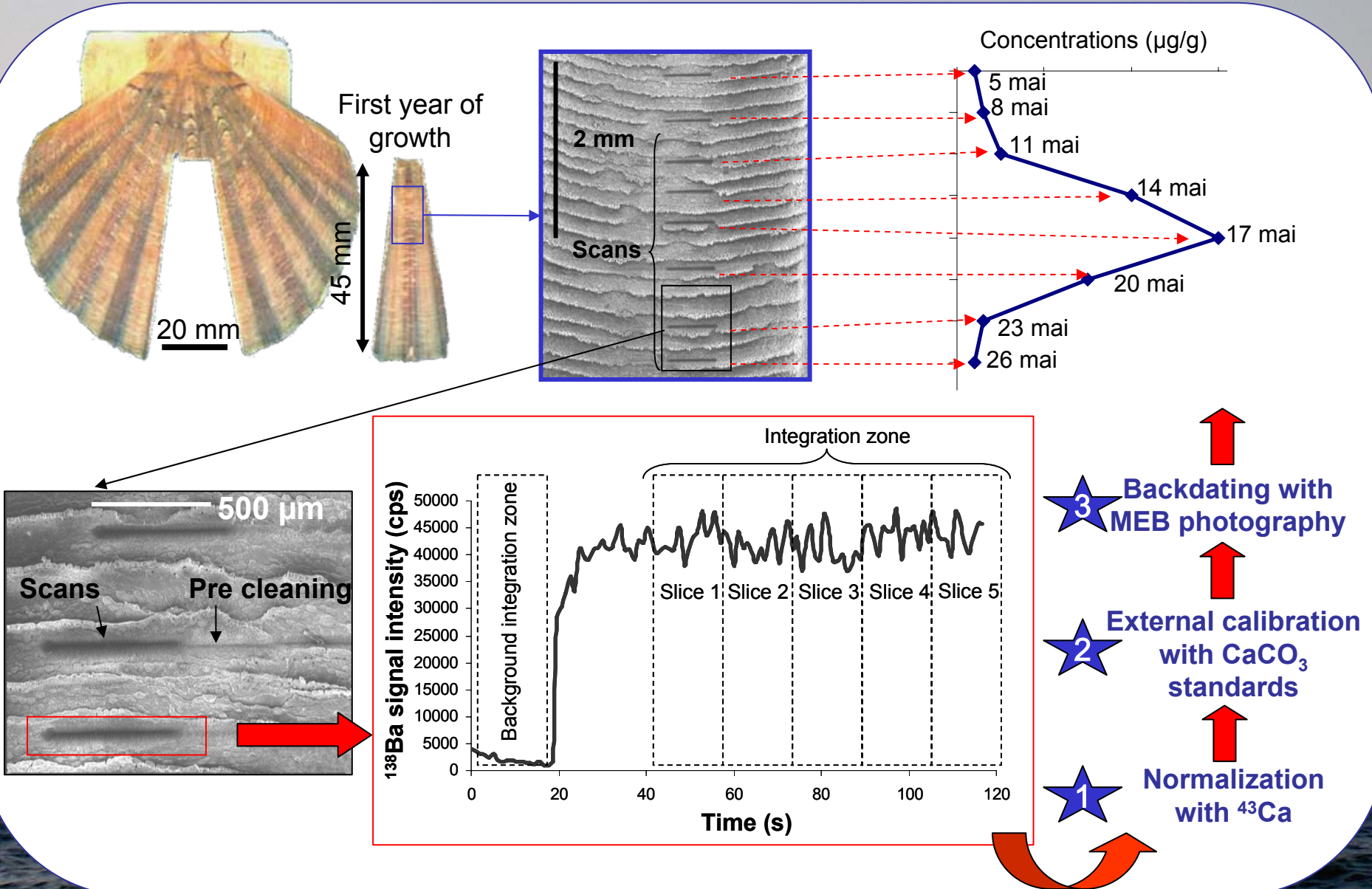
## 2. Methodological approach

### 2.2. Application to the Great Scallop shell

# 2. Methodological approach

## 2.2. Application to the Great Scallop shell

### Application to Scallop shells

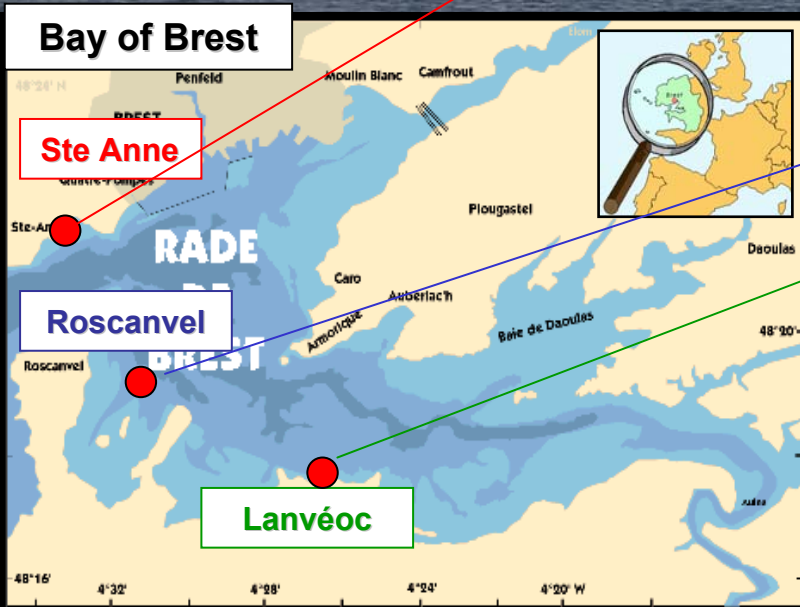
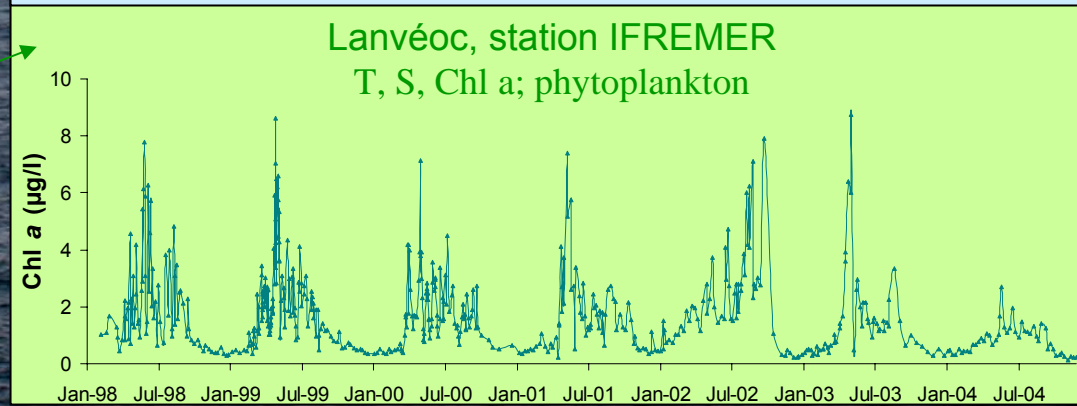
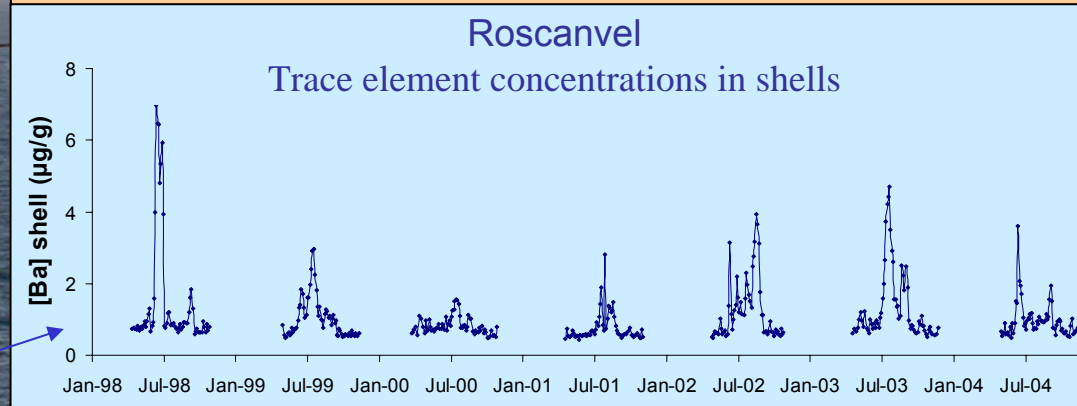
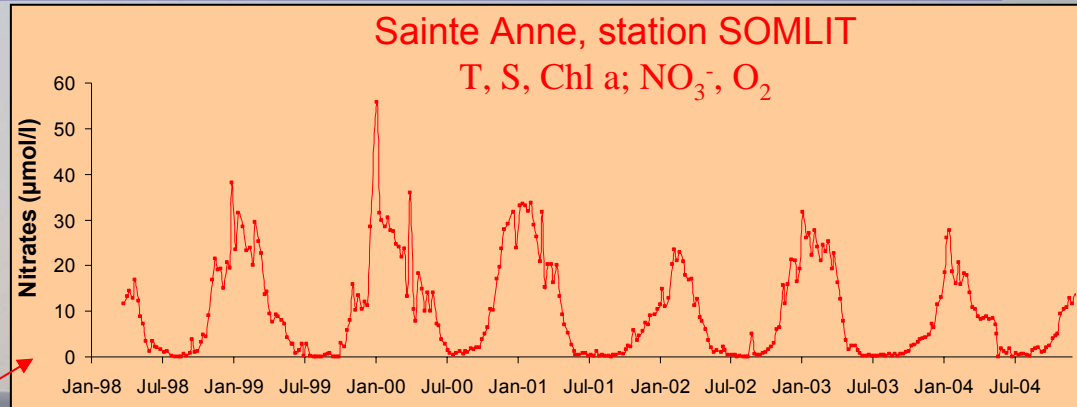




# 2. Methodological approach

## 2.2. Application to the Great Scallop shell

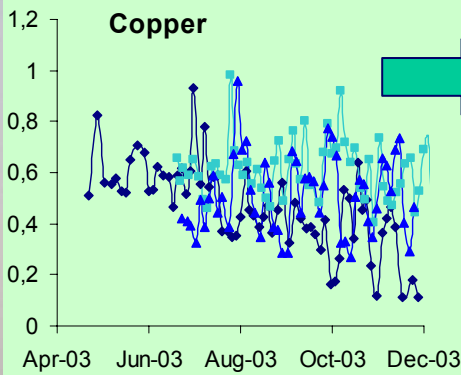
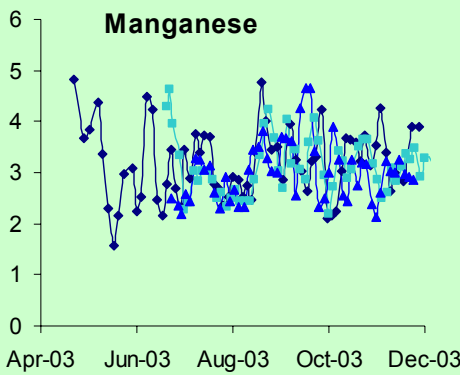
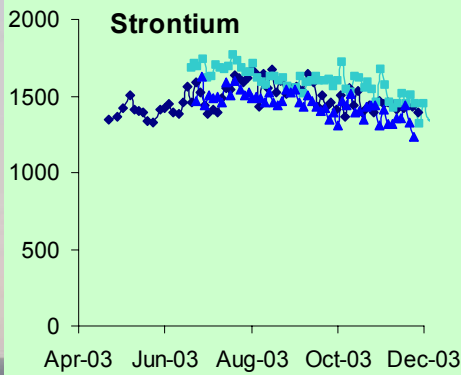
### Regular monitoring of coastal ecosystem: Bay of Brest, France



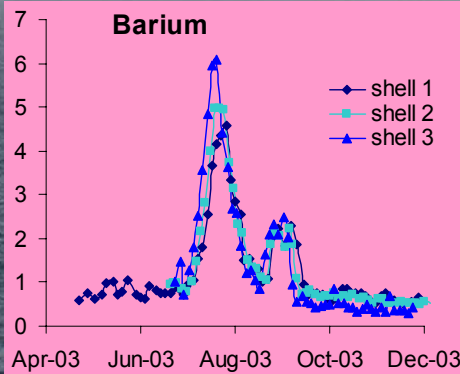
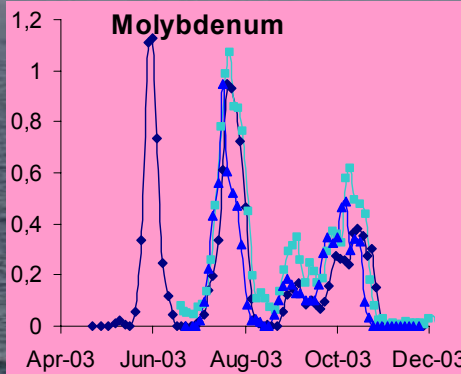
# 2. Methodological approach

## 2.2. Application to the Great Scallop shell

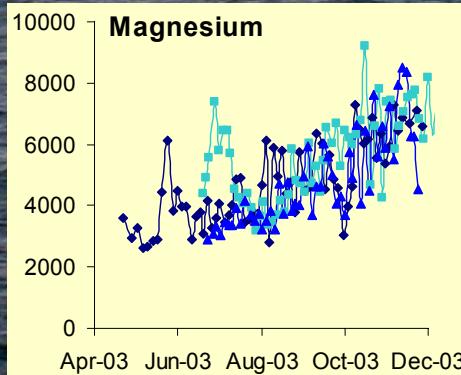
### Reproducibility in a same shell population



**Profile A:** steady state concentrations for Sr, Mn, Cu, Co, Sn, Pb



**Profile B:** steady state concentrations punctuated by episodic enrichments for Ba, Mo, Mn



**Profile C:** steady increasing concentrations

Concentrations ( $\mu\text{g.g}^{-1}$ )

An aerial photograph of a large body of water, possibly a bay or estuary, with a bridge crossing a narrow channel in the foreground. The water is a light blue-grey color, and the surrounding land is a mix of green vegetation and urban/industrial development. In the distance, there are more landmasses and a hazy horizon.

## **3. Significance of trace element shell profiles**

### **3.1. Background trace element shell concentrations**

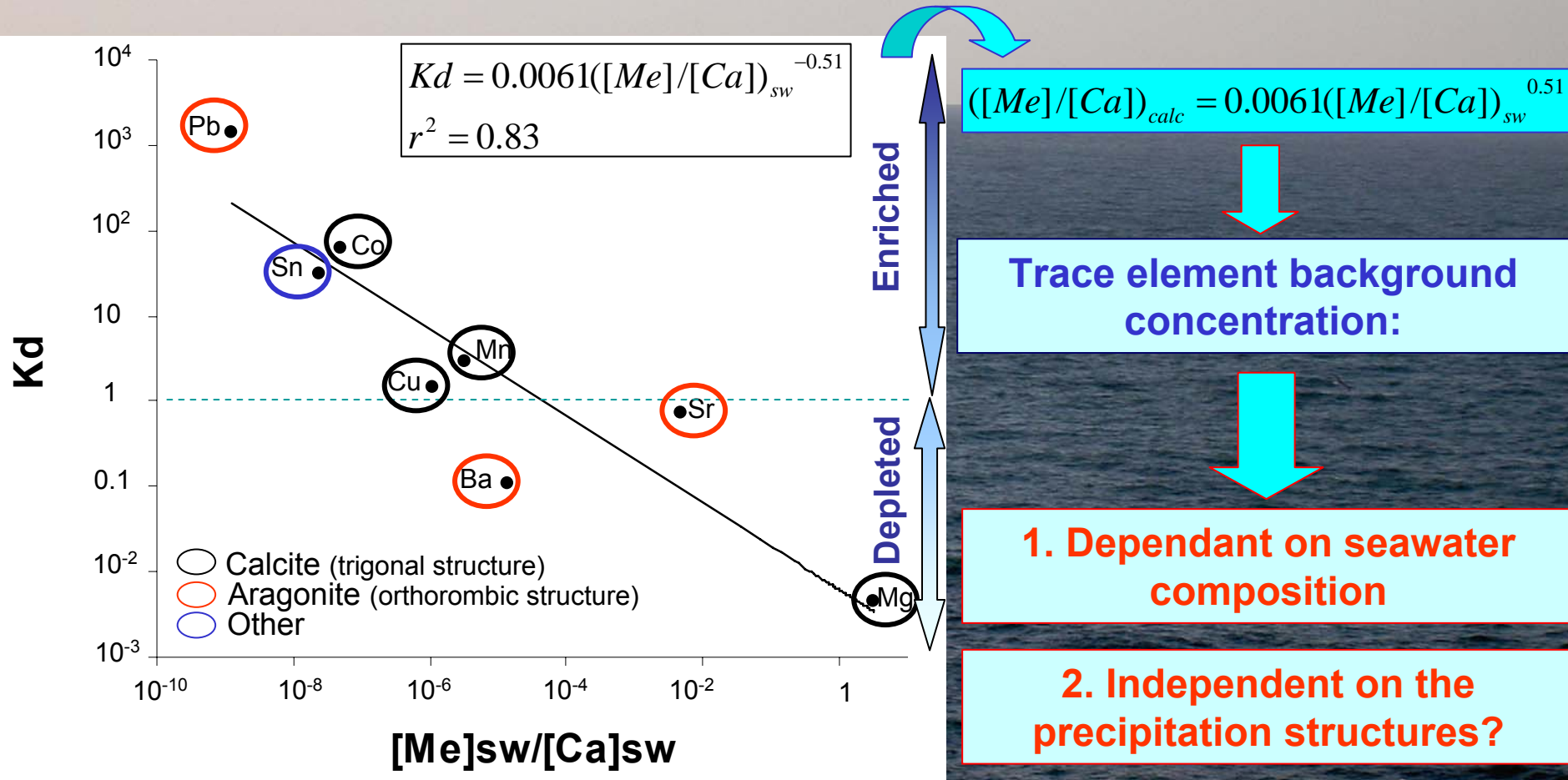


# 3. Significance of trace element shell profiles

## 3.1. Background trace element shell concentrations

- Background shell concentrations: 7-year period, 3 shells/year
- Trace element affinity with calcium carbonate matrix → partition coefficient  $K_d$

$$K_d = \frac{([Me]/[Ca])_{calc}}{([Me]/[Ca])_{sw}}$$



# 3. Significance of trace element shell profiles

## 3.1. Background trace element shell concentrations

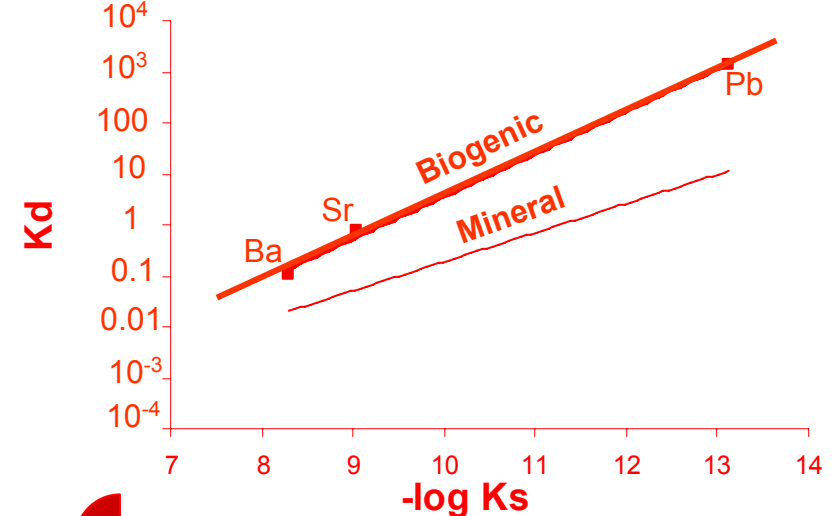
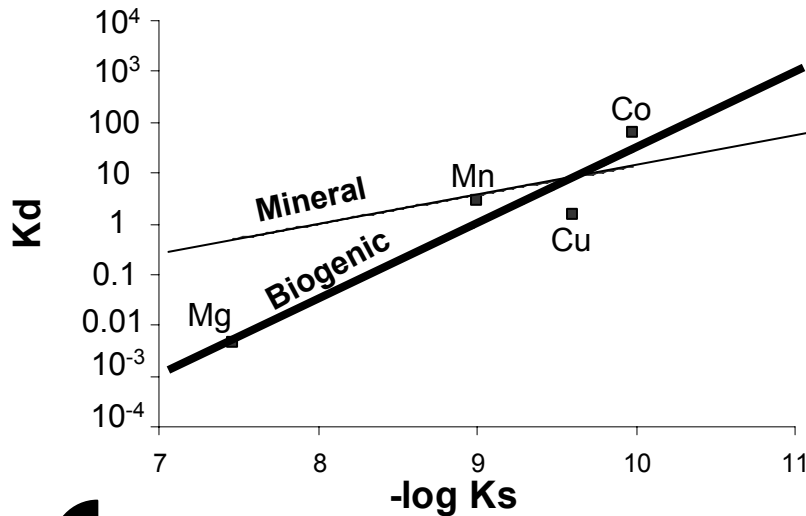
Structure of precipitation

Calcite

Aragonite

Ionic radii of  $Me^{2+} <$  Ionic radii of  $Ca^{2+}$

Ionic radii of  $Me^{2+} >$  Ionic radii of  $Ca^{2+}$



$$Kd = 5.10^{-14} Ks^{-1.48}; r^2 = 0.904$$

$$Kd = 2.10^{-8} Ks^{-0.83}; r^2 = 0.997$$

Trace element enrichment dependant on:

1. The ionic radii of  $Me^{2+}$

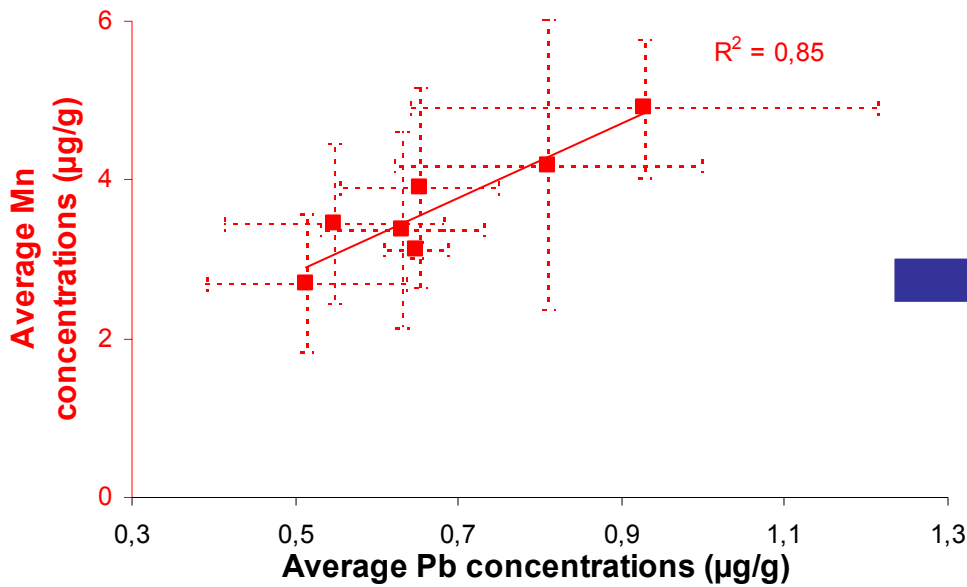
2. The solubility constants within  $CaCO_3$

3. The formation of biogenic calcite

# 3. Significance of trace element shell profiles

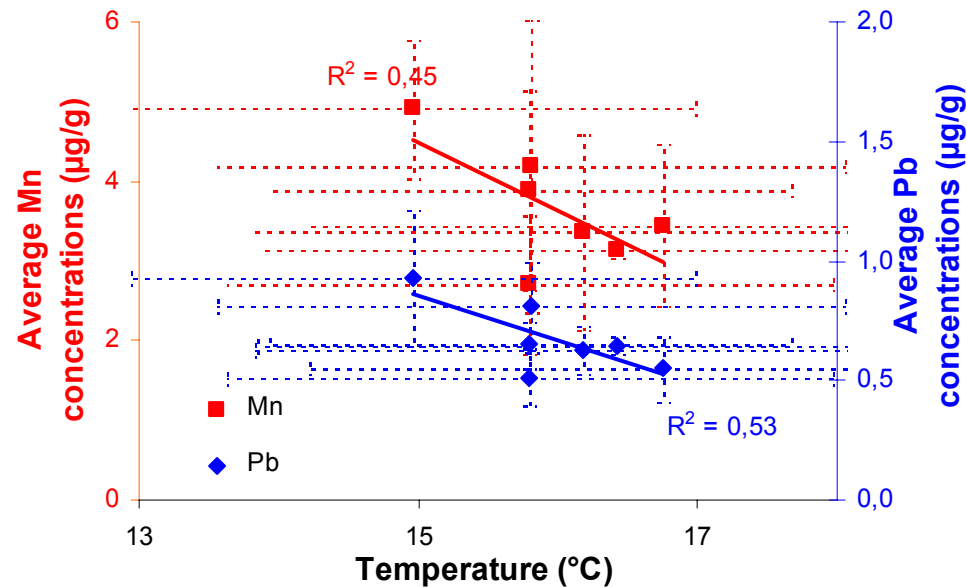
## 3.1. Background trace element shell concentrations

### Mn and Pb annual background concentrations (Bay of Brest, 1998-2004)



➤ Similar crustal sources?

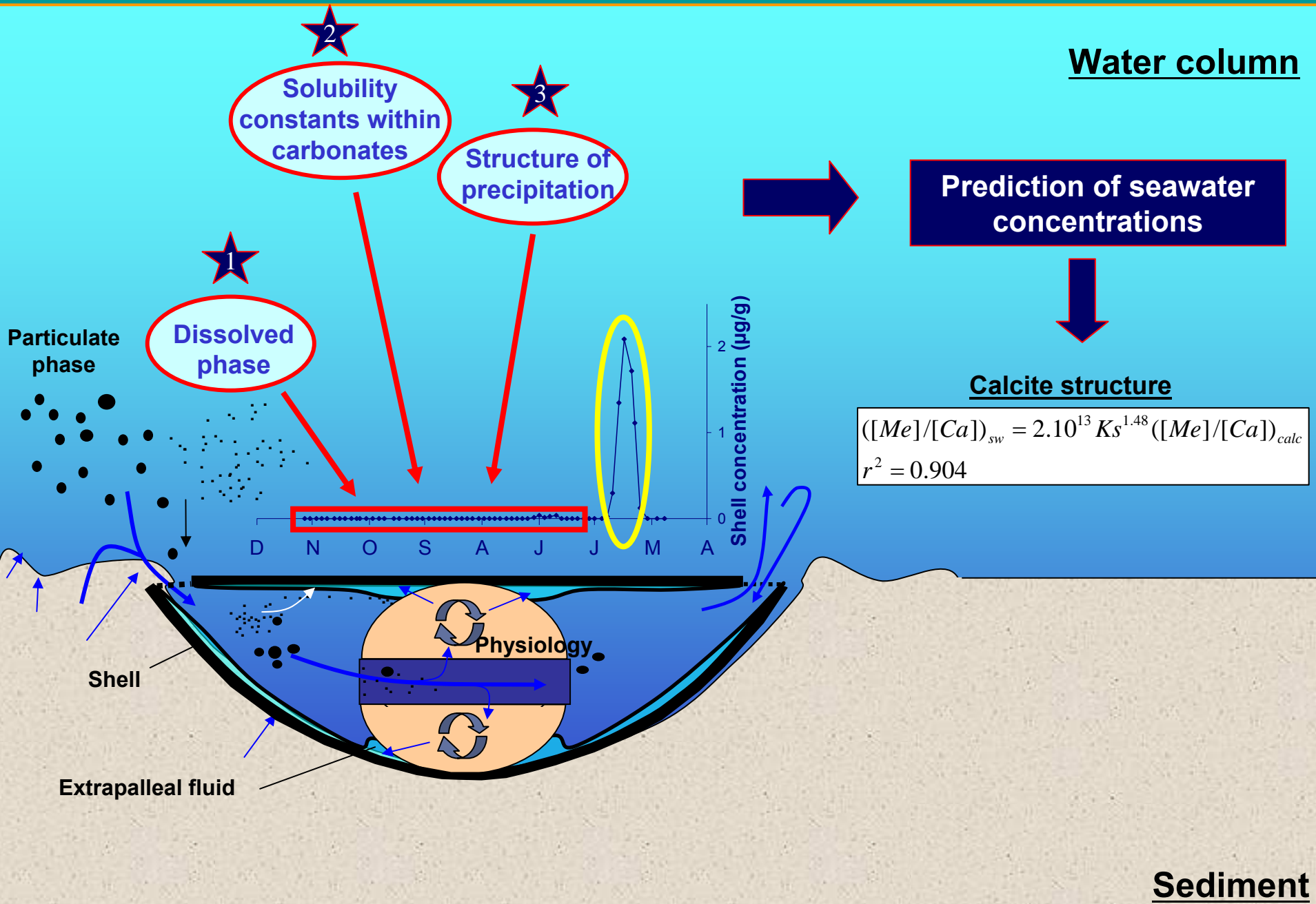
➤ Related to hydroclimatic conditions?





# 3. Significance of trace element shell profiles

## 3.1. Background trace element shell concentrations



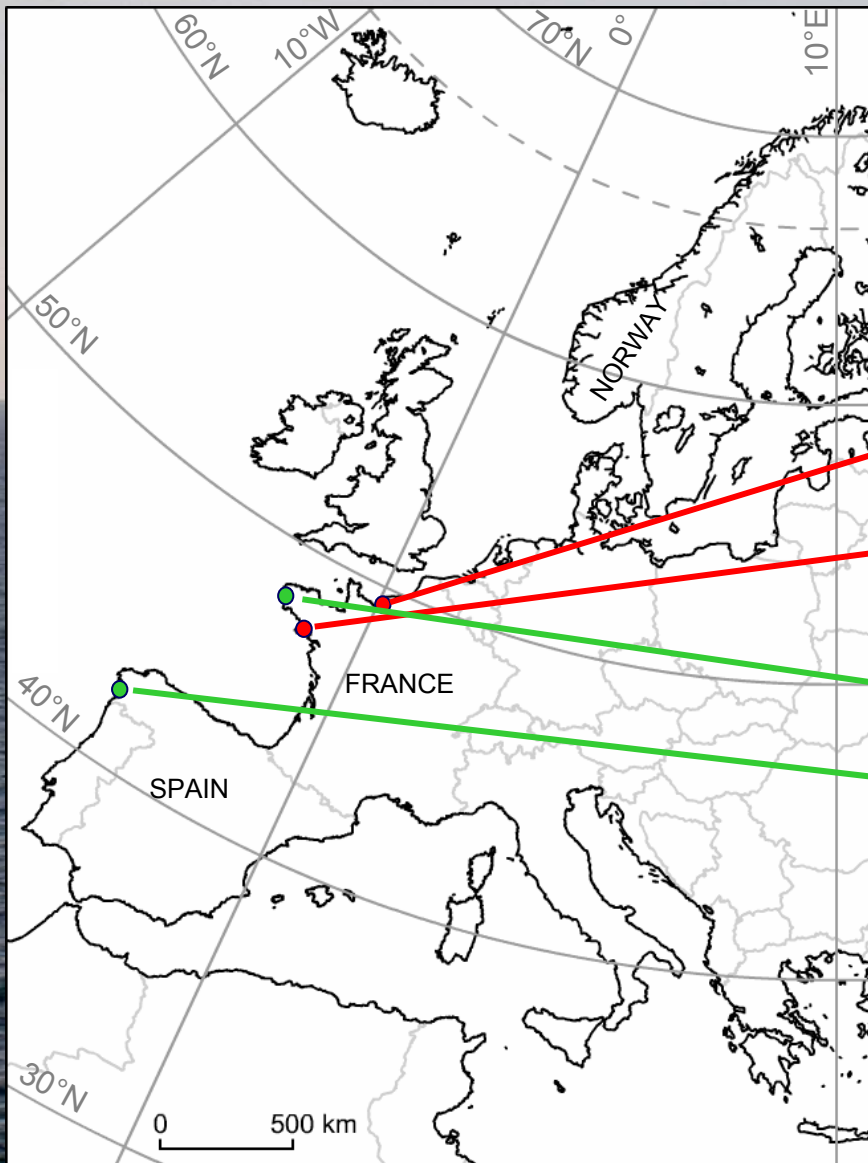
A photograph of a whale breaching the surface of the ocean, with a forested hillside in the background. The whale's dark, pointed dorsal fin is visible above the water, creating a splash. The water is dark blue with some white foam from the breach. The background shows a dark, forested hillside under a clear sky.

## **3. Significance of trace element shell profiles**

### **3.2. Episodic shell enrichments**

# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments



➤ Coastal environment influenced by major estuaries:

- Loire : Belle Ile or Quiberon (France);
- Seine: Seine bay (France).

➤ Coastal bay environment:

- Bay of Brest (France)
- Ria de Vigo (Spain)



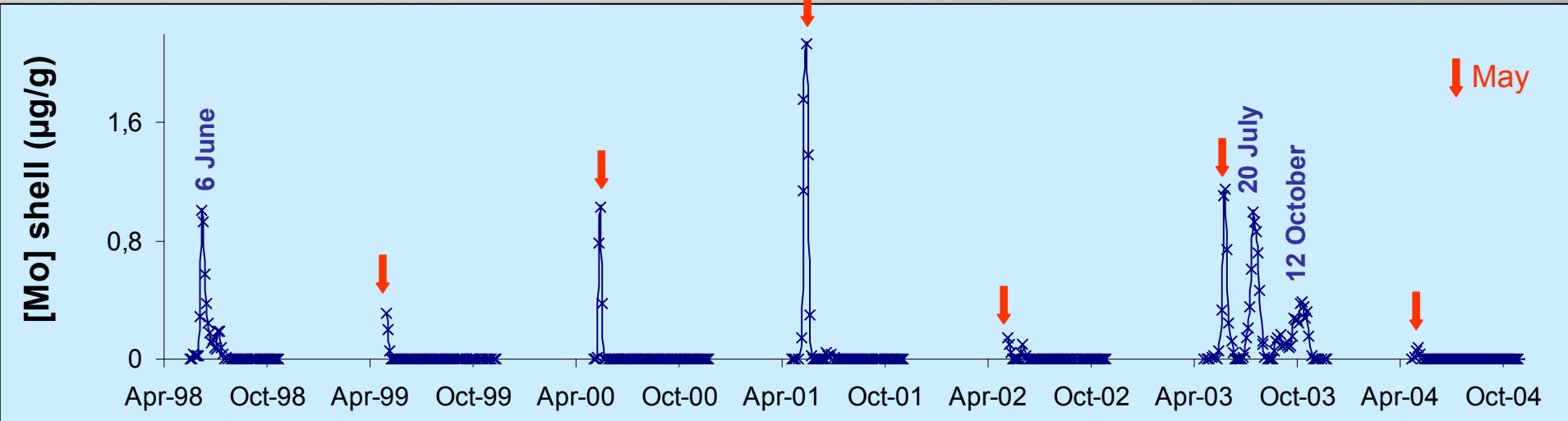


# 3. Significance of trace element shell profiles

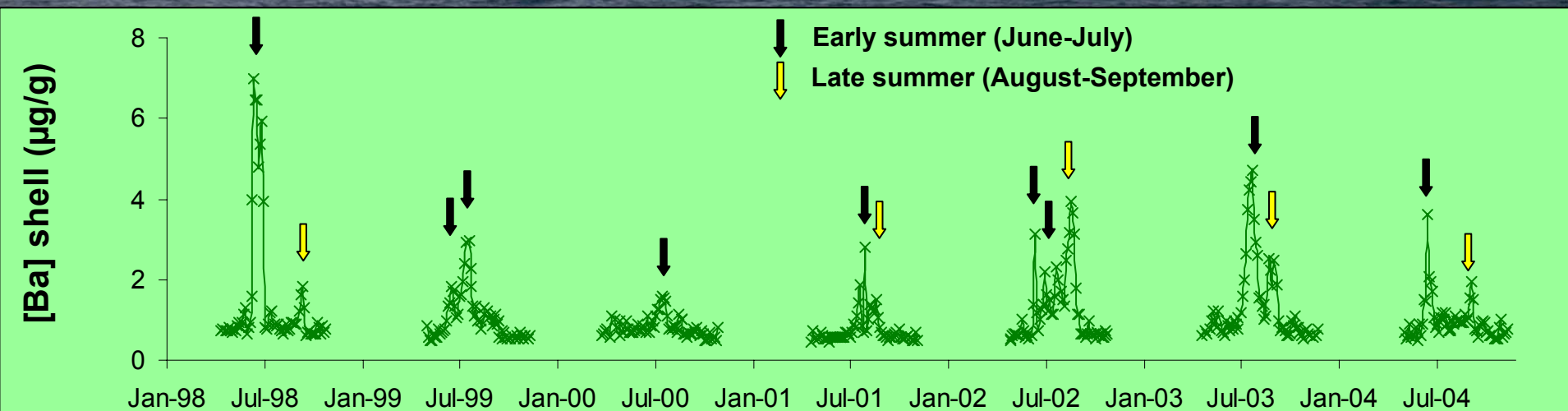
## 3.2. Episodic shell enrichments

### Mo and Ba shell profiles (Bay of Brest, 1998-2004)

#### Molybdenum



#### Barium



# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments

Molybdenum

Barium



### Episodic shell enrichments:

- Intensive (particularly for Mo);
- Ubiquitous in different coastal environments;
- Periodic occurrence:
  - in spring for Mo (generally in May);
  - in early or late summer for Ba.



- Comparison with shell growth rate
- Comparison with environmental monitoring variables:
  - Hydrological: temperature, salinity, chlorophyll a
  - Biological: dominant and recurrent phytoplankton species:
    - *Rhizosolenia spp./Pseudonitzschia spp.* (diatoms) for Mo
    - diatoms of *Chaetoceros spp./dinoflagellates of Gymnodinium spp.* for Ba

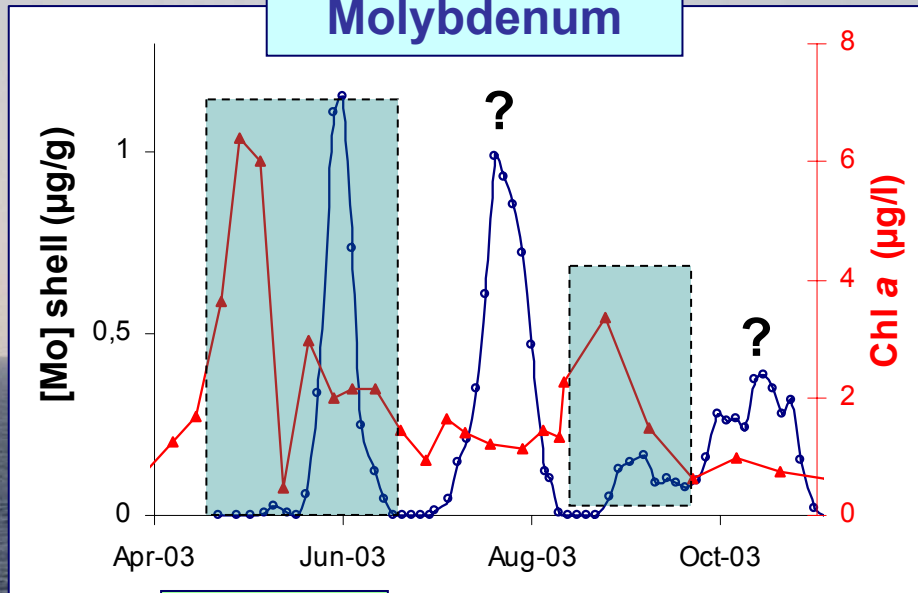


# 3. Significance of trace element shell profiles

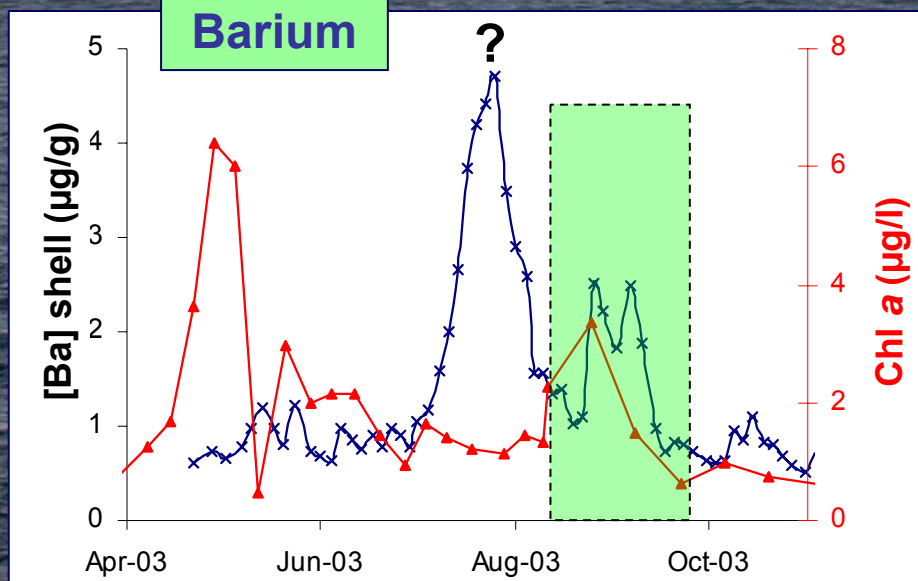
## 3.2. Episodic shell enrichments

### Comparison with chlorophyll *a* concentrations

#### Molybdenum



#### Barium



Statistical evaluation  
(1998-2004):

$r=0.28$ ,  $p>0.05$ ,  $n=37$



Influence of the total  
phytoplankton  
biomass?



Statistical evaluation  
(1998-2004):

➤ Early summer:  $r=0.22$ ,  $p>0.05$ ,  
 $n=20$

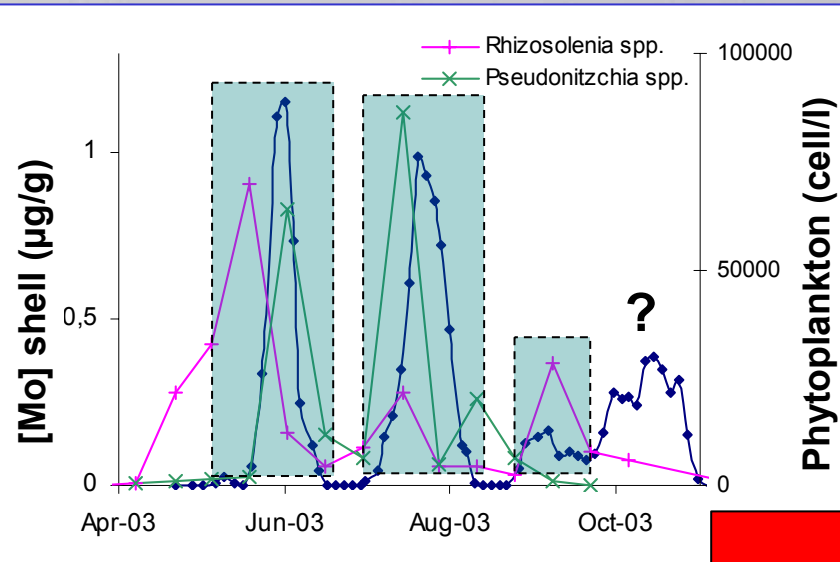
➤ Late summer:  $r=0.79$ ,  
 $p<0.05$ ,  $n=16$

# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments

### Comparison with phytoplankton speciation

Molybdenum

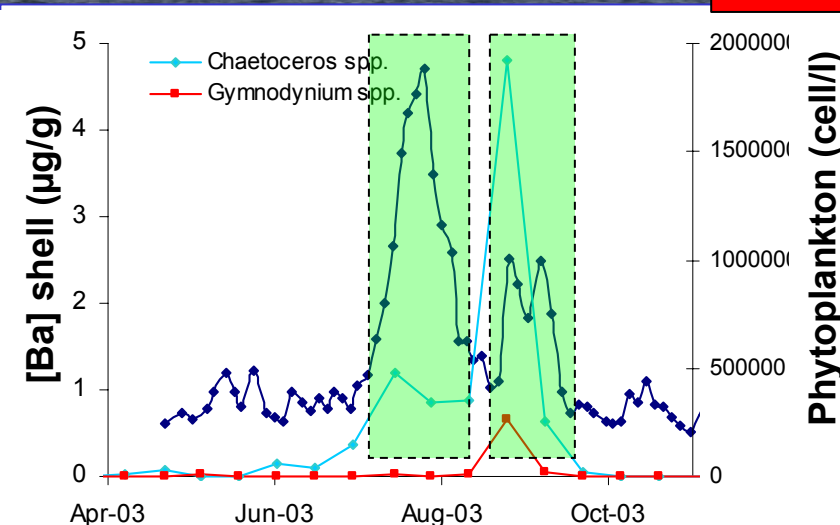


Statistical evaluation  
(1998-2004):

- *Pseudonitzschia* spp. ( $r=0.72$ ,  $p<0.05$ ,  $n=37$ )
- *Rhizosolenia* spp. ( $r=0.28$ ,  $p>0.05$ ,  $n=37$ )

Influence of the  
phytoplankton  
speciation?

Barium

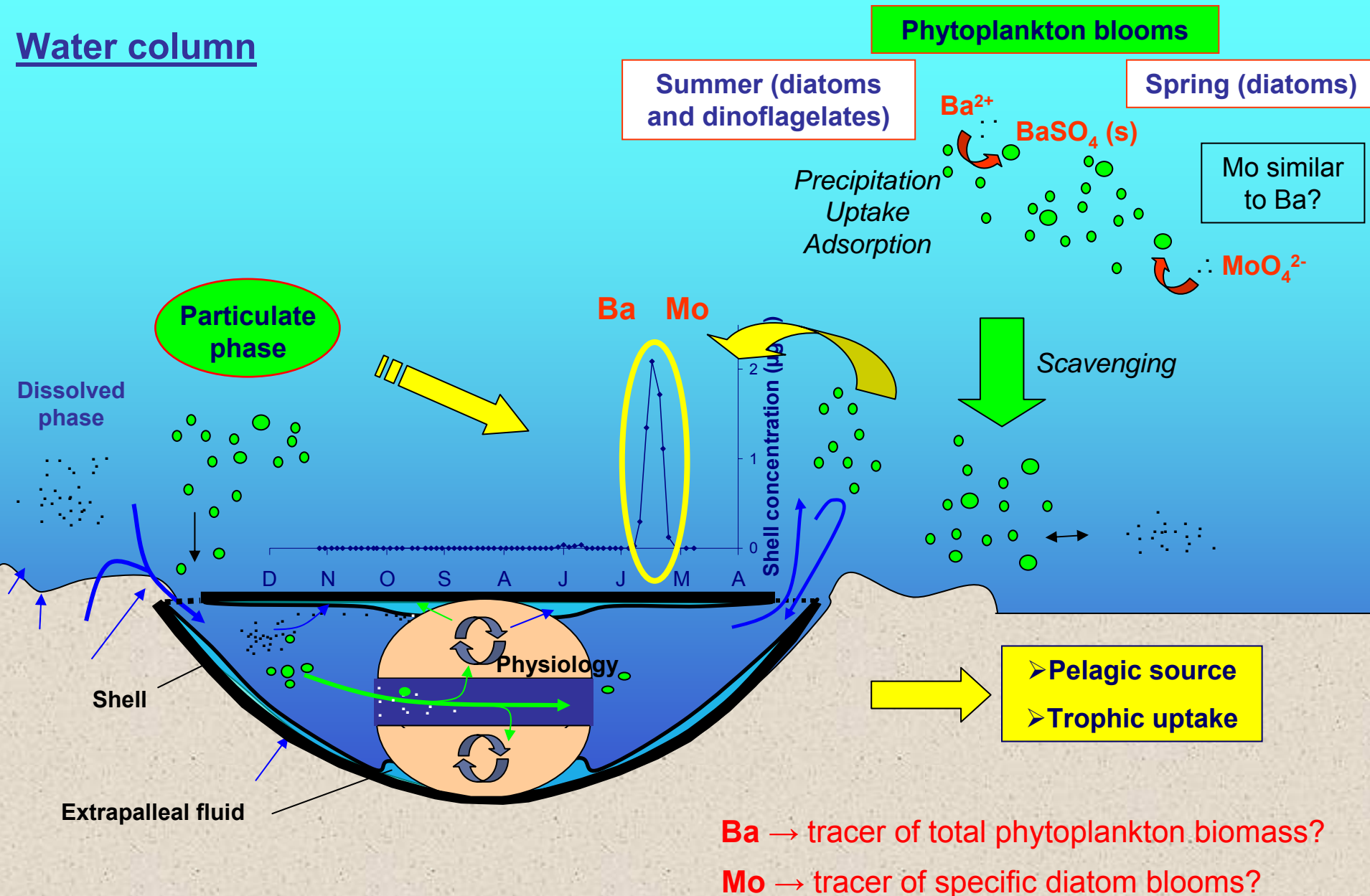


Statistical evaluation  
(1998-2004):

- Early summer: *Chaetoceros* spp. ( $r=-0.44$ ,  $p<0.05$ ,  $n=20$ )
- Late summer: *Gymnodinium* spp. ( $r=-0.01$ ,  $p>0.05$ ,  $n=16$ )

# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments



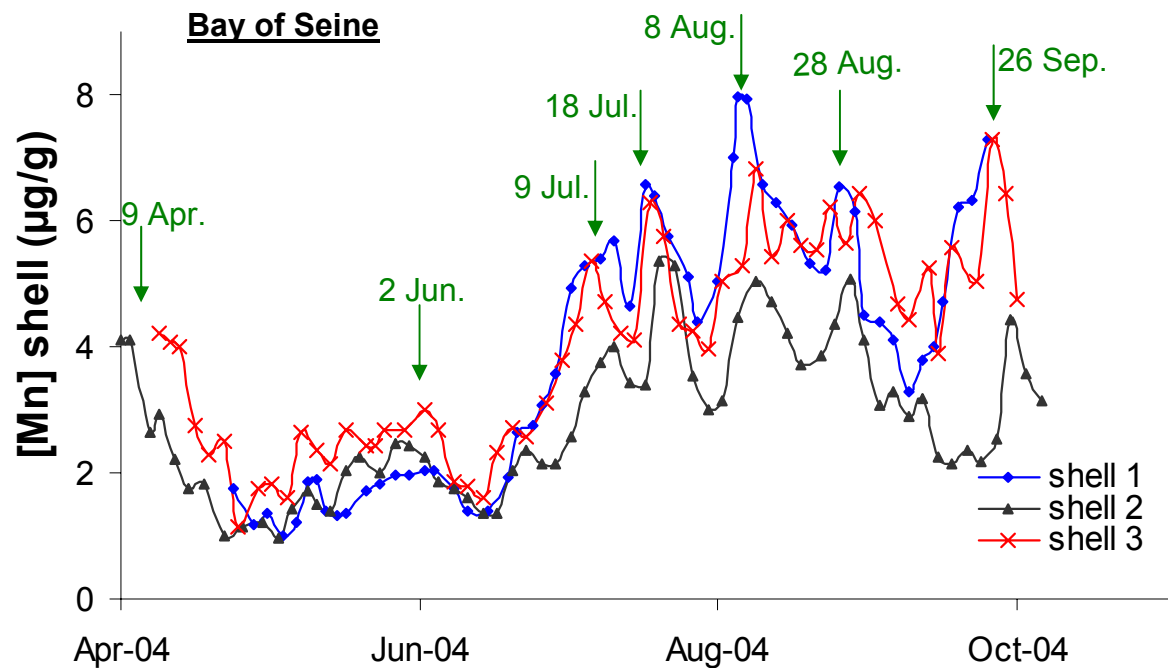
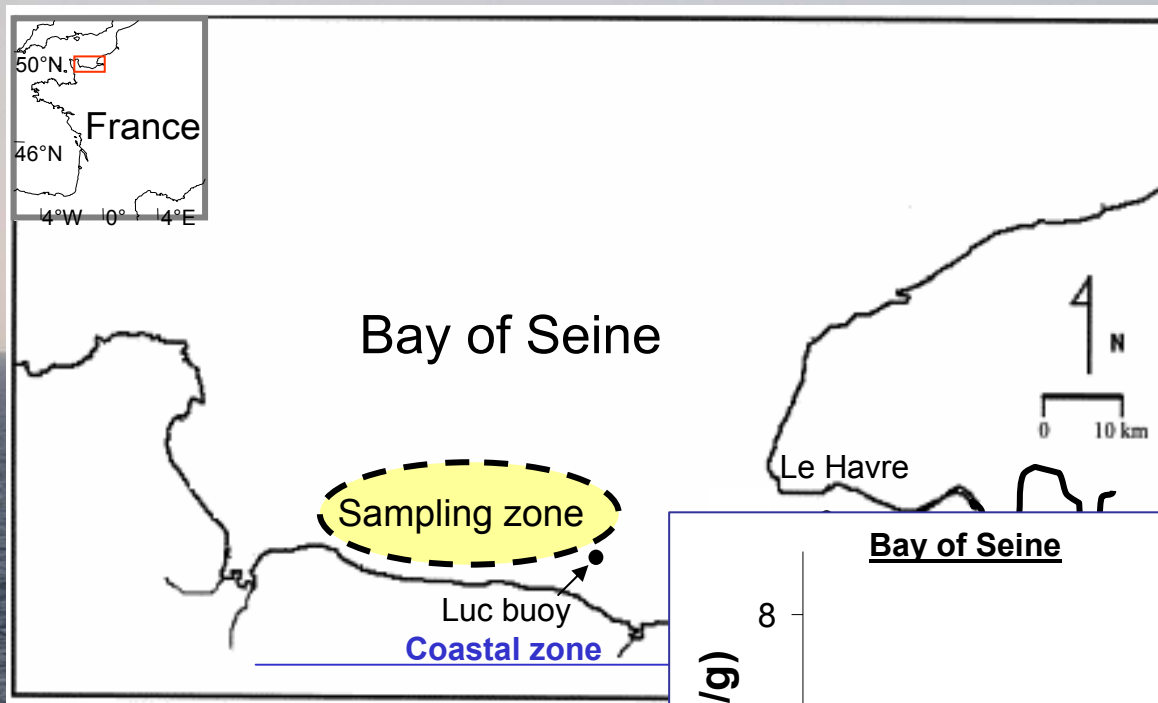
## Sediment



# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments

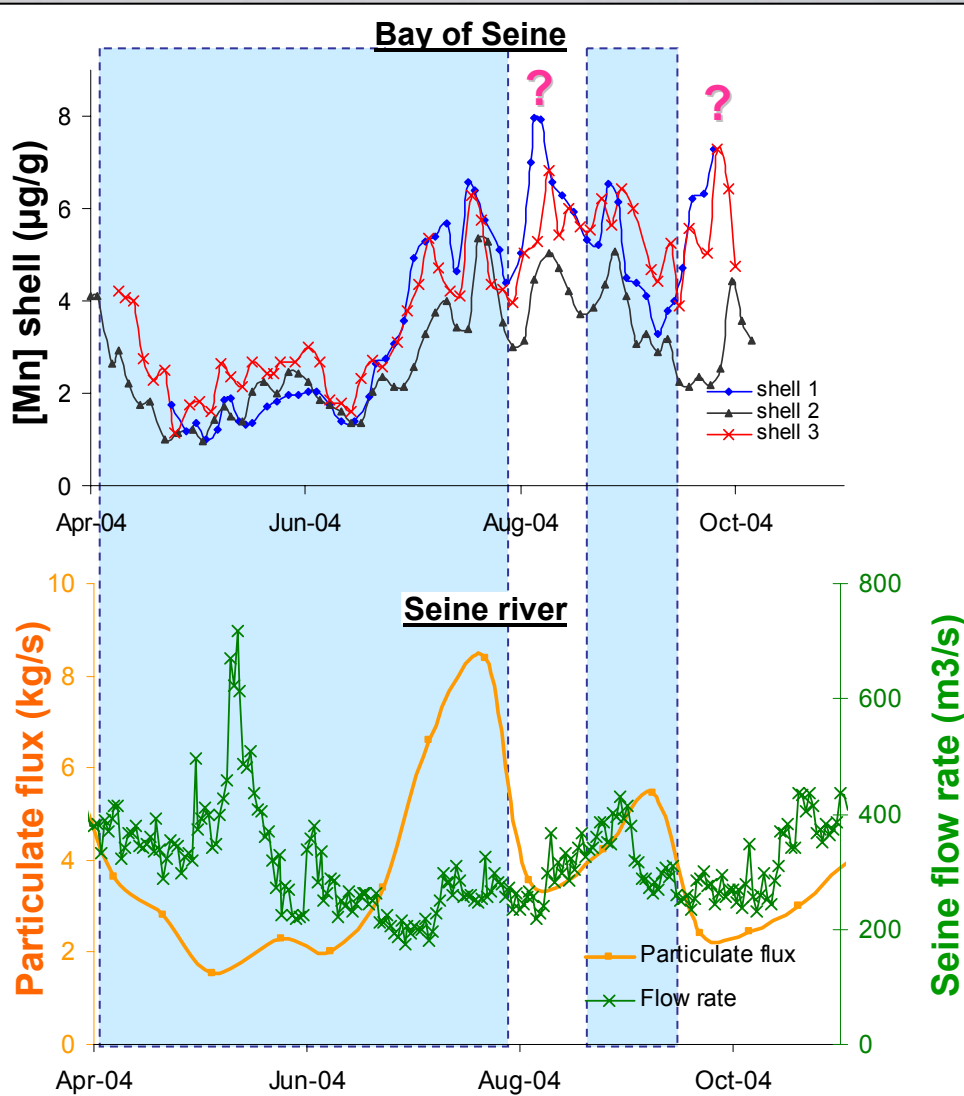
### Mn shell profiles (Seine bay, 2004)



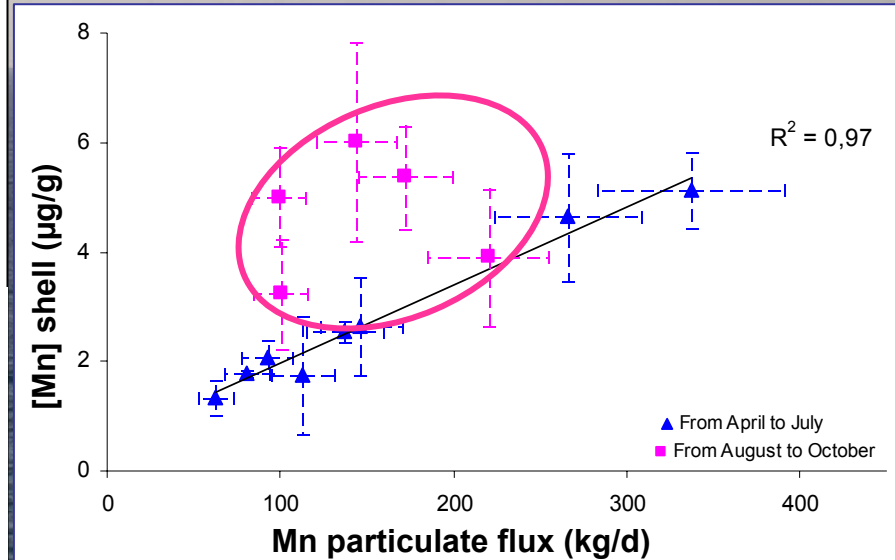
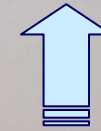
# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments

### Mn shell profiles (Bay of Seine, 2004): influence of riverine inputs



**Mn shell concentrations mainly influenced by riverine inputs**

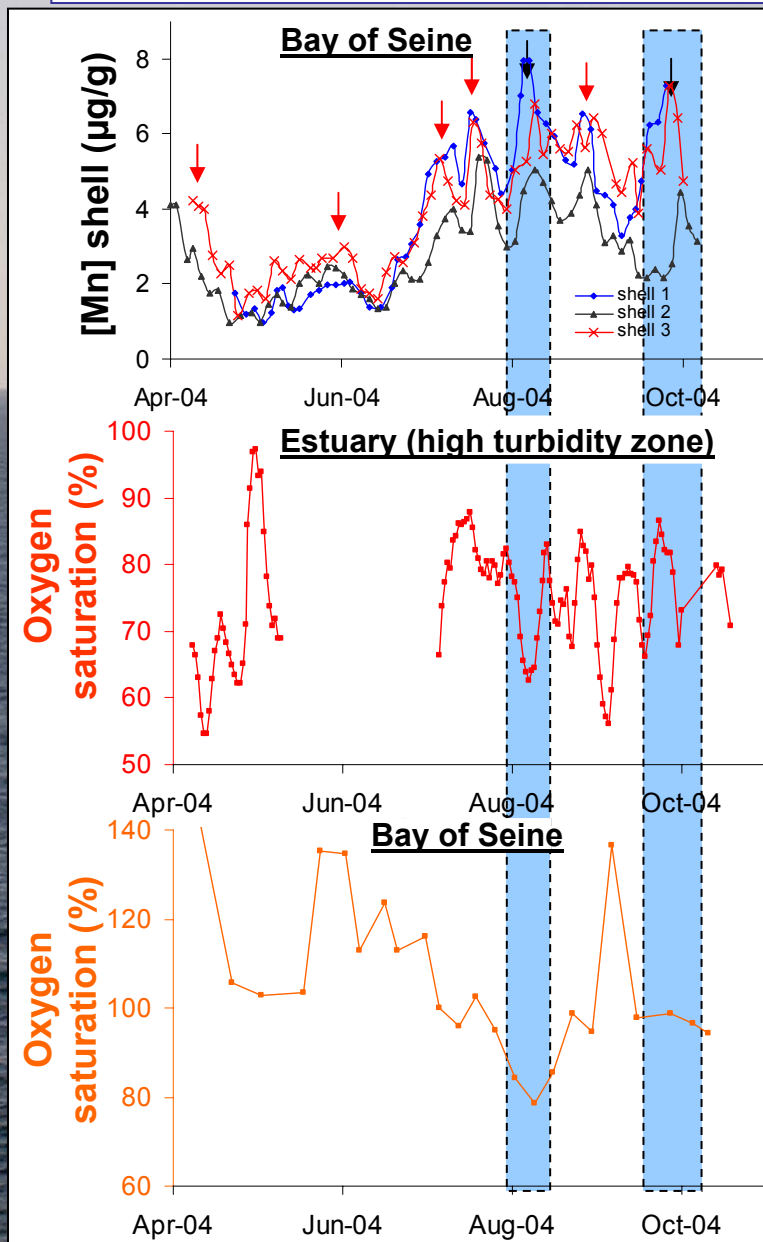


**Specific enrichment of Mn shell concentrations in late summer**

# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments

### Mn shell profiles (Seine bay, 2004): influence of redox conditions



**Specific summer Mn shell enrichments supported by reducing conditions :**

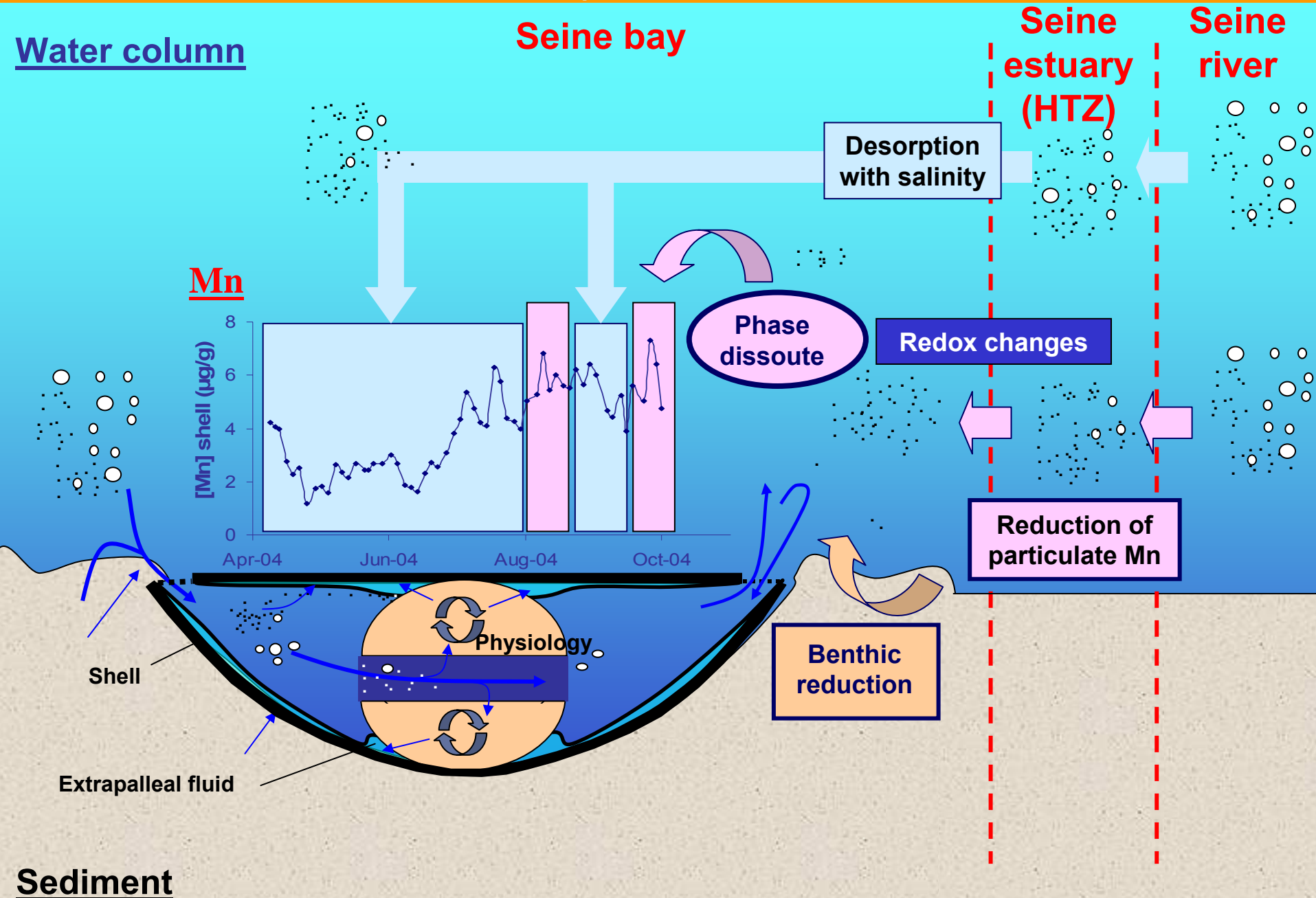
➤ in the estuary

➤ at SWI in the bay



# 3. Significance of trace element shell profiles

## 3.2. Episodic shell enrichments



## 4. Conclusion

# 4. Conclusion

## Scientific inputs

### ➤ Development of a bioanalytical tool: the Great Scallop + LA-ICP-MS

- Definition of quantitative and chronological trace element profiles along the calcite shell
- Methodological approach adaptable to others  $\text{CaCO}_3$  matrices

### ➤ Trace element profiles in *Pecten maximus* shells as an archive :

- with Ba and Mo of phytoplankton dynamic

  - Ba → summer total phytoplankton biomass?

  - Mo → phytoplankton speciation?

- with Mn of particulate riverine inputs and redox processes

### ➤ Trace element shell profiles → archive of transient events for coastal environment

- Significant and transient Mo shell enrichments during spring diatom blooms  
→ Mo as a conservative behavior in the seawater?



# 4. Conclusion

★ 1

## Analytical development (LCABIE)

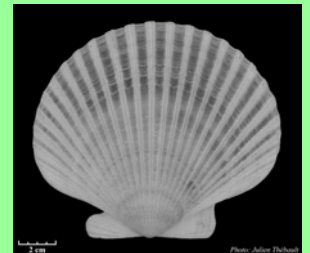
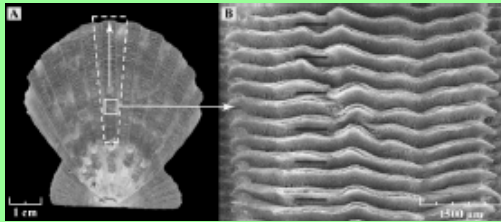
- Improvement of the detection limits, of the analysis time (programmation) → use of femtosecond laser
- Isotopic measurement (tracer of biogeochemical processes?) → use of femtosecond laser coupled with a multi collector (MC) ICP-MS.

★ 2

## Biological model (LEMAR)

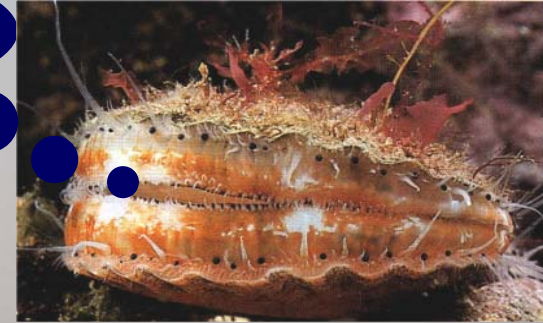
- Fossile or historical shells;
- Others species:

- *Argopecten purpuratus* (Chile)
- *Comptopallium radula* (New Caledonia)
- Polar species (Antartica)



# Acknowledgments

Thank you for your attention  
Merci pour votre attention



**Merci à tous les membres du LCABIE et ceux du LEMAR: cette alliance béarno-bretonne a largement contribué à l'aboutissement de cette thèse.  
Je tiens également à remercier tout mon entourage pour m'avoir toujours encouragée dans cette voie.**