Spectrometric characterization techniques applied to artworks belonging to the historic and cultural heritage

A. Martín Sánchez, M. J. Nuevo

Department of Physics, University of Extremadura, 06006 Badajoz, Spain

OUTLINE

- ✓ *The Region of Extremadura (Spain):*
  - ❖ *Extremadura in the world*
  - ❖ *A vast archaeological site*
- ✓ *Analytical Techniques and Samples:*
  - ❖ *A wide range of applications*
- ✓ *Some Results*
- ✓ *Conclusions*
- ✓ *Other works*

The Region of Extremadura (Spain)

Extremadura in the world



The region of Extremadura (Spain)



- 1 092 997 hab. (2,36%) – in 2015
- 41635 km² (8,25%) → A vast region

A vast Archaeological Site





➢ Different settlements:

- Palaeolithic and Neolithic vestiges
- Greeks and Phoenicians
- Romans
- Middle Age
  - Islamic buildings
  - Christian sites
- Modern Age
- … TODAY





The Region of Extremadura (Spain)

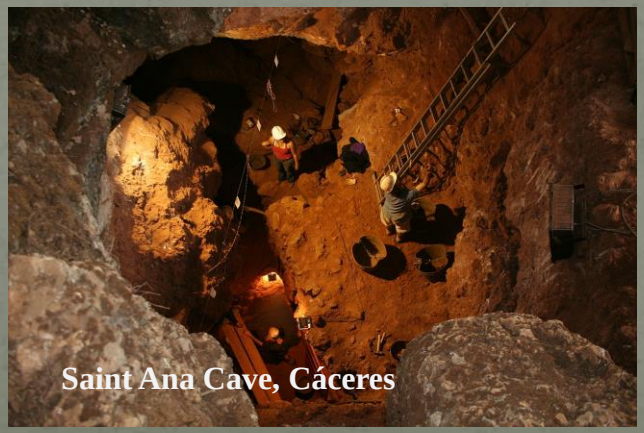
A vast Archaeological Site

Some examples:

- Prehistory
  - † Paleolithic – stone tools…
  - † Neolithic – megaliths, menhirs…
  - † Metal Age – copper, bronze, iron tools...



Maltravieso Cave, Cáceres



Saint Ana Cave, Cáceres



National Archaeological Museum, Madrid

The Region of Extremadura (Spain)

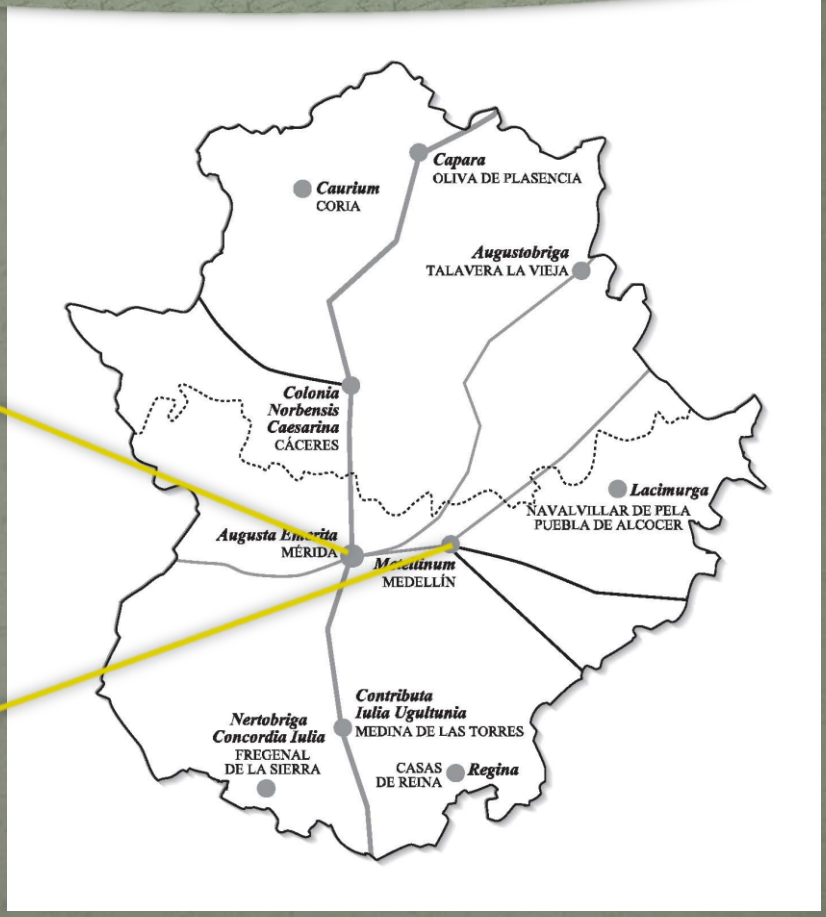
A vast Archaeological Site

- Roman Period

  Cities, theaters, circus, villas…







The Region of Extremadura (Spain)

A vast Archaeological Site

- Middle Islamic Christian Age

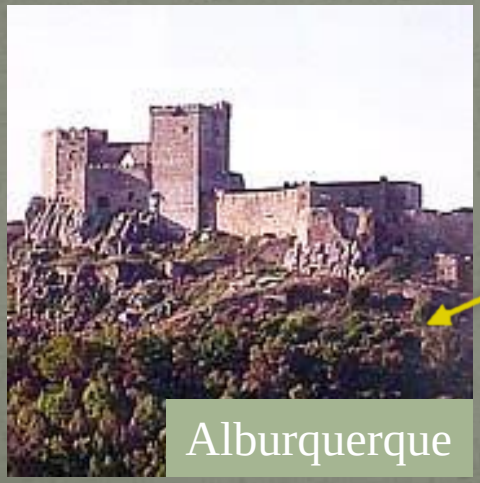
Castles…



Coria

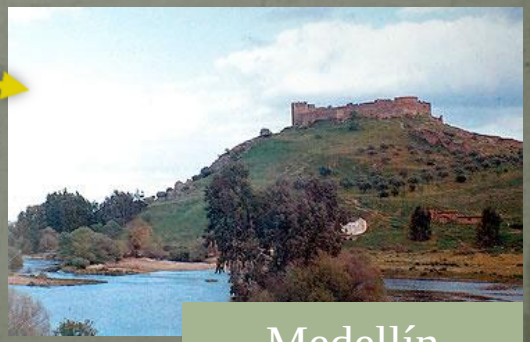


Trujillo



Alburquerque





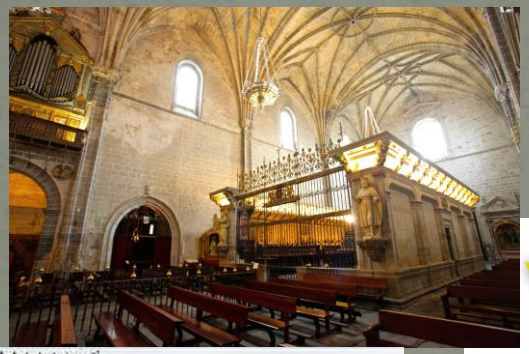
Medellín

The Region of Extremadura (Spain)

A vast Archaeological Site

Modern Age

Cathedrals, Churches…













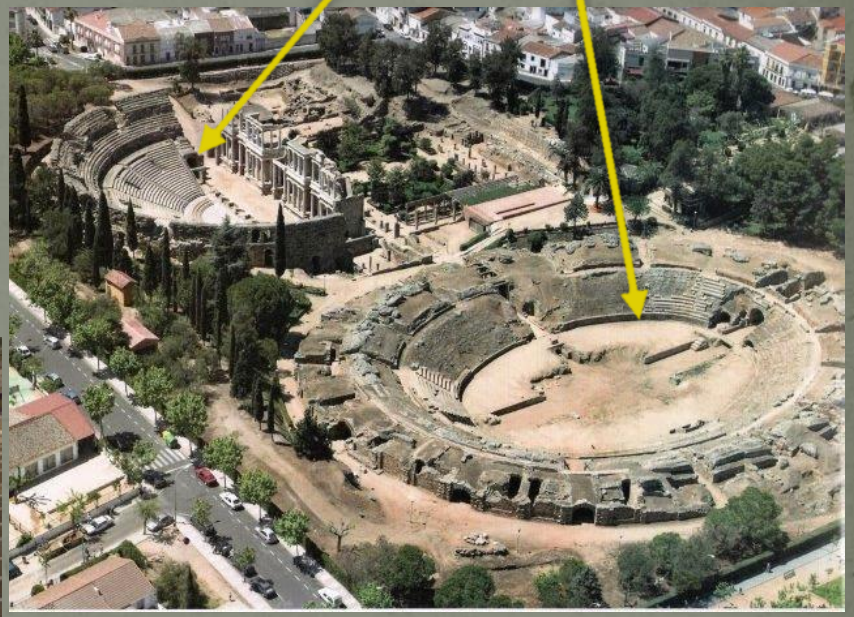
But...

A vast Archaeological Site

…especially remarkable

The Roman Period…

Mérida
Theater, Circus





A vast Archaeological Site

38º 57' 58.32" N,
Medellín…
5º 57' 21.74" W

"Cerro del Castillo"



Roman

Medieval





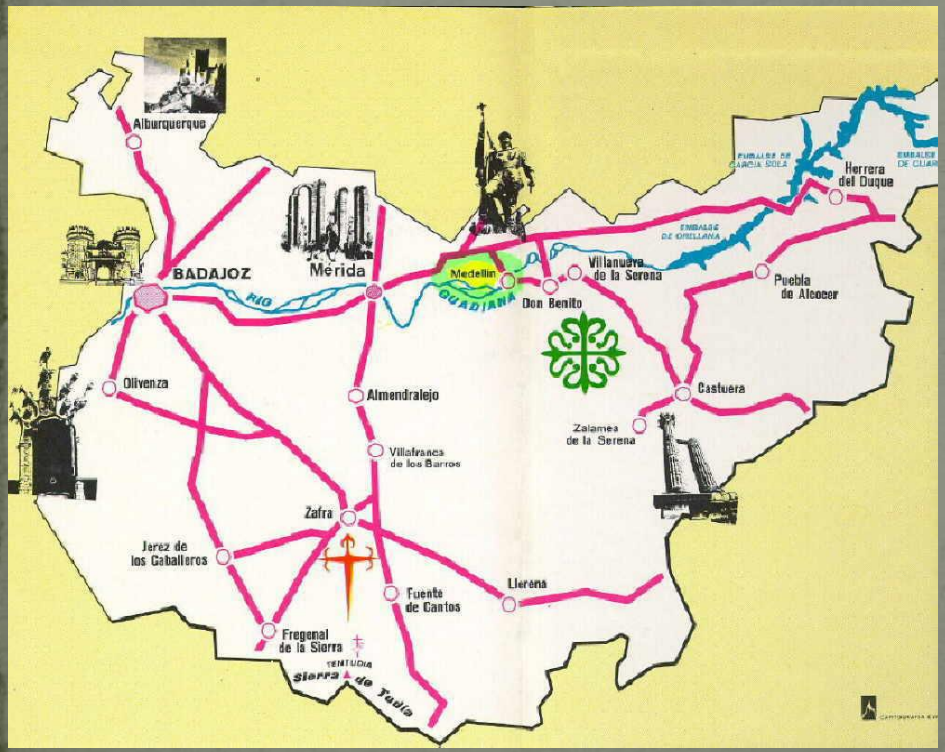




A vast Archaeological Site

… and surroundings

Roman Villa *La Majona*
(Don Benito)







Analytical techniques and samples

- *A wide range of applications*

In situ

- ✓ *X –Ray Fluorescence (EDXRF)*

In SAIUex

- ✓ *X-Ray Diffraction (XRD)*
- ✓ *Fourier transform Infrared (FTIR)*
- ✓ *Scanning Electron Microscopy (SEM-EDX)*

Analytical techniques and samples

*In situ (**Medellin and surroundings**)*

✓ *X-Ray Fluorescence (EDXRF)*

- ✧ *Scaenae front*
- ✧ Columns
- ✧ Sphinx

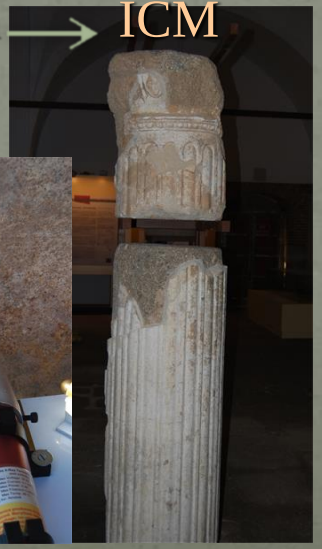
} TRM



- ✧ Walls → VR "La Majona"
- ✧ Pieces from the Museum → ICM











Analytical techniques and samples

*In situ (**Roman theater of Medellín** -TRM)*

✓ *X-Ray Fluorescence (EDXRF)*

- ***Scaenae front***
- Columns
- Sphinx









Analytical techniques and samples

In situ (Roman theater of Medellín -TRM)

✓ *X-Ray Fluorescence (EDXRF)*

- ✧ *Scaenae front*
- ✧ Columns
- ✧ Sphinx





Analytical techniques and samples

In situ (Roman theater of Medellín -TRM)

✓ *X-Ray Fluorescence (EDXRF)*

- ✧ *Scaenae front*
- ✧ **Columns**
- ✧ Sphinx





Analytical techniques and samples

In situ (Roman theater of Medellín -TRM)

✓ *X-Ray Fluorescence (EDXRF)*

- ✧ *Scaenae front*
- ✧ Columns
- ✧ **Sphinx**







Analytical techniques and samples

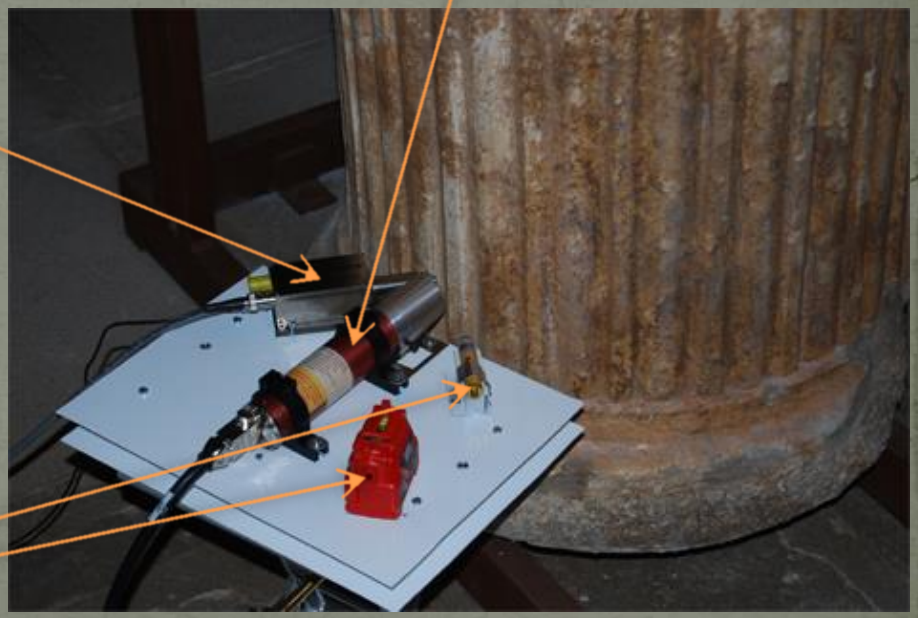
In situ

✓ *X-Ray Fluorescence (EDXRF):* **Technical details**

DETECTOR (XR-100CR. Amptek):
Si-PIN
Resolution: 220eV (FWHM, ^{55}Fe).
Window: 25μm (Be).

X-RAY TUBE (Eclipse III, Amptek):
Max Tension 30kV
Max. Intensity 100μA
Anode: Ag.
Collimator: 1.5mm





Two crossed lasers

In this work: 25kV, 10μA, 200-300s

Analytical techniques and samples

In situ

✓ *X-Ray Fluorescence (EDXRF):* **Technical details**

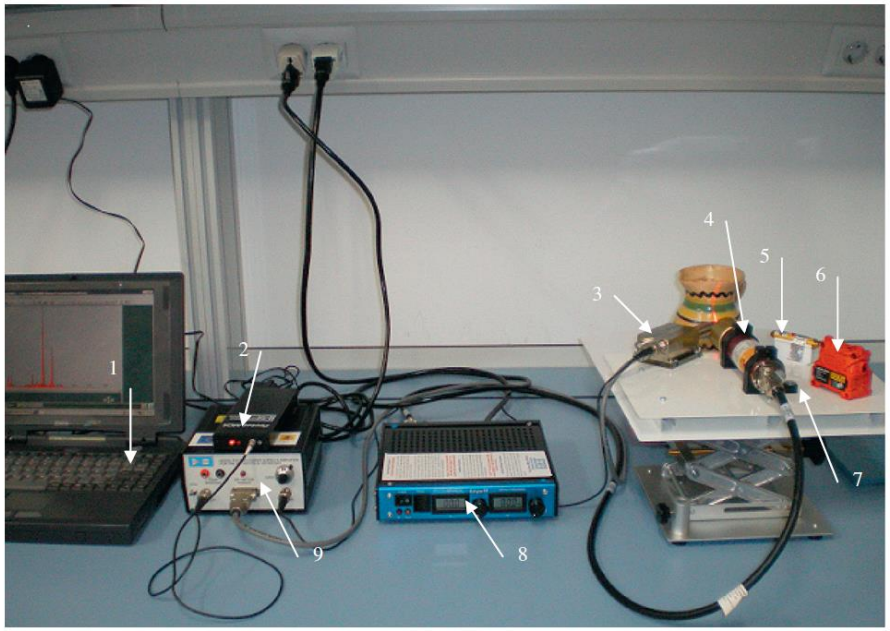


Fig. 1. XRF spectrometer system used in this work: (1) Laptop; (2) Multichannel analyzer (MCA); (3) Si-PIN detector and preamplifier; (4) X-ray tube; (5) Pointer laser; (6) Level laser; (7) Flat surface; (8) X-ray power supply controller; and (9) Power supply and amplifier for the detector.



Analytical techniques and samples

In situ

✓ *X-Ray Fluorescence (EDXRF)*

In SAIUex (research support facilities -Uex)

- ✓ *X-Ray Diffraction (XRD)*
- ✓ *Fourier transform Infrared (FTIR)*
- ✓ *Scanning Electron Microscopy (SEM-EDX)*

Roman Theater TRM		***Medieval Church ICM***	
M1-1	*UE9200*	M6-1	*UE640* (modern s. XVI-XVIII)
M1-2	"	M6-2	"
M2	*UE9070*	M7	*UE685* (Christian s. XIII?)
M3	*UE9089*	M8	*UE700* (Islamic s. XII-XIII?)
M4	*UE8619*		
M5	*1532-14*		

Analytical techniques and samples

In

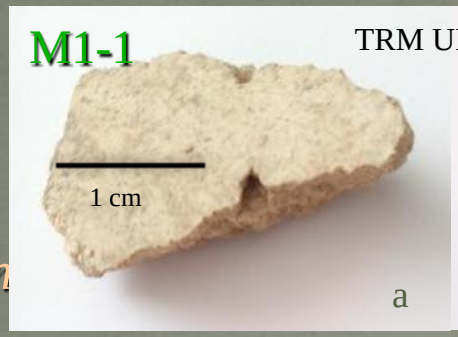
✓

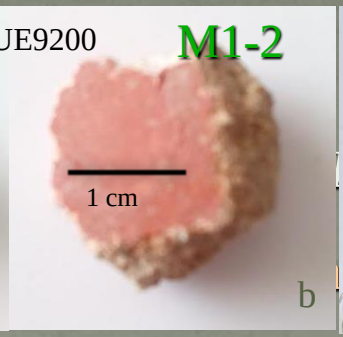
En

✓ s X (XRD)

✓

✓

















Roman Theater *TRM*		*Medieval Church* *ICM*	
M1-1	*UE9200*	M6-1	*UE640* (modern s. XVI-XVIII)
M1-2	"	M6-2	"
M2	*UE9070*	M7	*UE685* (Christian s. XIII?)
M3	*UE9089*	M8	*UE700* (Islamic s. XII-XIII?)
M4	*UE8619*		
M5	*1532-14*		

Analytical techniques and samples

In SAIUex : **technical details**

- ✓ ***X-Ray Diffraction** (XRD)*
- ✓ *Fourier Transform Infrared (FTIR)*
- ✓ *Scanning Electron Microscopy (SEM-EDX)*



Bruker D8 ADVANCE

Types of measure: **coupled** and **low-angle incidence** modes

- Range (º2θ): 20-70º
- Increment º2θ: 0.02º
- Counter time: 0.5s
- Radiation: K_α copper (1.54184 Å)
- Output mirror grid Göebel: 2.0 mm
- Type of detector: lineal Vantec (aperture 12º)

Analytical techniques and samples

In SAIUex : **technical details**

- ✓ *X-Ray Diffraction (XRD)*
- ✓ ***Fourier Transform Infrared** (FTIR)*
- ✓ *Scanning Electron Microscopy (SEM-EDX)*



FTIR (Nicolet iS10, Thermo Scientific)
Work mode: transmission
Sample: KBr Pellets
32 scans/spectrum
Range: from 400 to 4000 cm^{-1}

Analytical techniques and samples

- ✓ *X-Ray Diffraction (XRD)*
- ✓ *Fourier transform Infrared (FTIR)*
- ✓ ***Scanning Electron Microscopy*** *(SEM-EDX)*

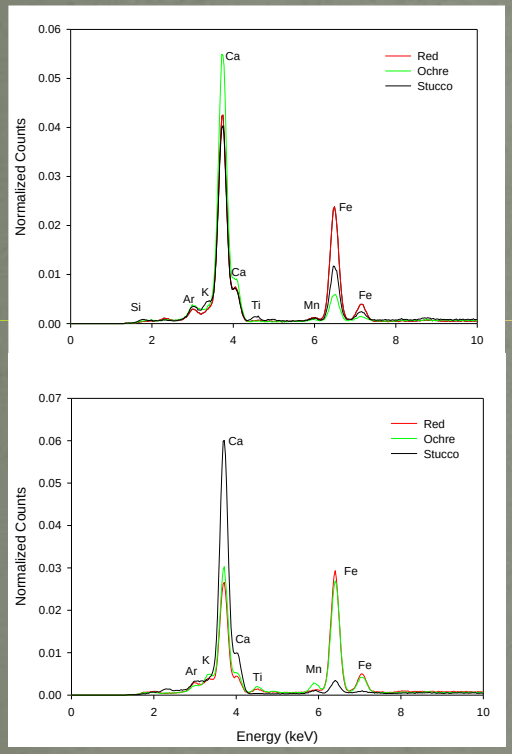


SEM
Quanta 3D FEG (FEI Company II)

- Work mode: e^- in low vacuum (10-130Pa)
- Detector: secondary electrons (SE) and back scattering dispersed electrons (BSED)
- Sample preparation: paint cross-section embedded in polyester resins
- μXRF analysis
- Elemental scan

Some results

✓ X-Ray Fluorescence



EDXRF spectra of the red and ochre pigments versus stucco from the ***Scaenae Frons*** and a column of the Roman Theater.

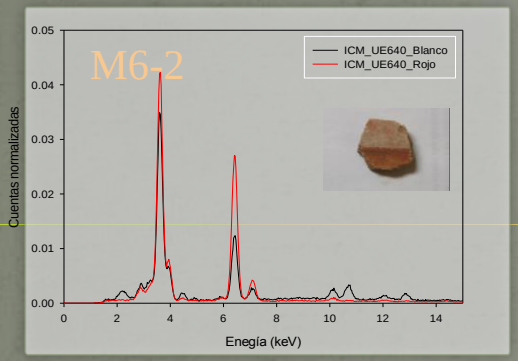
Fe/Ca	Red	Ochre	Black	Stucco	Marble
Scaenae Frons	1.20	0.26	-	-	-
Column1	0.43	0.35		0.56	
Column2	1.26	1.02	0.08	0.05	
Sphinx	-	0.03	-	-	0.03

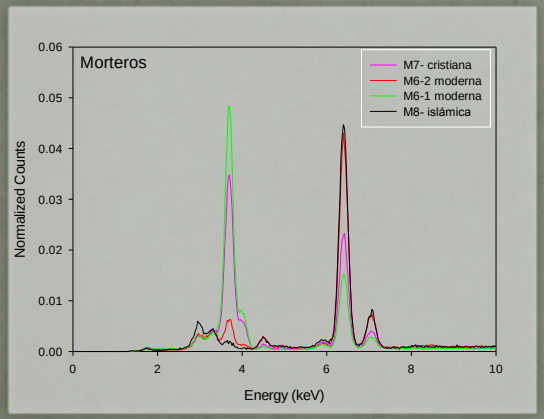
- Ca and Fe were the main found elements
- Mn, Ti, K and traces of S and Si
- Fe/Ca shows a higher Fe amount in red color respect to ochre color in the *Scaenae front* and columns.
- No differences in Fe/Ca in Sphinx.
- Uncertainty: $\Delta \approx 1\%$

❖ Similar results were found in the Roman Villa "La Majona"

Some results

✓ **X-Ray Fluorescence: Samples from the Archaeological Museum**





Pigments:

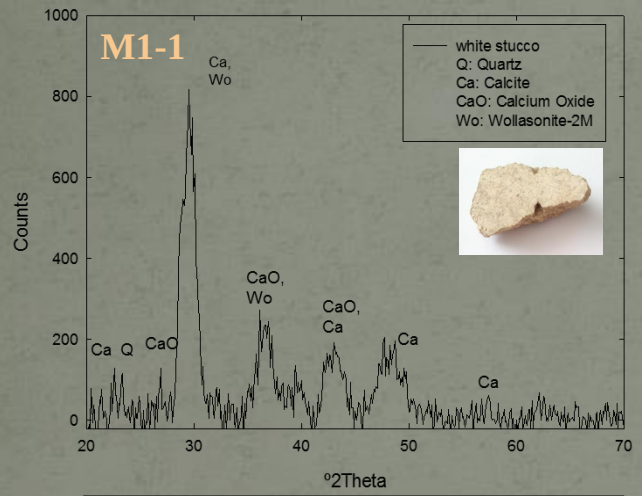
- Generally, Ca and Fe main elements with traces of Mn and Ti .
- Traces of S, Hg and Pb in M6-2 (modern) ➔ White lead and cinnabar?
- Remarkable presence of Pb in orange of M4 (Roman) ➔ Minium (Red lead)?

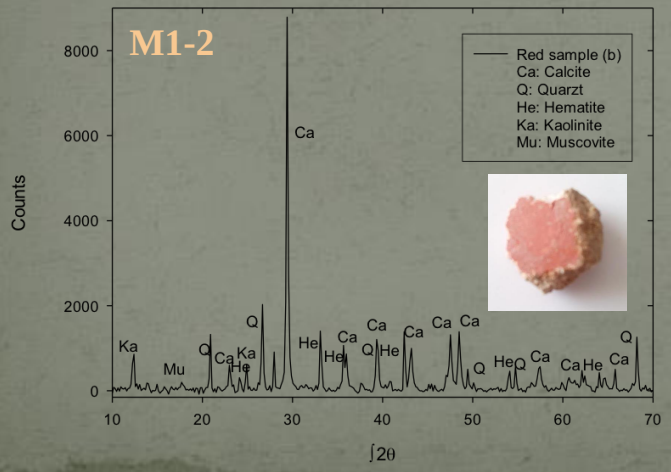
Mortars:

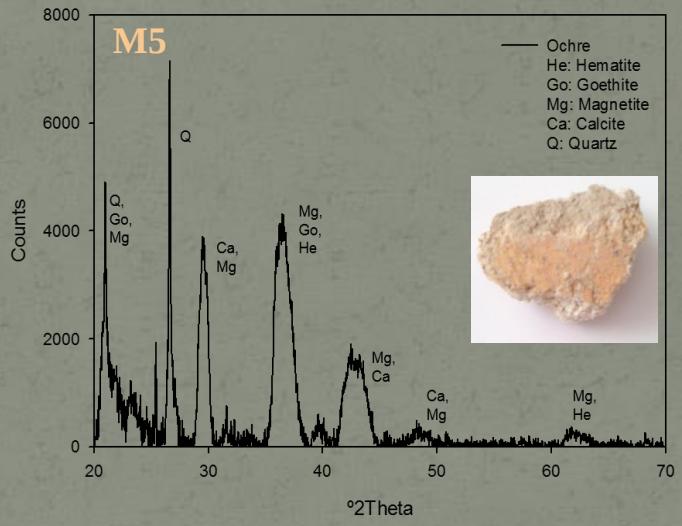
- Ca and Fe and traces of Mn, Ti, K and Si in M6 and M7
- Fe in M8 (Islamic -adobe)

Some results

✓ X-Ray Diffraction (XRD)



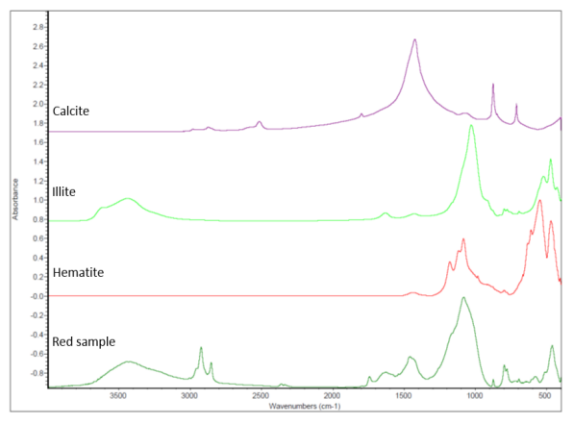




- Calcite and quartz present in all cases
- Hematite and Goethite in red and ochre

Some results

✓ Fourier Transform Infrared (FTIR)



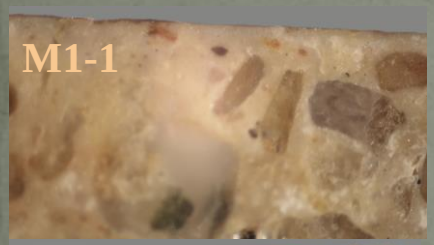
- The calcite presence is confirmed in all the cases.
- hematite is confirmed as the main component of red pigment.
- Presence of Illite confirming Si, K traces found by fluorescence analyses.

- Presence of signal around 3000 and 1745 cm^{-1} correspond to aliphatic (C-H) and ester (C=O) groups, respectively which suggests the usage of oil as a binder Ny Carlsberg Glyptotek (http://trackingcolour.com/objects/23)

Some results

✓ Scanning Electron Microscopy (SEM-EDX)

Cross section Optic Microscope (x100)





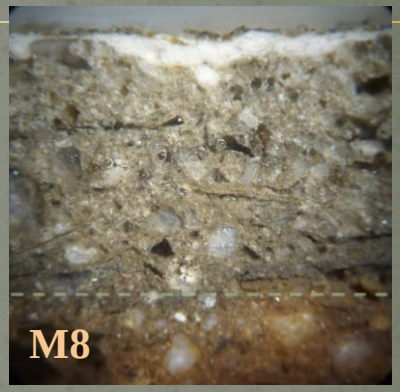












TRM

- Analogy in the mortar particle size distribution
- Remarkable differences in painting technique

ICM

- Remarkable differences in mortars

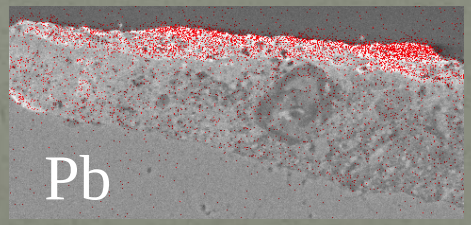
Some results

✓ Scanning Electron Microscopy (SEM-EDX)

- SEM analysis focused on studying structure, elemental composition elemental and thickness of the painting layer.
- Confirmation of Pb in the orange stripe of M4 (roman) ➔ Minium (Red lead)





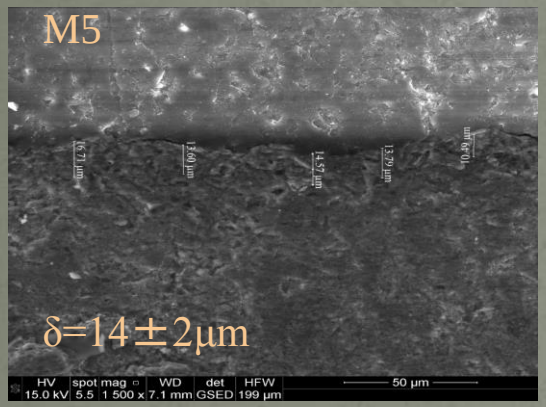


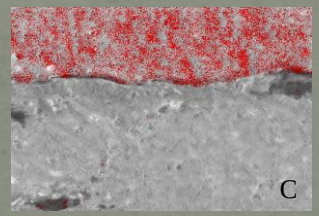
Some results

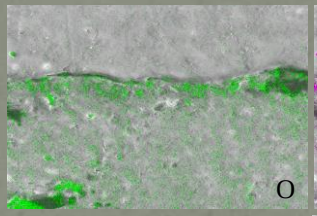
✓ Scanning Electron Microscope (SEM-EDX)

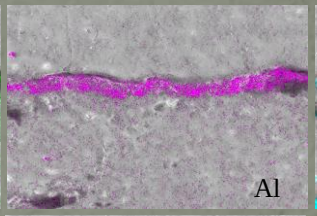


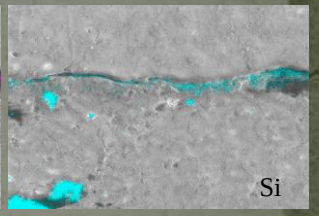


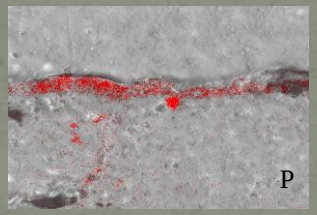


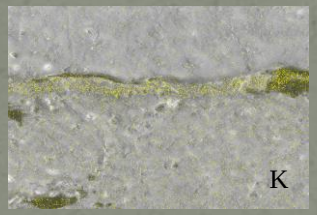


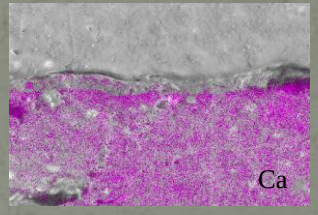


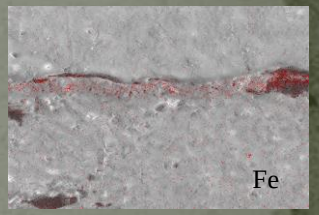












➢ No uniform structure layers but with same composition



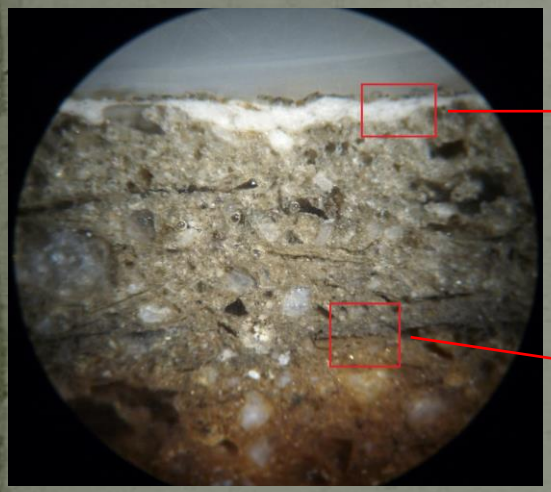
Some results

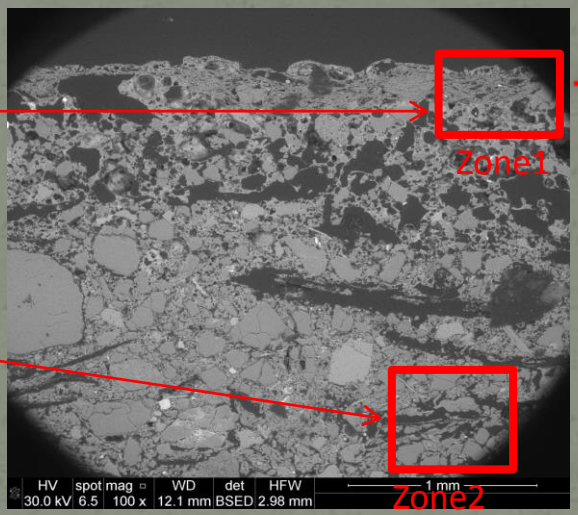


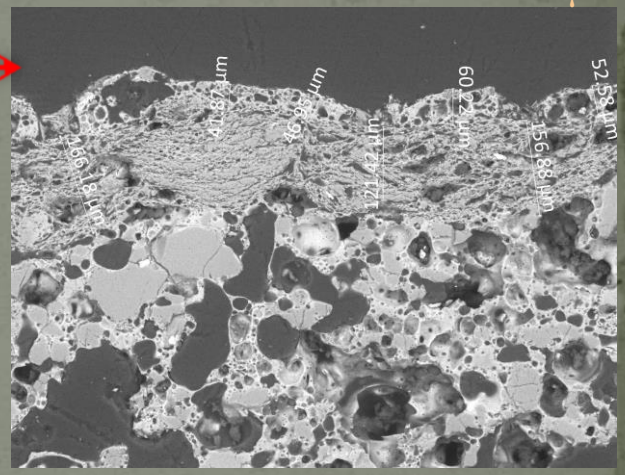
✓ **Scanning Electron Microscope (SEM-EDX)**

δ= 50±8μm

δ= 148±24μm







- No uniform porous layers but with similar composition, as can be observed from SEM maps performed at the interface.

Conclusions

✓ Several wall fragments belonging to different periods localized in a specific geographic area were analyzed and a comparison among materials and execution techniques was performed.

✓ Pigments, charges and binders were identified. The most elaborated works and a wide rage of pigments correspond to the roman period.

✓In some cases, the execution technique has been identified and some differences between organic and inorganic blinders has been found.

✓ This kind of study allows to obtain a greater knowledge about materials used in painting, the possible origin of these materials, the creation process and, thus, the more suitable method to guaranty the future preservation.

Other works

1. Pigments used in pottery

Application of XRF spectrometry to the study of pigments in glazed ceramic pots

M.J. NUEVO and A. MARTÍN SÁNCHEZ

Appl. Rad. Isot. 69, 574-579, **2011**





Other works

1. Pigments used in pottery



Fig. 3. Photographs of the ceramic vases: (a) PA; (b) TR; (c) BG; (d) PG1; (e) PG2.

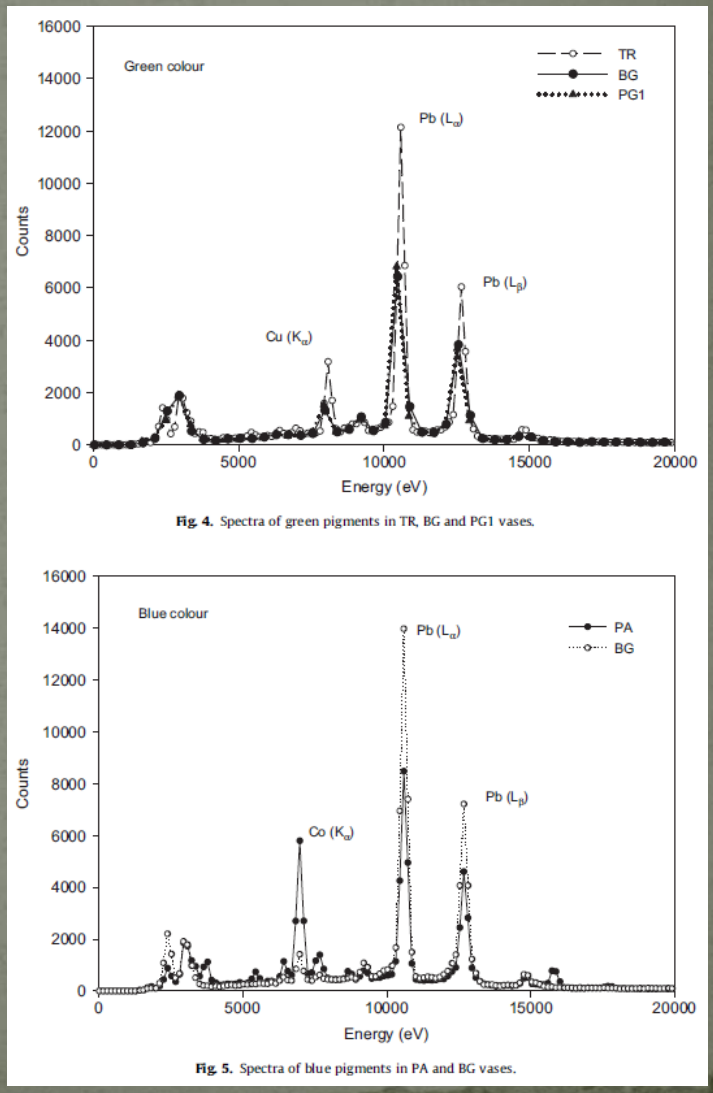


Fig. 4. Spectra of green pigments in TR, BG and PG1 vases.

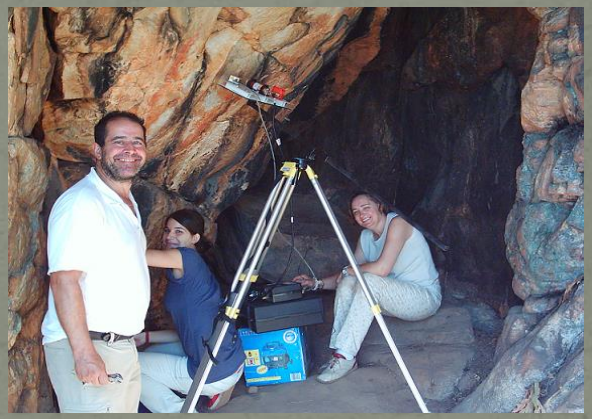
Fig. 5. Spectra of blue pigments in PA and BG vases.

Other works

2. Pigments in rock art



Abrigo dos Gaivões



Igreja dos Mouros

In situ EDXRF analysis of rock art pigments from "Abrigo dos Gaivões" and "Igreja dos Mouros" caves (Portugal)

M.J. NUEVO, A. MARTÍN SÁNCHEZ, C. OLIVEIRA and J. de OLIVEIRA

X-Ray Spectrometry 41, 1-5, **2011**

Other works

2. Pigments in rock art

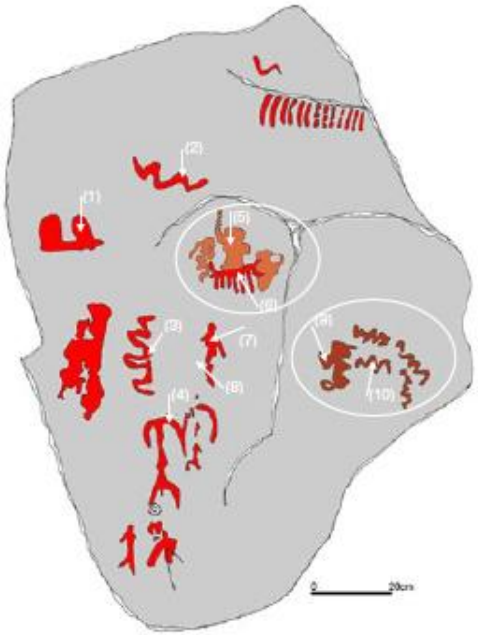


Figure 1. Schematic representation of the occidental panel from the 'Abrigo dos Galvões' shelter, with the studied points indicated.



Figure 2. Schematic representation of the central panel from the 'Abrigo dos Galvões' shelter, with the studied points indicated.

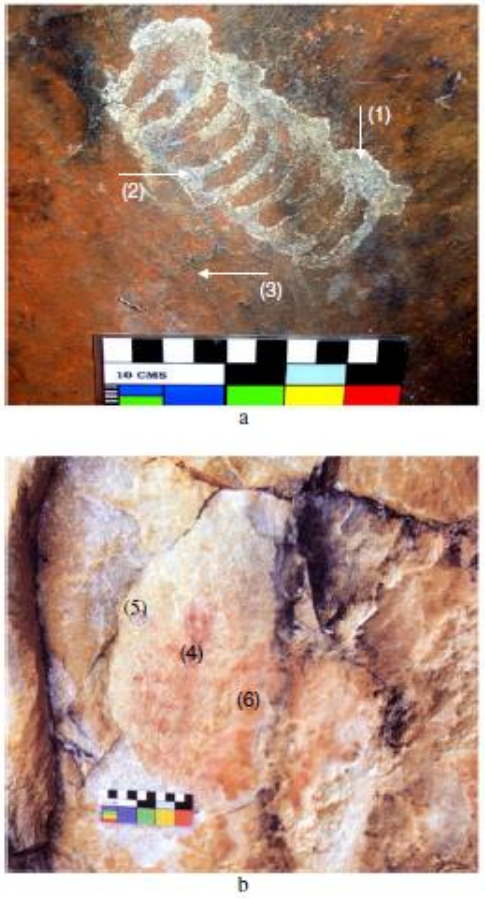


Figure 3. Figures from the 'Abrigo dos Mouros' cave: (a) white figure and (b) red figure, with the analysed points indicated.

Other works

3. Pigments in paintings.

Caracterización de los pigmentos en la obra del pintor costumbrista español Pérez Jiménez mediante XRF.

P. PAJUELO CABEZAS, M.J. NUEVO, A. MARTÍN SÁNCHEZ

Estudos Arqueológicos de Oeiras (Portugal), 2012.



De vuelta de la Fuente



El Ramito de Flores



Los Recién Casados

Other works

3. Pigments in paintings.



Other works

3. Pigments in paintings (restorations)





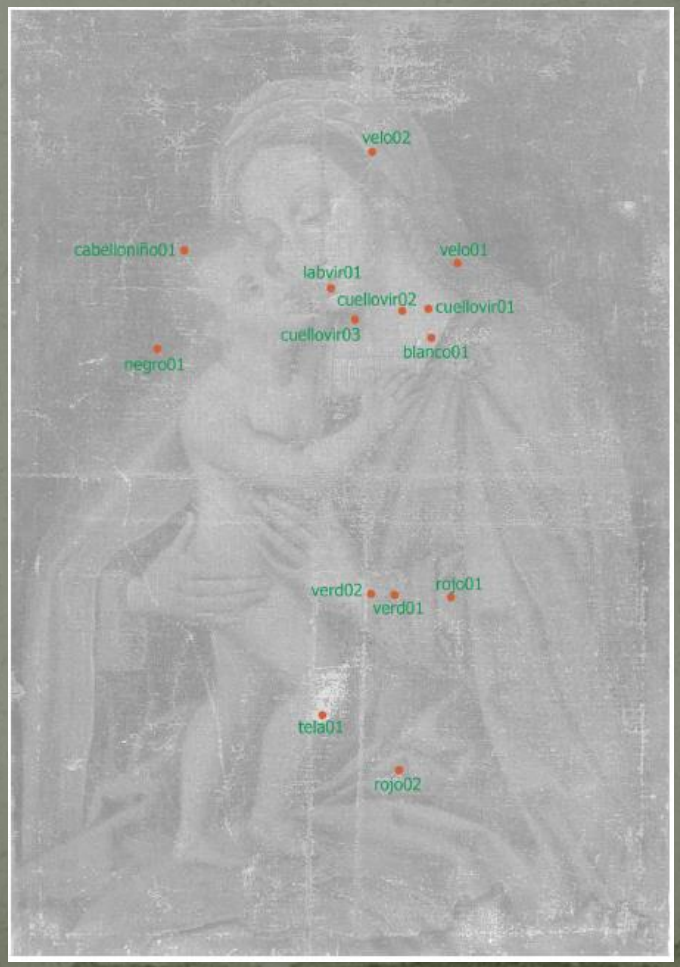




Other works

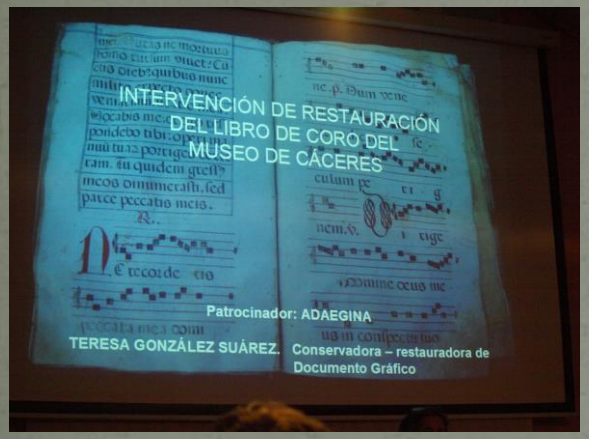
3. Pigments in paintings (restorations)





Other works

4. Analysis of inks in parchment







Caracterización de los materiales utilizados en libros antiguos mediante Fluorescencia de Rayos X (XRF) y Anatomía Comparada.

M. J. NUEVO, A. MARTÍN SÁNCHEZ, T. GONZÁLEZ SUÁREZ, M.A. OJEDA

Actas del X Congreso Ibérico de Arqueometría, (España), 2014

Other works

4. Analysis of inks in parchment



Acknowledgements

SAEM

(**S**ervicio de **A**nálisis **E**lemental
Elemental and Molecular A

SACSS

(**S**ervicio de **A**
Analysis and Ch
de **S**ólidos y **S**uperficies)
lids and Surfaces

Gracias



JUNTA DE EXTREMADURA

(GR10160, FEDER)

Thank you