SCIENCE & PAST

MASTERING MATERIALS TO KNOW OUR HERITAGE

Zaragoza February 1-3 2017

Studying ancient ceramics:

from the supply of raw materials to the laboratory

Elisabetta Gliozzo

The life of a pot

- **RAW MATERIALS SUPPLY AND PREPARATION**
- **SHAPING, COATING AND FIRING TECHNOLOGY**
- **DISTRIBUTION AND USE**
- **POST DEPOSITIONAL PROCESSES**
- **CONSERVATION AND RESTORATION**

Ceramic materials: the research

- **Significant research objectives**
  - **Production site, distribution site, available reference groups, local raw materials investigated…**
- **Representative sampling**
  - **Typology, stratigraphy, chronology, conservation state…**
- **Appropriate methodology**
  - **Destructive/ non destructive, bulk/superficial, chemical/mineralogical/….**
- **Rigorous presentation and interpretation of the results**
- **Dissemination (archaeology/archaeometry)**

Case 1. Building materials - production site

- **Research questions**
  - **Raw materials supply**
  - **Production technology**
  - **(Dating)**
- **Sampling criteria**
  - **Typology, stratigraphy, chronology → pottery**
  - **Typology, stratigraphy, chronology → kiln**
  - **Geology → 'local' clayey and sandy materials**

Both wastes and finished products !!!

Case 1. Building materials - production site

- **Analytical techniques**

  - **Destructive**
  - **Chemical**
  - **Mineralogical**
  - **Petrographic**
  - **Geotechnical tests**

Same for ceramics, kiln and raw materials !!!

Case 1. Building materials - production site

Bulk chemical analyses

1. **X-ray fluorescence (XRF)**
2. **Inductively coupled plasma mass spectroscopy (ICP-MS)**
3. **Neutron activation (NA)**

1	2	3
"Heavy" sample	"Light" sample	Also non-destr.
Widely available	Available	Scarcely available
Very fast	~Fast	Fast/slow
The cheapest	Not too expensive	Rather expensive

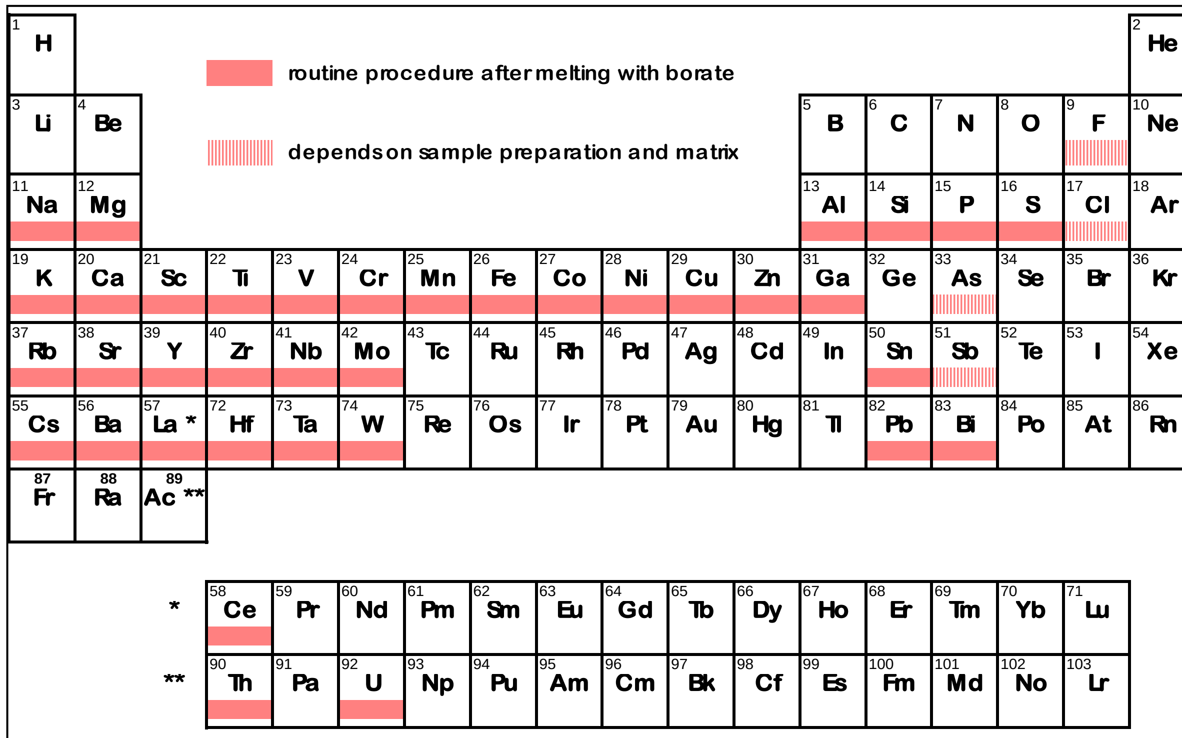
PRECISION & ACCURACY

Case 1. Building materials - production site

Heavy and light samples !!!

PRECISION & ACCURACY

XRF → From B to U
ICP-MS → From Li to U … no problem with light or trace elements! Lower detection limits (ppb) and higher accuracy than XRF



Case 1. Building materials - production site

PRECISION & ACCURACY

Estimated detection limits for INAA

Sensitivity (picograms)	**Elements**
1	Dy, Eu
1 - 10	In, Lu, Mn
10 - 100	Au, Ho, Ir, Re, Sm, W
100 - 10^3	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
10^3 -10^4	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
10^4 -10^5	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
10^5 -10^6	F, Fe, Nb, Ne
10^7	Pb, S

Mainly used for the determination of traces. Usually, it is necessary to use complementary techniques in order to determine the wt% of some elements (in particular some major elements, Pb and S).

Sample can remain radioactive for many years, requiring handling and <u>disposal protocols</u> for low-level to medium-level radioactive material.

Case 1. Building materials - production site

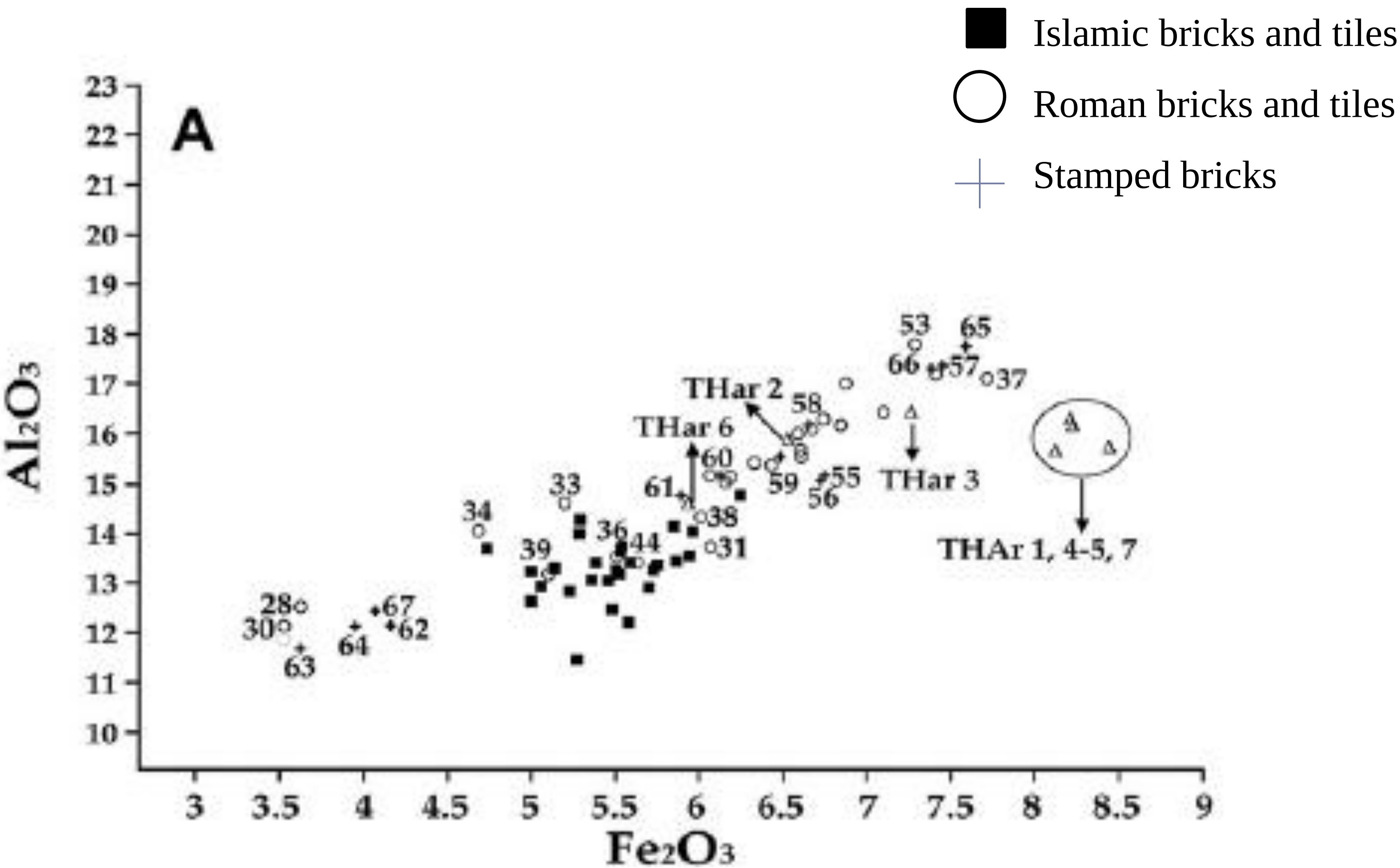
~Sand / Clay

Identity card

	Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	V	Cr	Co	Ni	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Pb	Ce	Th	U
Bricks	THI 55	56.71	0.83	14.89	6.63	0.07	2.23	13.90	0.77	2.00	0.24	1.56	164	163	18	50	105	86	355	28	168	17	308	25	22	52	10	3
	THI 56	57.80	0.81	14.91	6.66	0.07	1.98	13.83	0.77	1.95	0.25	0.80	161	160	18	51	110	87	356	28	169	17	303	33	18	68	9	3
	THI 57	53.77	0.89	16.42	7.05	0.08	2.21	11.01	0.60	2.12	0.48	5.20	154	149	21	56	102	90	339	27	165	17	487	27	31	84	11	2
	THI 58	54.24	0.83	15.69	6.45	0.08	2.53	14.21	0.68	1.97	0.31	2.85	130	145	18	53	108	59	362	27	173	16	468	25	25	70	10	2
	THI 59	55.22	0.78	14.51	6.06	0.07	2.04	12.38	0.63	1.50	0.25	6.41	131	129	16	47	91	74	286	25	181	15	511	26	24	54	9	2
	THI 60	51.97	0.73	13.62	5.50	0.07	2.18	13.49	0.47	1.50	0.32	9.99	114	116	16	45	85	64	319	24	180	14	688	27	25	50	9	2
	THI 61	53.70	0.72	13.49	5.39	0.07	2.17	13.63	0.56	1.43	0.31	8.39	115	117	15	42	86	66	294	24	177	14	423	24	24	57	8	2
	THI 62	50.63	0.49	10.98	3.76	0.11	1.85	20.81	0.42	1.20	0.14	9.50	73	98	19	49	70	74	195	27	125	10	380	21	19	40	7	3
	THI 63	45.87	0.54	9.81	3.04	0.03	1.33	21.32	0.27	1.52	0.24	15.91	62	75	10	25	44	46	216	19	163	10	410	13	26	35	7	2
	THI 64	49.22	0.46	10.72	3.49	0.12	1.82	20.83	0.41	1.09	0.18	11.54	69	85	12	47	71	66	219	26	121	9	343	22	19	38	8	2
	THI 65	53.34	0.89	16.73	7.15	0.07	2.09	10.94	0.69	2.17	0.20	5.57	165	154	27	54	113	94	309	27	144	17	383	34	23	43	10	3
	THI 66	56.03	0.88	17.17	7.32	0.07	2.49	11.60	1.09	2.33	0.19	0.67	183	161	22	58	109	98	322	28	159	18	314	27	17	74	11	3
	THI 67	52.82	0.57	11.36	3.72	0.05	2.89	17.36	1.05	1.31	0.22	8.50	65	86	15	29	66	76	361	25	181	13	436	18	24	26	10	2
Clays	THar 1	63.20	0.90	14.49	7.53	0.14	1.14	4.01	0.24	0.98	0.13	7.11	140	82	115	48	68	82	87	27	221	14	364	35	40	80	9	2
	THar 2	49.99	0.69	13.61	5.60	0.07	1.51	11.99	0.47	1.71	0.19	14.05	114	77	75	43	86	74	239	21	155	11	286	21	25	52	7	1
	THar 3	51.86	0.73	14.26	6.31	0.07	1.53	9.69	0.45	1.80	0.21	12.95	123	83	80	47	97	83	214	22	162	12	292	30	27	63	8	1
	THar 4	62.92	0.87	14.90	7.59	0.09	1.41	3.09	0.27	1.08	0.12	7.53	139	83	105	47	68	83	87	27	221	14	305	36	37	77	8	2
	THar 5	65.58	0.88	15.18	7.66	0.08	1.09	1.61	0.28	0.91	0.10	6.51	144	94	100	44	59	77	73	27	236	14	278	36	36	89	8	2
	THar 6	57.96	0.66	13.23	5.39	0.07	1.32	9.78	0.53	1.56	0.34	9.03	106	72	85	38	75	60	146	19	232	9	239	27	34	54	5	1
	THar 7	64.42	0.90	14.66	7.89	0.06	1.48	2.72	0.39	0.90	0.06	6.38	131	94	100	46	66	82	102	28	238	14	294	38	36	62	8	2

- Marine
- Lacustrine
- Fluvial

Case 1. Building materials - production site



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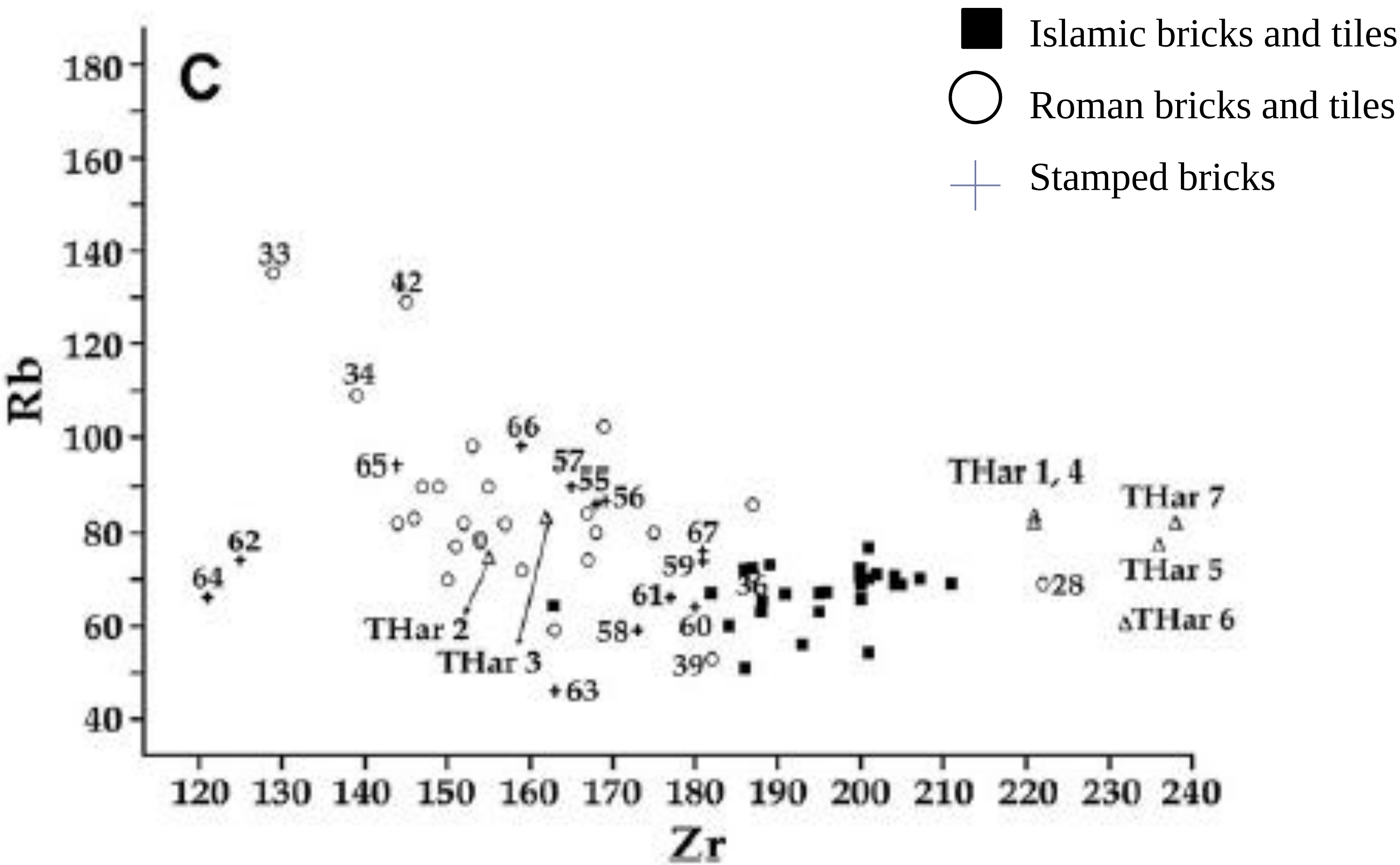
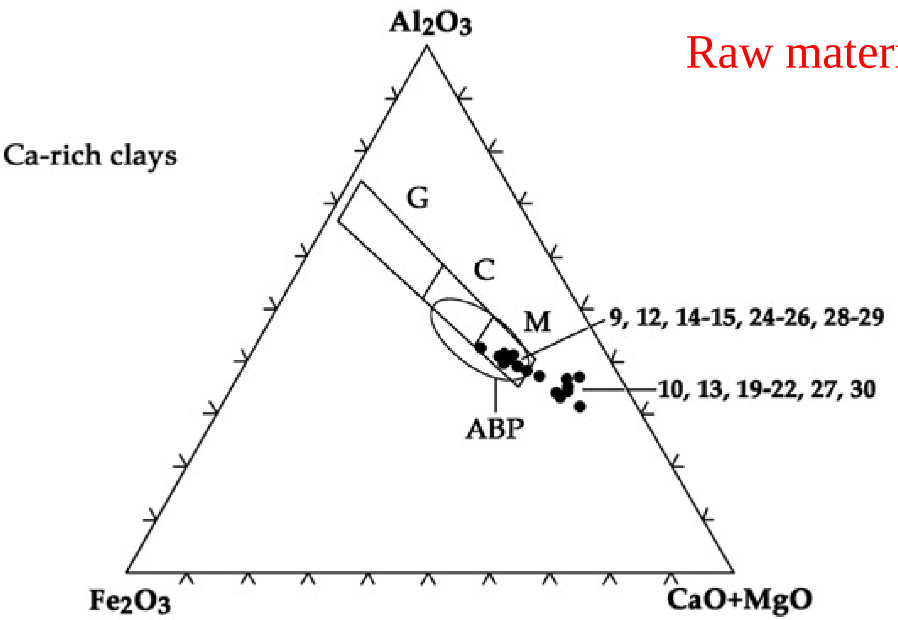
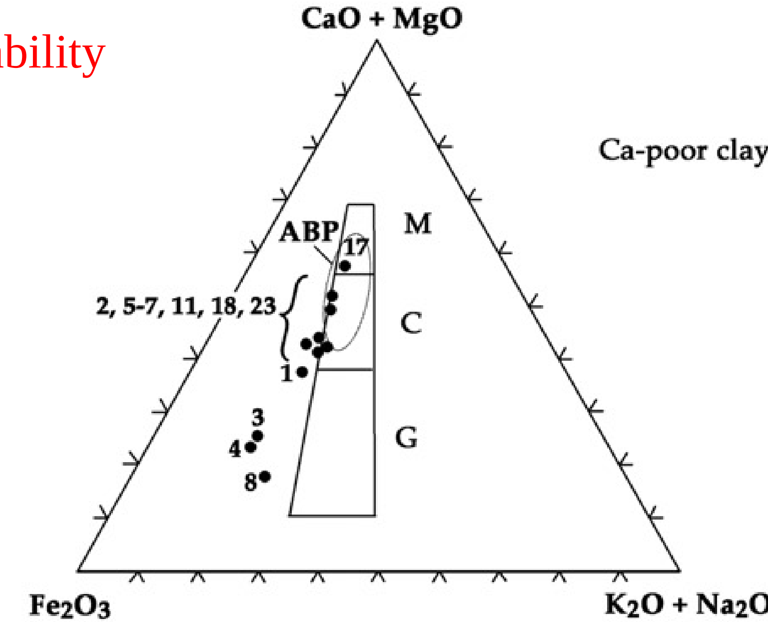


Case 1. Building materials - production site

Raw materials suitability

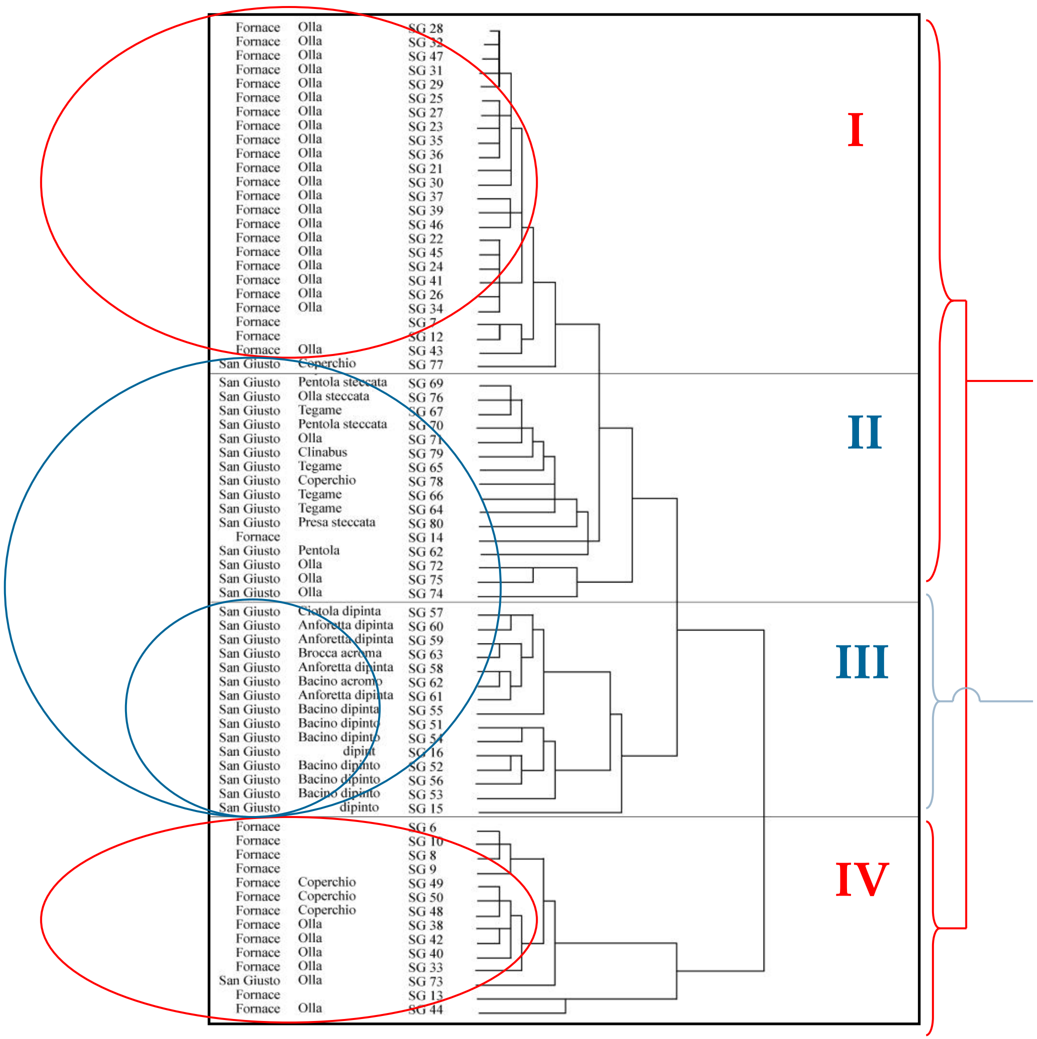




Ternary diagrams after Vincenzini and Fiori (1976).
M stands for majolica, C for cottoforte (i.e. semigres) and G for gres

Qualitative 'opinions' on ancient craftsmen skills!
"High/low technological level" → what does it mean?

Case 1. Building materials - production site



Qtz, Sa, Pl, cpx, amph., micas, Fe- Ti- oxides, opaques, primary and secondary calcite, Volcanic lithic fragments.

Qtz, Kfs, Pl, Micas, Fe-Ti-oxides, secundary calcite Sandstone

Case 1. Building materials - production site

Mineralogical and petrographic analyses

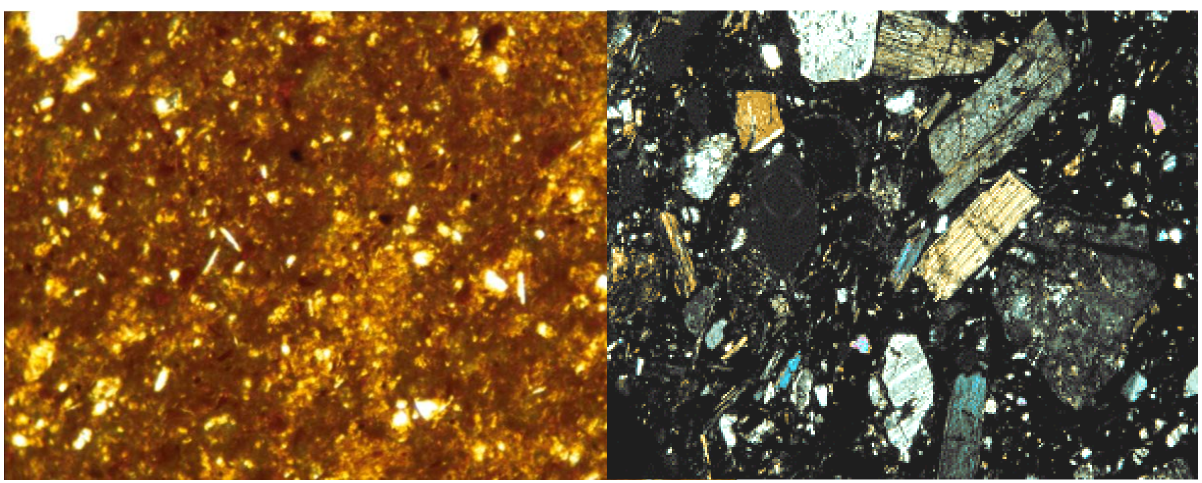
1. **Optical microscopy (OM)**
2. **X-ray diffraction (XRD)**

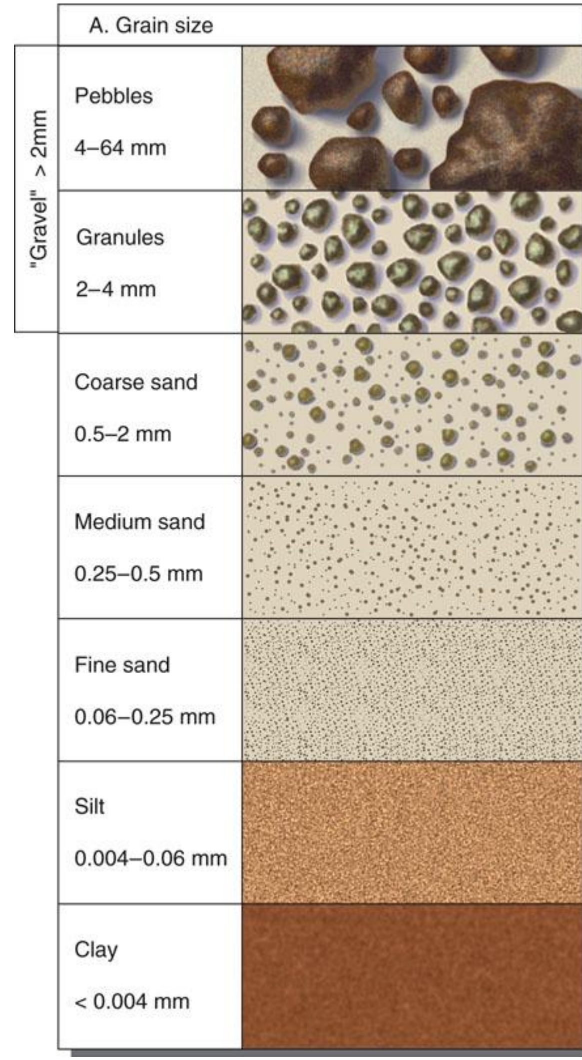
} **complementary**

1		2
Destructive		**Destr. / non-destr.**
"Heavy" sample		**"Light" sample**
Layer	⟷	**Bulk**
Widely available		**Widely available**
Time consuming		**Fast (qualitative)**
(Very cheap)		**Relatively cheap**

Case 1. Building materials - production site

- Optical microscopy - Textural features
  - Clayey/sandy matrix
  - Grain size
  - Roundness, sphericity
  - Orientation
  - Porosity





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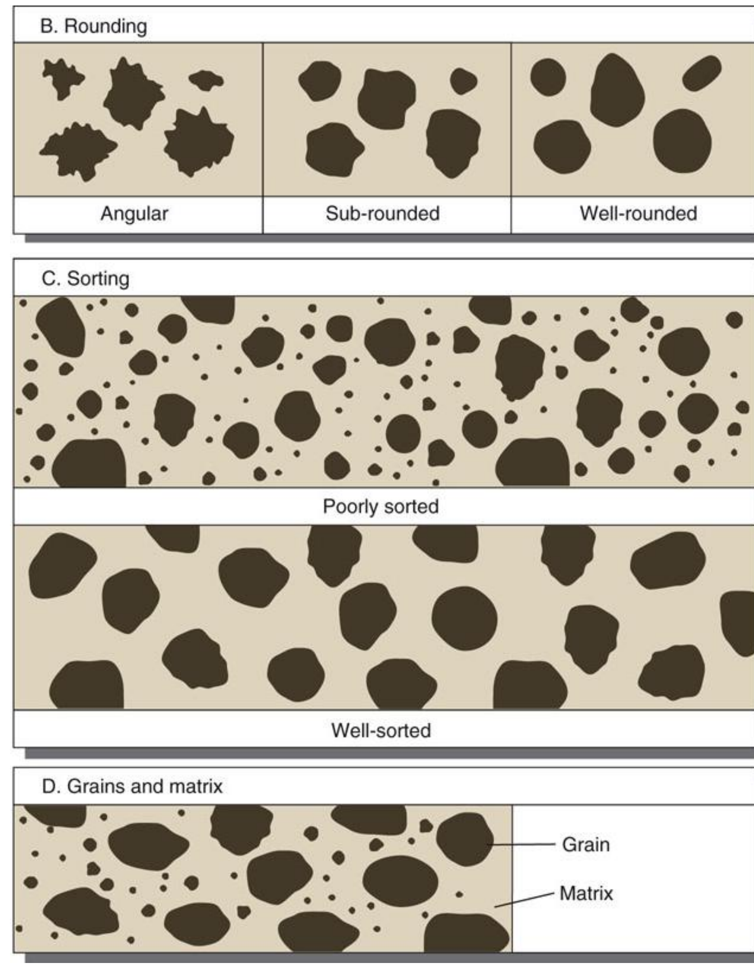

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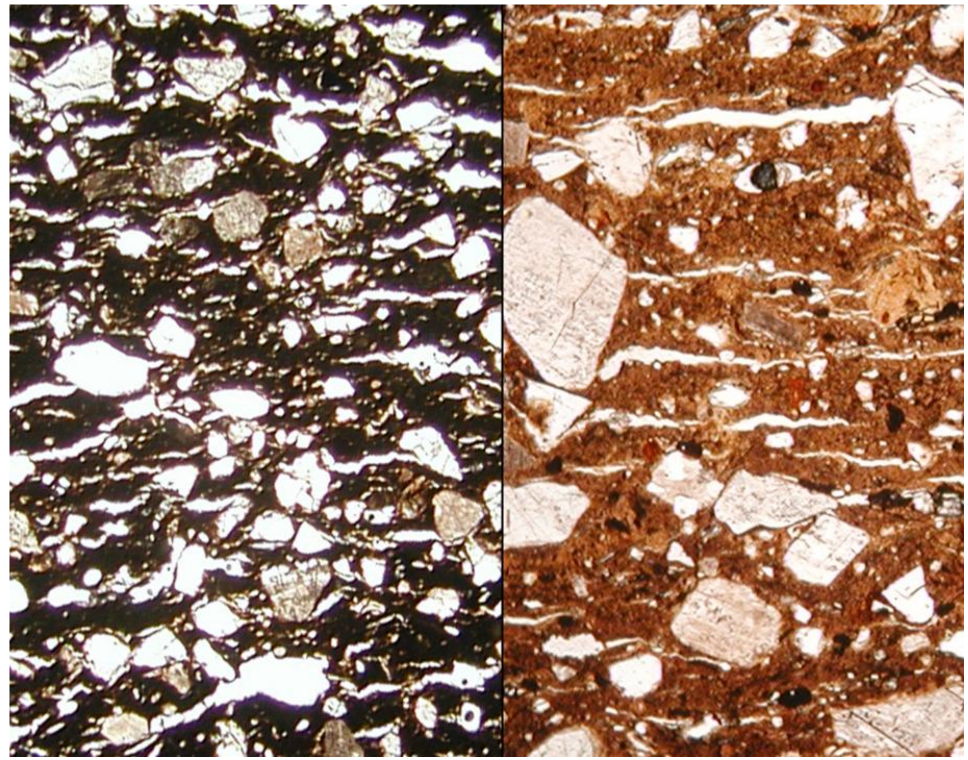
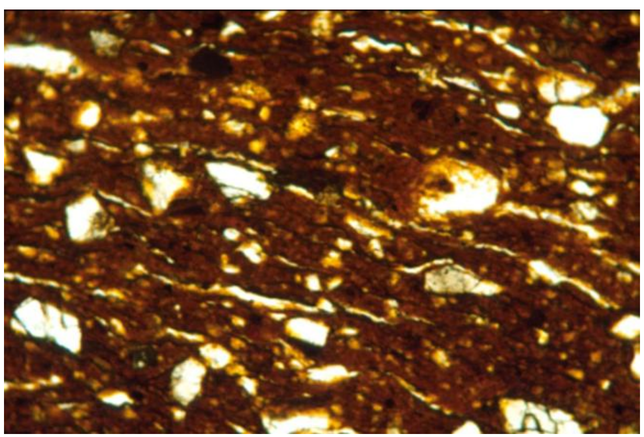


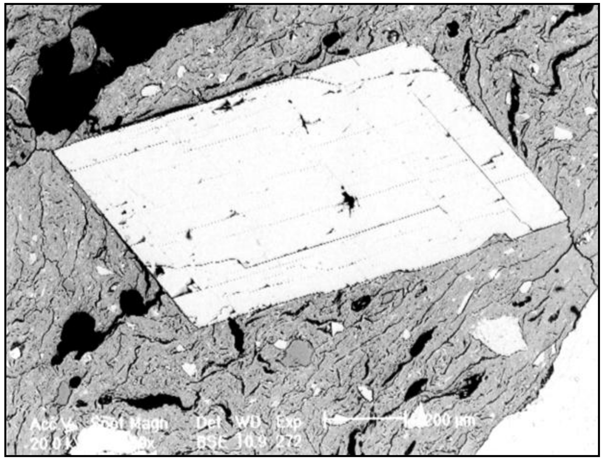


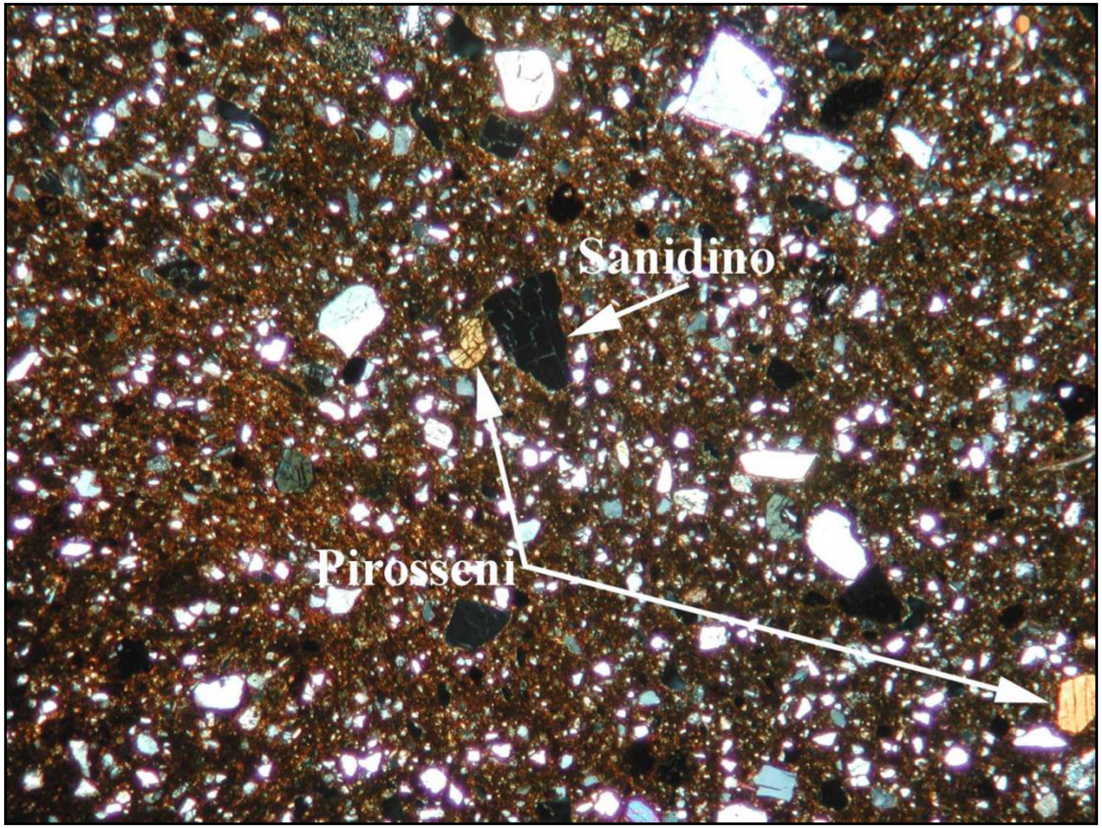
Case 1. Building materials - production site

- Optical microscopy - Qualitative and quantitative characterization of **mineralogical phases**, lithic fragments and microfauna
  - Phases %
  - Natural inclusions

  vs. temper

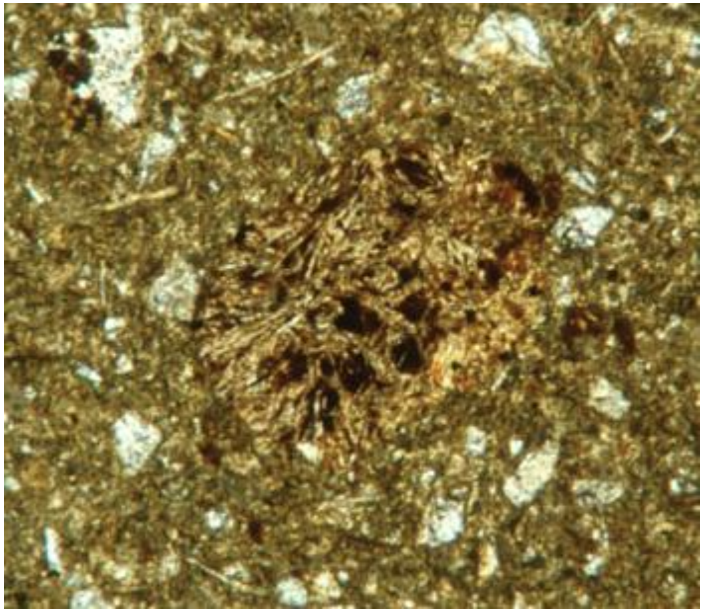
Sparry calcite (SEM-EDS)

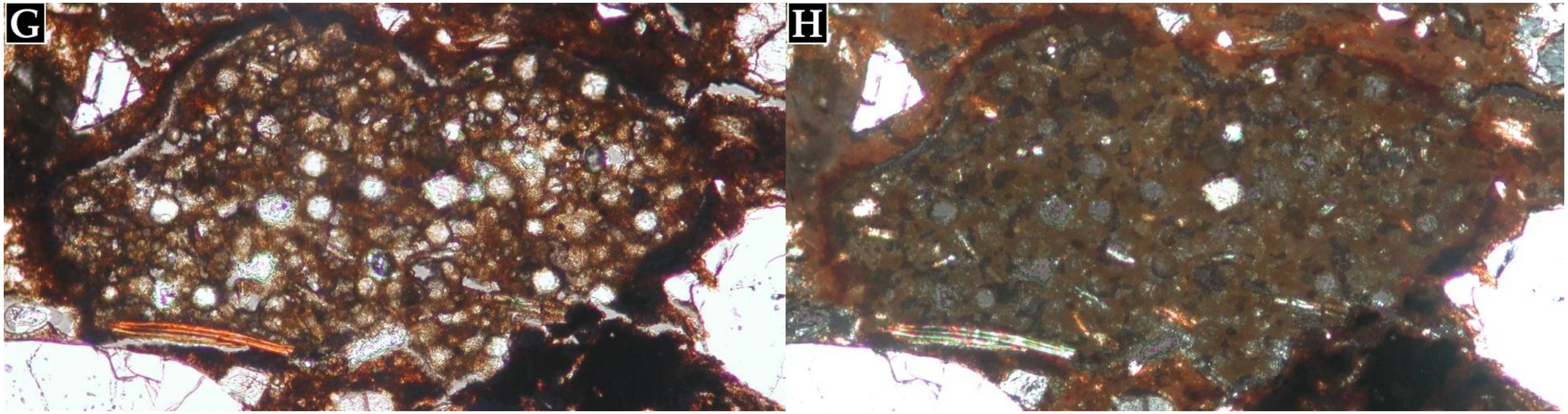




Case 1. Building materials - production site

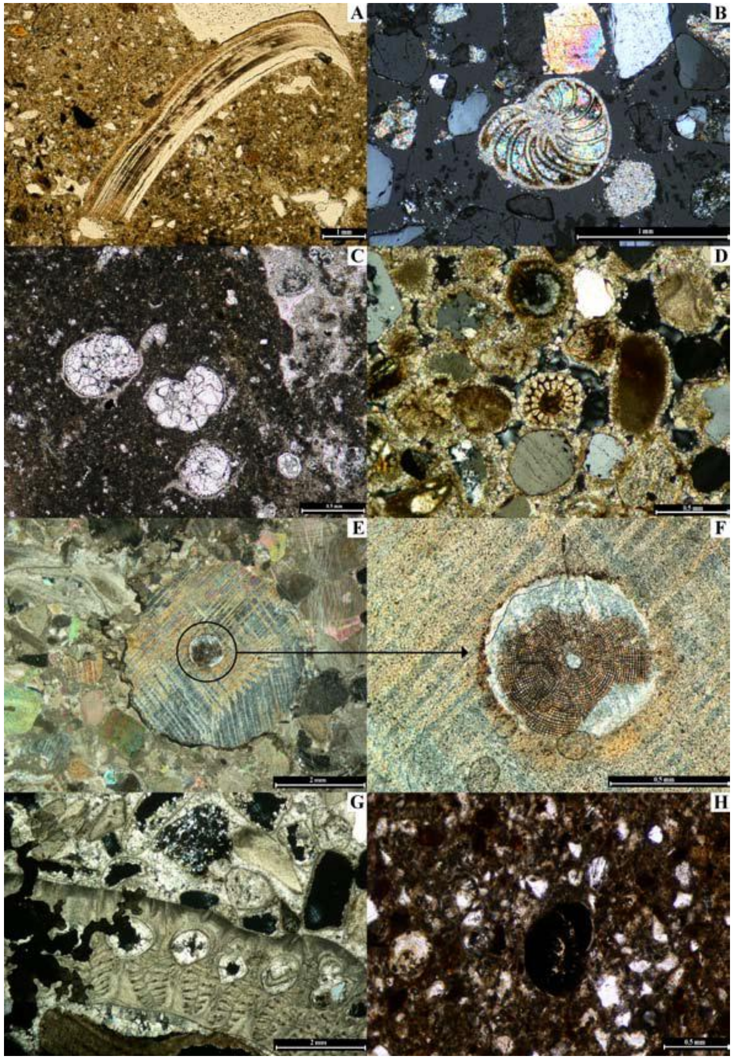
- Optical microscopy - Qualitative and quantitative characterization of mineralogical phases, **<u>lithic fragments</u>** and microfauna





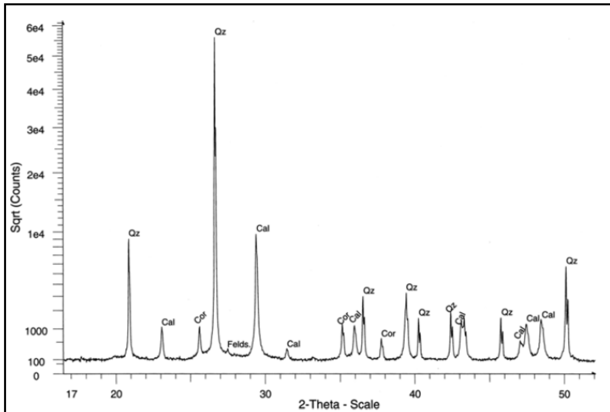
Case 1. Building materials - production site

- Optical microscopy - Qualitative and quantitative characterization of mineralogical phases, lithic fragments and **microfauna**

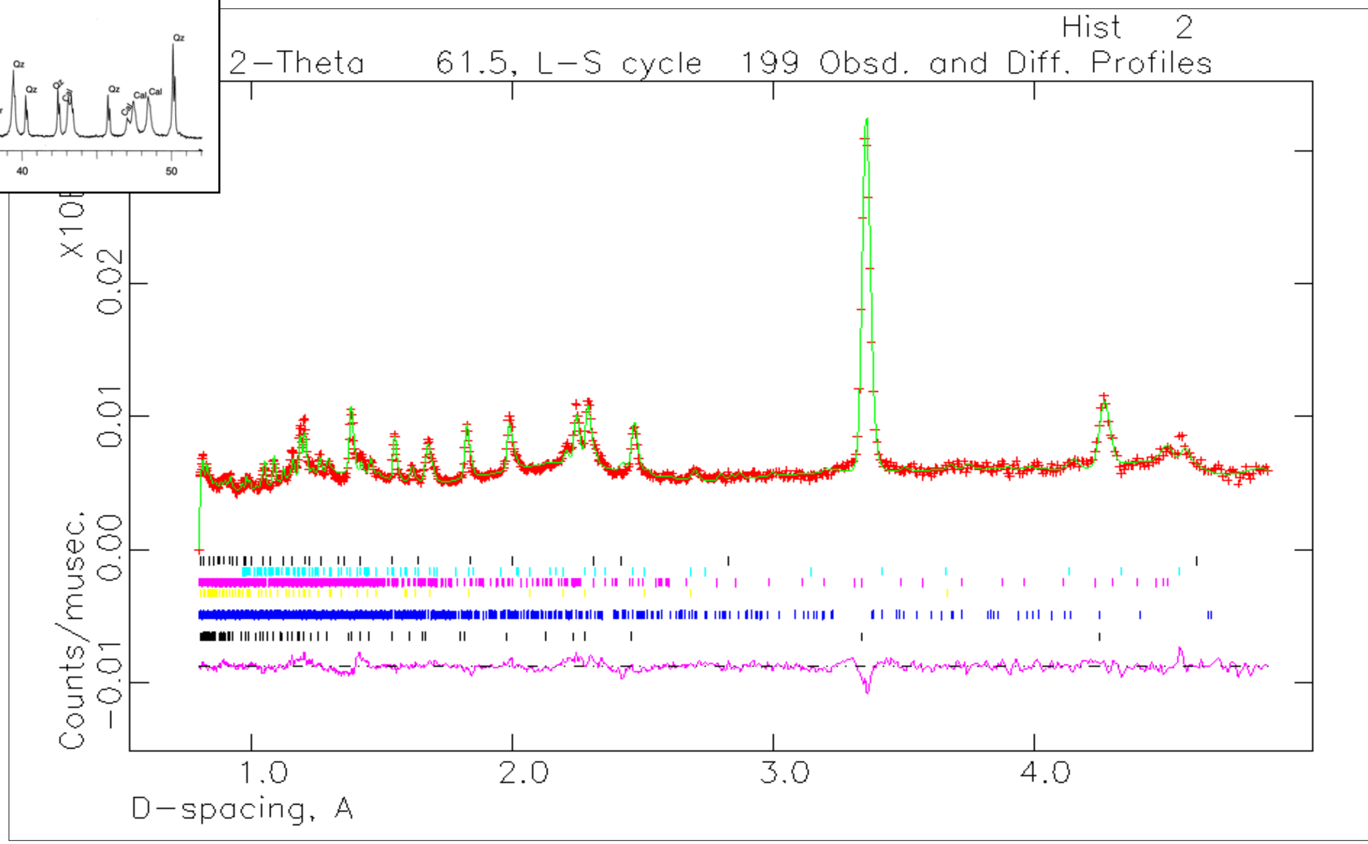


a) Mollusc;
b) Benthic (i.e. live on or within the seafloor sediment) foraminifer *Nonion boueanum*
c) Plactonic (i.e. floaters in the water column at various depths) foraminifera
d) Echinid
e) Echinid with a foraminifer in the nucleus
f) =
g) Briozoa
h) Benthic foraminifer substituted by iron oxides

Case 1. Building materials - production site



Quartz: 83%
Hematite 5 %
Plagioclase: 12 %
Small amounts of mica



Qualitative

Quantitative

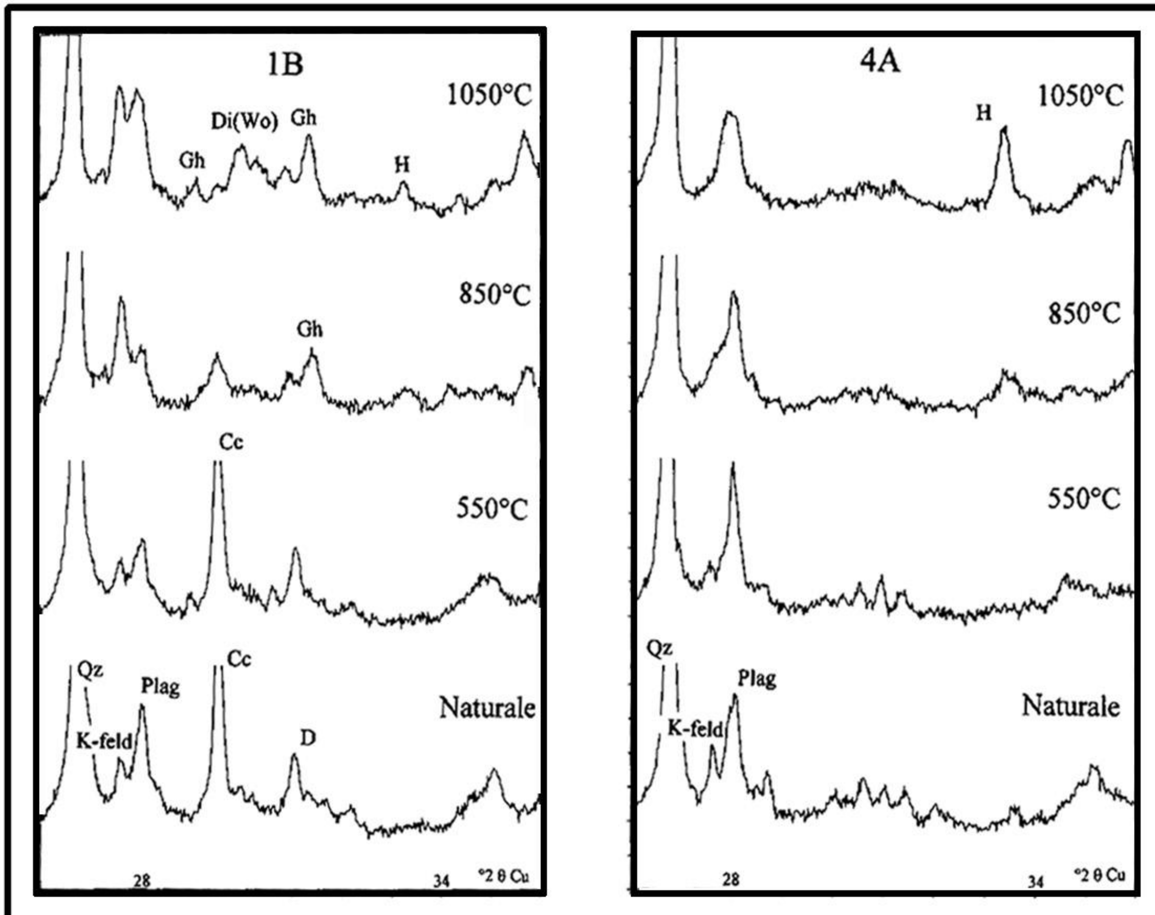
Case 1. Building materials - production site

Diffrattogrammi RX dei campioni 1B e 4A; dal basso verso l'alto sono riportate: l'argilla di partenza e le successive cotture a 550, 850, 1050°C.

Qz=quarzo
K-feld=feldspato potassico
Plag=plagioclasi
Gh=gehlenite
Di(Wo)=diopside (wollastonite)
H=ematite
C=calcite
D=dolomite

FIRING TEMPERATURES

Ca-rich clay **Ca-poor clay**

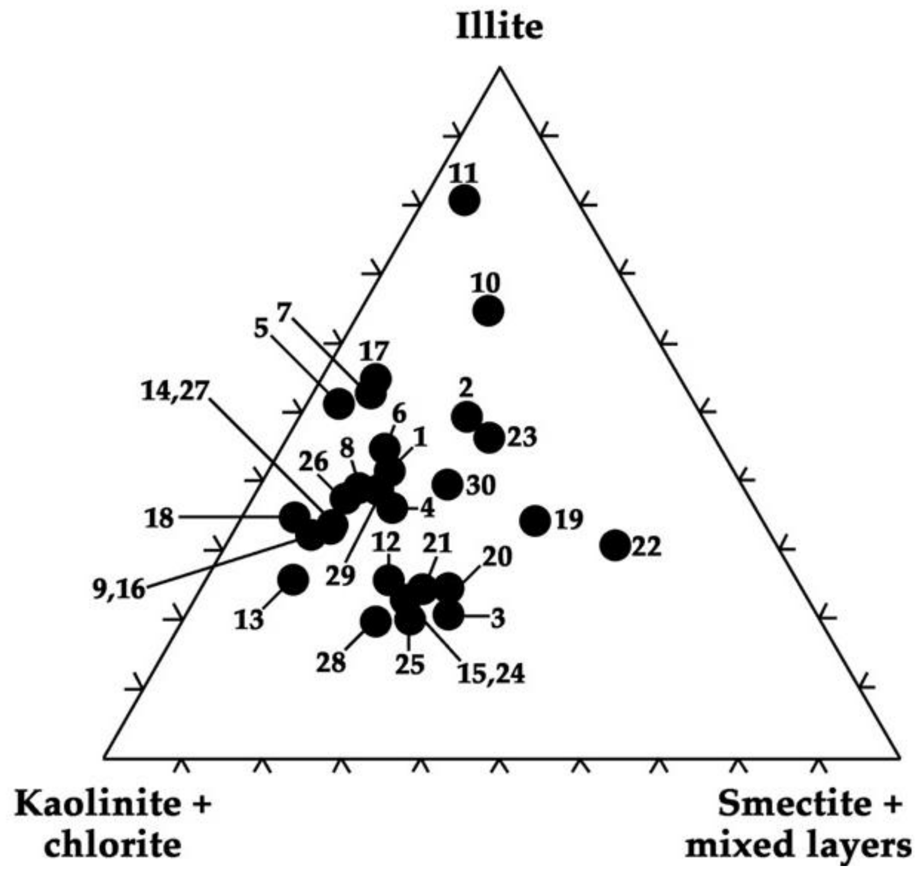


Duminuco, Riccardi, Messiga, Setti (1996). *Ceramurgia* (5), 281-288.

Case 1. Building materials - production site

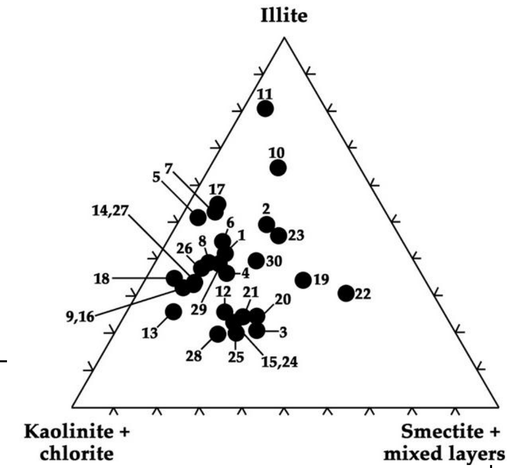
The clay-size fraction assemblages is determined using oriented samples. The clay fraction (below 2 μm) is isolated in settling tubes by gravity sedimentation, following Stokes' law.
Clay samples are placed on glass slides and allowed to dry in order to make oriented samples and XRD patterns are taken after air drying and glycol solvation.
The samples are X-rayed in the range 4–40°2θ with a step size of 0.02°2θ and a measuring time of 2 s/step. Additionally, the range 27.5–30.6°2θ is measured with a step size of 0.01°2θ and a measuring time of 4 s/step in order to better resolve the peaks of kaolinite and chlorite (Biscaye, 1965).

Phase analyses on the clay fraction



Case 1. Building materials - production site

Phase analyses on the clay fraction



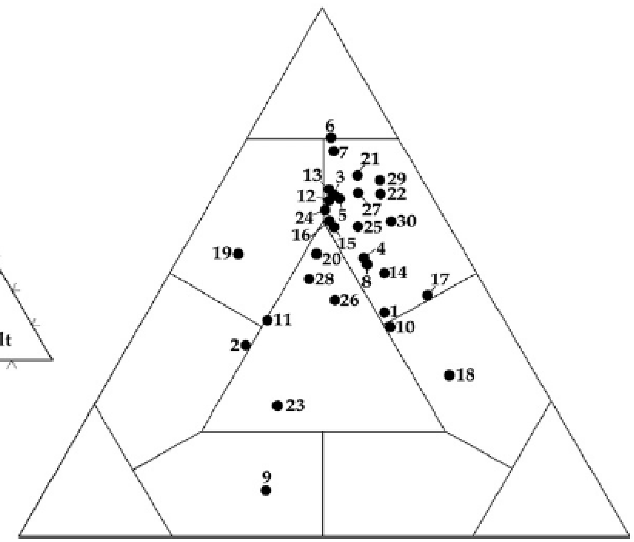
CLAY MINERALS BEHAVIOUR

Illite **Chlorite** **Kaolinite**	**Relatively coarsed grain, non expandable**
Chlorite-Vermiculite **Illite-Smectite**	**Fine grained, expandable, increase plasticity**
Smectite **Vermiculite**	**Fine grained, highly expandable, greatly increase plasticity**

Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

	Sample # 	Sand wt.%	Silt wt.%	Clay wt.%
1	1	19	39	43
	4	17	30	52
	10	19	41	40
	11	38	20	41
	15	19	22	59
	23	45	30	25
	26	26	29	45
2	2	45	19	37
	3	16	19	65
3	5	15	20	63
	6	11	13	74
	7	12	15	73
4	8	17	31	51
	9	55	36	9
	14	15	35	50
	17	10	44	46
	18	14	55	31
5	12	17	19	64
	13	16	18	66
	16	19	21	60
	19	37	9	54
	20	24	22	54
	21	10	21	68
	22	8	27	66
	24	19	19	62
	25	15	26	59
	27	12	23	66
	28	28	23	49
	29	7	25	68
	30	9	31	60



Particle size distribution. The classification used here is that of Shepard (1954) (shown on the left) with the sand, silt, and clay-size fractions based on the Wentworth (1922) scale.

Case 1. Building materials - production site

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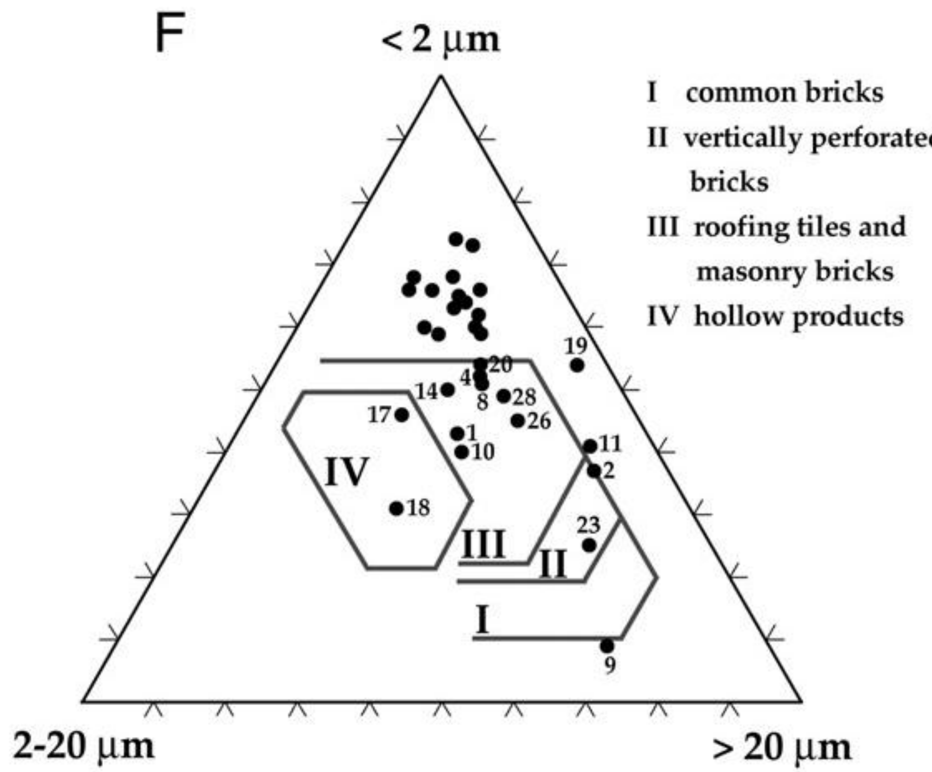
2	2	45	19	37
	3	16	19	65
3	5	15	20	63
	6	11	13	74
	7	12	15	73
4	8	17	31	51
	9	55	36	9
	14	15	35	50
	17	10	44	46
	18	14	55	31
5	12	17	19	64
	13	16	18	66
	16	19	21	60
	19	37	9	54
	20	24	22	54
	21	10	21	68
	22	8	27	66
	24	19	19	62
	25	15	26	59
	27	12	23	66
	28	28	23	49
	29	7	25	68
	30	9	31	60

Particle size distribution



Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

LDS mm
10.0
10.7
7.3
6.4
13.5
8.5
10.7
11.4
15.0
10.7
13.6
13.6
13.5
3.5
9.2
9.2
7.0
10.0
12.2
12.3
10.2
12.0
13.1
15.1
12.1
11.4
13.4
11.4
12.4
11.7

ATTERBERG LIMITS

Linear shrinkage limit → The boundary between the semi-solid and solid states.

The maximum water content at which the reduction in water content will not cause decrease in total volume of soil but the increase in moisture content will cause an increase in moisture content.
http://www.aboutcivil.org/atterberg-limits.html

Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

LL wt.%
49
52
41
44
64
42
59
39
66
60
69
66
58
31
48
49
40
57
60
59
53
55
64
78
60
63
67
61
63
58

ATTERBERG LIMITS

Liquid limit → The boundary between the liquid and plastic states (i.e. the water content at which the behavior of a clayey soil changes from plastic to liquid)

The moisture content at which it takes 25 drops of the Casagrande cup to cause the groove to close over a distance of 13.5 millimetres (0.53 in) is defined as the liquid limit. (http://expeditionworkshed.org/workshed/liquid-and-plastic-limit-tests/)

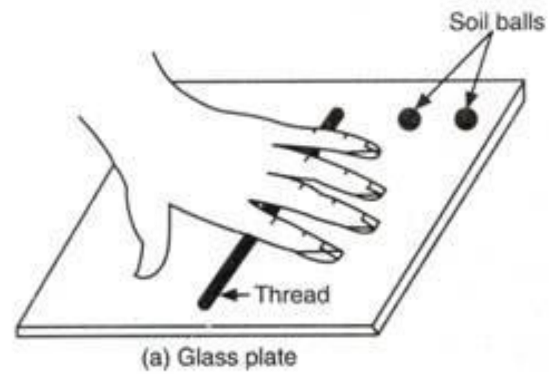
Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

PL
wt.%
24
23
16
17
26
22
30
16
26
24
20
21
22
17
20
20
18
25
20
26
19
22
22
27
26
29
22
29
27
24

ATTERBERG LIMITS

Plastic limit → The boundary between the plastic and semi-solid states.

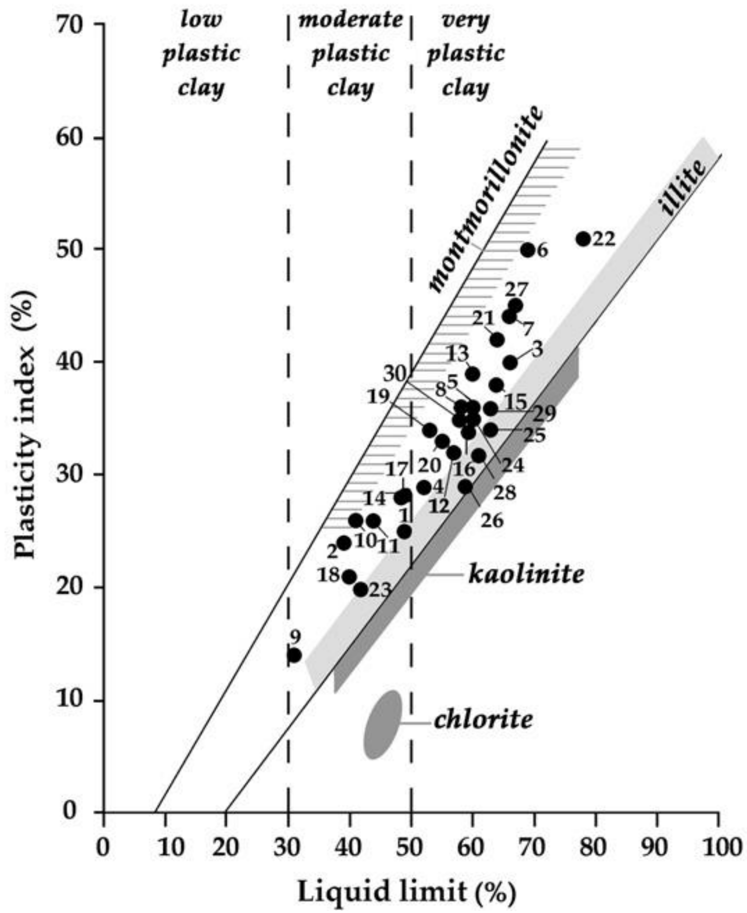


The water content at which the soil begins to crumble when rolled into threads of specified size. The Plastic Limit, also known as the lower plastic limit, is the water content at which a soil changes from the plastic state to a semisolid state.

Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

LL	PL
wt.%	wt.%
49	24
52	23
41	16
44	17
64	26
42	22
59	30
39	16
66	26
60	24
69	20
66	21
58	22
31	17
48	20
49	20
40	18
57	25
60	20
59	26
53	19
55	22
64	22
78	27
60	26
63	29
67	22
61	29
63	27
58	24



Plasticity chart

Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)

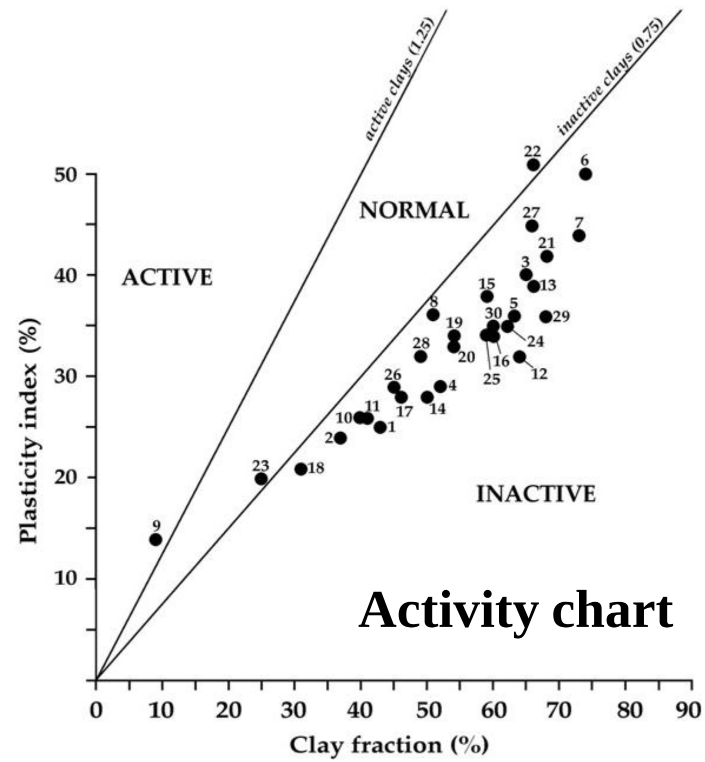
Ip wt.%	A	
25	0.59	Inactive
29	0.55	Inactive
26	0.64	Inactive
26	0.64	Inactive
38	0.66	Inactive
20	0.80	Normal
29	0.65	Inactive
24	0.64	Inactive
40	0.61	Inactive
36	0.56	Inactive
50	0.67	Inactive
44	0.61	Inactive
36	0.70	Inactive
14	1.57	Active
28	0.54	Inactive
28	0.62	Inactive
21	0.69	Inactive
32	0.51	Inactive
39	0.60	Inactive
34	0.56	Inactive
34	0.63	Inactive
33	0.61	Inactive
42	0.62	Inactive
51	0.78	Normal
35	0.56	Inactive
34	0.57	Inactive
45	0.68	Inactive
32	0.65	Inactive
36	0.53	Inactive
35	0.58	Inactive

Plasticity Index (PI)

The range of water content over which a soil exhibits plastic properties.

Plasticity index =
Liquid Limit – Plastic Limit

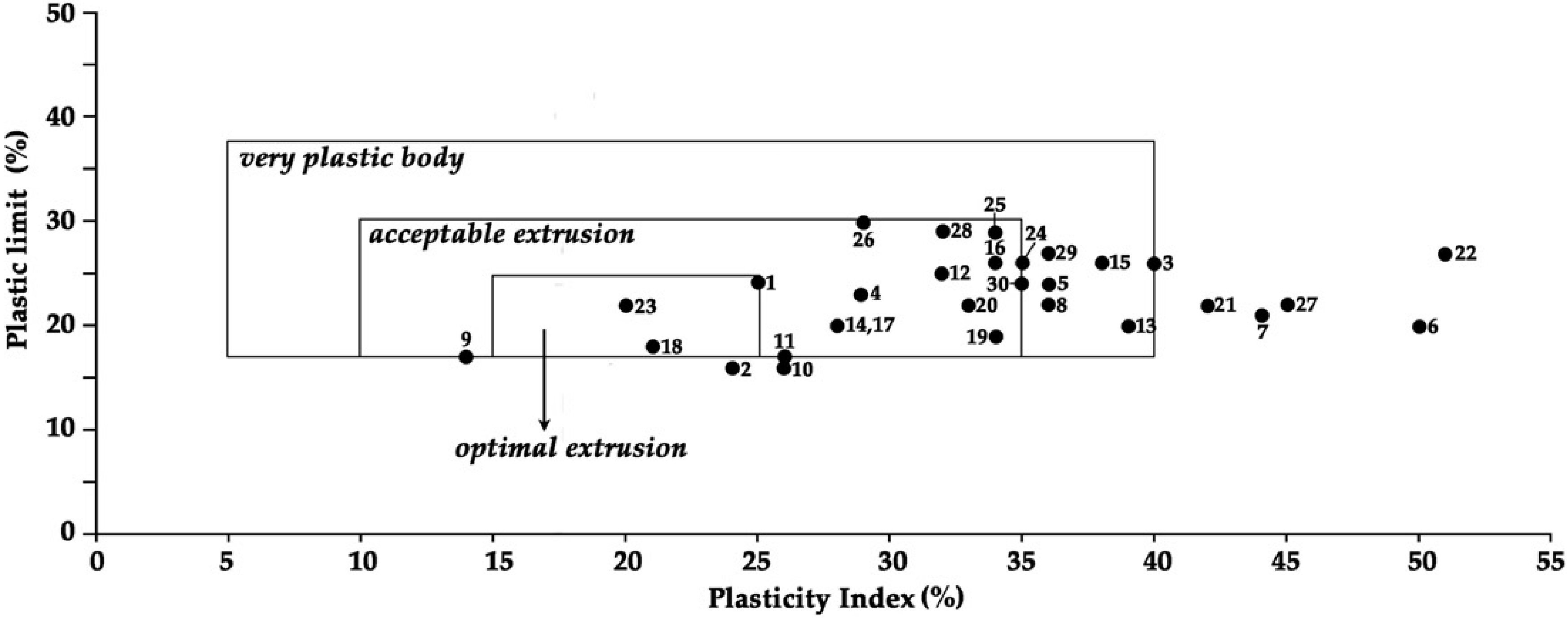
$$I_p = LL - PL$$



Activity chart

Case 1. Building materials - production site

Geotechnical analyses and tests (ceramics and clays)



Classification of moulding behaviour after Marsigli and Dondi (1997).

Case 2. Coated fine ware - distribution site

- Research questions
  - **Local production or import?**
  - **Trade routes**
  - **Production technology – ceramic body and coating**
- Sampling criteria
  - **Typology, stratigraphy, chronology → pottery**
  - **Geology → ‘local’ clayey ~~and sandy~~ materials**

Case 2. Coated fine ware - distribution site

Analytical techniques

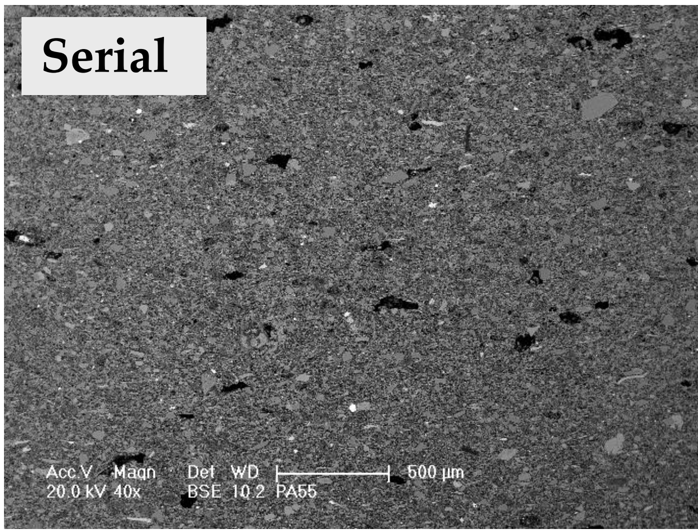
1. Optical microscopy (OM)…………………………………… B (C)
2. Scanning electron microscopy (SEM-EDS) ……..…………………..…. B C
3. Trasmission electron microscopy (TEM) ……………………….. C
4. X-ray fluorescence (XRF) + portable XRF ……………………….. B C
5. Inductively coupled plasma mass spectroscopy (ICP-MS) …….….. B
6. Neutron activation (NA) ……………………………………..…. B
7. X-ray diffraction (XRD) ……………………………………. B C
8. Syncrothron radiation X-ray diffraction (SR-XRD) …………..…. C
9. Neutron diffraction (ND) ……………………………………. B
10. X-ray absorption spectroscopy (XAS) …………………………. C

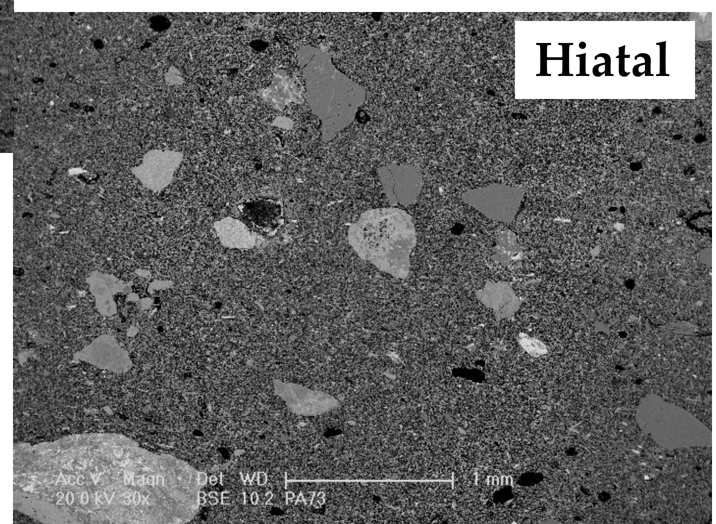
Case 2. Coated fine ware - distribution site

Scanning electron microscopy

Texture – clay body

The observation is not influenced by colours!!





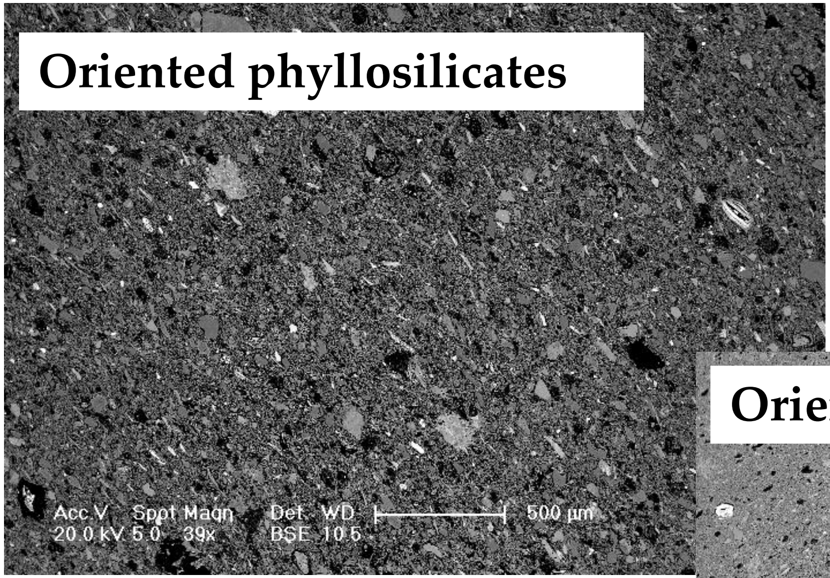
What does it tell you?

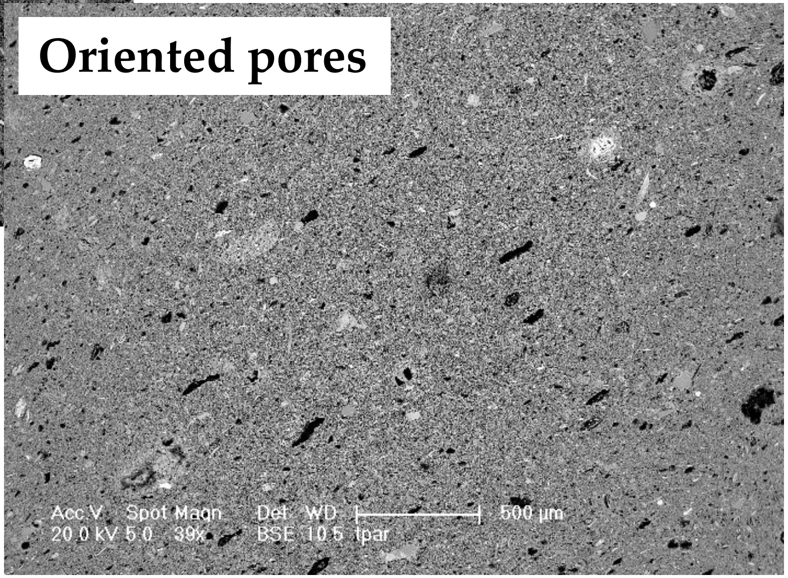
- supply materials, tempering

Information already achieved by OM

Case 2. Coated fine ware - distribution site

Scanning electron microscopy





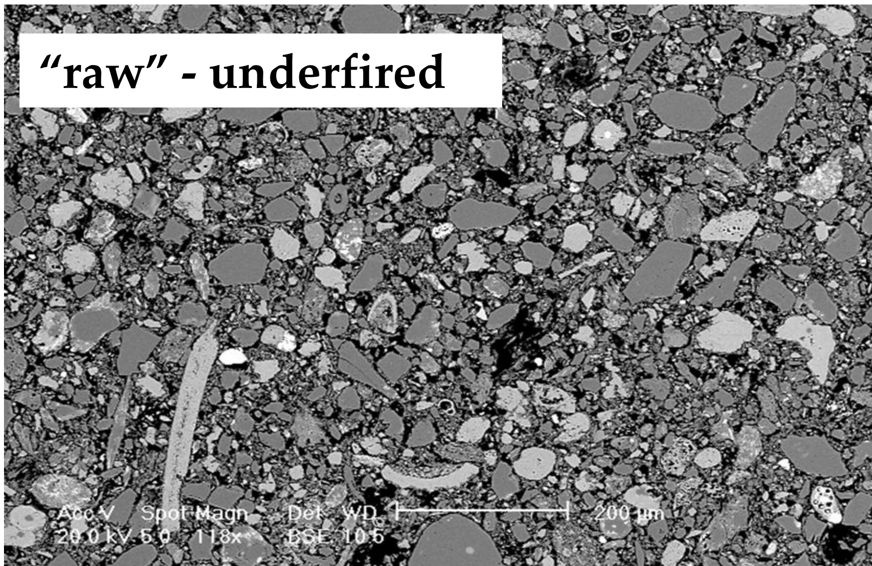
What does it tell you?

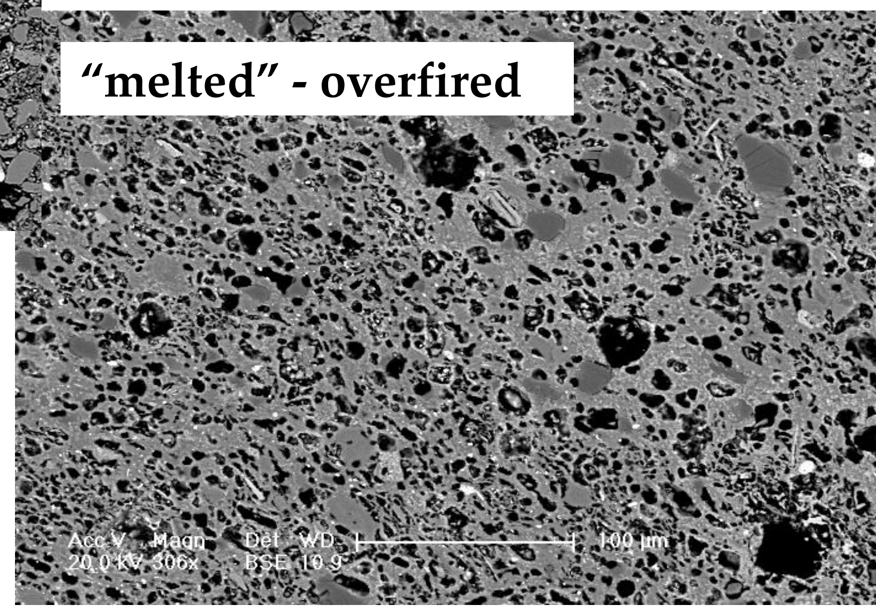
-production technology

Information already achieved by OM

Case 2. Coated fine ware - distribution site

Scanning electron microscopy





What does it tell you?

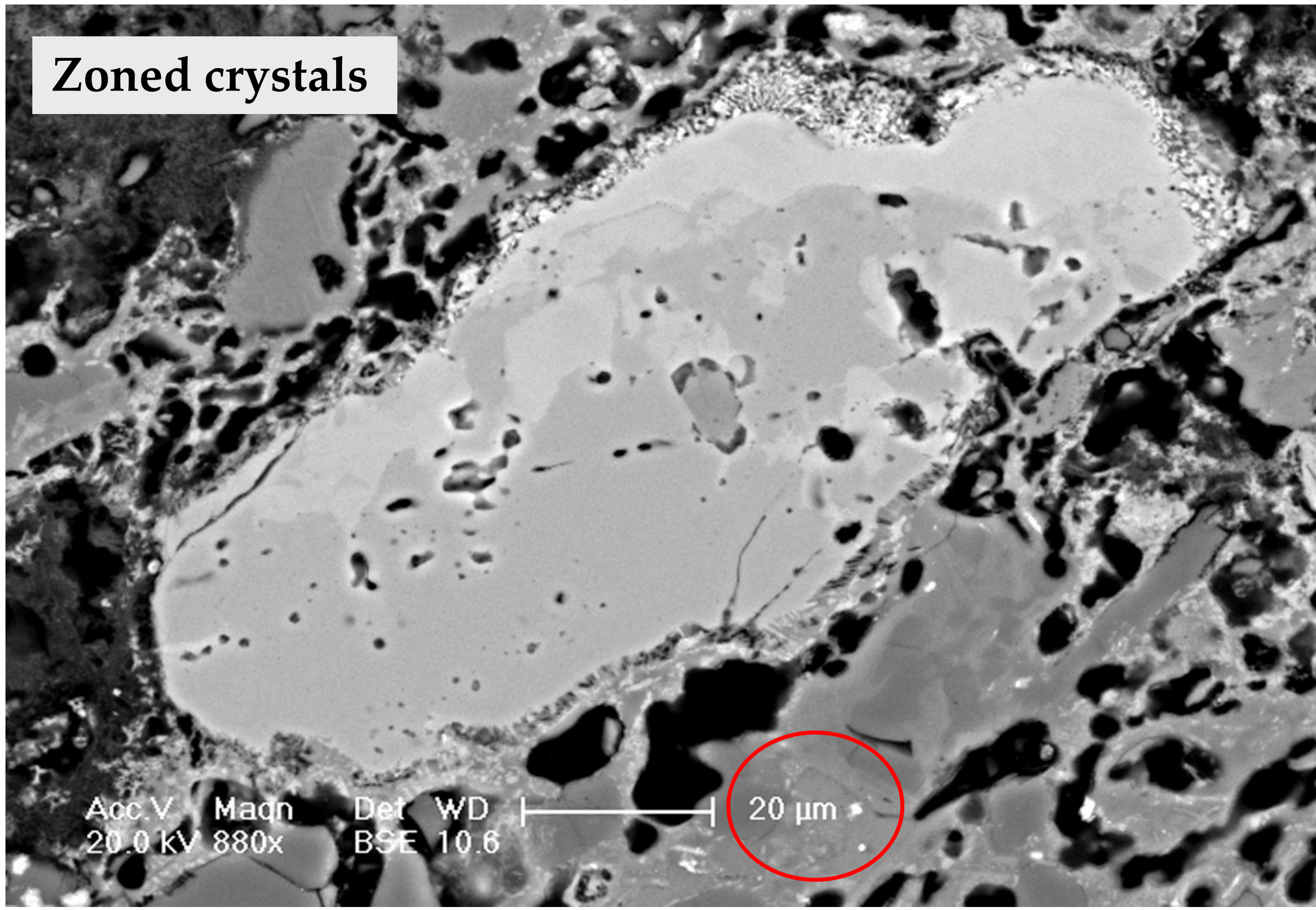
-sintering

Case 2. Coated fine ware - distribution site

Scanning electron microscopy

Zonation

Reaction rims

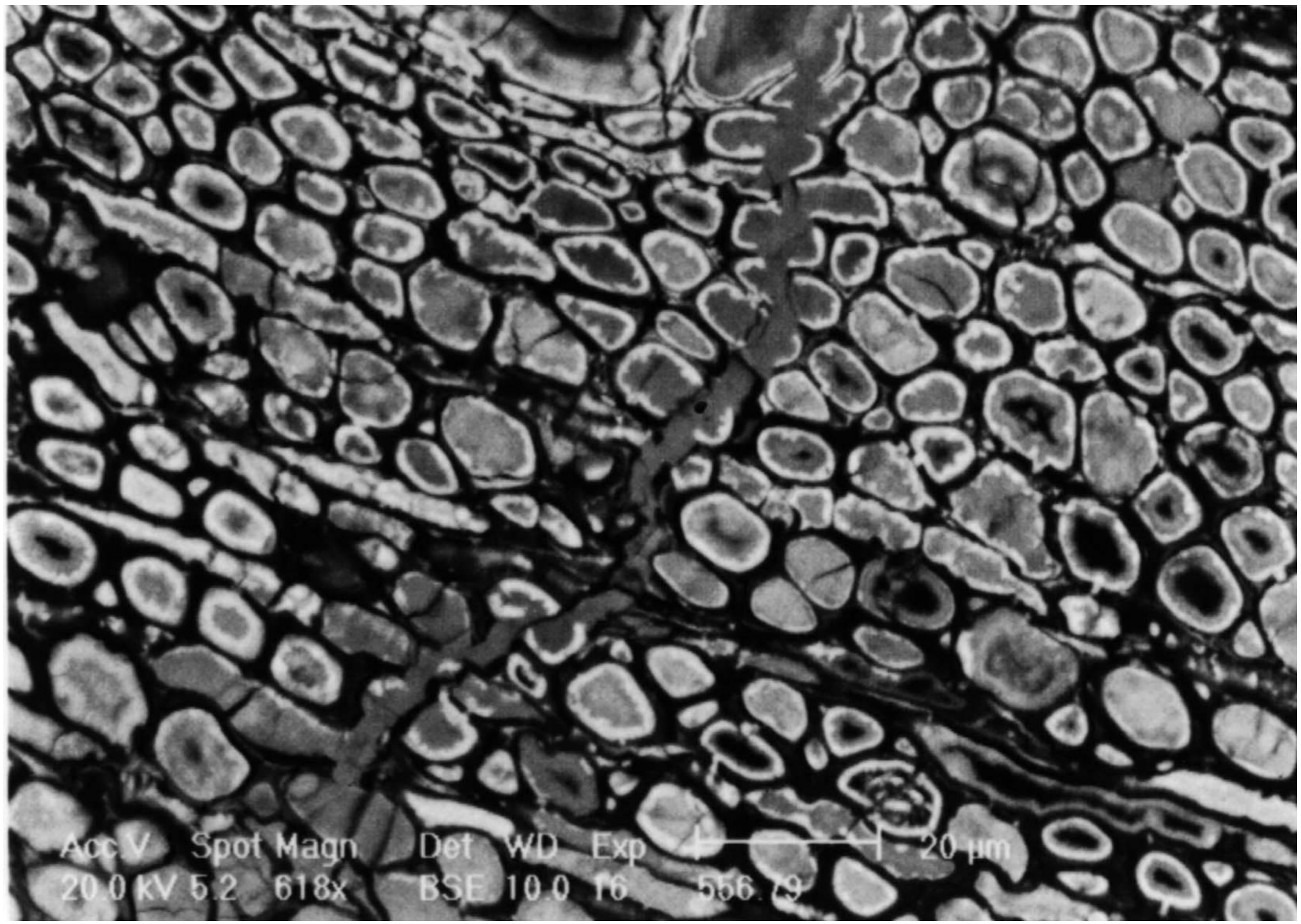


Case 2. Coated fine ware - distribution site

Scanning electron microscopy

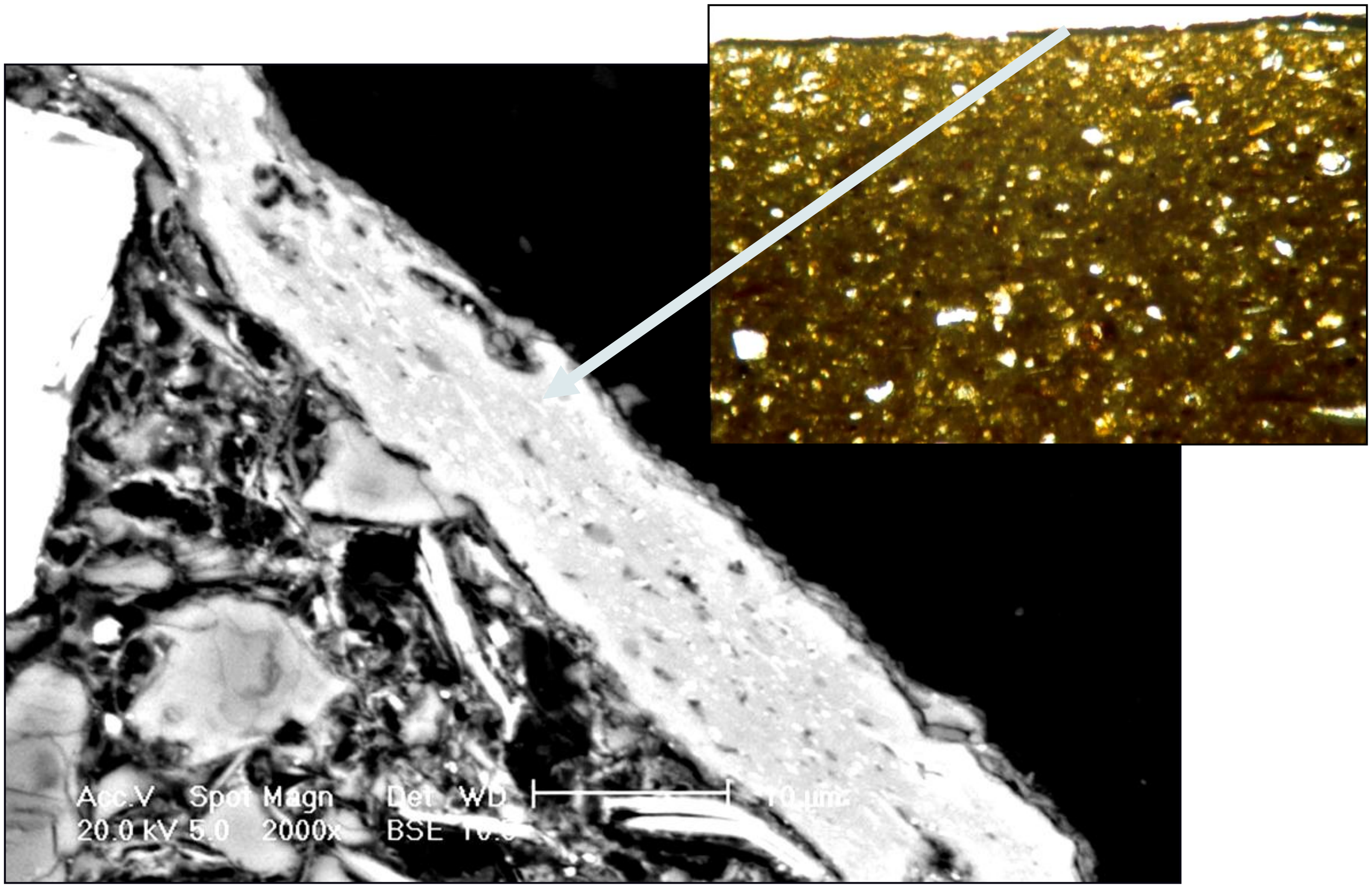
Rose – raw ceramic (not fired)

Vegetal remains



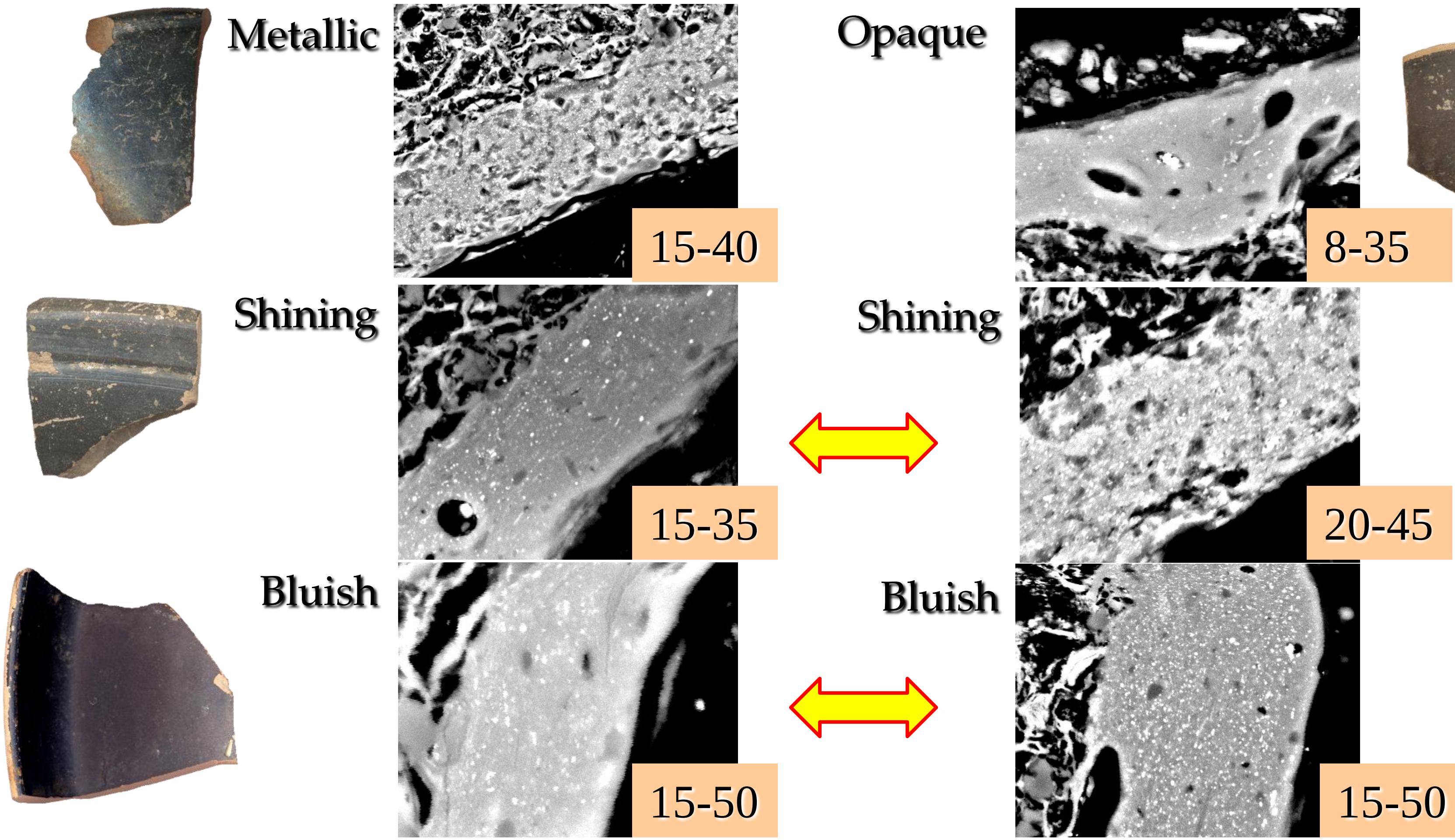
Case 2. Coated fine ware - distribution site

Scanning electron microscopy



Case 2. Coated fine ware - distribution site

Scanning electron microscopy



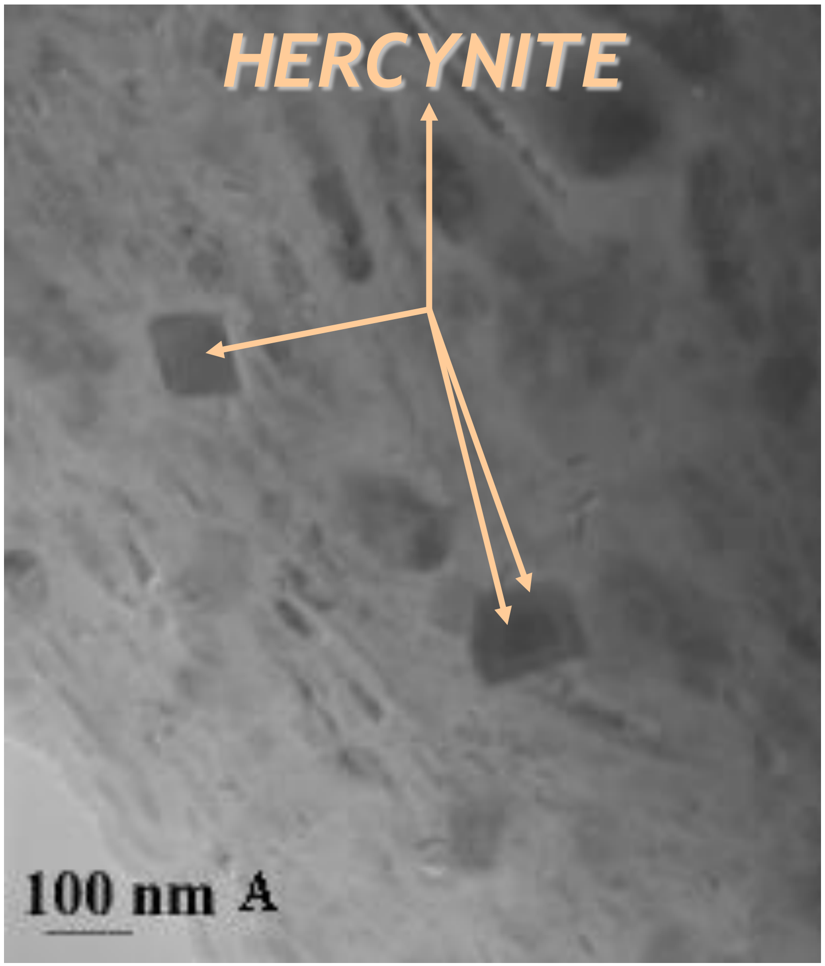
Case 2. Coated fine ware - distribution site

Scanning electron microscopy

	opaque	shining	metallic	bluish
SiO_2	49,52	50,07	47,54	47,16
Al_2O_3	28,09	28,40	28,85	29,06
TiO_2	0,33	0,41	0,24	0,38
FeO	12,53	12,40	13,96	14,11
MgO	2,65	2,64	1,98	2,29
CaO	0,90	0,81	1,09	0,89
Na_2O	0,34	0,17	0,14	0,23
K_2O	5,6	5,24	6,19	5,88

Case 2. Coated fine ware - distribution site

Trasmission electron microscopy



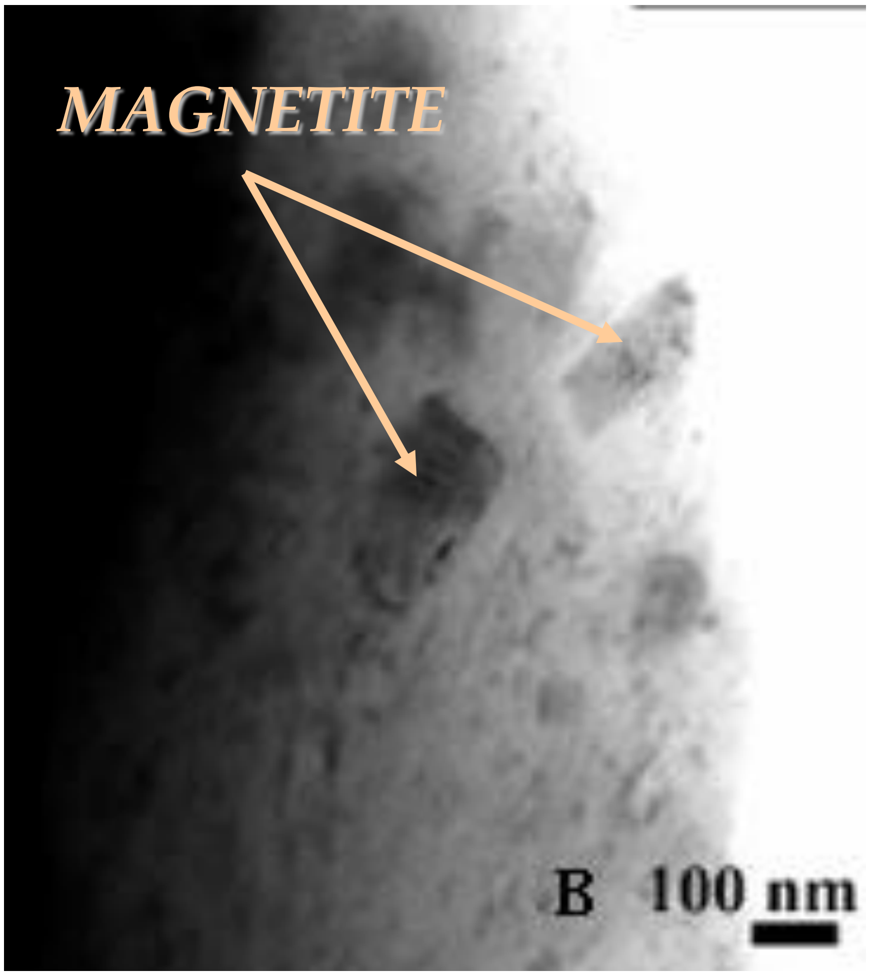
BLUISH

Nucleus: intermediate composition between hercynite, magnetite, spinell s.s.

Rim:
Hercynite with minor magnetite in solid solution

Case 2. Coated fine ware - distribution site

Trasmission electron microscopy



METALLIC

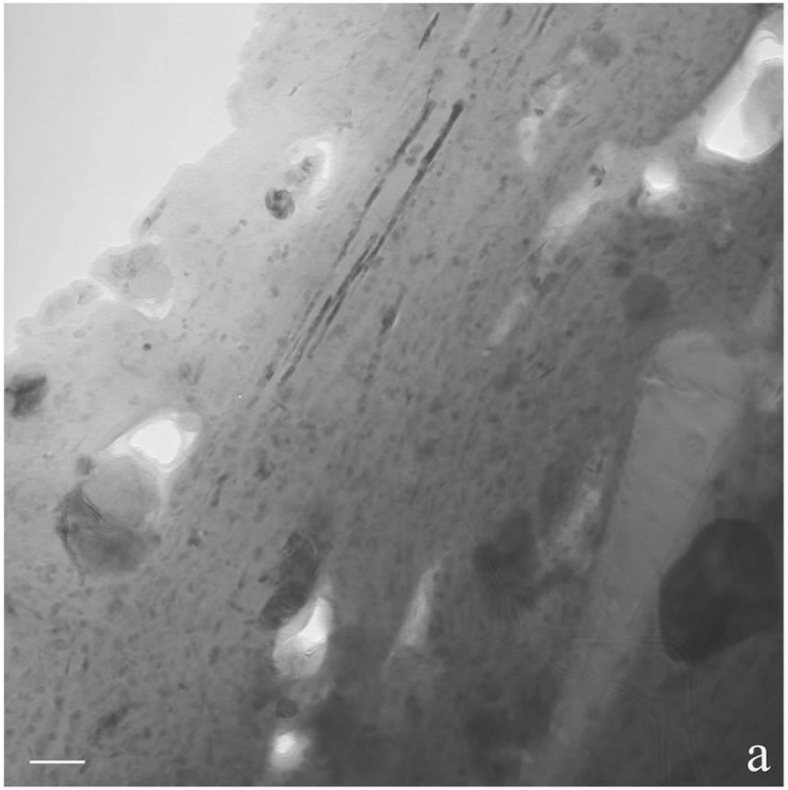
Magnetite with minor hercynite and spinel s.s. in solid solution

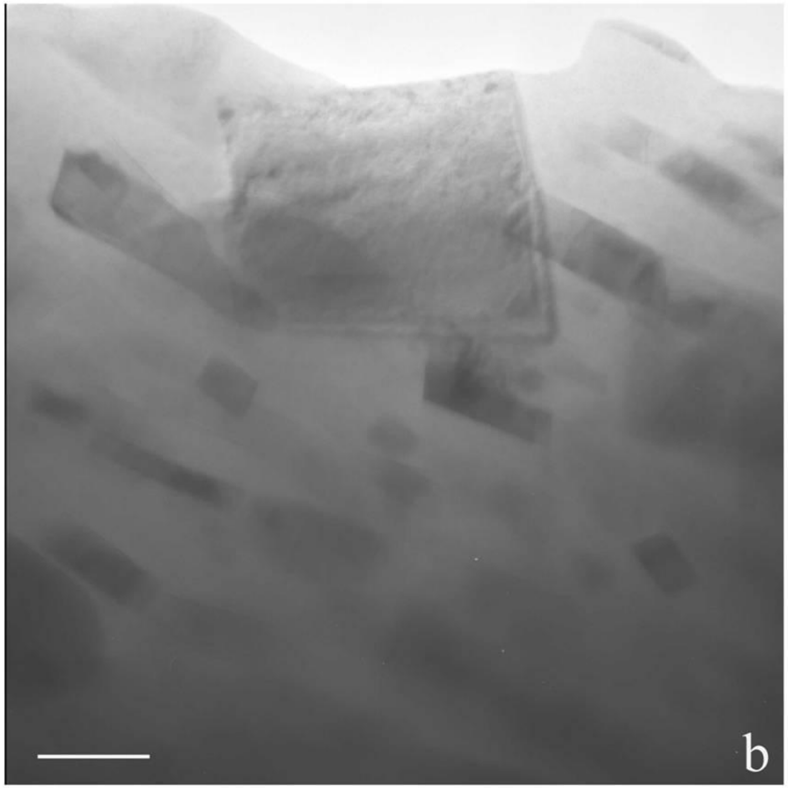
Case 2. Coated fine ware - distribution site

Trasmission electron microscopy

MISFIRED - Hematite

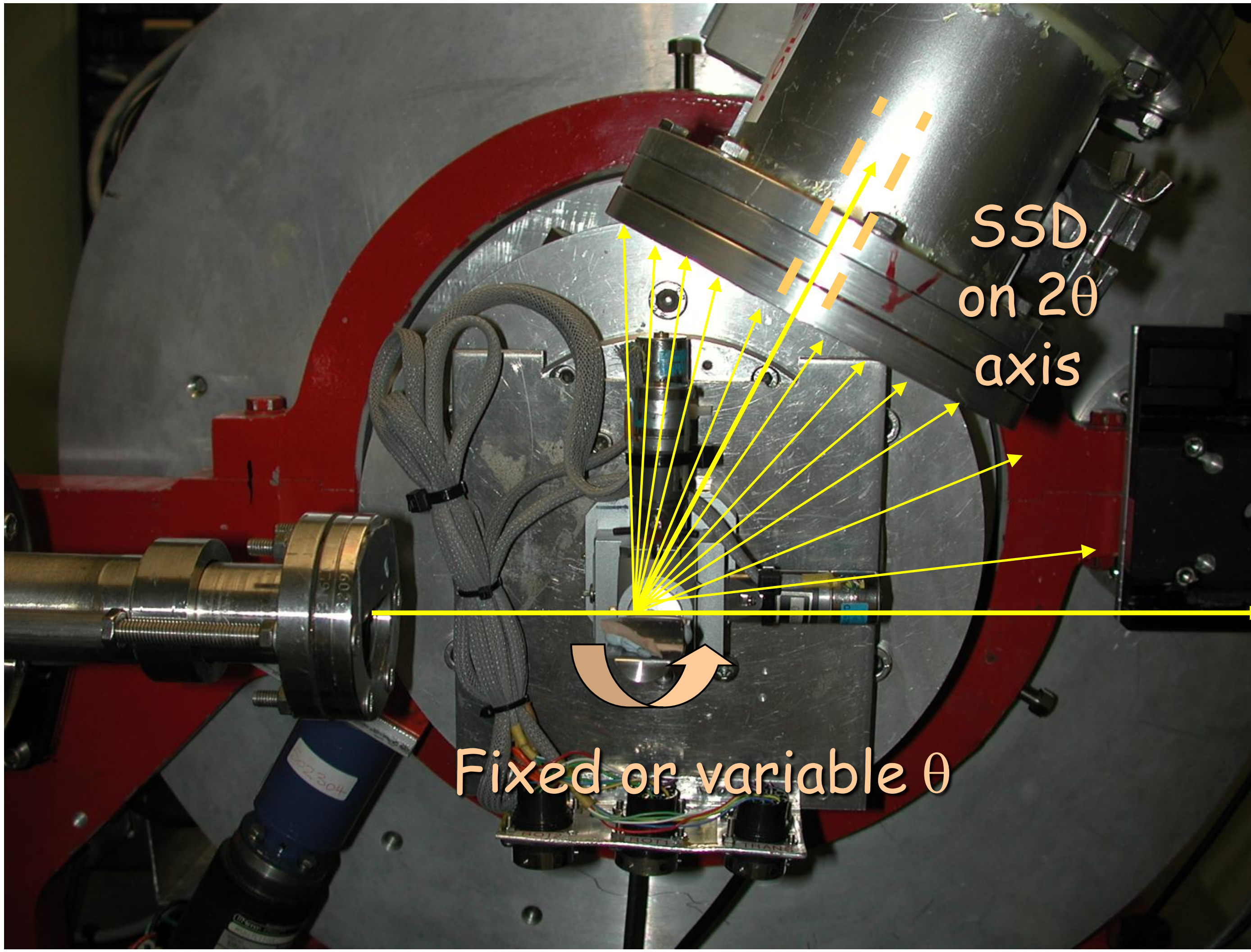
OPAQUE - Hercynite and magnetite





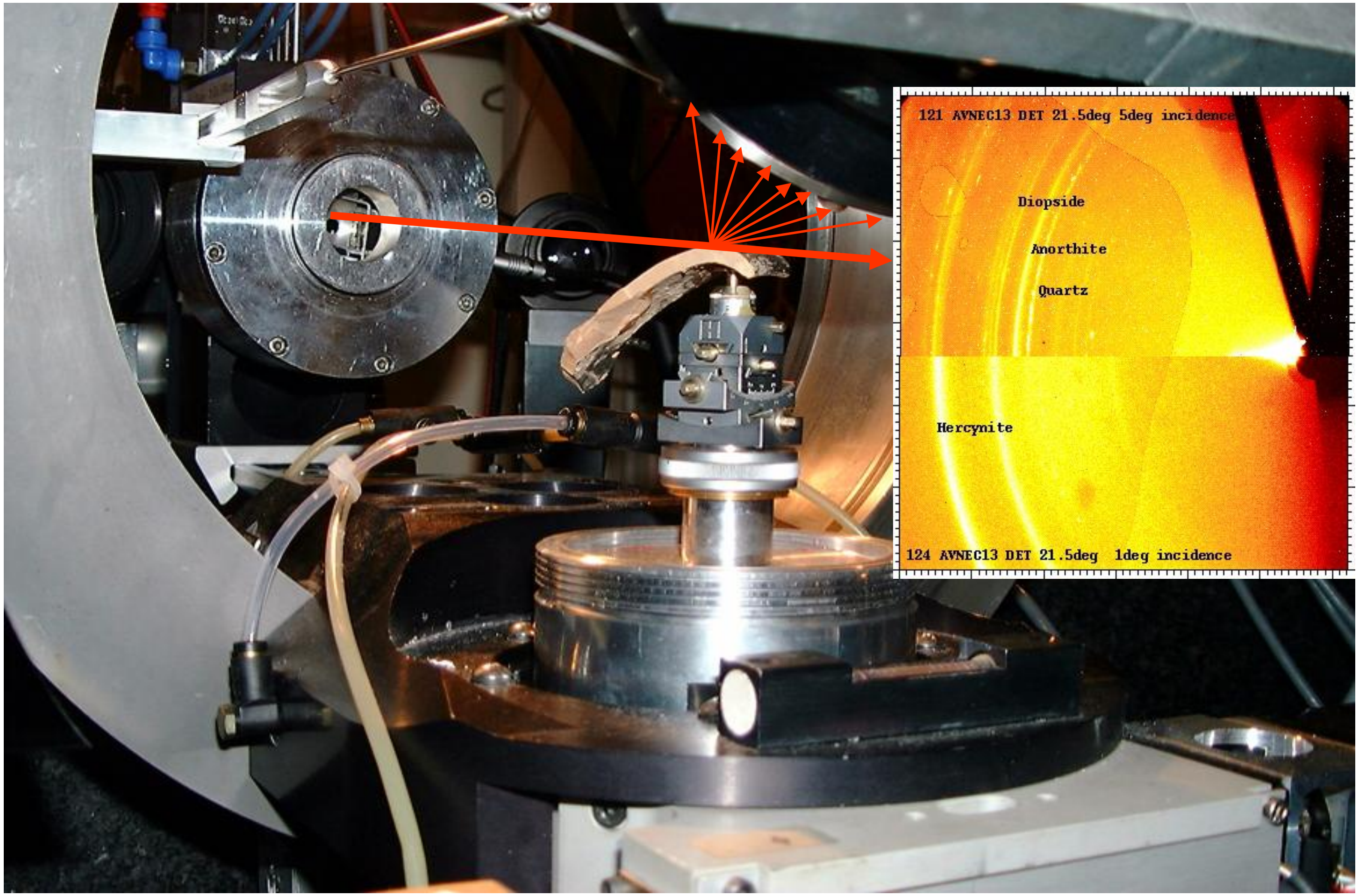
Case 2. Coated fine ware - distribution site

SR-XRD



Case 2. Coated fine ware - distribution site

SR-XRD



Case 2. Coated fine ware - distribution site

Hematite

$Fe^{3+}{}_2O_3$

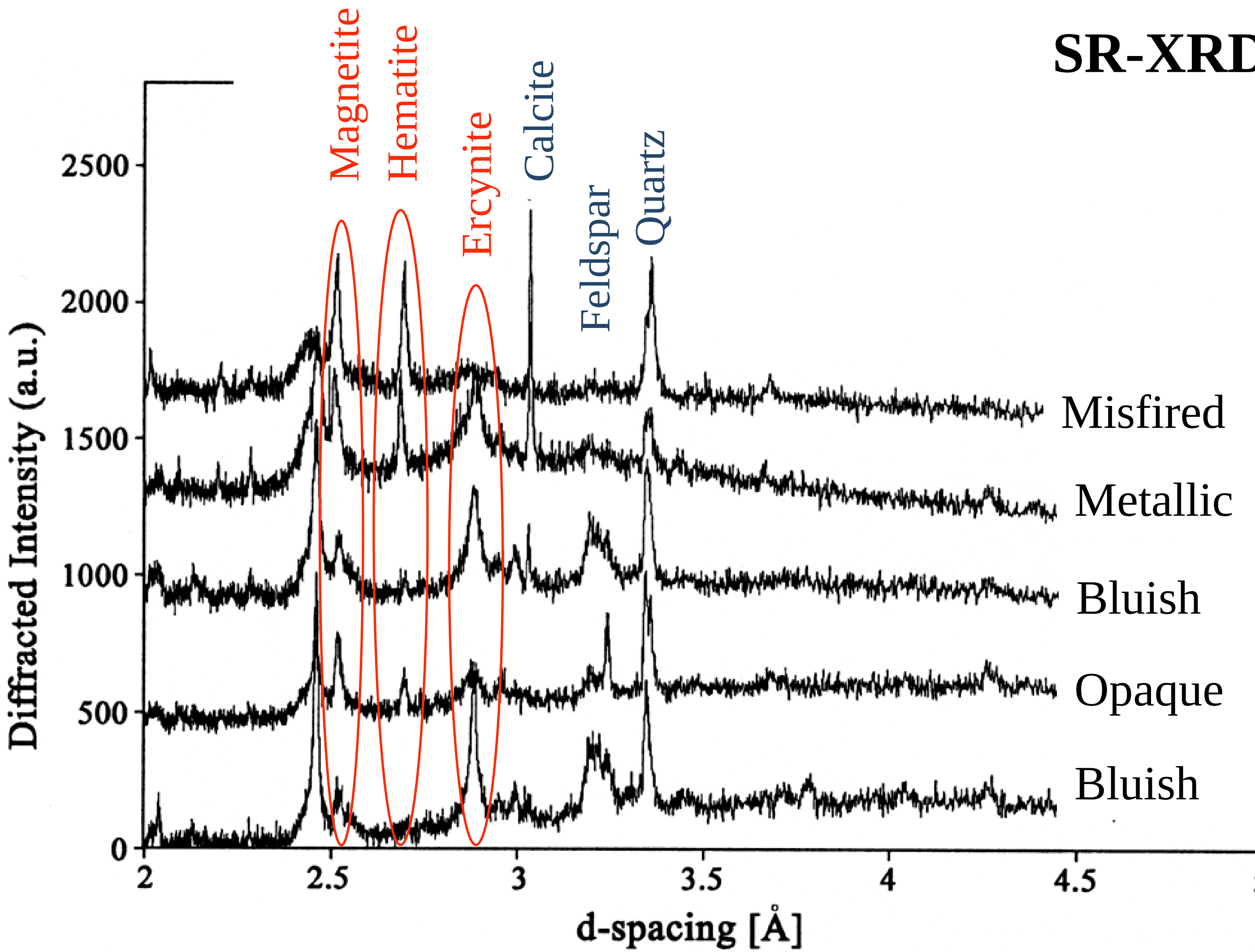
Hercynite

$Fe^{2+}Al_2O_4$

Magnetite

$Fe^{2+}Fe^{3+}{}_2O_4$

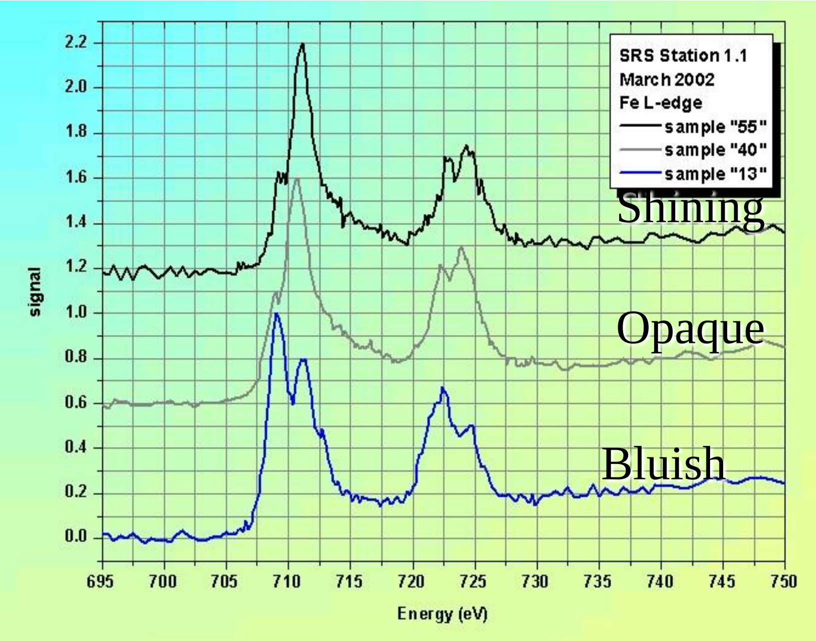
SR-XRD



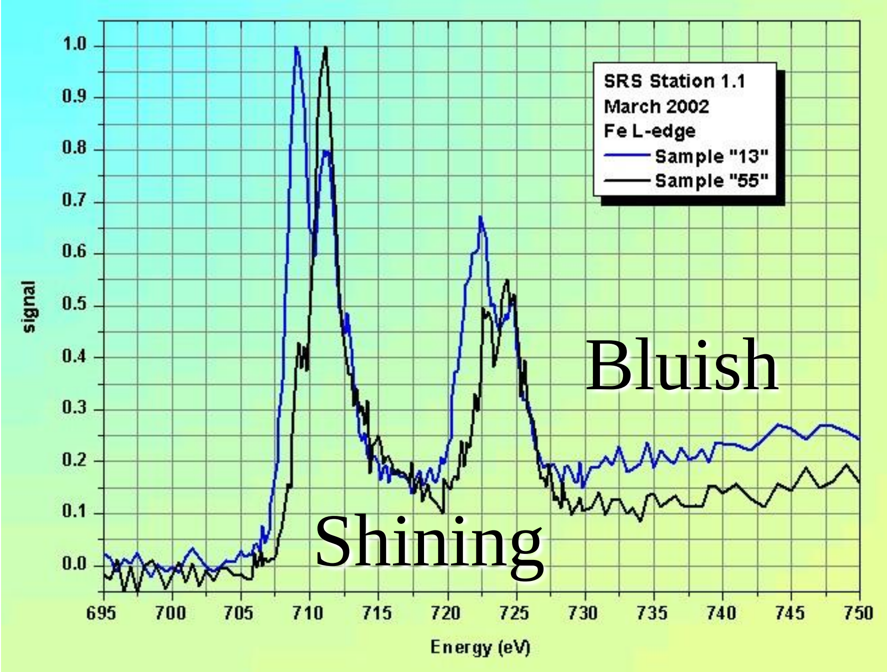
Case 2. Coated fine ware - distribution site

X-ray Absorption Spectroscopy (XAS)

~1mm penetration depth



$Fe^{2+} \longleftrightarrow Fe^{3+}$



Case 2. Coated fine ware - distribution site

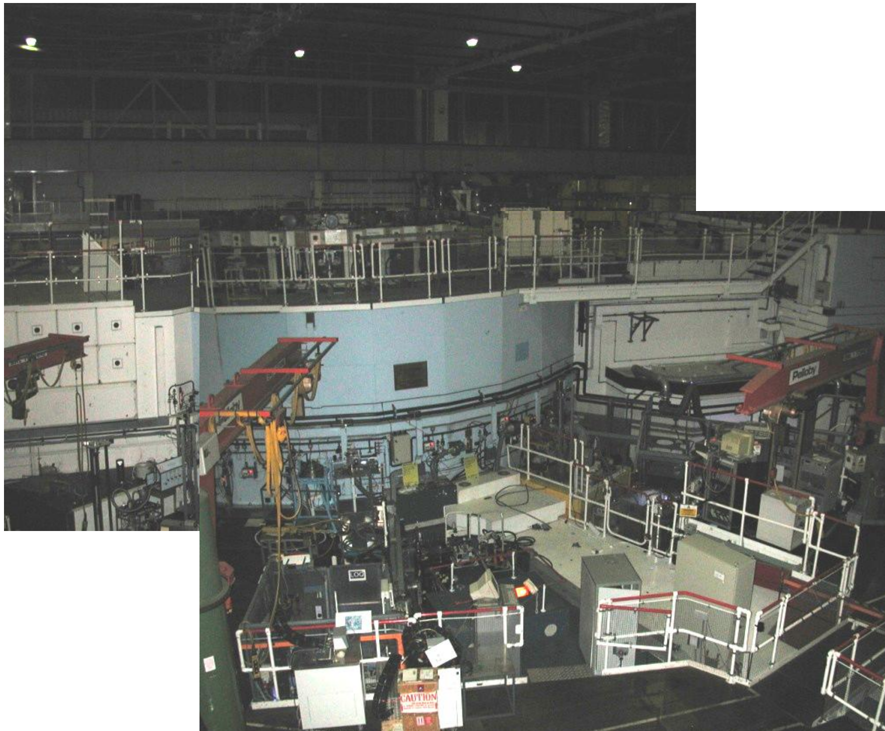
Oxidising vs. reducing

MISFIRED
HEMATITE - OXIDISING

METALLIC
MAGNETITE WITH MINOR HERCYNITE – PREV. OXIDISING

BLUISH
HERCYNITE WITH MINOR MAGNETITE – PREV. REDUCING

Case 2. Coated fine ware - distribution site



Neutron diffraction →
NON DESTRUCTIVE
bulk mineralogical analysis

6/7 HOURS
4/5 DAYS RADIOACTIVE
SCARCELY AVAILABLE

Case 2. Coated fine ware - distribution site

PORTABLE X-RAY FLUORESCENCE (XRF)

Non destructive

Very rapid

Unexpensive

Limited penetration (few tens of μm)

<u>LOW ACCURACY</u>

<u>Perfect for a preliminary diagnosis, sampling and *unica* !!!</u>

Major risk: from Museums without explanatory panels to Museums with lots of panels including false information