Clay bodies of ancient tiles:

Correlation between Ionoluminescence signal and manufacturing conditions

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Outline

- Set-up and Analytical techniques
  - Ionoluminescence, PIXE and PIGE
  - external vs. in vacuum beam
- The samples: clay bodies of ancient tiles
- Results and Discussion
- Summary

Equipment: IBA techniques

Tandem Peletrón (model: 9SDH-2) at Universidad Nacional Autónoma de México, UNAM.

External proton beam set-up *:

PIXE: 2 X-ray detector for light and heavy elements,
RBS: 1 particle detector
PIGE: 1 gamma detector (HGe)
IL: USB2000 Ocean Optics Spectrometer, optical fibres (1 mm diameter).

Experimental conditions:

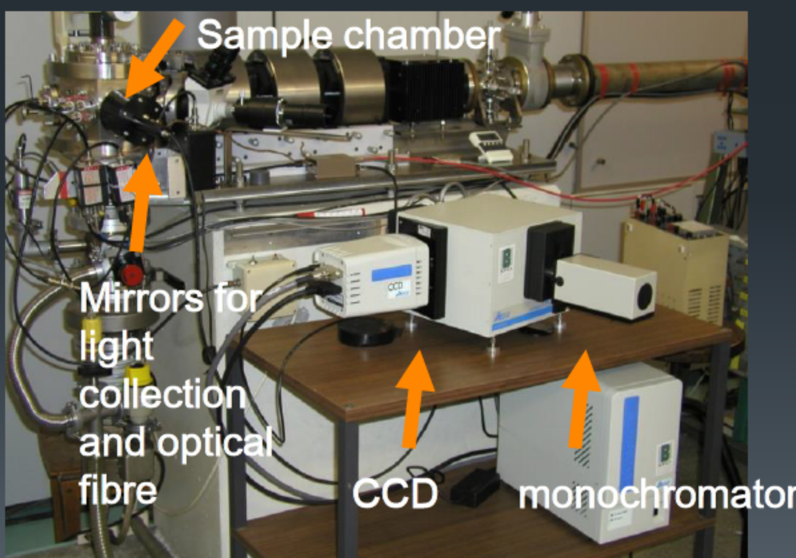
Energy: 3 MeV, protons
Exposure time: 3-4 s for IL; 5 min. for PIXE/PIGE and RBS
Beam current: 3 nA
Beam size: 2-3 mm diameter

* H. Calvo del Castillo et al, Anal. Bioanal. Chem. (2007) 387:869-878

http://www.fisica.unam.mx//peletron/

Equipment: IBA techniques

2.5 MV Van Van de Graaff accelerator at Campus Tecnológico e Nuclear, CTN/IST in Portugal.



Nuclear microprobe under vacuum conditions:

PIXE: 1 Si X-ray detector,
RBS: 1 particle detector,
IL * : Jobin-Yvon/Horiba (Triax 190) Spectrometer, optical fibre and a Symphony CDD detection system.

Experimental conditions:

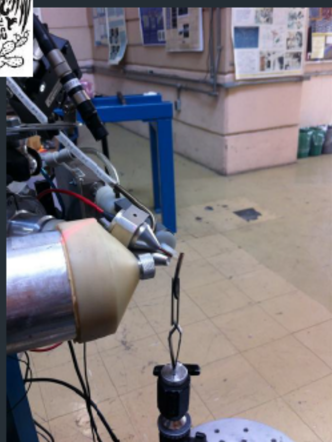
Energy: 2 MeV, protons
Exposure time: 3-4 s for IL; 10 min. for PIXE/RBS
Beam current: < 1 nA
Beam size: 10x10 μm^2

* N. F. Santos et al, Nucl. Instr. Methods, B (2013) 306:195-200

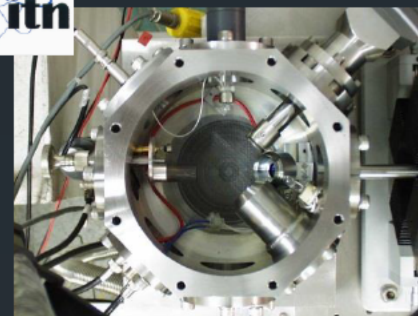
http://www.itn.pt/facilities/pt_lab_ion_beam.htm

Experimental: external vs vacuum

Broad beam: 2-3 mm
3,0 MeV



Micro-beam: 10x10 μm^2
2 MeV



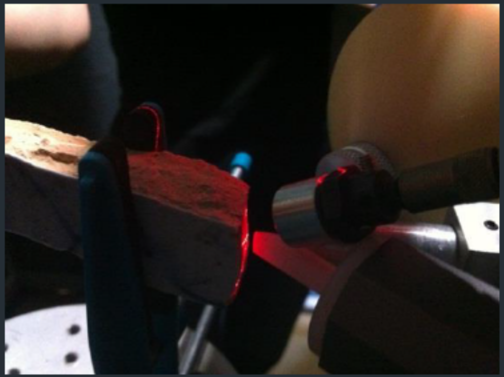
External beam	Vacuum beam
✓ Higher energies, ✓ High beam currents, >nA	✓ Lower energy, ✓ Lower beam currents, <1nA ✓ Can raster the surface or analyse small areas
• Can damage the samples: • Glaze, • Newest clays.	• The light signal is low: • Problems related with the signal detection.
Used to study the clays of the tiles.	Used to study particular features of the clays and the glaze colours.

The samples

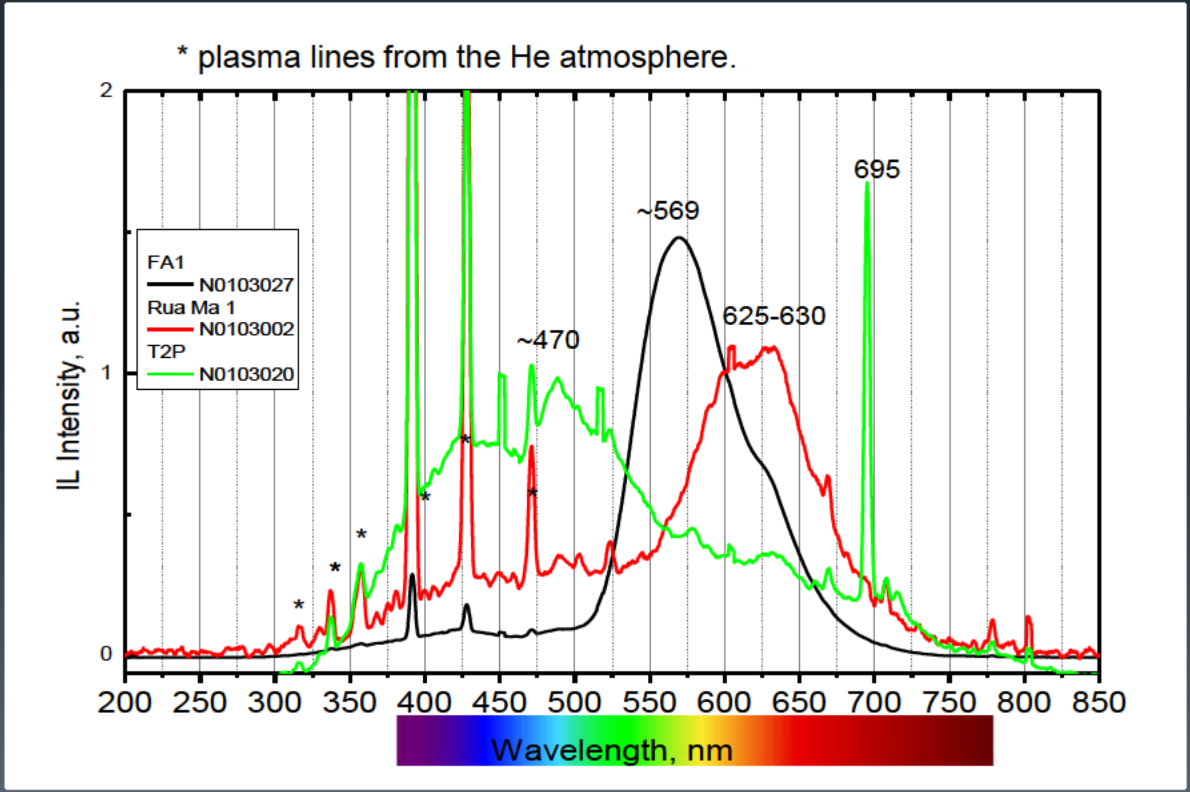
					
T2P XX c.	FA XX c.	FL1 XIX c., last quarter	MR1 XVIII c., last quarter	CSJ2P XVIII c., 3^{rd} quarter	ABS1 XVIII c., 3^{rd} quarter

				
RSM1 XVIII c., 3^{rd} quarter	RSM2B XVIII c., 2^{nd} half	SE1 XVIII c., 2^{nd} half	Vista Lisboa Res. XVIII c. 1st half	Marc XVIII c., 2^{nd} half
				
Rua Madalena 1 XVIII c. 1st half	Rua Madalena 2 XVIII c. 1st half	Vista Lisboa Exp. XVIII c. 1st half	BA1 XVII, last quarter	AA2P XVII, 2^{nd} half

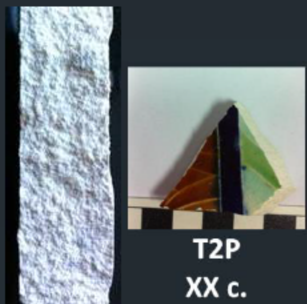
Ionoluminescence results



Based on the light emission, the set of tiles was classified in 3 main groups, according wit the maximum:



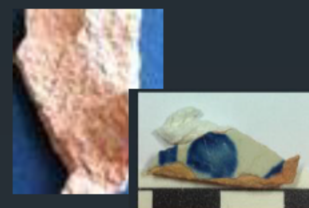
Ionoluminescence results



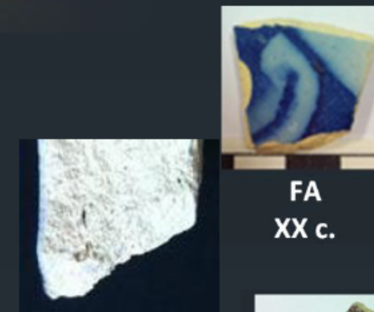
T2P
XX c.

Rua Madalena 1
XVIII c. 1st half

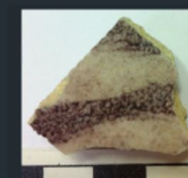
Marc
XVIII c., 2nd half



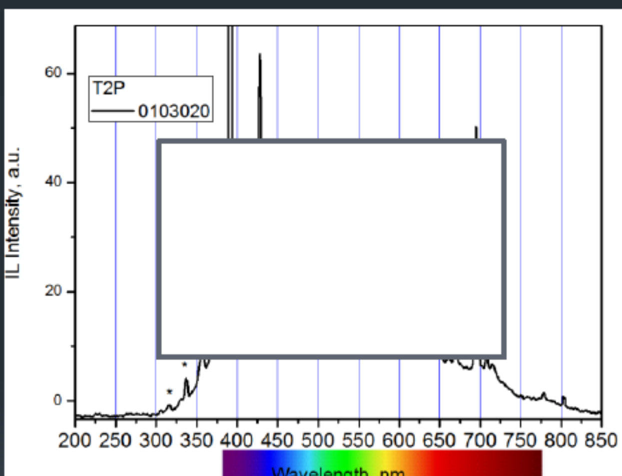
FL1
XIX c., last quarter



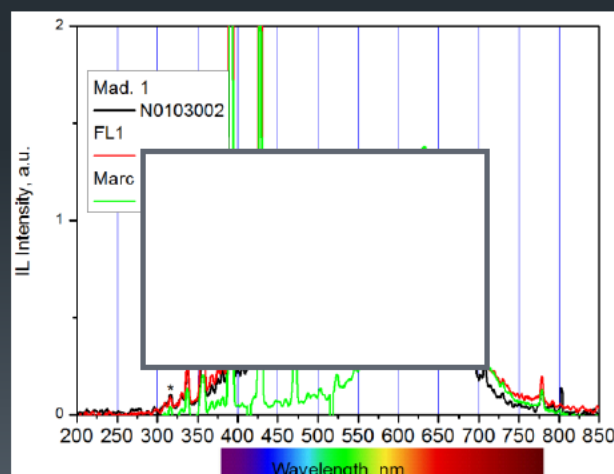
FA
XX c.



MR1
XVIII c., last quarter

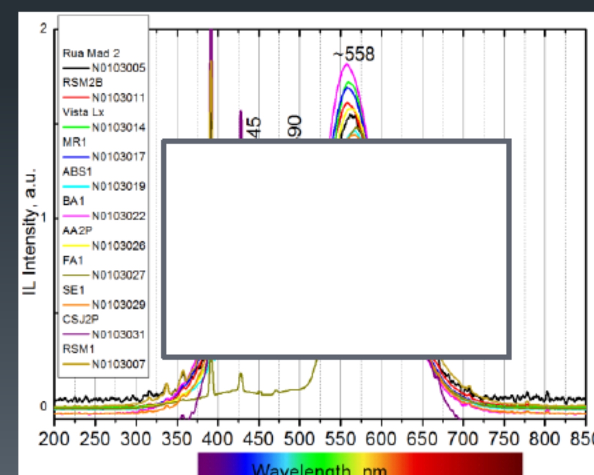


IL signal, type B



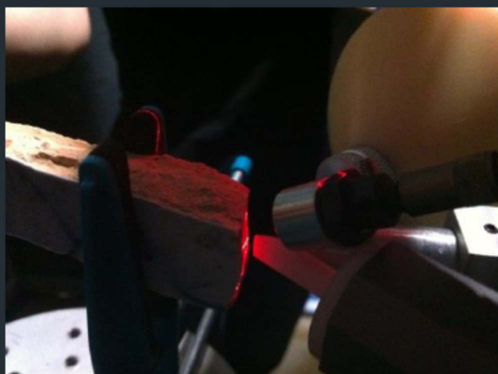
IL signal, type A

Most of the tiles show this IL signal.

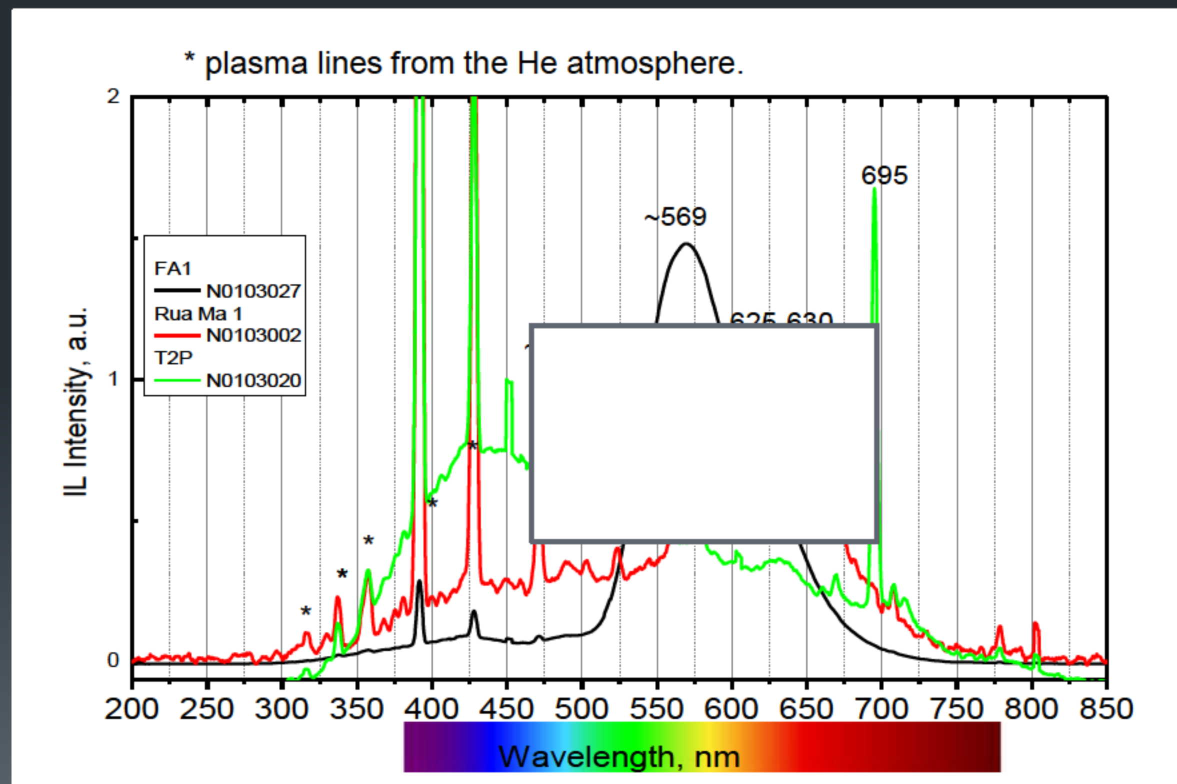


IL signal, type C

Ionoluminescence results



Based on the light emission, the set of tiles were classified in 3 main groups:



The groups are independent of:

- **the date,**
- **the clay colour,**
- **the composition?**

Body tiles: manufacturing

- Clay minerals,
- Fluxes (lower temperatures) as feldspars,
- metal oxides
- silica
- Additives intentionally added as calcite, or not but which are strongly dependent on the local geology

During the firing process the paste suffers physical and chemical alterations, depending on the temperature, heating cycles or the atmosphere inside the kiln.

The calcite decomposes at temperatures above 800 ºC, and it incorporates ions (as Fe) into the lattice.

Body tiles: manufacturing

Raw materials

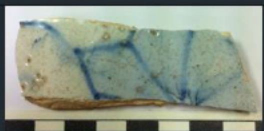
Firing process (temperature, time)

Cooling down:
fast (quenching) or slow process

These conditions will affect:

- the colour (ions of Fe);
- the porosity,
- hardness,
- final composition , etc..

Ionoluminescence results: Group A

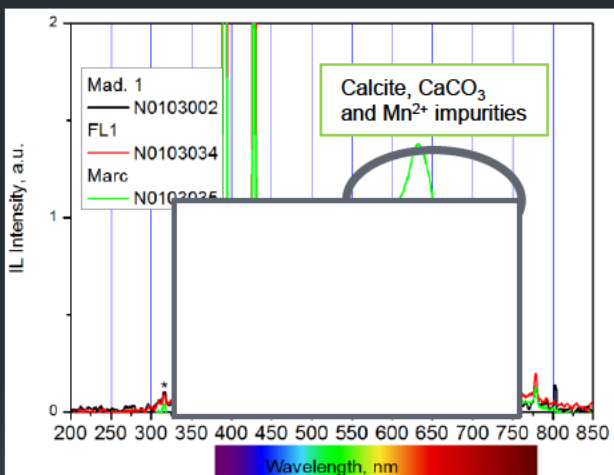


Rua Madalena 1
XVIII c. 1st half

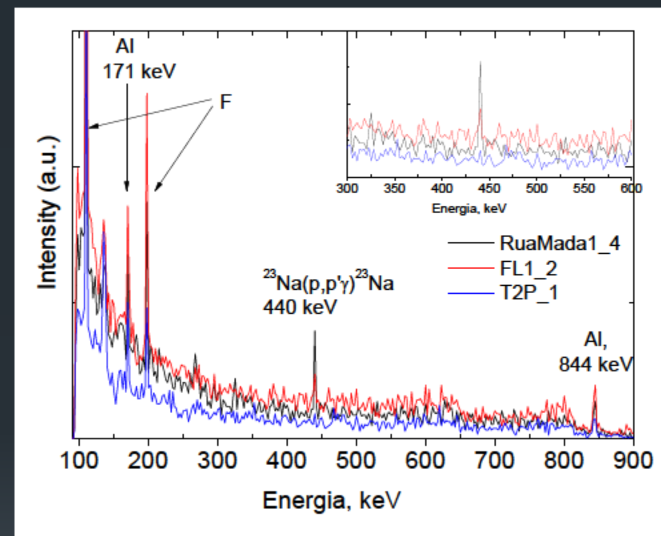
FL1
XIX c., last quarter

Marc
XVIII c., 2^{nd} half

The firing temperature was not high enough to decompose the starting carbonates minerals ($CaCO_3$) which typically occur between 800 and 950 ºC.



IL signal, type A

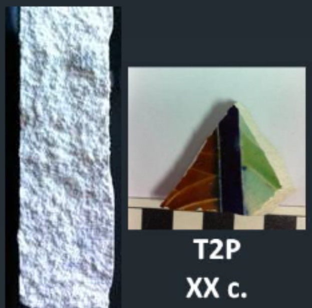


These are the unique samples where Na was identified by PIGE.

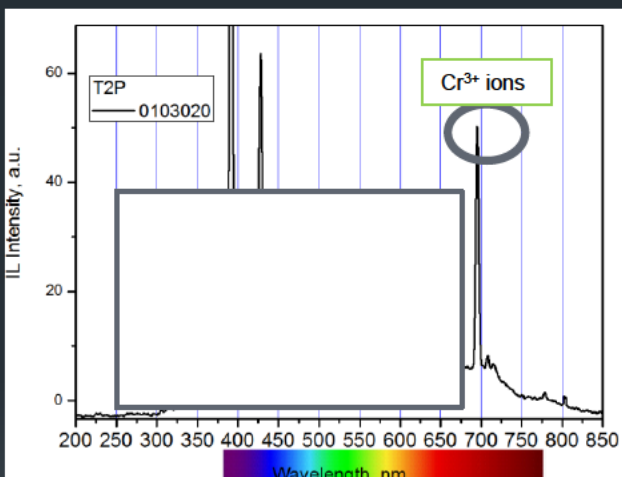
Sodium fluxes (as soda feldspar or sodium carbonate) were used to reduce the melting temperature.

* H. Calvo del Castillo et al, Anal. Bioanal. Chem. (2007) 387:869-878

Ionoluminescence results: Group B



T2P
XX c.



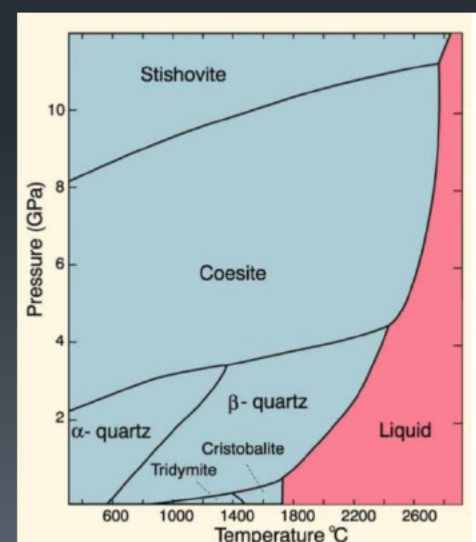
IL signal, type B

Igneous quartz: cristobalite and tridymite.

High temperature polymorphs of silica.

Considering the phase diagram for SiO_2, they are only possible under low pressure and high temperature (>1000ºC and 1400ºC) conditions.

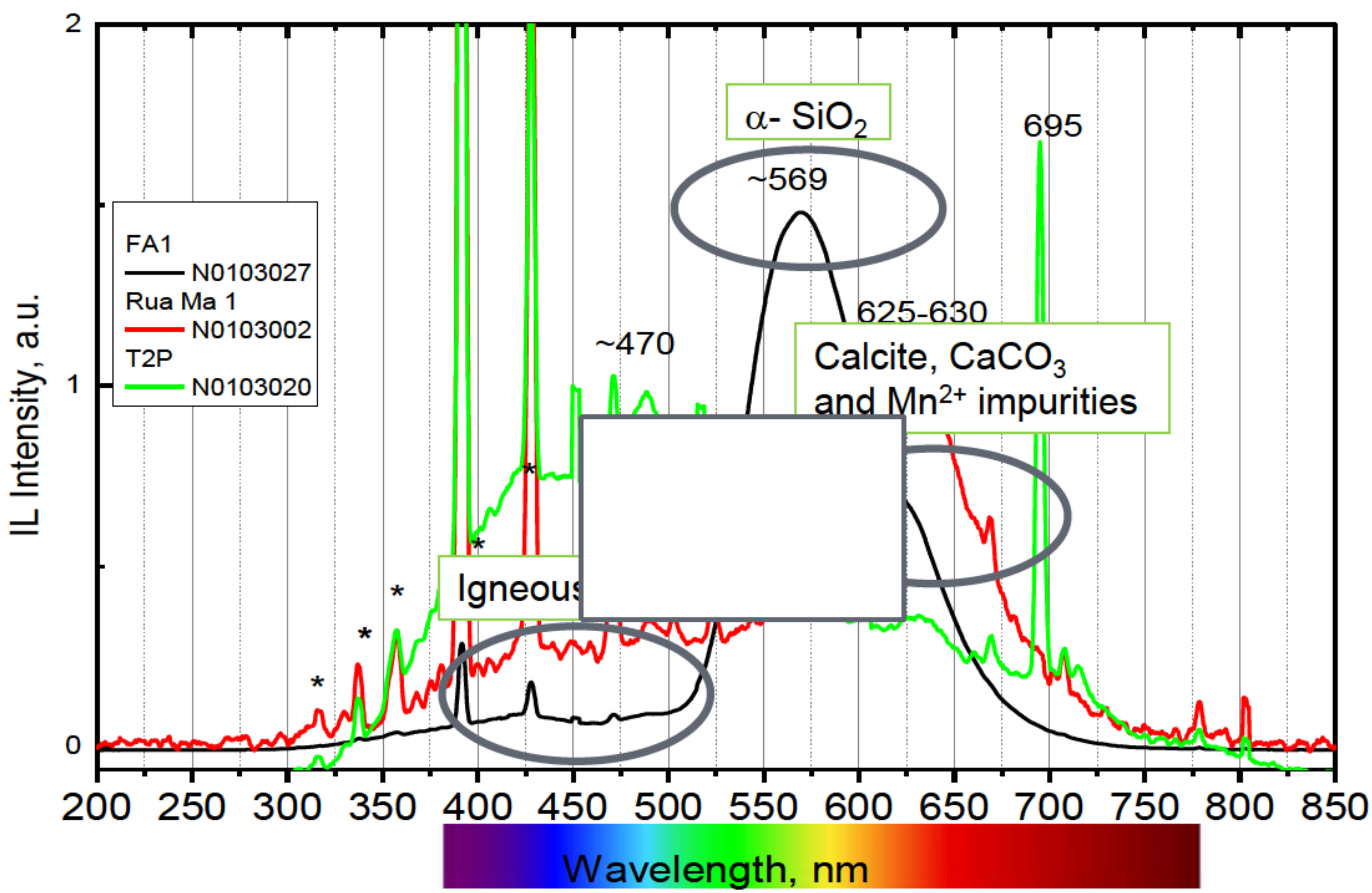
They are metastable when **fast** cooling down occurs.



M. Kayama et al. 9th Meeting of the Int. Mineralogical Association (2006).

Ionoluminescence results

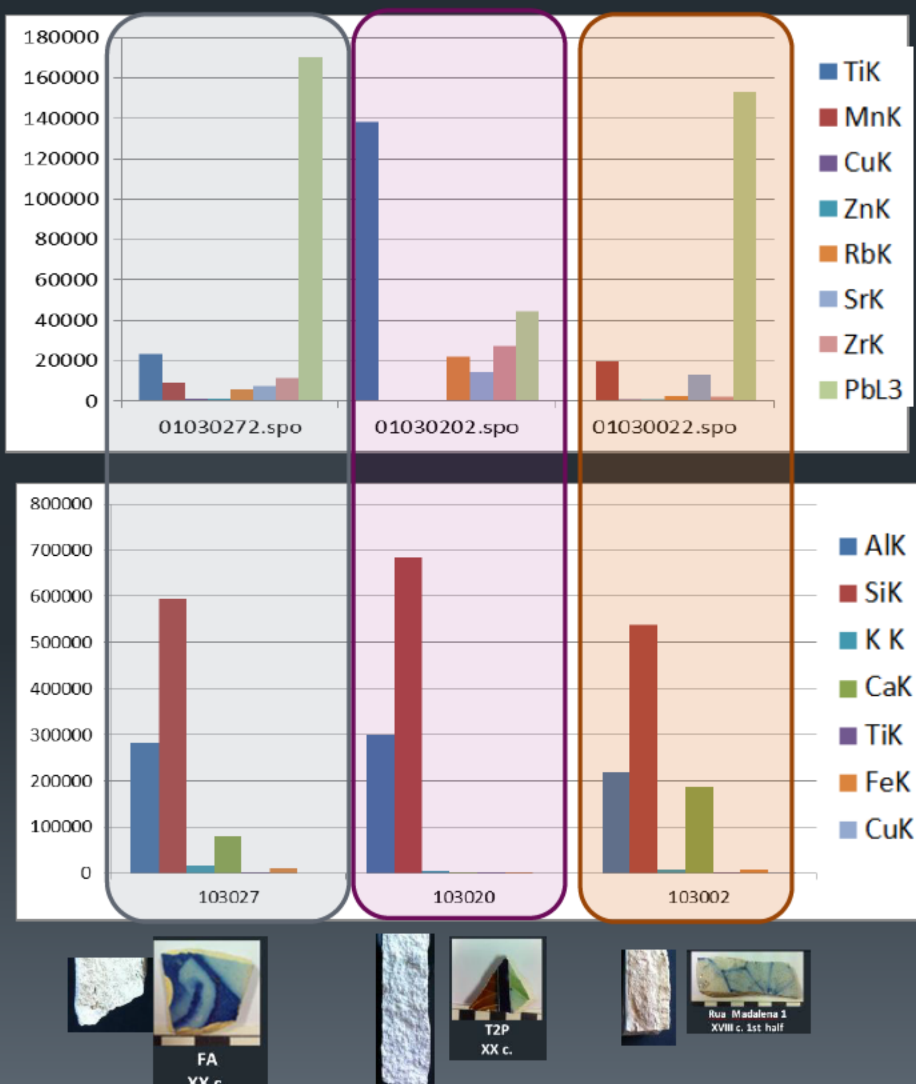
* plasma lines from the He atmosphere.



M. Kayama et al. 9th Meeting of the Int. Mineralogical Association (2006).

PIXE composition results

Type C Type B Type A

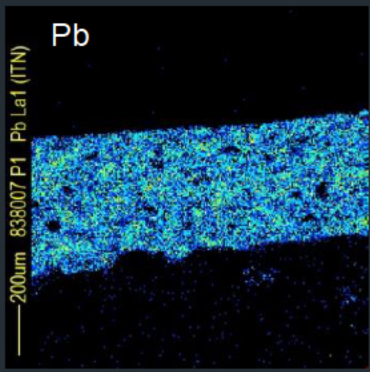


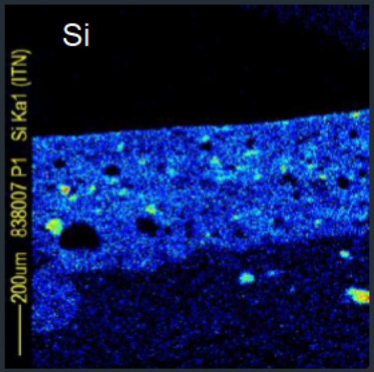
In terms of composition, there are also differences:

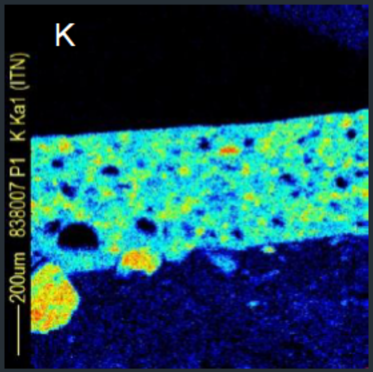
- Group B: highest concentration of Ti (white colour), Si and Al.
- Group C: high concentration of Al and Si.
- Group C and A: high concentration of Pb. Where?

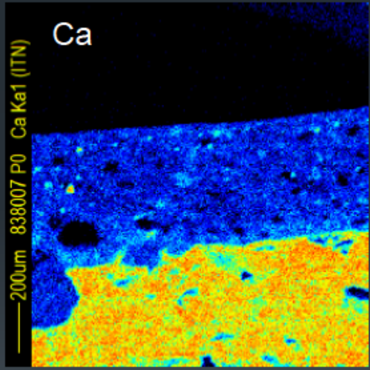
Not in the starting materials….

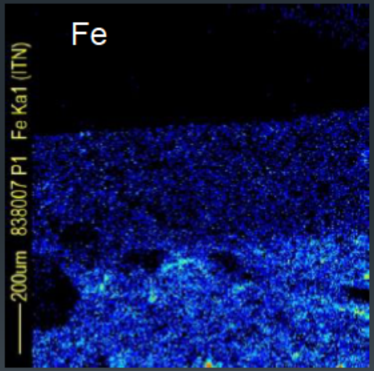
PIXE results









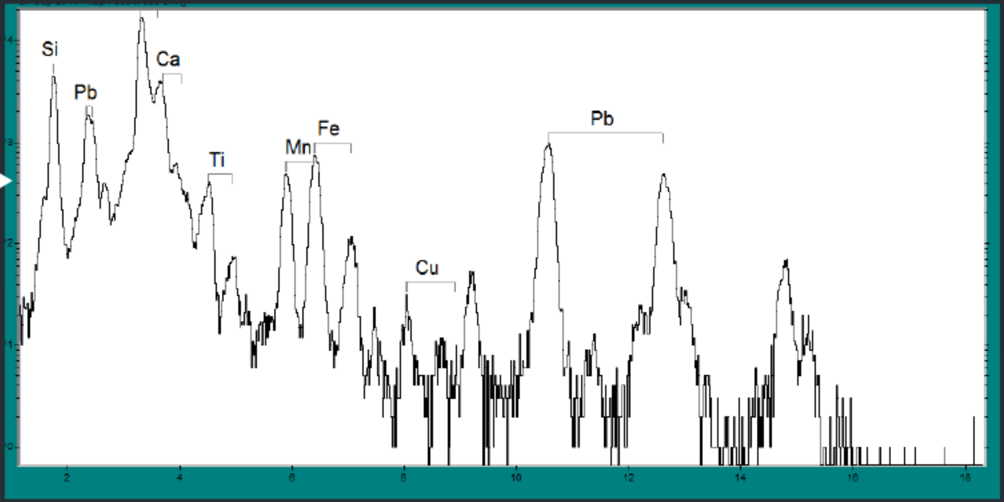


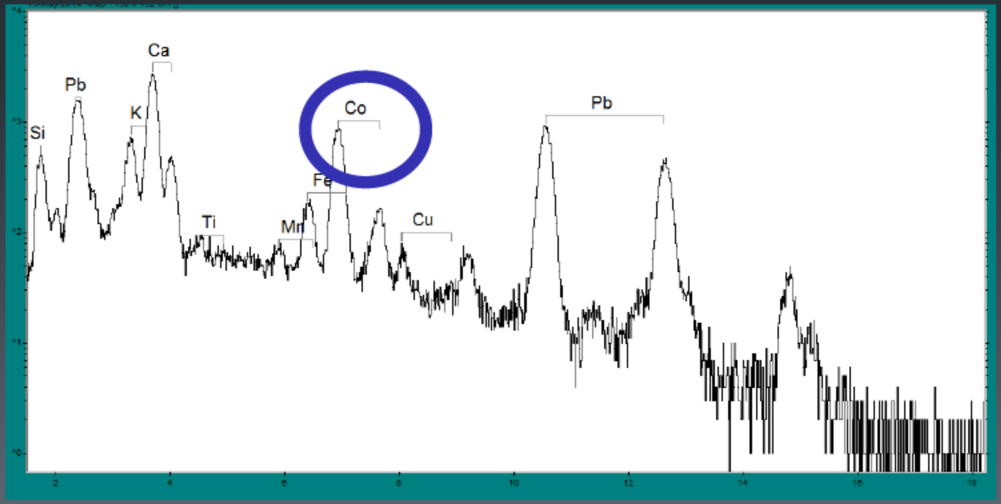
The Pb in the clay body comes from the glaze. Lead migrates thanks to the high porosity of the ceramic body: capillarity effect.

In the glaze, the PbO was used to reduce the melting point.

PIXE results

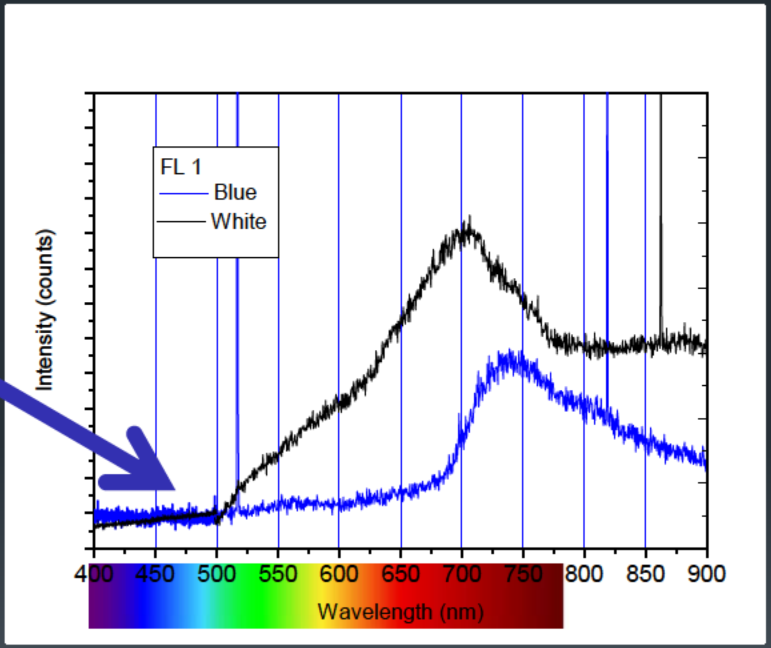
FL1
XIX c., last quarter





PIXE + IL results


FL1
XIX c., last quarter



Conclusions

IL signal can be an alternative characterization technique to classify the composition of clays just in **few** seconds. Sample preparation is not needed.

Other techniques as XRD: take more time and the sample should be powder.

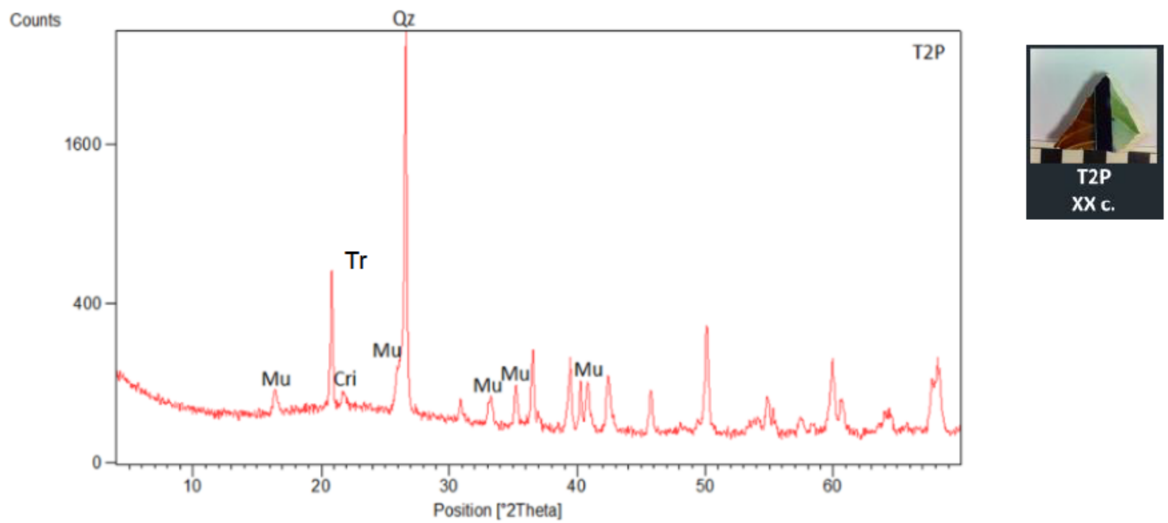


Fig. 2 – X-ray diffraction pattern of a 20th century tile body enhancing the presence of mullite (a high temperature aluminium phase). Qz: Quartz; Mu: Mullite; Cri: Cristobalite. Tr: Tridymite

* M.I. Dias et al. Proc. Int. Conf. Azulejar, Aveiro, Portugal (2012).

Conclusions

IL signal can be an alternative characterization technique to classify the composition of clays just in **few** seconds. Sample preparation is not needed.

Other techniques as XRD: take more time and the sample should be powder.

The IL signall jointly with the composition from PIXE and PIGE can give us information about:

- starting materials,
- temperature of firing process,
- cooling down process.

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M.I. Prudêncio
L.C. Alves

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Gracias
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http://www.itn.pt/projs/microfex/index.html