

# Materials Properties, Use and Conservation: Construction Materials and Binders

## Pozzolanicity beyond Vitruvius

Michele Secco



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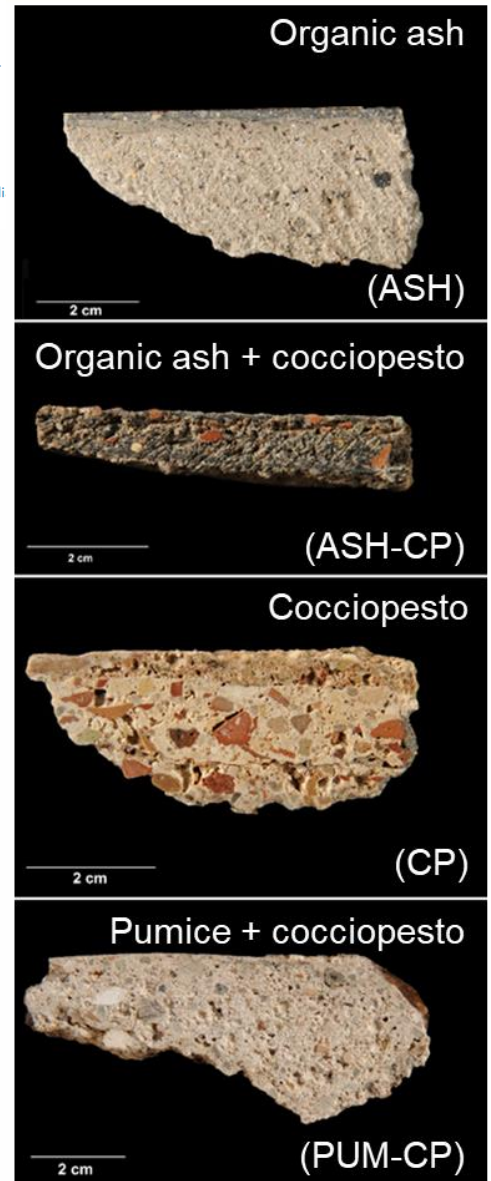
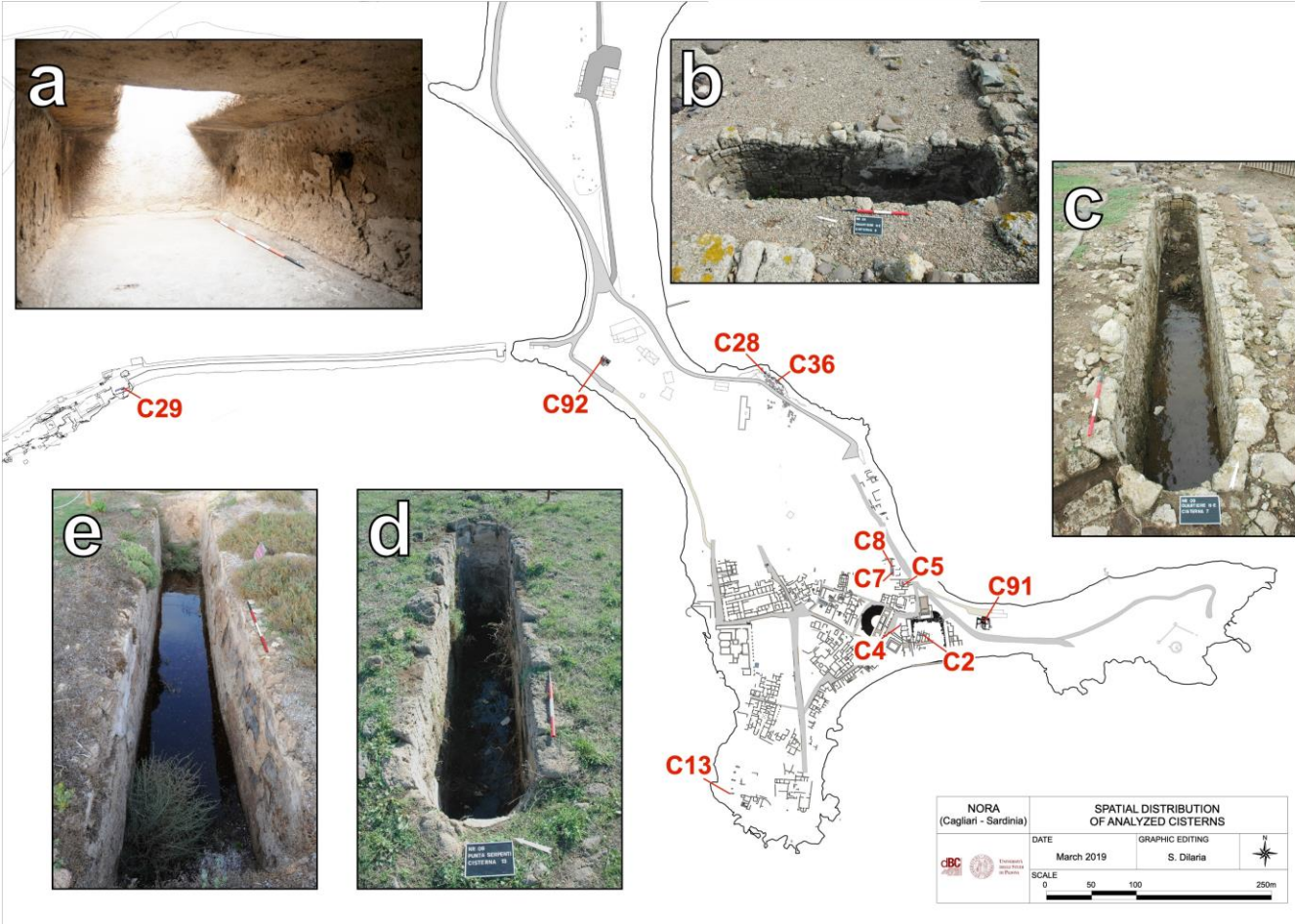
Journal of Cultural Heritage

Volume 44, July–August 2020, Pages 63–82

Original article

Technological transfers in the Mediterranean on the verge of Romanization: Insights from the waterproofing renders of Nora (Sardinia, Italy)

Michele Secco <sup>a, b, c, d, e</sup>, Simone Dilaria <sup>a</sup>, Jacopo Bonetto <sup>a</sup>, Anna Addis <sup>c</sup>, Sergio Tamburini <sup>d</sup>, Nereo Preto <sup>e</sup>, Giuli Ricci <sup>b, e</sup>, Gilberto Artoli <sup>b, e</sup>



NORA (Cagliari - Sardinia)		SPATIAL DISTRIBUTION OF ANALYZED CISTERNS	
DATE	March 2019	GRAPHIC EDITING	S. Dilaria
SCALE	0 50 100 250m		



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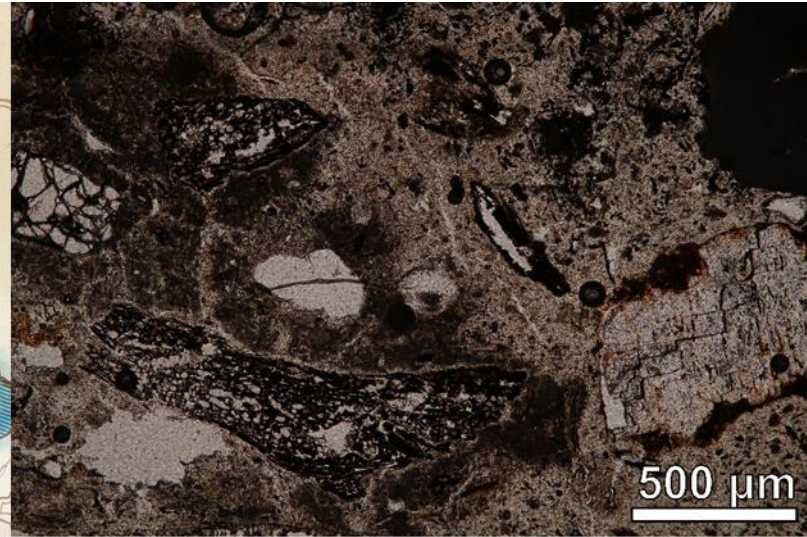
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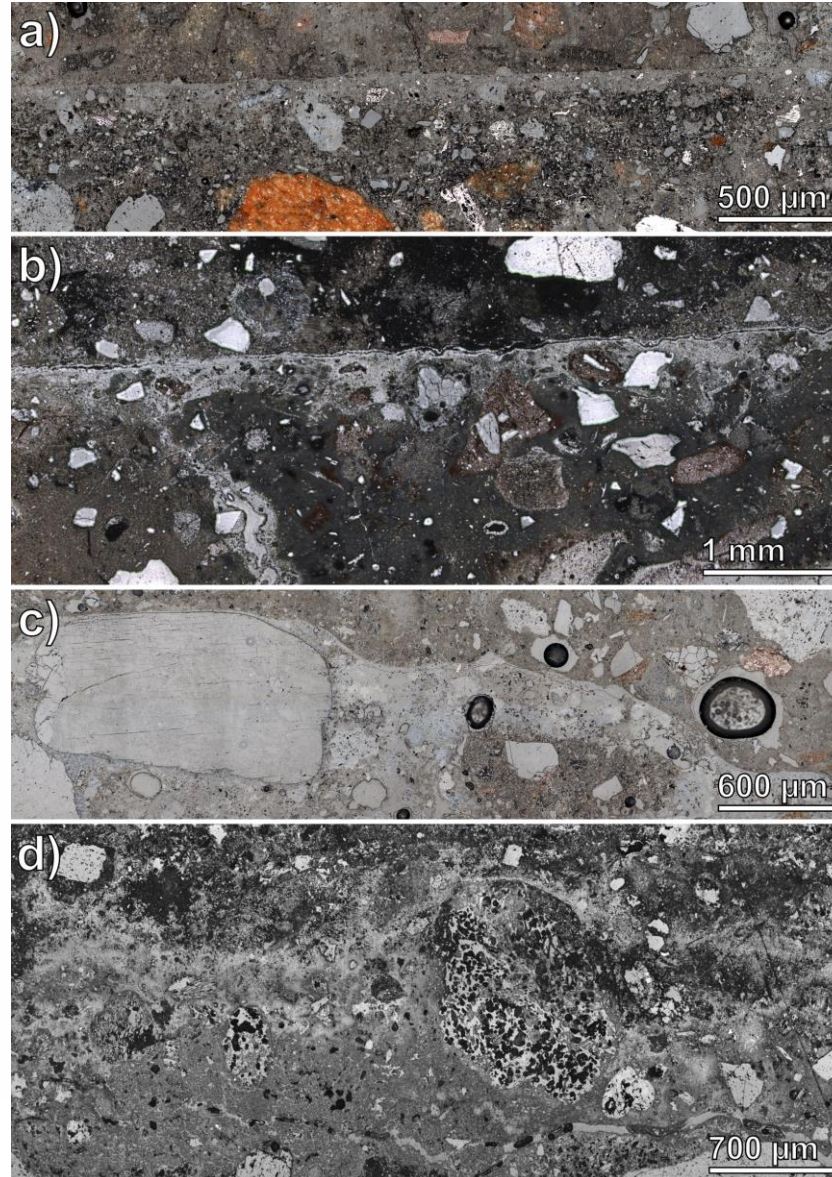


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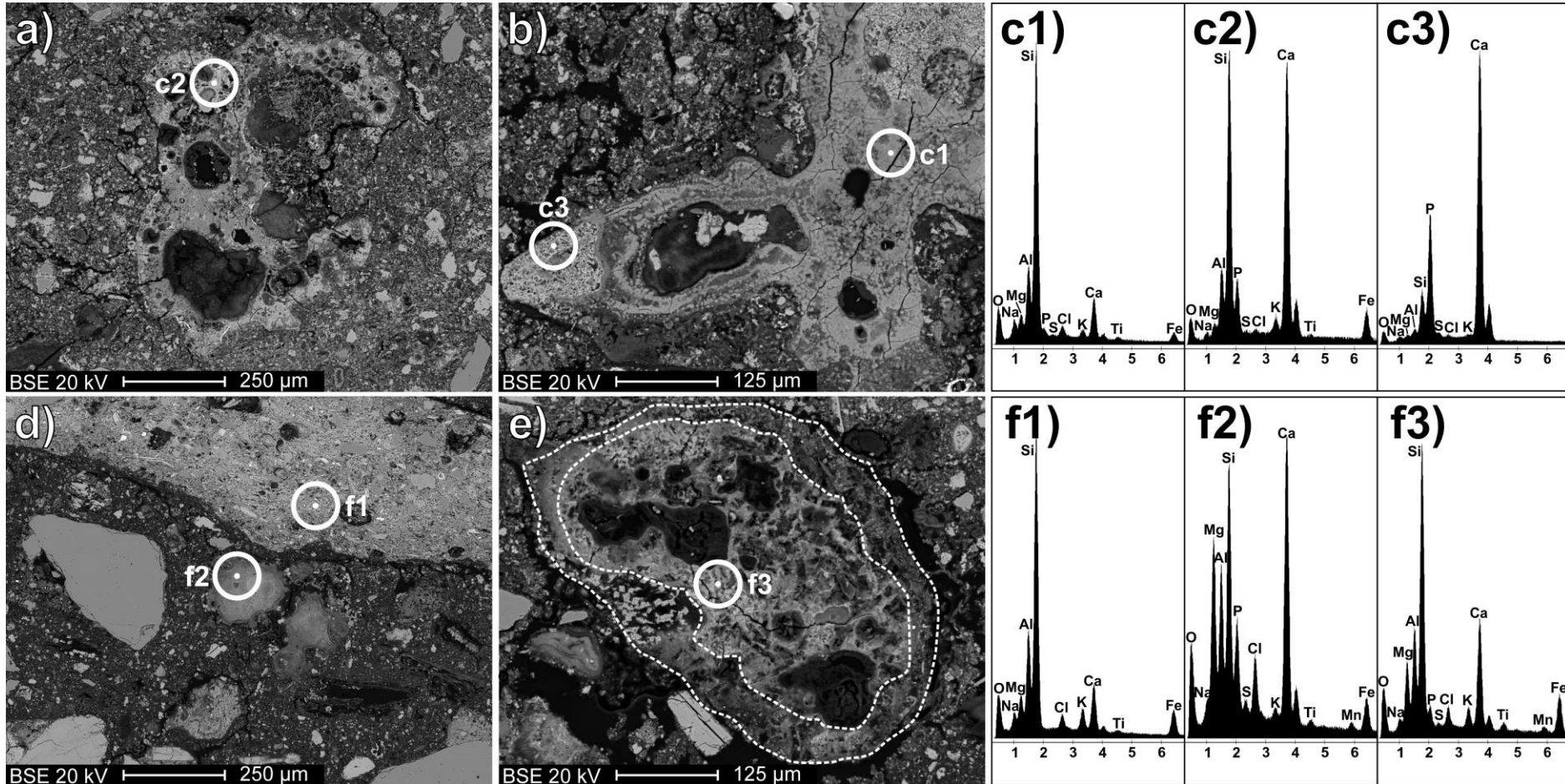
# Nora, Sardinia, Italy

Nora cisterns wall coating systems													
Cistern	C2	C4	C5	C7	C8	C13	C28	C29	C36	C91	C92	C92-lw	
Typology	bathtub	bathtub	bathtub	bathtub	bathtub	bathtub	rock-grave	rectangular	rock-grave	bathtub	rock-grave		
Construction chronology	150-75 B.C.E.						Roman age		Roman age	Roman age	1 <sup>st</sup> - 2 <sup>nd</sup> C.E.	2 <sup>nd</sup> - half 1 <sup>st</sup> B.C.E.	Roman age
Coating phases	<b>Constr.</b>	ASH-CP ASH-CP	ASH-CP	ASH ASH-CP	ASH-CP ASH-CP	ASH-CP	ASH ASH	ASH-CP CP CP	ASH-CP	CP PUM-CP PL	ASH-CP PL	CP	
	<b>rest. 1</b>		PUM-CP PUM-CP	ASH-CP ASH-CP PUM-CP	ASH-CP PUM-CP		CP	ASH-CP ASH-CP PUM-CP	CP PUM-CP		ASH-CP PL		
	<b>rest. 2</b>		PUM-CP	PUM-CP PUM-CP PUM-CP PUM-CP			CP	PUM-CP				PUM-CP	
	<b>rest. 3</b>			PUM-CP									
Coating systems	<b>CS1a</b>	ASH ASH				<b>CS1b</b>	ASH-CP ASH-CP	ASH-CP ASH-CP	ASH ASH-CP	CP-CL-ASH PL			
	<b>CS2a</b>	CP-CL-ASH PUM-CP	CP-CL-ASH CP-CL-ASH PUM-CP			<b>CS2b</b>	CP PUM-CP PL	PUM-CP PUM-CP PUM-CP PUM-CP	PUM-CP		<b>CS3</b>	CP CP CP	
<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <h3>CS1</h3> <p>CS1a      CS1b</p> </div> <div style="text-align: center;"> <h3>CS2</h3> <p>CS2a      CS2b</p> </div> <div style="text-align: center;"> <h3>CS3</h3> </div> </div>													



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## SEM-EDS ASH



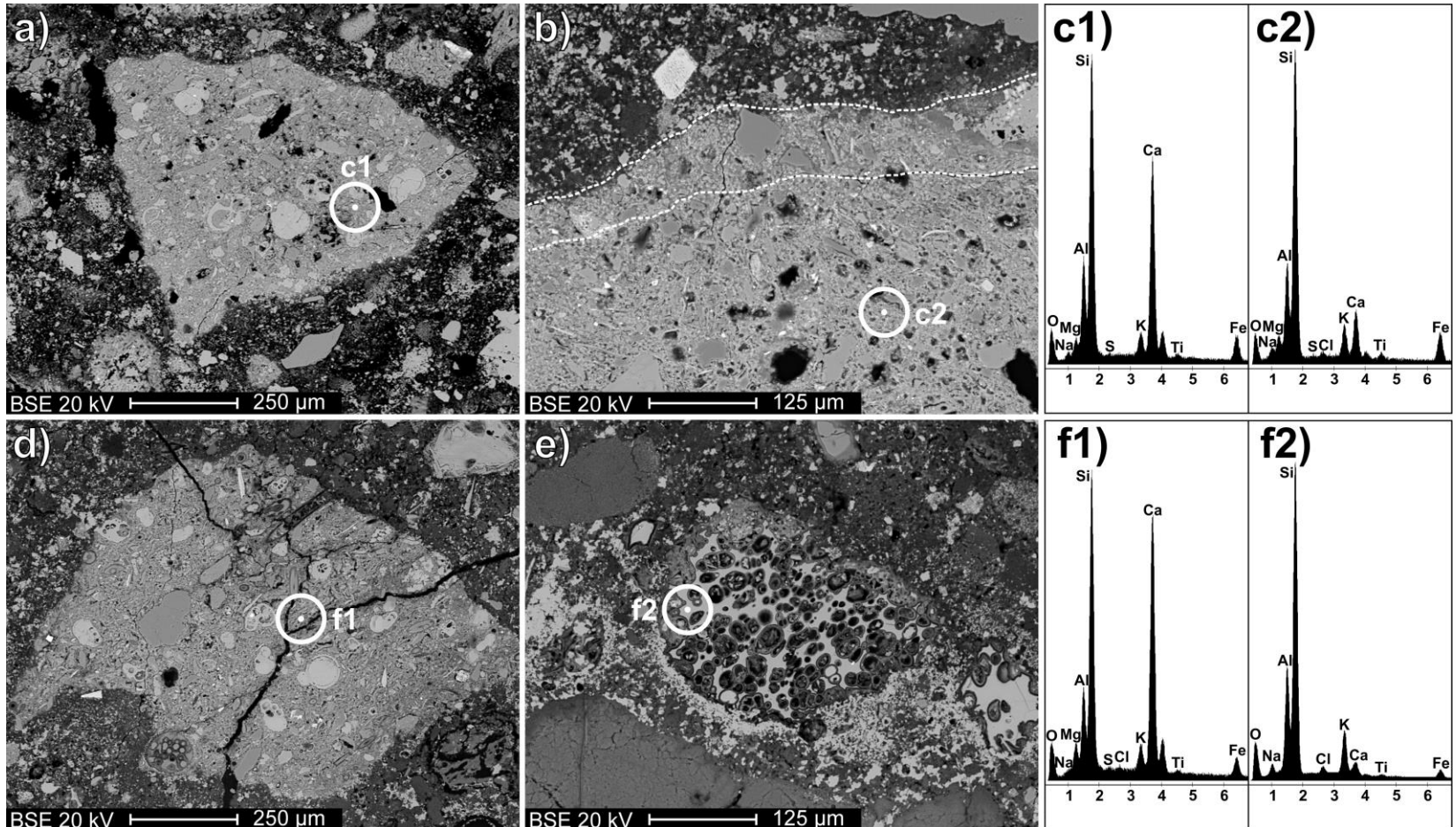
## ASH-CP

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## SEM-EDS CP



## PUM-CP

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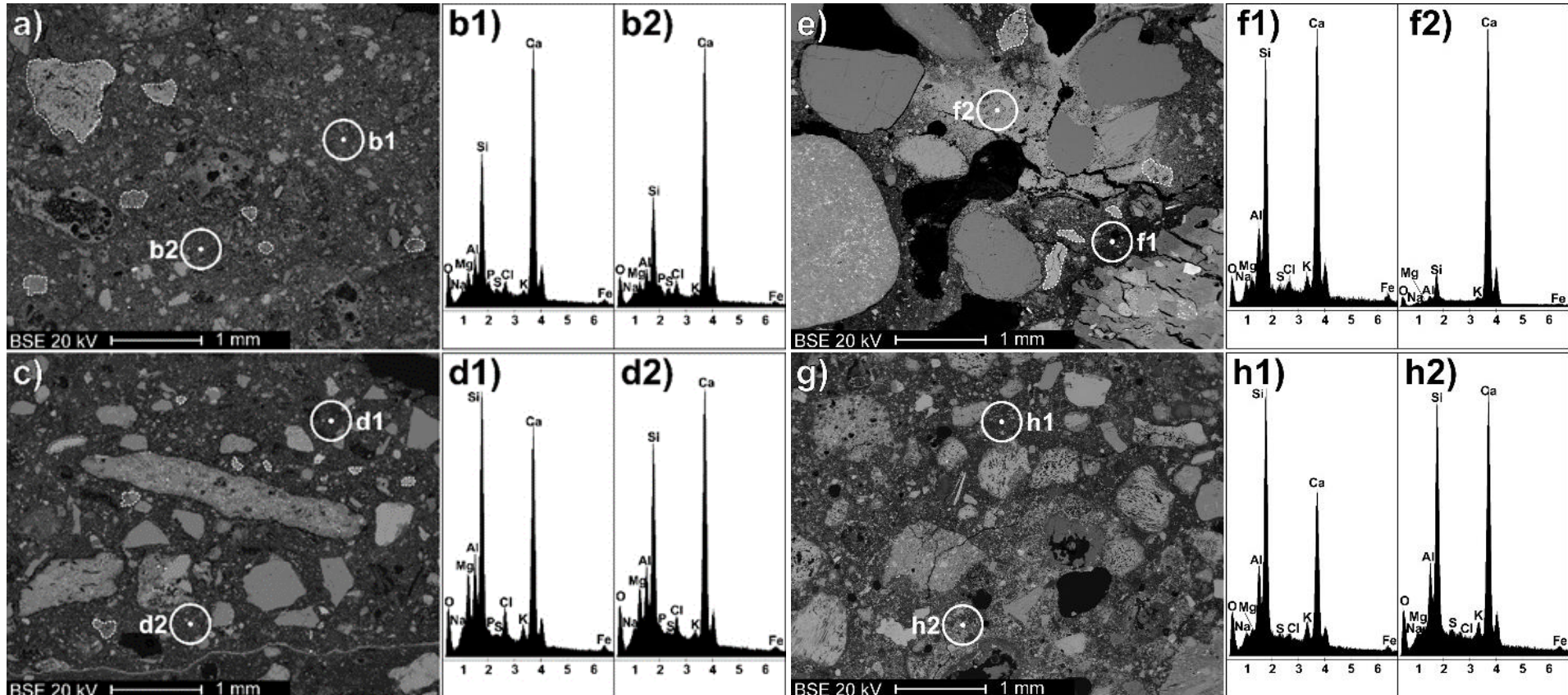


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## SEM-EDS

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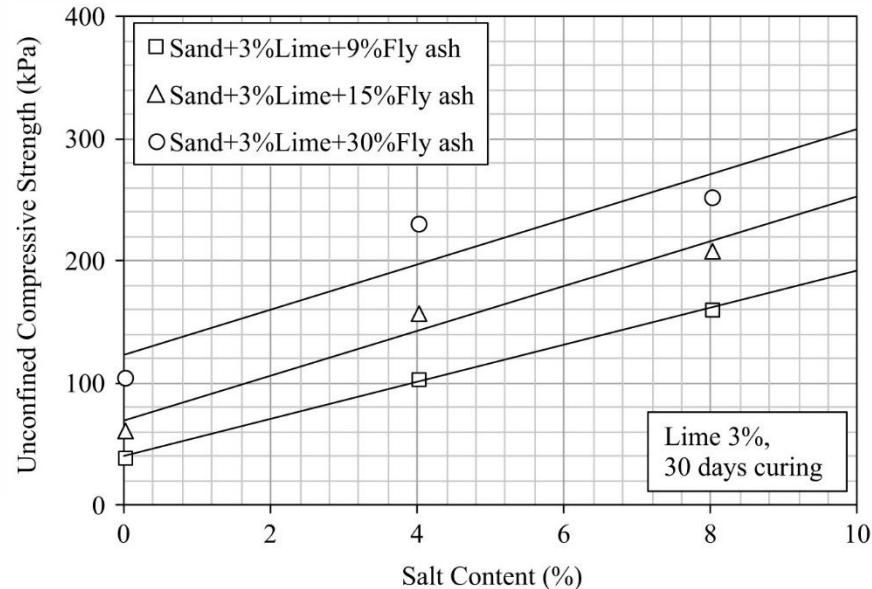
### CP



### ASH-CP

### PUM-CP

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Karim et al., 2017



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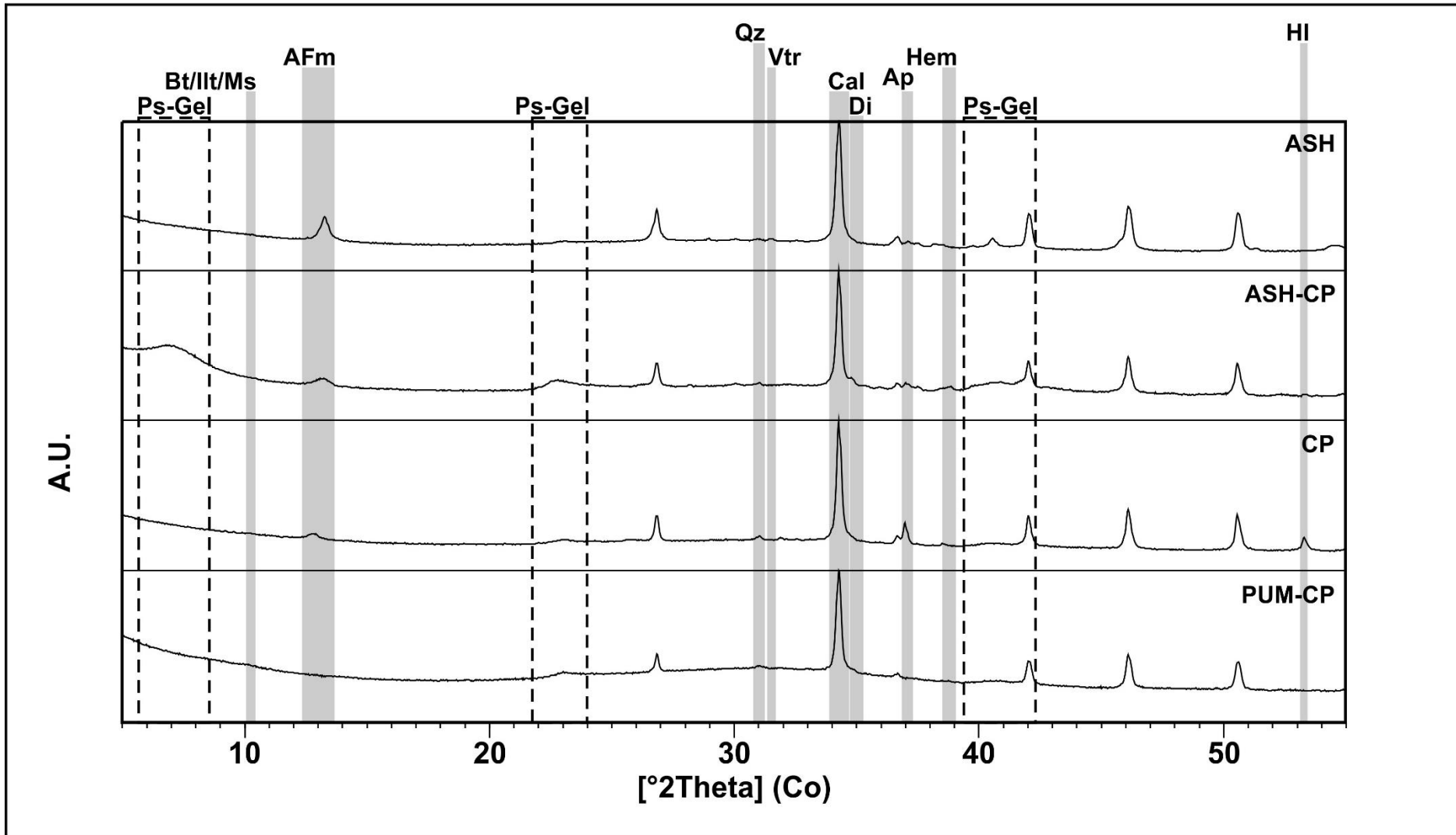
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## XRPD, BINDER FRACTION



## Magnesium silicate hydrate (M-S-H) gel

Cement and Concrete Research 73 (2015) 228–237



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Cement and Concrete Research

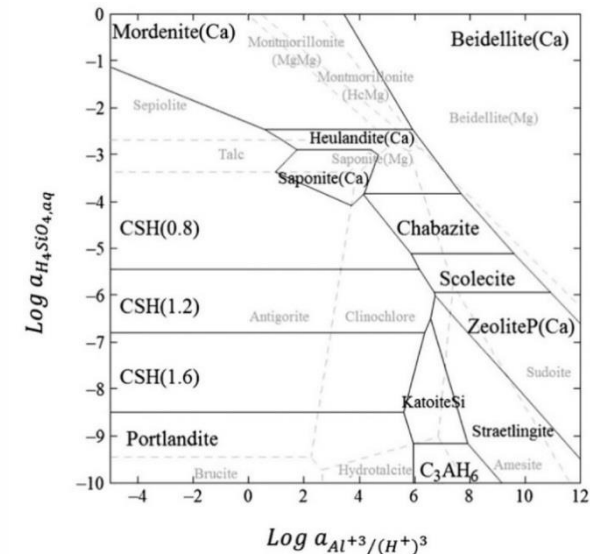
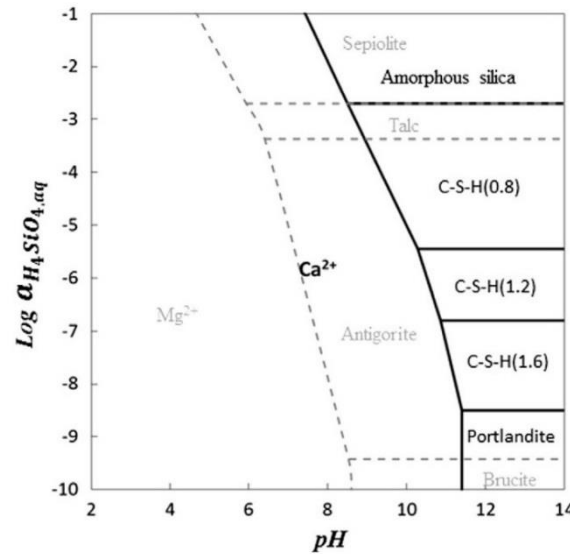
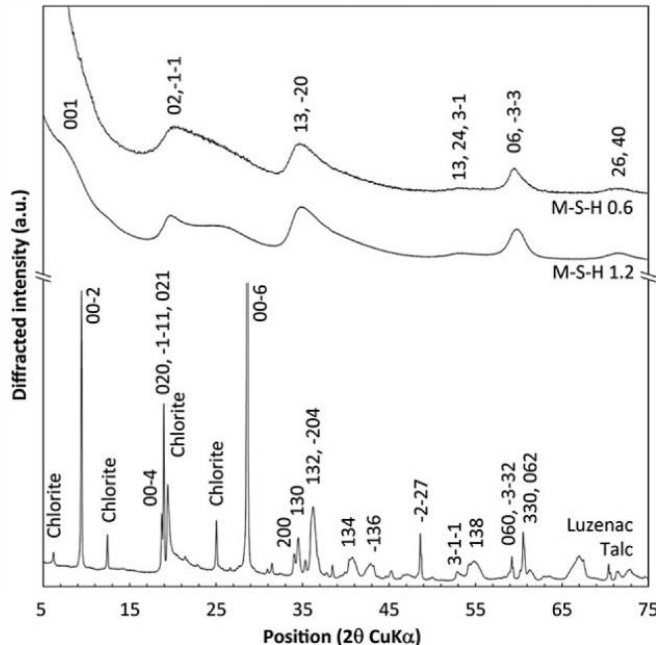
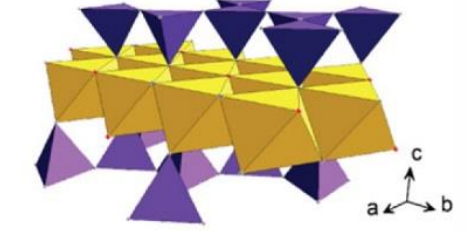
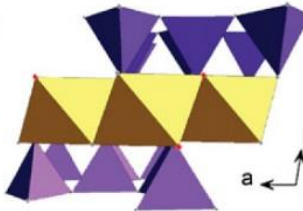
journal homepage: <http://ees.elsevier.com/CEMCON/default.asp>



Crystal structure of magnesium silicate hydrates (M-S-H): The relation with 2:1 Mg–Si phyllosilicates

Cédric Roos<sup>a,b,\*</sup>, Sylvain Grangeon<sup>b</sup>, Philippe Blanc<sup>b</sup>, Valérie Montouillout<sup>c</sup>, Barbara Lothenbach<sup>d</sup>, Pierre Henocq<sup>a</sup>, Eric Giffaut<sup>a</sup>, Philippe Vieillard<sup>e</sup>, Stéphane Gaboreau<sup>b</sup>

<sup>a</sup> Andra – Scientific Division, 1-7 Rue Jean Monnet, Parc de la Croix Blanche, 92298 Chatenay-Malabry Cedex, France  
<sup>b</sup> BRGM, 3 Avenue Claude Gallemis, 45060 Orléans Cedex 2, France  
<sup>c</sup> CNRS, CEMMFL, UPR 3079, 45071 Orléans, France  
<sup>d</sup> Empa, Laboratory for Concrete & Construction Chemistry, Überlandstrasse 129, 8600 Dübendorf, Switzerland  
<sup>e</sup> Université de Poitiers-CNRS, UMR2285 IC2MP, Equipe HydrASA, Poitiers 86022, France



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Cement and Concrete Research 79 (2016) 323–332



Contents lists available at ScienceDirect

## Cement and Concrete Research

journal homepage: <http://ees.elsevier.com/CEMCON/default.asp>



### Properties of magnesium silicate hydrates (M-S-H)

Dominik Nied <sup>a,b,1</sup>, Kasper Enemark-Pedersen <sup>c</sup>, Emilie L'Hopital <sup>b</sup>, Jørgen Skibsted <sup>c</sup>, Barbara Lothenbach <sup>b</sup>

<sup>a</sup> HeidelbergCement Technology Center GmbH, 69181 Leimen, Germany  
<sup>b</sup> Empa, Laboratory for Concrete & Construction Chemistry, 8600 Dübendorf, Switzerland  
<sup>c</sup> Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 Århus C, Denmark



Construction and Building Materials 131 (2017) 549–557



Contents lists available at ScienceDirect

## Construction and Building Materials

journal homepage: [www.elsevier.com/locate/conbuildmat](http://www.elsevier.com/locate/conbuildmat)



### Performance and microstructure of MgO-SiO<sub>2</sub> concrete under different environments

C. Sonat, W.W. Teo, C. Unluer\*

School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore



Thermochimica Acta 655 (2017) 251–261



Contents lists available at ScienceDirect

## Thermochimica Acta

journal homepage: [www.elsevier.com/locate/tca](http://www.elsevier.com/locate/tca)



### Investigation of the performance and thermal decomposition of MgO and MgO-SiO<sub>2</sub> formulations

C. Sonat, C. Unluer\*

School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore



Physics and Chemistry of the Earth 99 (2017) 158–167



Contents lists available at ScienceDirect

## Physics and Chemistry of the Earth

journal homepage: [www.elsevier.com/locate/pce](http://www.elsevier.com/locate/pce)



### Traditional Portland cement and MgO-based cement: a promising combination?

Monica Tonelli <sup>a</sup>, Francesca Martini <sup>b</sup>, Lucia Calucci <sup>c</sup>, Marco Geppi <sup>b,c</sup>, Silvia Borsacchi <sup>c</sup>, Francesca Ridi <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry "Ugo Schiff" & CSGI, University of Florence, Sesto Fiorentino (FI), 50019, Italy  
<sup>b</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa 56124, Italy  
<sup>c</sup> Istituto di Chimica dei Composti OrganoMetallici, Consiglio Nazionale delle Ricerche – CNR S.S. di Pisa, Pisa 56124, Italy



Construction and Building Materials 131 (2017) 526–535



Contents lists available at ScienceDirect

## Construction and Building Materials

journal homepage: [www.elsevier.com/locate/conbuildmat](http://www.elsevier.com/locate/conbuildmat)



### Strength and workability of magnesium silicate hydrate binder systems

H.M. Tran\*, A. S. S. S.

Department of Civil and Natural Resources Engineering, University of Canterbury, Christchurch, New Zealand



Cement and Concrete Research 41 (2011) 439–442



Contents lists available at ScienceDirect

## Cement and Concrete Research

journal homepage: <http://ees.elsevier.com/CEMCON/default.asp>



### Development of low pH cement systems forming magnesium silicate hydrate (M-S-H)

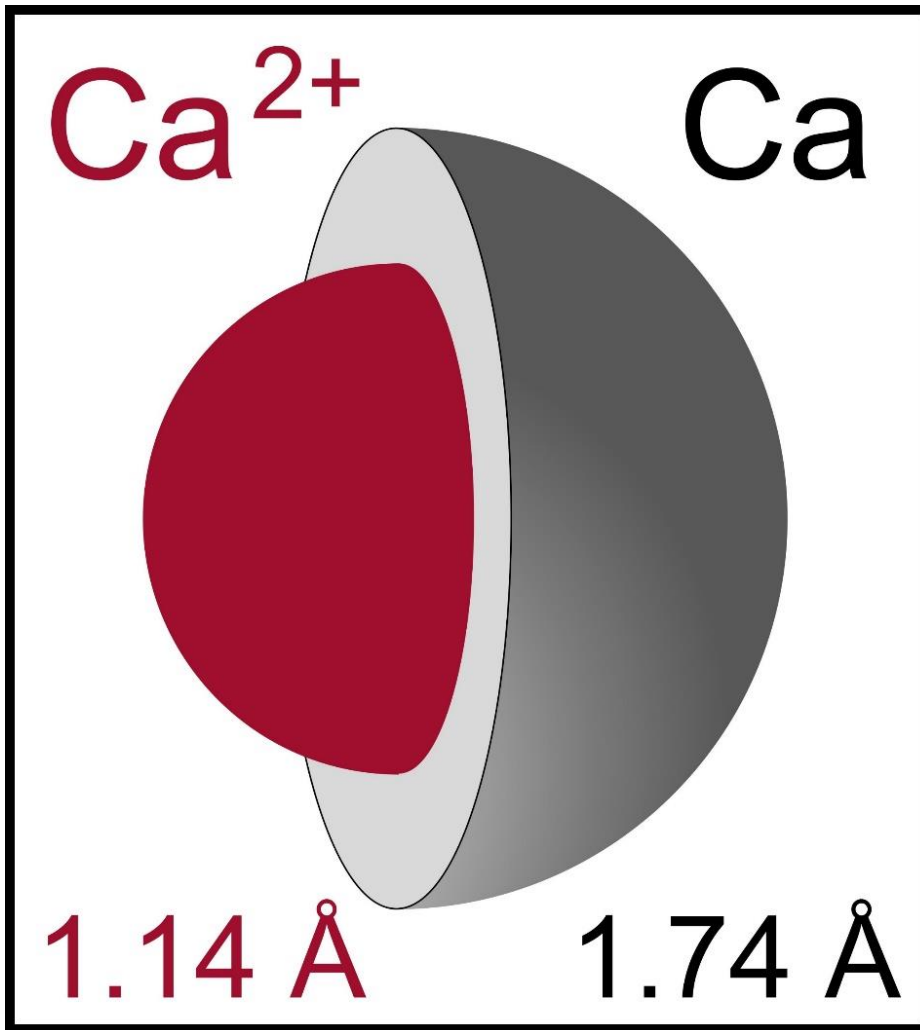
Tingting Zhang <sup>a,b</sup>, C.R. Cheeseman <sup>a,\*</sup>, L.J. Vandeperre <sup>b</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom  
<sup>b</sup> Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

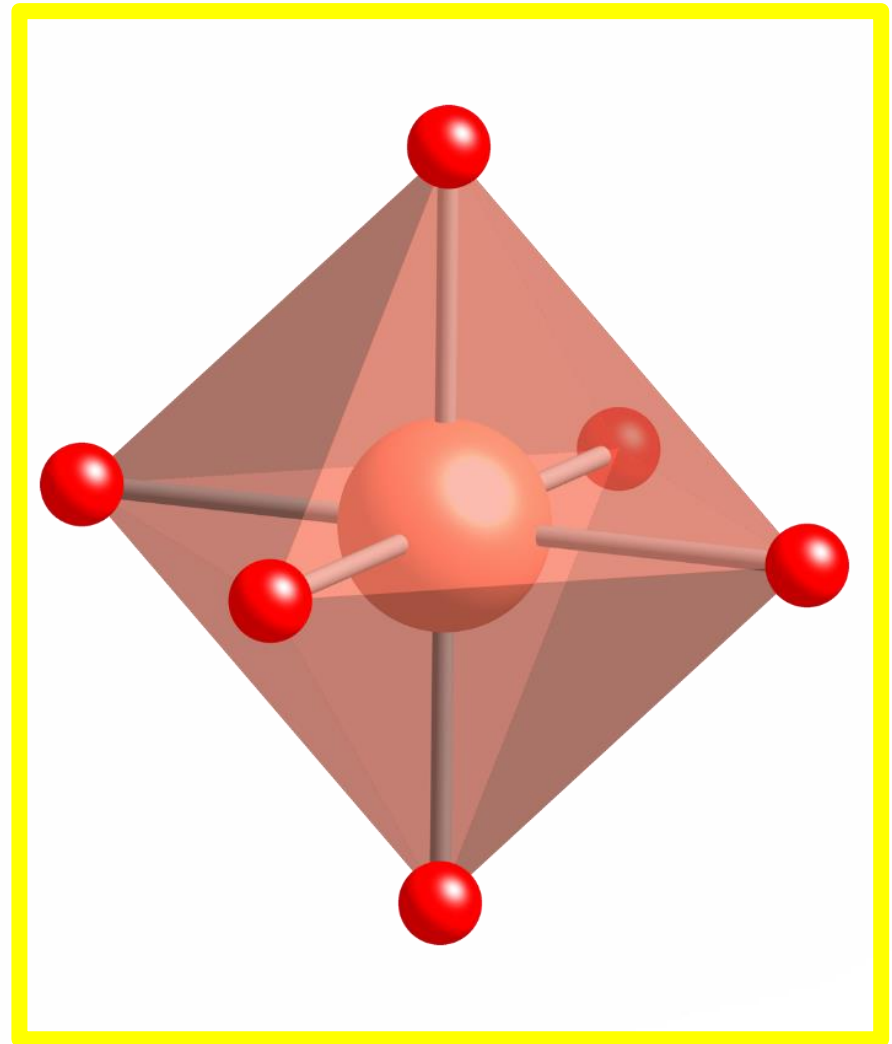
Romans had done it already!

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Shannon, 1976



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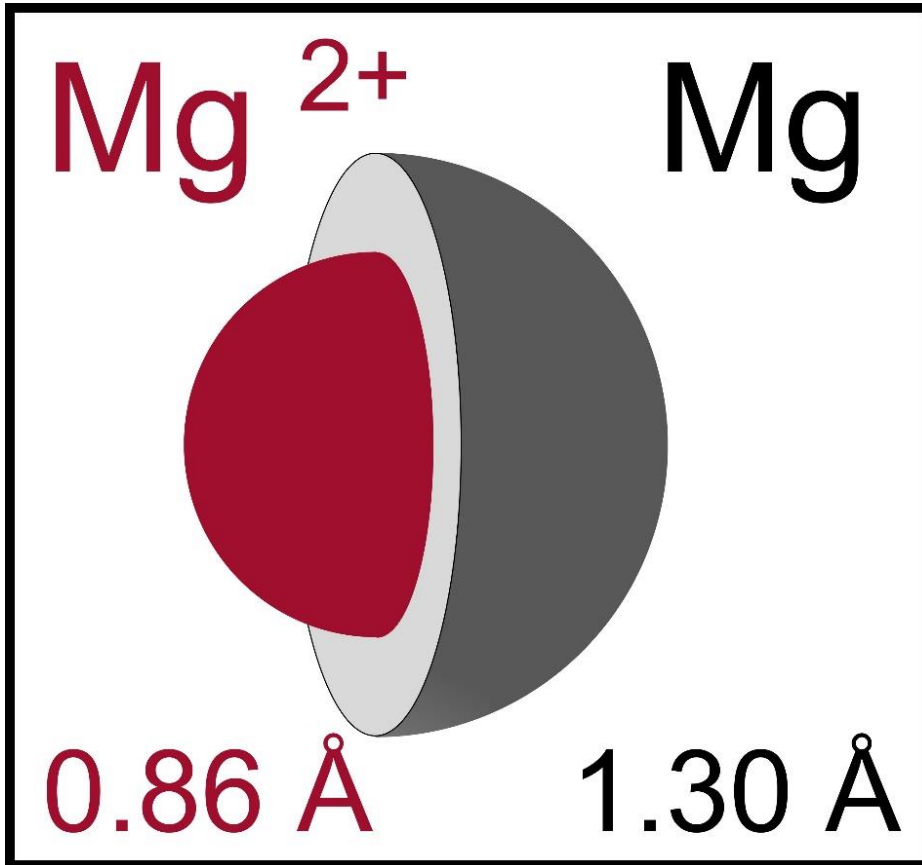
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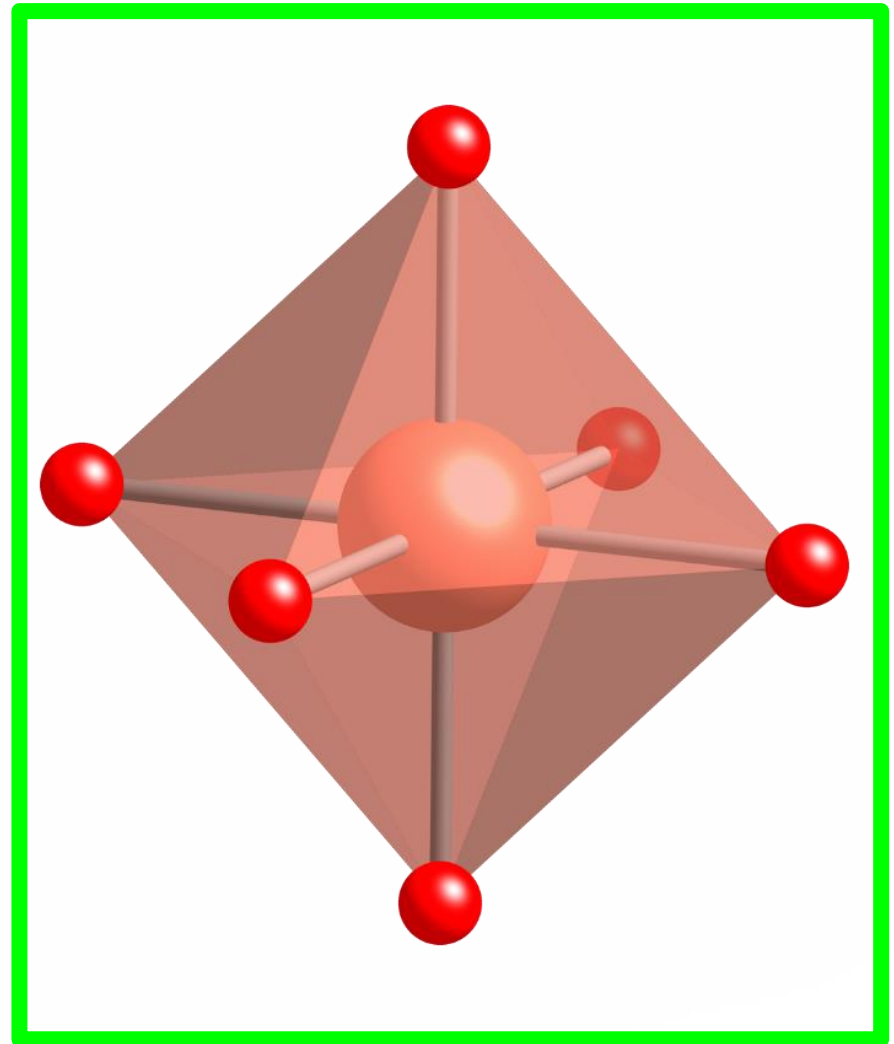
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Shannon, 1976

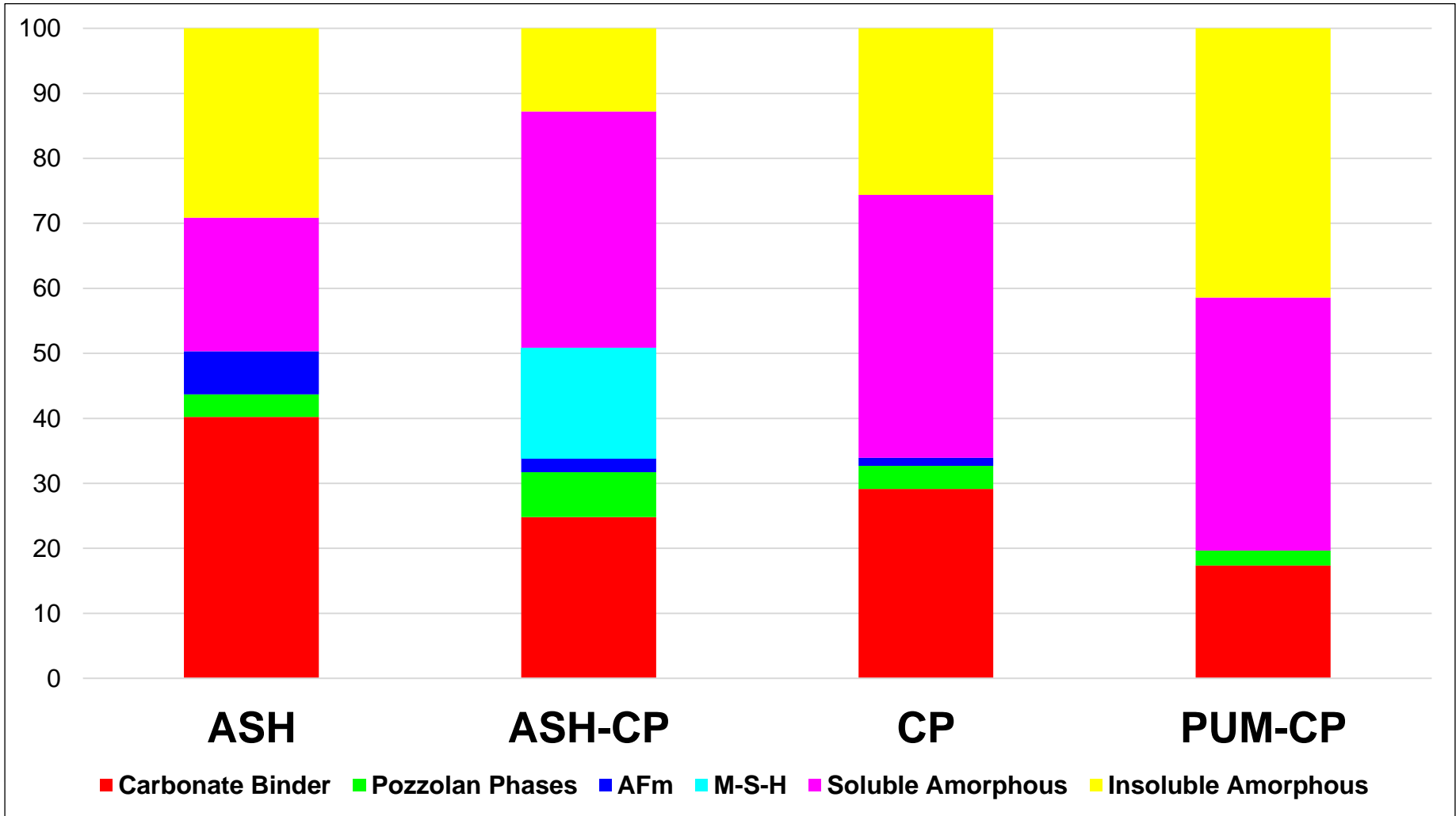


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## ACID ATTACK + XRPD, BINDER FRACTION

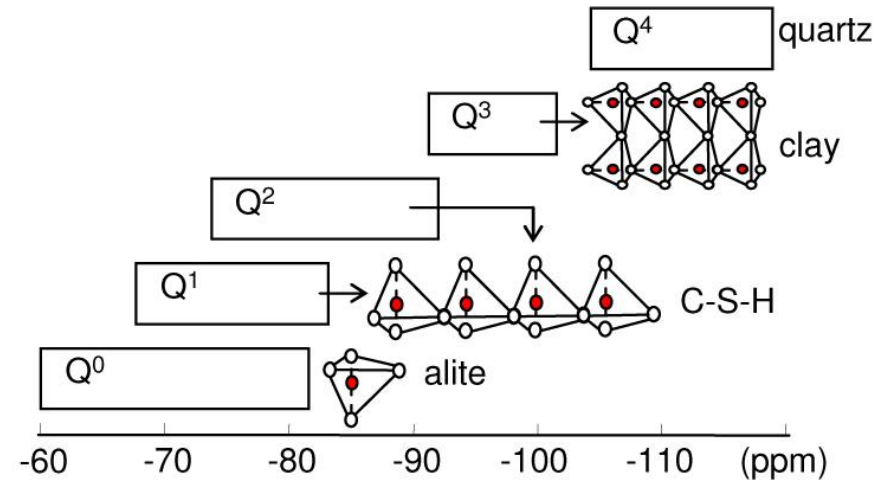


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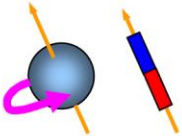
## SOLID-STATE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY



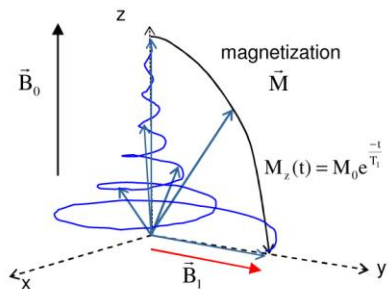
### <sup>29</sup>Si chemical shift ranges of silicates



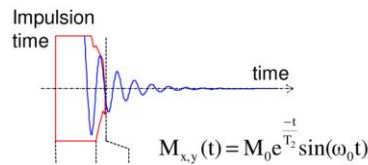
The nucleus and the spin



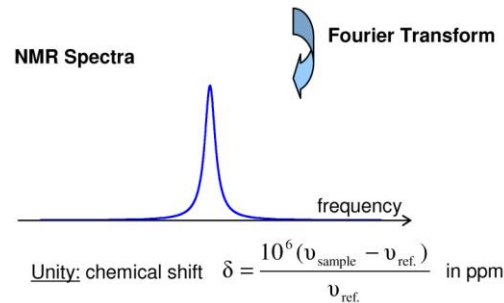
Experiment



Free induction decay (fid)



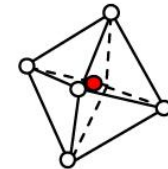
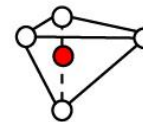
NMR Spectra



### <sup>27</sup>Al chemical shift ranges of aluminates

Al in alite, C-S-H

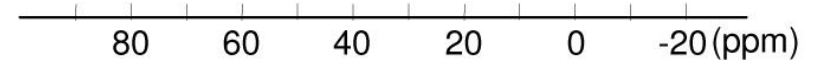
ettringite, AFm



Al(IV)

V

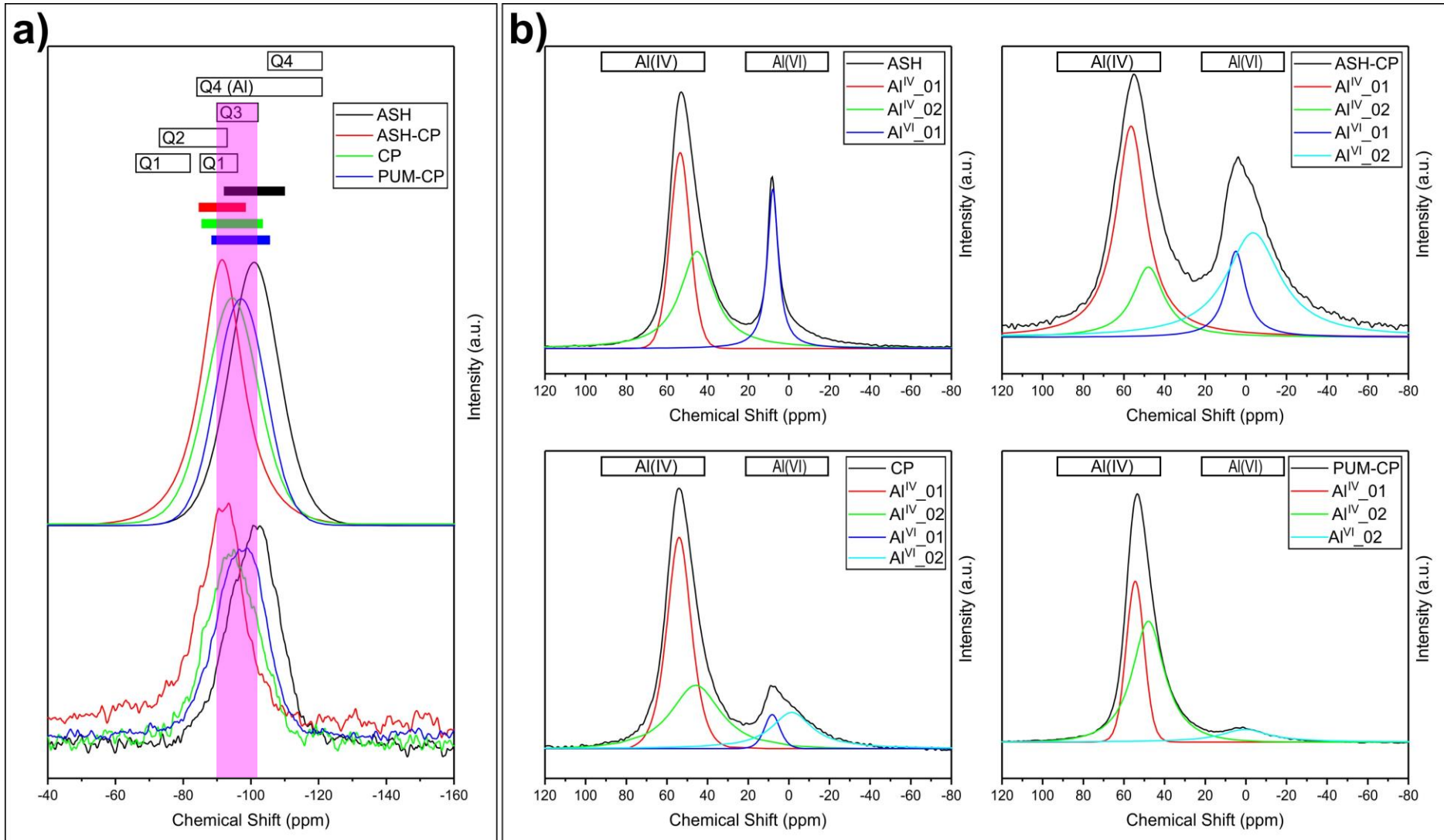
Al(VI)





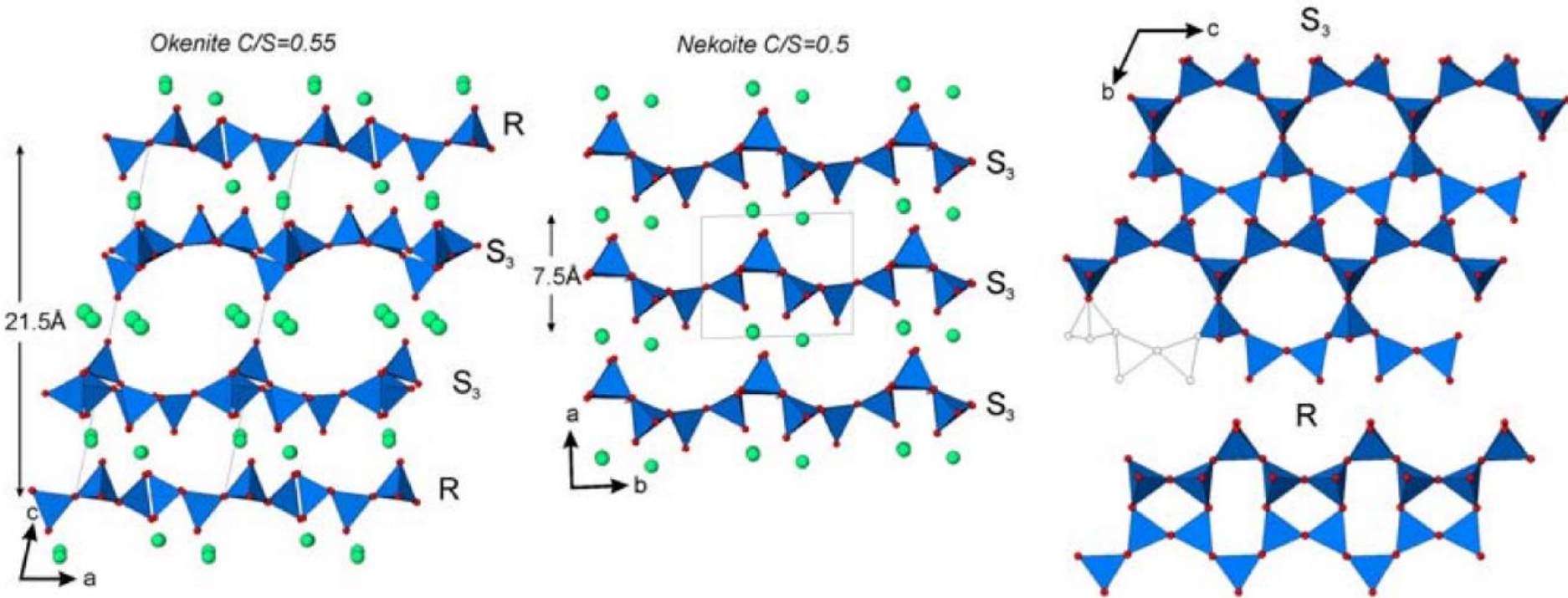
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## SS-NMR, BINDER FRACTION



# Nora, Sardinia, Italy

## Hybrid inosilicate/phyllosilicate C-S-H gel



Garbev et al., 2002

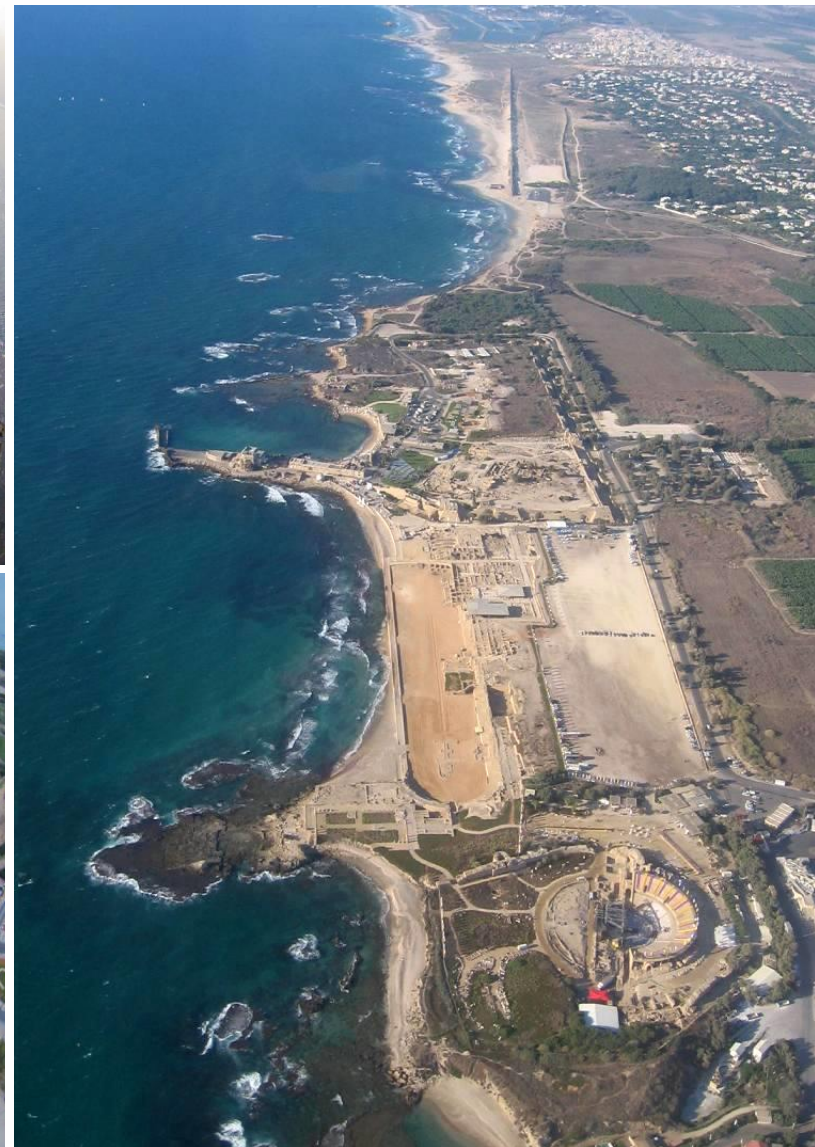


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Hohfelder et al., 2007



# Caesarea Maritima, Israel



Hohfelder et al., 2007



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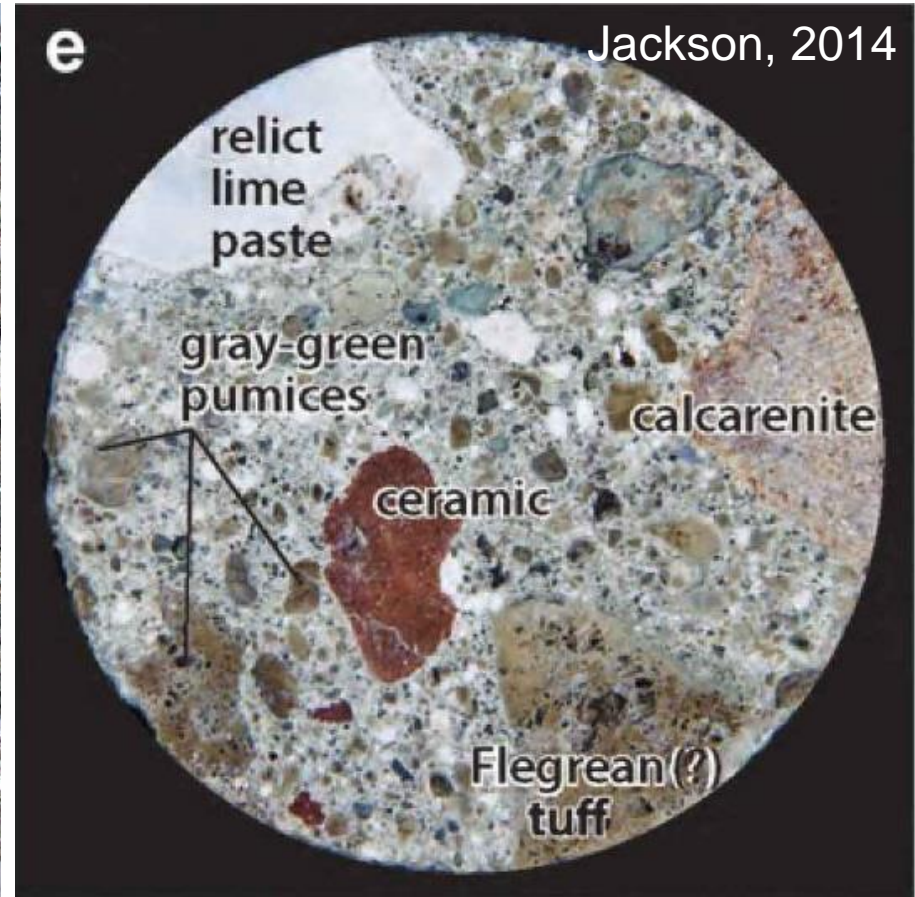
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Hohfelder et al., 2007

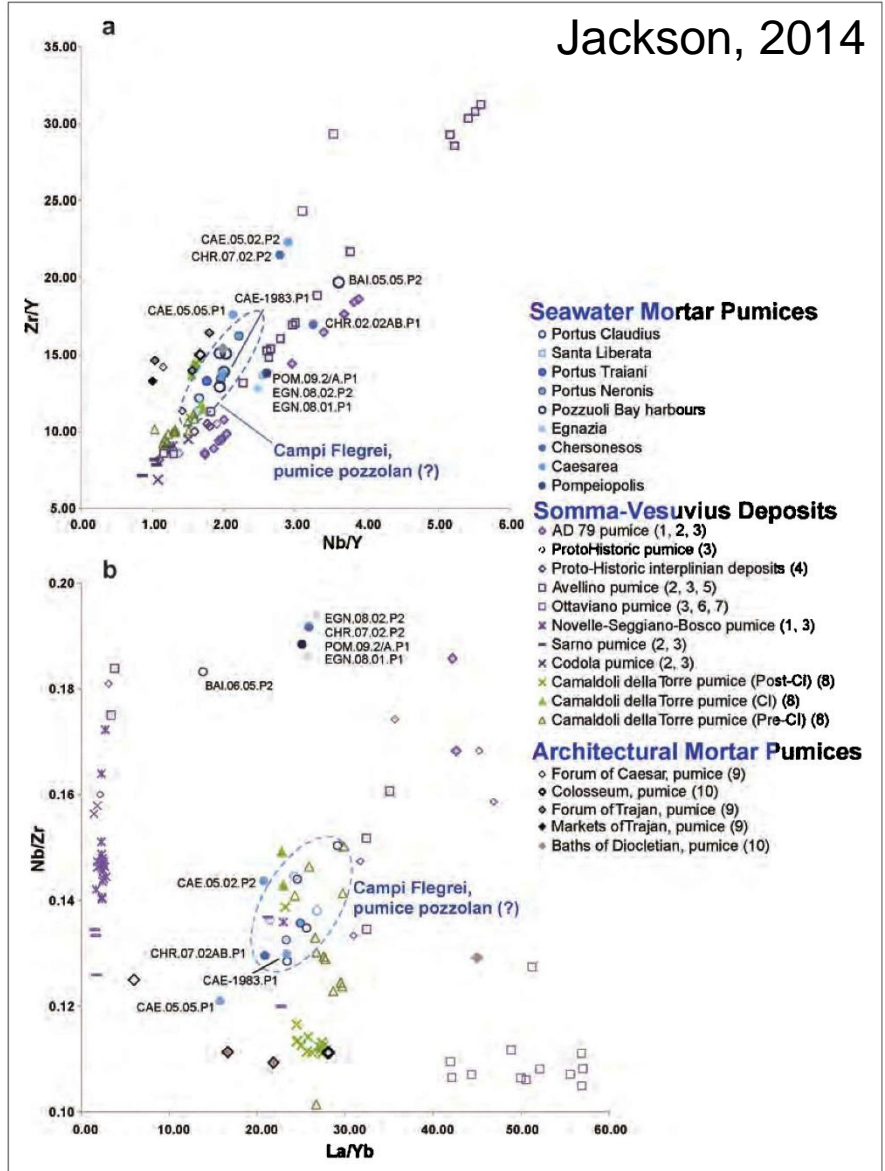
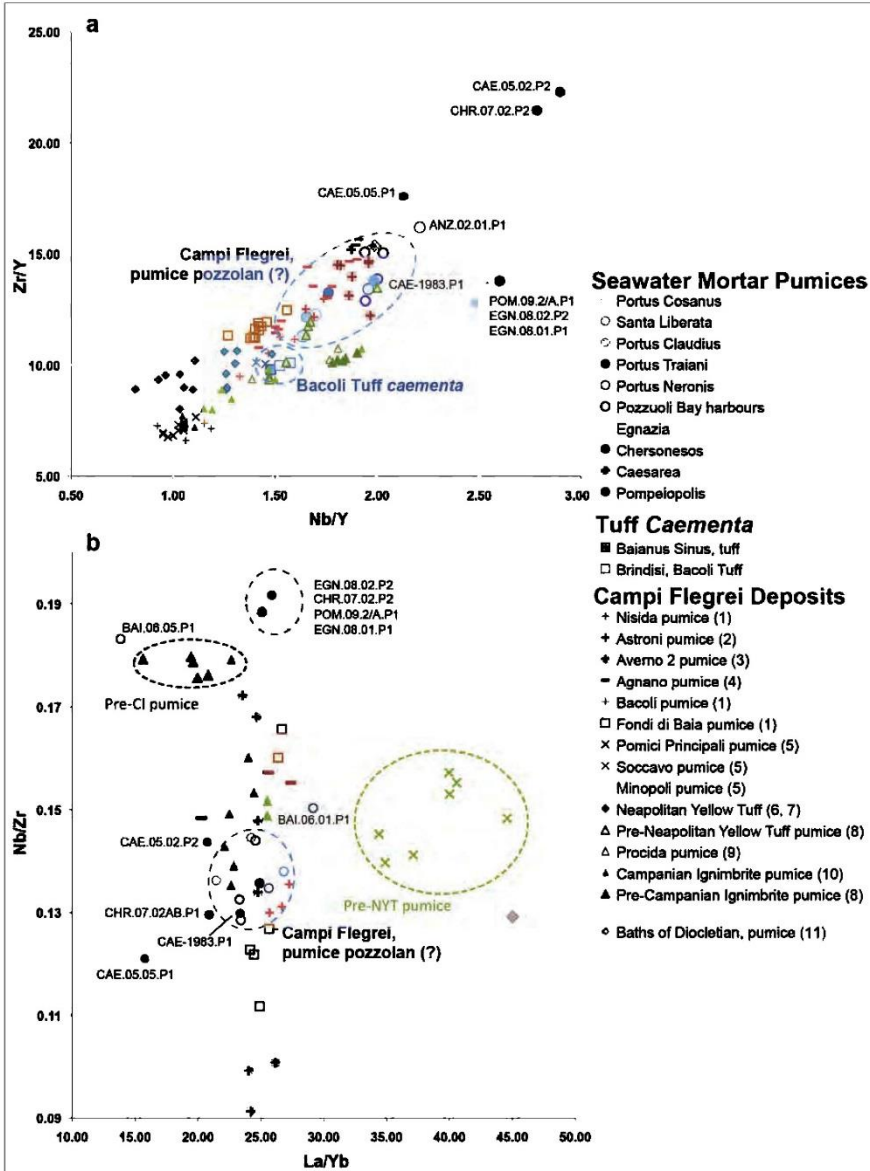


Jackson, 2014



# Caesarea Maritima, Israel

Jackson, 2014



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Cementation processes of Roman pozzolanic binders from Caesarea Maritima (Israel)

Michele Secco<sup>a,b,\*</sup>, Yotam Asscher<sup>c</sup>, Giulia Ricci<sup>b,d</sup>, Sergio Tamburini<sup>e</sup>, Nereo Preto<sup>d</sup>, Jacob Sharvit<sup>c</sup>, Gilberto Artioli<sup>b,d</sup>

<sup>a</sup> University of Padova, Department of Cultural Heritage (DBC), Italy

<sup>b</sup> University of Padova, Inter-Departmental Research Center for the Study of Cement Materials and Hydraulic Binders (CIRCe), Italy

<sup>c</sup> Israel Antiquities Authority (IAA), Israel

<sup>d</sup> University of Padova, Department of Geosciences, Italy

<sup>e</sup> National Research Council, Institute of Condensed Matter Chemistry and Technologies for Energy (CNR-ICMATE), Italy



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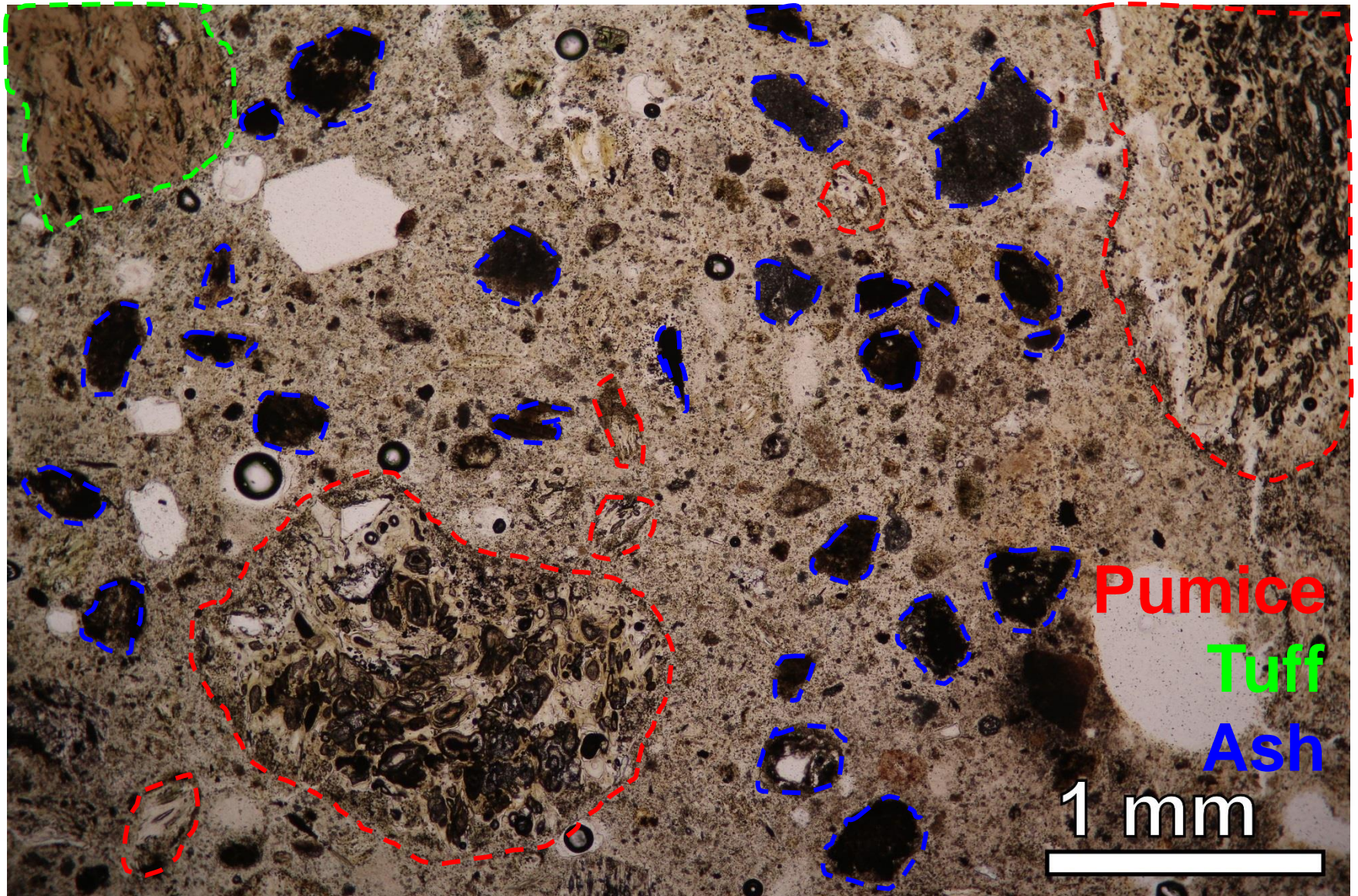
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e dei Leganti Idraulici

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Materials Properties, Use and Conservation:  
Construction Materials and Binders



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Pumice

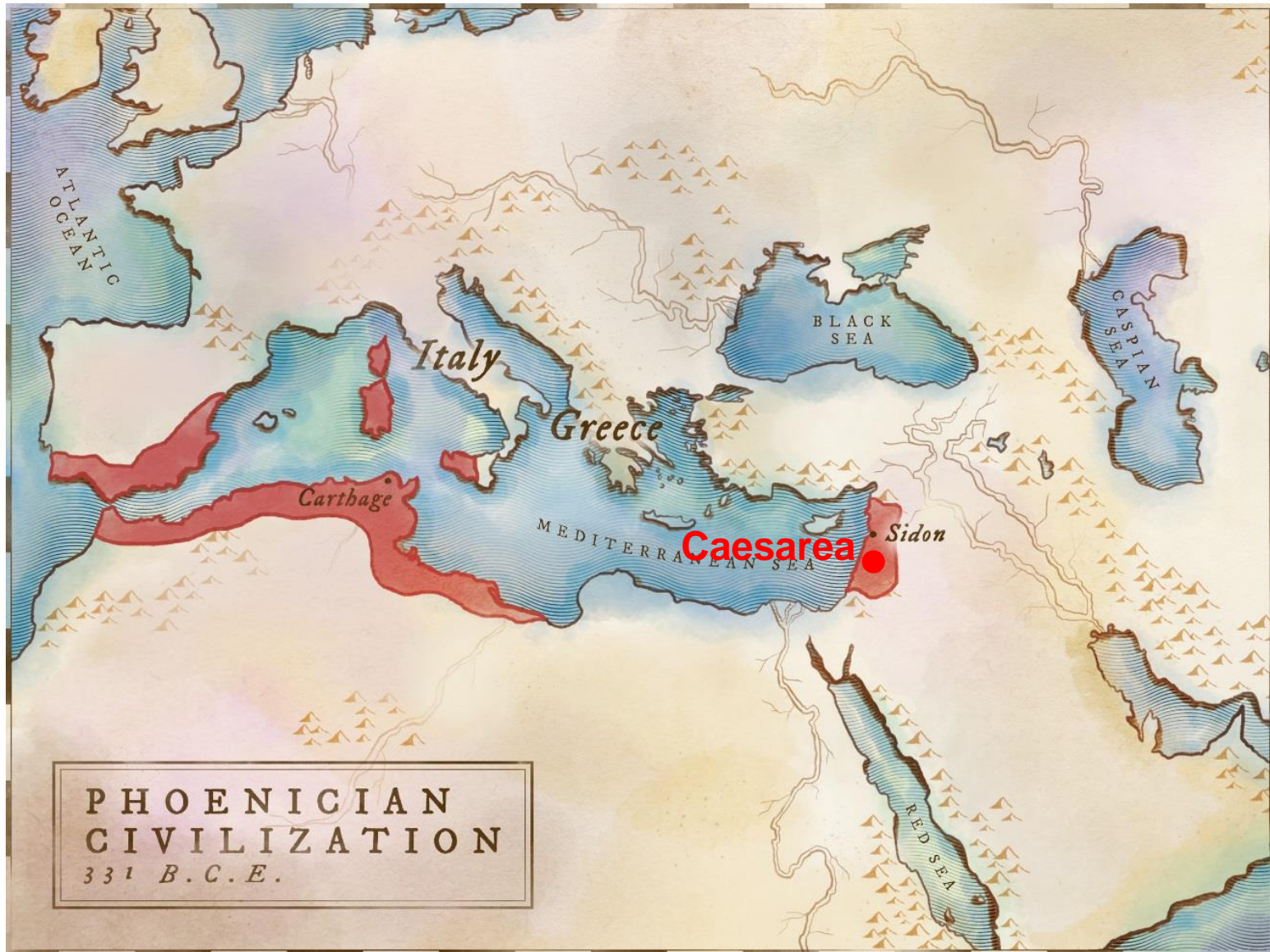
Tuff

Ash

1 mm



# Caesarea Maritima, Israel



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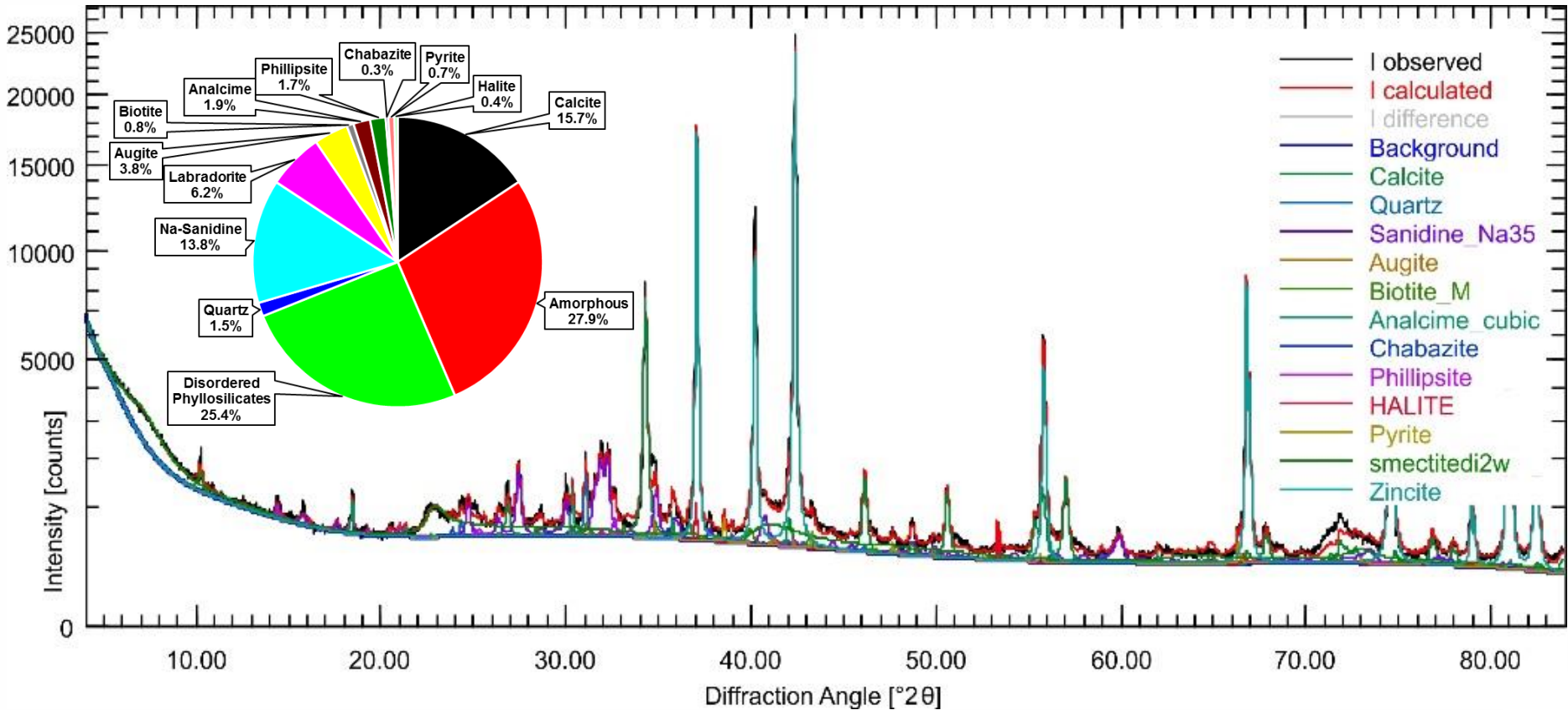
DIAGNOSTICA - RILIEVO - TECNOLOGIE

**Materials Properties, Use and Conservation:  
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# Caesarea Maritima, Israel

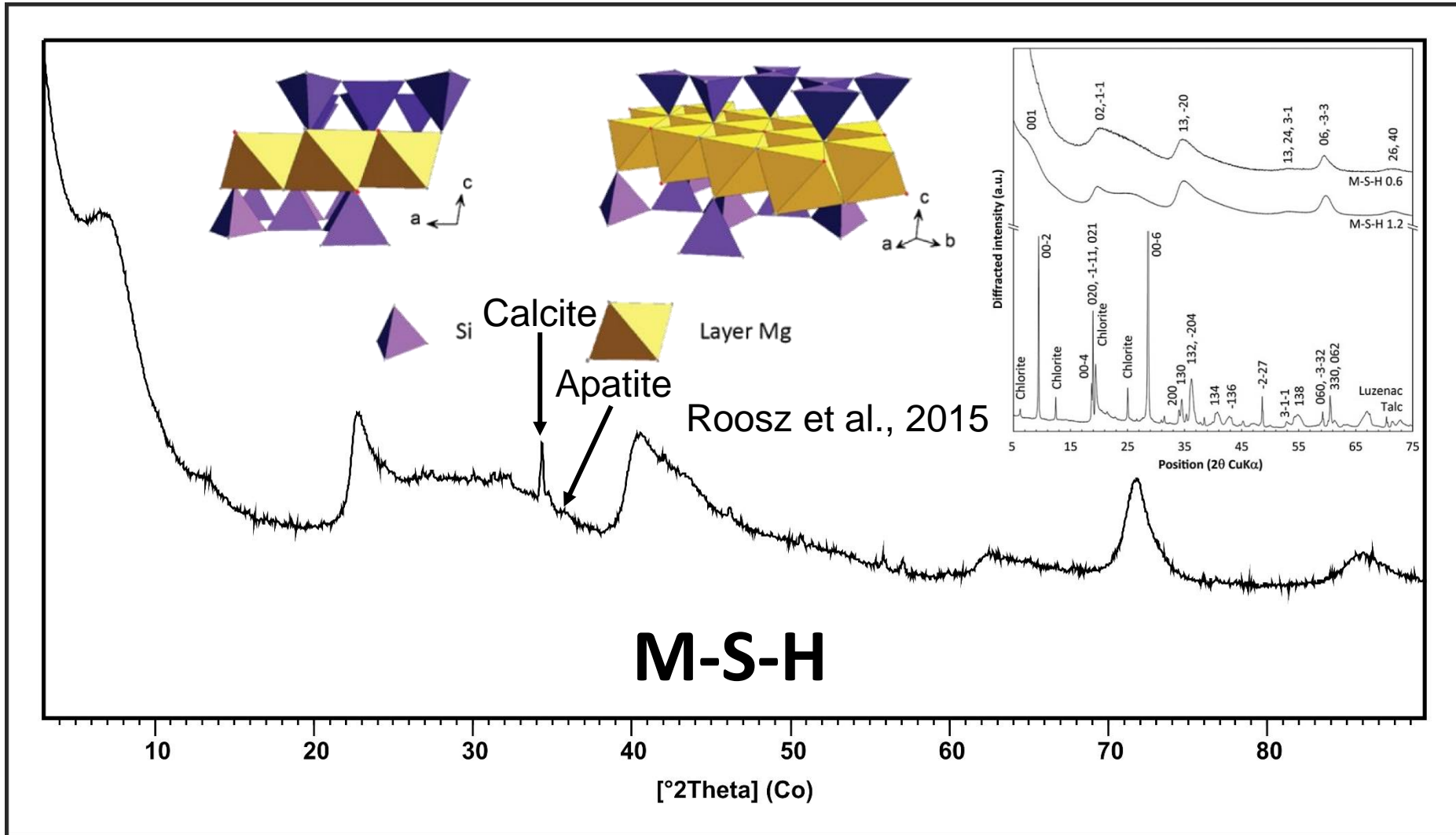
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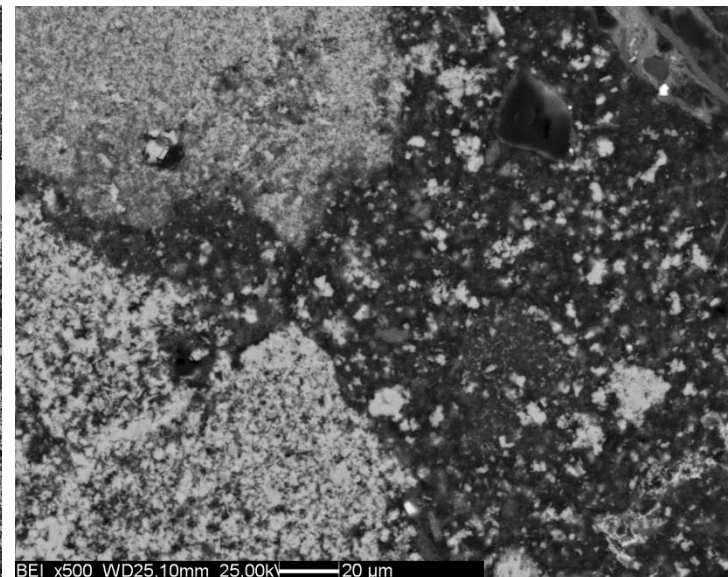
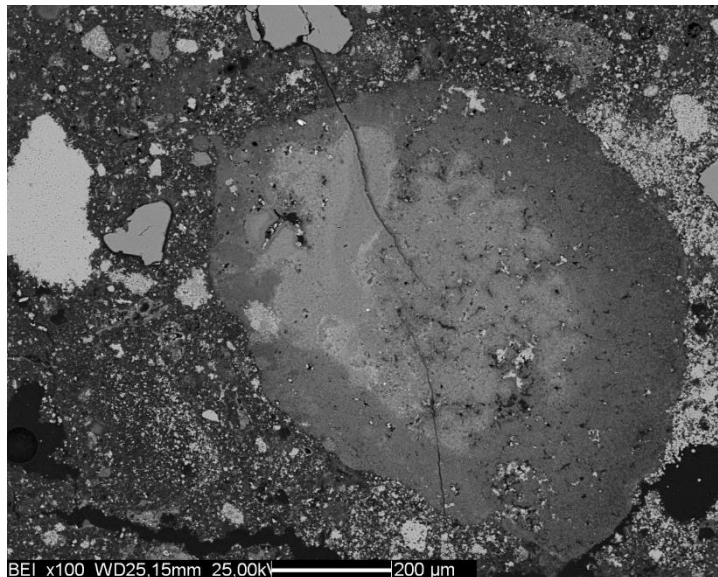
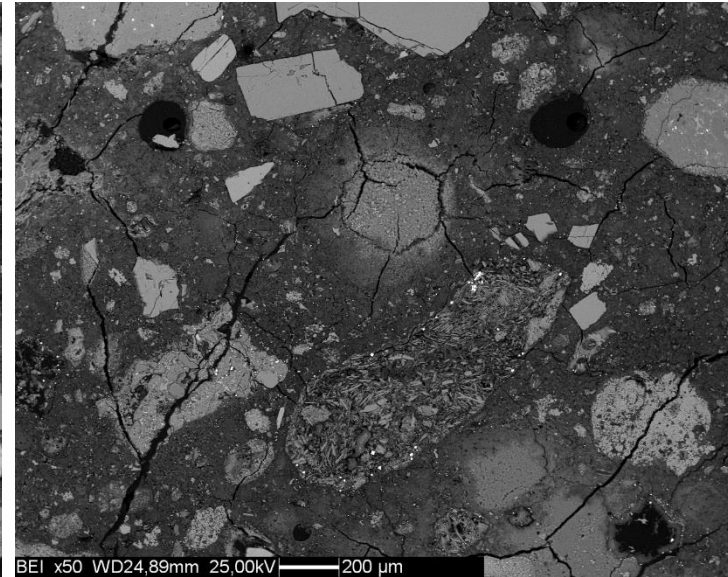
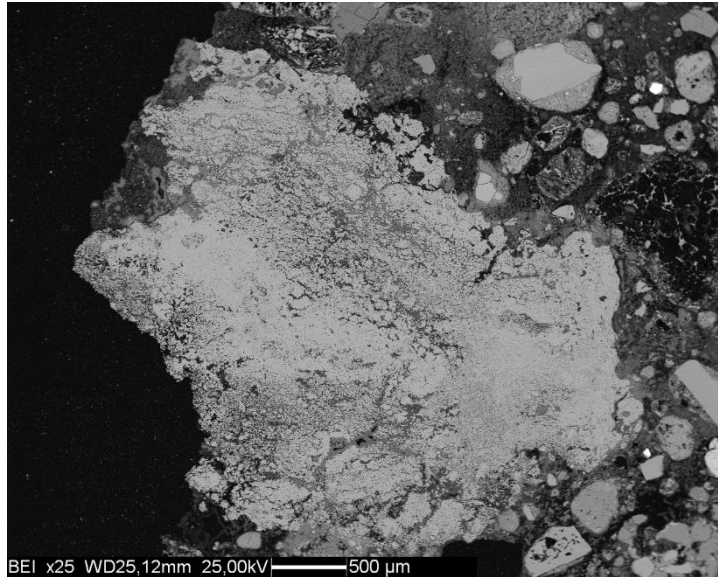
# Caesarea Maritima, Israel

## XRPD, BINDER FRACTION



**M-S-H**

# Caesarea Maritima, Israel





# Caesarea Maritima, Israel

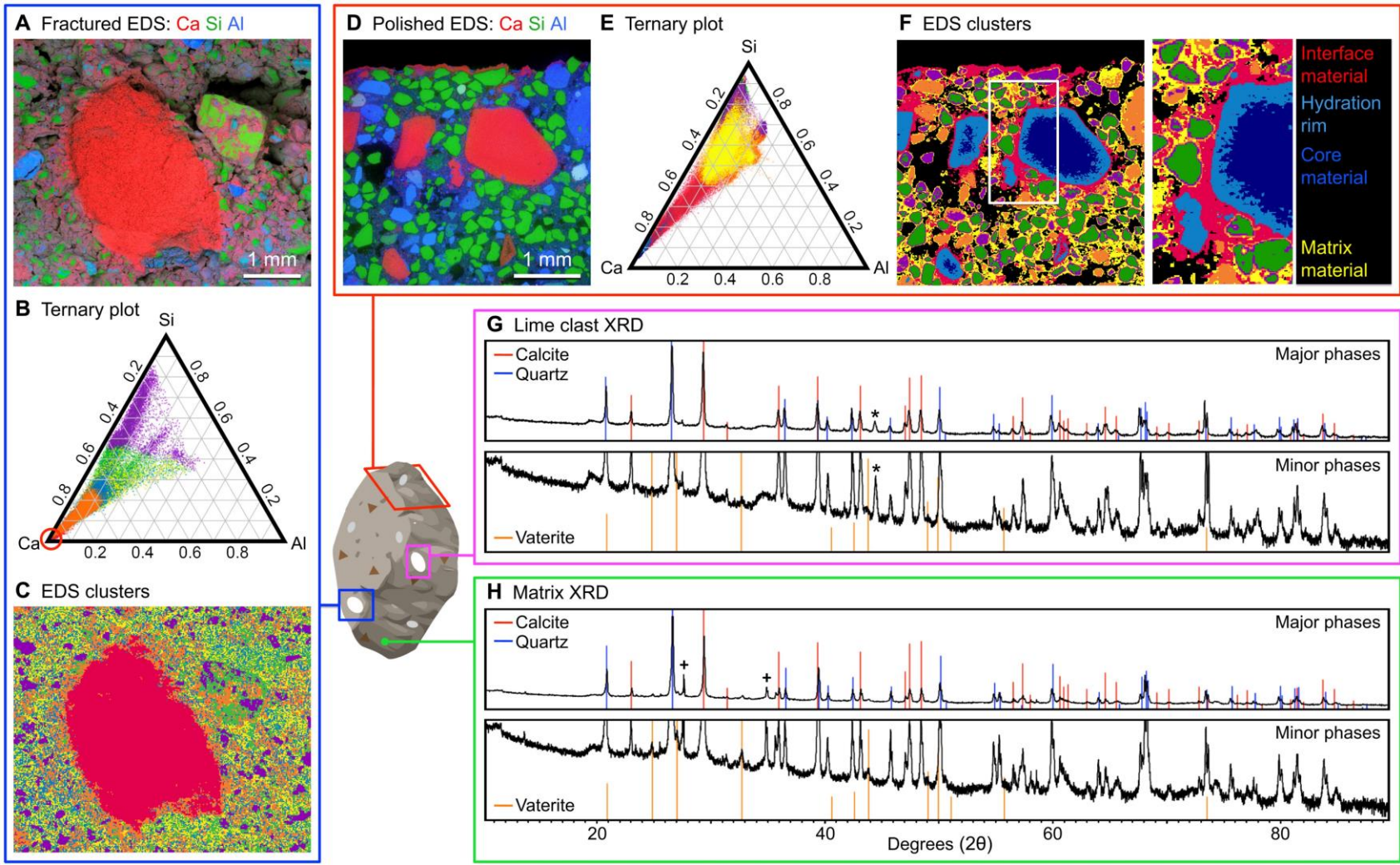
## HOT LIME MIXING





# Caesarea Maritima, Israel

## HOT LIME MIXING



Seymour et al., 2023

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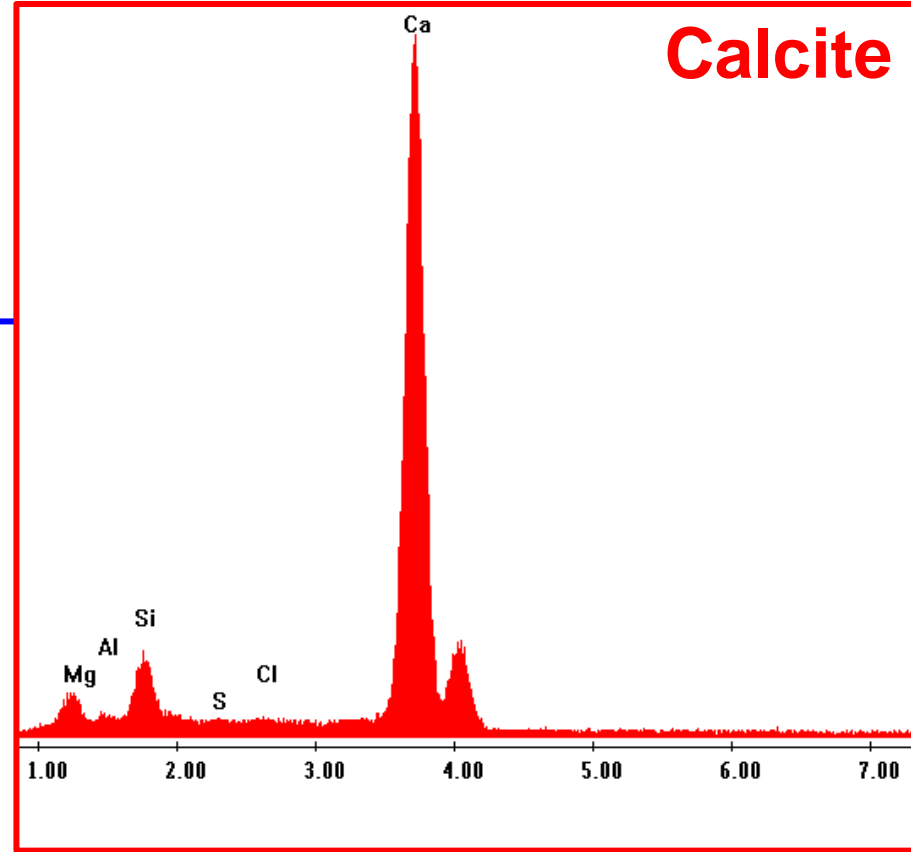
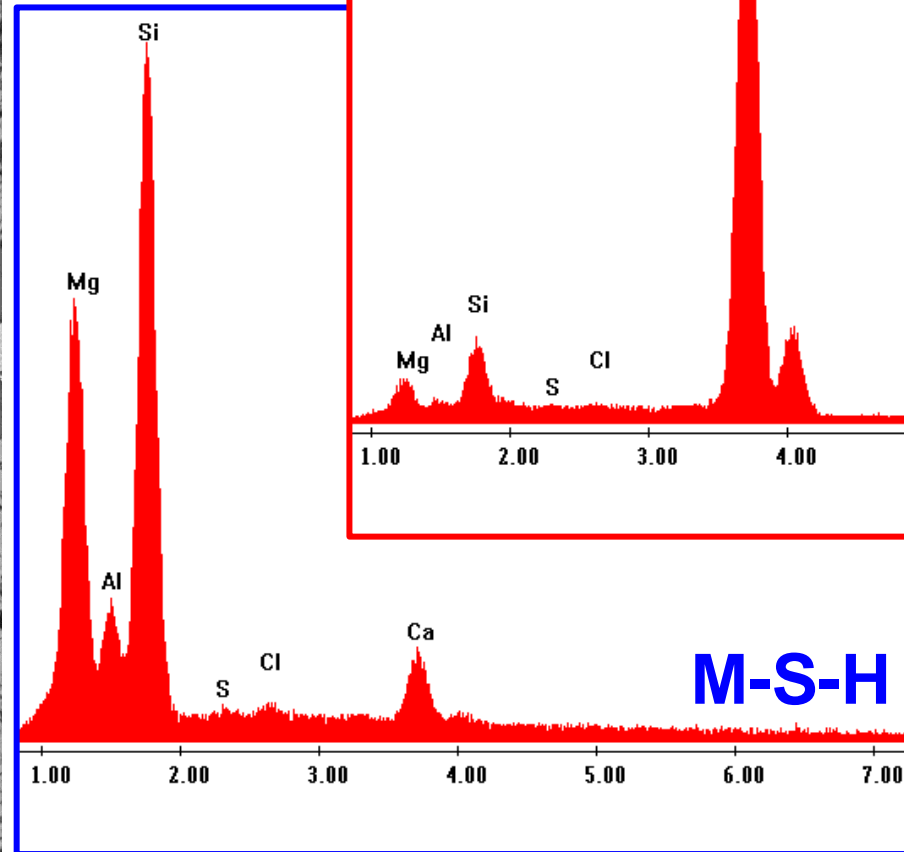
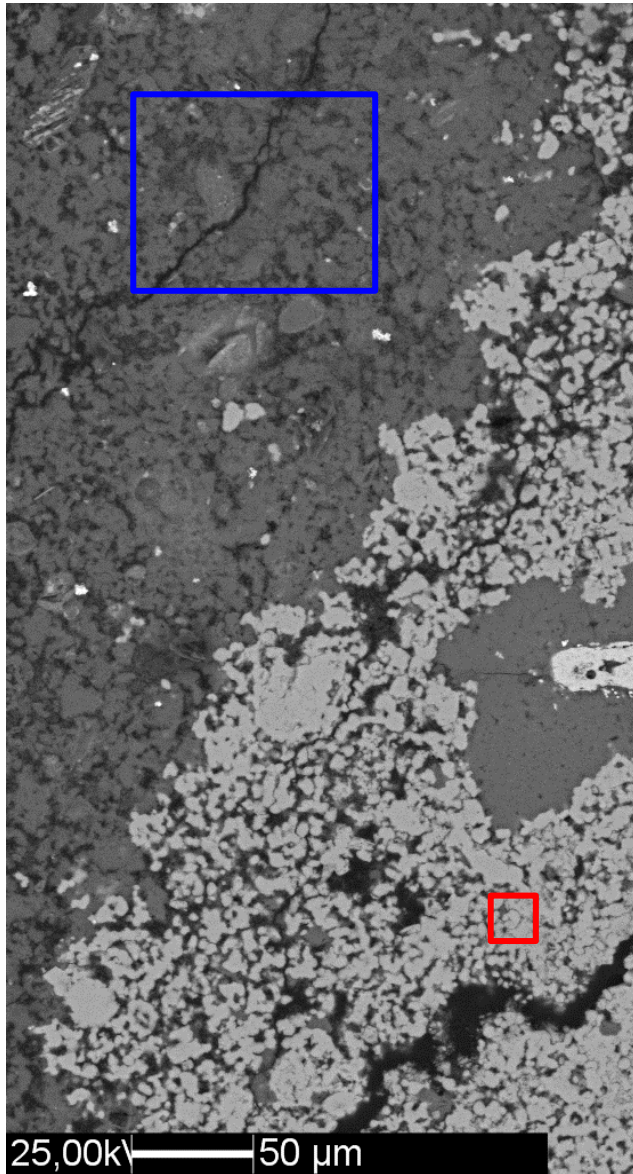
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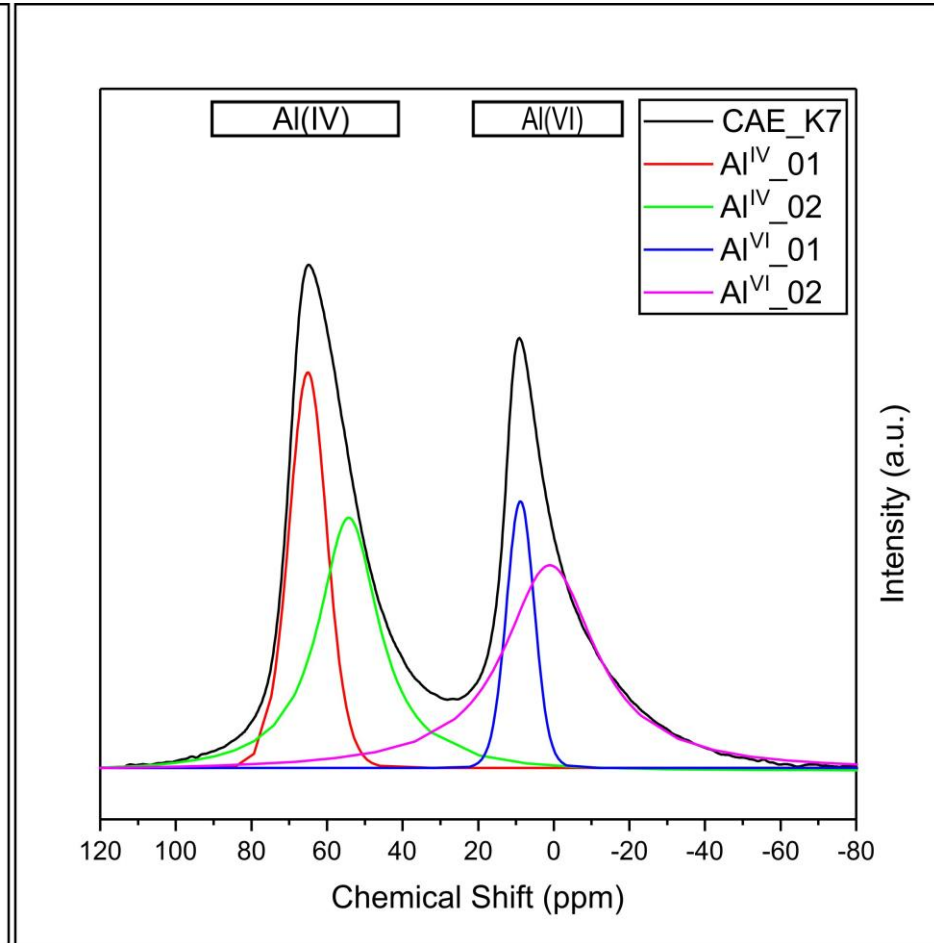
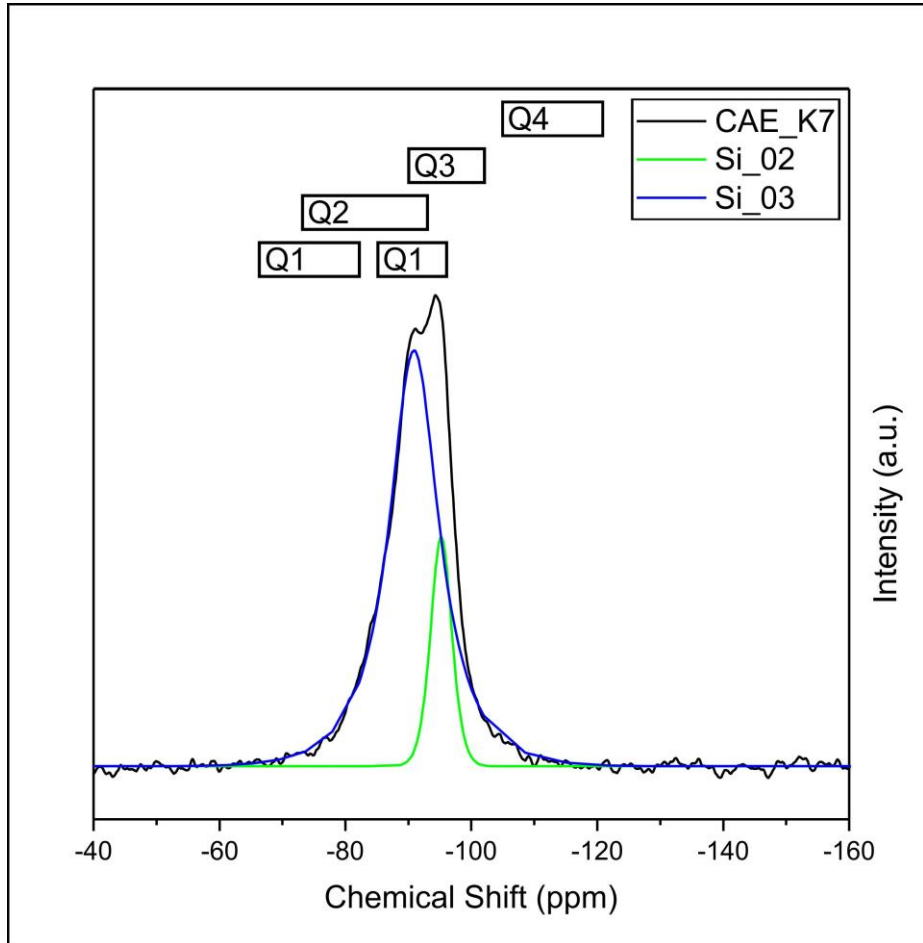


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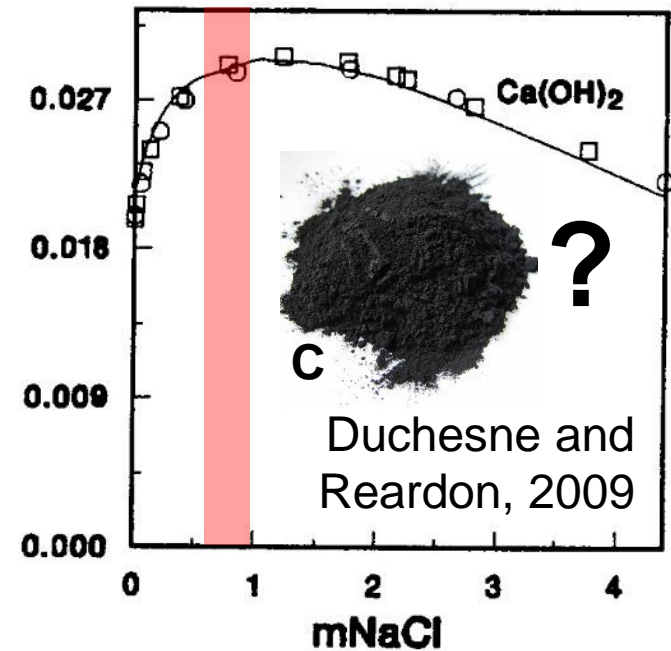
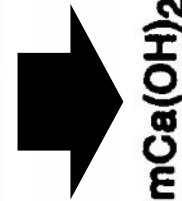
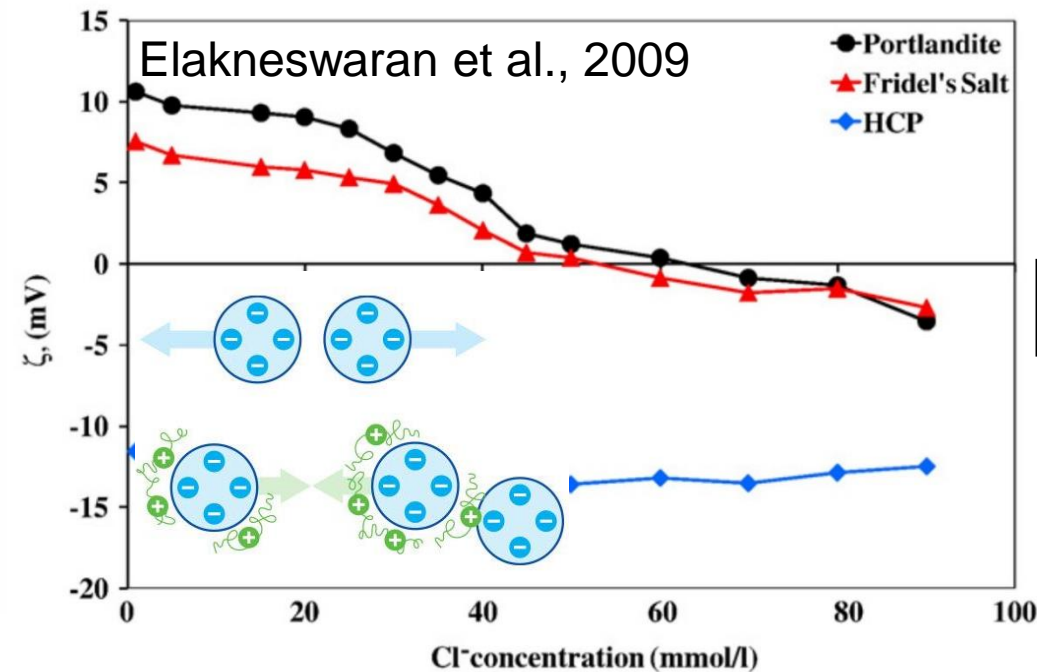
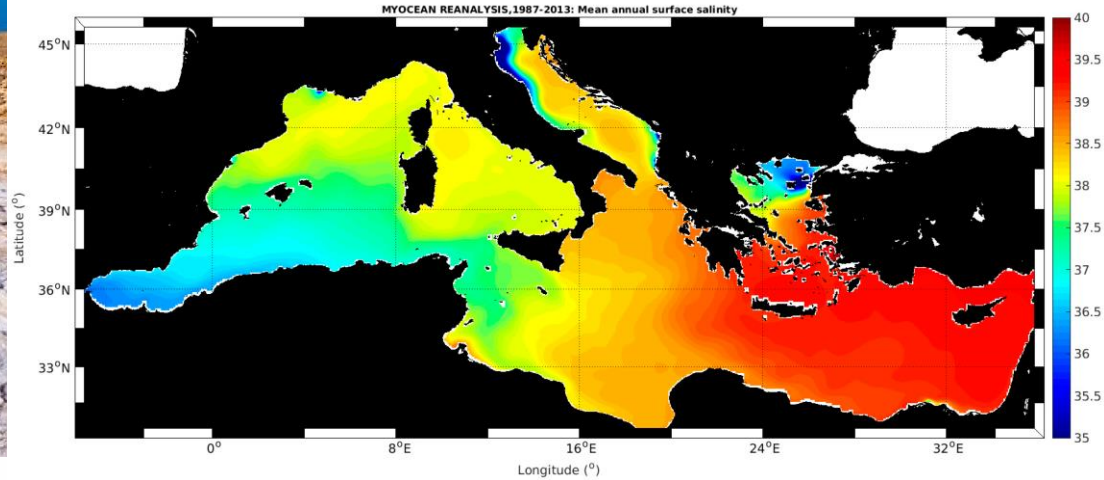
# Caesarea Maritima, Israel

## SS-NMR, BINDER FRACTION

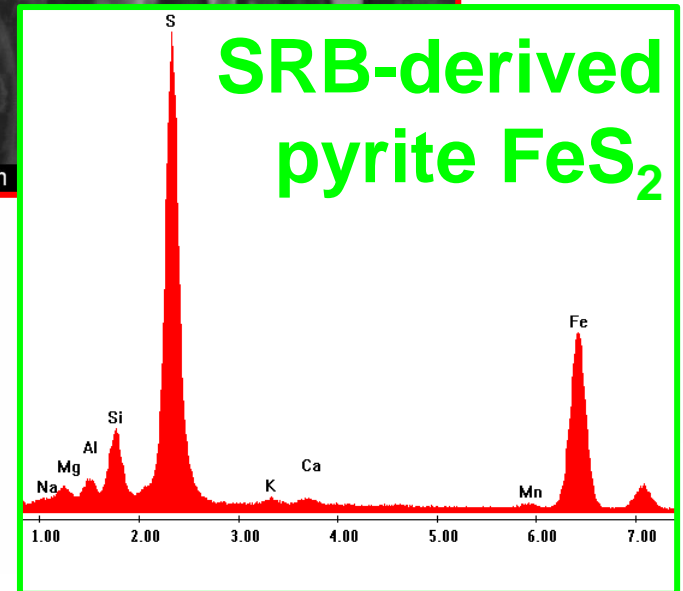
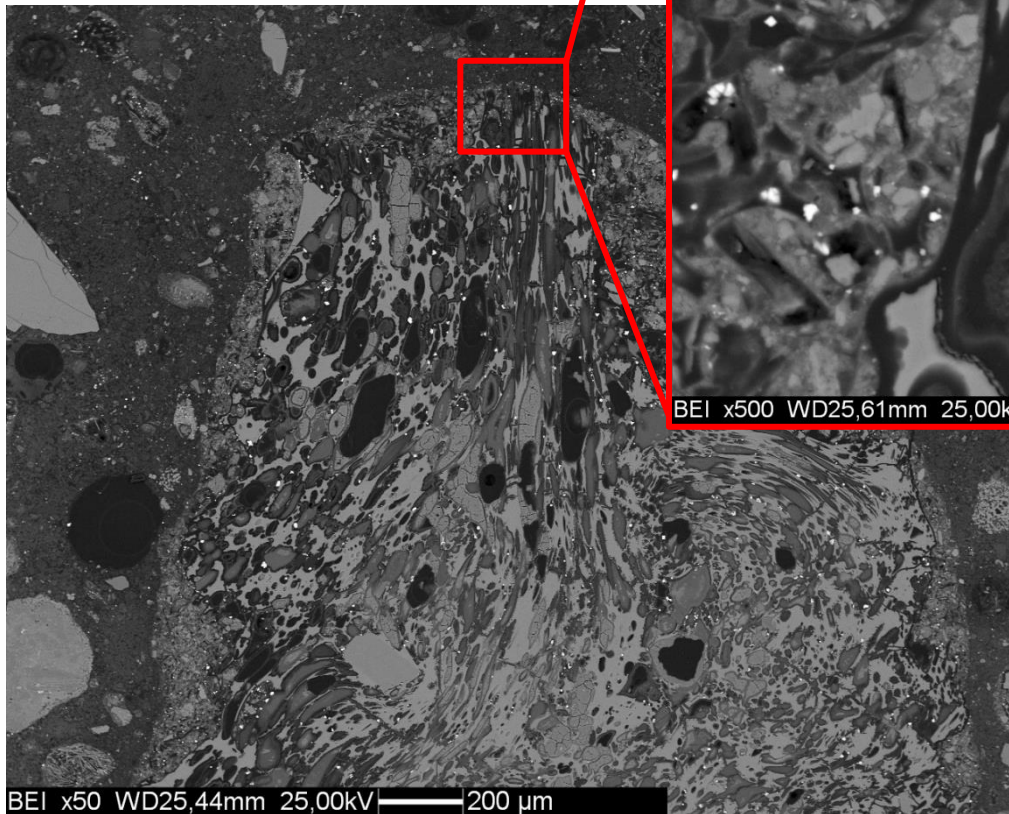




# Caesarea Maritima, Israel

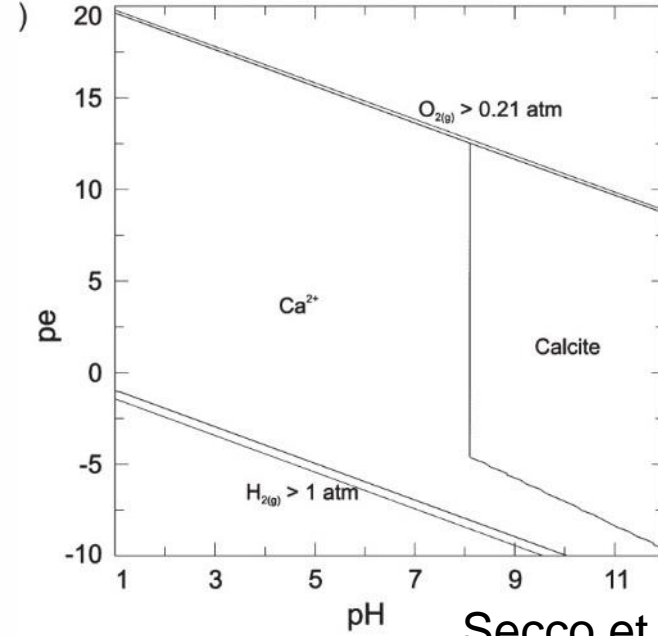
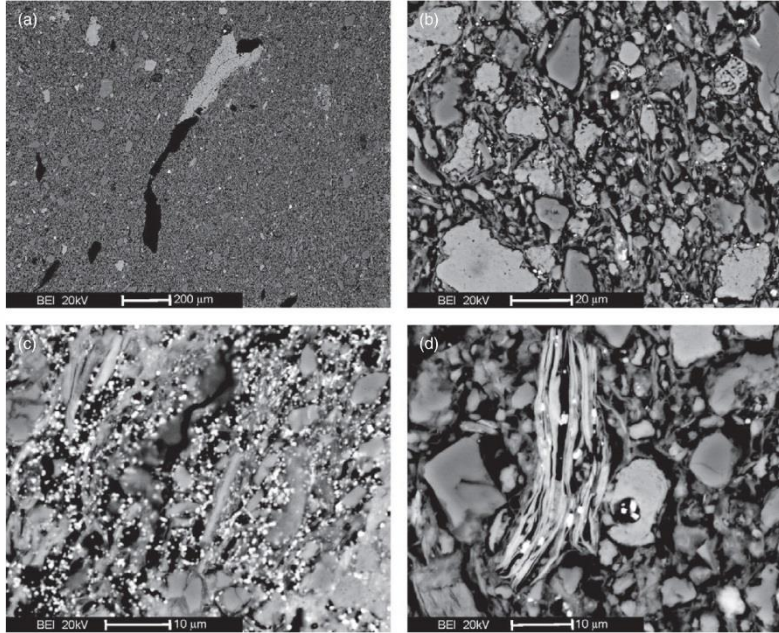


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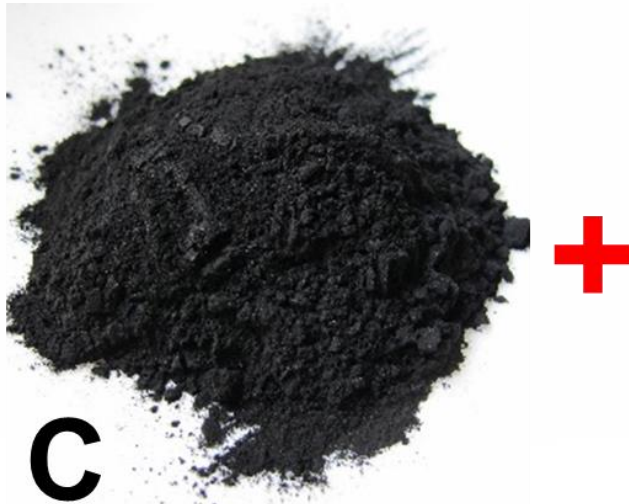




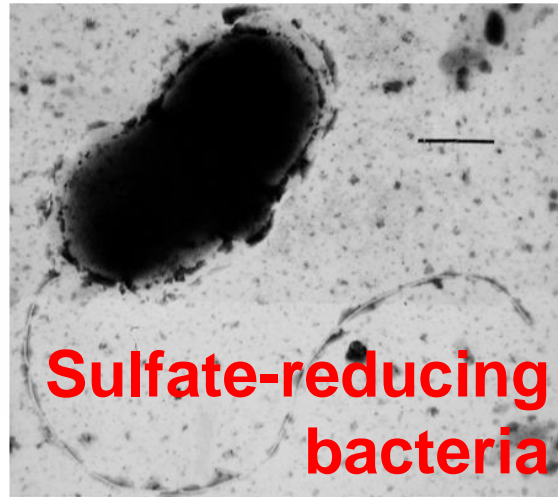
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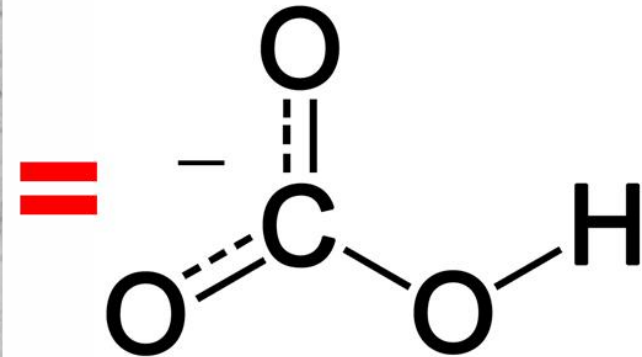
Secco et al., 2011



C

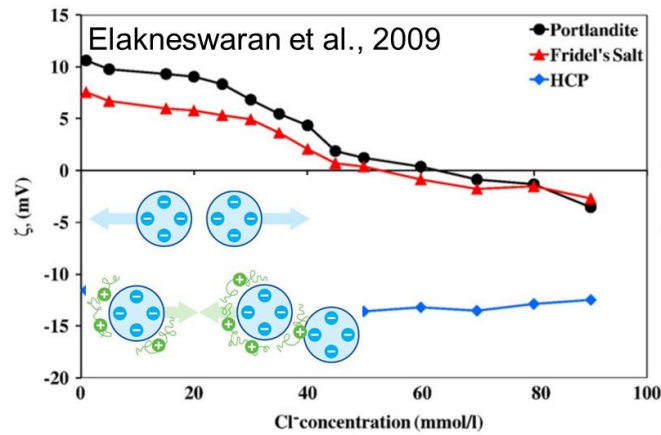
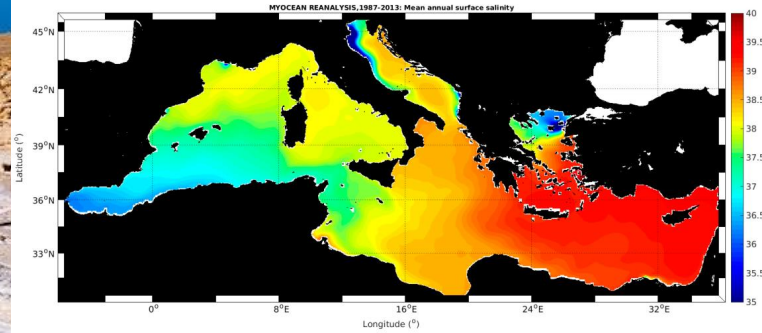


Sulfate-reducing  
bacteria

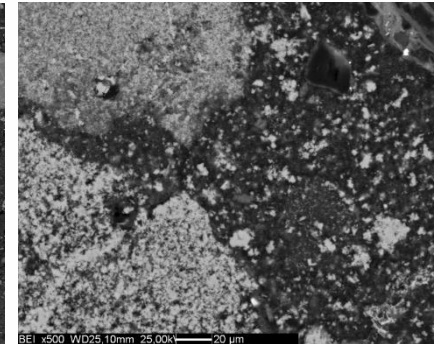
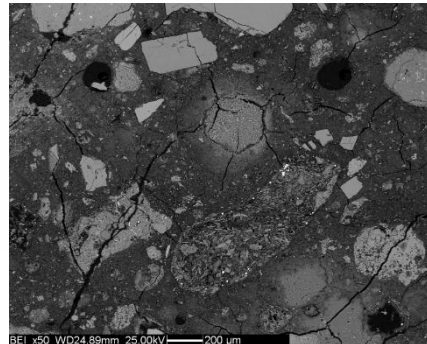
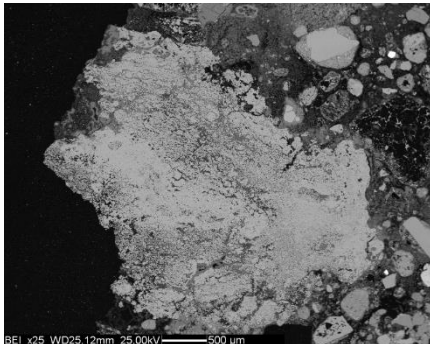
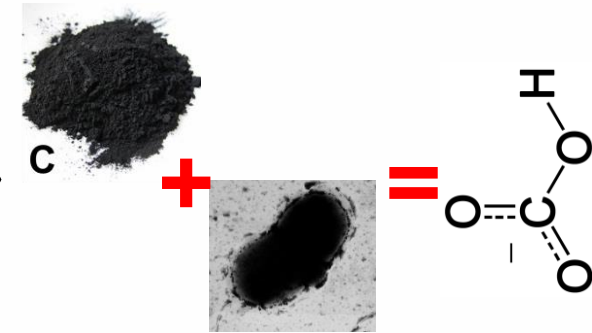
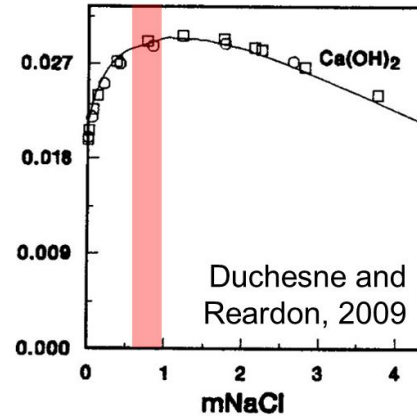


Materials Properties, Use and Conservation:  
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mCa(OH)<sub>2</sub>



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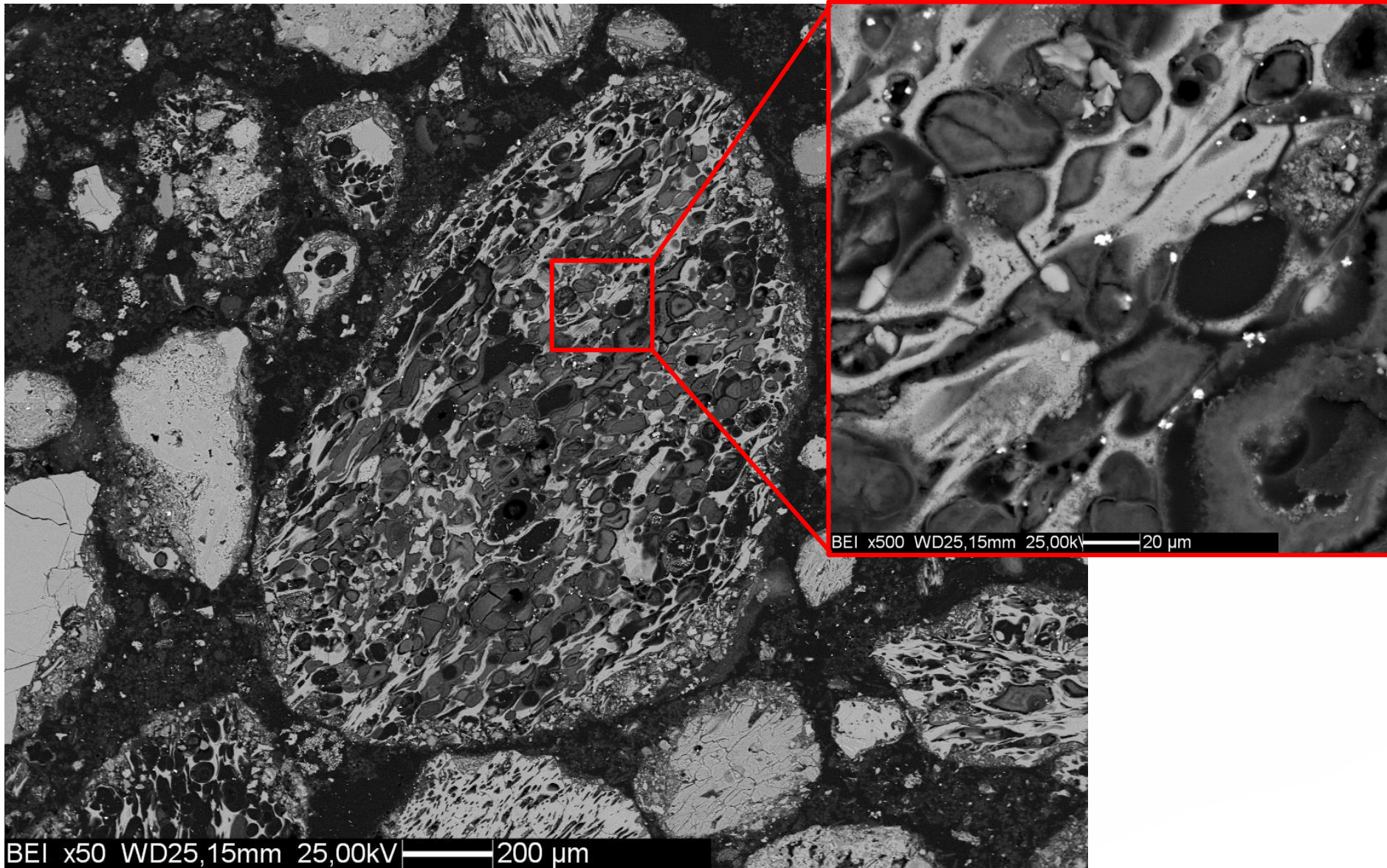
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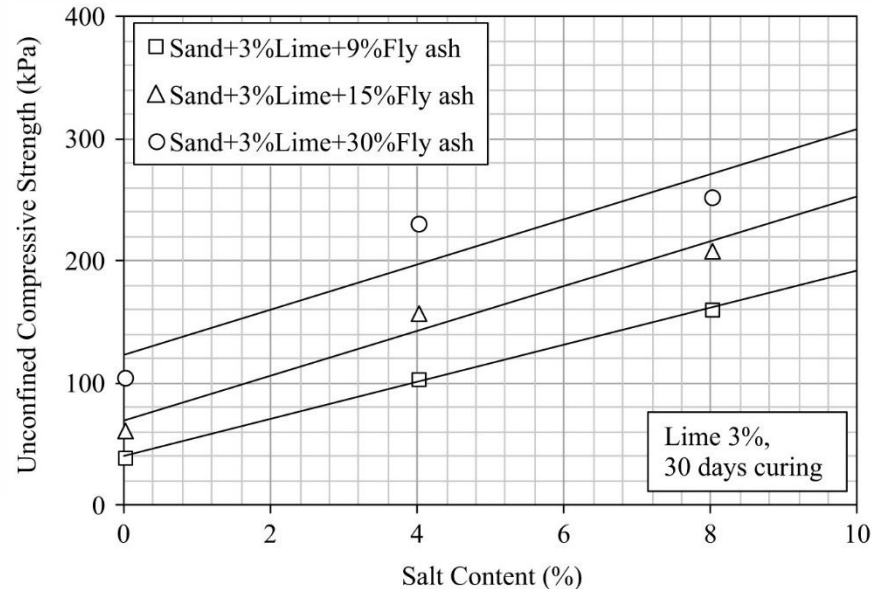
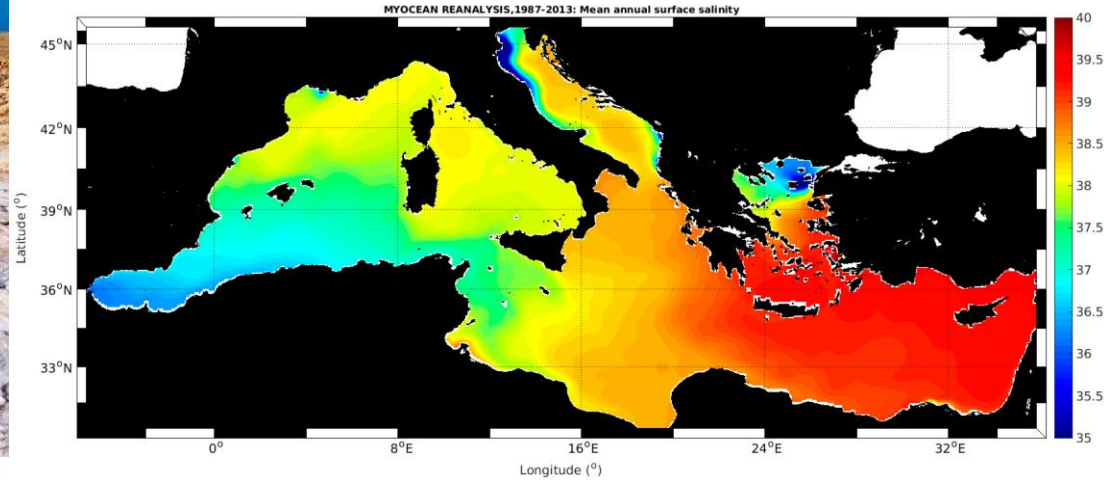
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# Caesarea Maritima, Israel



Karim et al., 2017



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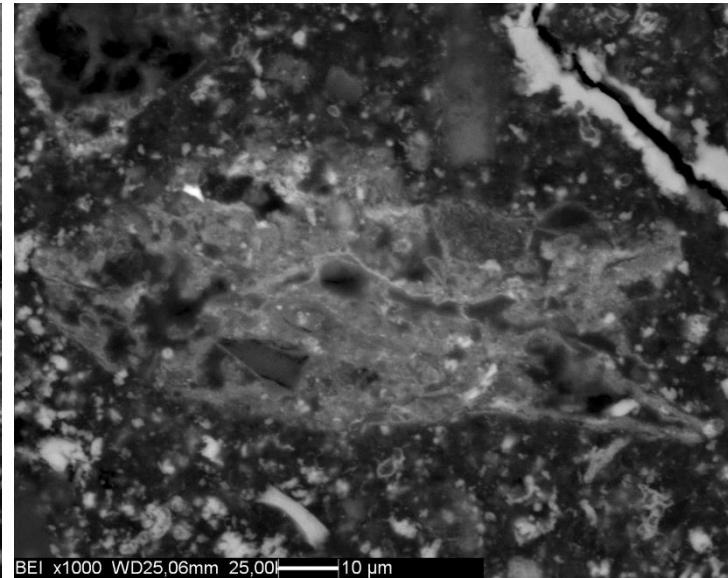
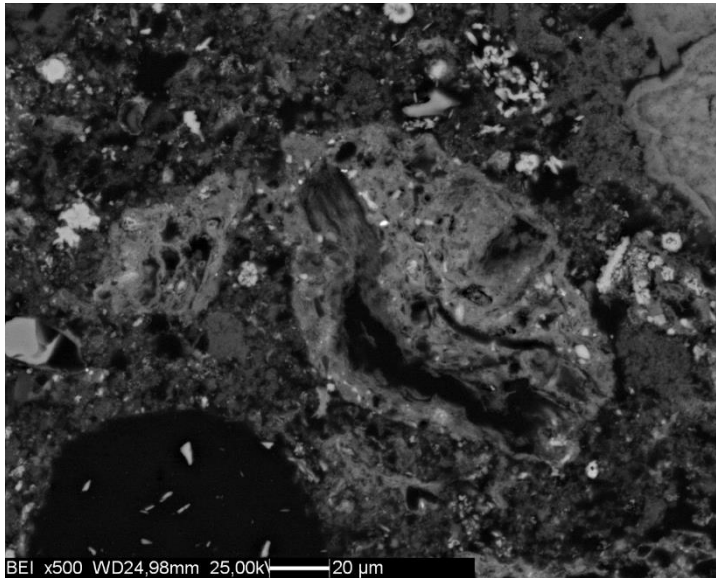
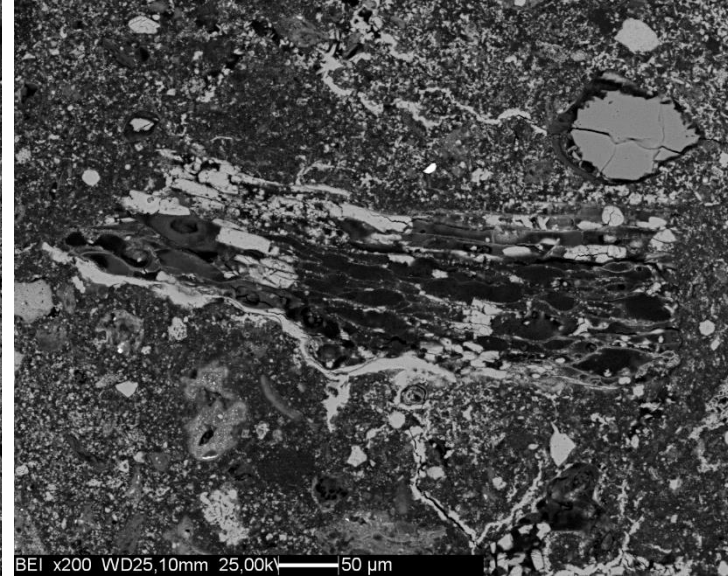
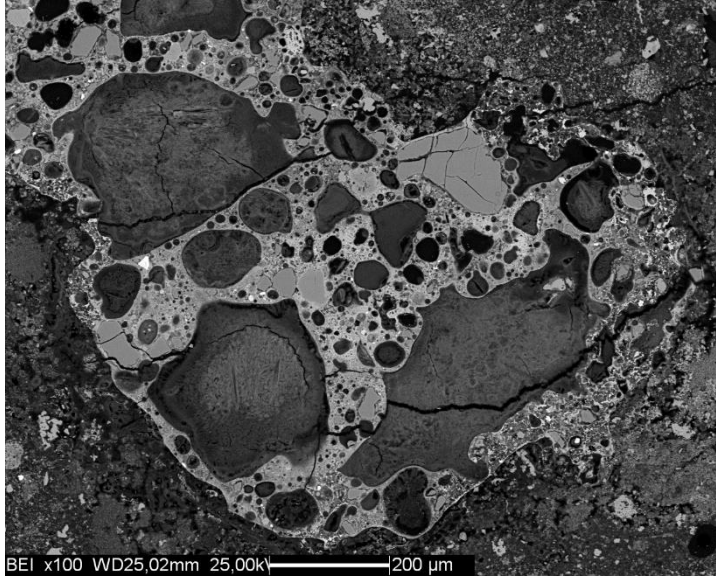
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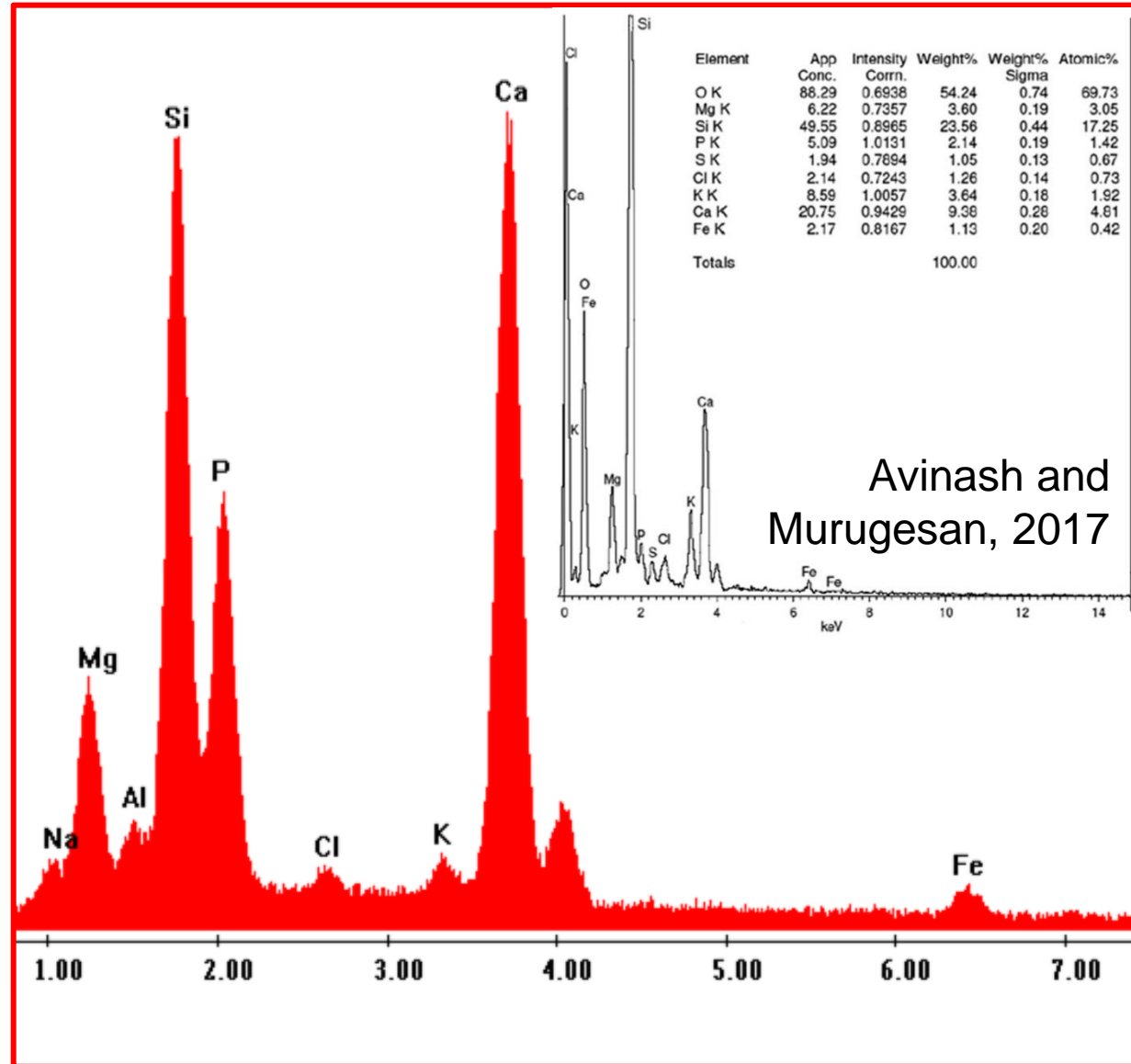
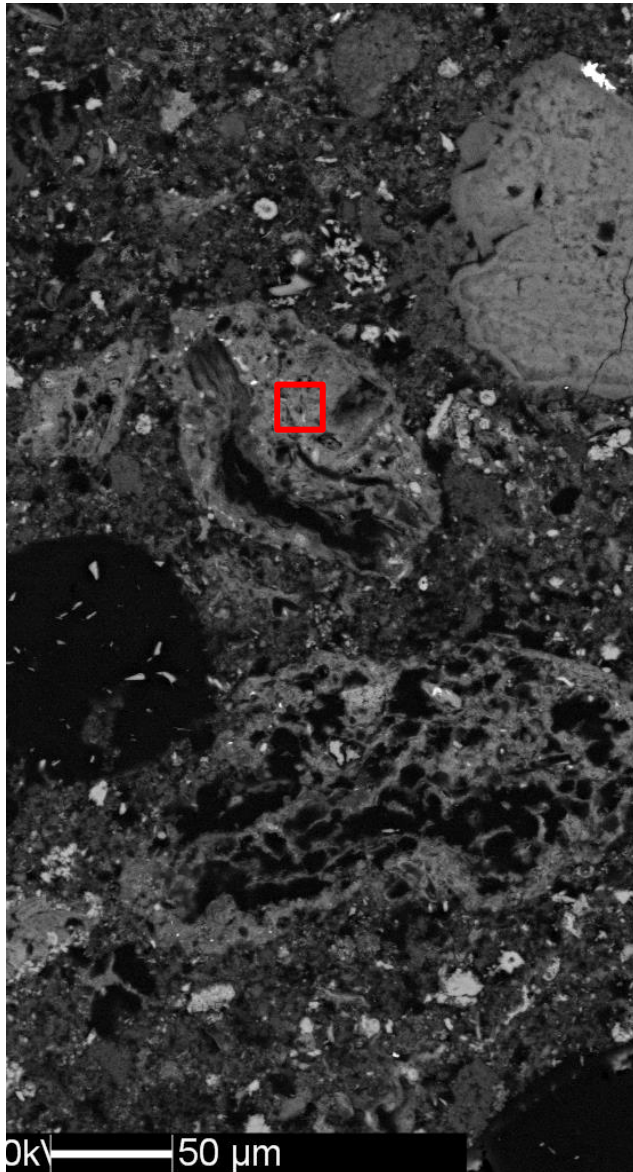
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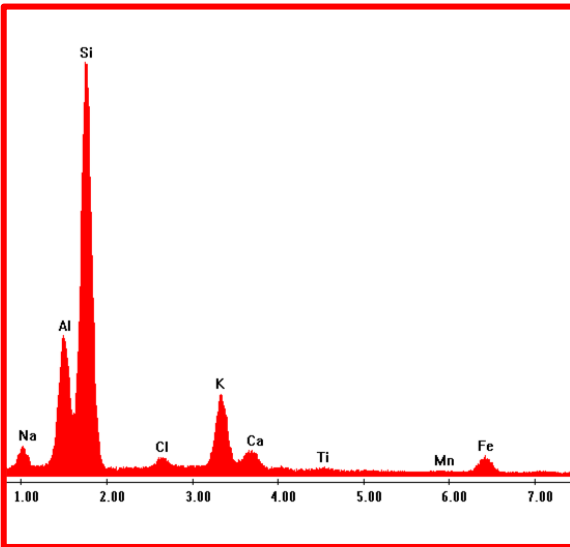
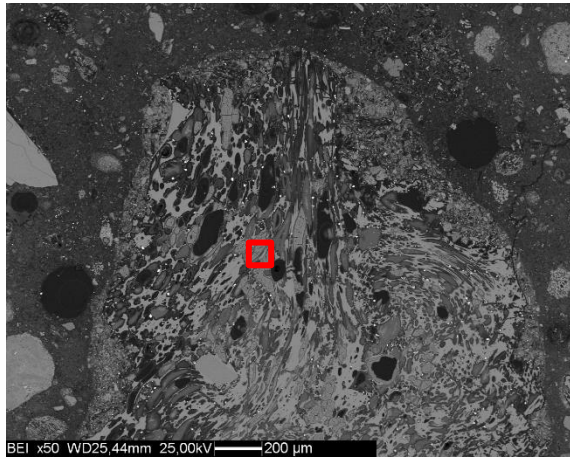
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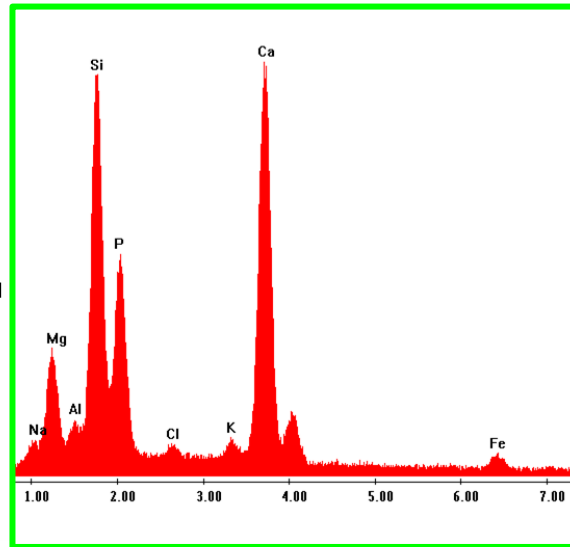
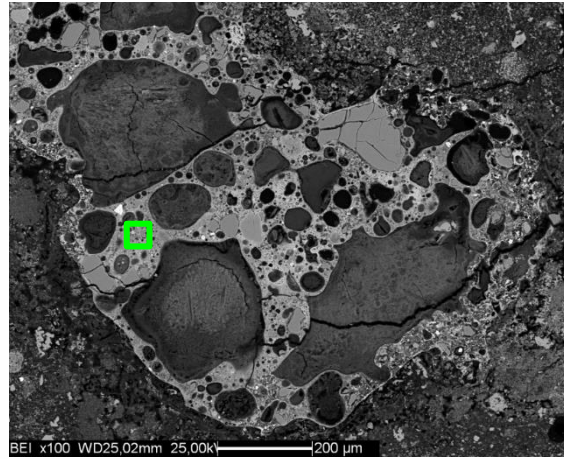


# Caesarea Maritima, Israel

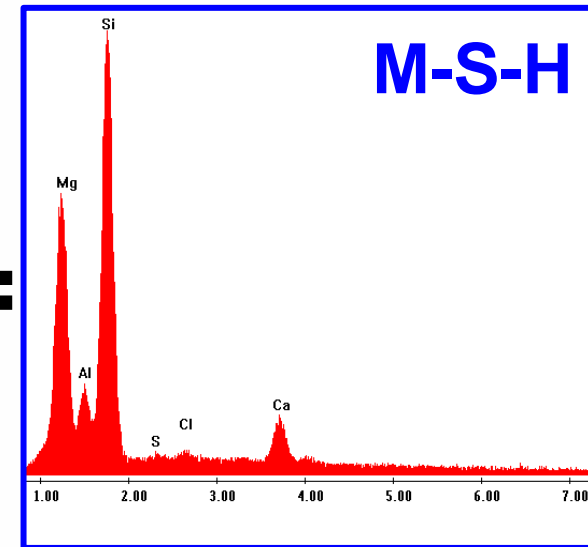
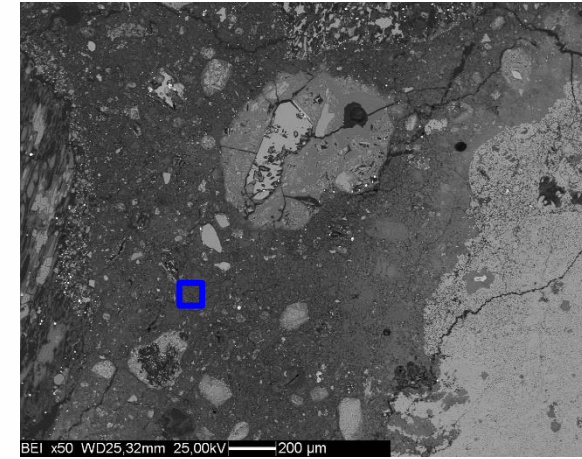
## Pumice



## Ash



## Binder



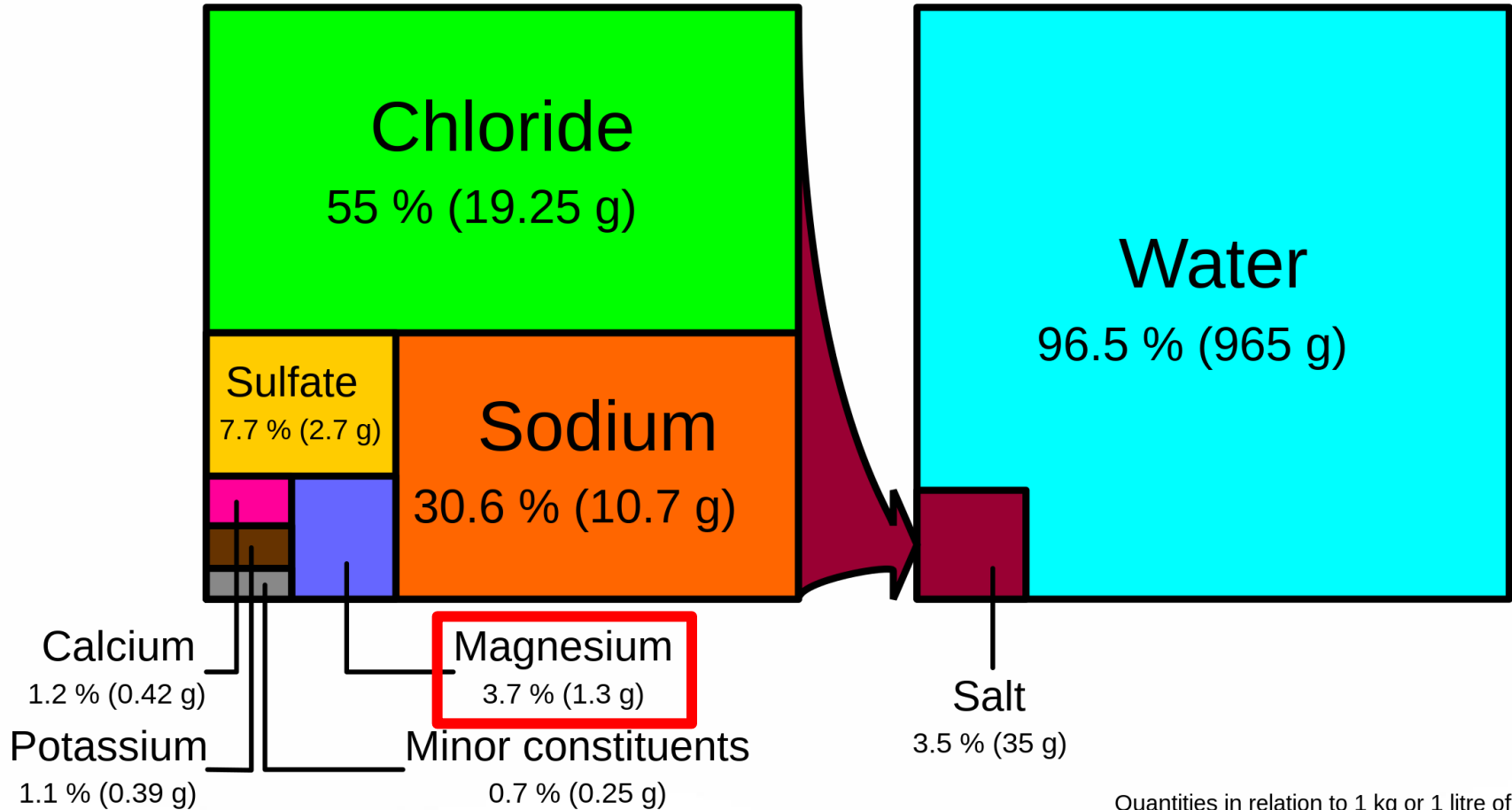
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## Sea salts

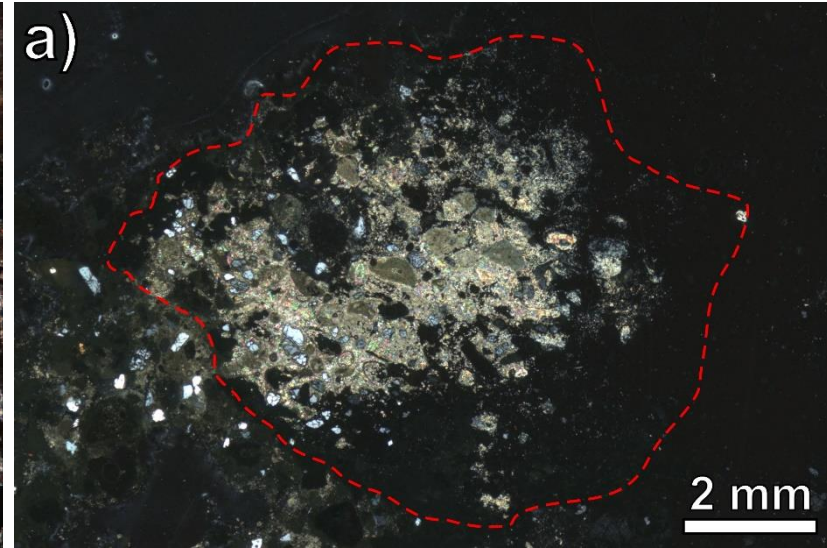
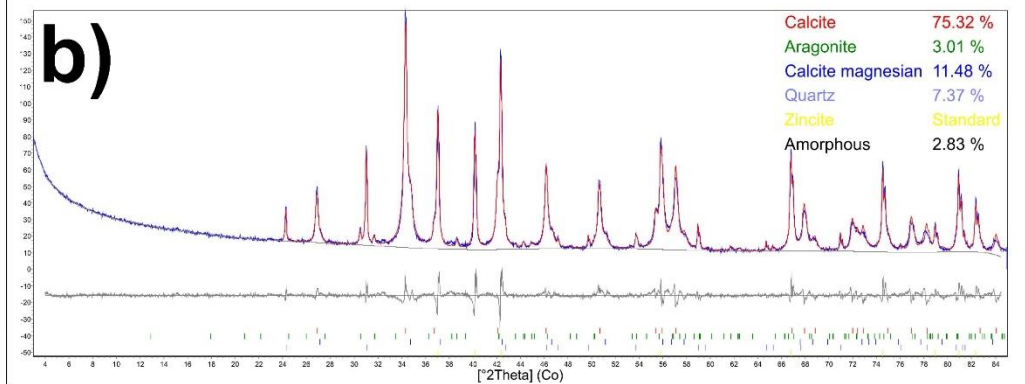
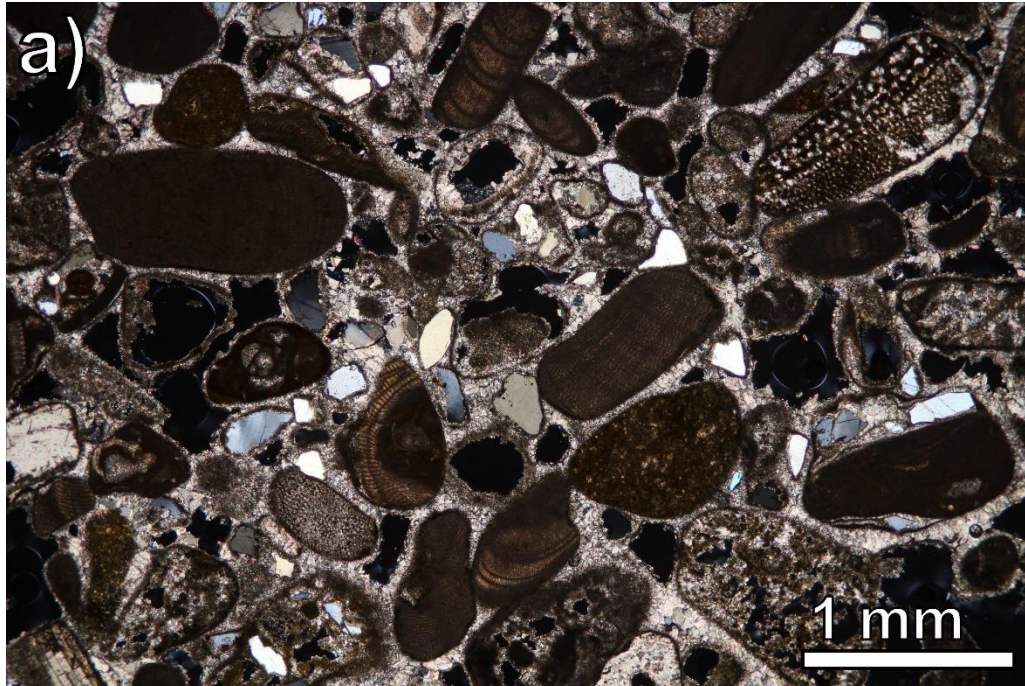
## Sea water



Quantities in relation to 1 kg or 1 litre of sea water.



# Caesarea Maritima, Israel



Contents lists available at ScienceDirect  
**Cement and Concrete Research**  
 journal homepage: <http://www.elsevier.com/locate/cemcon>

**A** Carbonate halos  
 Dolomitic rims  
 200µm

The so-called alkali-carbonate reaction (ACR) – Its mineralogical and geochemical details, with special reference to ASR  
 Tetsuya Katayama  
 Kawasaki Geological Engineering Co. Ltd., 2-11-13 Minami, Minato-ku, Tokyo, 108-8338, Japan

$$\text{CaMg}(\text{CO}_3)_2 + 2\text{MOH} \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCO}_3 + \text{M}_2\text{CO}_3 \quad (1.1)$$

(dolomite) (brucite) (calcite) (thermonatrite)

$$\text{M}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{MOH} + \text{CaCO}_3 \quad (1.2)$$

where:  
 M = K, Na or Li

**B** Dol, Carbonate halo, Calc, Brucite, Dolomitic rim, Brucite  
 10µm

**F** ASR gel, Calc, Mg(OH)<sub>2</sub>, ASR gel  
 10µm

**C** Carbonate halos  
 Dolomitic rims  
 200µm

**E** Dedolomitization, ASR gel, ASR gel  
 100µm



# Zairo Theatre, Padova





# Zairo Theatre, Padova



# Zairo Theatre, Padova



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# Zairo Theatre, Padova



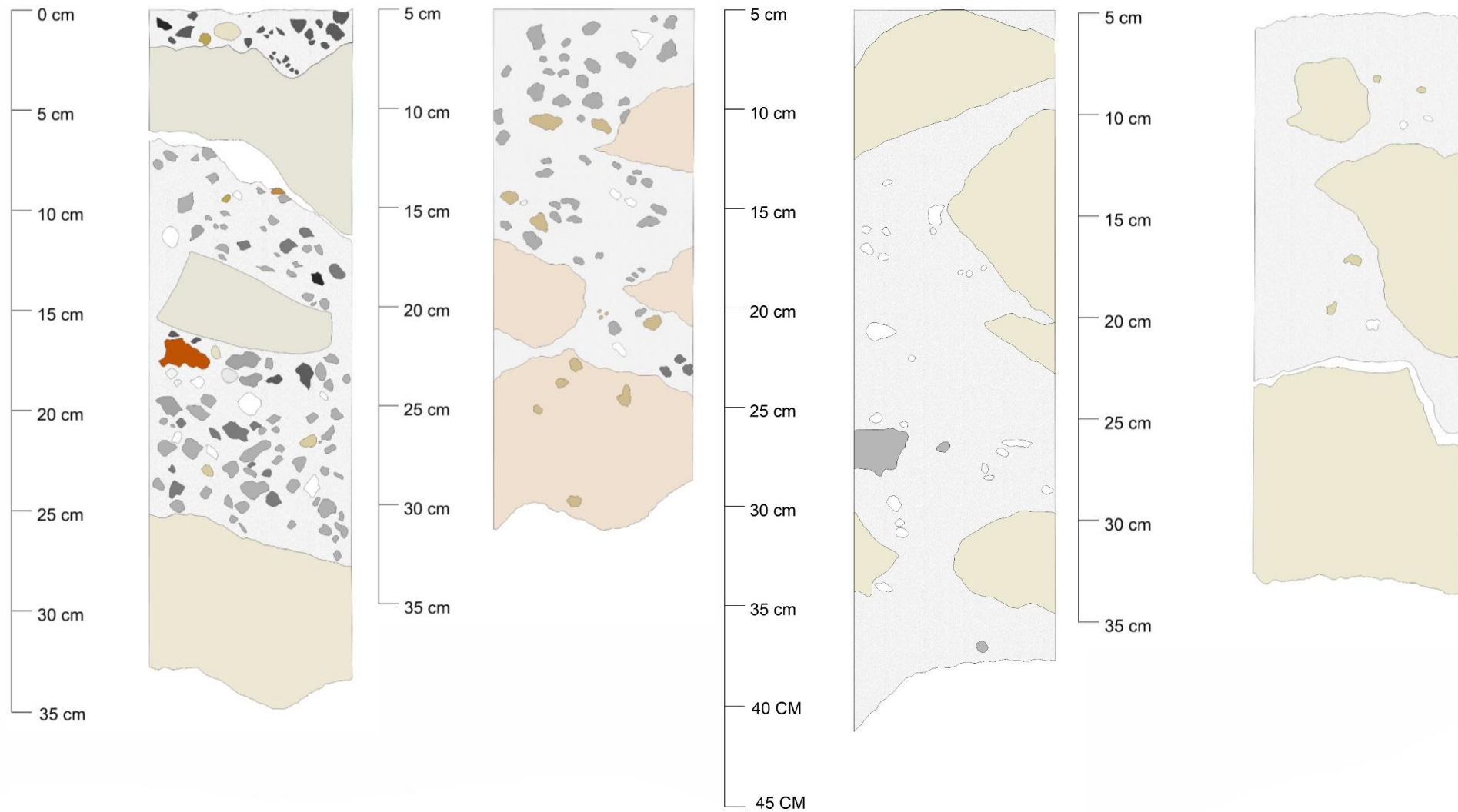


# Zairo Theatre, Padova

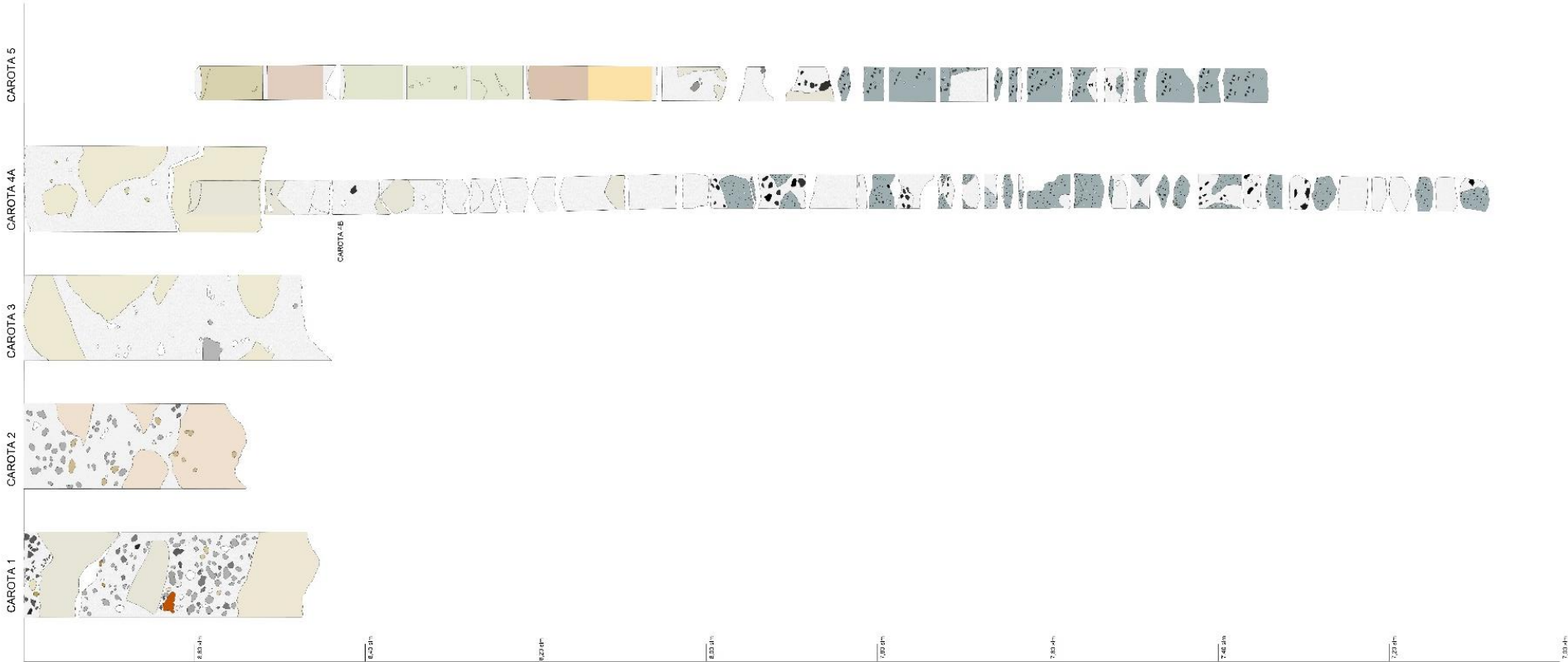




# Zairo Theatre, Padova

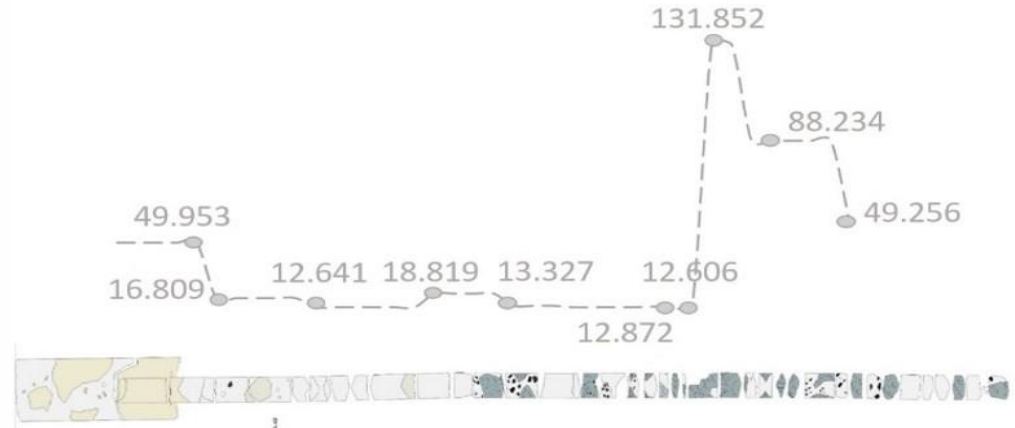


# Zairo Theatre, Padova



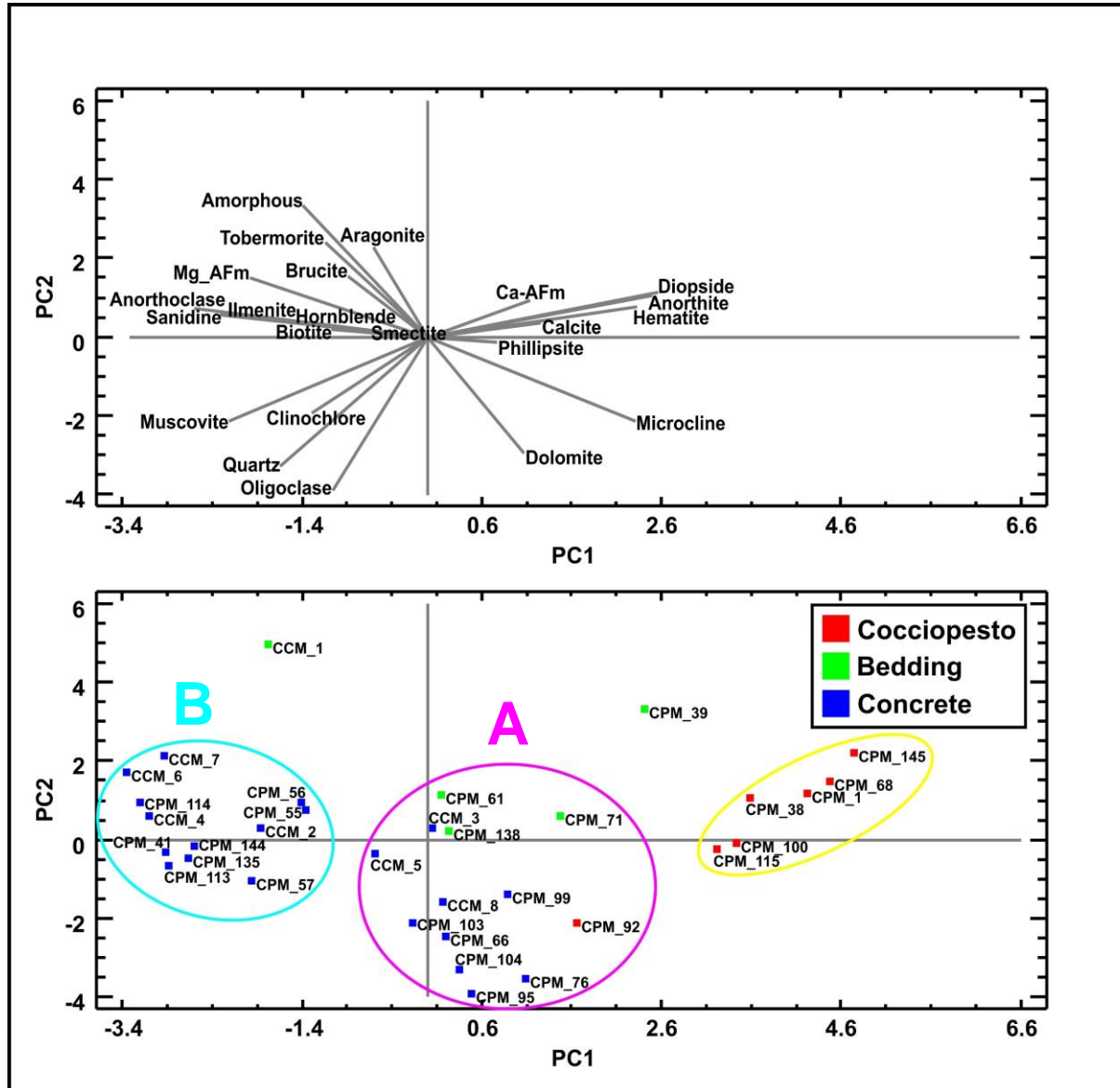


# Zairo Theatre, Padova



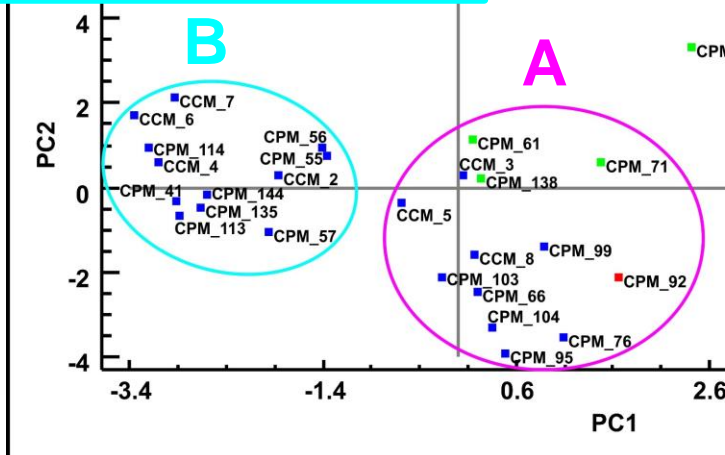
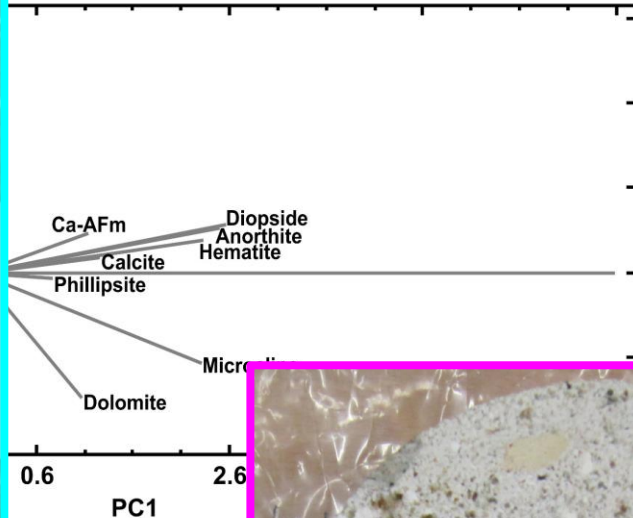
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1.V	90	50	102.443	16.11

# Zairo Theatre, Padova



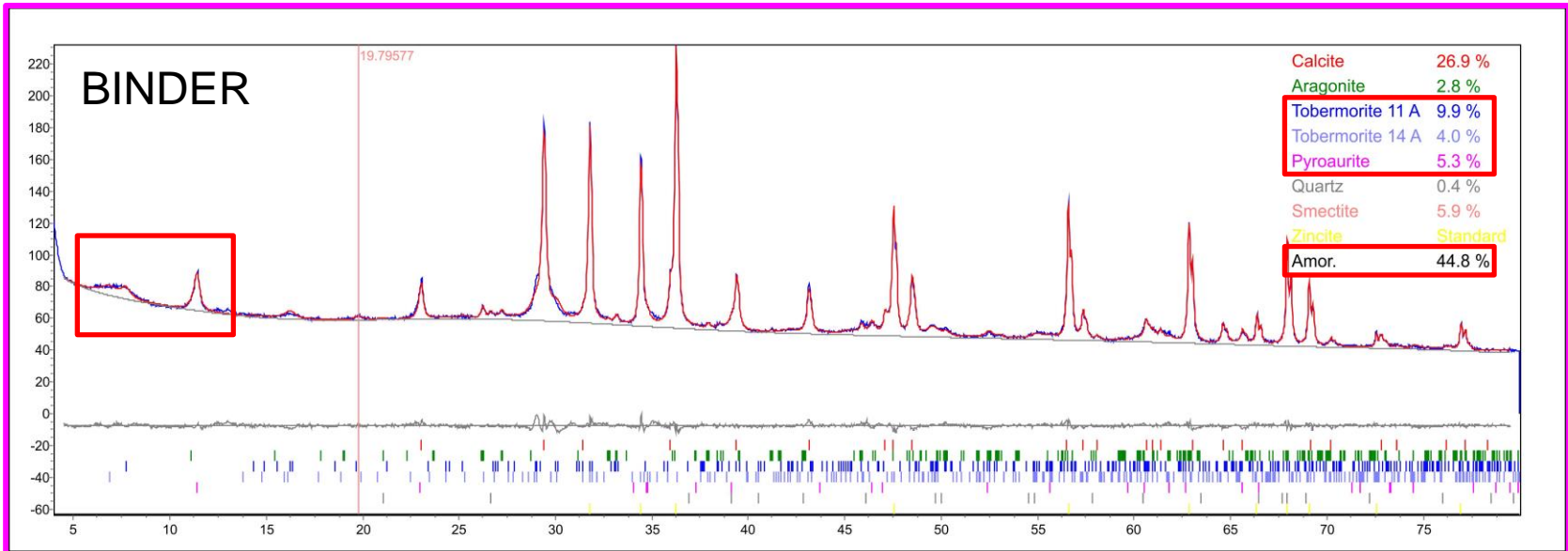
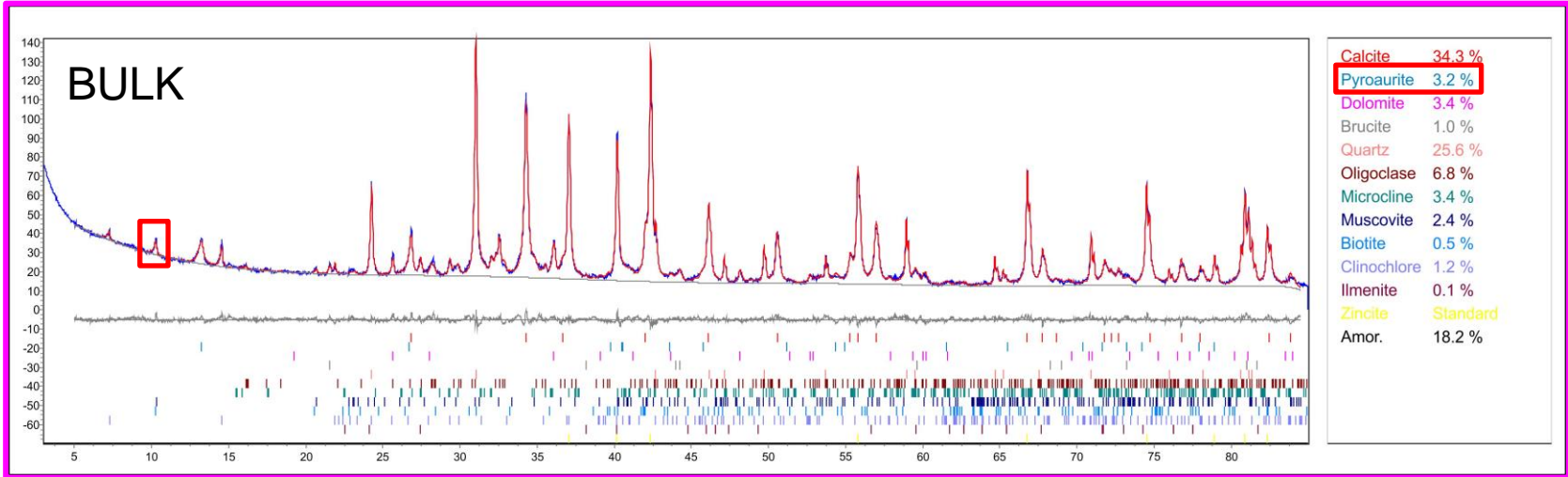


# Zairo Theatre, Padova



# Zairo Theatre, Padova

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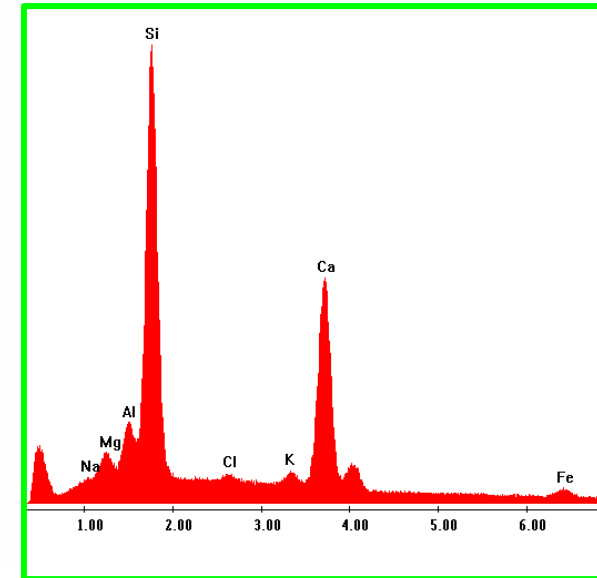
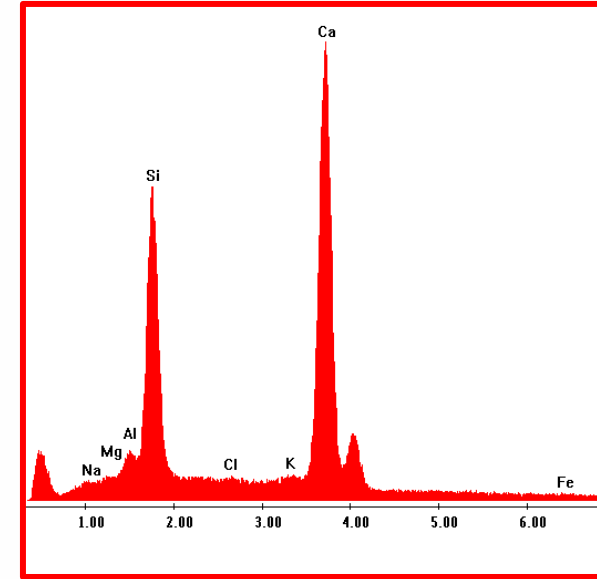
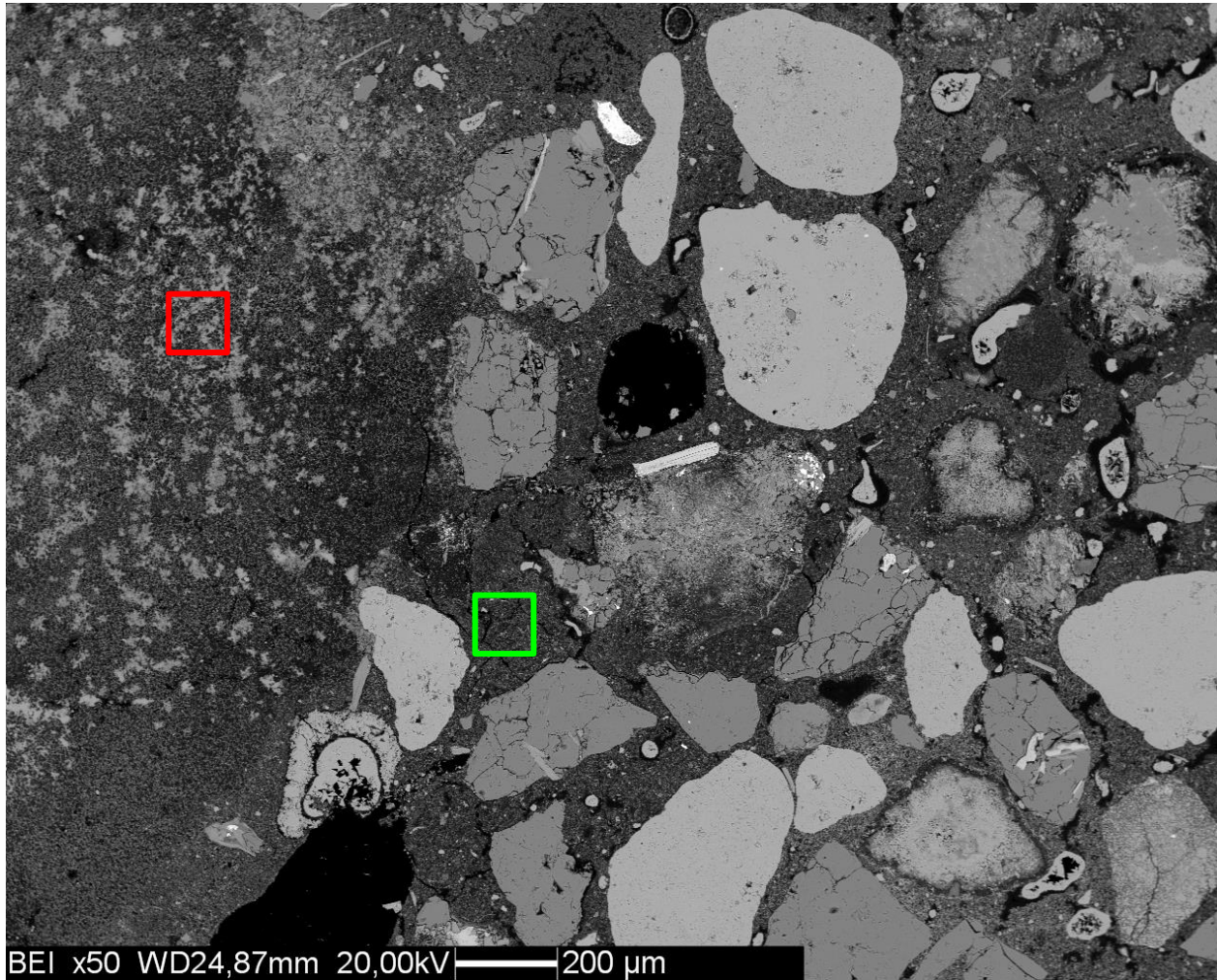
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# Zairo Theatre, Padova

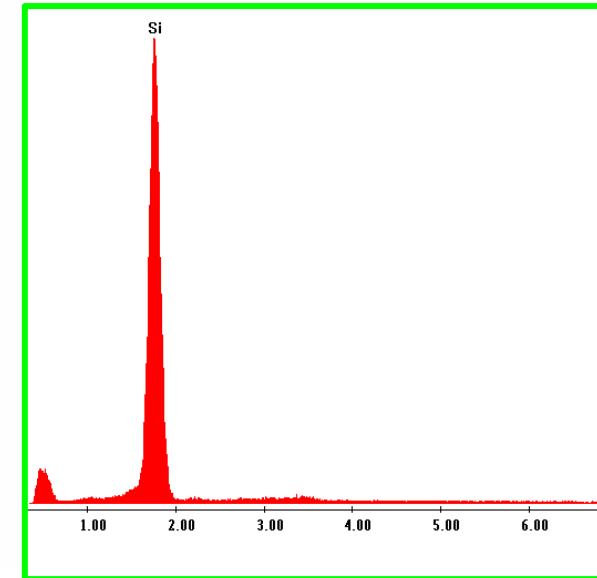
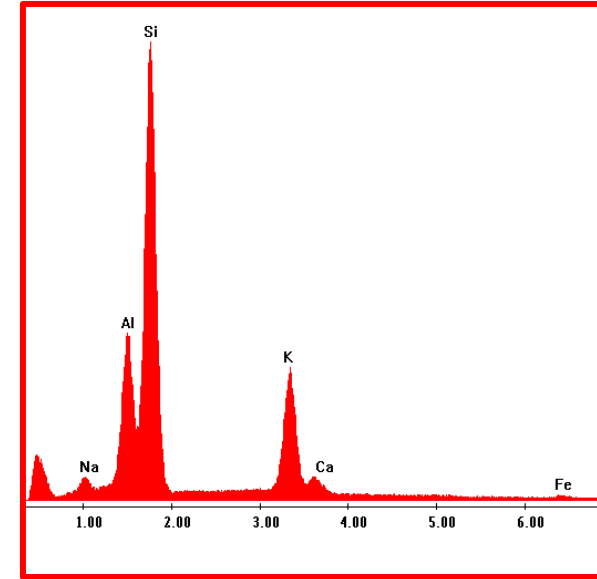
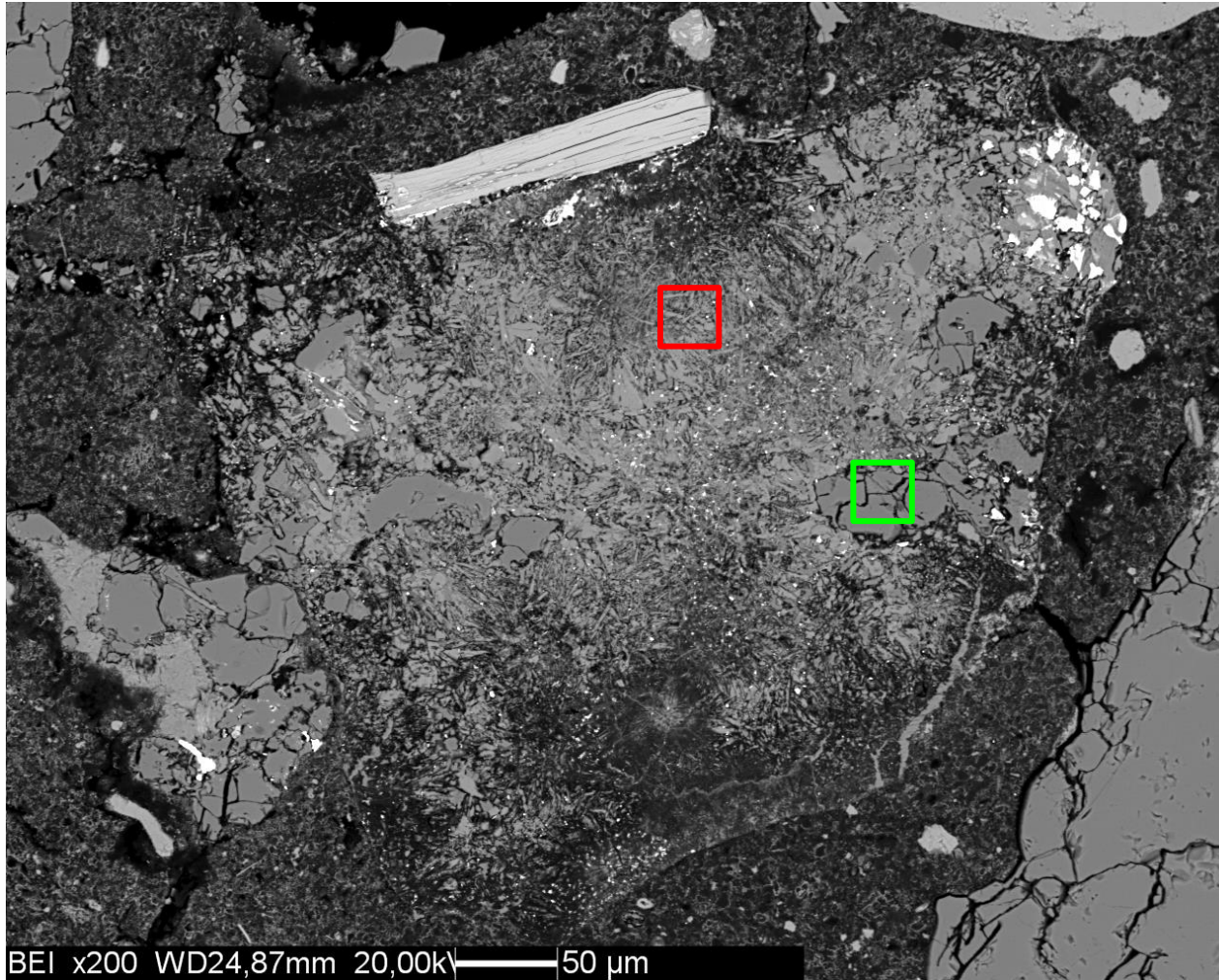
# A





# Zairo Theatre, Padova

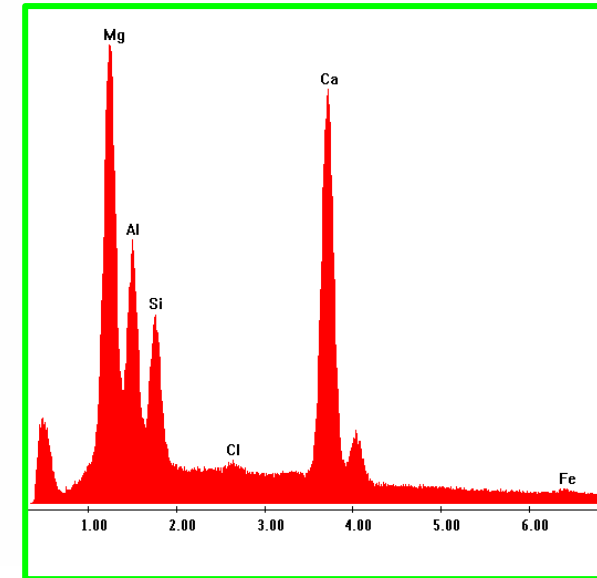
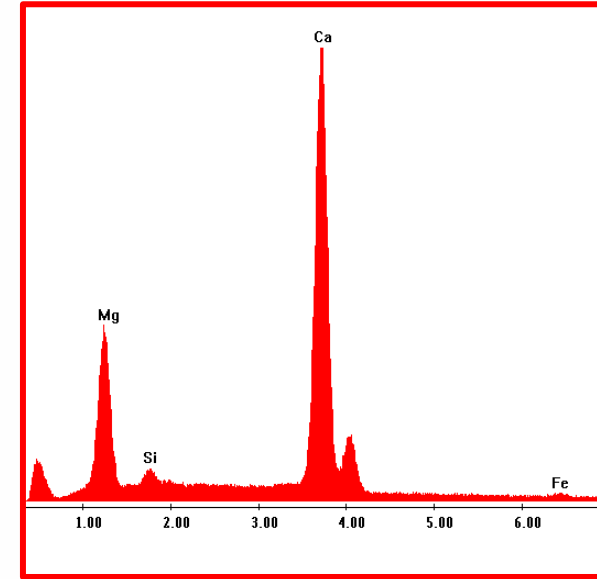
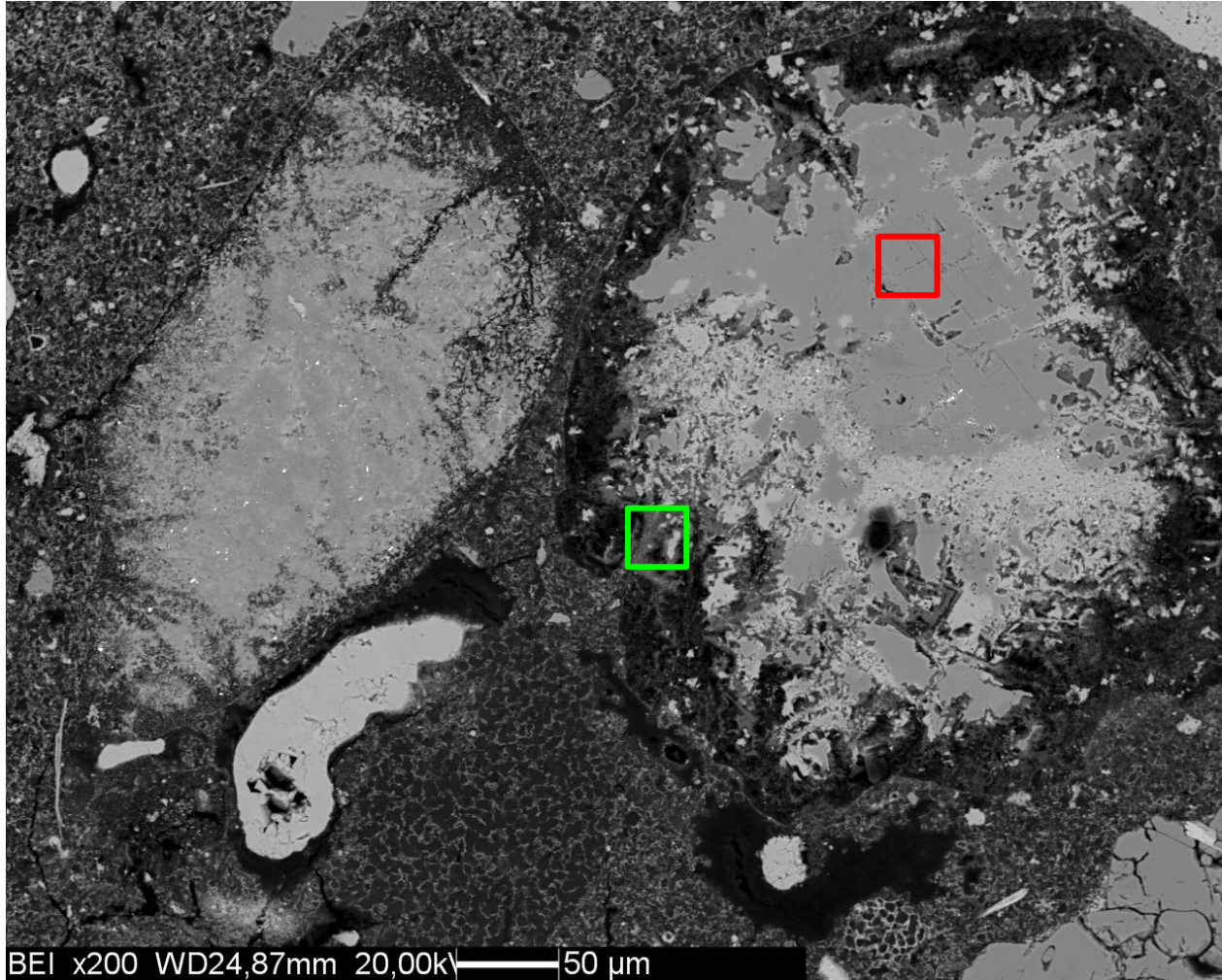
# A





# Zairo Theatre, Padova

# A



# Zairo Theatre, Padova



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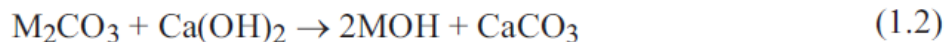
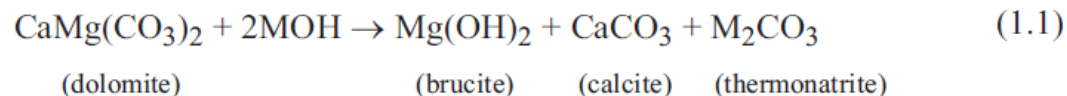
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The so-called alkali-carbonate reaction (ACR) – Its mineralogical and geochemical details, with special reference to ASR

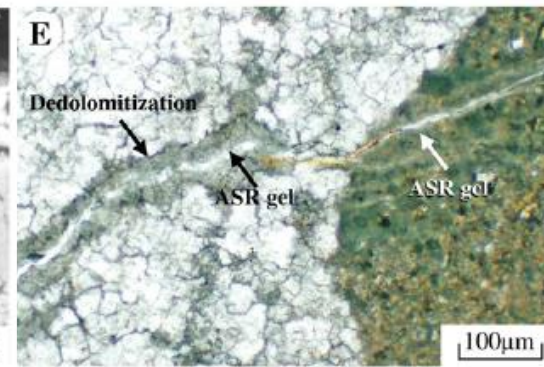
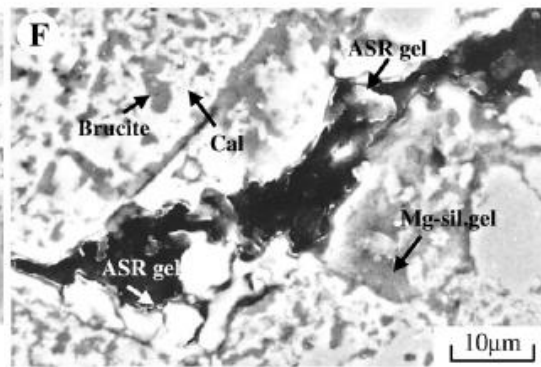
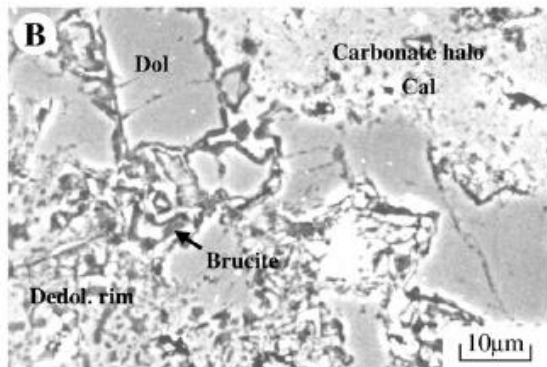
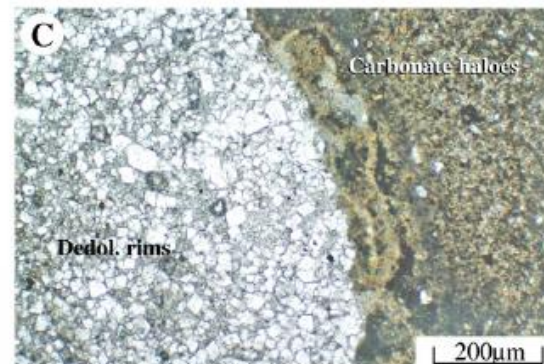
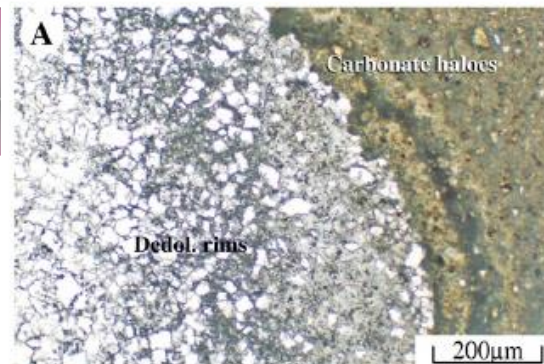
Tetsuya Katayama

Kawasaki Geological Engineering Co. Ltd., 2-11-15 Mita, Minato-ku, Tokyo, 108-8338, Japan



where:

M = K, Na or Li



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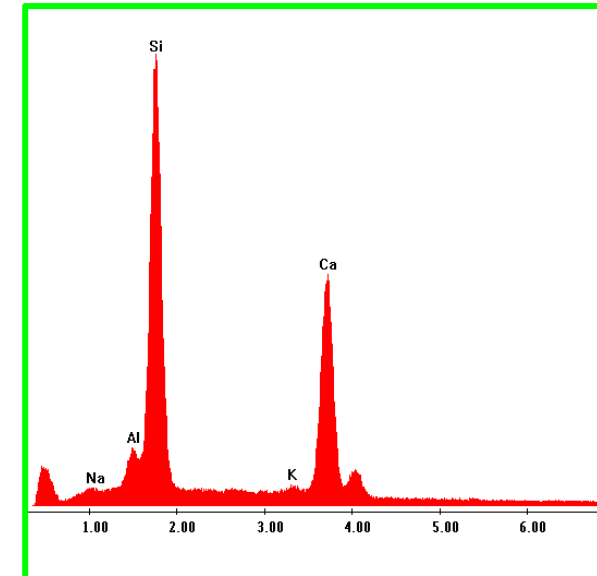
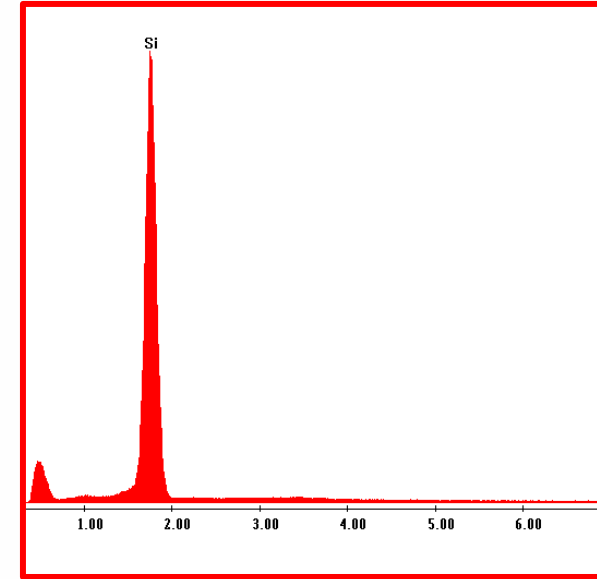
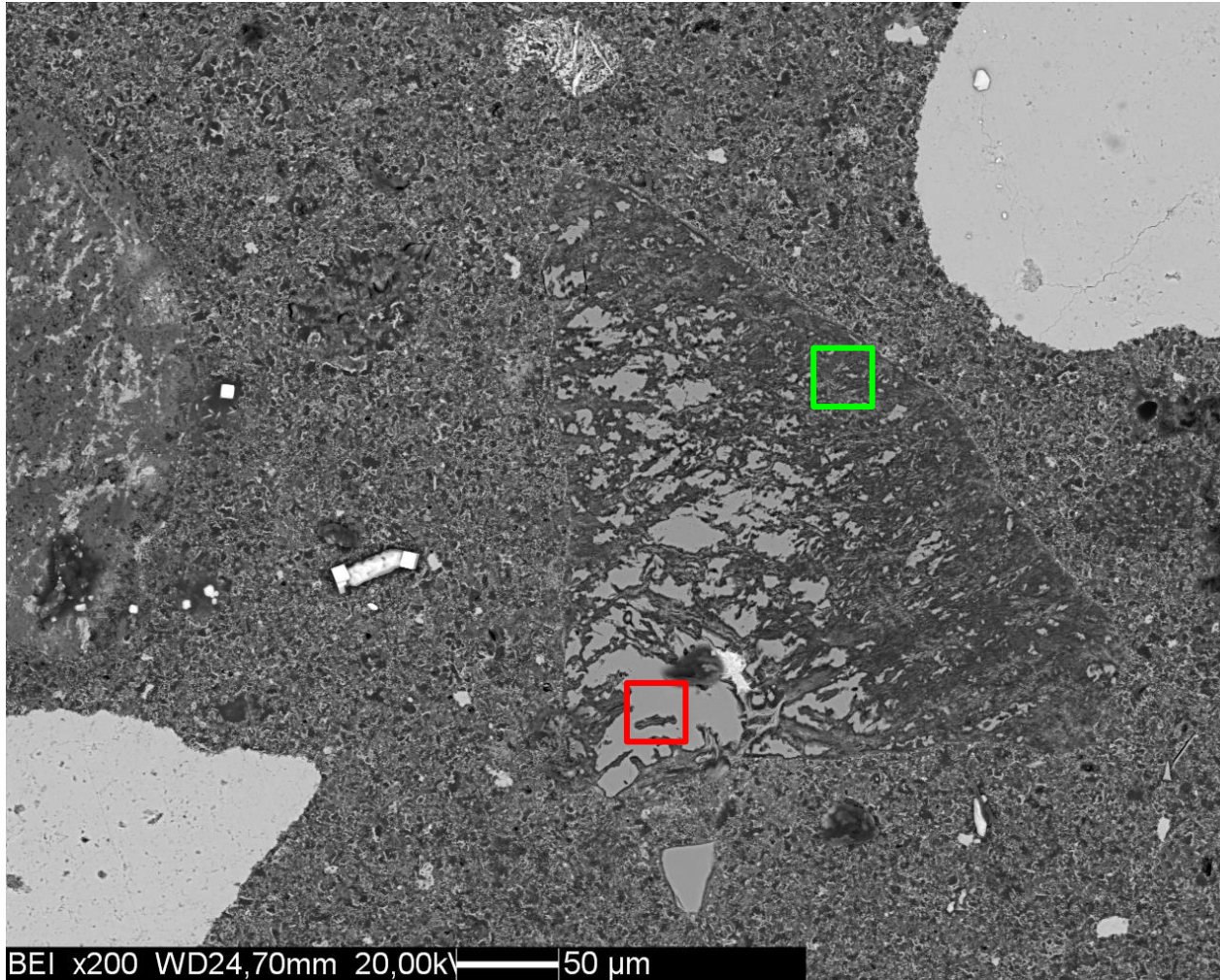
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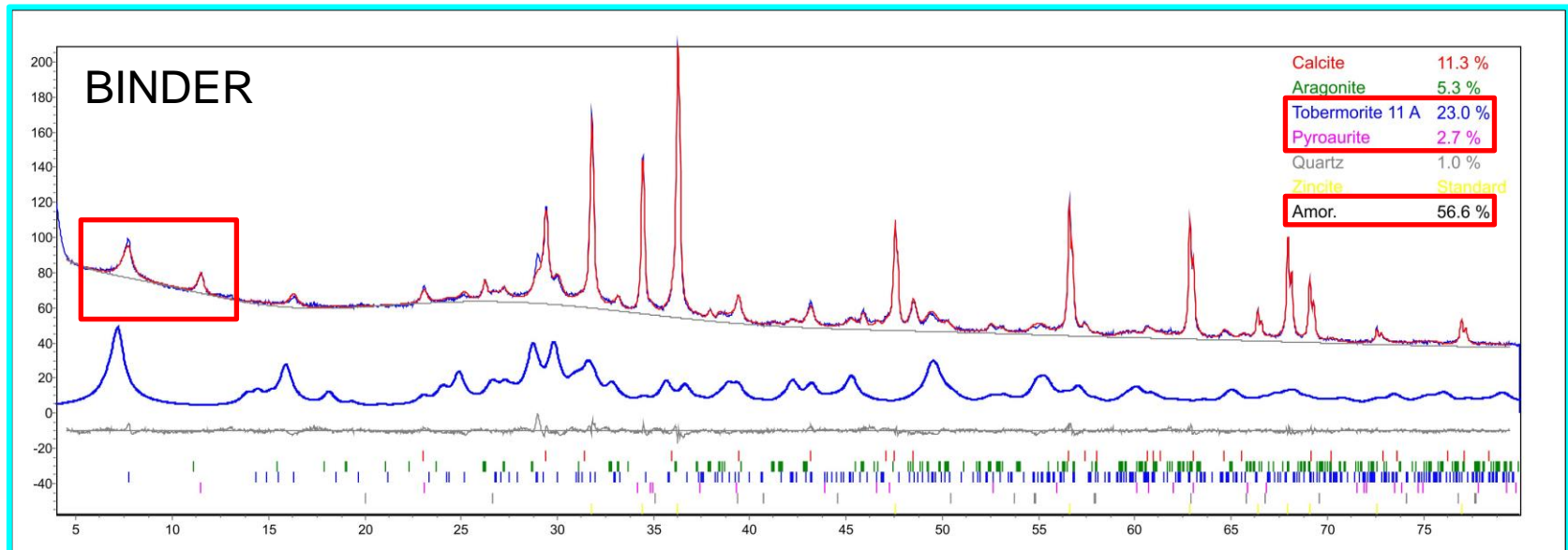
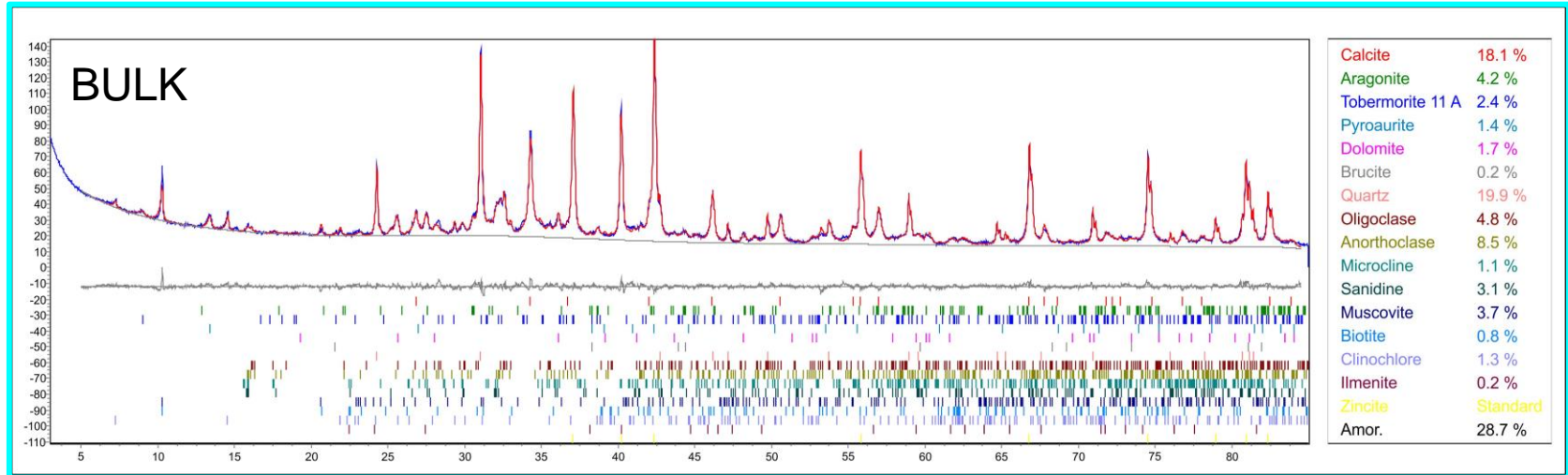
# Zairo Theatre, Padova

# A



# Zairo Theatre, Padova

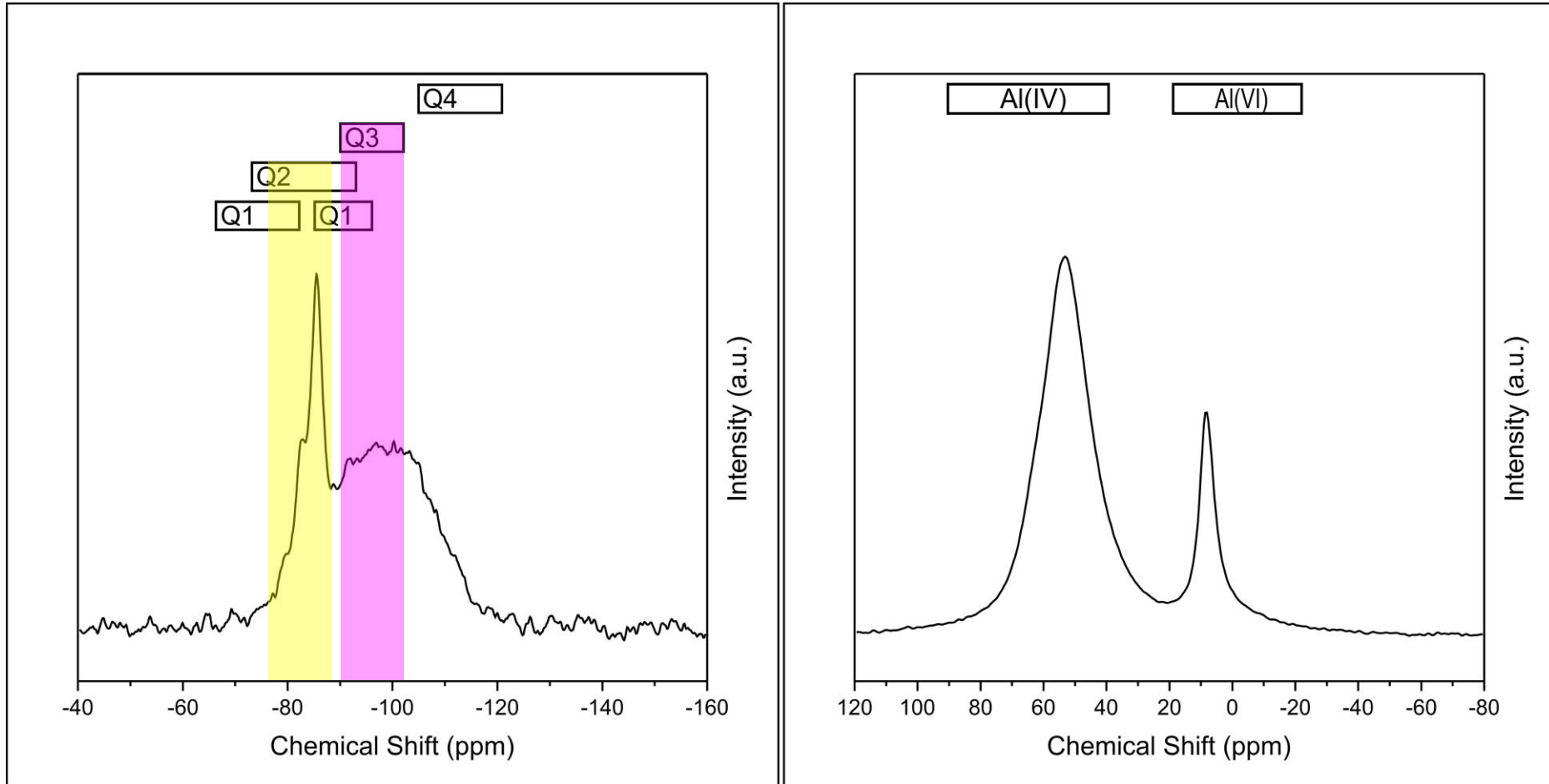
B





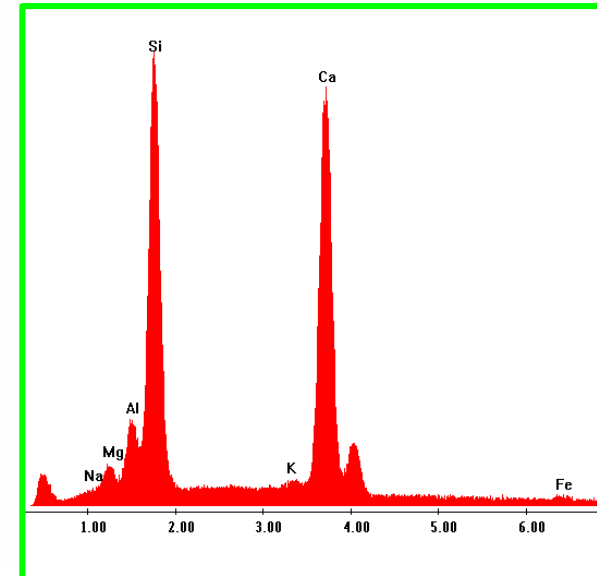
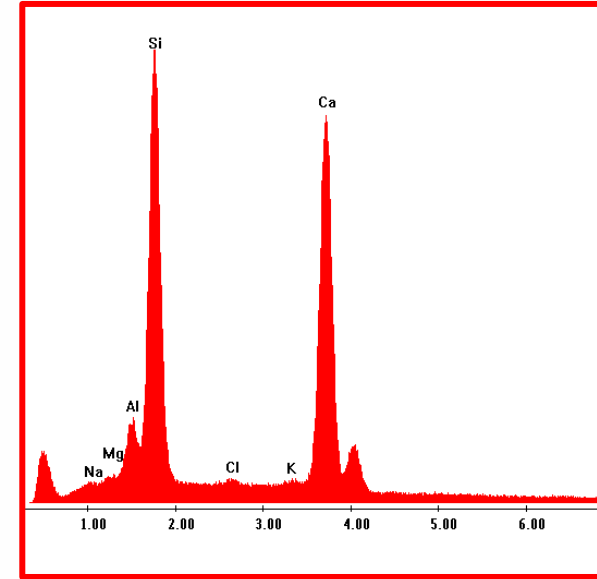
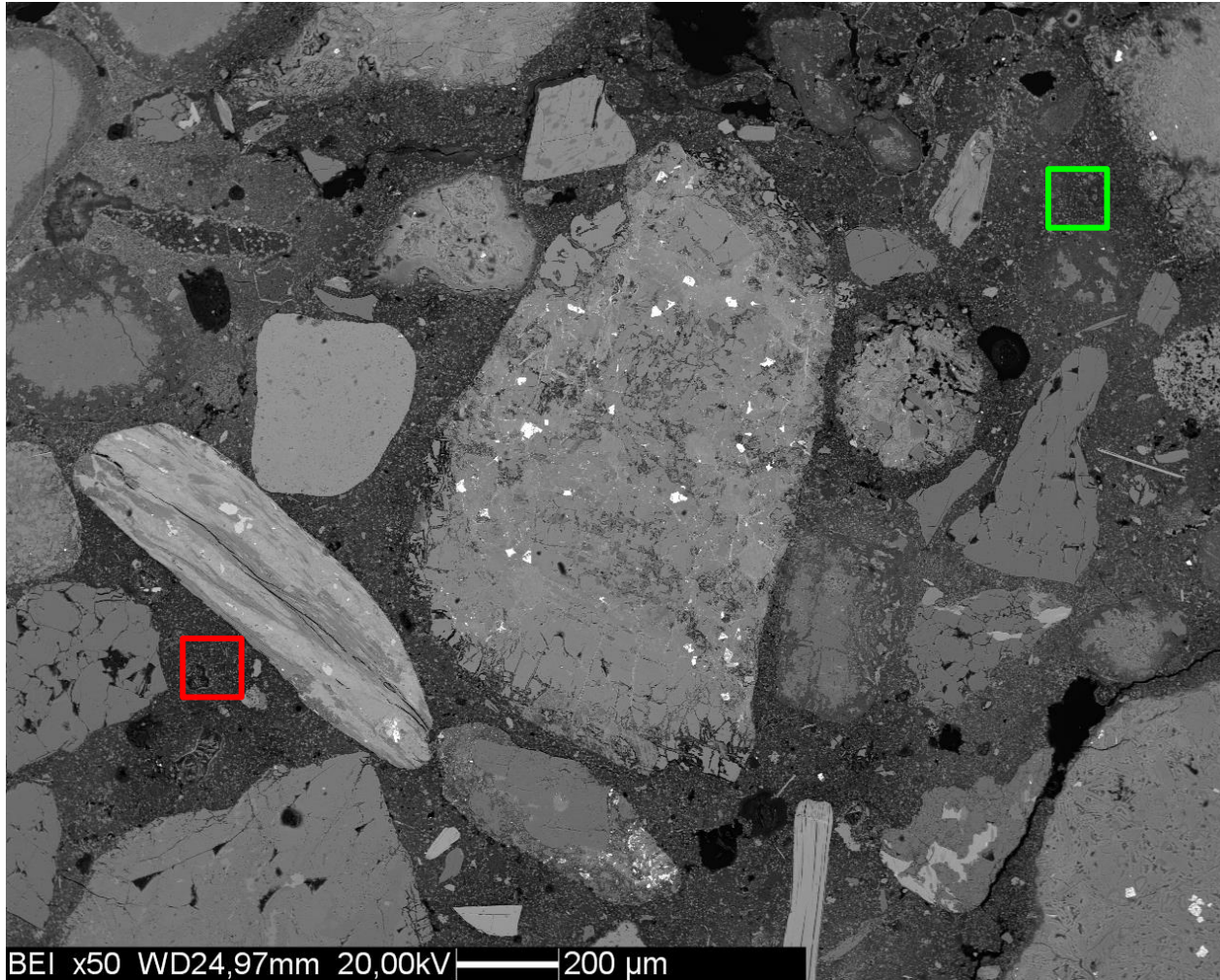
# B

## SS-NMR, BINDER FRACTION



# Zairo Theatre, Padova

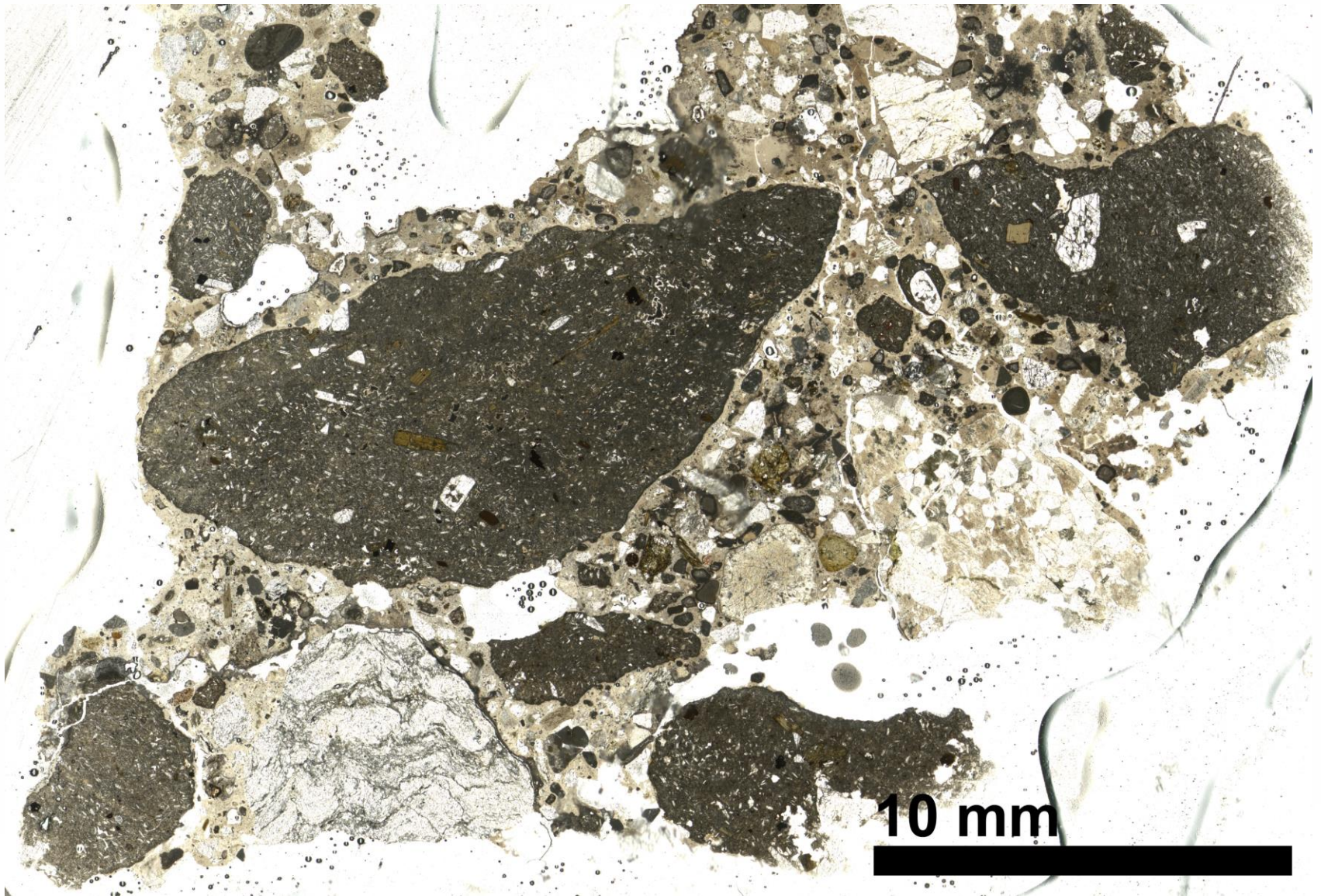
## B





# Zairo Theatre, Padova

B



10 mm



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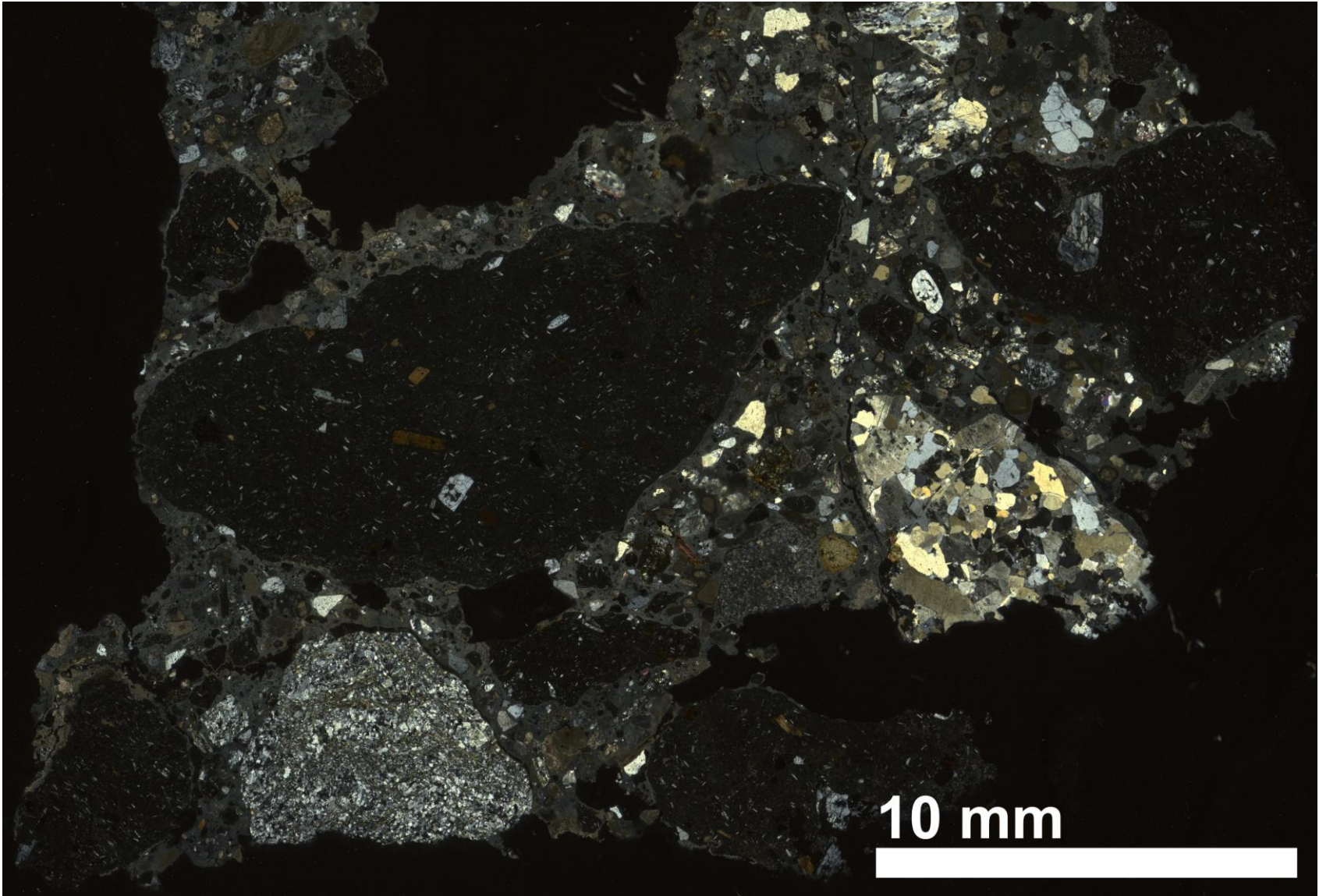
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10 mm



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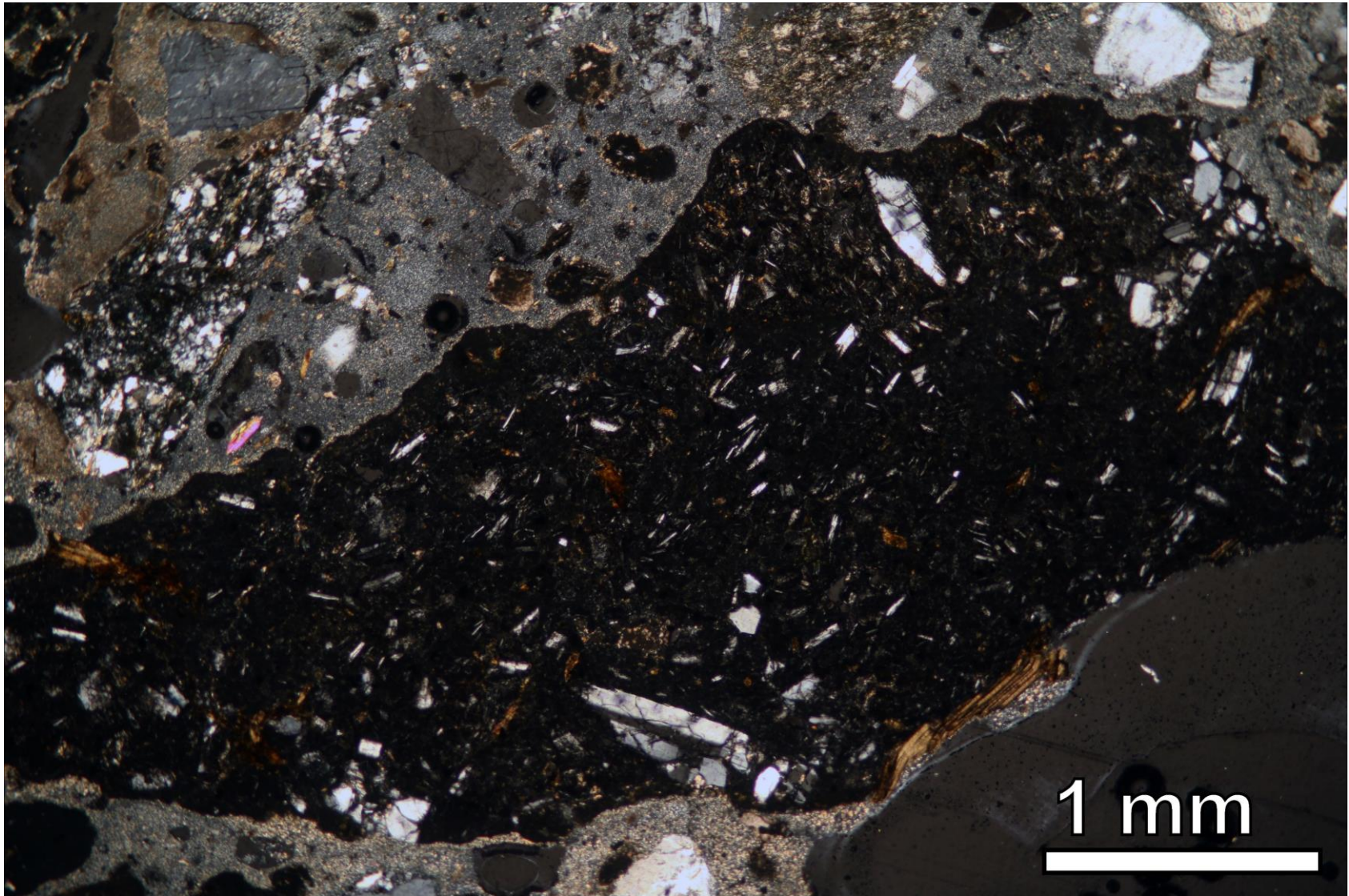
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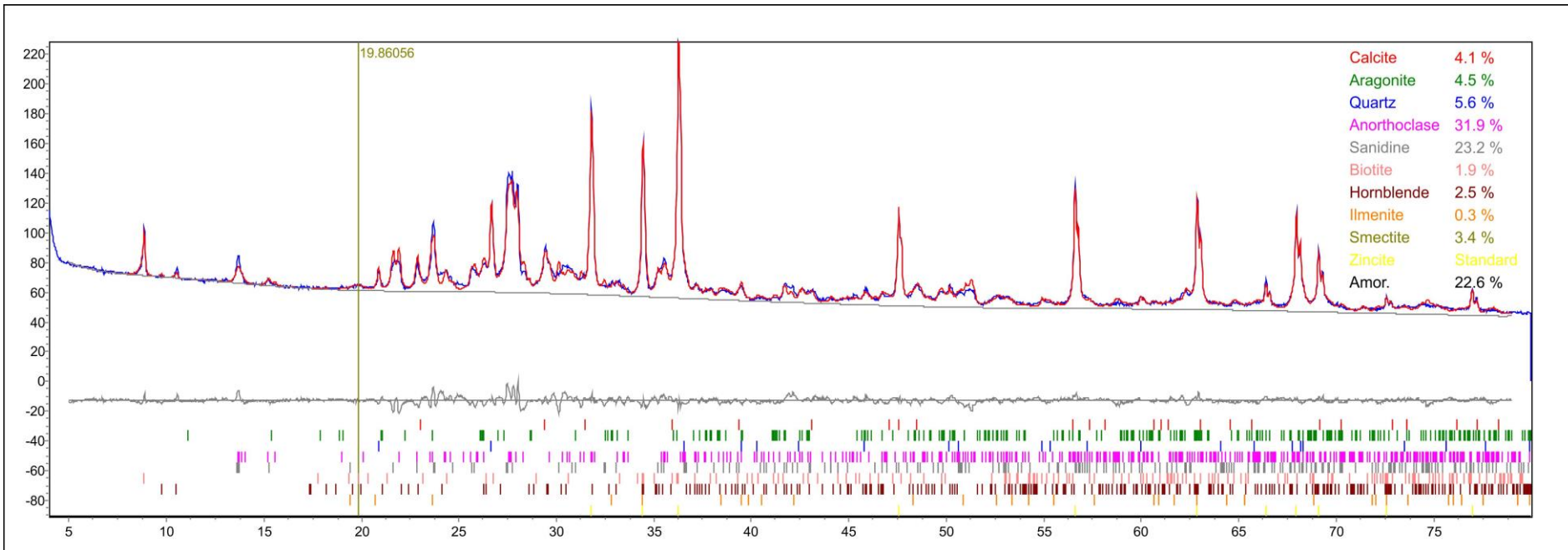
# Zairo Theatre, Padova

B



# Zairo Theatre, Padova

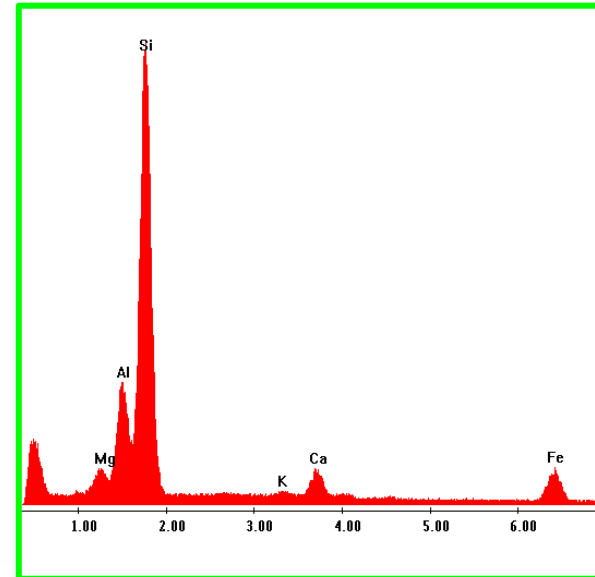
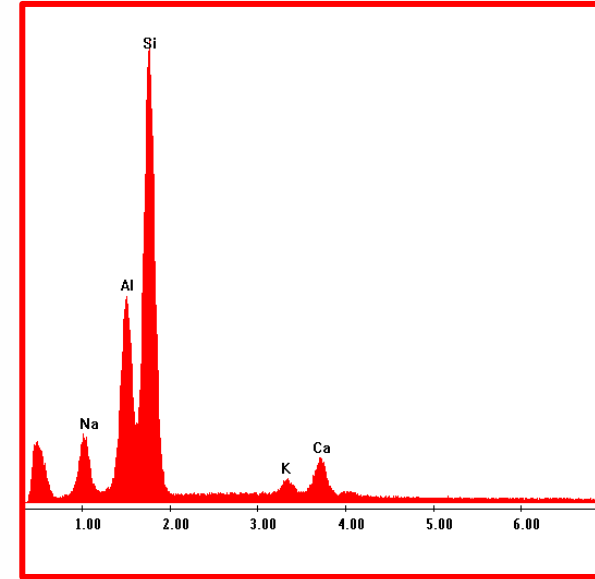
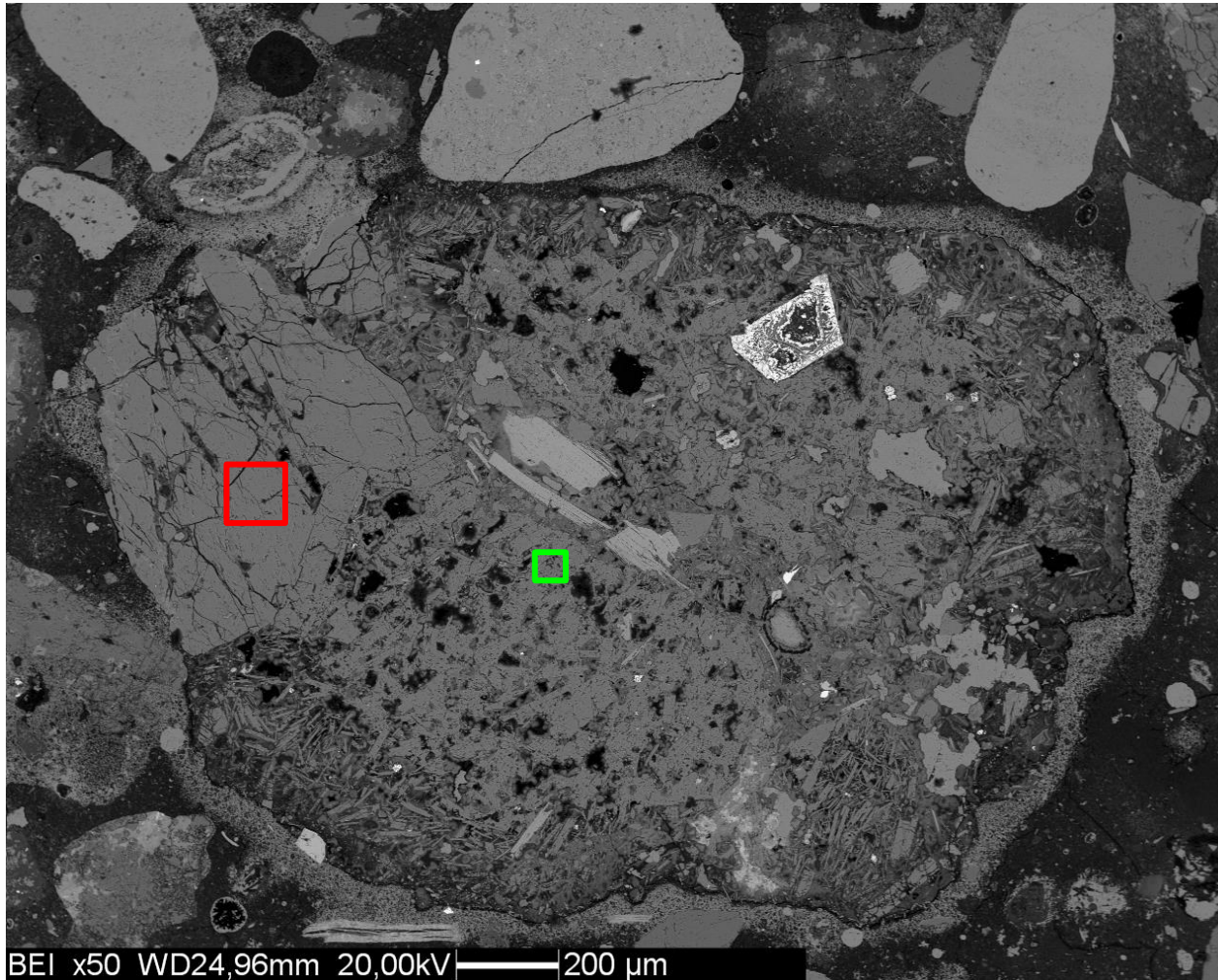
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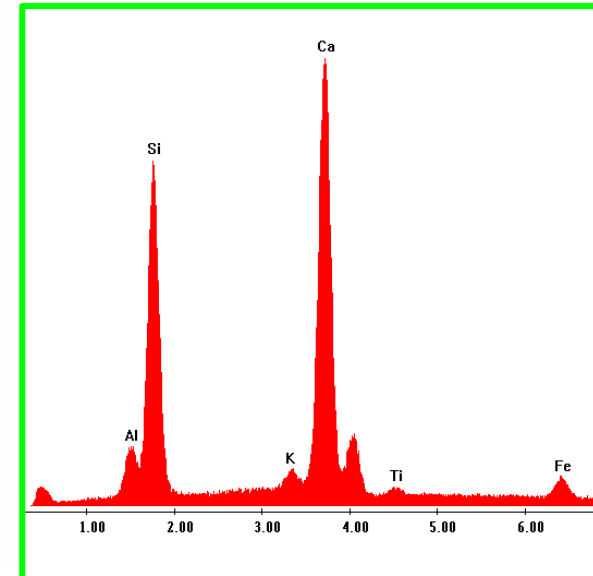
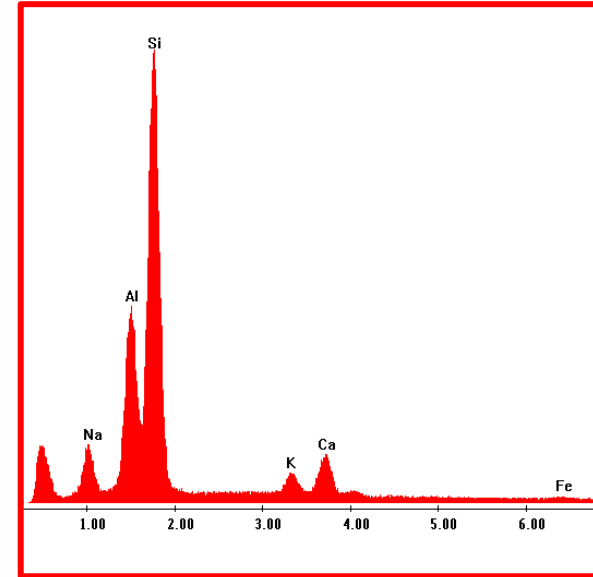
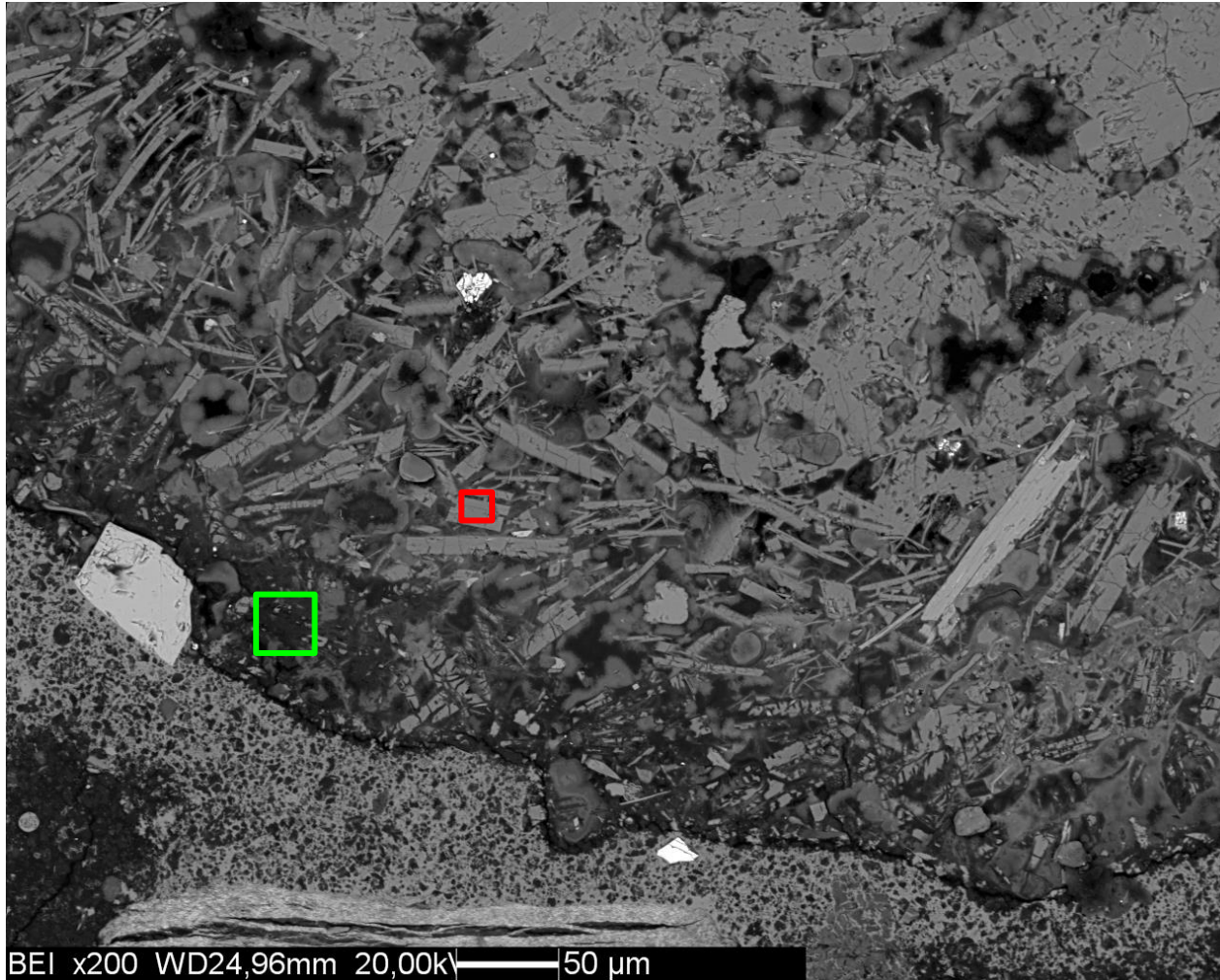
# Zairo Theatre, Padova

## B



# Zairo Theatre, Padova

## B





# Zairo Theatre, Padova

## Euganean Hills



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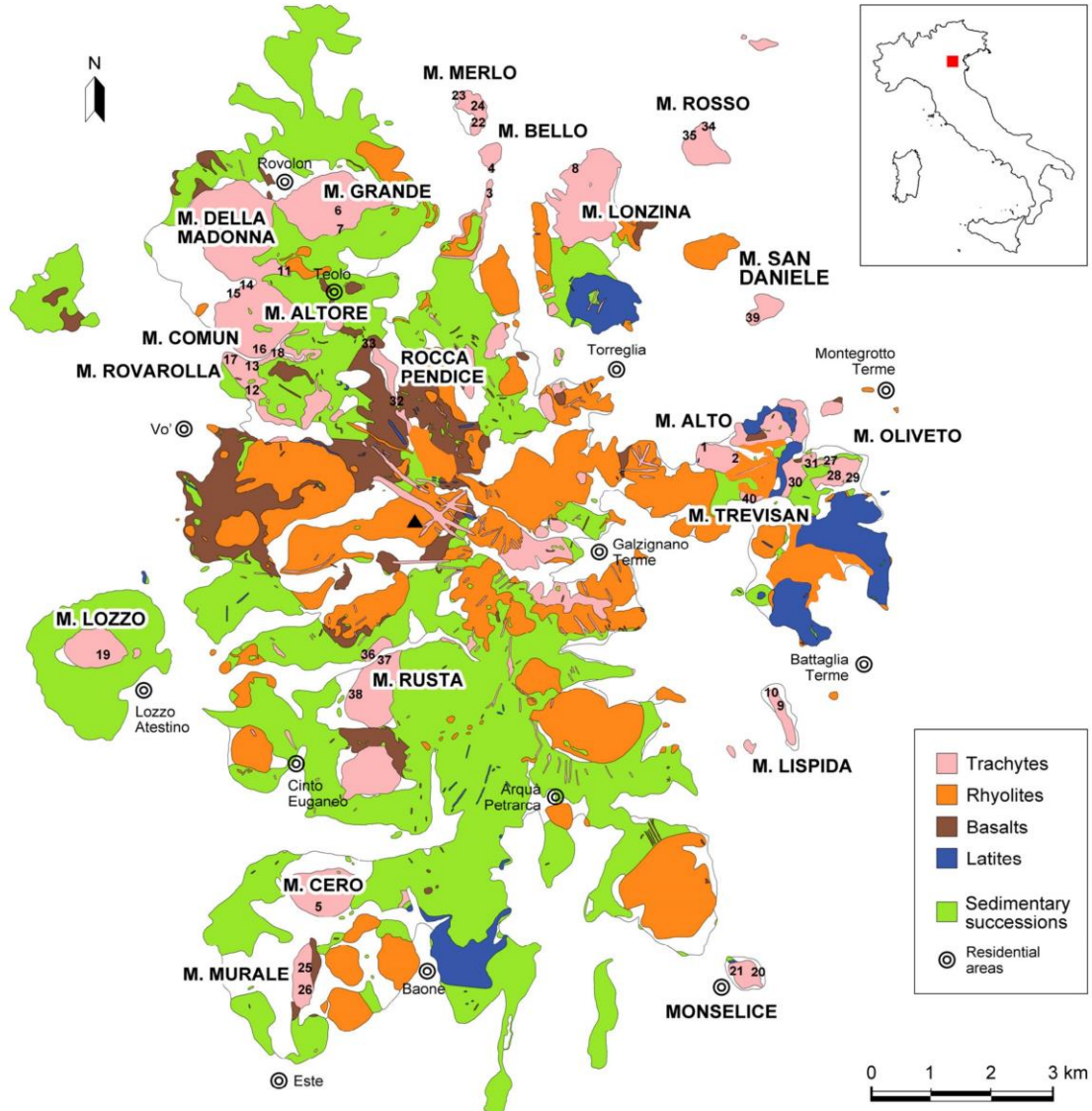
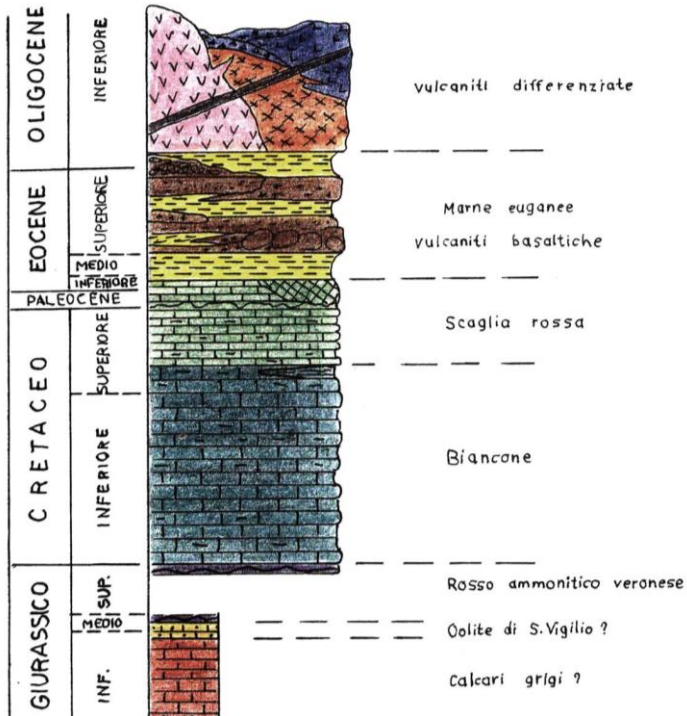
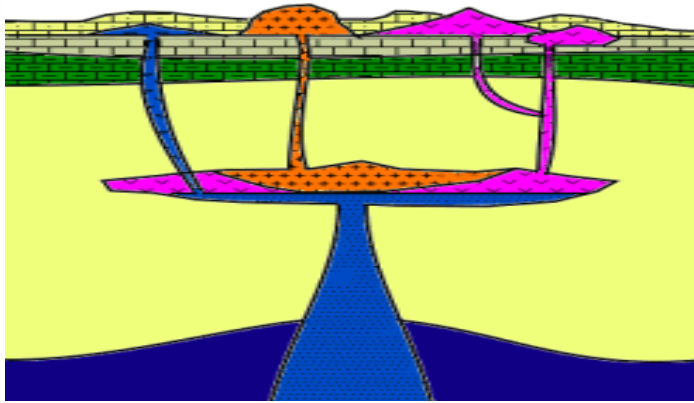
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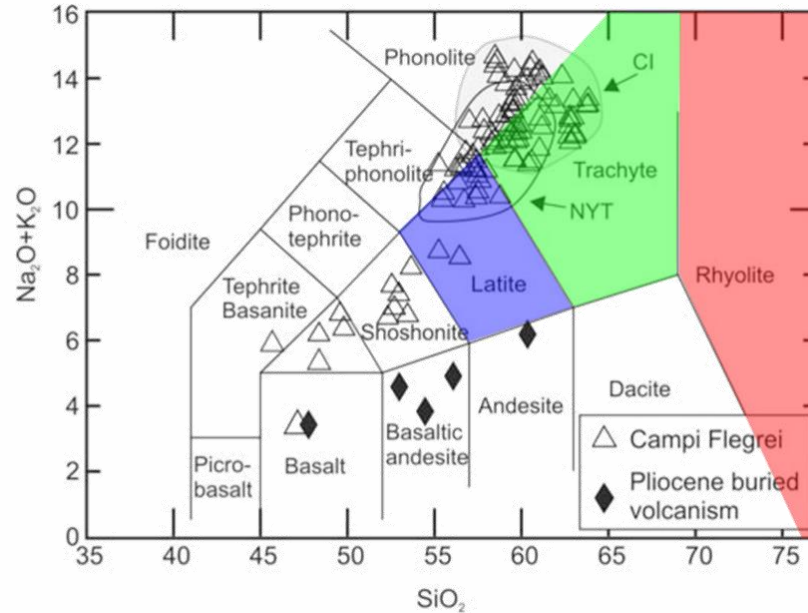


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Rhyolite

Trachyte

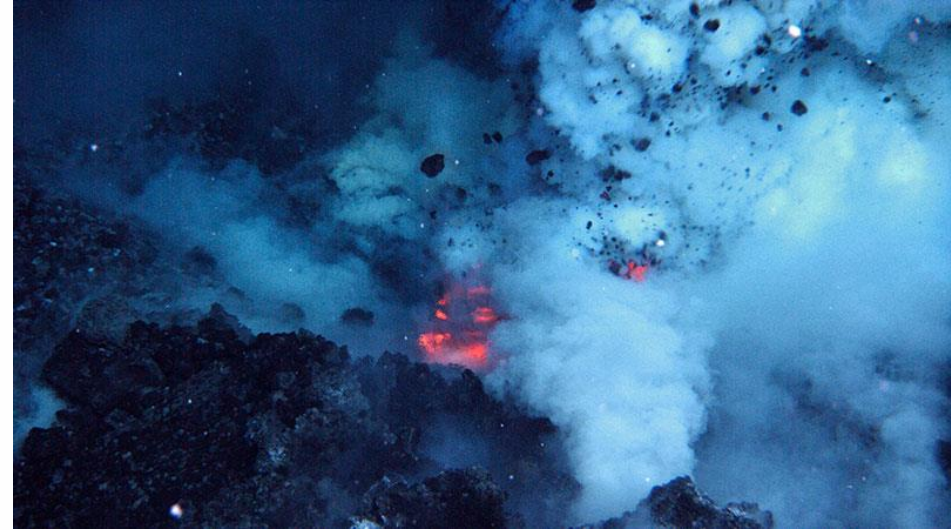
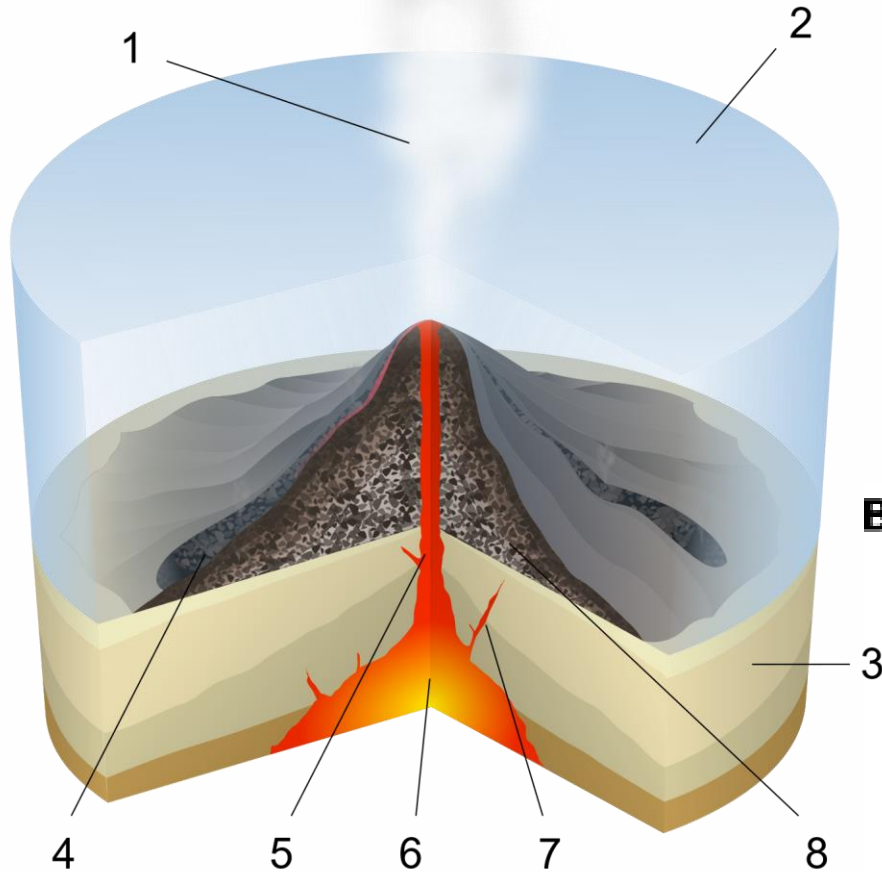
Latite



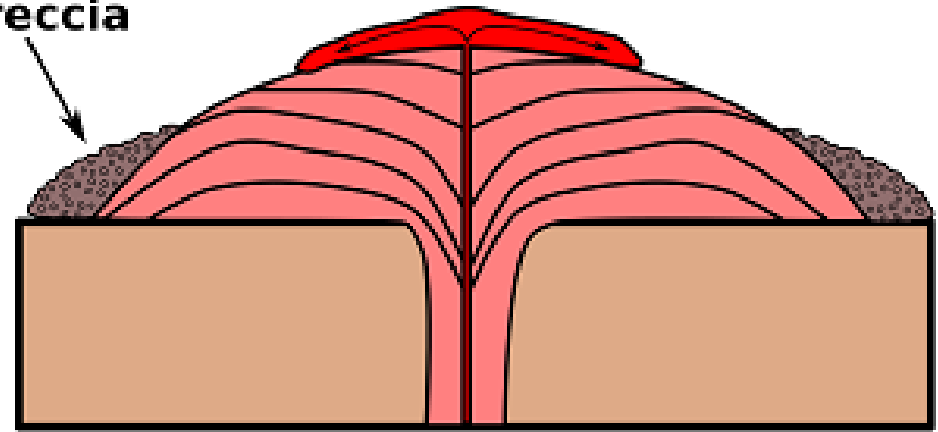
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## Submarine eruptions



Breccia





# Zairo Theatre, Padova

## Volcanic breccias in the Euganean Hills



Google Earth



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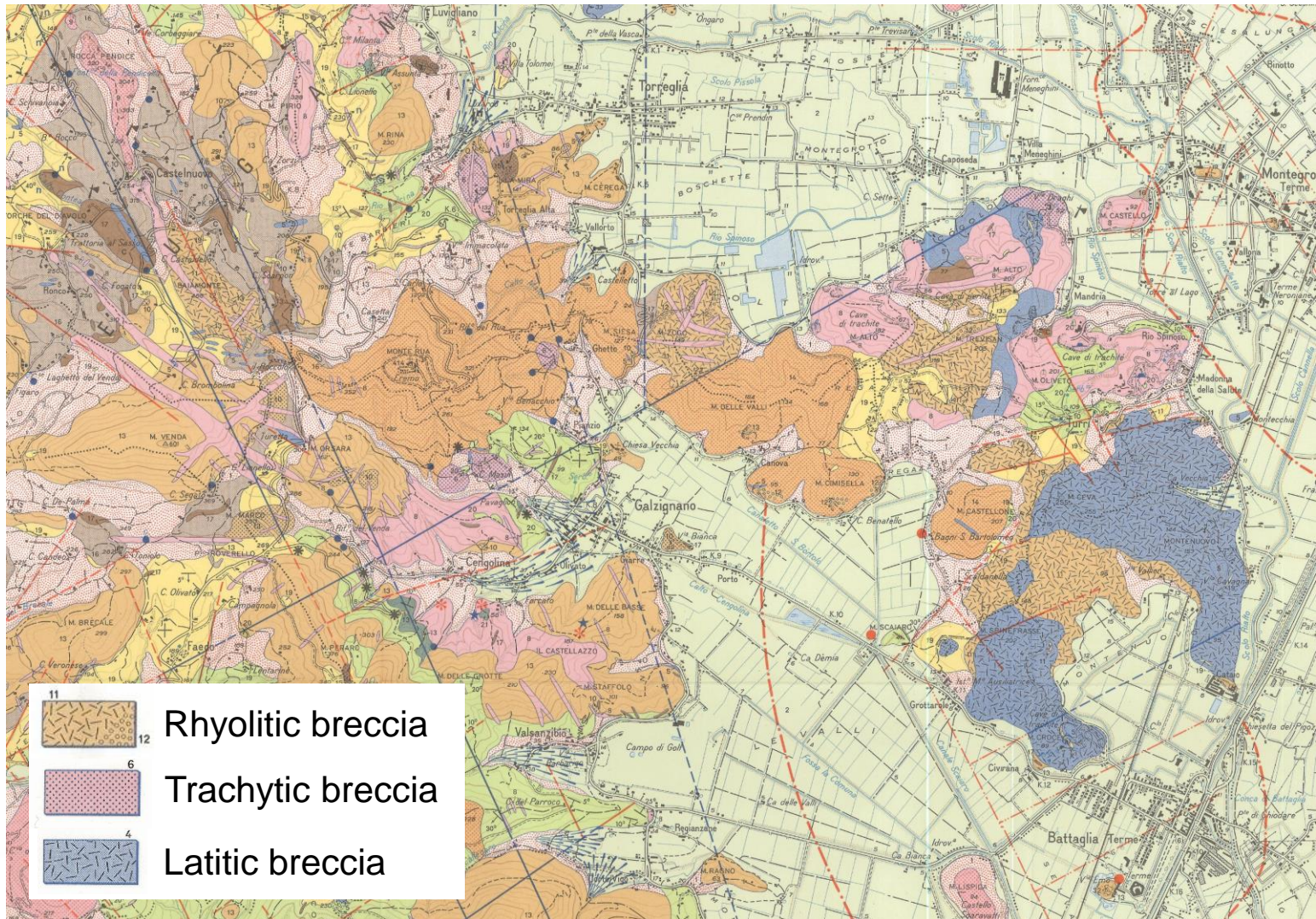
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## Volcanic breccias in the Euganean Hills





# Zairo Theatre, Padova

## Volcanic breccias in the Euganean Hills





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## Volcanic breccias in the Euganean Hills



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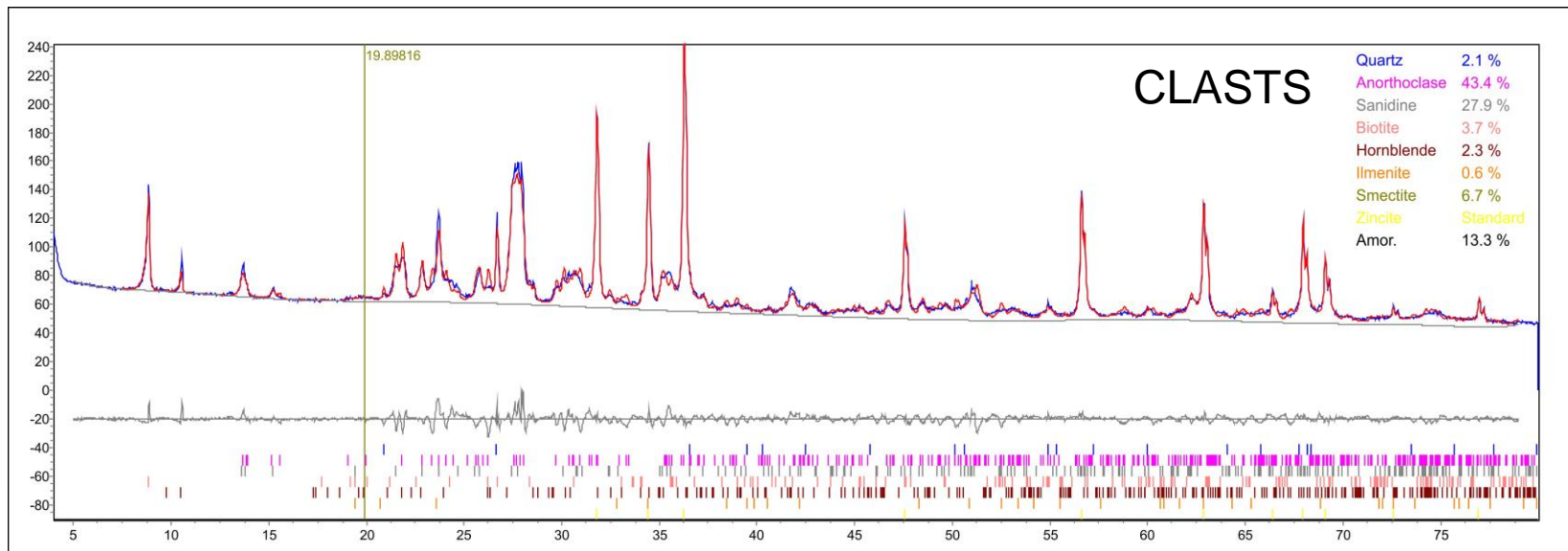
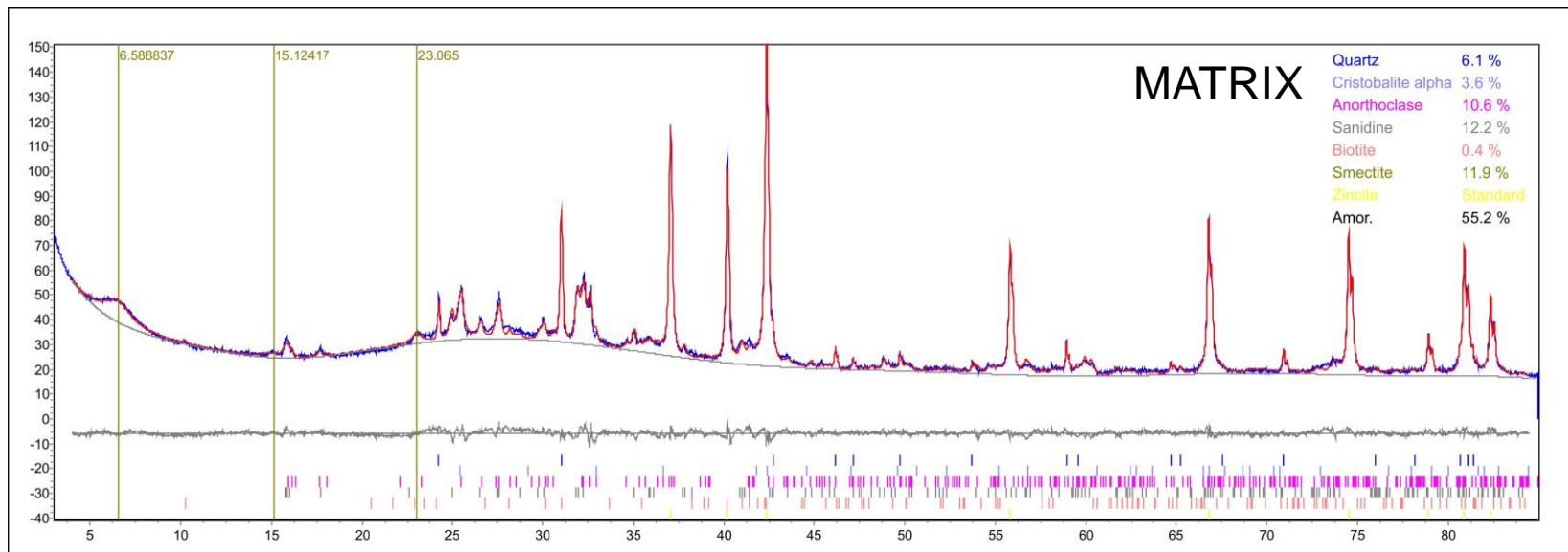
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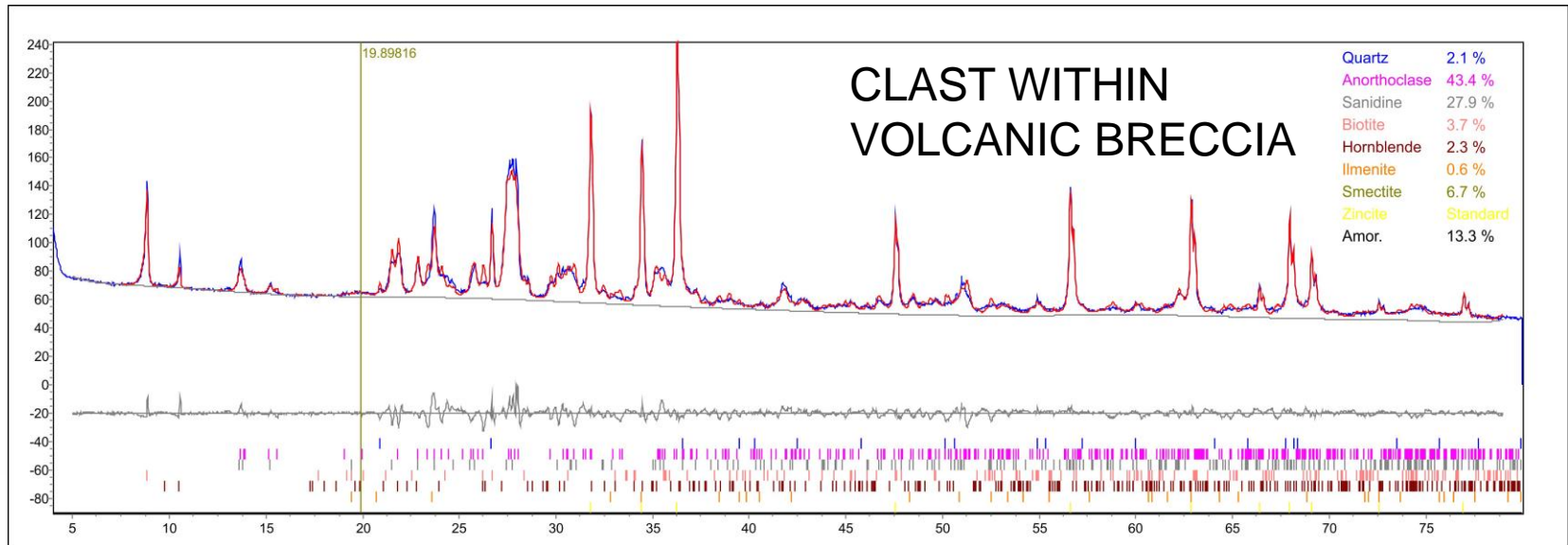
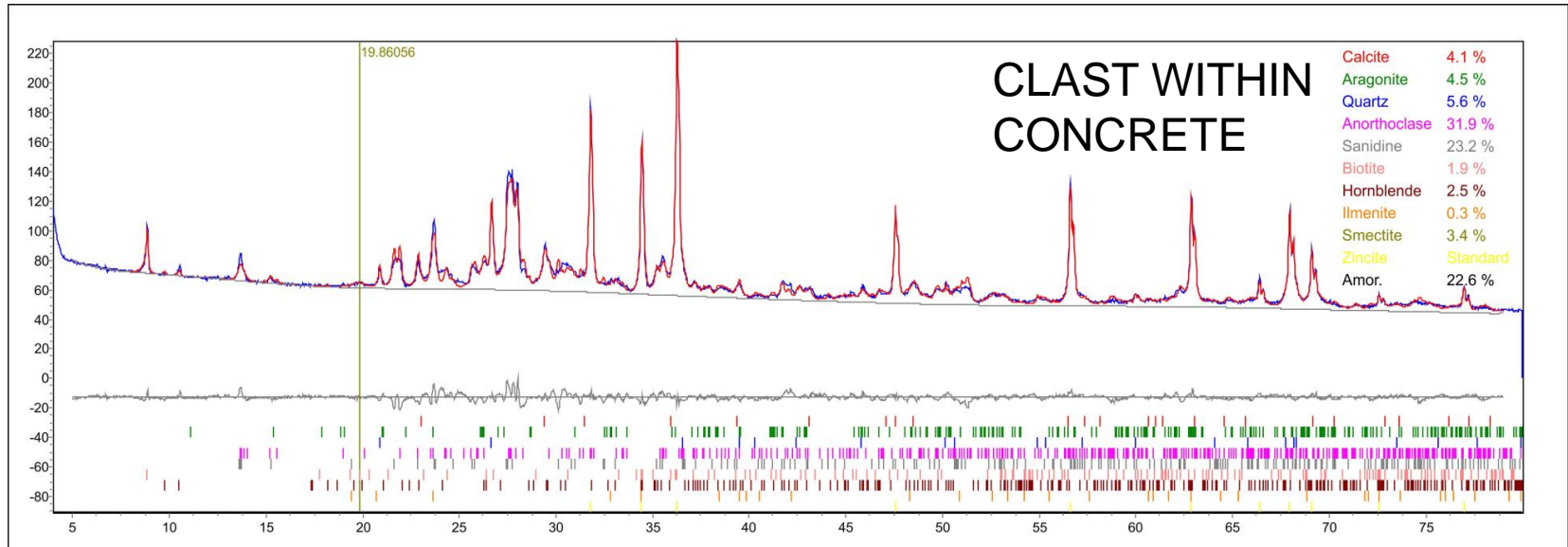
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# Padova Amphitheatre



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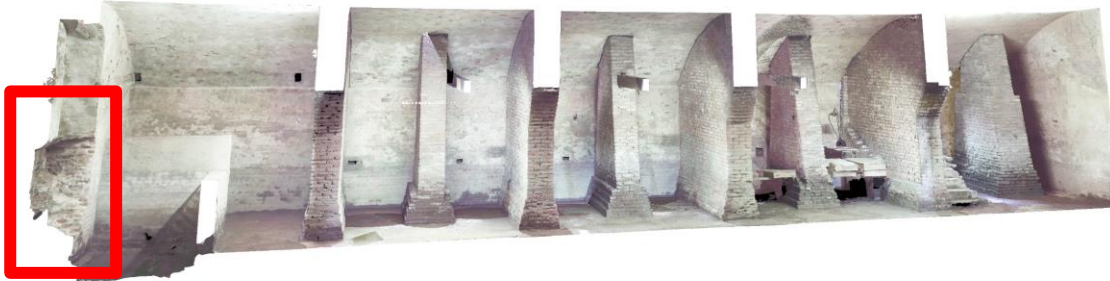
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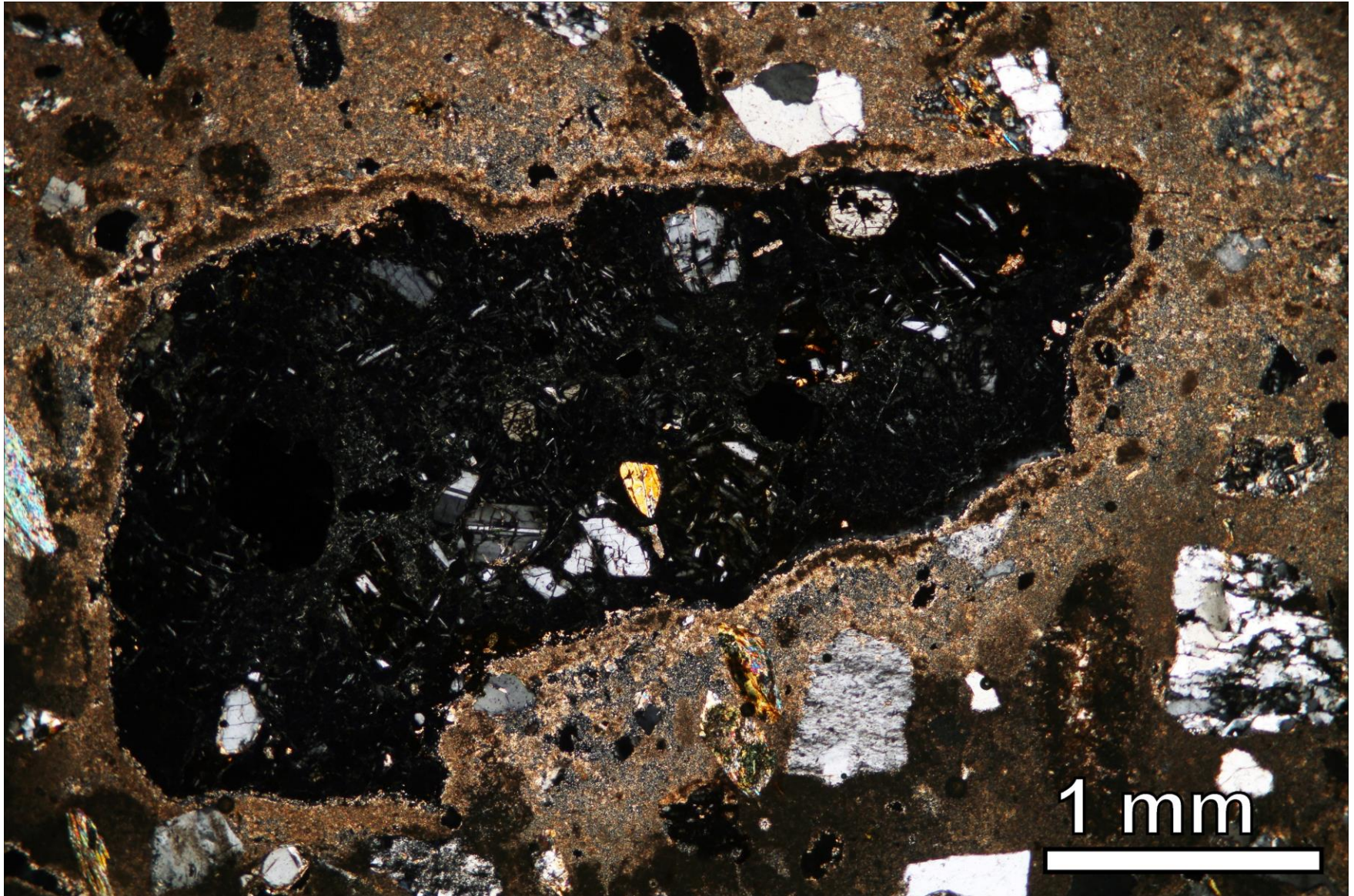


# Padova Amphitheatre



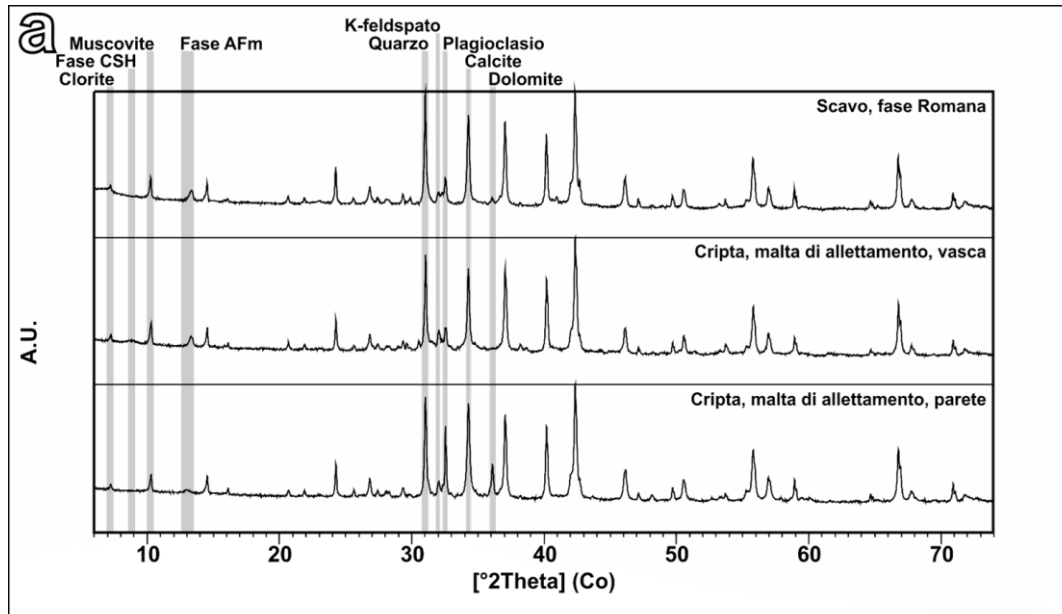
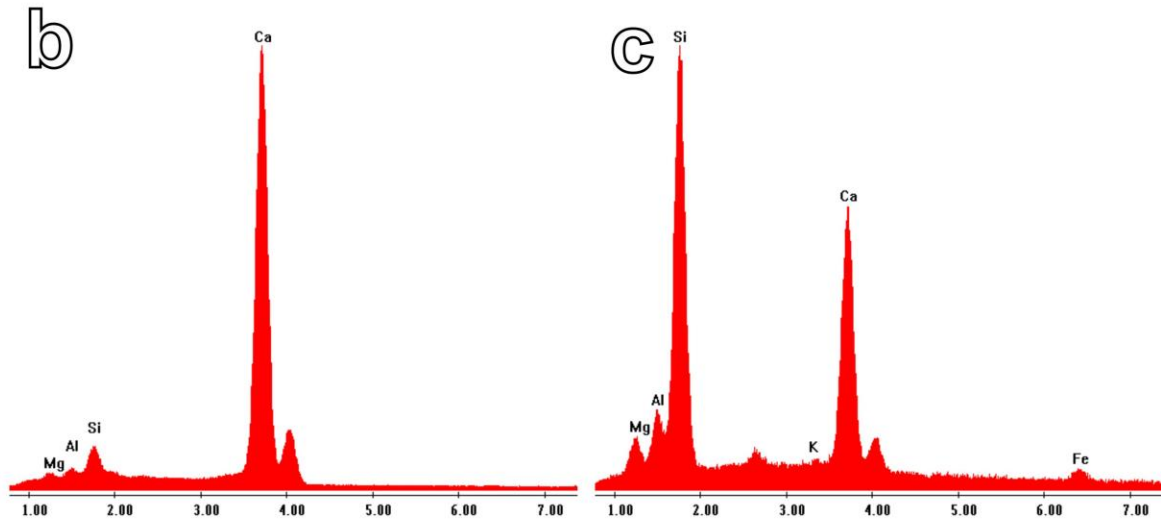
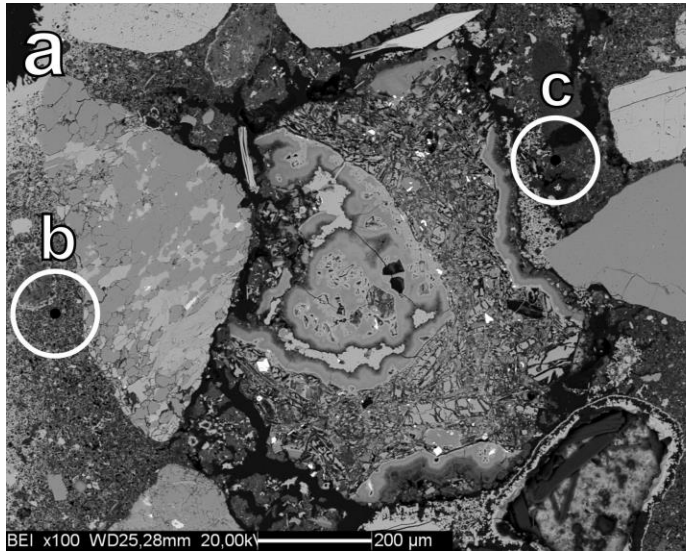


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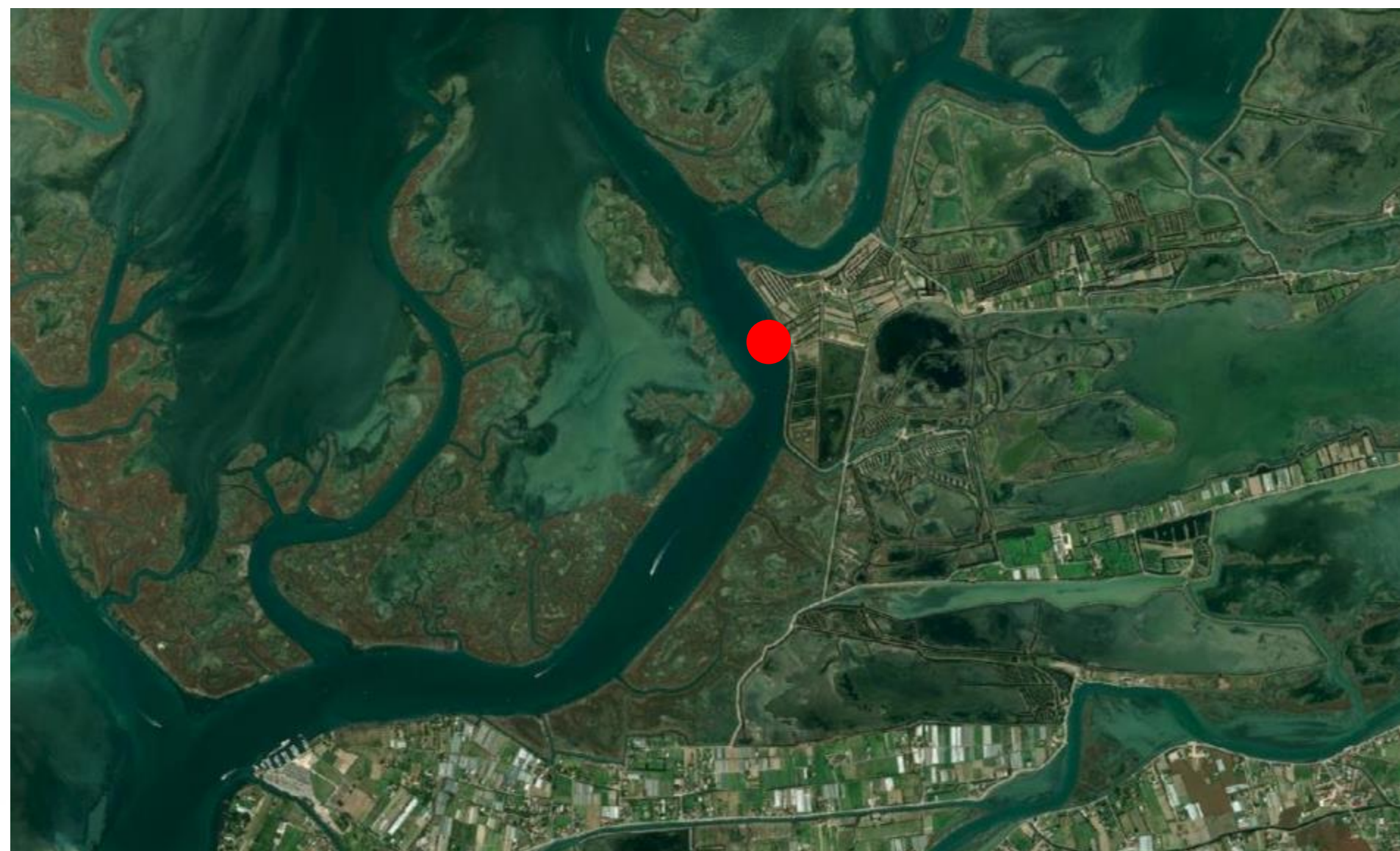
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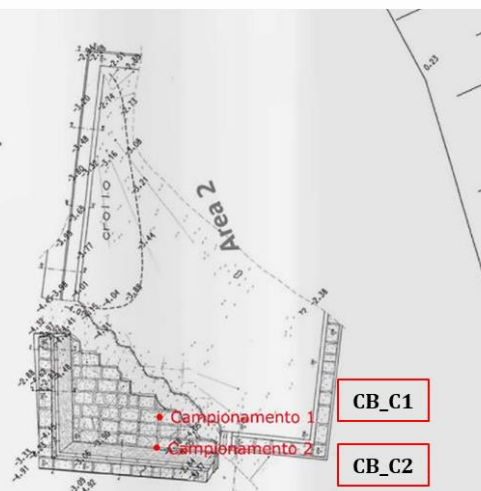
# Northern Venice Lagoon – Cà Ballarin

Ca' Ballarin 7 2020 Molo		CB_7_M
Ca' Ballarin 7 2020 blocco G		CB_7_G
Ca' Ballarin molo blocco A	malta campione	CB_7_A
Ca' Ballarin campionamento 1 cisterna	fuga tra i mattoni - legante	CB_C1
Ca' Ballarin campionamento 2 cisterna	allettamento tra muro e pavimentazione - leggero strato di malta sopra	CB_C2



5 cm

CB\_7\_G



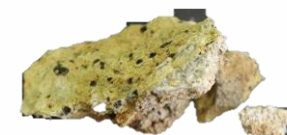
CB\_C1

CB\_C2



5 cm

CB\_C1



5 cm

CB\_C2



CB\_7\_A

CB\_7\_M



5 cm

CB\_7\_M

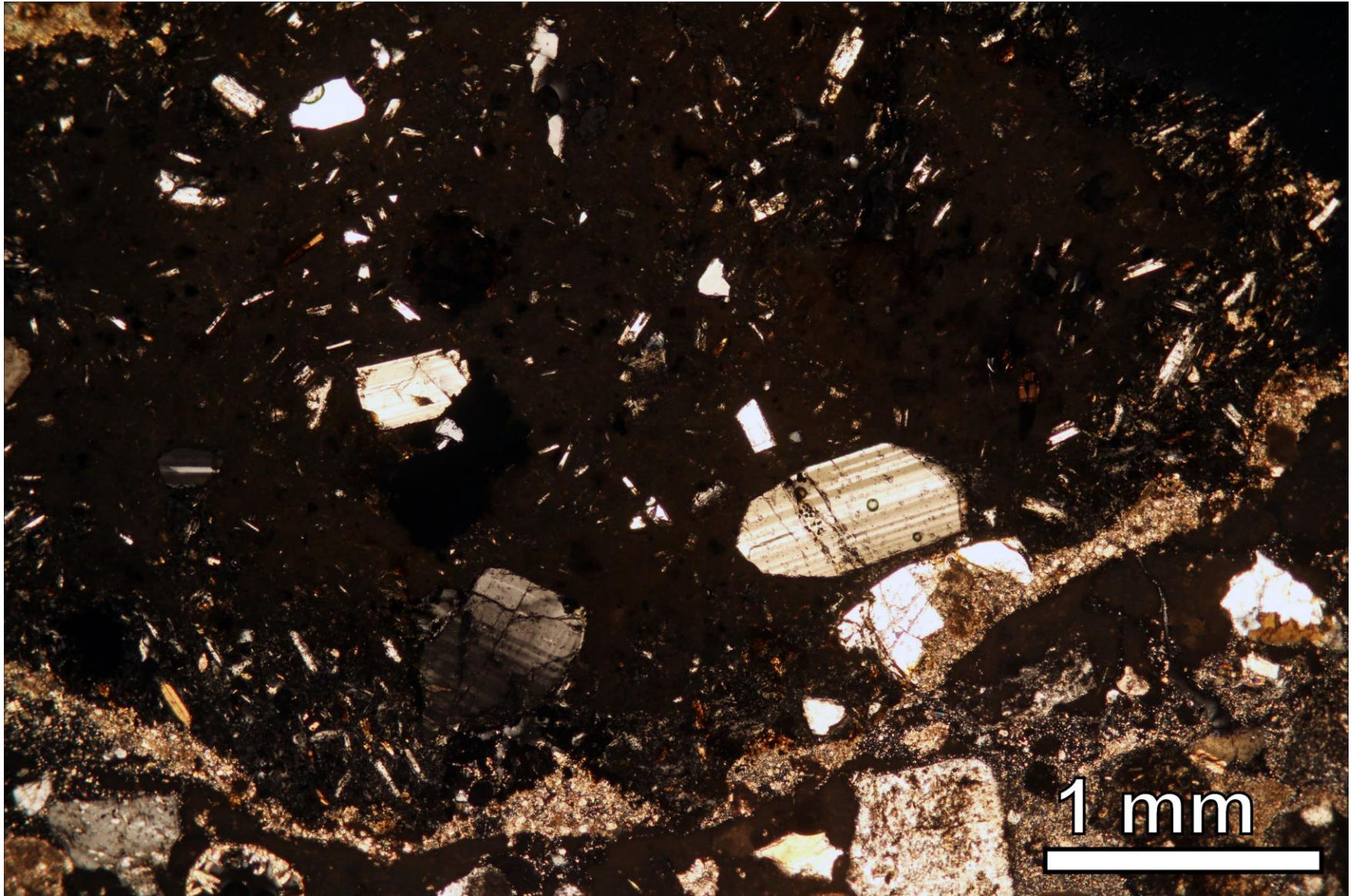


5 cm

CB\_7\_A



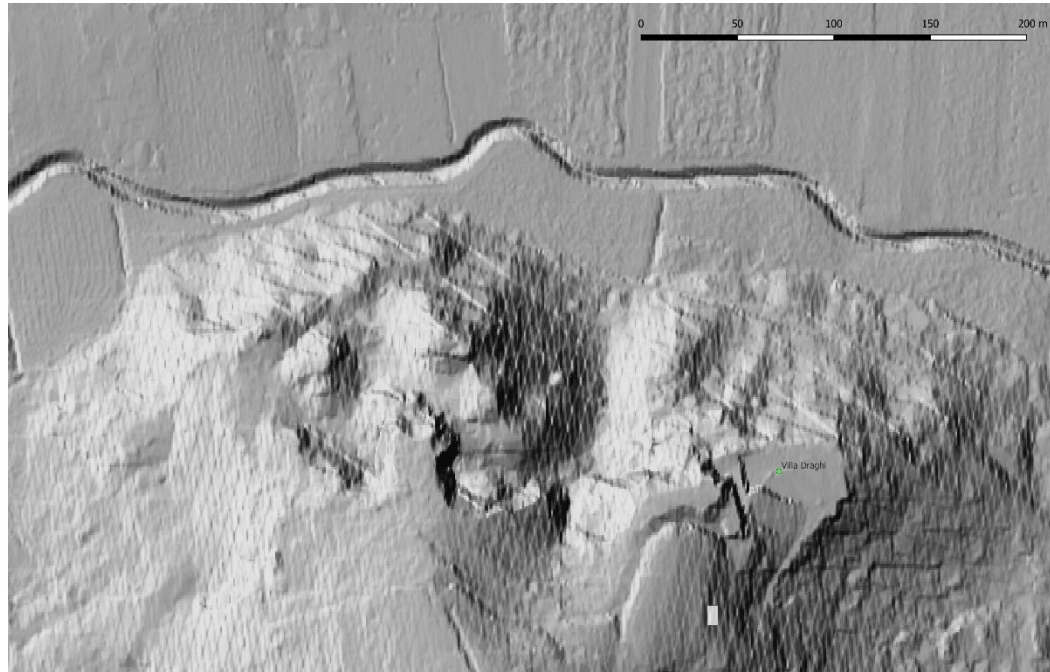
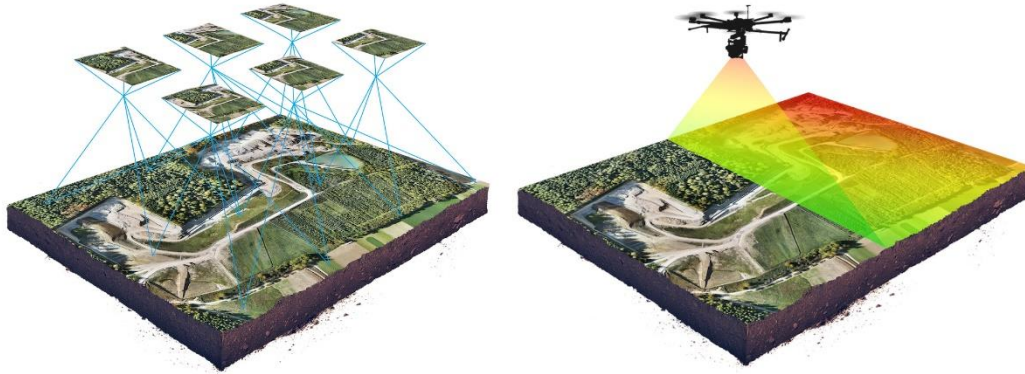
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# The Euganean Pozzolan

## In search of ancient quarries



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