



LABORATOIRE INTERDISCIPLINAIRE  
DES ENVIRONNEMENTS CONTINENTAUX



# Fadi HAJJ

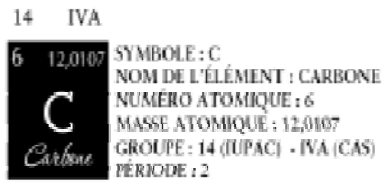
Where do you come from,  
enigmatic wood?



Supervised by:  
**Anne POSZWA**

# I. Context

14 IVA  
6 12,0107  
SYMBÔLE : C  
NOM DE L'ÉLÉMENT : CARBONE  
NUMÉRO ATOMIQUE : 6  
MASSE ATOMIQUE : 12,0107  
GROUPE : 14 (IUPAC) - IVA (CAS)  
PÉRIODE : 2



- MASSES ATOMIQUES DES ISOTOPES LES PLUS STABLES ENTRE ACCOLADES
- MASSES ATOMIQUES DONNÉES À 6 CHIFFRES SIGNIFICATIFS

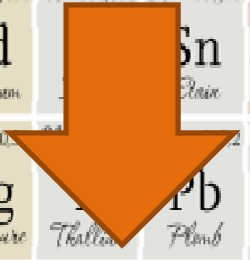
NOUVEAUX MÉTAUX	ALCOÏDES
MÉTAUX ALCALINS	HALOGÈNES
MÉTAUX ALCALINO-TERREUX	GAZ NOBLES
MÉTAUX DE TRANSITION	LANTHANIDES
MÉTAUX PAUVRES	ACTINIDES

5 10,811	6 12,0107	7 14,0067	8 15,9994	9 18,9984	10 20,1797
B Bore	C Carbone	N Azote	O Oxygène	F Fluor	Ne Néon
13 26,9815	14 28,0855	15 30,9738	16 32,065	17 35,453	18 39,948

38  
**Sr**  
Strontium  
87.62



$^{87}\text{Sr}/^{86}\text{Sr}$  varies with the type of the bedrock



Sr isotopic ratio is one of the best isotopic tools to trace provenance

57 138,906	58 140,116	59 140,908	60 144,242	61 (145)	62									
La Lanthane	Ce Cerium	Pr Praseodyme	Nd Neodyme	Pm Prométhium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutécium
89 (127)	90 232,038	91 231,036	92 238,029	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (259)	103 (262)
Ac Actinium	Th Thorium	Pa Protactinium	U Uranium	Np Neptunium	Pu Plutonium	Am Americium	Cm Curium	Bk Berkelium	Cf Californium	Es Einsteinium	Fm Fermium	Md Mendelevium	No Nobelium	Lr Lawrencium

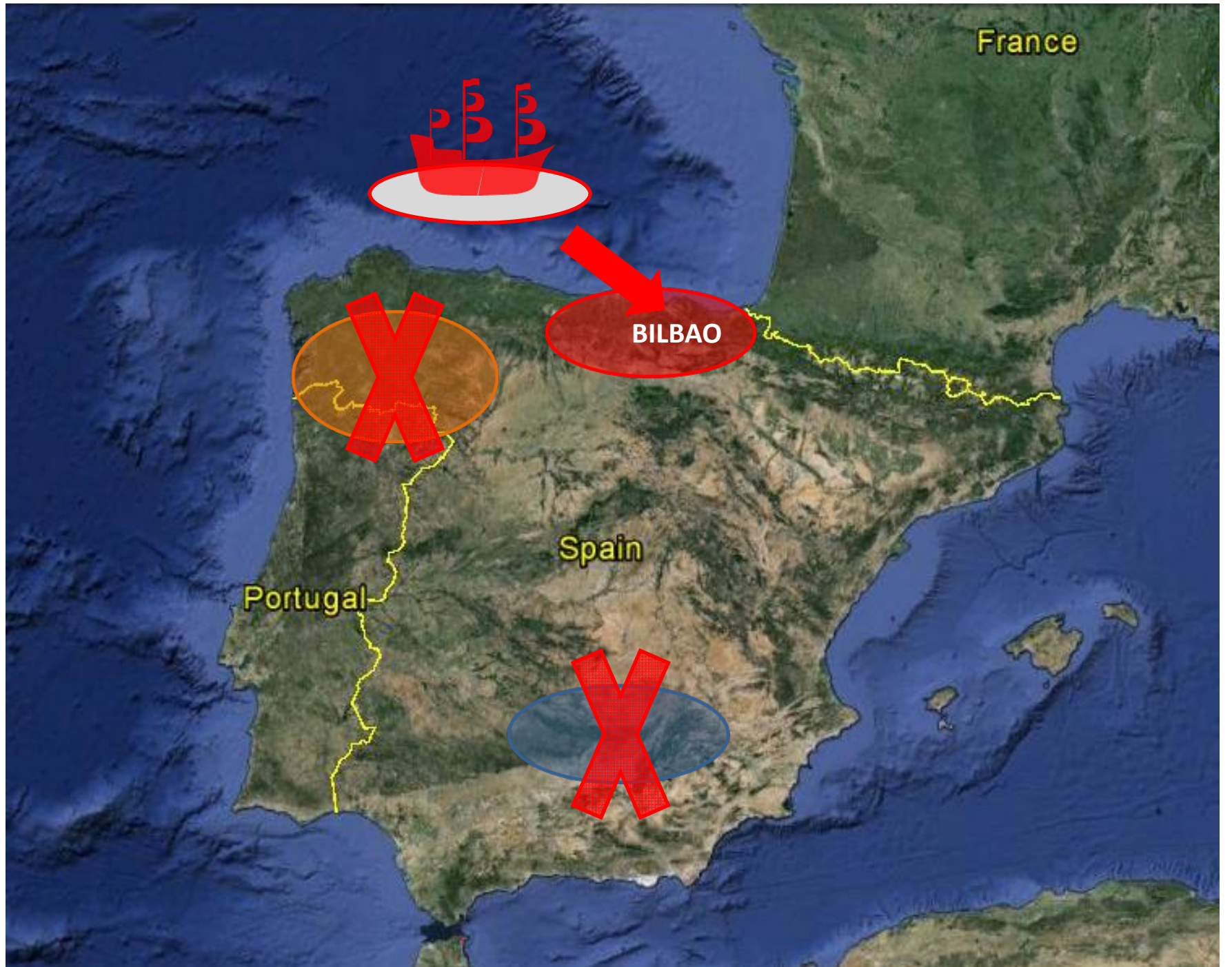


France

Spain

Portugal





France

BILBAO

Spain

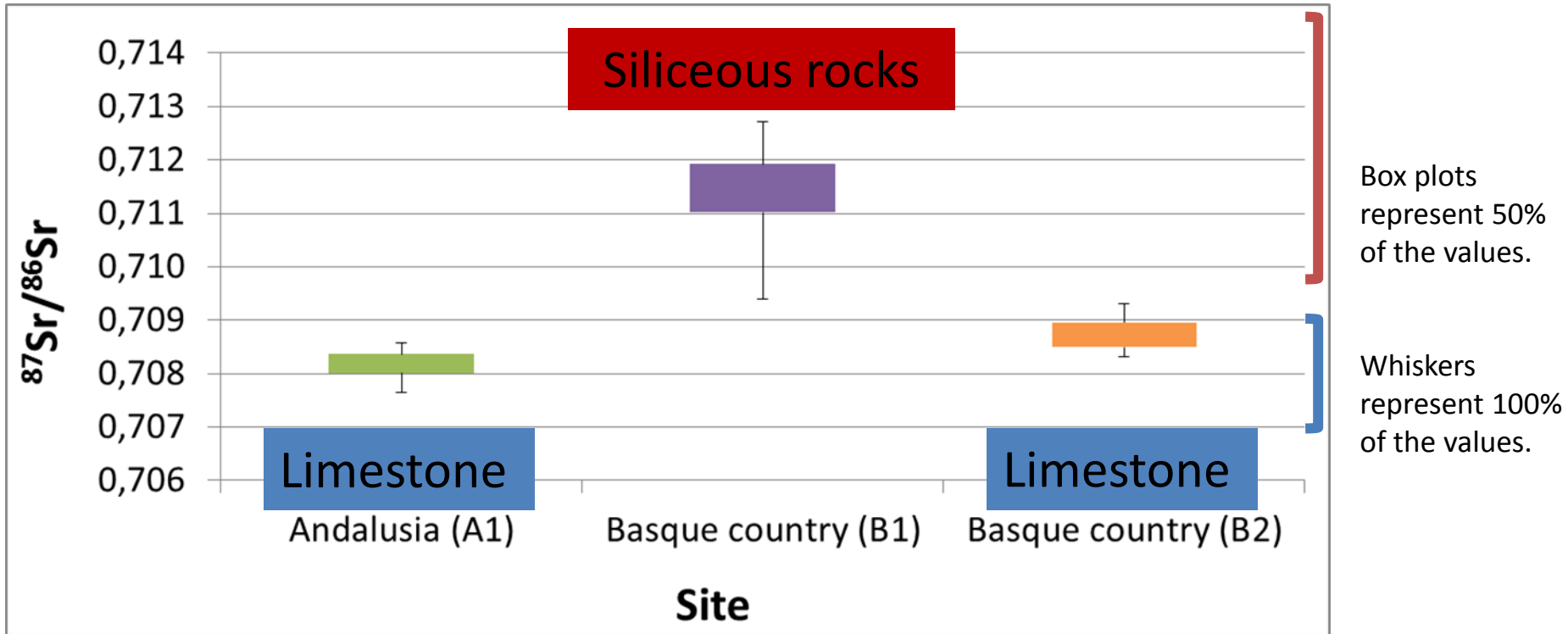
Portugal

# II. Results

1. Wood from living trees
2. Relation between rock-soil-wood isotopic ratios
3. Wood from shipwrecks

# II.1. Results from living trees

## Box plots of the living trees isotopic signature



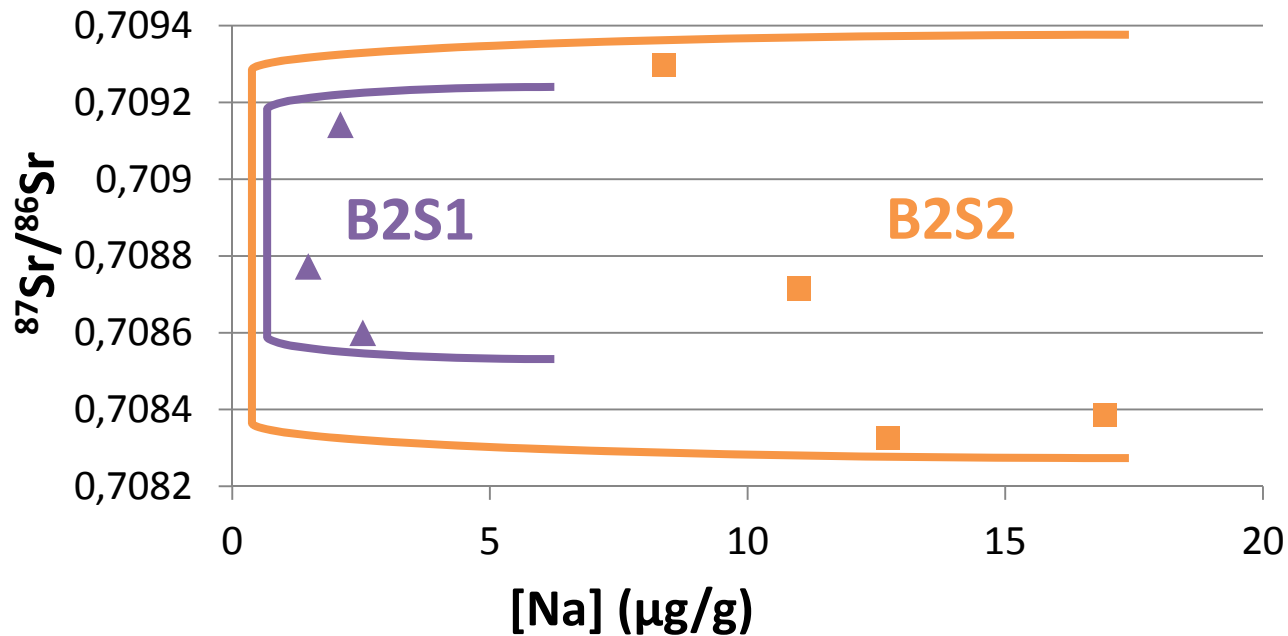
**Specific signature for each site → linked to rock type**

# Another way for discrimination within a site

Example: Basque country B2

B2S1: AZK

B2S2: UZK

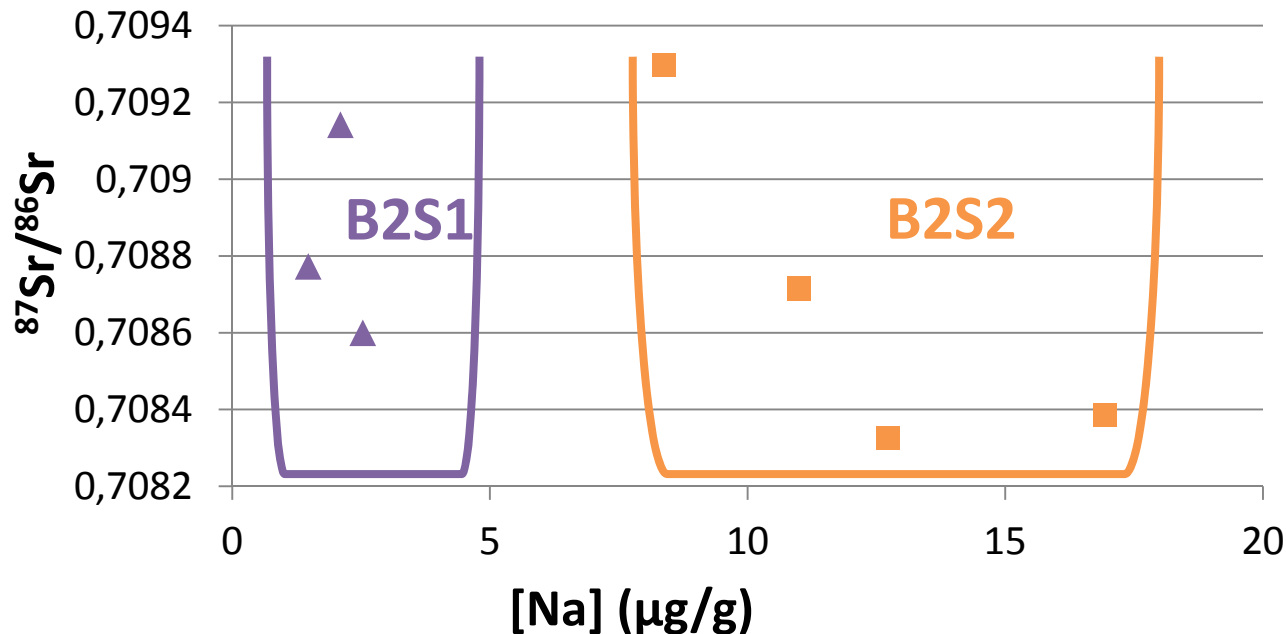


# Another way for discrimination within a site

Example: Basque country B2

B2S1: AZK

B2S2: UZK



**Higher Na concentration in wood indicate proximity from the coasts**



# II.2. Results from rock and soil analyses

## Soil description

SOL	Code terrain	Test HCl sol	Couleur	Description macroscopique									Texture	Informations		
				Taille des			Nature des grains									
				Argiles	Silts	Sables	Calcite	Dolomite	Quartz	Muscovite	Biotite	Oxydation (orange)			Oxyde de fer	
A1	S1	LIN101	-	10YR 3/6 dark yellowish brown	X	X					X?			X	Limono-argileux	
		LIN113	-	2,5Y 2,5/1 black	X	X									Limono-argileux	Certains agrégats réagissent à HCl
		LIN201	-	2,5Y 2,5/1 black	X	X							X		Limono-argileux	
	NAV405	+	10YR 2/2 very dark brown		X		X?	X?				X?			Limono-argileux	
	NAVE08	-	10YR 2/2 very dark brown		X										Limoneux	Beaucoup de MO
B1	S1	OIR101	-	10 YR 8/2 very pale brown	X	X					X				Argilo-limoneuse	
		OIR104	-	10 YR 5/3 brown		X	X			X	X			X	Limono-sableux	
		OIR111	-	10 YR 5/2 grayish brown	x	X	X				X		X		Limono-sableuse	Quartz anguleux émoussés, concrétions mangasiques
	S2	OIR204	+	10 YR 7/3 very pale brown	X	X		X					X		Argilo-limoneuse	Grains de calcite visibles
		OIR205	+	10 YR 5/2 grayish brown		X		X				X?	X	X	Argilo-limoneuse	
	S2	ART001	-	2,5 Y 4/3 olive brown		X	X			X	X		X	X	Limono-(sableux)	Quartz anguleux émoussés
		ART002	-	2,5 Y 5/3 light olive brown	x	X	X			X	X		X	X	Limono-sableux	Quartz anguleux émoussés
ART004		-	2,5 Y 5/4 light olive brown		X	X			X	X		X	X	Limono-sableux		
B2	S1	AZK004	-	10 YR 4/3 brown	X	X					X				Argilo-limoneux	
		AZK005	-	10 YR 4/3 brown	X	X									Argilo-limoneux	

 9 representative soil samples were selected for isotopic analyses

# II.2. Results from rock and soil analyses

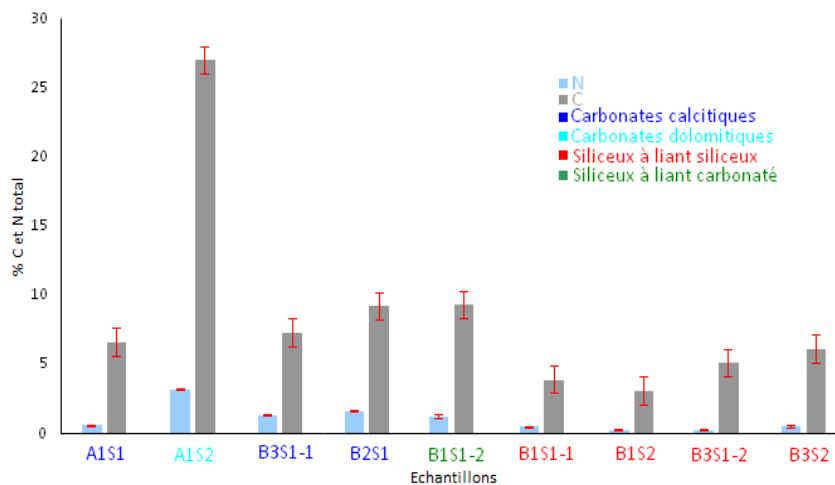
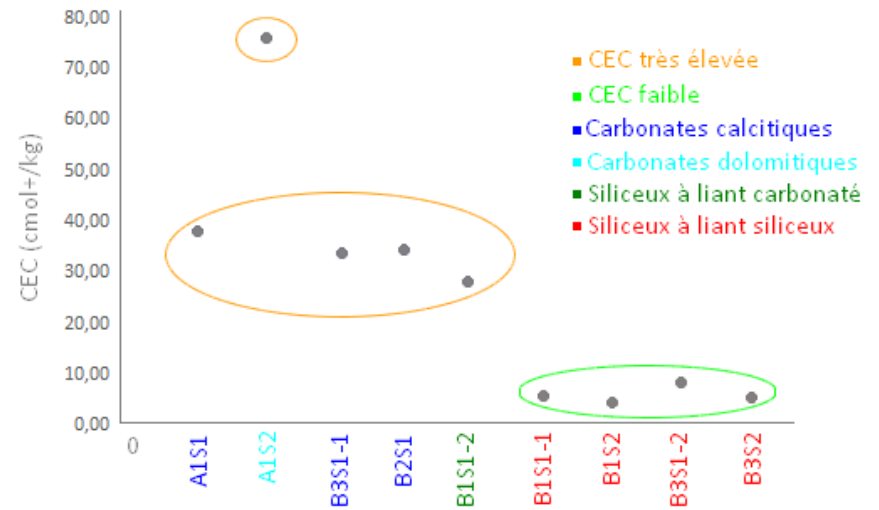
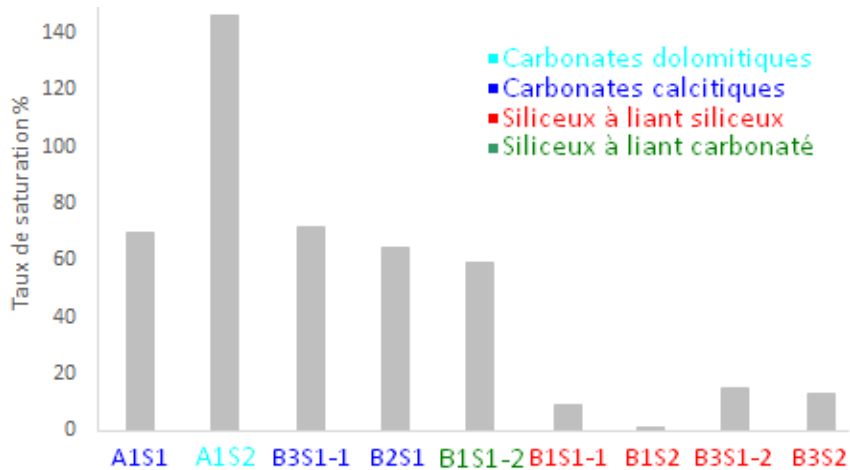
## Rock description

ROCHE	Code terrain	Test HCl roche	Description macroscopique											Nom roche	Informations	
			Liant		Nature des grains											
			Matrice	Ciment	Calcite	Dolomite	Quartz		Muscovite	Biotite	Feldspaths	Argiles	Oxydation (orange)			Oxyde de fer
Silts	Sables															
A1	S1	LIN101	+		X		X			X?			X	X?	Wackstone	
		LIN113	+	X		X		X					X		Wackstone	Clastes biogéniques
		LIN201	+	X		X		X							Wackstone	Clastes biogéniques
	S2	NAV405	+		X?	X							X	X?	Wackstone dolomitique	
		NAVE08	+	X		X	X								Wackstone dolomitique	
B1	S1	1	OIR101	-	X			X		X			X		Argilite-silteuse	
			OIR104	-				X		X			X		Argilite-silteuse	
		OIR111	-	X			X	X	X		X		X	X	Greywacke	Feldspath visible
	2	OIR204	+	X		X	X					X			Siltite à matrice carbonatée	
		OIR205	+			X	X							X?	Siltite à matrice carbonatée	
	S2	ART001	-		X		X	X	X				X	X	Siltite-schisteuse	Veine de quartz
		ART002	-	x	X			X	X				X	X	Arénite-schisteuse	Très altérée
ART004		-				X		X?	X?				X?			
B2	S1	AZK004	+			X		X?								
		AZK005	+	X		X									Mudstone	Veine de calcite, entroques

 9 representative rock samples were selected for isotopic analyses

# II.2. Results from rock and soil analyses

## Analyses on the 9 selected soil and rock samples

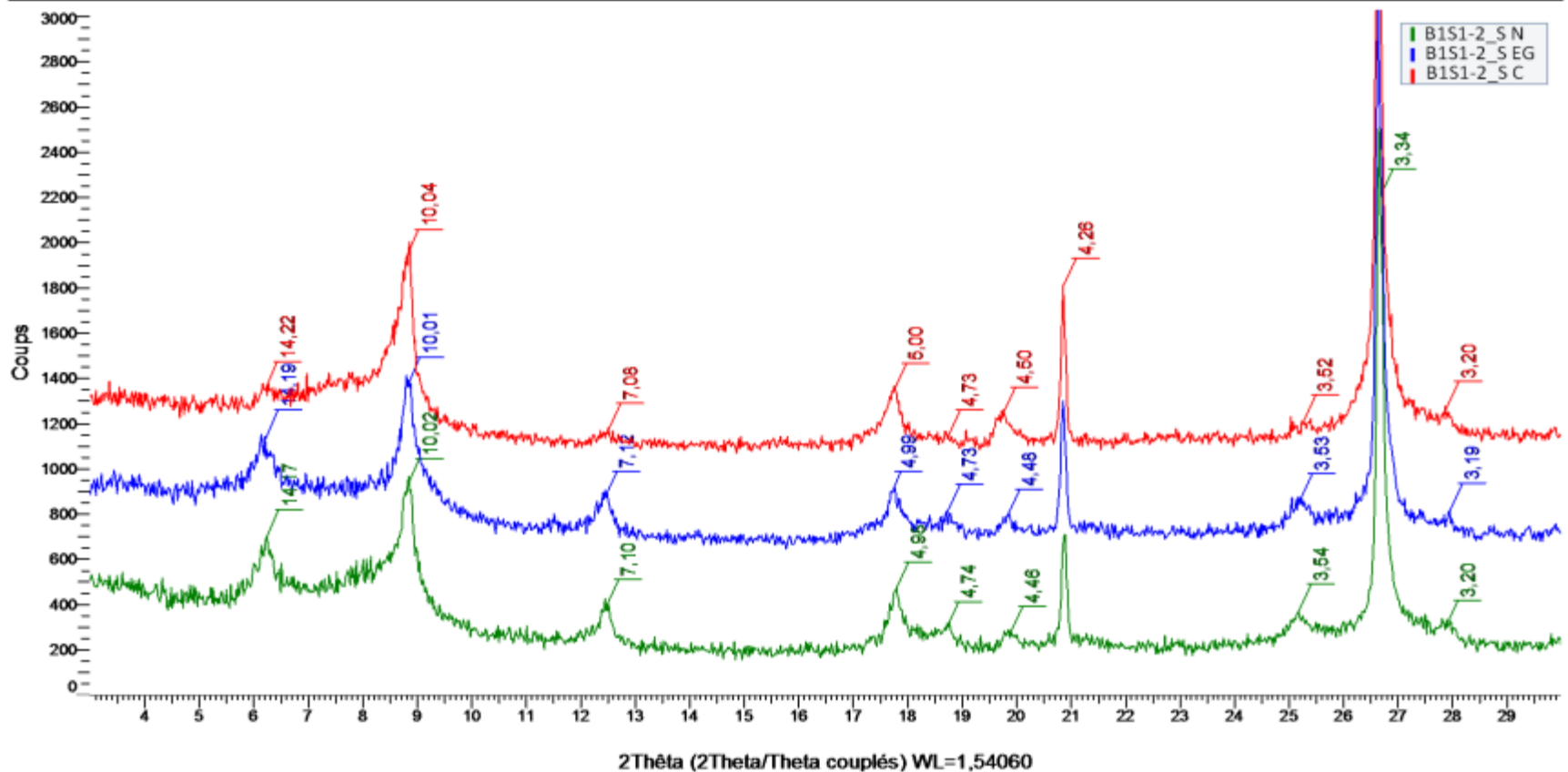


**Significant difference between values from calcareous and siliceous samples**

# II.2. Results from rock and soil analyses

## XRD (X-ray diffraction) analyses

B1S1-2 Suspension de sol





## II.2. Results from rock and soil analyses

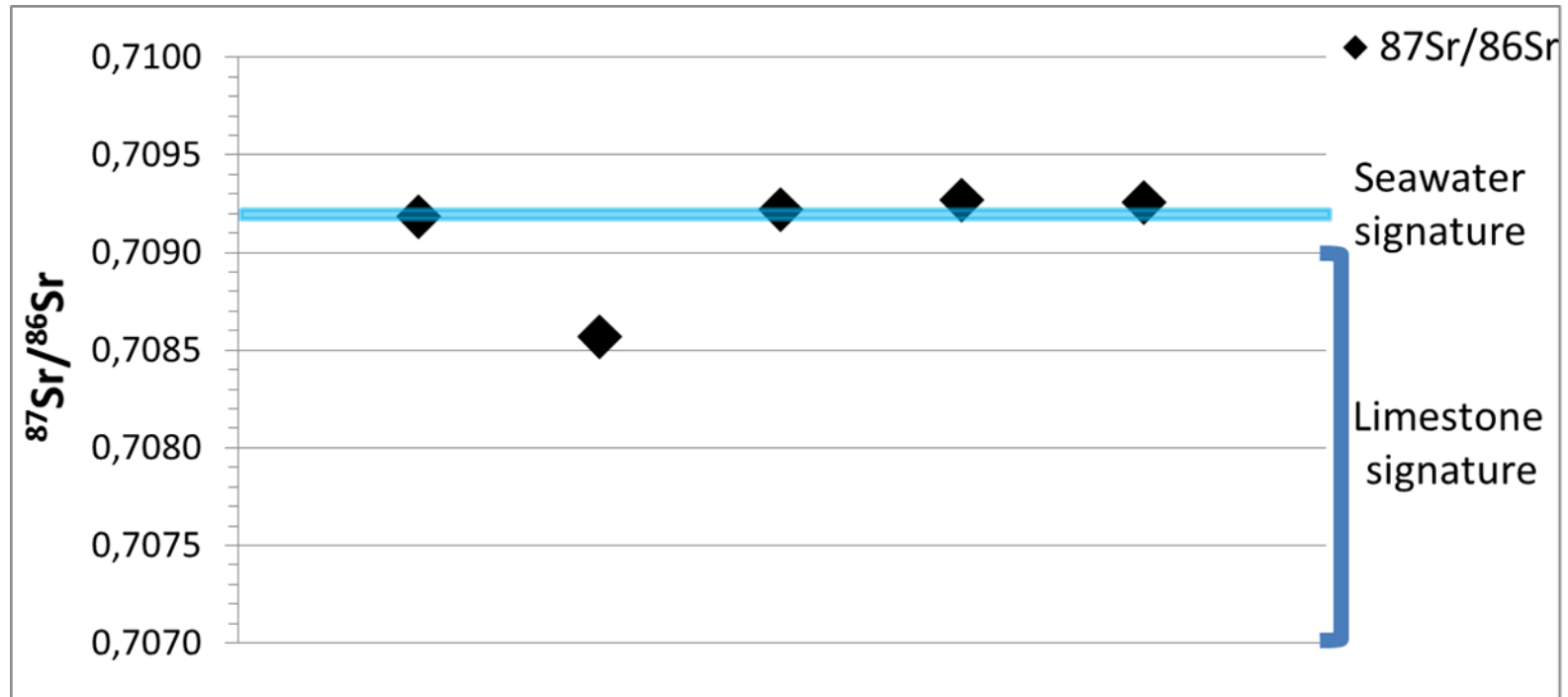
Do we have a correlation between the Sr isotopic ratios of rocks, soils and trees?



Undergoing analyses

# II.3. Results from shipwreck timbers

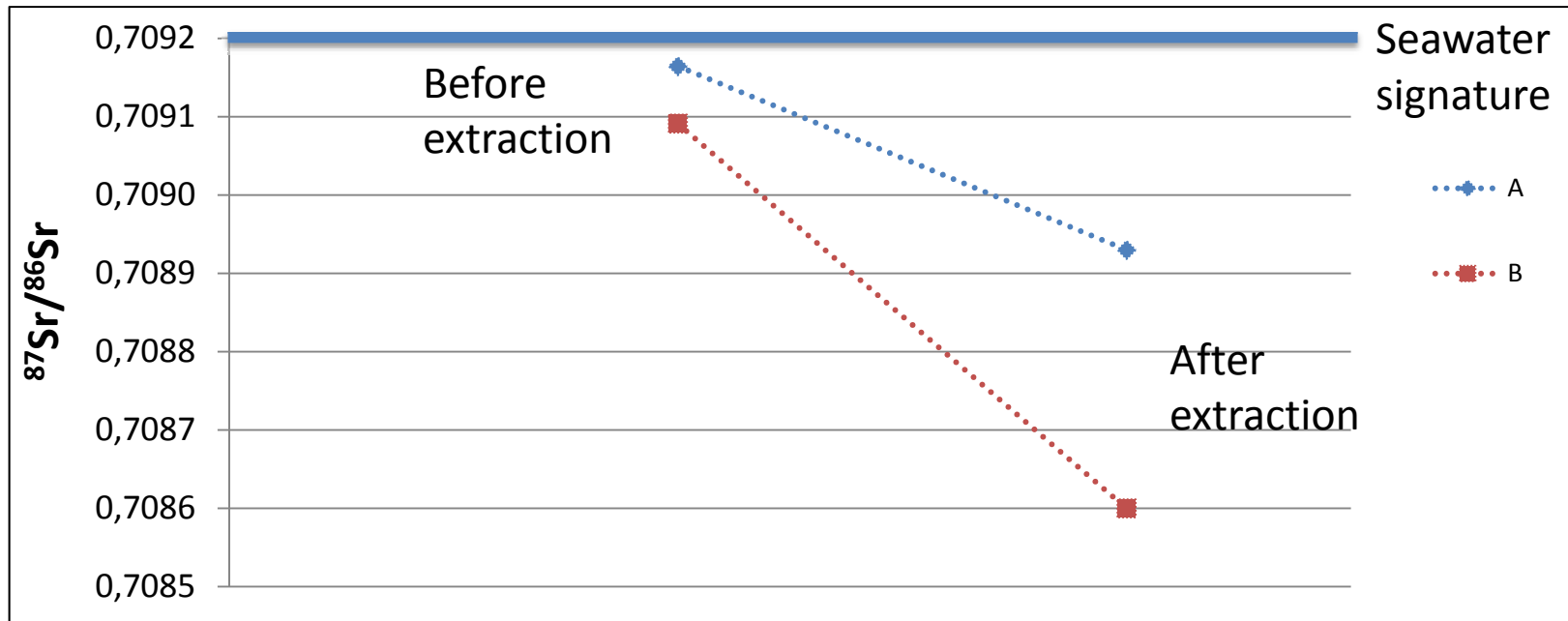
## First analyses of wood from Ribadeo shipwreck



**Wood from shipwreck are contaminated by sea water elements**

# II.3. Results from shipwreck timbers

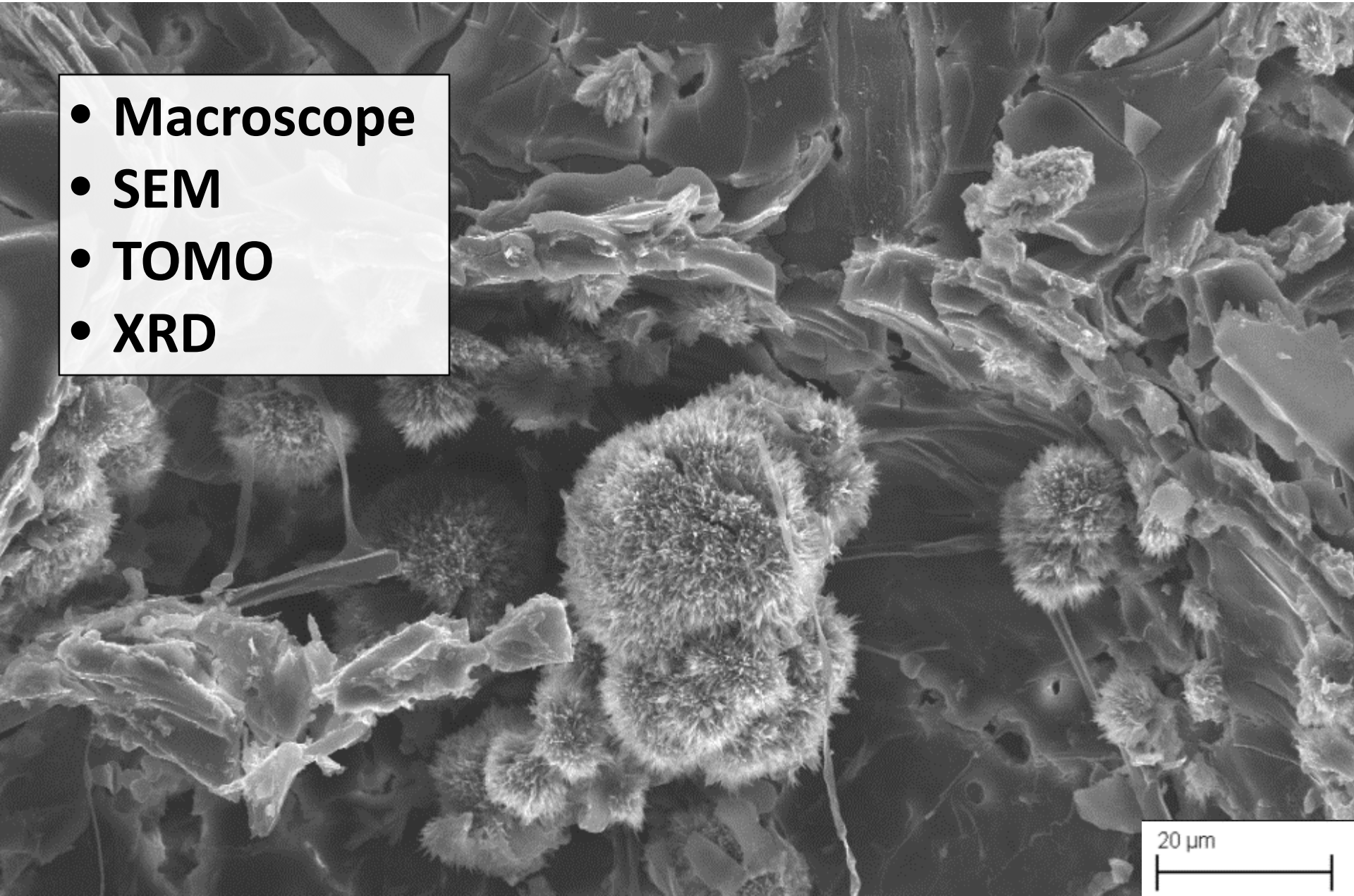
## First extraction results



**Sea water elements were extracted from the wood but the extraction is not complete**

## II.4. Characterization of the contamination

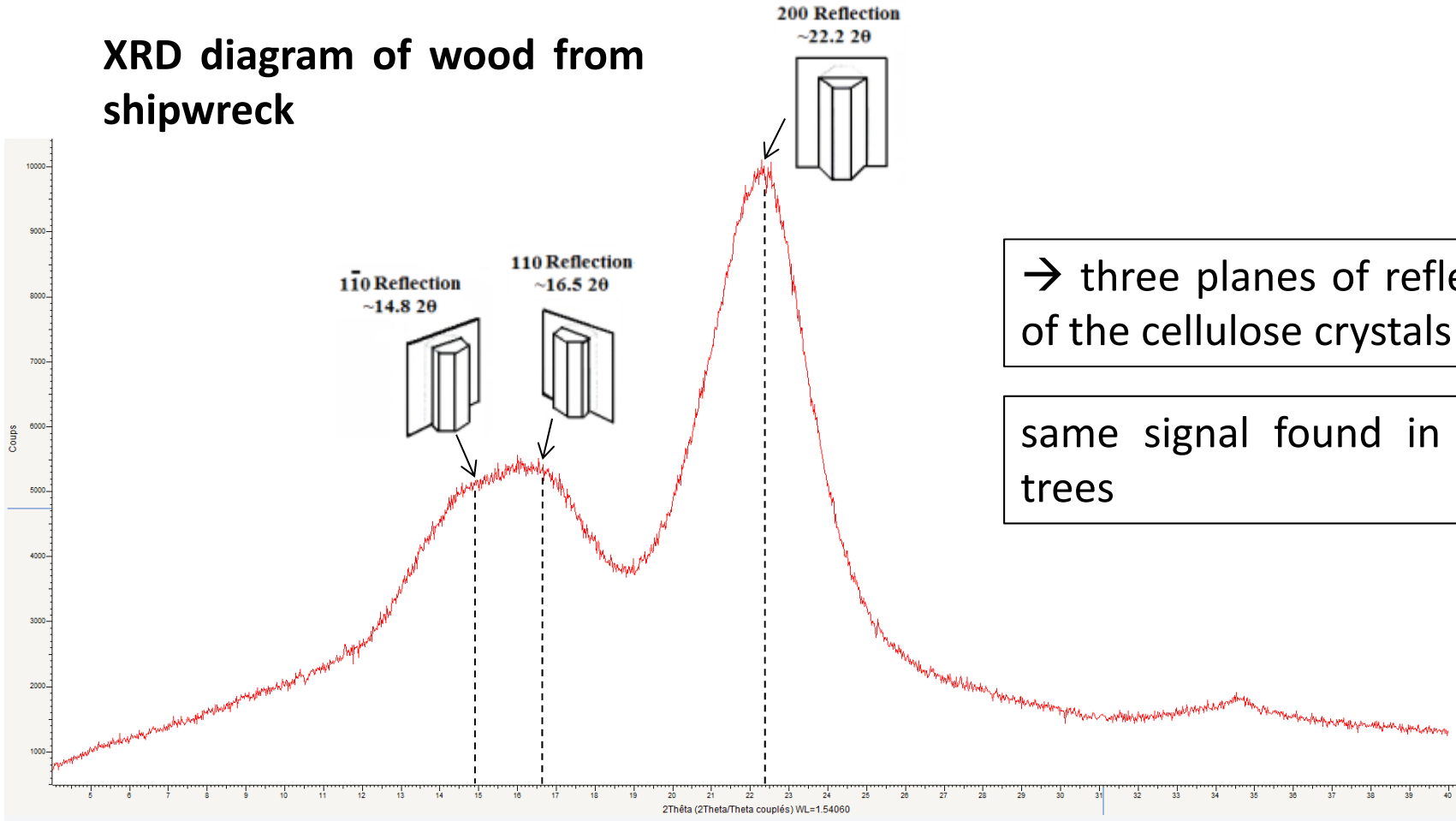
- **Macroscope**
- **SEM**
- **TOMO**
- **XRD**





# II.4. Characterization of the contamination

XRD diagram of wood from shipwreck



→ three planes of reflection of the cellulose crystals

same signal found in living trees

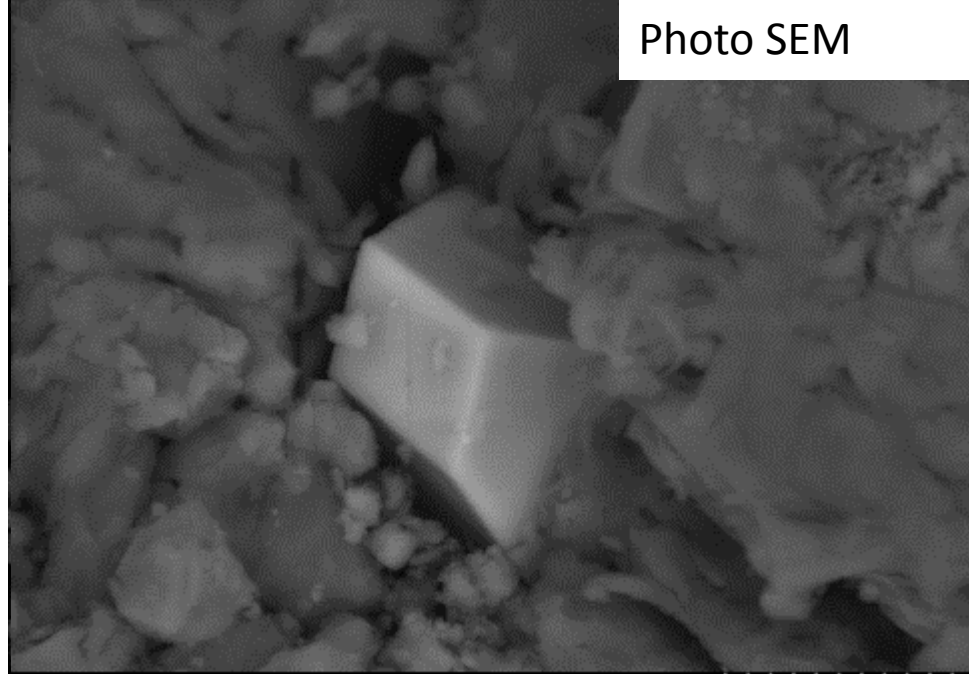
**Common peaks for wood samples**

# Sometimes other peaks ...

XRD diagram from another sample

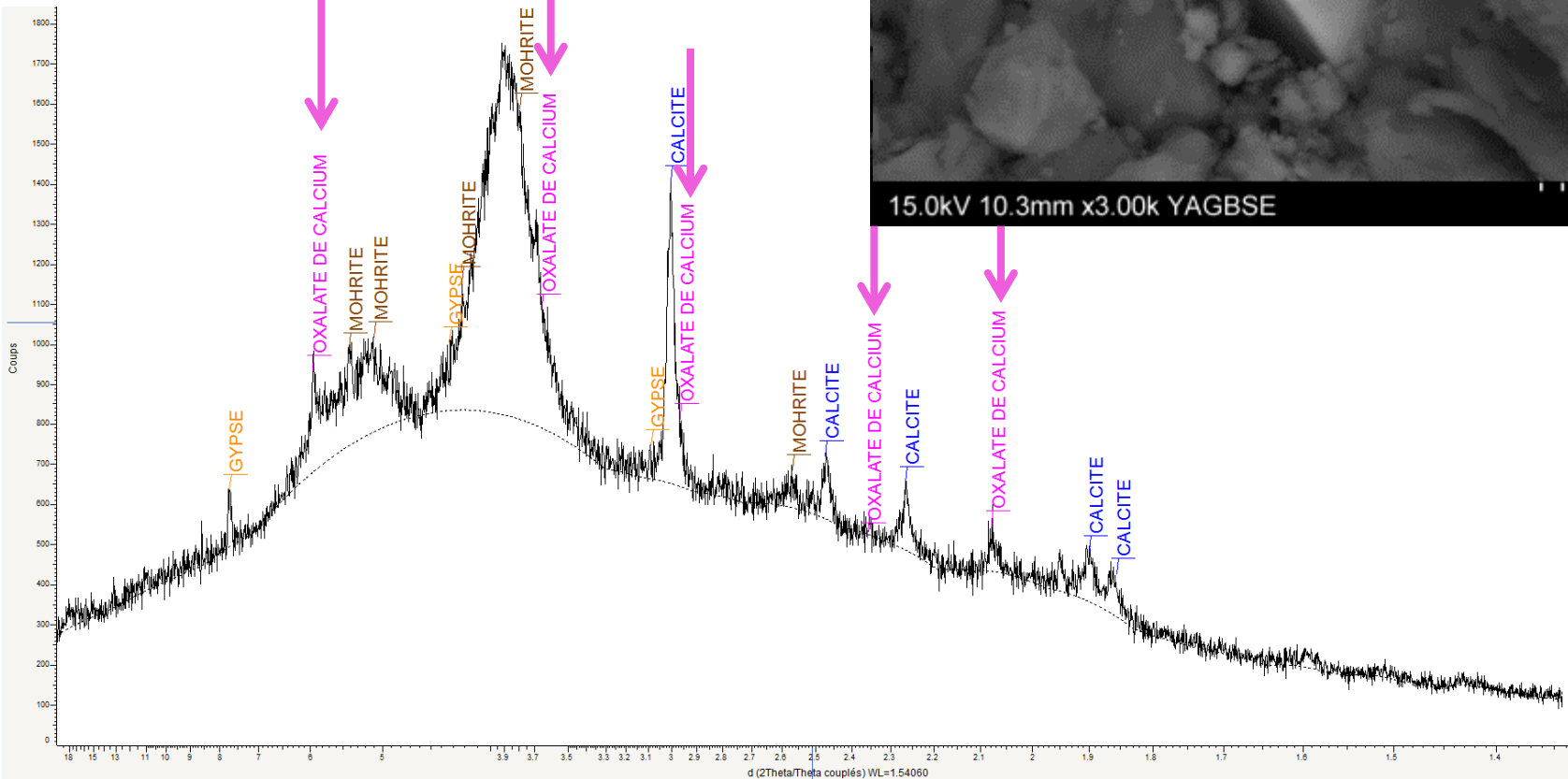
Calcium oxalates:  $\text{Ca}(\text{COO})_2$

Photo SEM



15.0kV 10.3mm x3.00k YAGBSE

10.0um



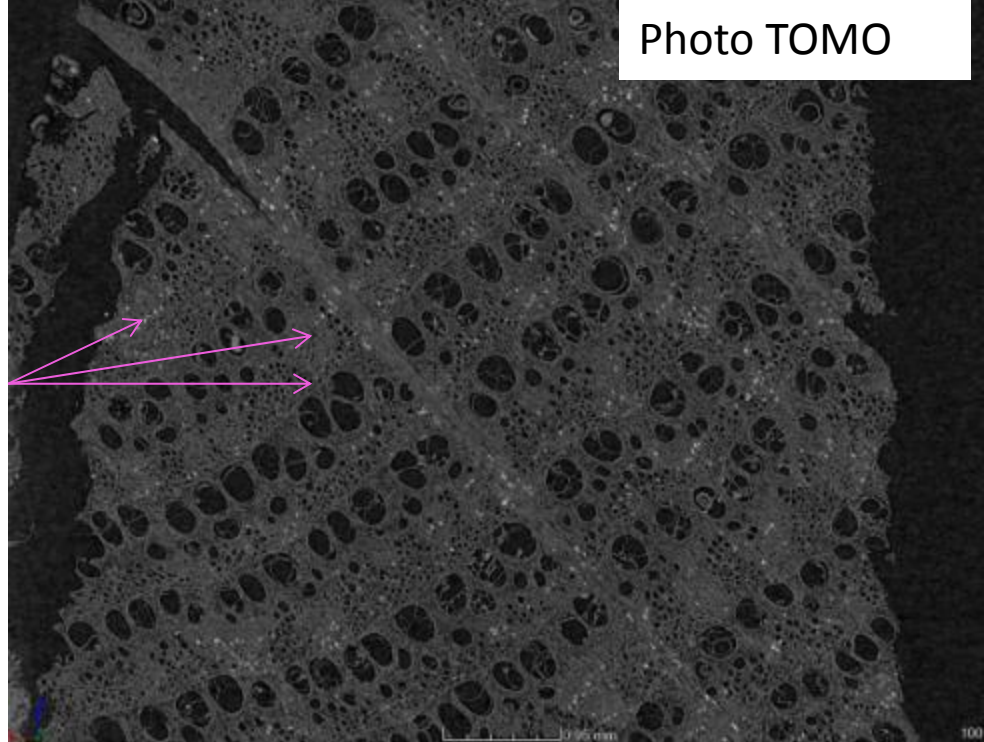
# Sometimes other peaks ...

XRD diagram from another sample

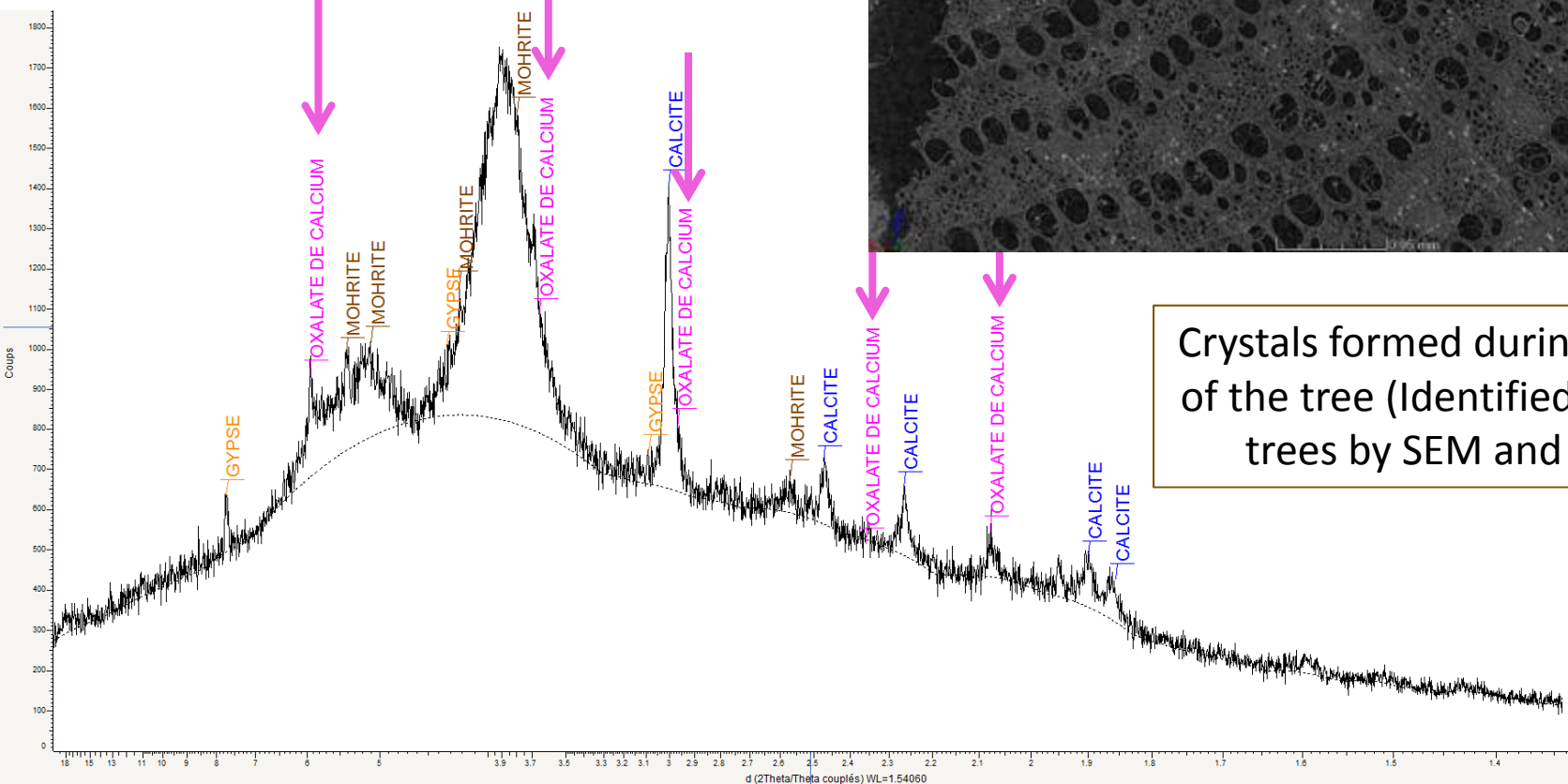
Calcium oxalates:  $\text{Ca}(\text{COO})_2$

Photo TOMO

Oxalates



Crystals formed during the life of the tree (Identified in living trees by SEM and XRD)



**Oxalates still present in wood from shipwrecks**

# More peaks ...

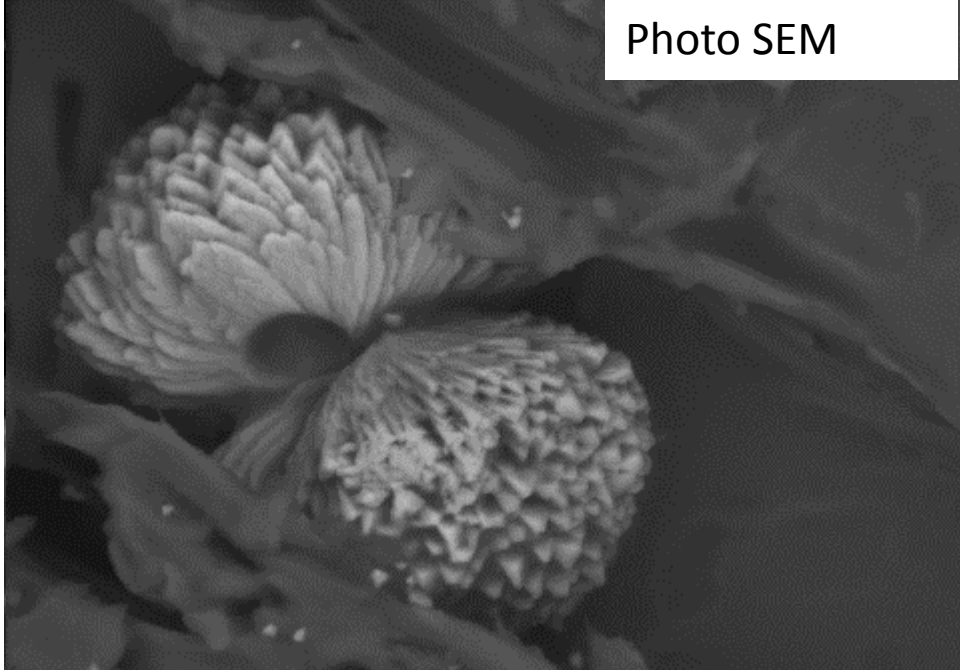
## XRD diagram from another sample

Calcium oxalate :  $\text{Ca}(\text{COO})_2$

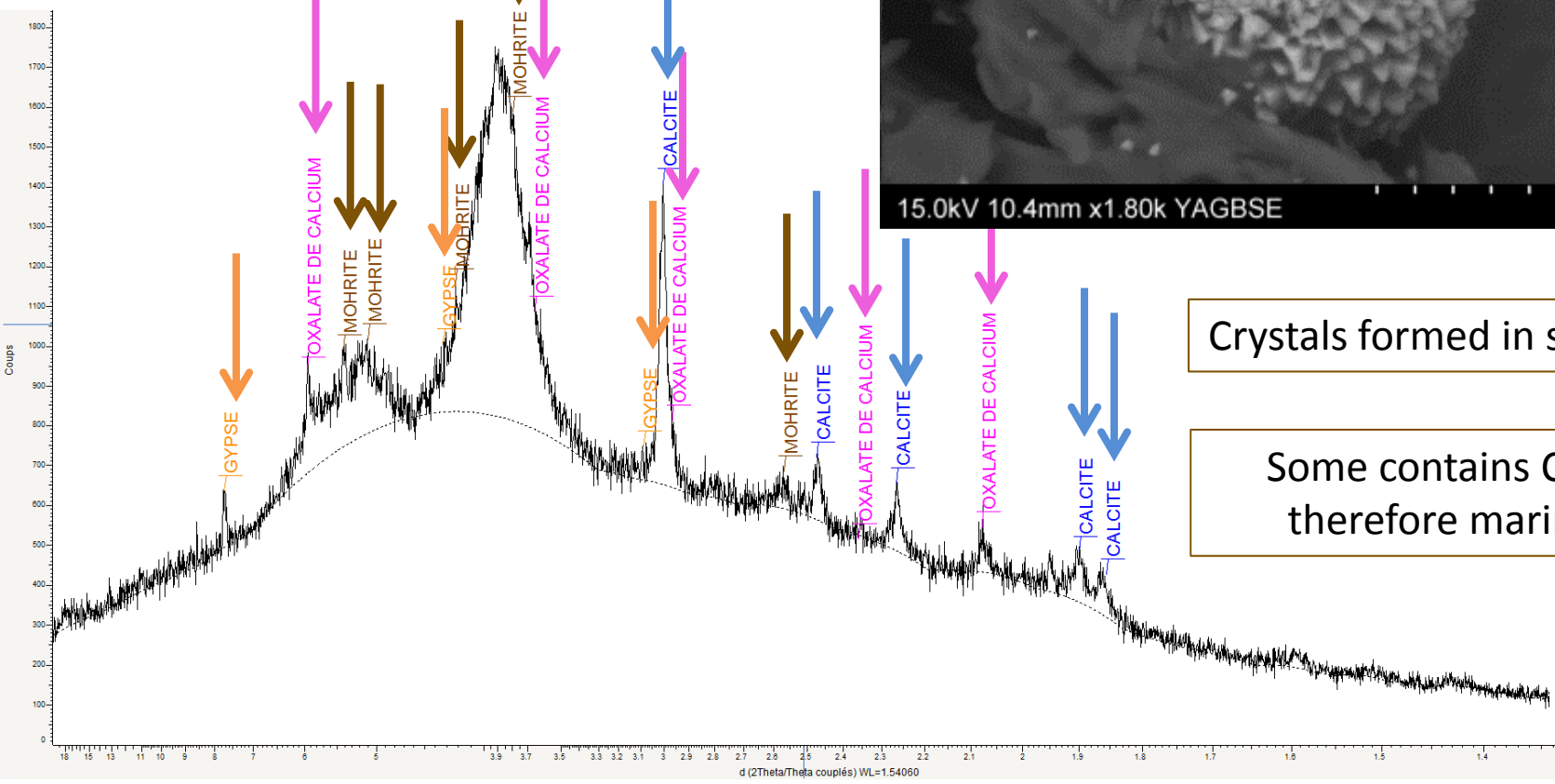
Mohrite :  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$

Gypsum :  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Calcite :  $\text{CaCO}_3$



15.0kV 10.4mm x1.80k YAGBSE 30.0um



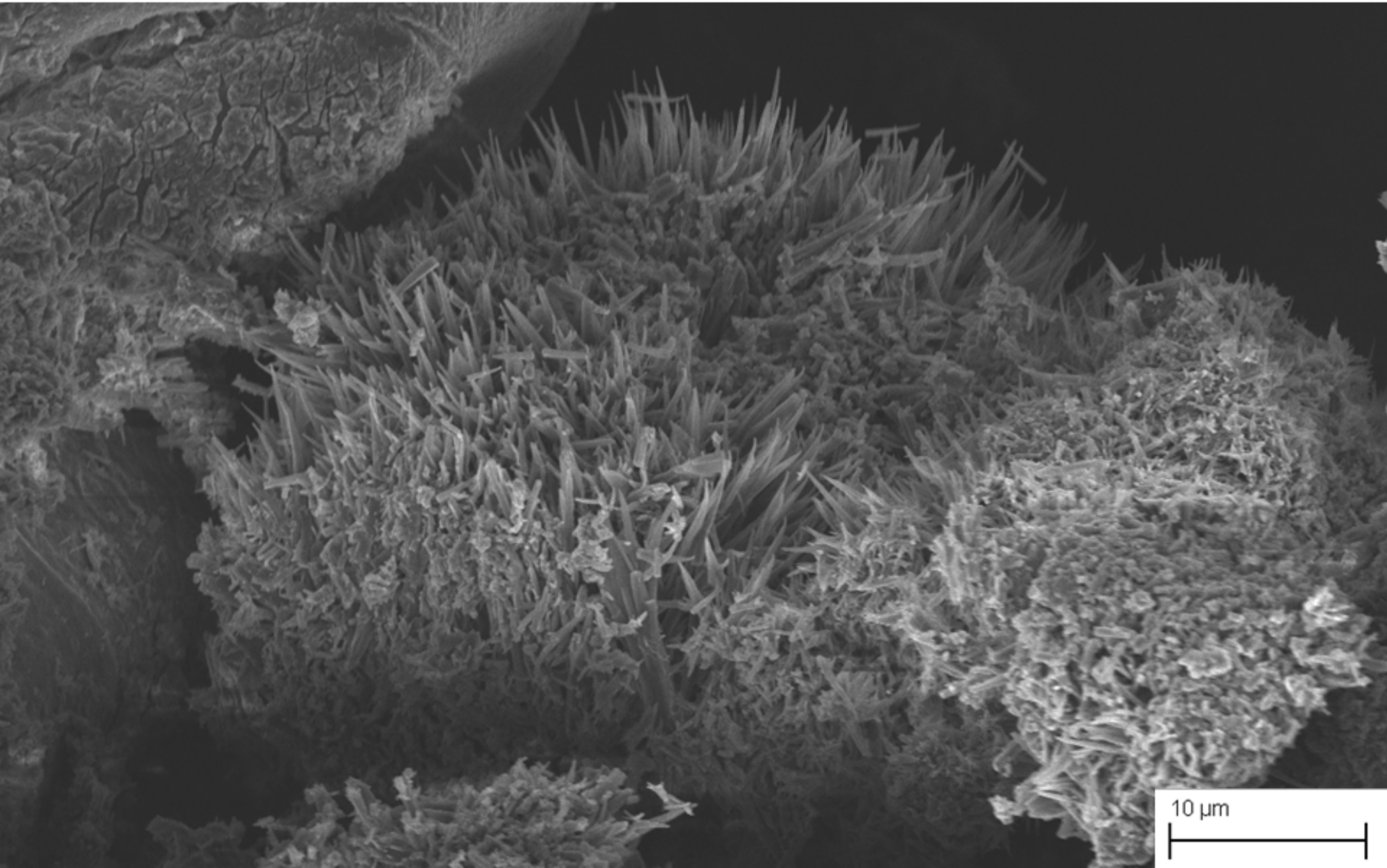
Crystals formed in sea water

Some contains Ca and therefore marine Sr

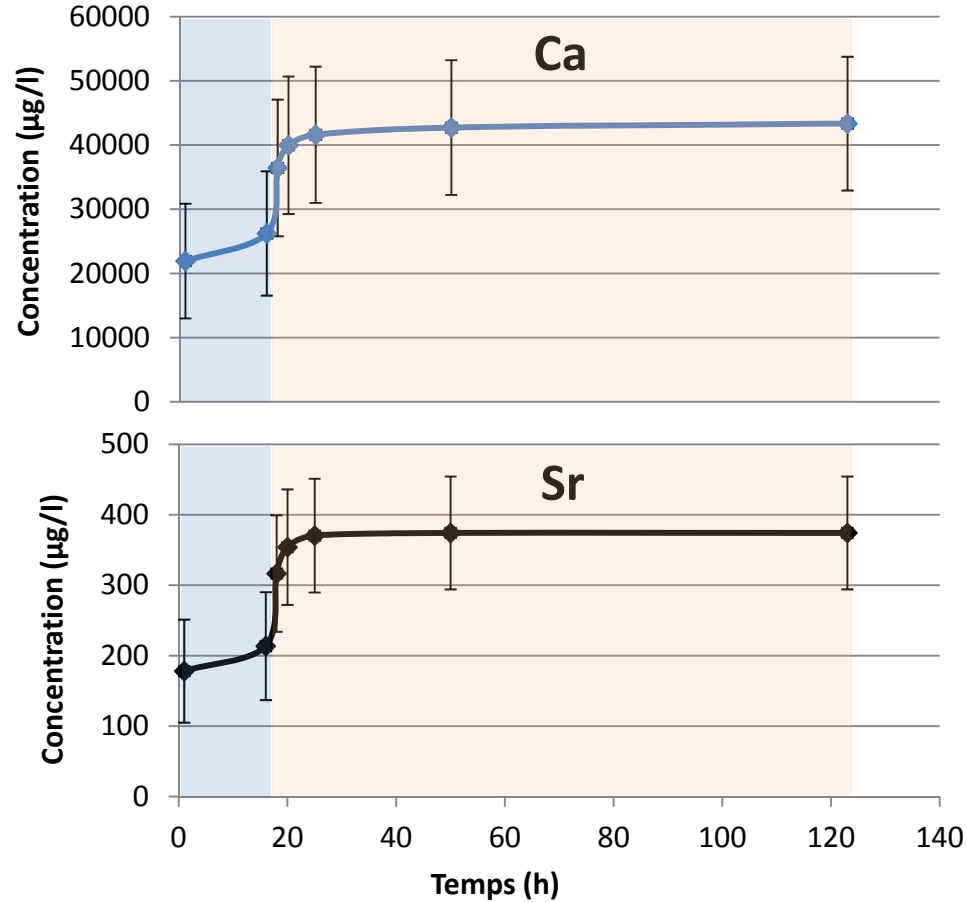
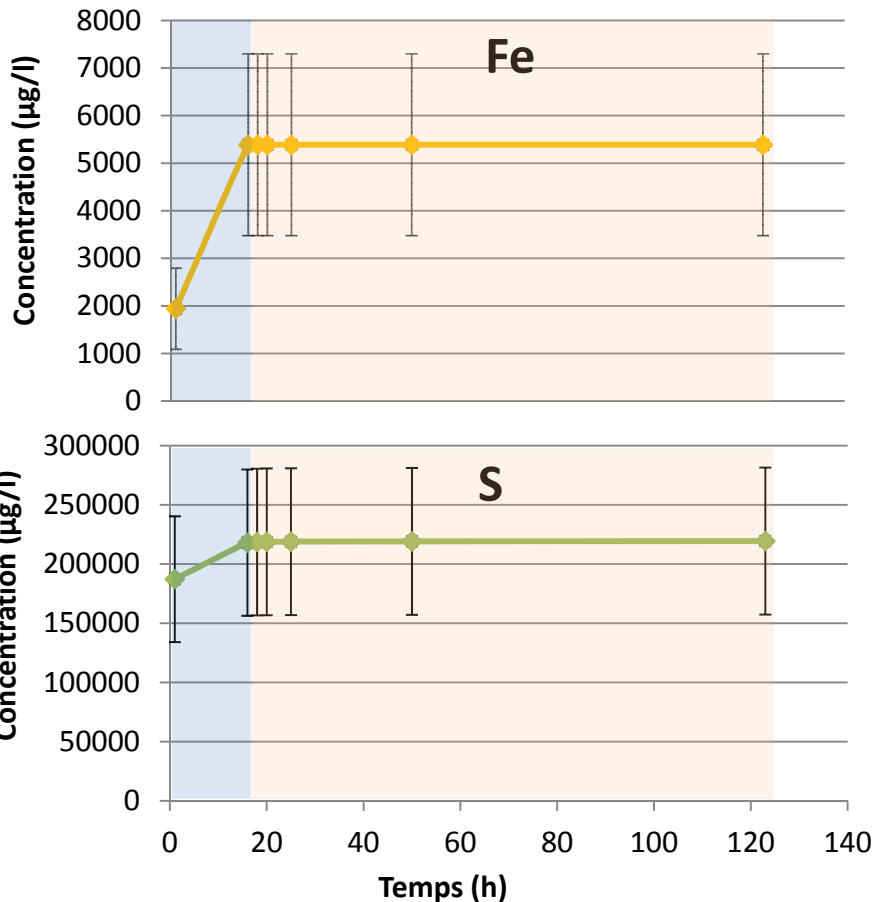
Possible contamination of the wood signature with marine elements in the crystals



## II.5. Extraction protocol to eliminate the contamination



# Example of extraction applied on a wood from shipwreck from the 18th century (BAY 01W 2S)



Fe and S are eliminated by water

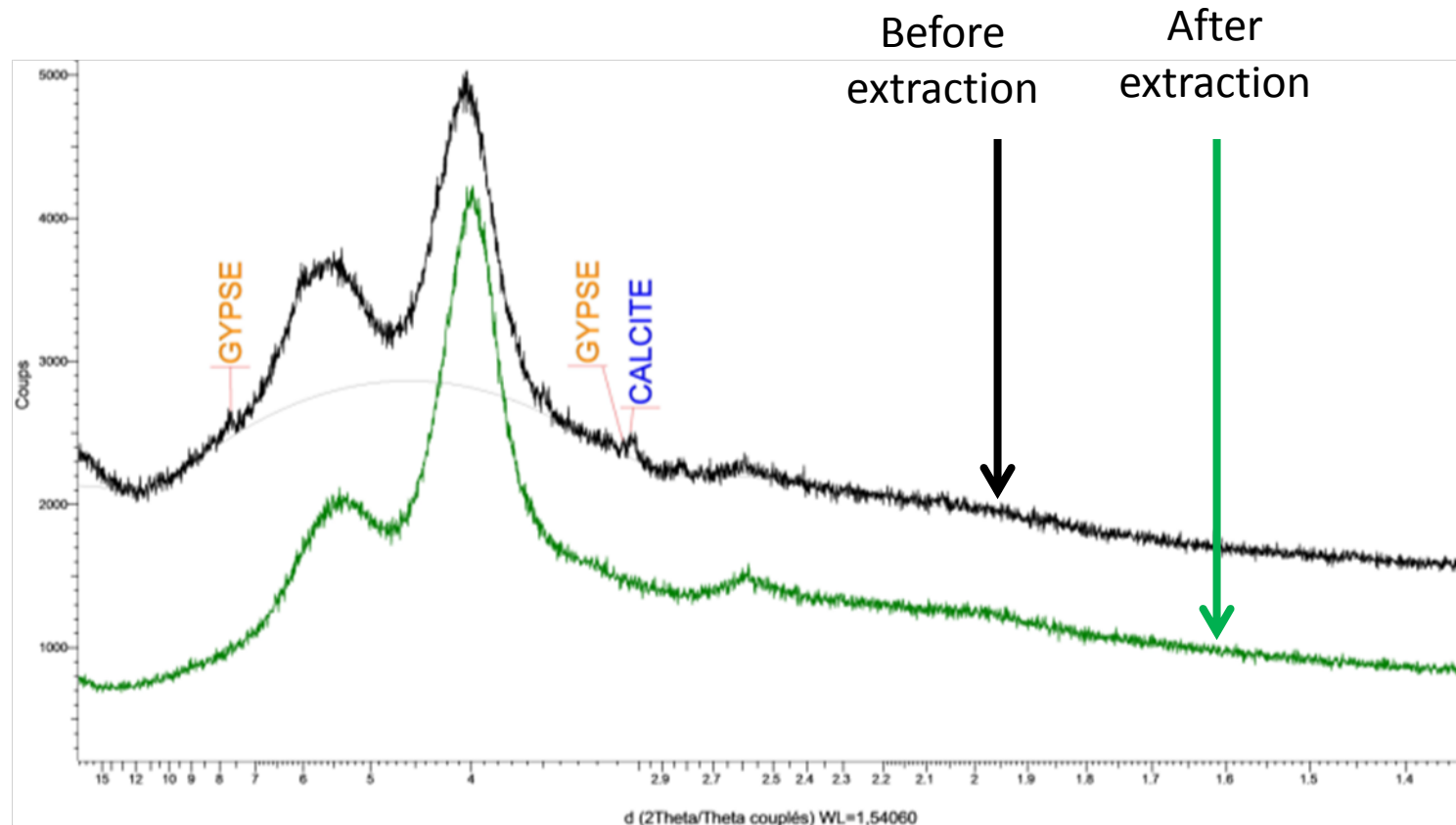
Ca and Sr are extracted by water (in sulfates) and by NH<sub>4</sub>Ac (exchangeable)

Similar results for three other shipwrecks

**Does that mean that we extracted the totality of seawater elements?**

# II.5. Extraction protocol to eliminate the contamination

Verification of the minerals present before and after the extraction on BAY 01W 2S



**Elimination of Gypsum and Calcite by the extraction**



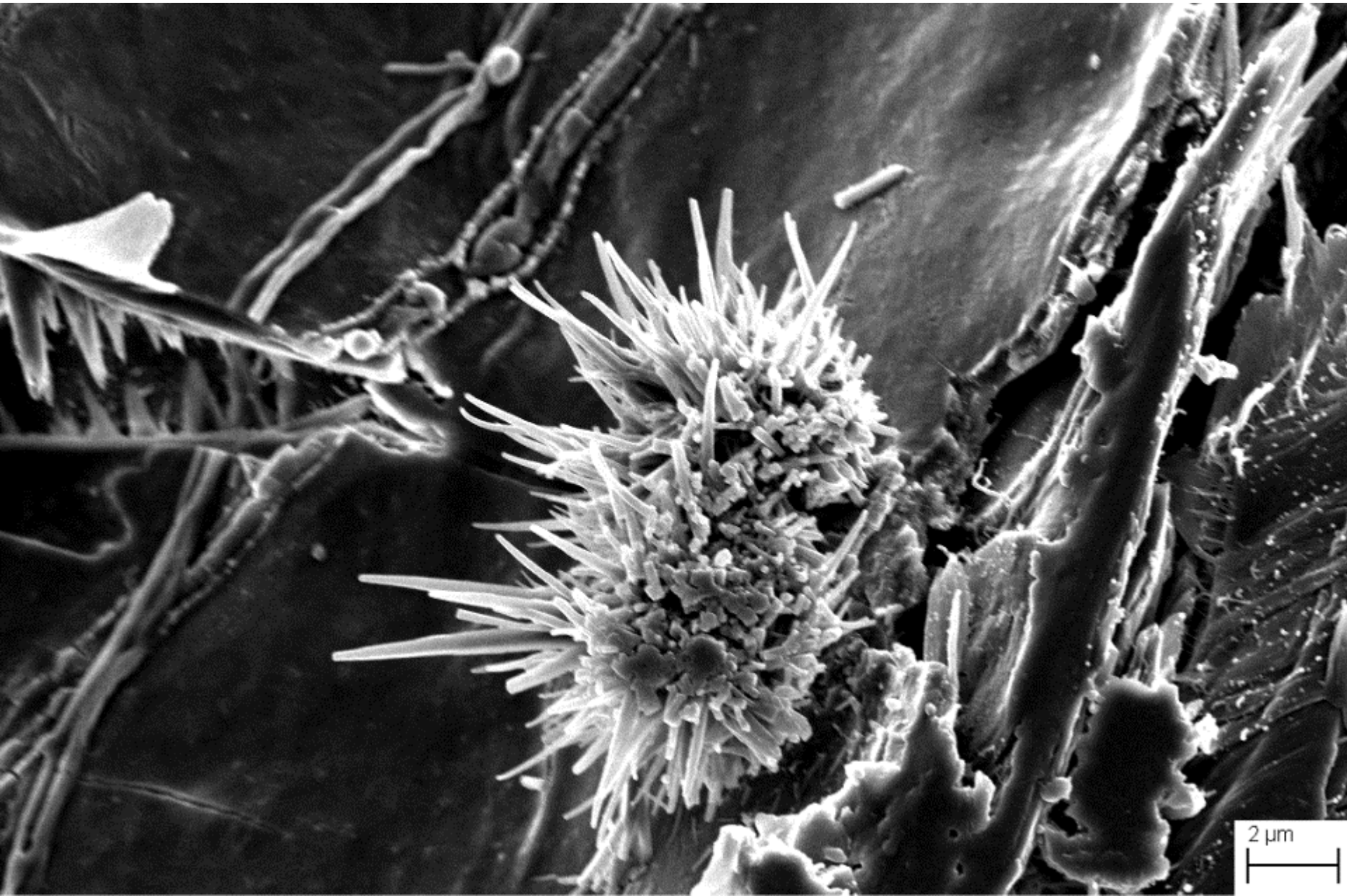
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UNIVERSITÉ  
DE LORRAINE

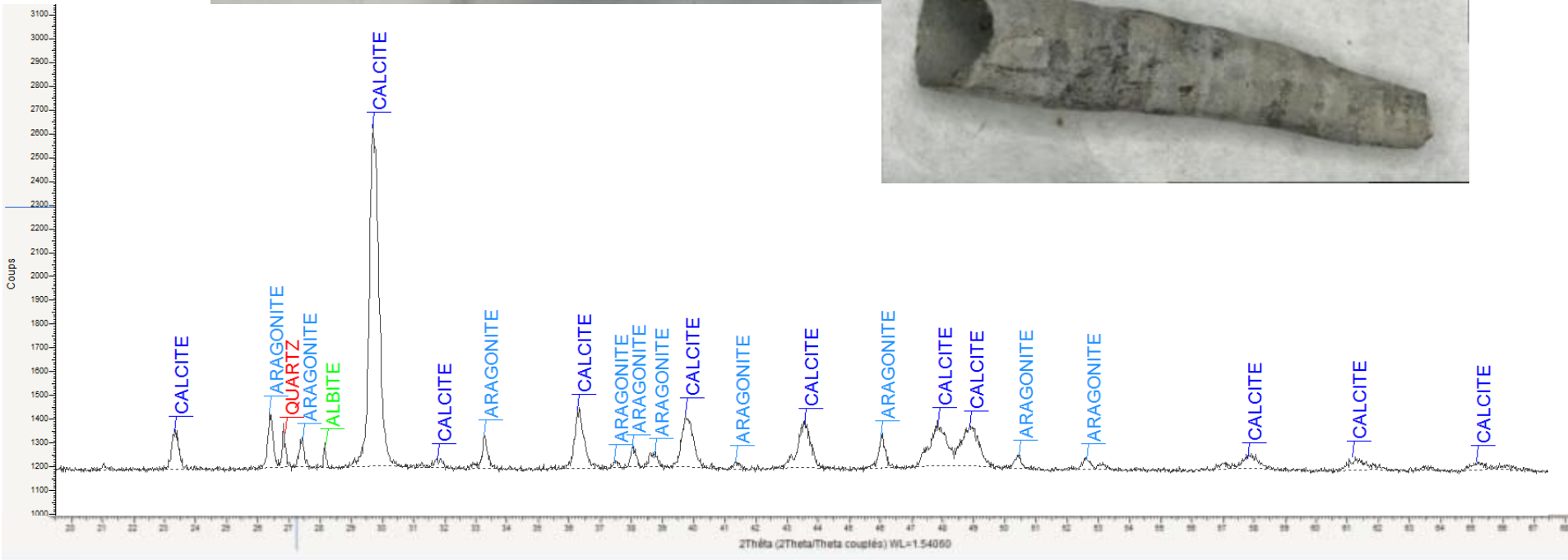


Thank you for your attention!

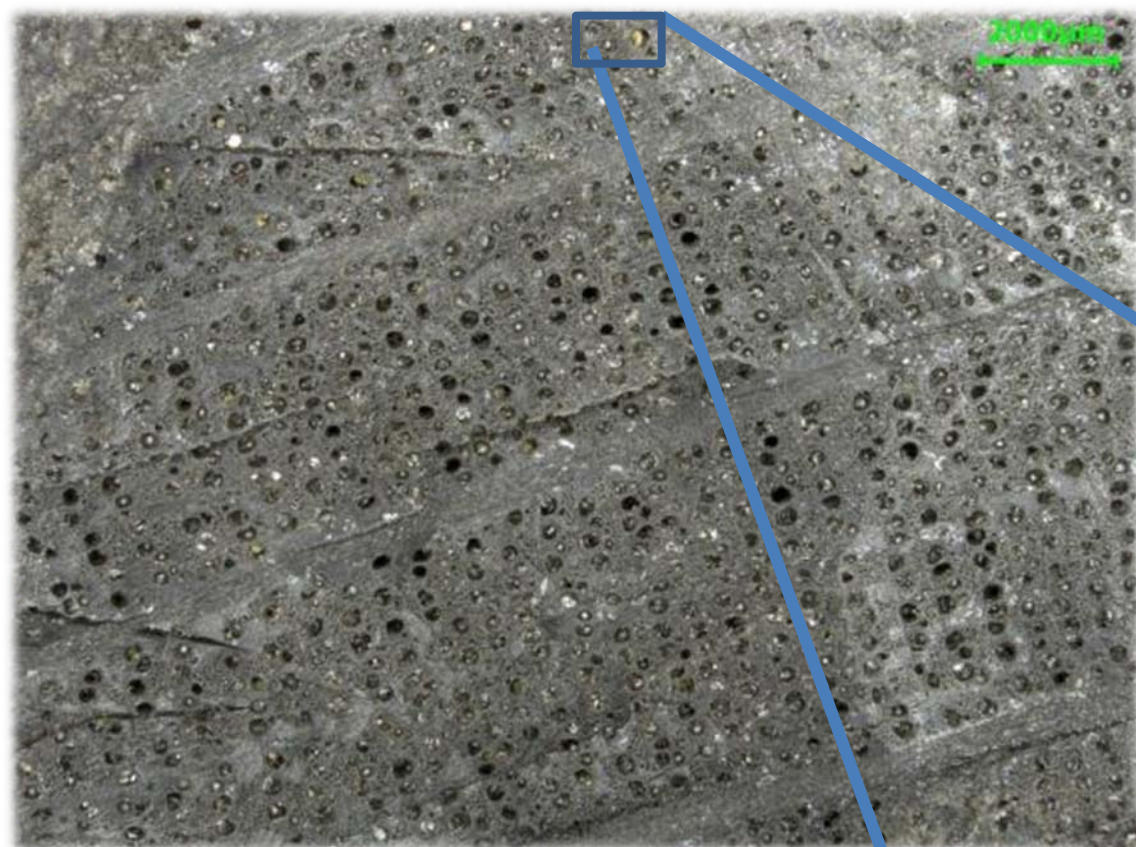




Calcite :  $\text{CaCO}_3$   
 Aragonite :  $\text{CaCO}_3$   
 Quartz :  $\text{SiO}_2$   
 Albite :  $\text{NaAlSi}_3\text{O}_8$





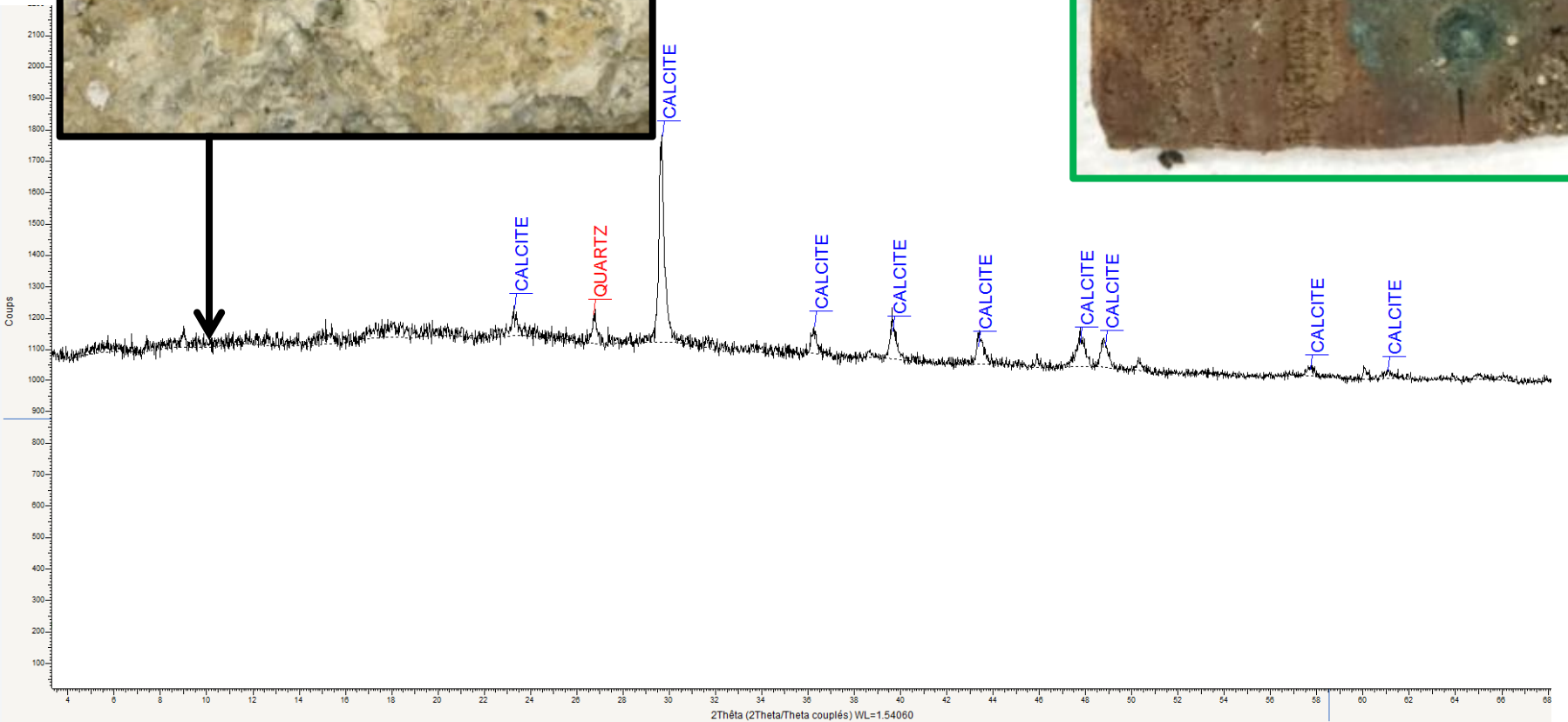


# Pas vraiment étonnant ...



Calcite :  $\text{CaCO}_3$

Quartz :  $\text{SiO}_2$

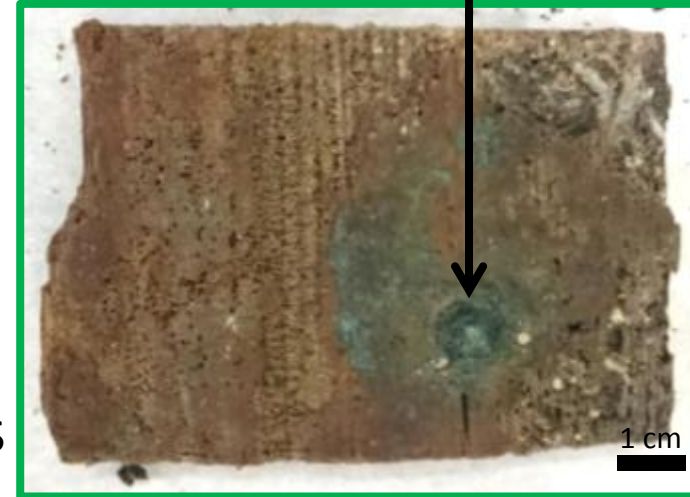


# Pas vraiment étonnant ...

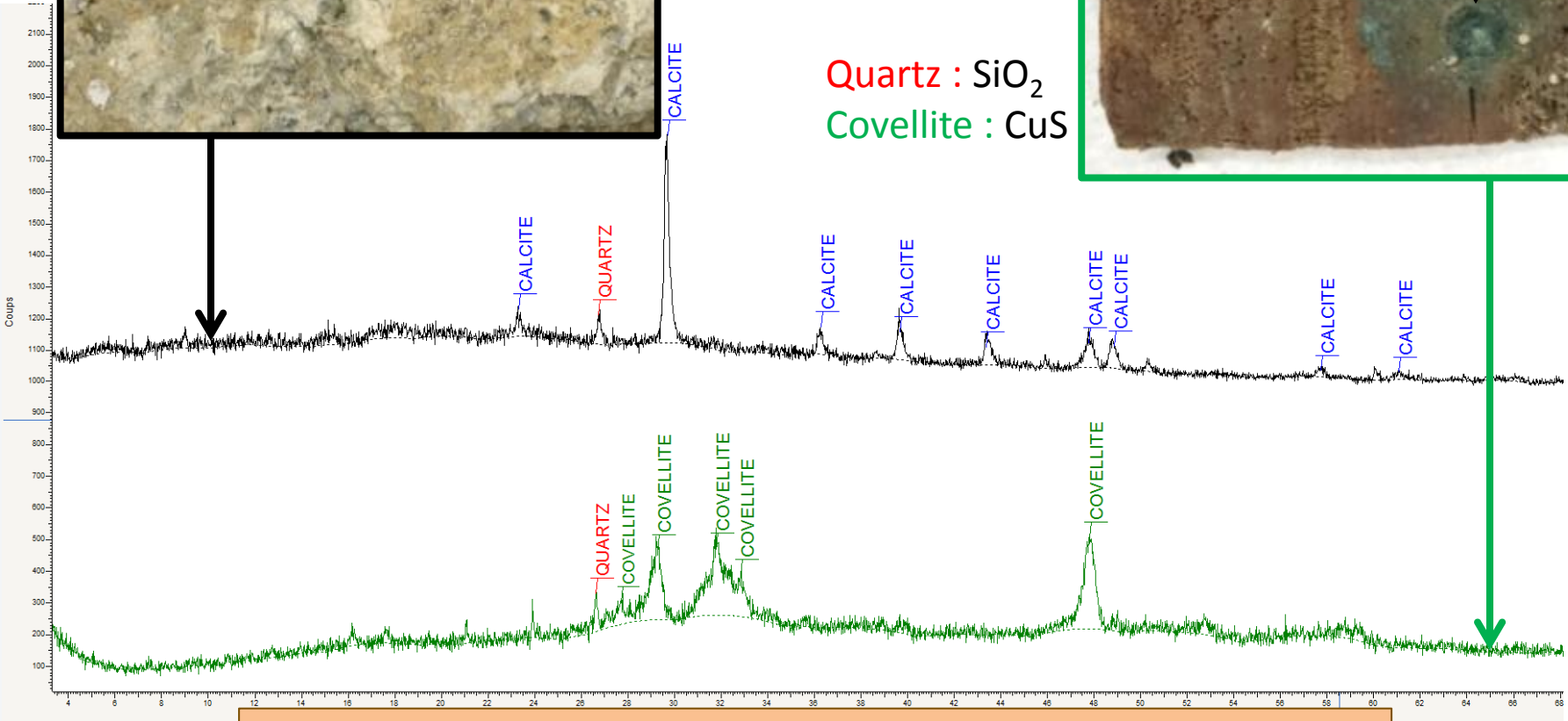
Clou !



Calcite :  $\text{CaCO}_3$   
Quartz :  $\text{SiO}_2$



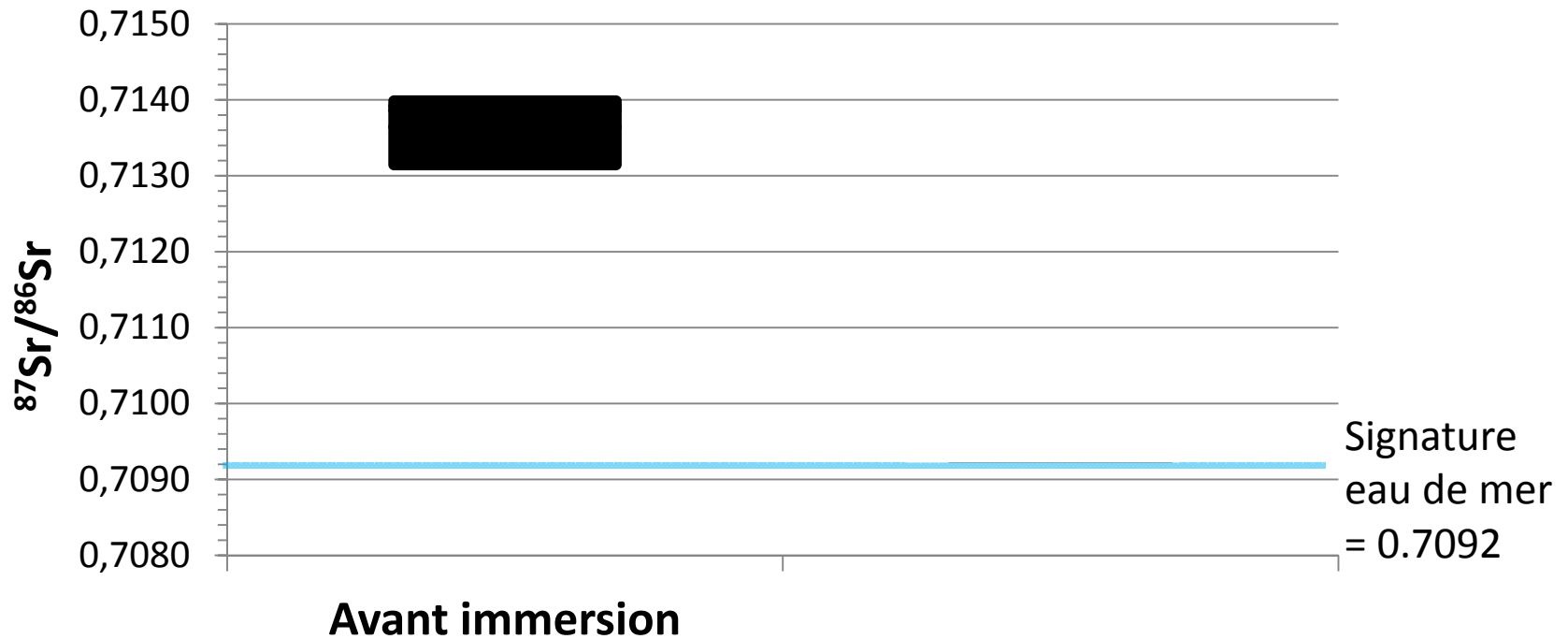
Quartz :  $\text{SiO}_2$   
Covellite :  $\text{CuS}$



**Dégradation du signal bois intense en surface  
(précipitations, contamination par autres matériaux ...)**

# II.1. Premières analyses de bois

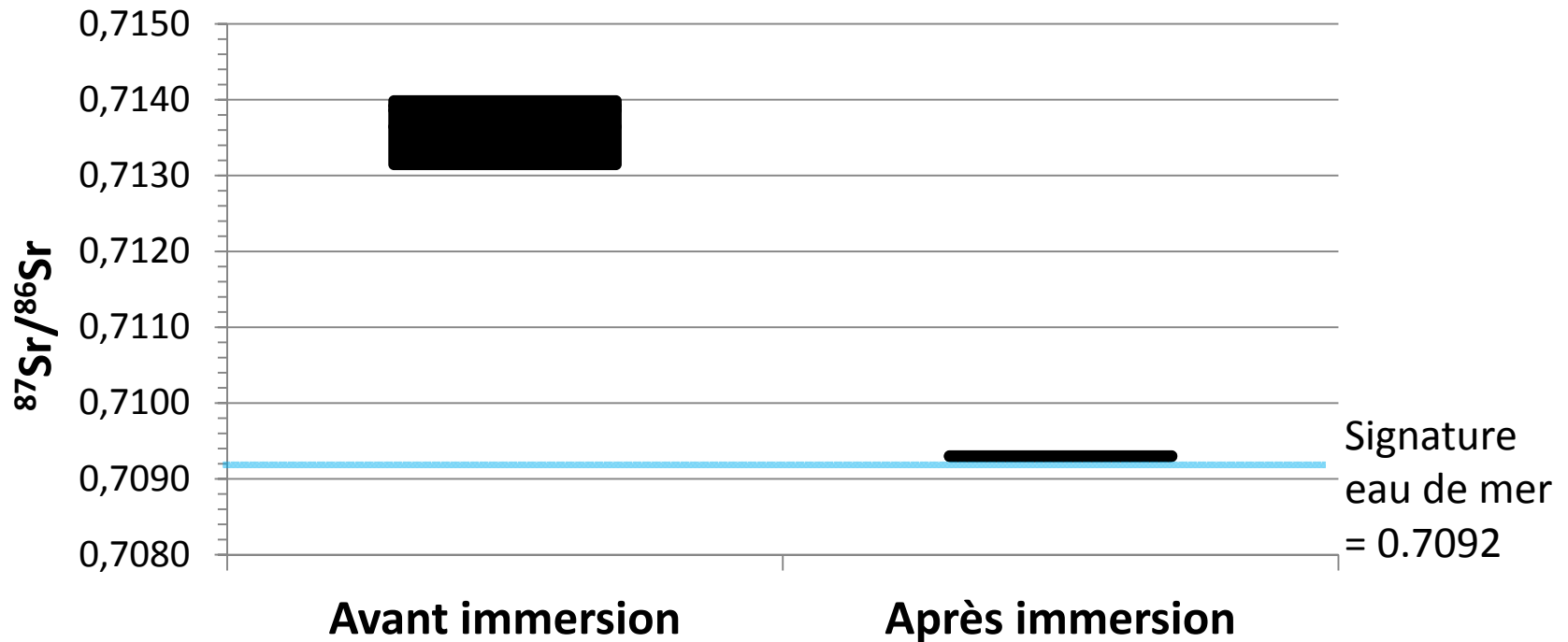
Comparaison du rapport  $^{87}\text{Sr}/^{86}\text{Sr}$  d'un bois de cathédrale avant et après immersion dans l'eau de mer





## II.1. Premières analyses de bois

Comparaison du rapport  $^{87}\text{Sr}/^{86}\text{Sr}$  d'un bois de cathédrale avant et après immersion dans l'eau de mer



**Evolution rapide de la signature d'un bois vers une signature eau de mer**

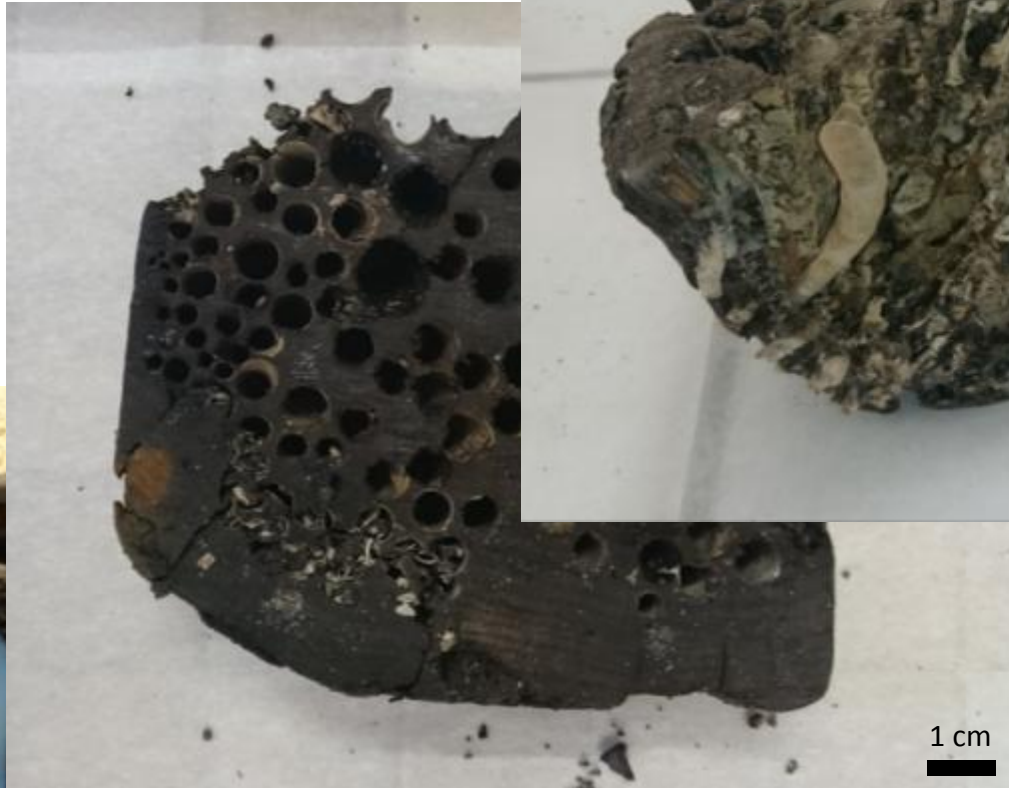
# 1<sup>er</sup> type de bois étudié : bois actuel



Échantillonnage difficile  
Analyses sans surprises



# 2<sup>ème</sup> type de bois étudié : bois archéologique



Échantillonnage facile  
Mais qu'analyse-t-on?!