ForSEAdiscovery

LIEC LABORATOIRE INTERDISCIPLINAIRE DES ENVIRONNEMENTS CONTINENTAUX

UNIVERSITÉ DE LORRAINE

Fadi HAJJ

Where do you come from, enigmatic wood?

Supervised by:

Anne POSZWA

I. Context

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

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


France
Spain
Portugal

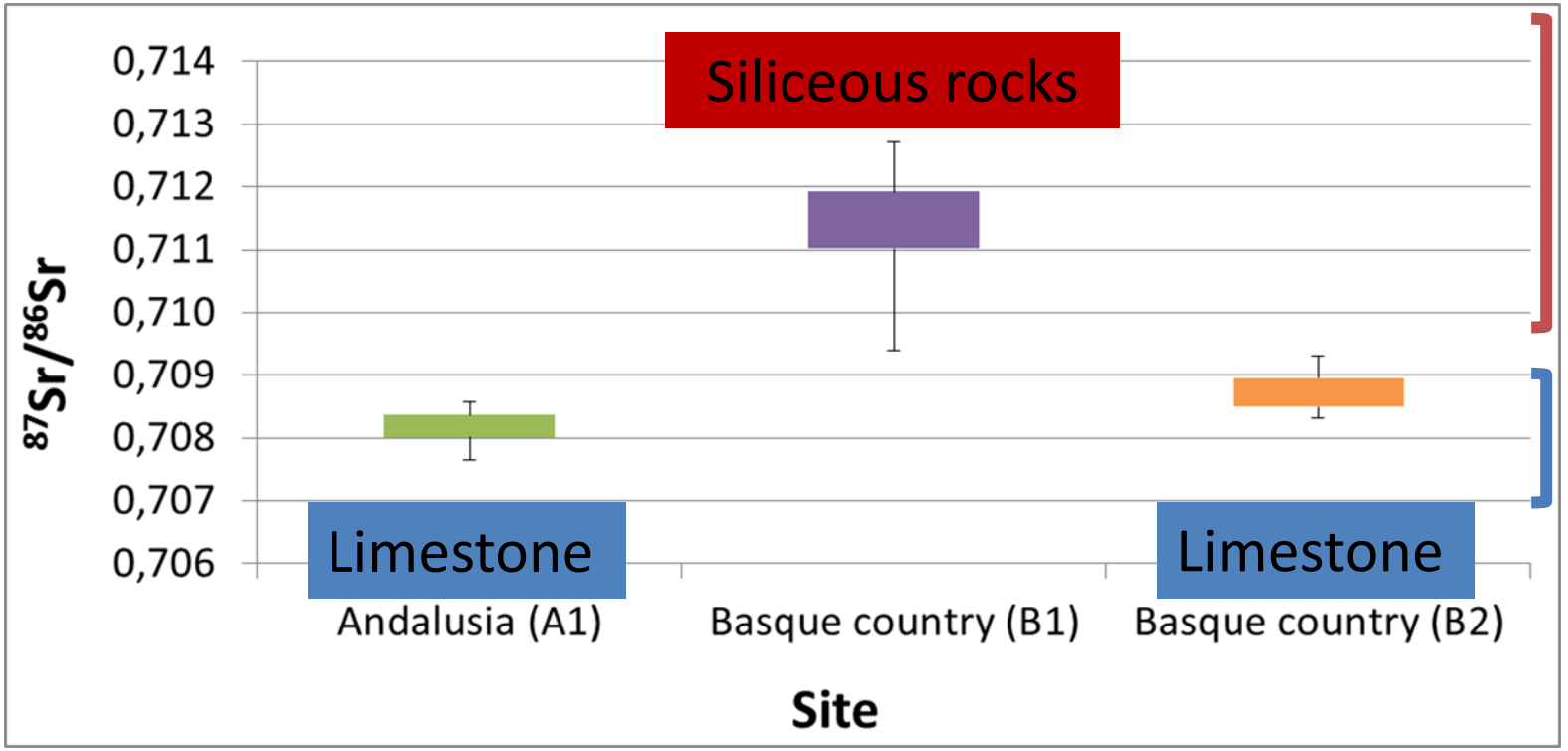

France
BILBAO
Spain
Portugal

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



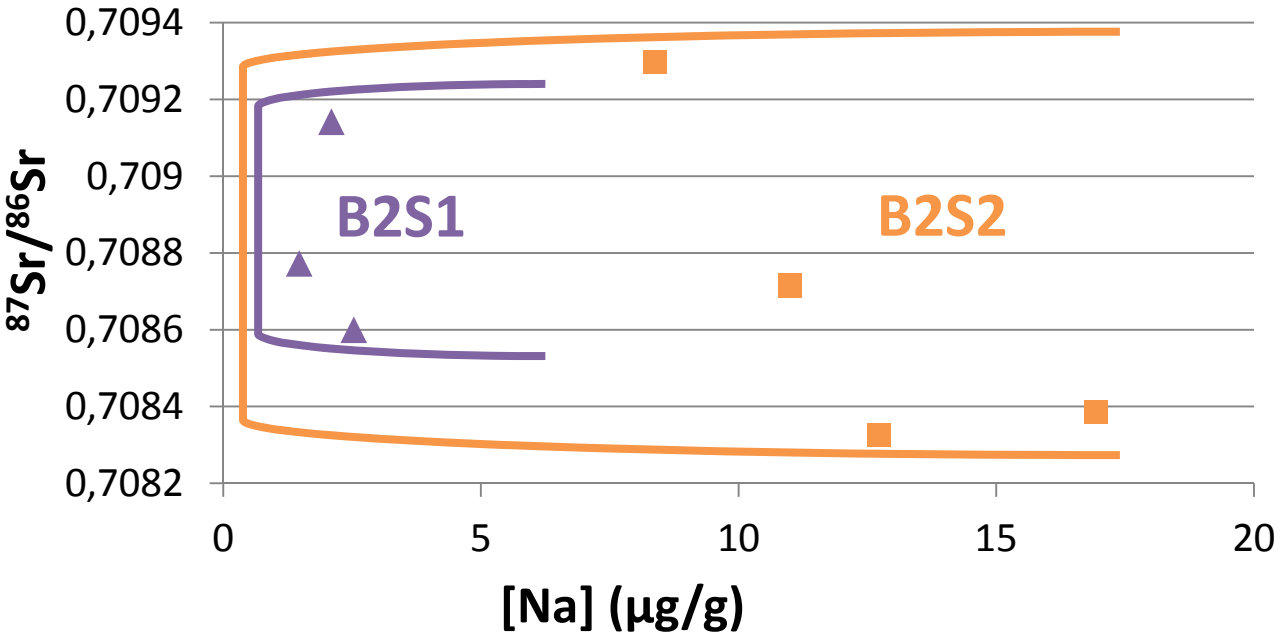
Box plots represent 50% of the values.

Whiskers represent 100% of the values.

Specific signature for each site → linked to rock type

Another way for discrimination within a site

Example: Basque country B2
B2S1: AZK
B2S2: UZK



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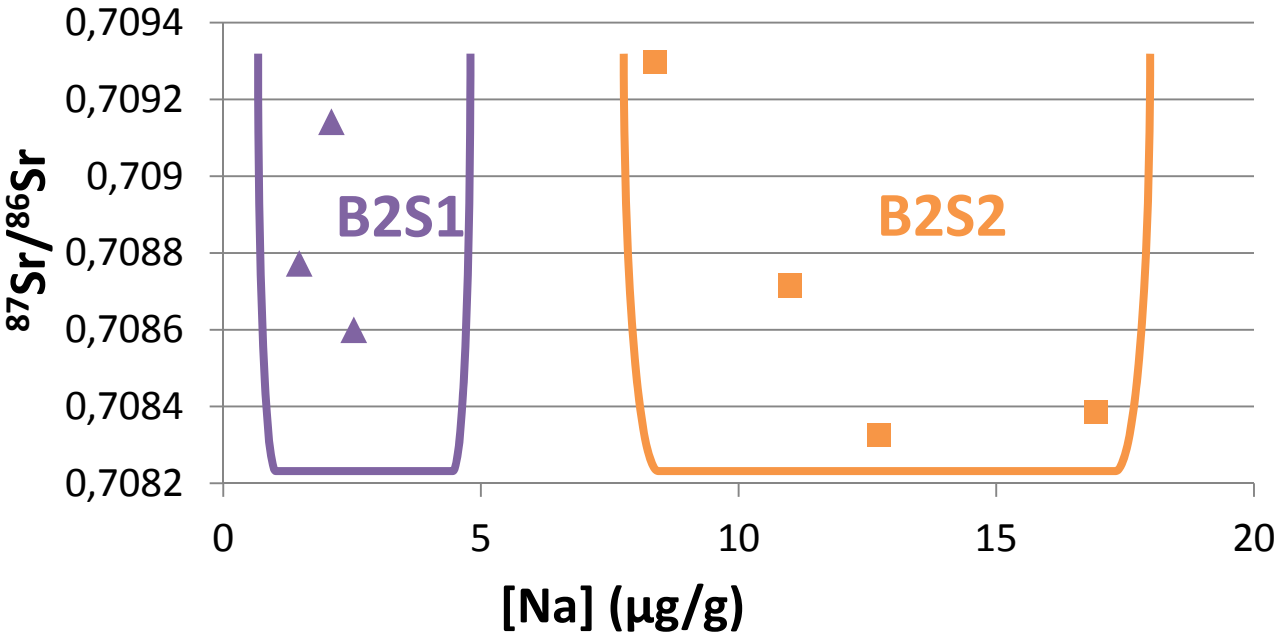


Higher Na concentration in wood indicate proximity from the coasts

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 1	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
		S1 2	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

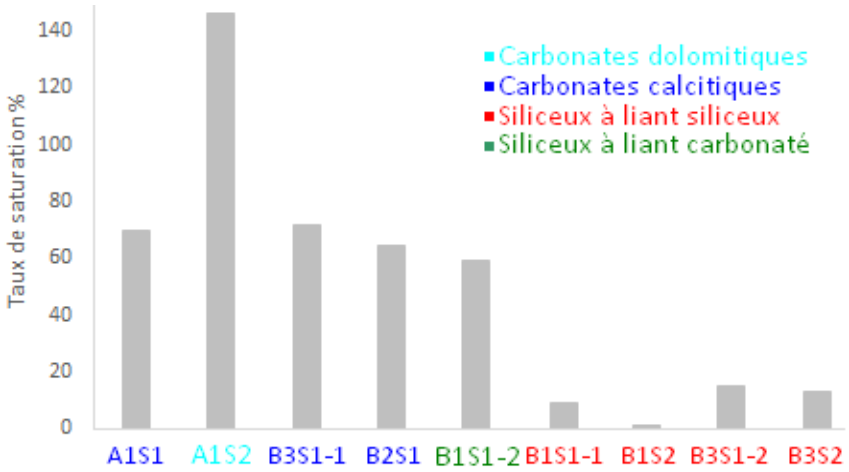
Rock description

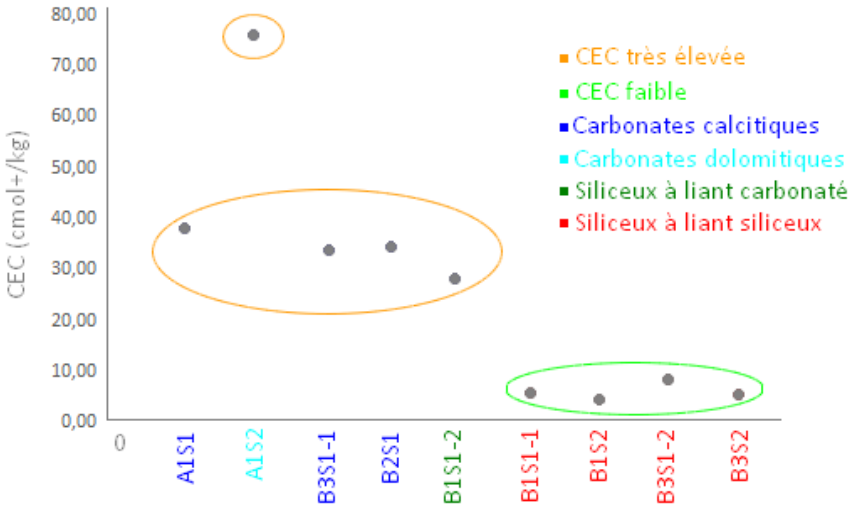
ROCHE		Code terrain	Test HCl roche	Description macroscopique												Nom roche	Informations
				Liant		Nature des grains											
								Quartz									
				Matrice	Ciment	Calcite	Dolomite	Silts	Sables	Muscovite	Biotite	Feldspaths	Argiles	Oxydation (orange)	Oxyde de fer		
A1	S1	LIN101	+			X		X			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
	S1 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

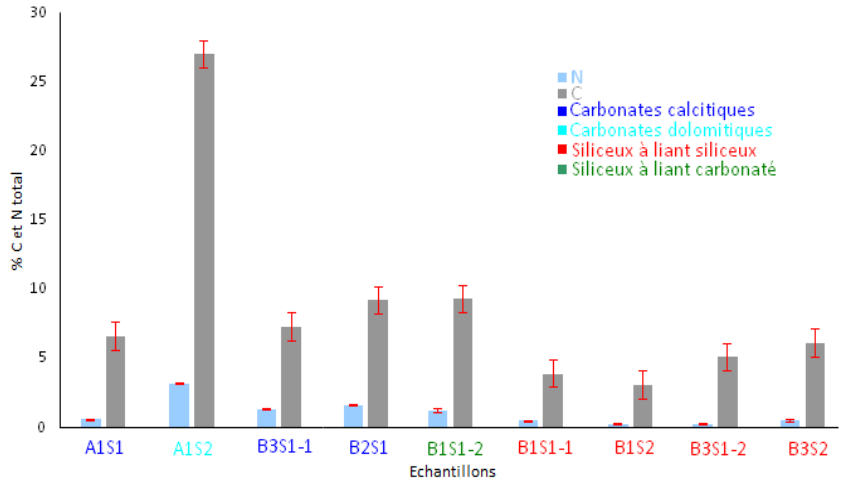
➡ **9 representative rock samples were selected for isotopic analyses**

II.2. Results from rock and soil analyses

Analyses on the 9 selected soil and rock samples



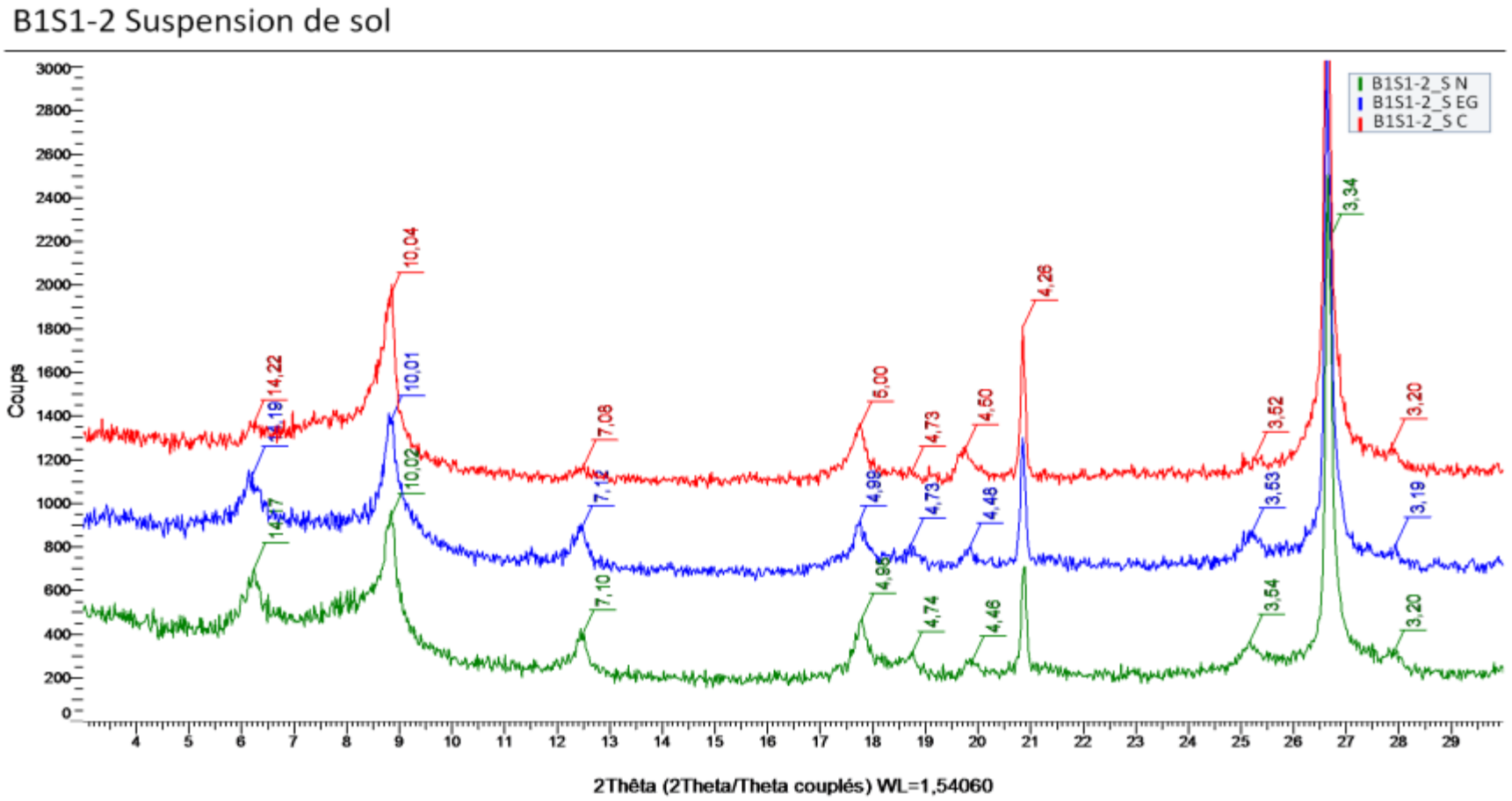




Significant difference between values from calcareous and siliceous samples

II.2. Results from rock and soil analyses

XRD (X-ray diffraction) analyses



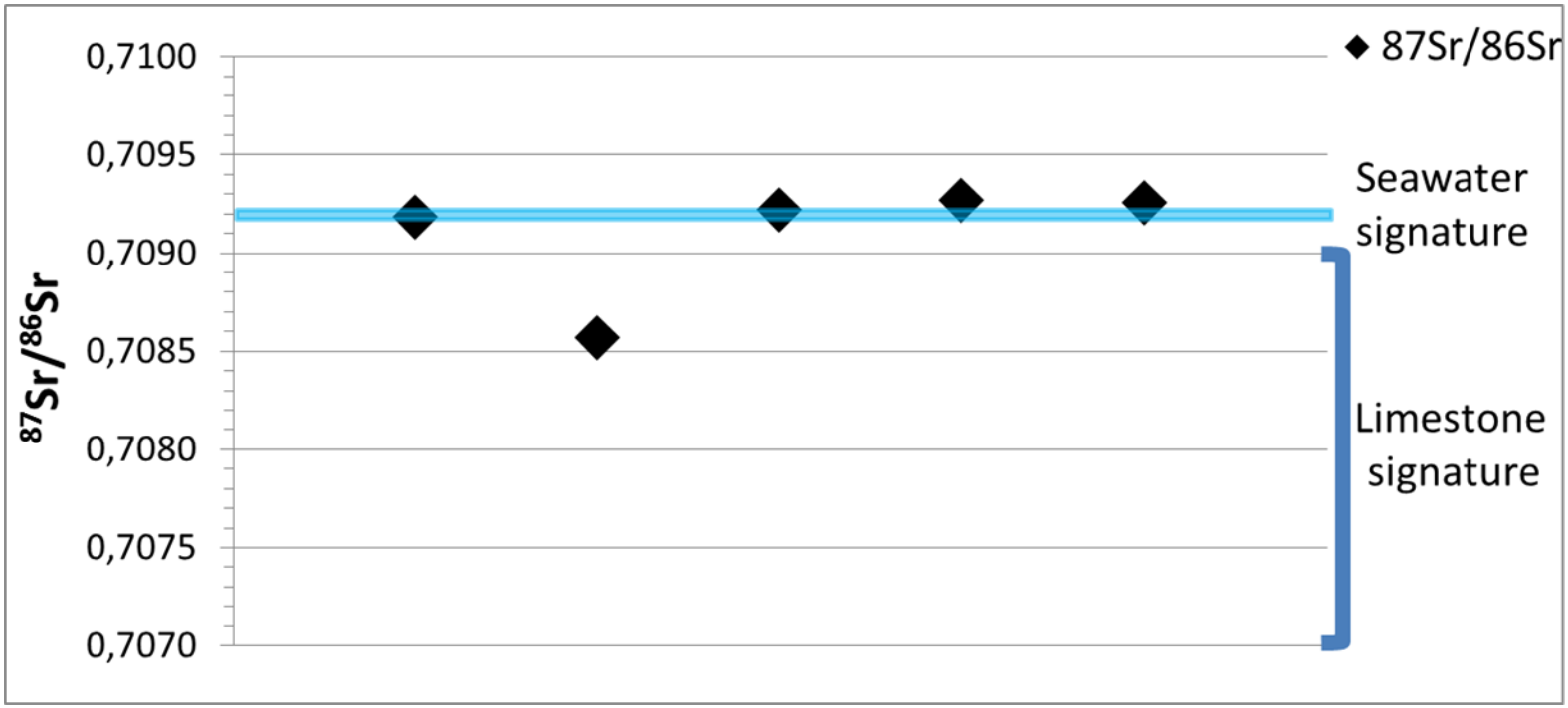
II.2. Results from rock and soil analyses

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

Undergoing analyses

II.3. Results from shipwreck timbers

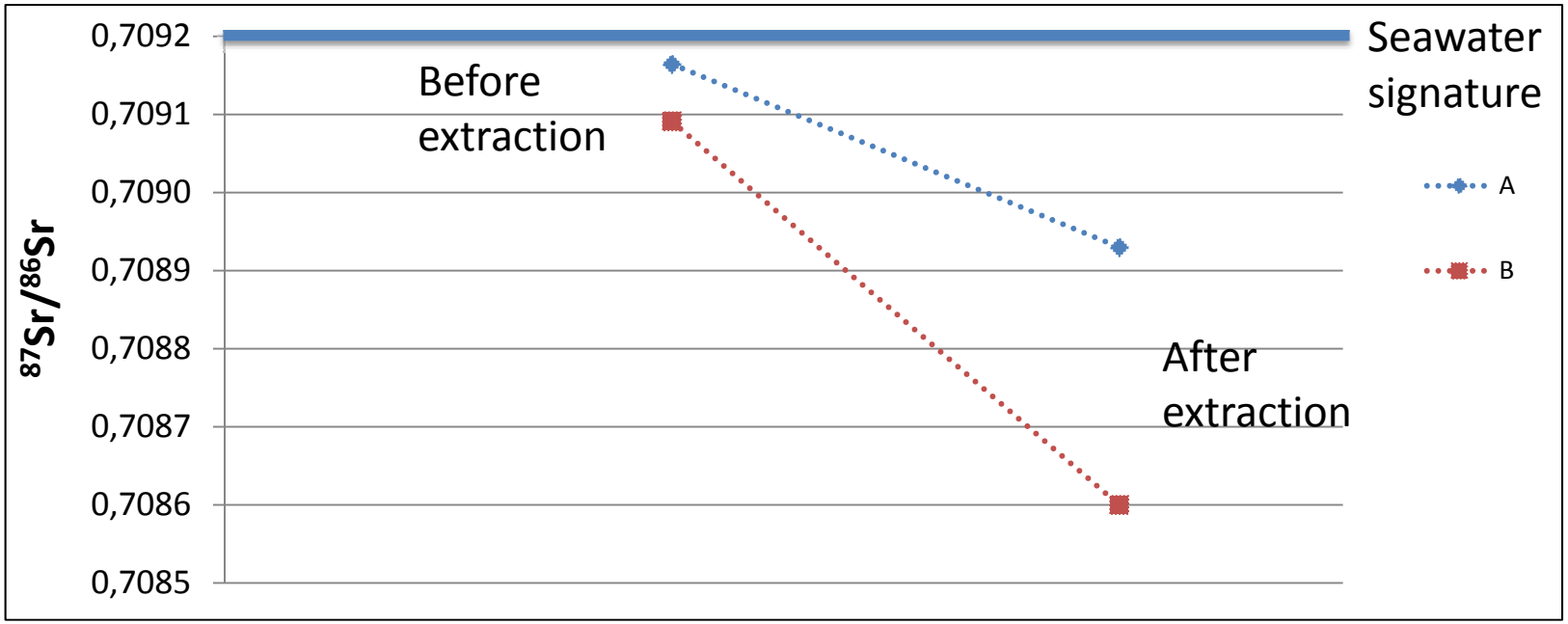
First analyses of wood from Ribadeo shipwreck



Wood from shipwreck are contaminated by sea water elements

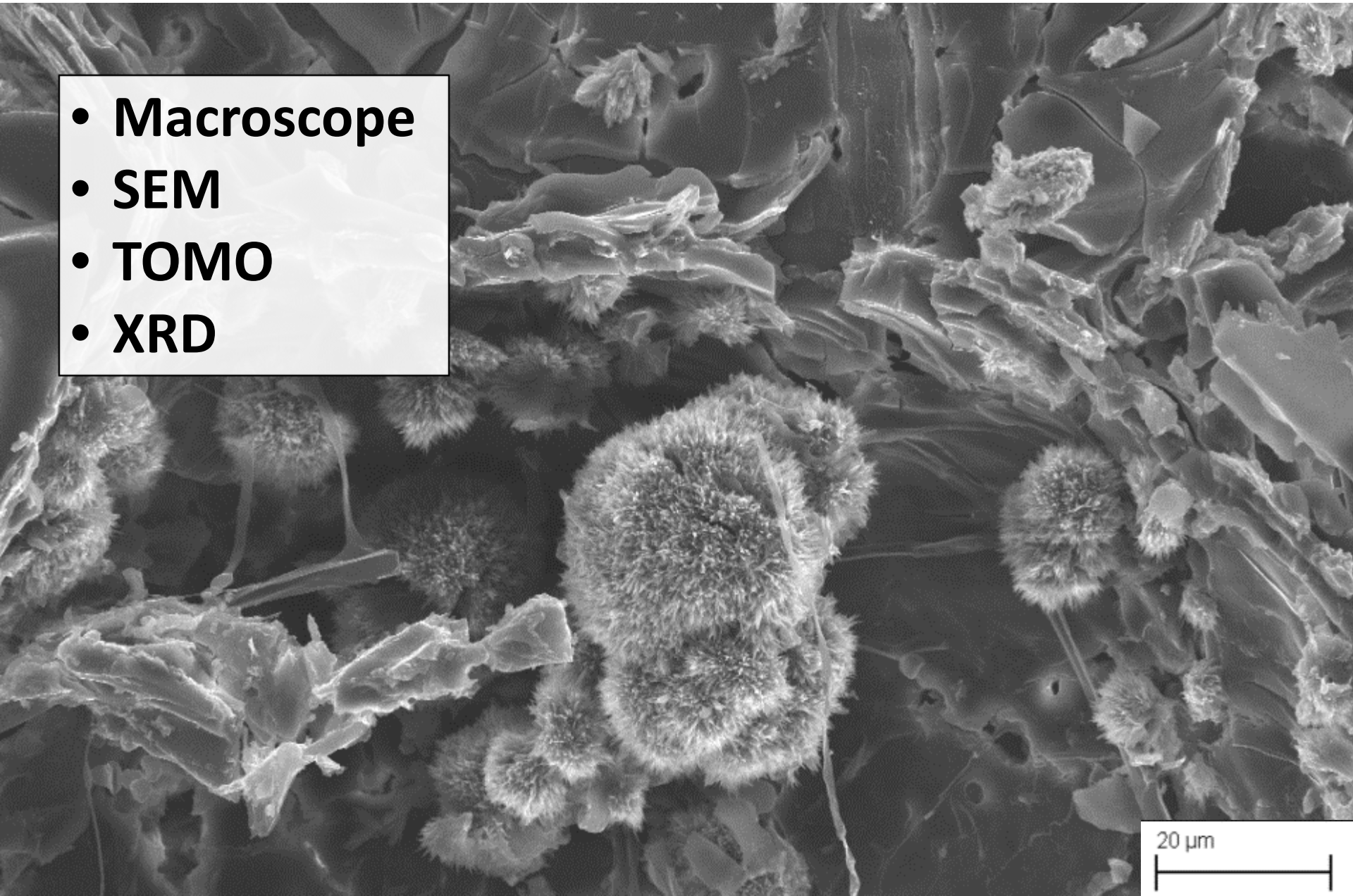
II.3. Results from shipwreck timbers

First extraction results



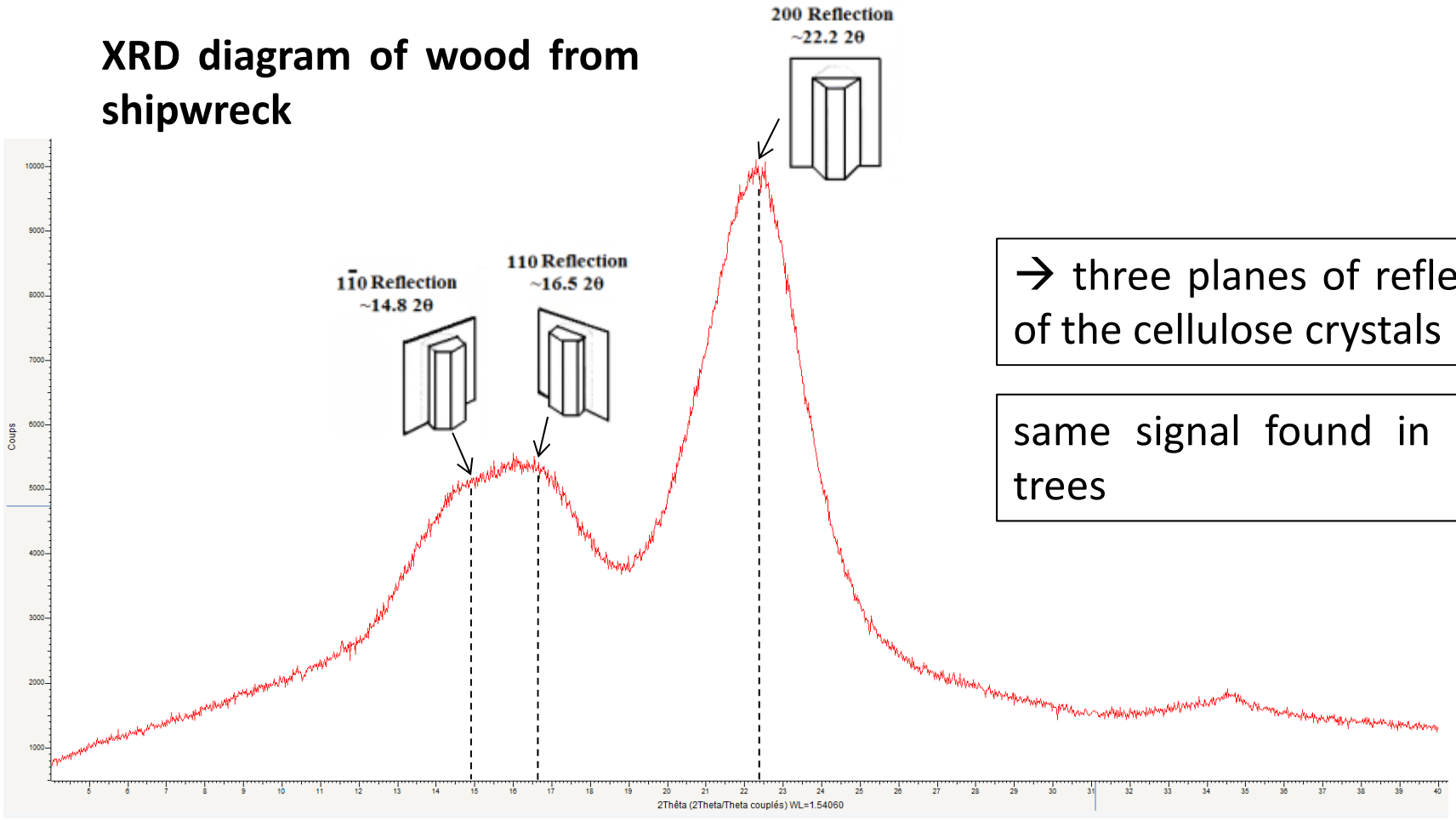
Sea water elements were extracted from the wood but the extraction is not complete

II.4. Characterization of the contamination



II.4. Characterization of the contamination

XRD diagram of wood from shipwreck



→ three planes of reflection of the cellulose crystals

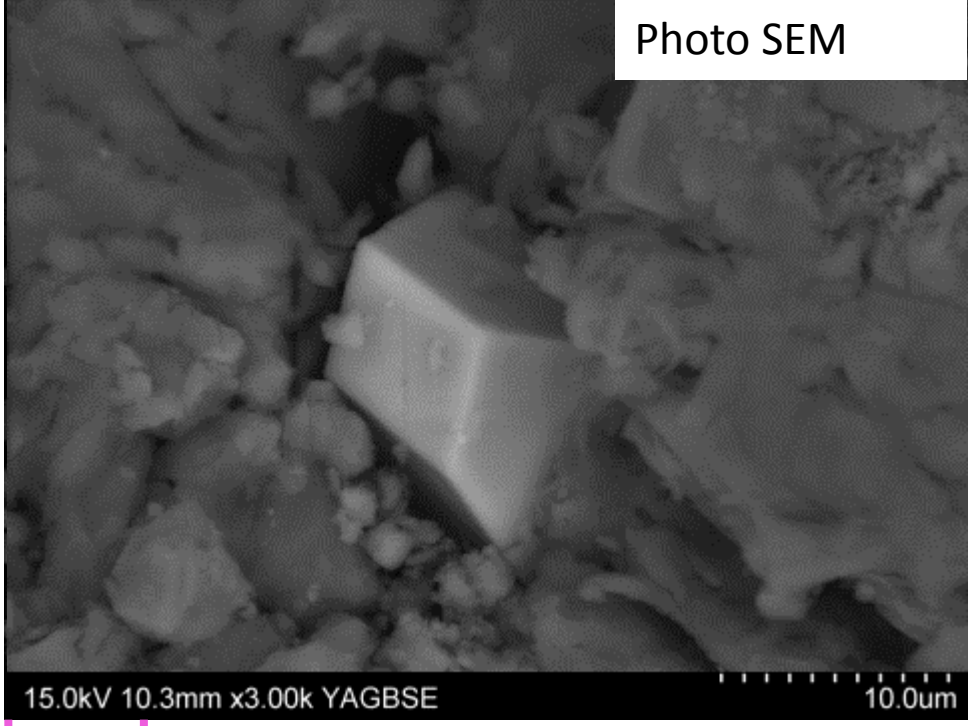
same signal found in living trees

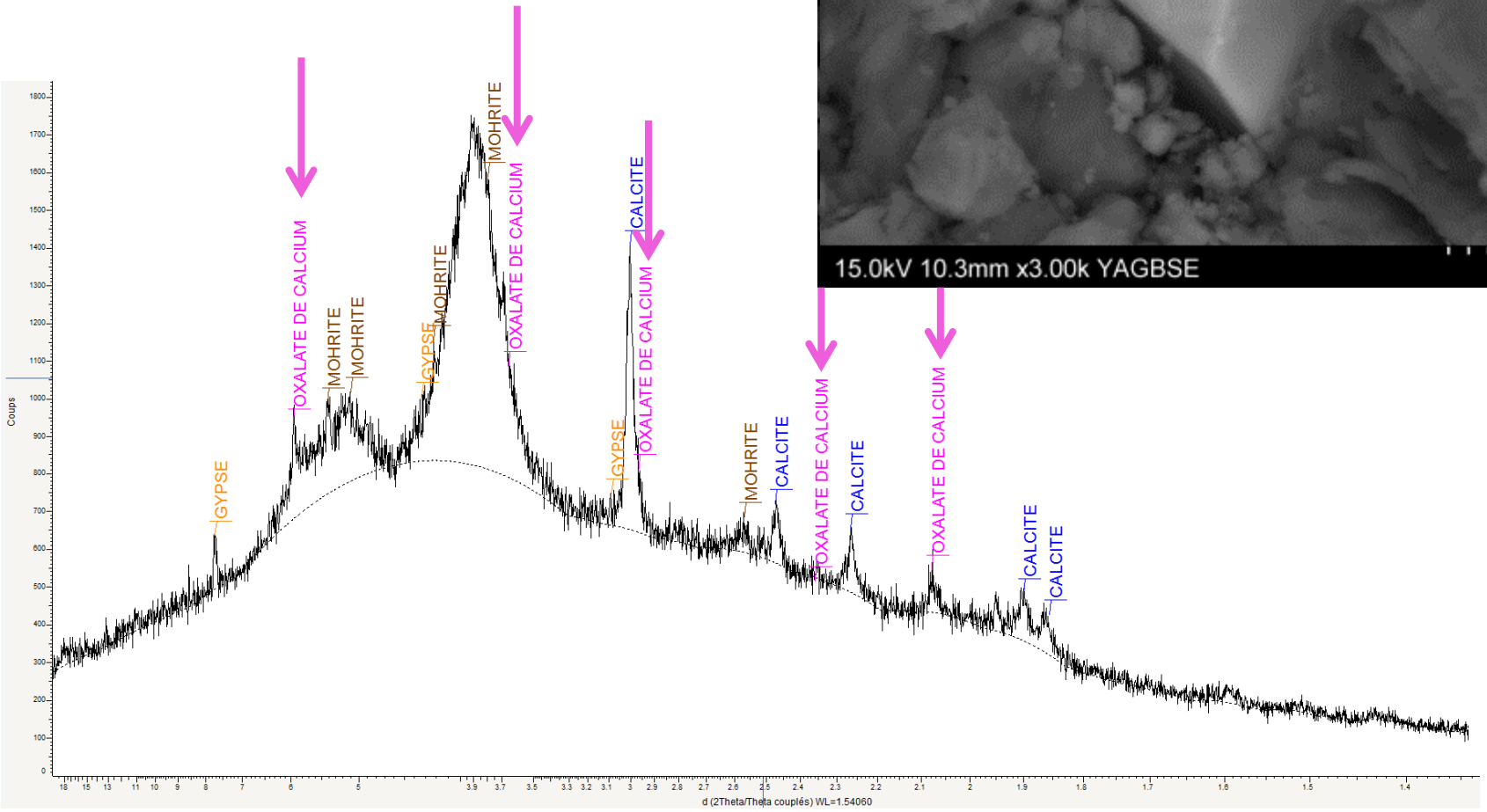
Common peaks for wood samples

Sometimes other peaks …

XRD diagram from another sample

Calcium oxalates: $Ca(COO)_2$

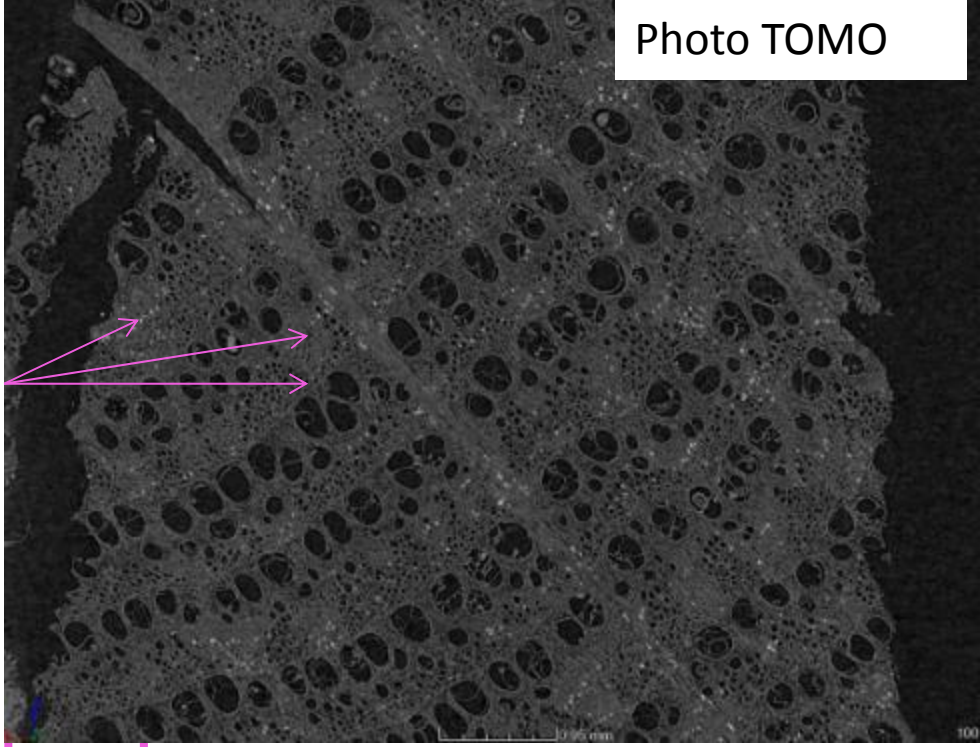


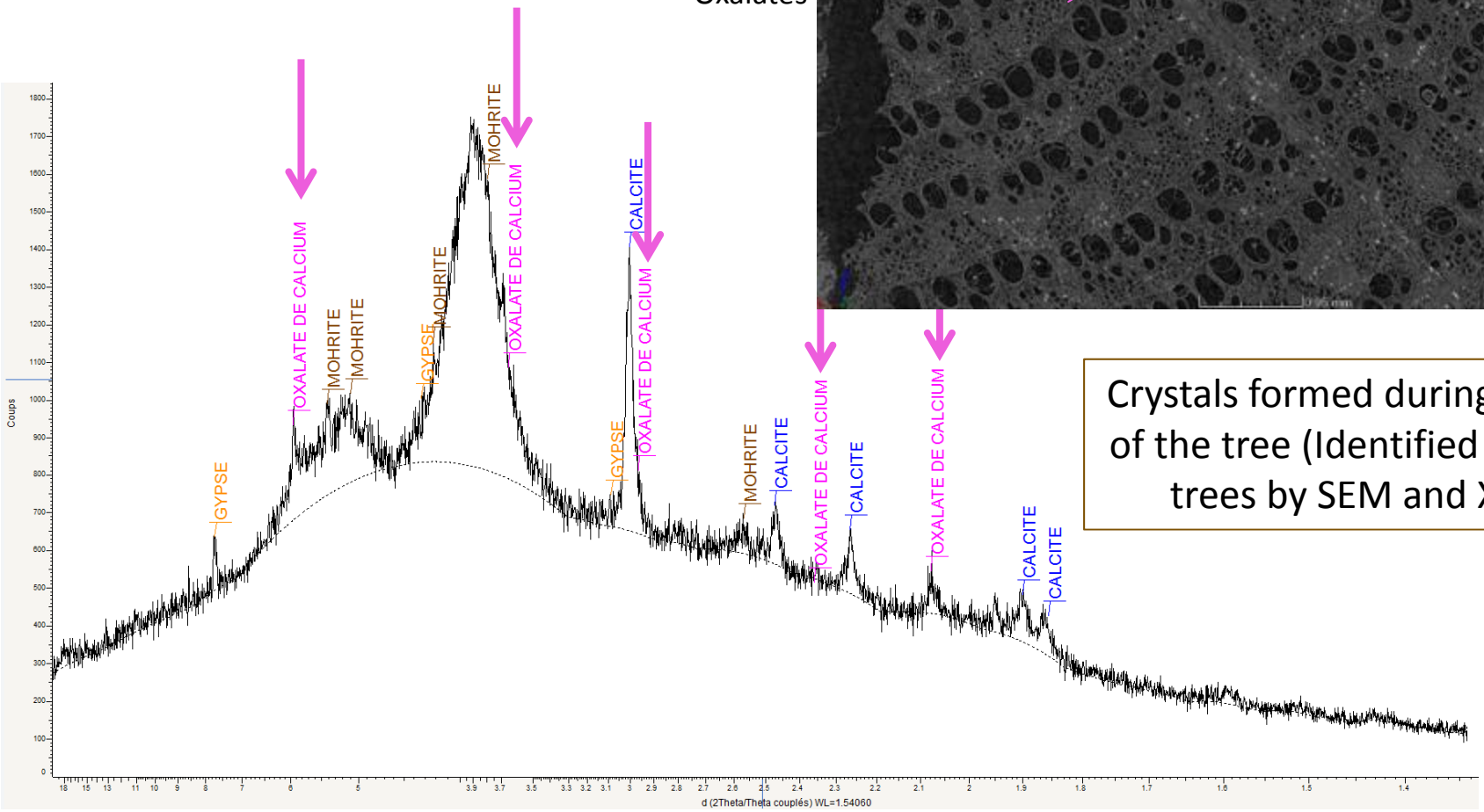


Sometimes other peaks …

XRD diagram from another sample

Calcium oxalates: $Ca(COO)_2$





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 …

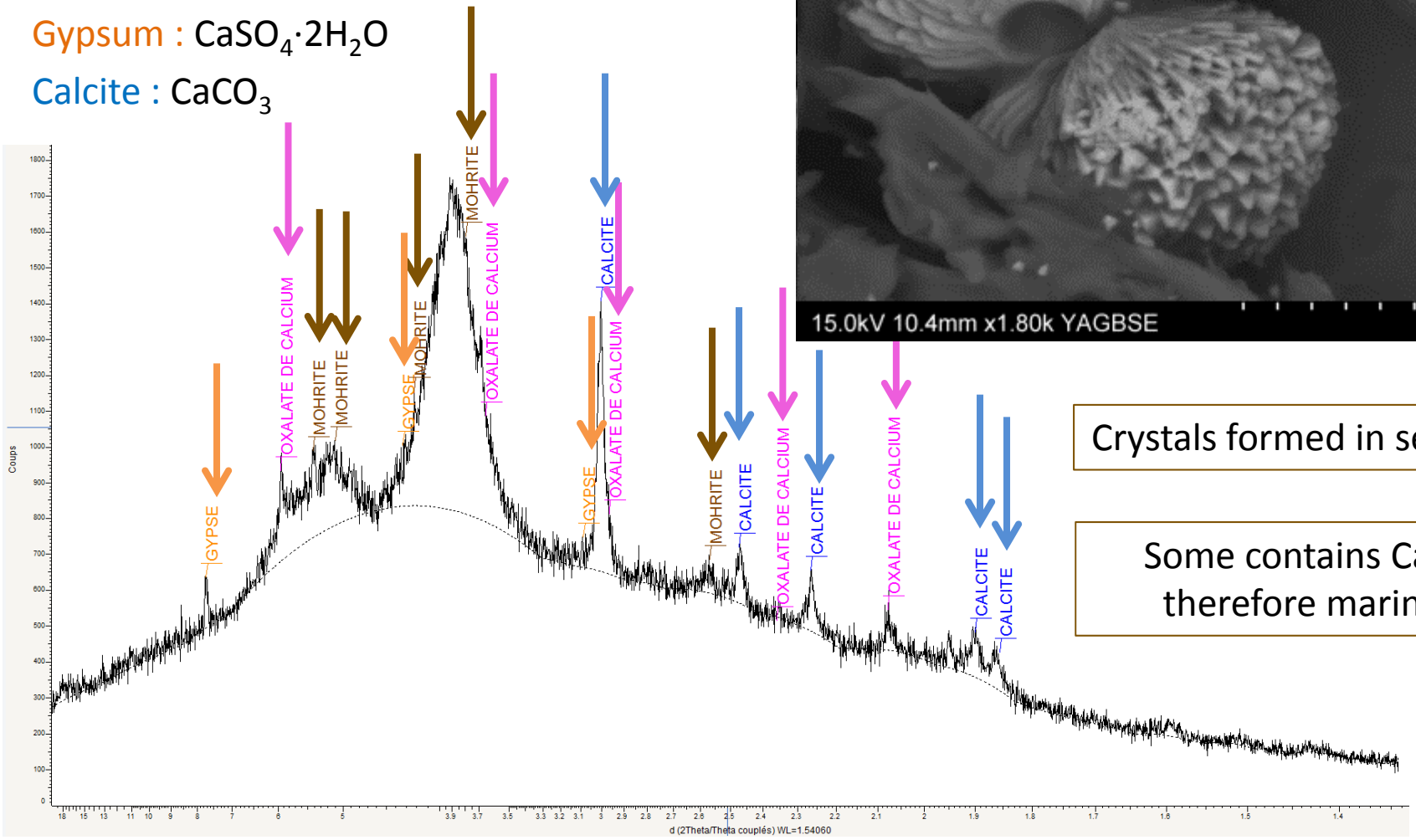
XRD diagram from another sample

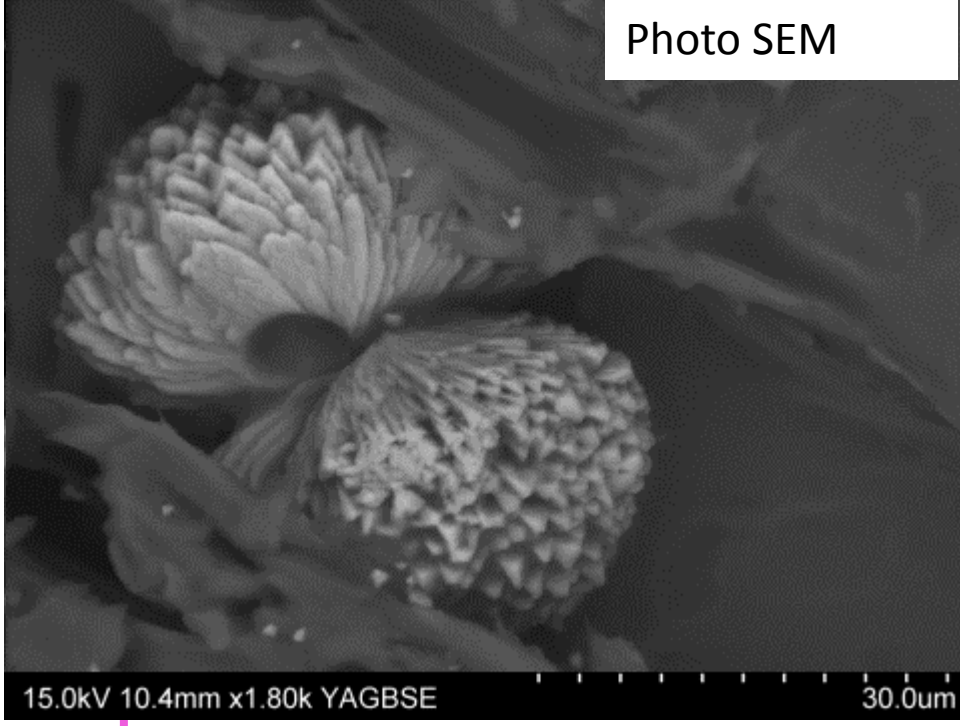
Calcium oxalate : $Ca(COO)_2$

Mohrite : $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$

Gypsum : $CaSO_4 \cdot 2H_2O$

Calcite : $CaCO_3$



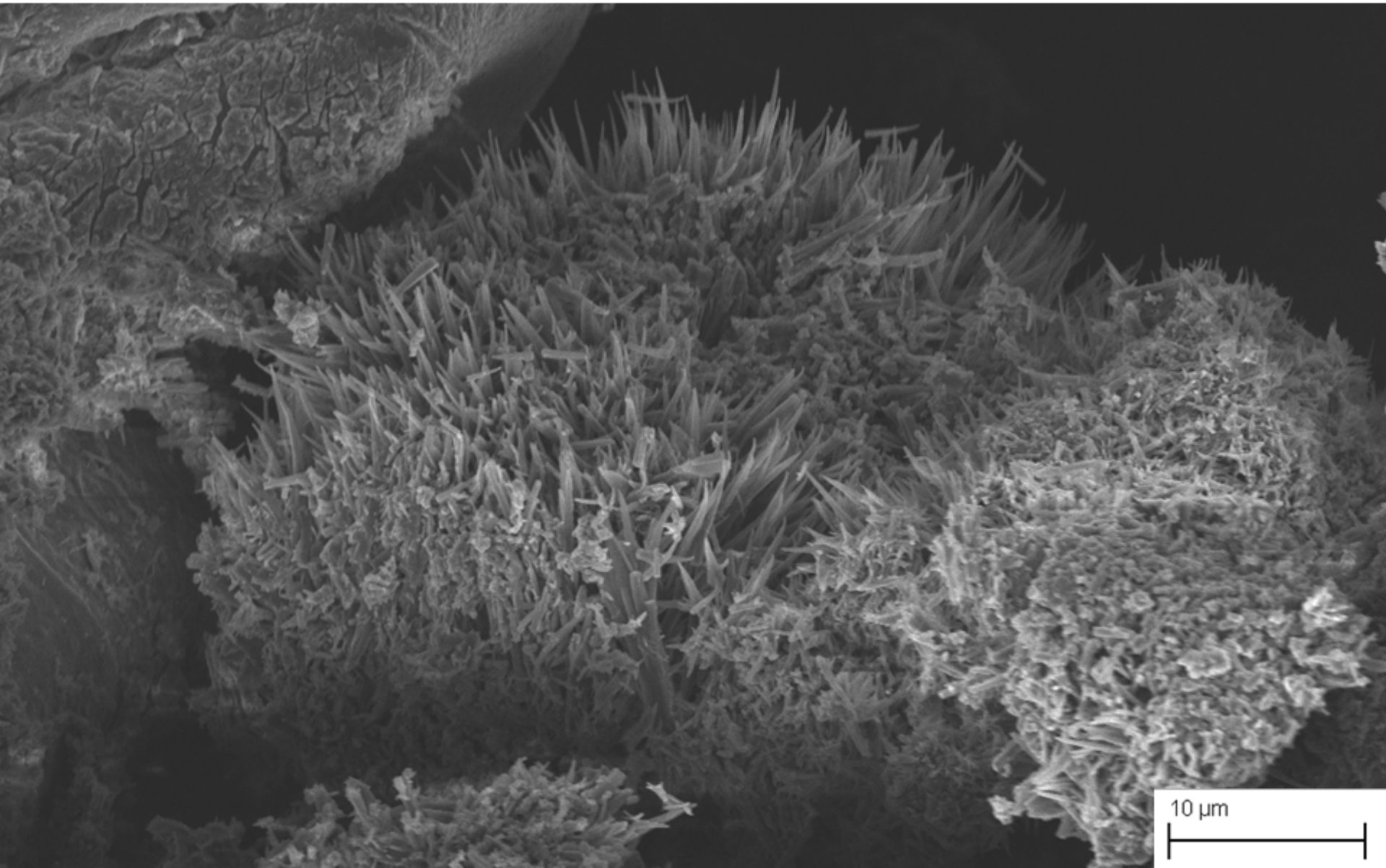


Crystals formed in sea water

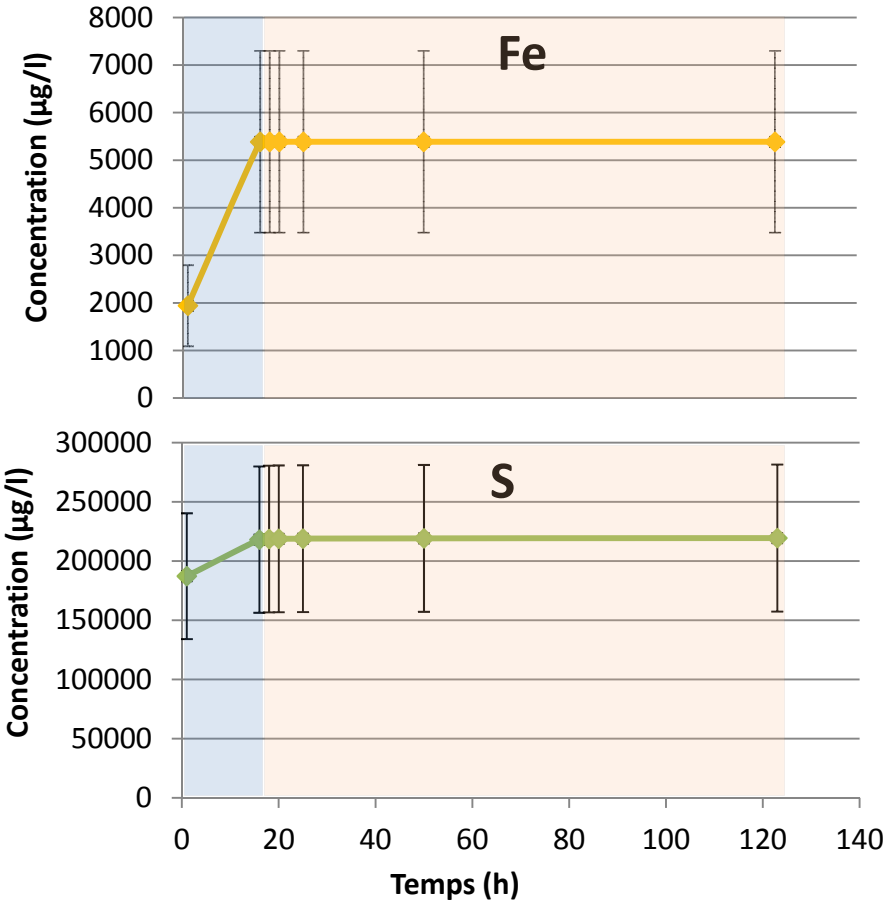
Some contains Ca and therefore marine Sr

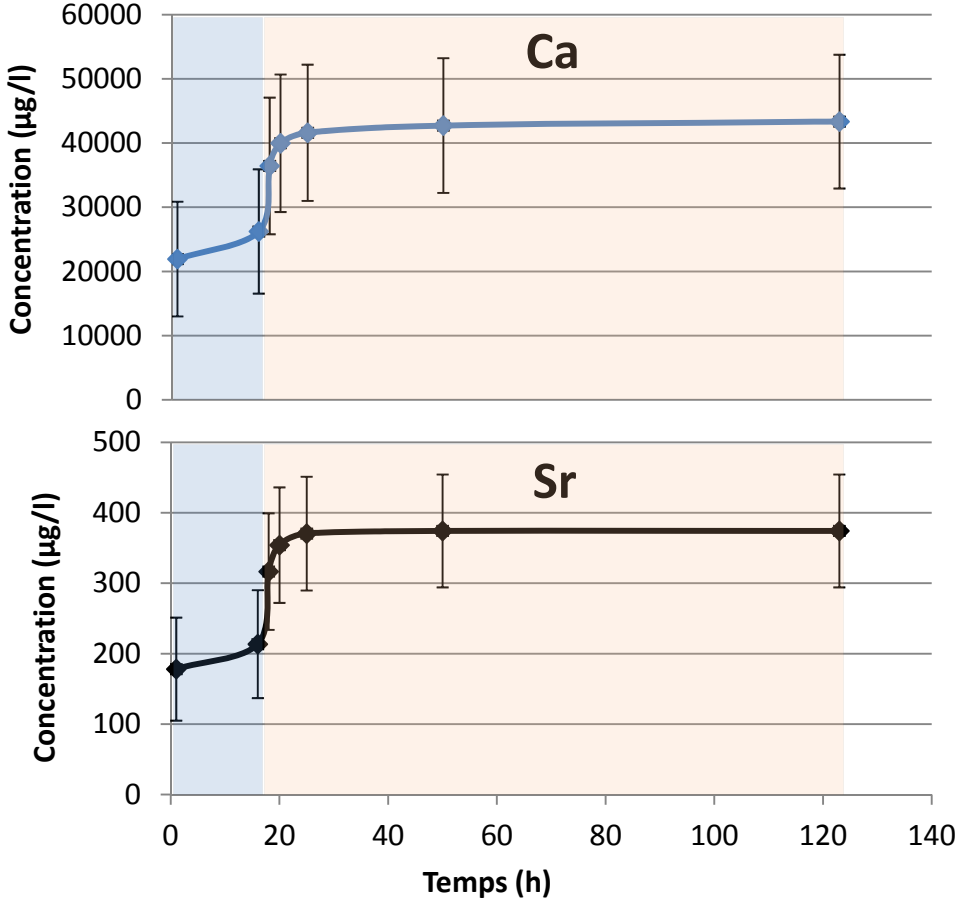
Possible contamination of the wood signature with marine elements in the crystals

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

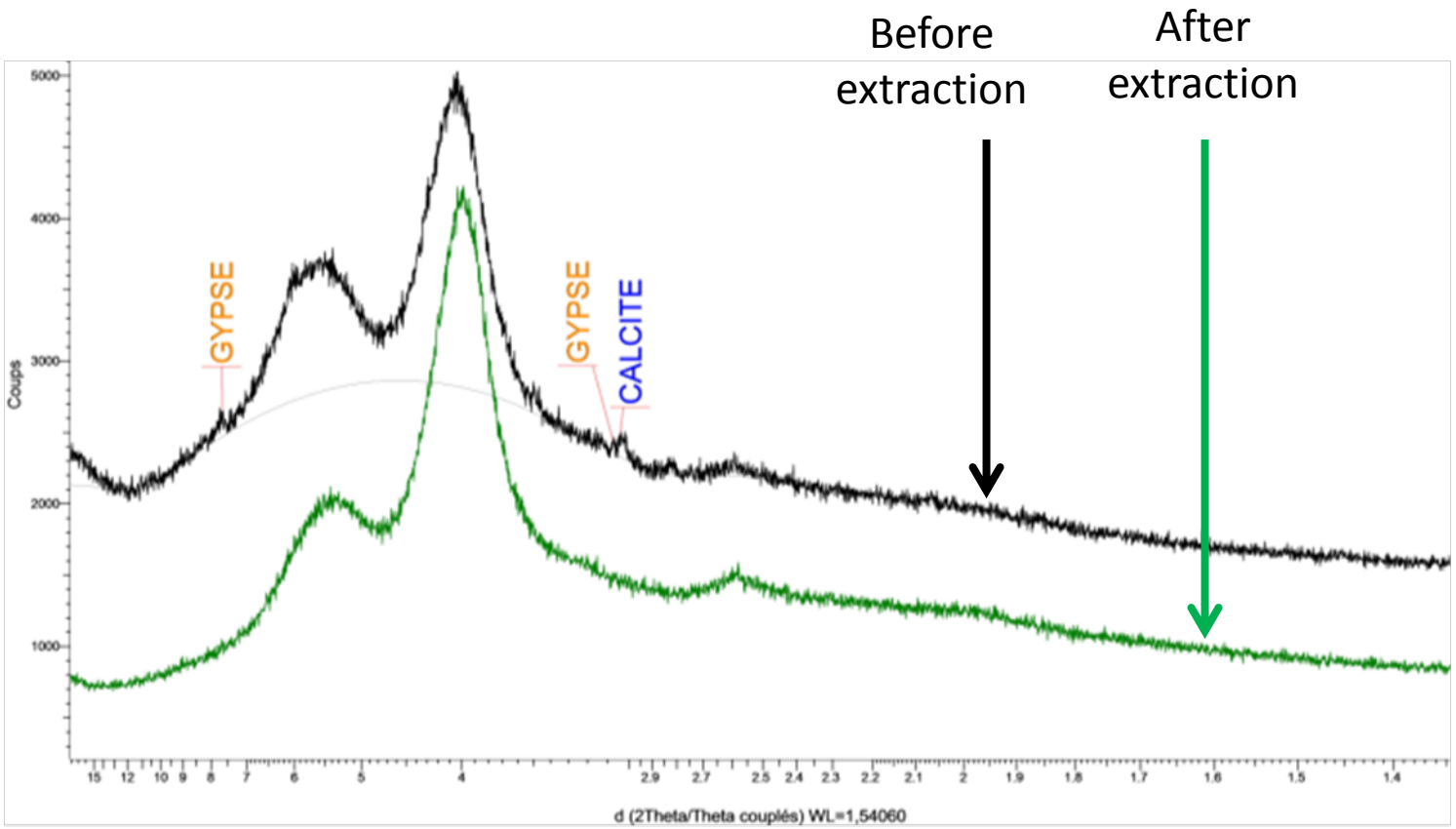
Ca and Sr are extracted by water (in sulfates) and by NH4Ac (exchangeable)

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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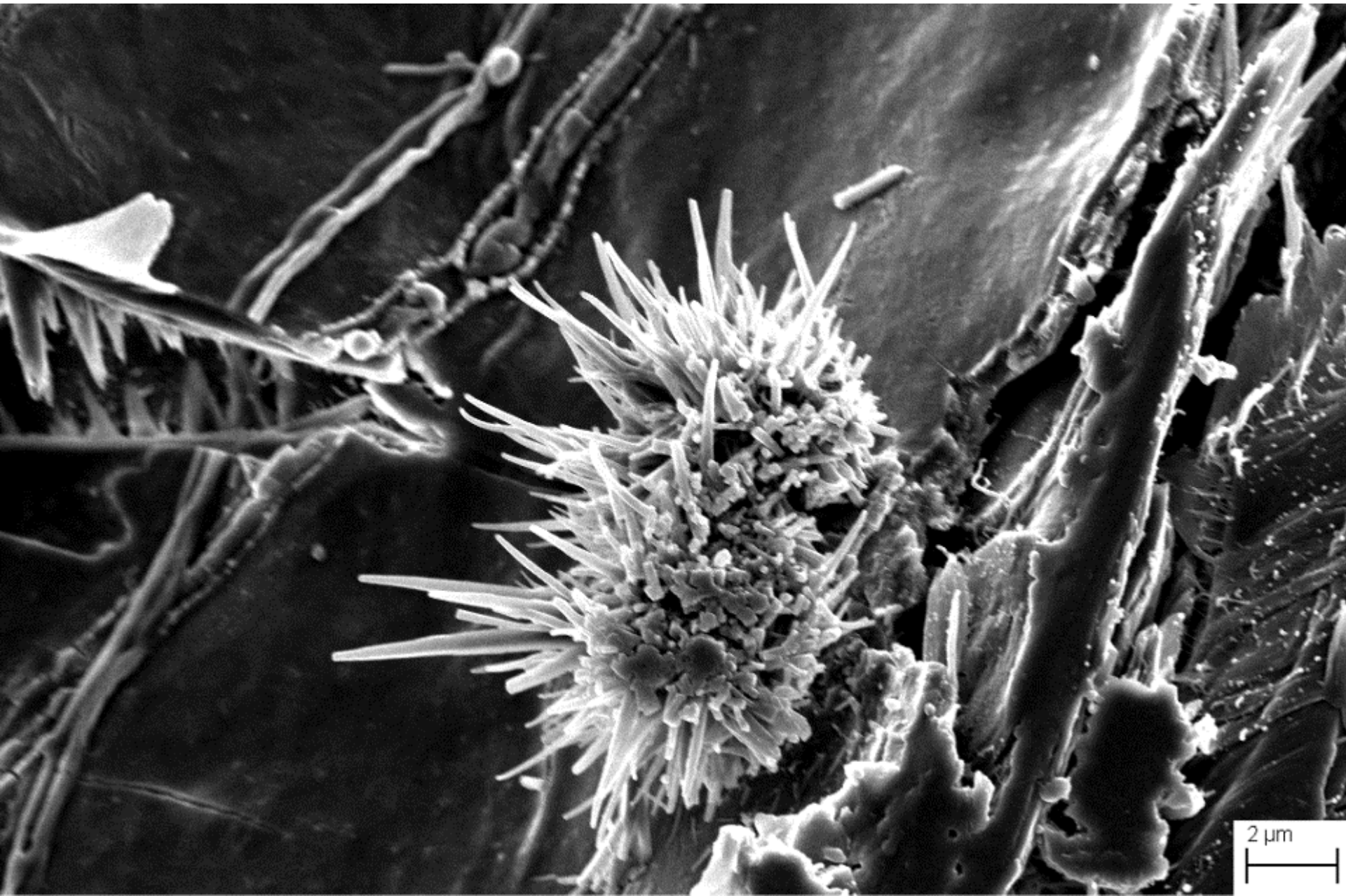
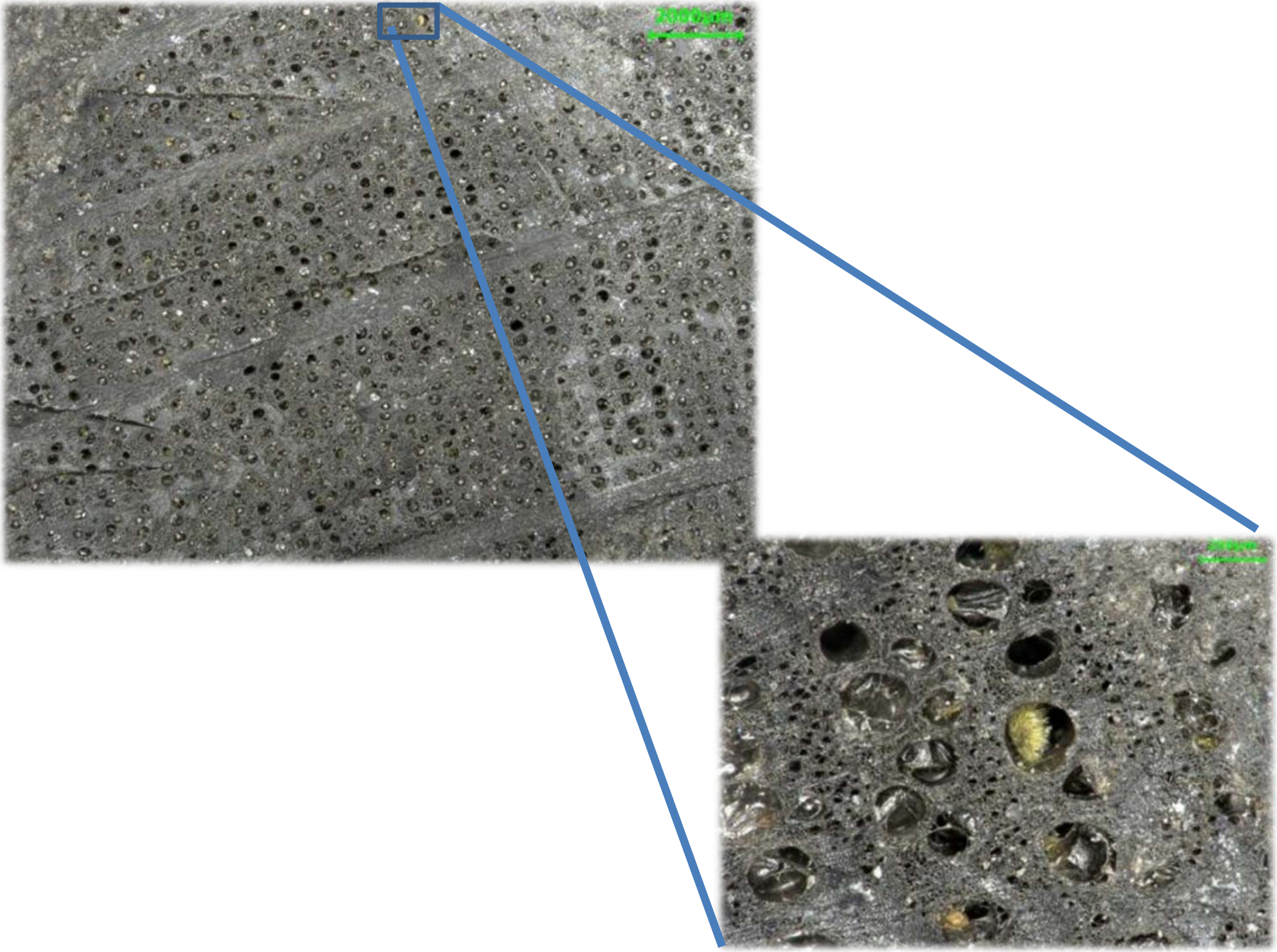
Thank you for your attention!



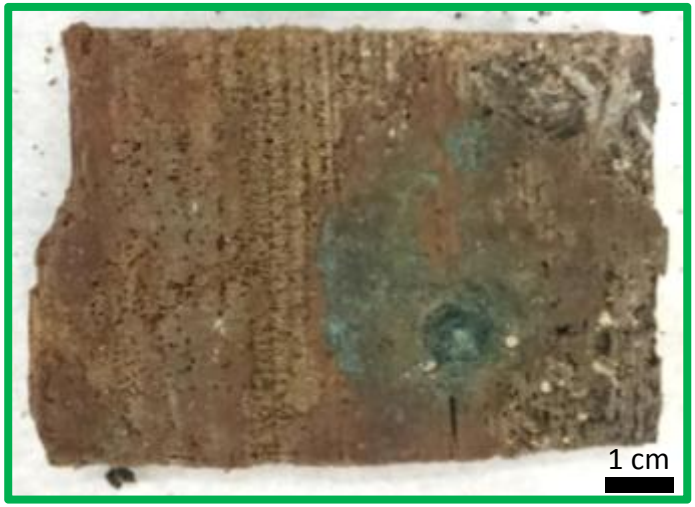
Calcite : $CaCO_3$
Aragonite : $CaCO_3$
Quartz : SiO_2
Albite : NaAlSi3O8

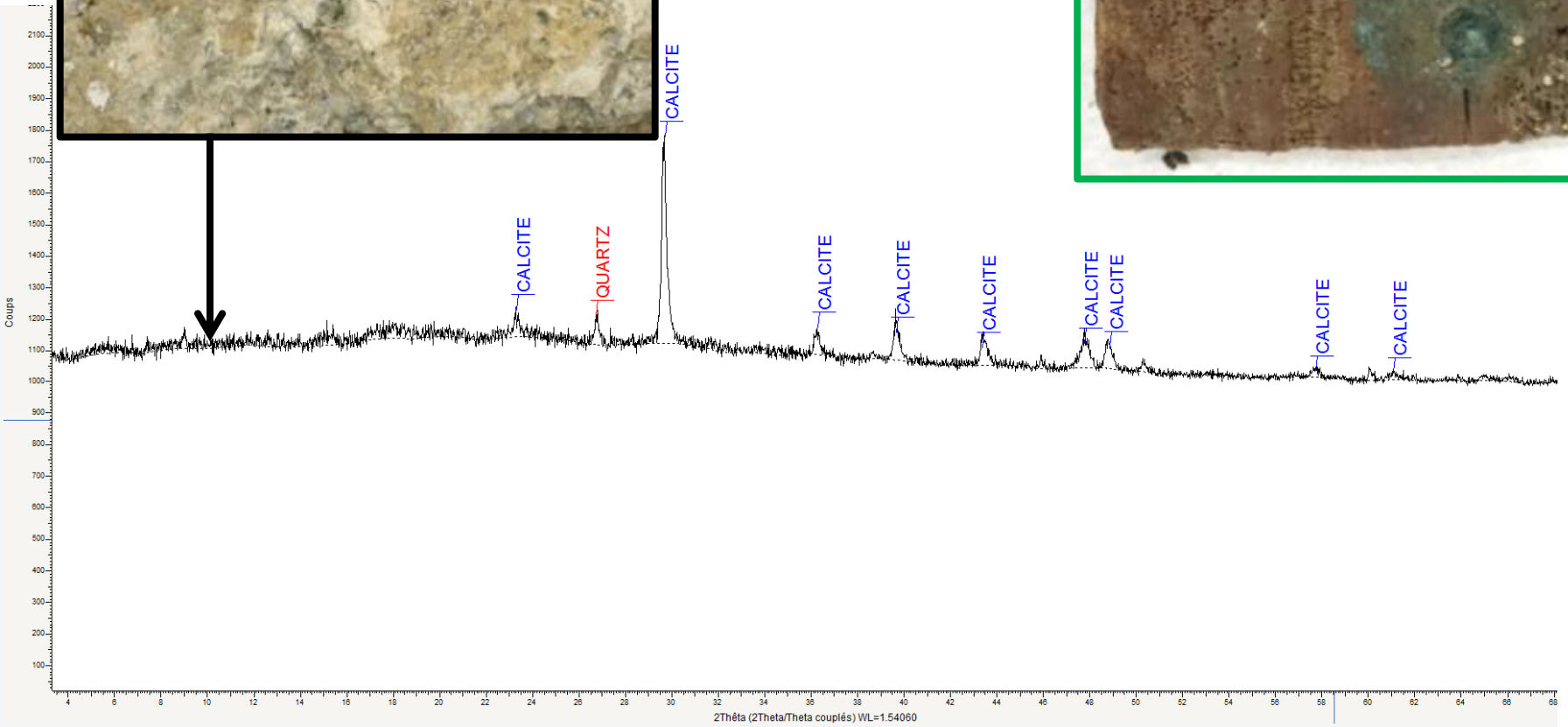


Pas vraiment étonnant ...

Calcite : $CaCO_3$

Quartz : SiO_2



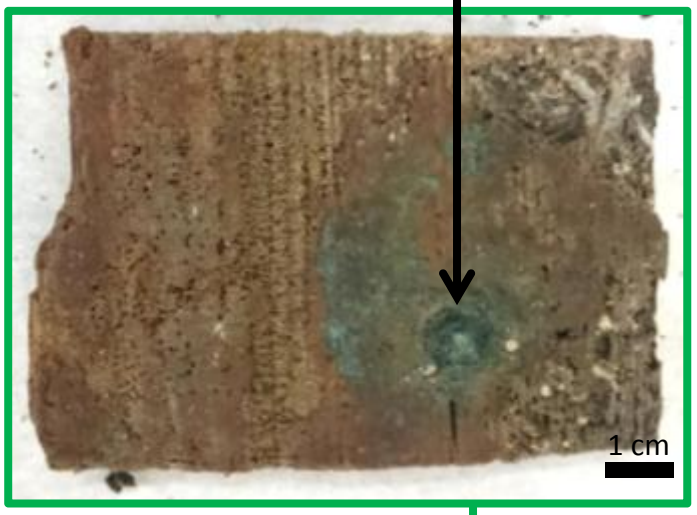


Pas vraiment étonnant ...

Clou !

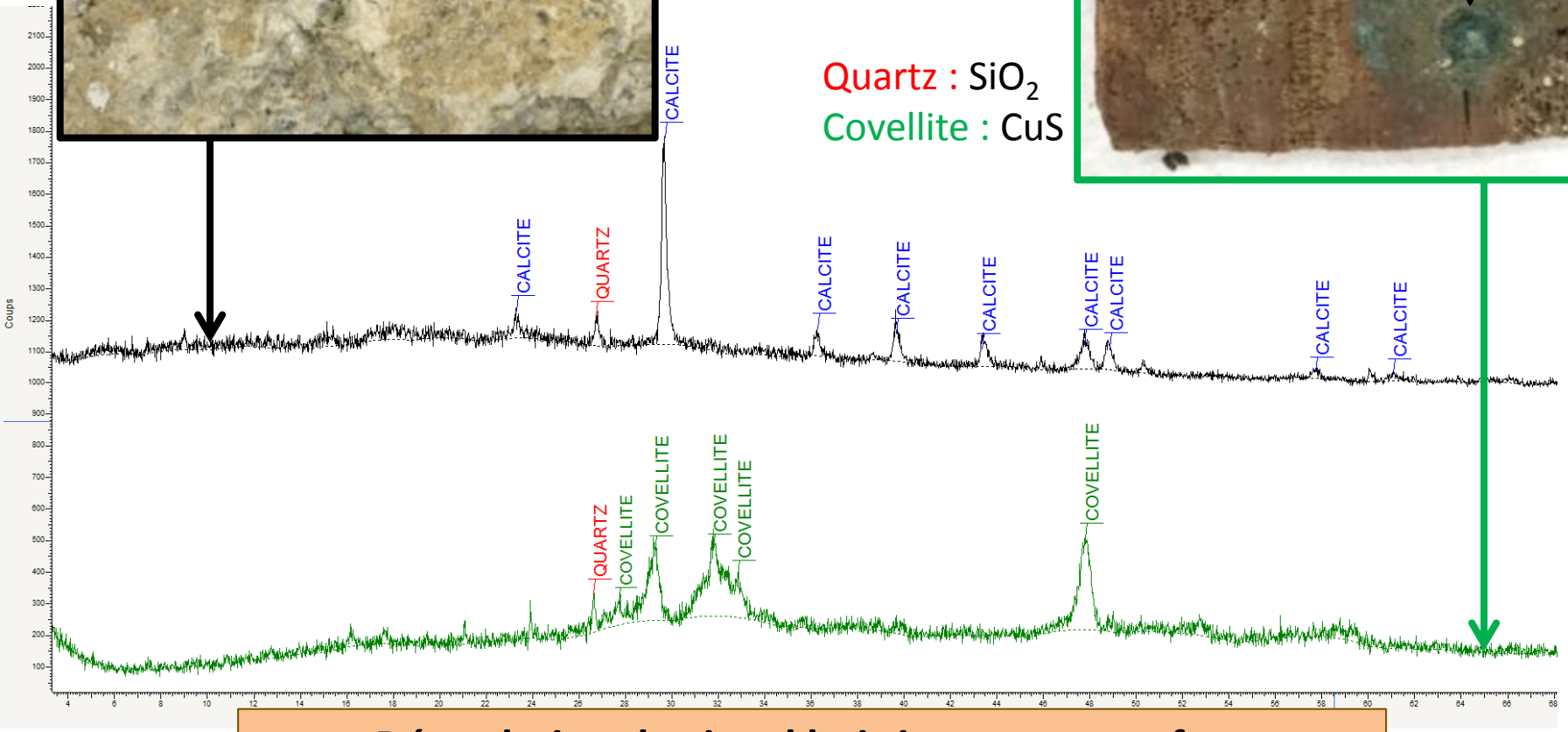
Calcite : $CaCO_3$

Quartz : SiO_2



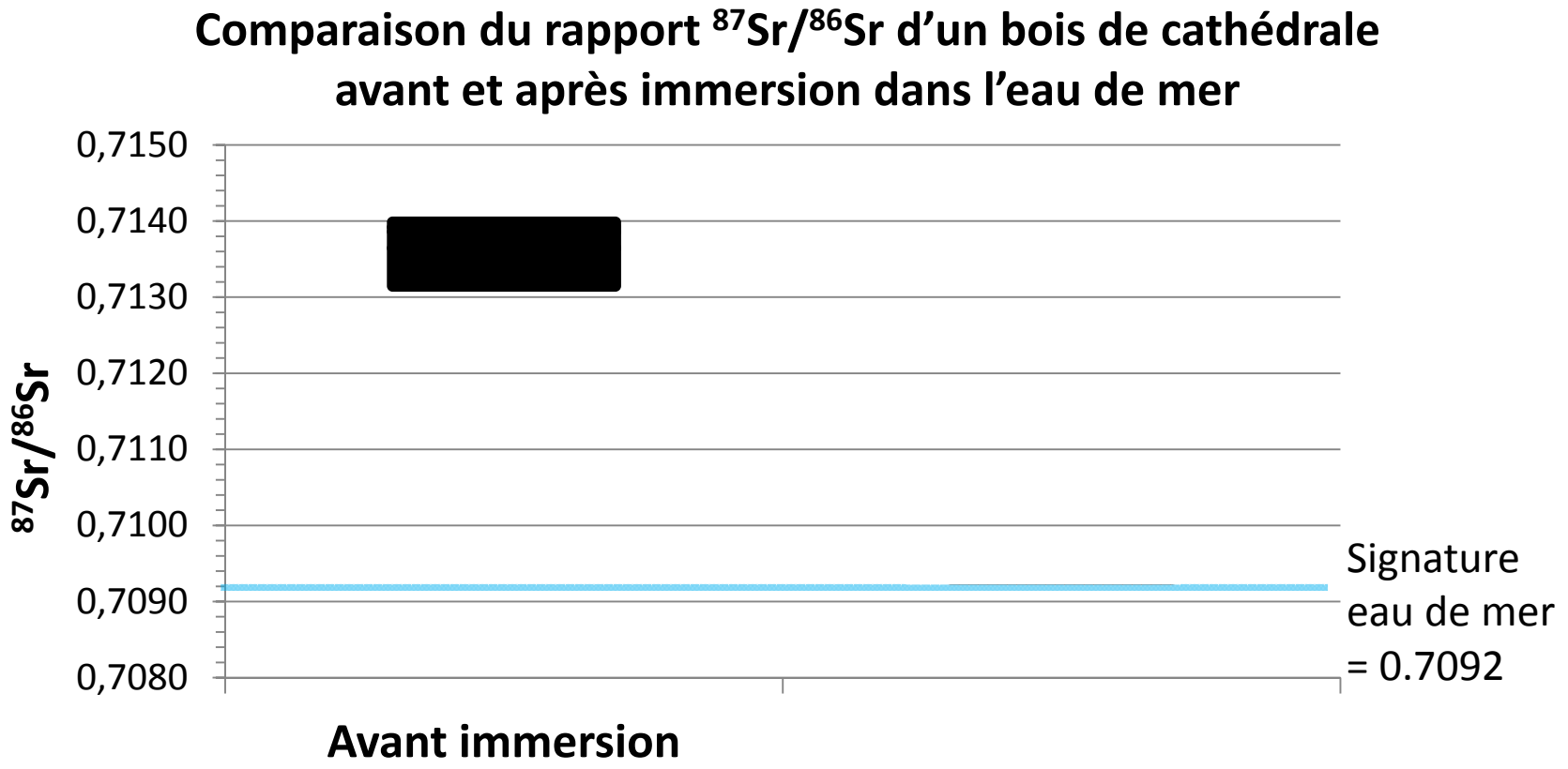
Quartz : SiO_2

Covellite : CuS

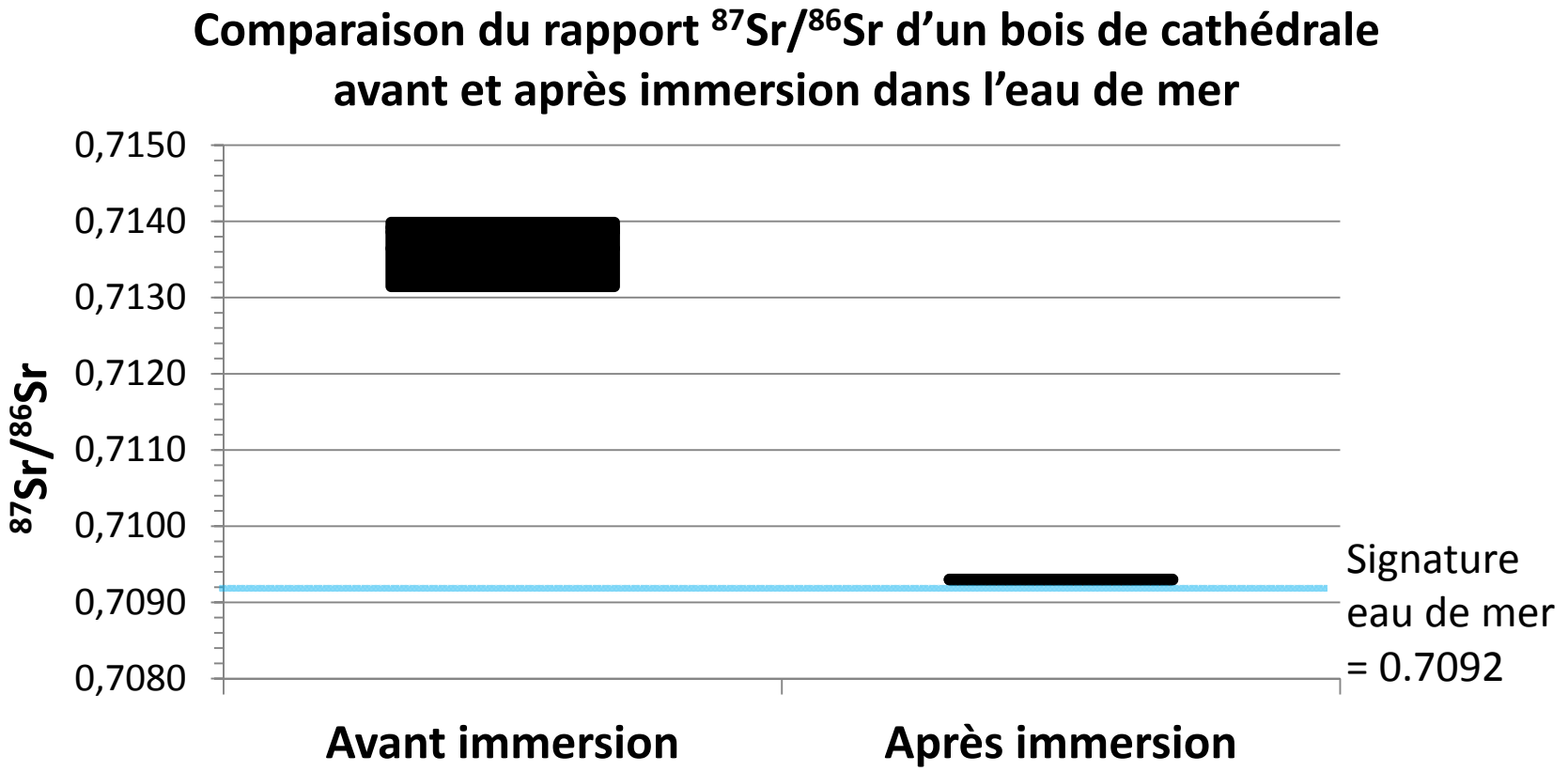


Dégradation du signal bois intense en surface (précipitations, contamination par autres matériaux …)

II.1. Premières analyses de bois

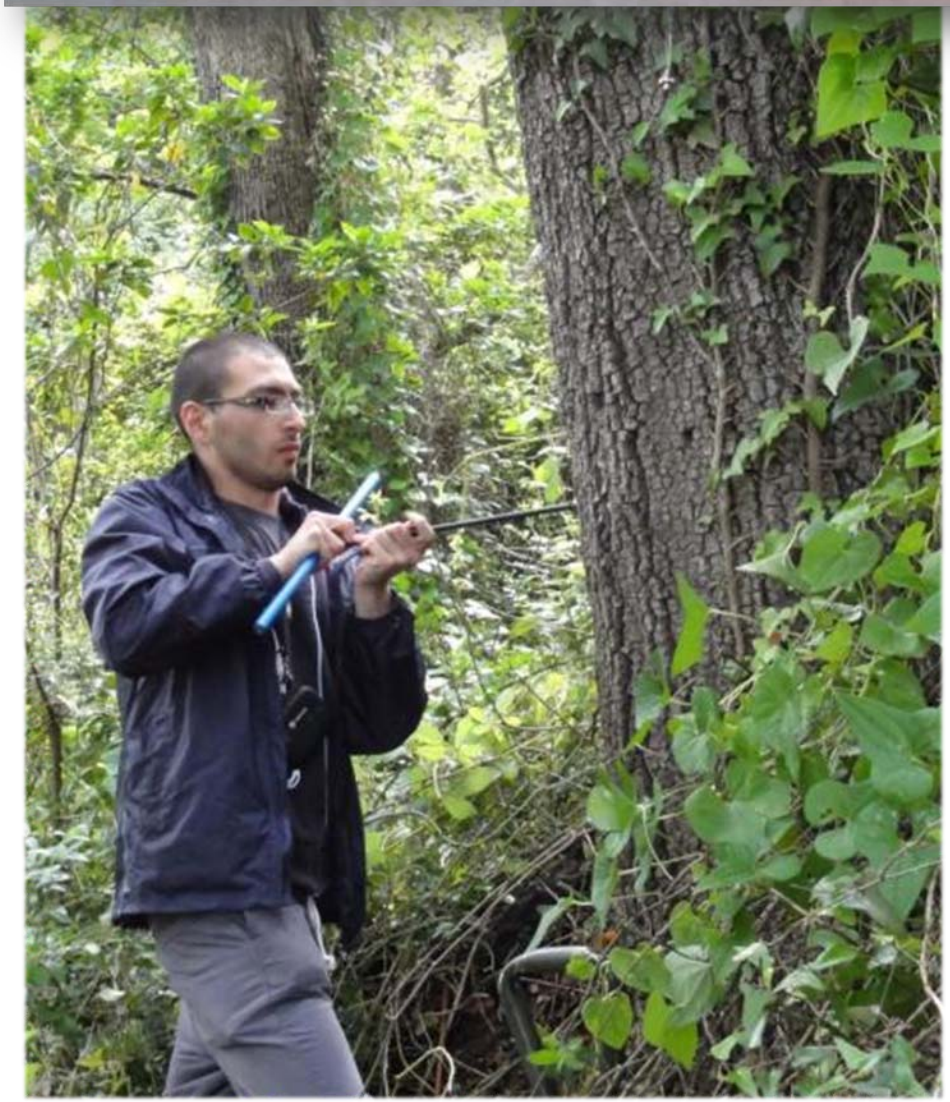


II.1. Premières analyses de bois



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

1er type de bois étudié : bois actuel



Échantillonnage difficile
Analyses sans surprises

2ème type de bois étudié : bois archéologique

Échantillonnage facile

Mais qu'analyse-t-on?!