



# INFN diagnostic campaigns in the ADAMO project

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# Why scientific analyses are applied on cultural heritage?

- Characterization of the materials employed and manufacture processes



Knowledge of the technical advances of an artists and/or cultures

- Diagnostic analyses of the original chemical composition and restoration treatments



Supporting the activities of restorers before-during-after the restoration

- Authentication of the artefacts based on the chemical-physical properties of the materials used



Supporting the activities of historian, art critics and art dealers

- Monitoring of the environmental conservative conditions and the *status quo* of the artefacts



Evaluation of the conservative practices.  
Performing a systematic check of the *status* of an artefact, before and after temporary loans

# Which techniques are more successful for our aims?

There is NO general answer

It depends on the chemical and physical properties of the artefact and on the aims. However, it is important knowing that scientific techniques could be divided in:

## Non-Destructive and Non-invasive Analyses

- X-ray Fluorescence Spectroscopy

## Micro-Destructive Analyses

### Elemental analyses

- Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray micro-analysis (EDX)

### Molecular analyses

- Imaging multispettrale (UV, VIS, NIR, SWIR)
- Portable Raman Spectroscopy
- Portable Infrared Spectroscopy
- Reflectance Spectroscopy
- Micro-Raman Spectroscopy
- Micro-FT-IR Spectroscopy with conventional and Synchrotron radiation Source

### Structural analyses

- Termography

# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Case studies

*Easel Paintings*



*Pottery*

*Metals and  
corrosion products*

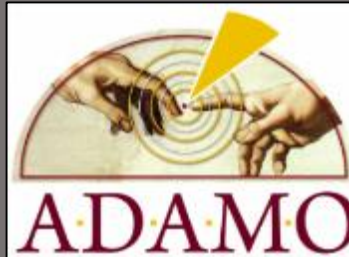




# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Easel Paintings

ADAMO site of interest:  
Palazzo Chigi (Ariccia, Rome)



“The Drunkenness of Noah” painted by Andrea Sacchi

PURPOSE:

Visualization of the underdrawings and  
“*pentimenti*”



Reconstruction of the artistic  
production of the artist



Catanzaro, Museo  
Provinciale



Berlino, Staatliche Museen,  
Gemäldegalerie



TECHNIQUE: Infrared Reflectography (IRR)

# "The Drunkenness of Noah" painted by Andrea Sacchi

VISIBLE



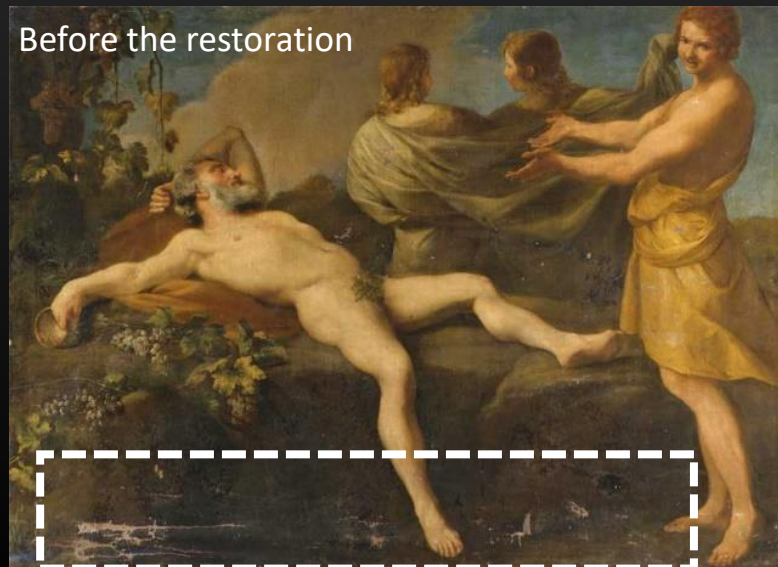
REFLECTOGRAPHY Near Infrared (NIR)



REFLECTOGRAPHY Shortwave Infrared (SWIR)



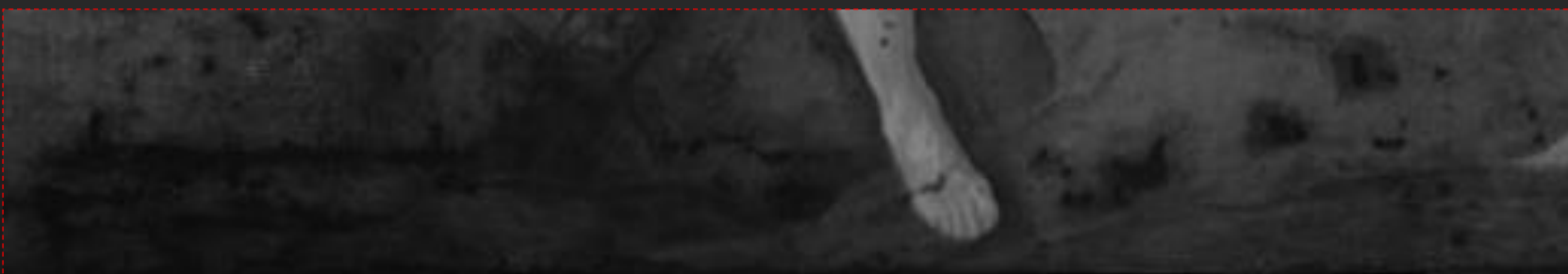
Before the restoration



Before the restoration



REFLECTOGRAPHY Shortwave Infrared (SWIR)



The infrared reflectography may highlights modern restoration due the infrared absorption of the materials used



# “The Drunkenness of Noah” painted by Andrea Sacchi



REFLECTOGRAPHY Near Infrared (NIR)



REFLECTOGRAPHY Shortwave Infrared (SWIR)



Before the restoration





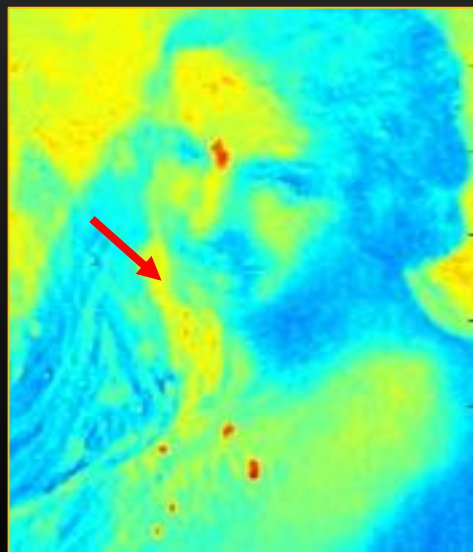
# “The Drunkenness of Noah” painted by Andrea Sacchi



Three important pentimenti: 1) the face of the figure placed on the left side was shifted; 2) the figure placed in the background right side shows short hair in the reflectograms.



REFLECTOGRAPHY SWIR



PRINCIPAL COMPONENT ANALYSIS (PCA)

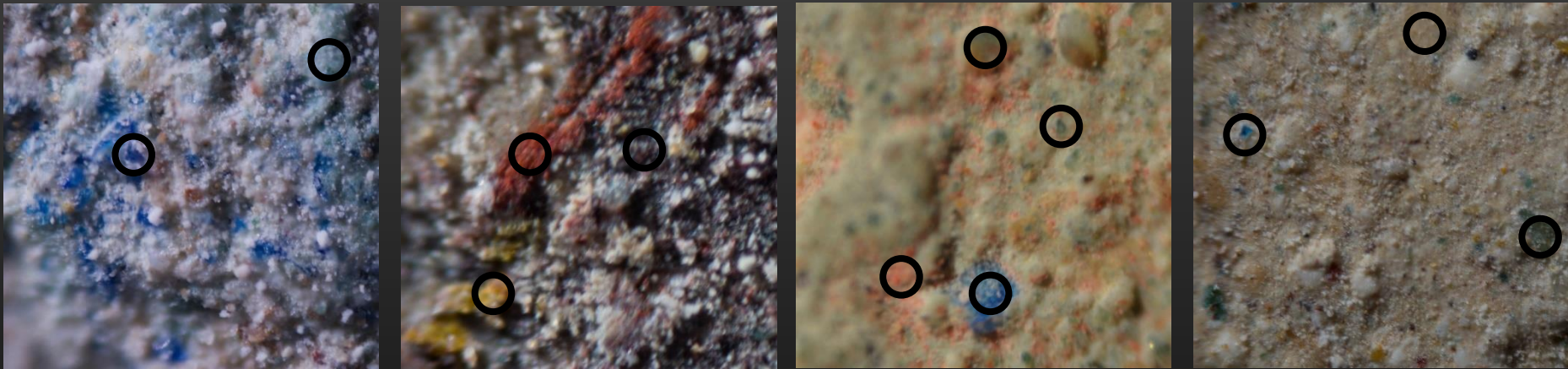
3) the figure in the foreground shows two faces: the older version seems smaller than the last one.

On the other hand, PC2 evidences few details not clearly identified both in the InGaAs image: here the chin of the earlier version of the Ham's face seems to have undergone changes

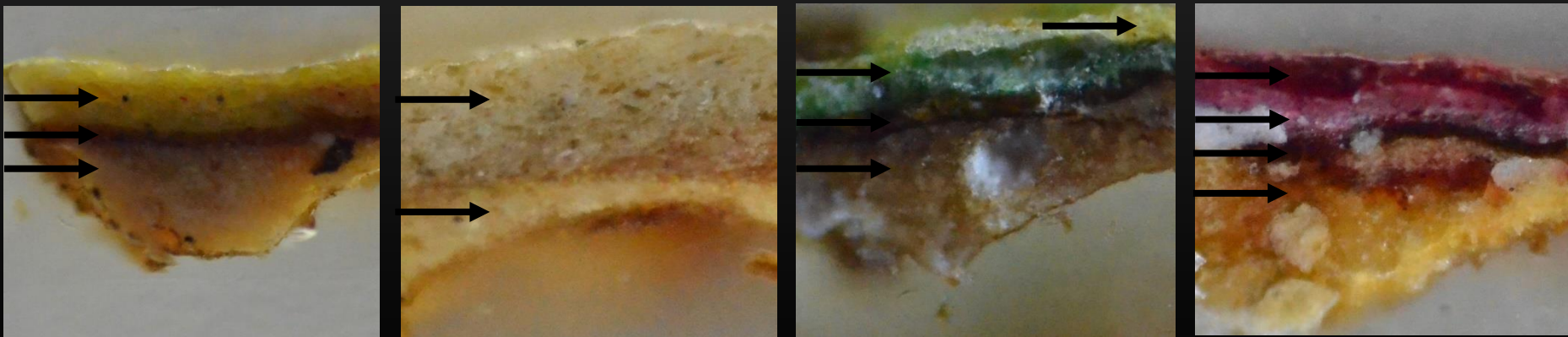
# Why it is necessary to perform micro-destructive analyses?

The composition of materials used for realizing artefacts is generally composed by inhomogeneous and stratified structures

Pictorial Surfaces



Cross sections of paintings





# Restoration of “Adoration of the Magi” attributed to El Greco

## QUESTION:

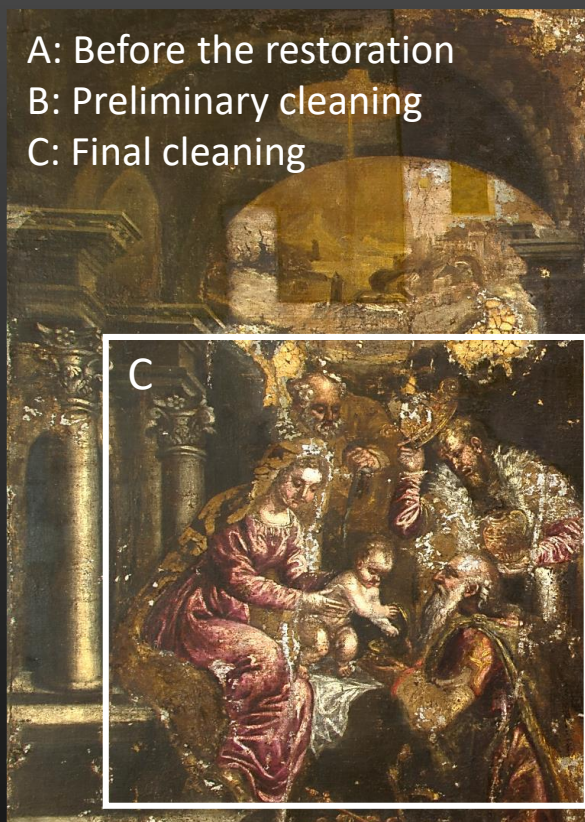
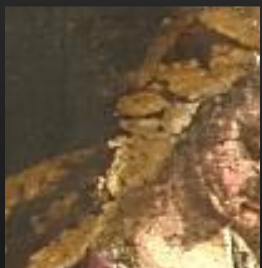
Why the painting is brown?



It is covered by several varnish layers



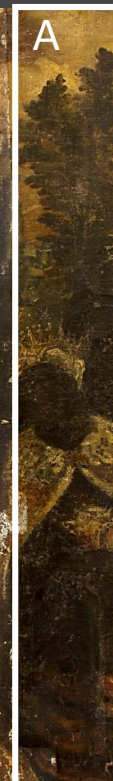
Some pictorial layers are brown, such as the Virgin’s veil, the sky



A: Before the restoration

B: Preliminary cleaning

C: Final cleaning



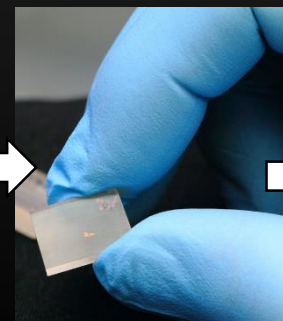
Realization of microsamples



Microsampling



Embedding in resin



Trasversal cut

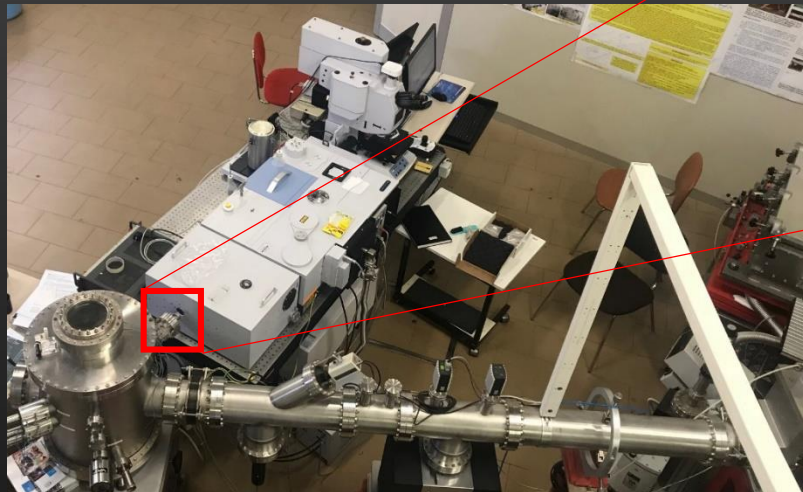


Polishing

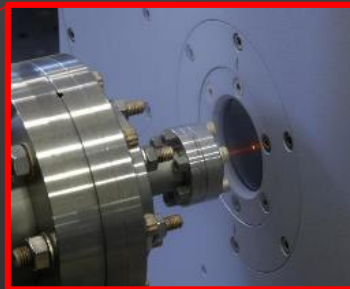


Which kind of analyses may be performed on cross sections for the molecular and elemental analyses?

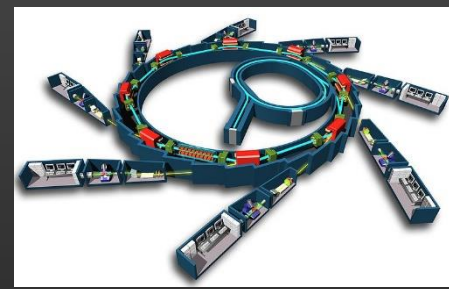
Micro-infrared Spectroscopy (FTIR) with Synchrotron radiation source



1



2



3



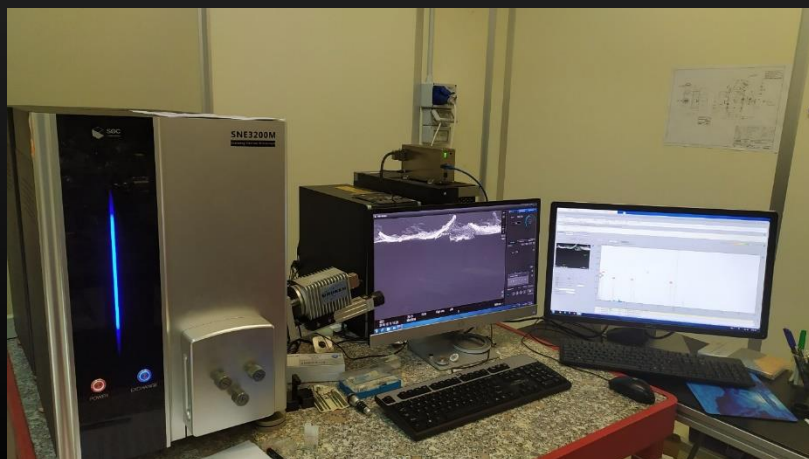
4

1 Synchrotron source

2 Schematic overview of a Synchrotron Facility

3 Synchrotron Radiation Facility at Frascati (Dafne - Light)

4 Synchrotron Radiation Facility at Trieste (Elettra)



Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray micro-analysis (EDX)

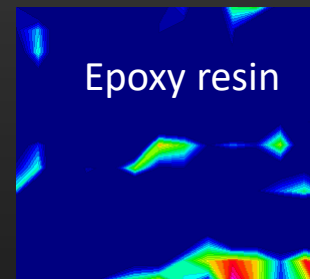
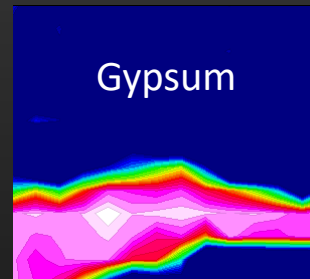
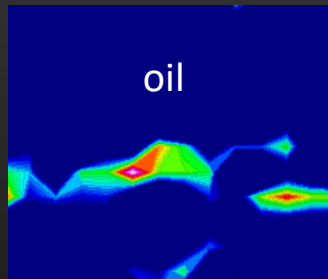
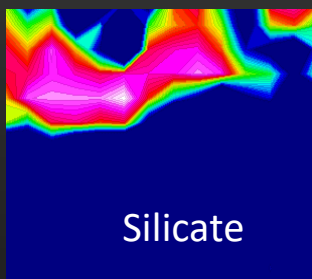
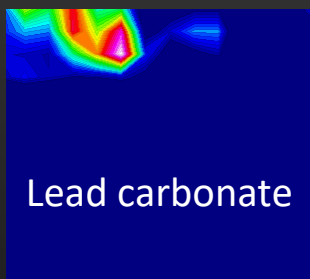
# Restoration of "Adoration of the Magi" attributed to El Greco (Accademia di San Luca, Rome)

Molecular composition



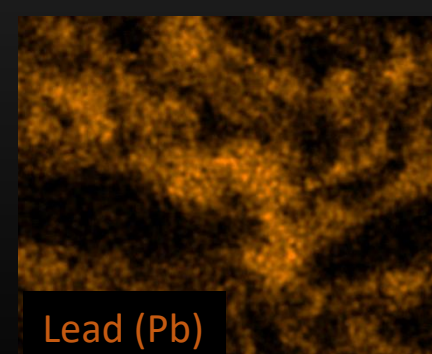
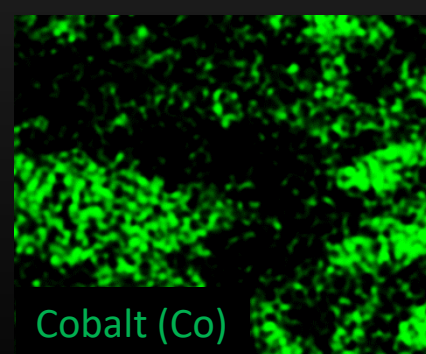
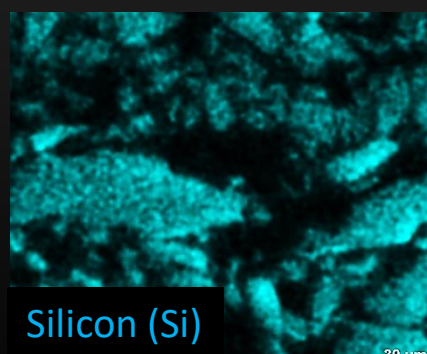
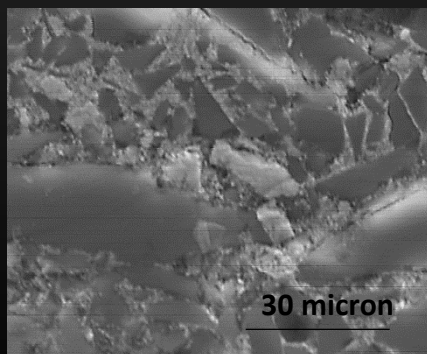
Lead carbonate  
Silicate  
Oil  
Gypsum  
Epoxy resin

Infrared spectroscopy imaging (Synchrotron radiation source)



Elemental composition

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray micro-analysis (EDX)



Brown pigment



Smalt (Cobalt glass)

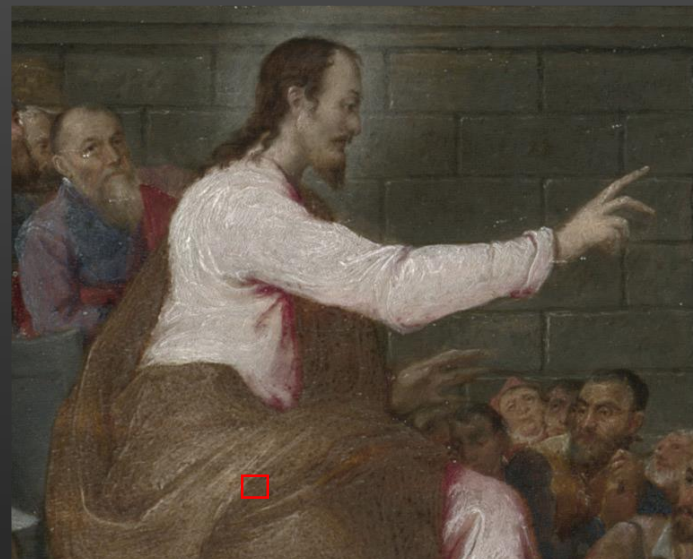


## Smalt degradation

### Blue mantles of the Vergin



## Browning of the Christ's mantle



Optical  
microscopy



UV  
fluorescence  
optical  
microscopy



# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Pottery

Campana reliefs from the Palatine Hill and Colosseum Valley in Rome

PURPOSE:

Which pigments are used?



Is it possible to take  
micro-samples?

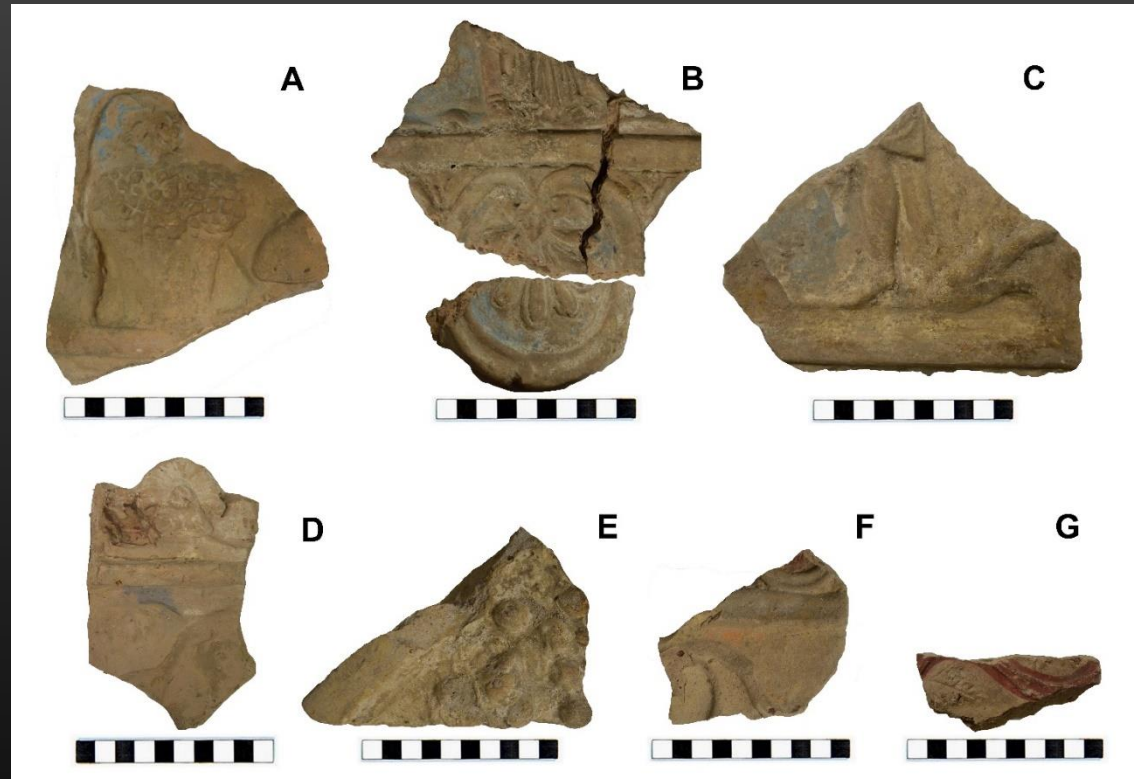
**NO**



Non invasive  
and  
non-destructive approach



X-ray fluorescence (XRF) Spectroscopy  
Fiber Optical Reflectance Spectroscopy (FORS)  
Photo-induced luminescence (PIL) imaging



# Campana reliefs from the Palatine Hill and Colosseum Valley in Rome



X-ray fluorescence (XRF)	Fiber Optical Reflectance Spectroscopy (FORS)	Photo-induced luminescence (PIL) imaging
Detection of LEAD (Pb)	No characteristic spectral features	NO

## MINIUM ( $Pb_3O_4$ )



X-ray fluorescence (XRF)	Fiber Optical Reflectance Spectroscopy (FORS)	Photo-induced luminescence (PIL) imaging
Detection of IRON (Fe)		NO

HEMATITE ( $Fe_2O_3$ )  
or  
RED OCHRE  
(hematite and silicates)

# Campana reliefs from the Palatine Hill and Colosseum Valley in Rome

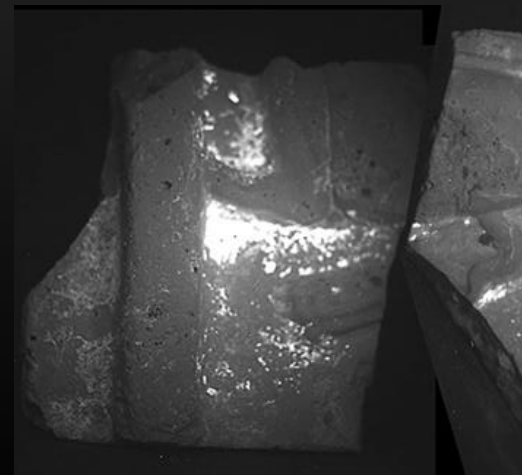


BLUE PIGMENT

X-ray fluorescence (XRF)	Fiber Optical Reflectance Spectroscopy (FORS)	Photo-induced luminescence (PIL) imaging
Detection of COPPER (Cu)	<p>The graph plots Reflectance (%) on the y-axis (ranging from 20 to 60) against Wavelength (nm) on the x-axis (ranging from 400 to 900). Three blue arrows point to specific peaks in the spectrum: one at approximately 480 nm, another at 580 nm, and a third at 720 nm.</p>	<p>A black and white image showing the result of photo-induced luminescence (PIL) imaging. A bright, curved, and somewhat irregular white area is visible against a dark background, indicating the presence of the pigment.</p>

EGYPTIAN BLUE  
(cuprorivaite  $\text{CaCuSi}_4\text{O}_{10}$   
and quartz  $\text{SiO}_2$ )

Egyptian blue could be detected by PIL imaging also in absence of evident traces of colour





# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Metals and corrosion products

### Copper-based Greek and Roman coins from Pompeii

Inv. no.	Coin	Inv. no.	Coin
C1-9	Republican as (III-II century BC)	C11-12	Republican as (II-I century BC)
C1-41	Republican as (III-II century BC)	C11-56	Pseudo-Ebusus (II century-early I century BC)
C1-12	Republican as (III-II century BC)	C14-15	Imperial quadrans (Caligula, 39-41 AD)
C1-38	Ebusus or pseudo-Ebusus (II century-early I century BC)	C14-6	Unknown coin
C7-12	Imperial quadrans (Caligula, 39-41 AD)	C18-9	Imperial as (early I century AD)
C5-1	Pseudo-Ebusus (II century-early I century BC)	C19-40	Republican as (153 BC)
C11-11	Unknown coin	C19-51	Republican as (III-II century BC)
		C24-31	Massalia (150/130-100 BC)

Imperial as



Pseudo-Ebusus



#### QUESTION:

- Which is the alloy of these coins?



X-ray fluorescence spectroscopy  
Scanning Electron Microscopy (SEM) coupled with  
Energy Dispersive X-ray micro-analysis (EDX)

- Which corrosion products cover the bulk?

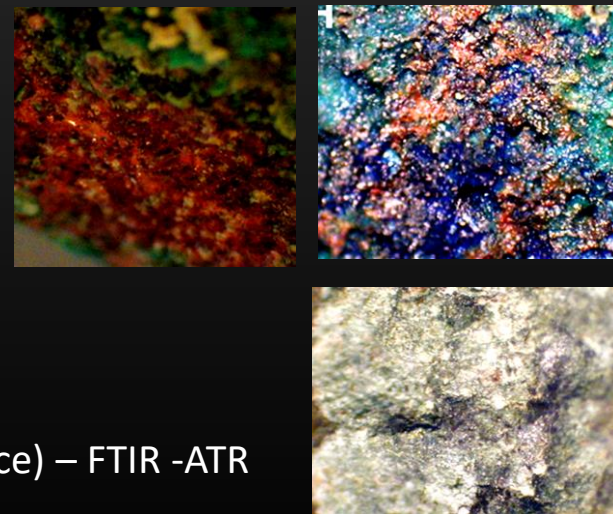


Is it possible to take micro-samples? **YES**

micro-destructive  
approach

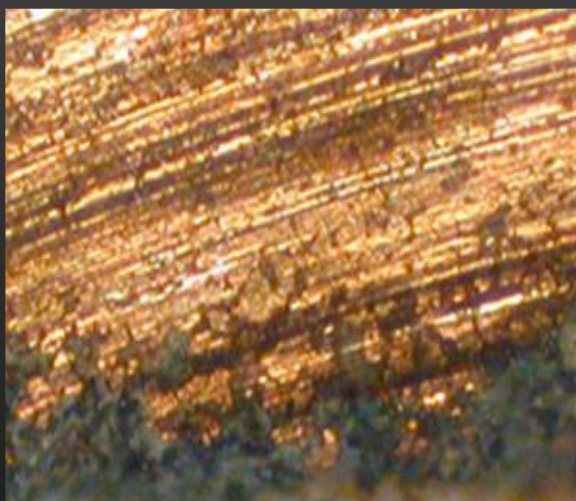


Infrared Spectroscopy (conventional source) – FTIR -ATR  
Micro-Raman spectroscopy



# Copper-based Greek and Roman coins from Pompeii

## X-ray fluorescence spectroscopy

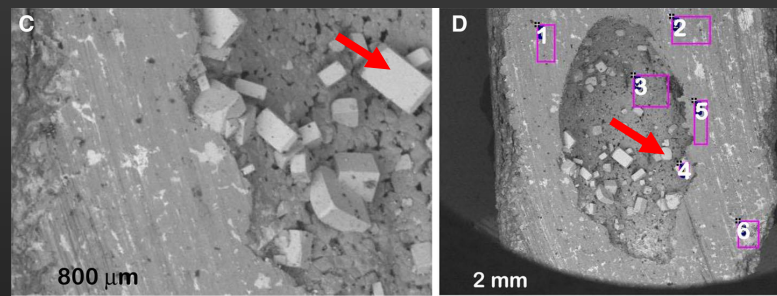


Imperial as, Ebusus and Massalia coins contain copper, tin and lead → **Bronze**  
Imperial as and quadrants have been minted with copper

Inv. No.	Cu	Sn	Pb
C1-9	x	x	x
C1-41	x	x	x
C1-12	x	x	x
C1-38	x	x	x
C7-12	x	n.d.	n.d.
C5-1	x	x	x
C11-11	x	x	n.d.
C11-12	x	x	x
C11-56	x	x	x
C14-15	x	n.d.	n.d.
C14-6	x	x	x
C18-9	x	n.d.	n.d.
C19-40	x	tr	x
C19-51	x	x	x
C24-31	x	n.d.	x

x, present; tr, low concentration (<1 wt.%); n.d., not detected

## Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray micro-analysis (EDX)



SEM-EDS analysis (mass %)					
Area	Fe	Cu	As	Sn	Pb
1	n.d.	86.5	1.1	4.0	8.4
2	n.d.	84.6	n.d.	3.4	12.0
3	n.d.	70.1	2.2	3.1	24.6
4	n.d.	10.0	n.d.	n.d.	90.0
5	0.9	83.0	n.d.	3.6	12.5
6	n.d.	19.9	n.d.	1.7	78.4

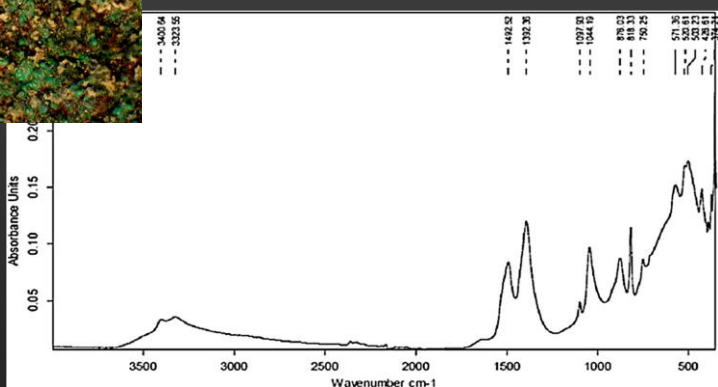
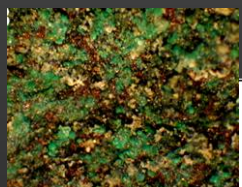


Several parallelepiped-shaped small crystals are found inside pore. The EDS analysis of a small crystal (4 area) revealed a high amount of Pb. Lead crystallizes in the cubic system and it is quite uncommon in nature. In this coin, optimal conditions for the growth of lead micro-crystals might have occurred.

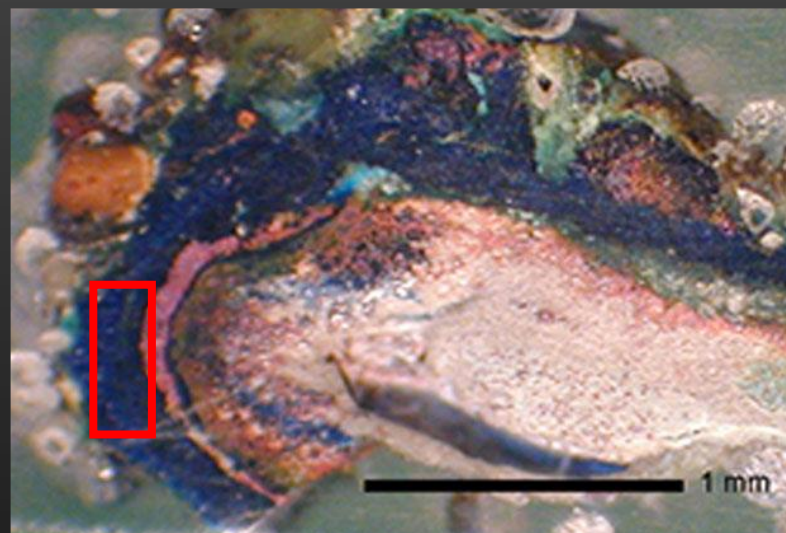
# Copper-based Greek and Roman coins from Pompeii

## Infrared Spectroscopy (conventional source)

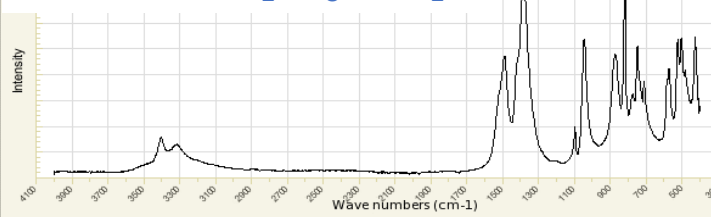
FTIR - ATR



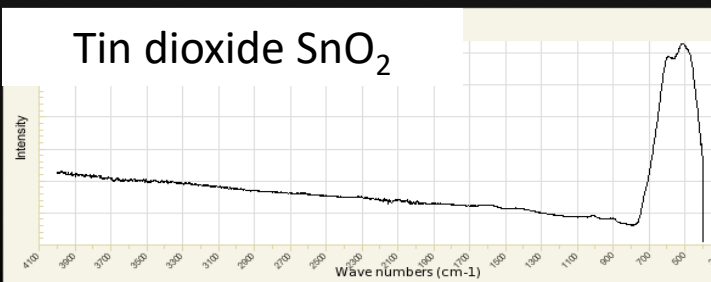
## Micro-Raman spectroscopy



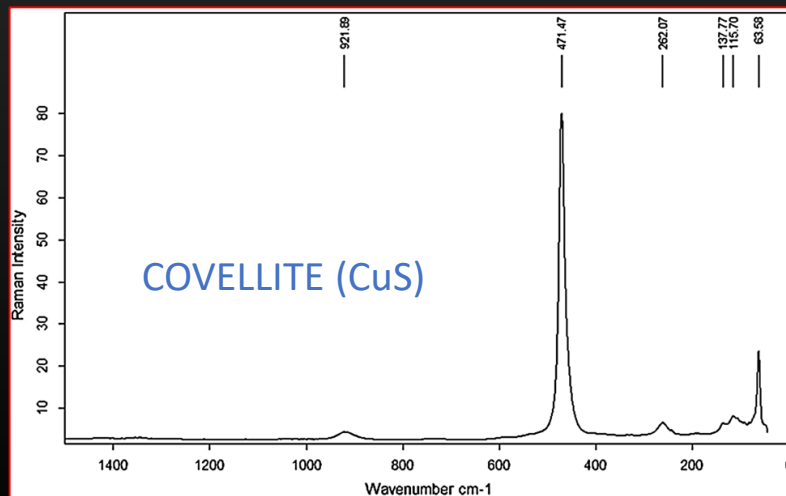
Malachite  $[\text{Cu}_2\text{CO}_3(\text{OH})_2]$



Tin dioxide  $\text{SnO}_2$



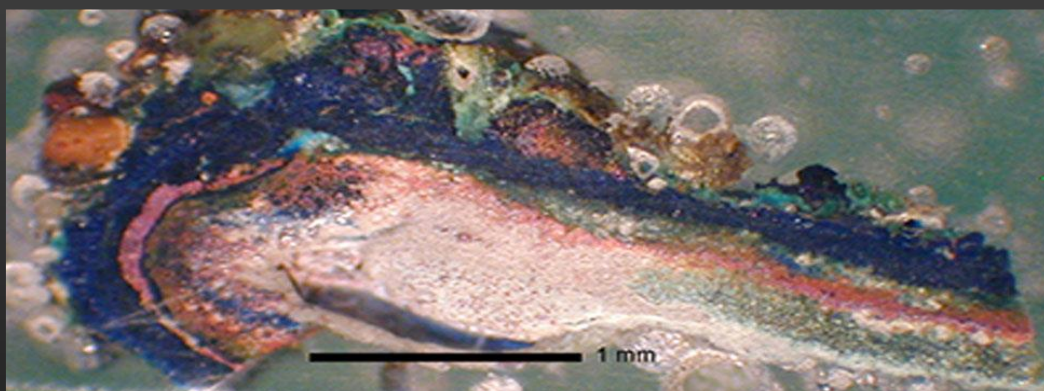
Reference spectra





## Copper-based Greek and Roman coins from Pompeii

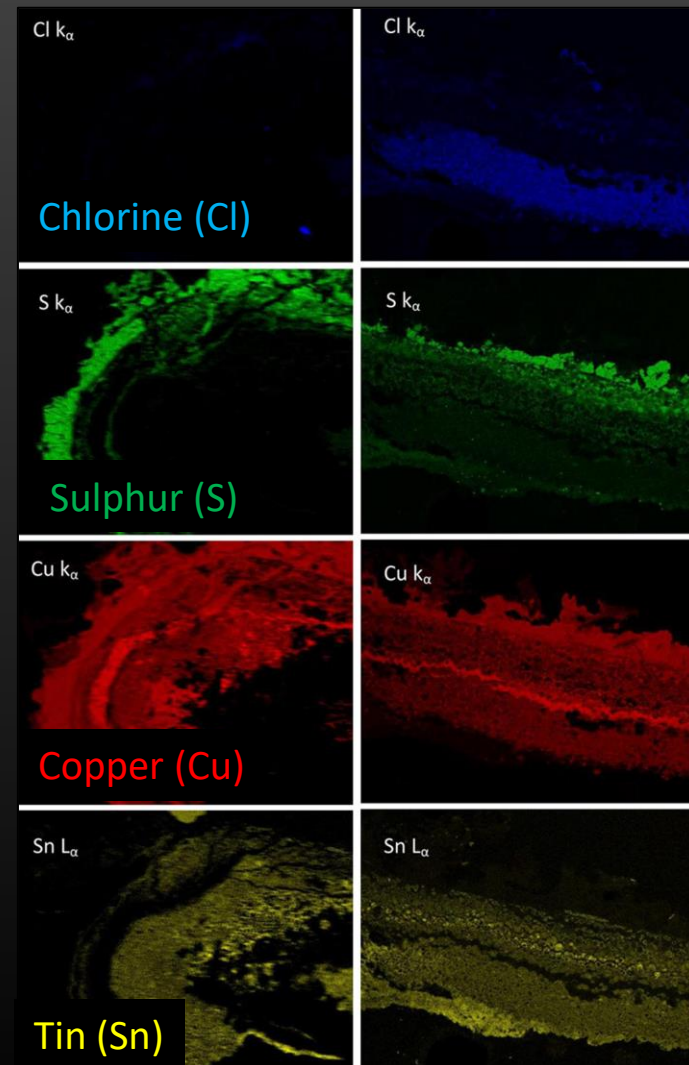
Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray micro-analysis (EDX)

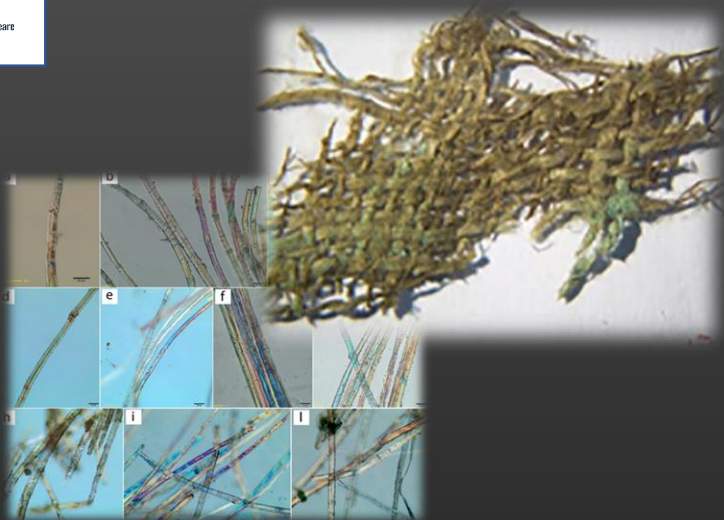


The entire corrosion stratigraphy is well described in terms of the distribution of copper, tin, chlorine, sulphur elements, obtained by SEM–EDS mapping

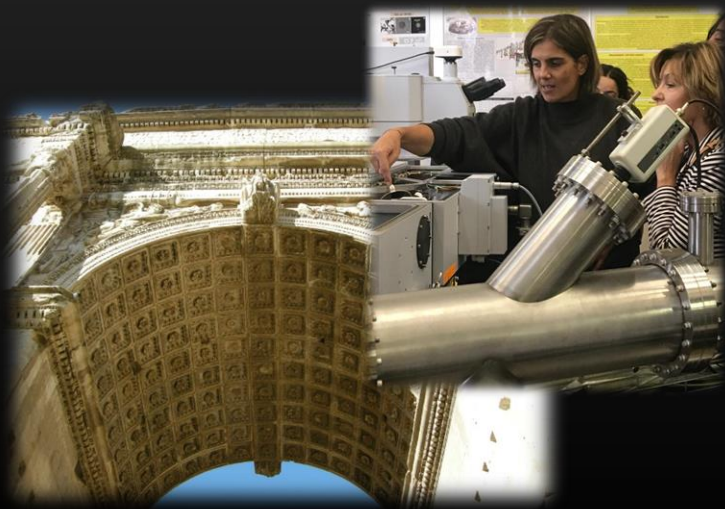
The external dark blue patinas are enriched with copper and sulphur (covellite), while the chlorine content suggests the presence of *bronze disease*

The elemental maps of Cu and Sn showed banded corrosion products in which copper-based layers alternate with Cu–Sn ones





## Cases Study: Mural Paintings, Historical Monuments and Archeological textiles



# DIAGNOSTIC ISSUES RELATED TO:

## MURAL PAINTINGS AND ARCHITECTURE:

Impossibility to move the artworks (frescoes, mural paintings) / insurance problems related to movement of fragments:

- *In situ* application of analytical techniques → The case of Palazzo Chigi, Ariccia
- Microsampling → The case of Septimius Severus Arch, Rome



## ARCHEOLOGICAL TEXTILES

- Could be found in bad conservation conditions (burnt)
- No reference standard (difficult comparing modern fibers with ancient ones)



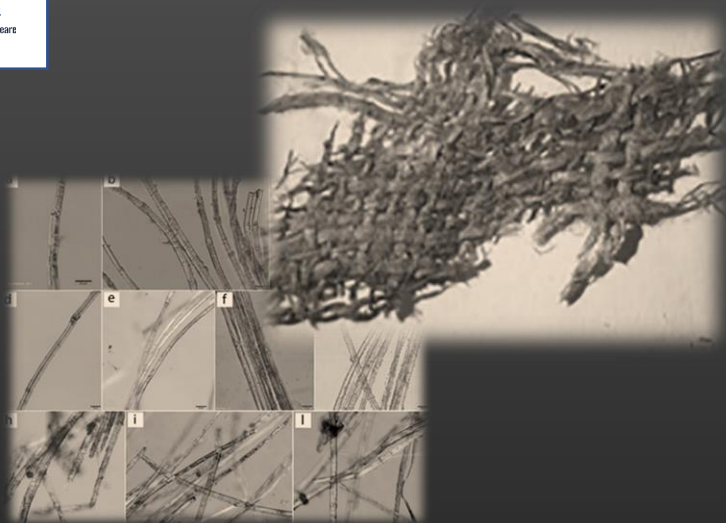
## WHY TO APPLY DIAGNOSTIC ANALYSES?

- Characterization of constituent's materials
- Characterization of degradation products
- Information about the conservation state of the studied artwork

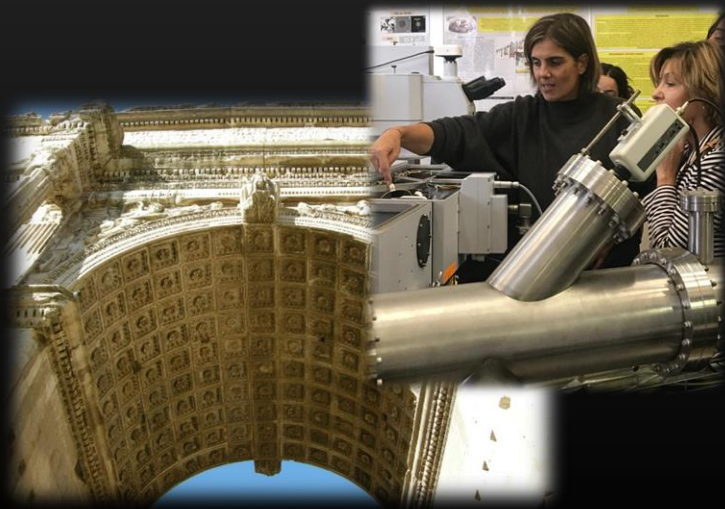
**To plan restoration and/or conservation interventions.**







# Mural Paintings and Historical Monuments





# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Mural Paintings

ADAMO site of interest:  
Palazzo Chigi (Ariccia, Rome)



**DTC** LAZIO  
DISTRETTO TECNOLOGICO  
BENI E ATTIVITÀ CULTURALI  
CENTRO DI ECCELLENZA

*San Giuseppe con il Bambino* by *Gian Lorenzo Bernini* (1663)

PURPOSE:

Characterization of painting's materials



Represents the unique autograph artwork of Bernini, considered the most important artist of Italy's baroque



# STUDY OF THE CONSERVATION STATE: GRAZING LIGHT

VISIBLE

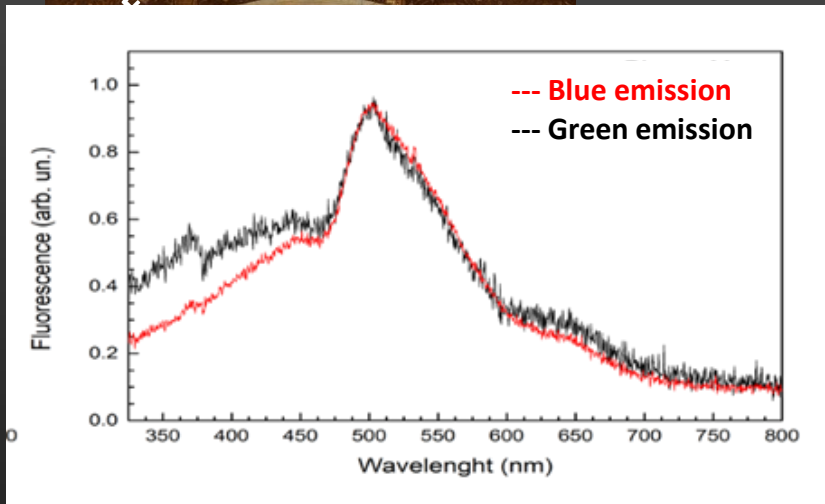


GRAZING LIGHT



- Obtained by illuminating the surface on one side by using a halogen lamp with angles of incidence always higher than  $80^\circ$  compared to the normal object.
- An amplification of the three-dimensional aspect of the surface is obtained.
- Useful to obtain information on the technique of execution and the state of conservation.

# STUDY OF THE CONSERVATION STATE: UV FLUORESCENCE

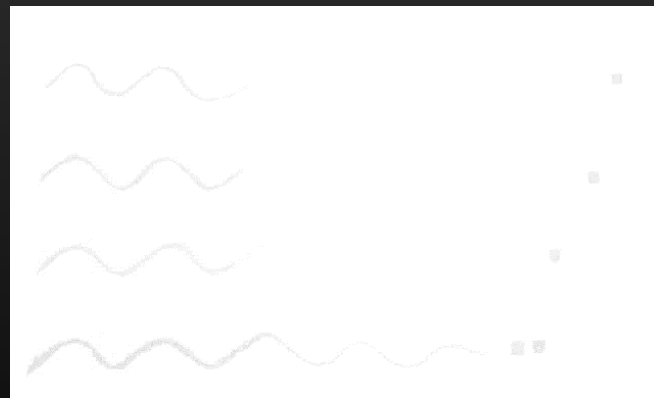
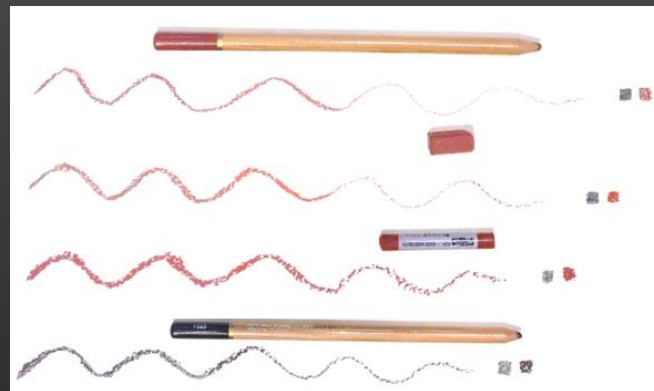


- Obtained by illuminating the artwork with an UV lamp
- Information about the superficial layer
- Absence of syntetich materials (dark areas)
- Two areas characterized by different fluorescence (blue and green)



# CHARACTERIZATION OF CONSTITUENT'S MATERIALS: IR REFLECTOGRAPHY

VISIBLE

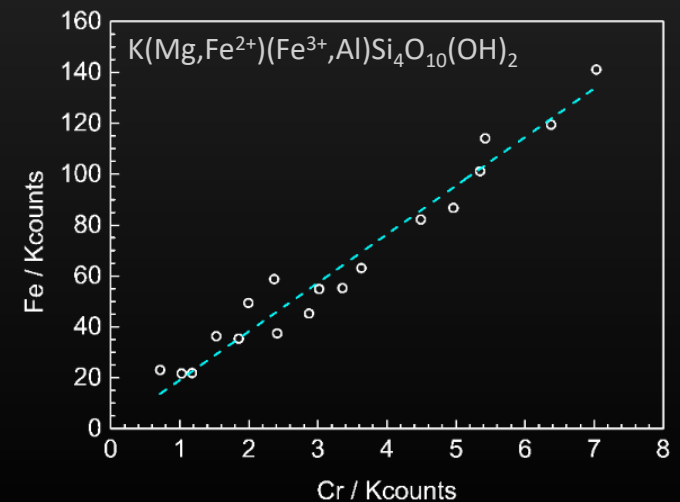
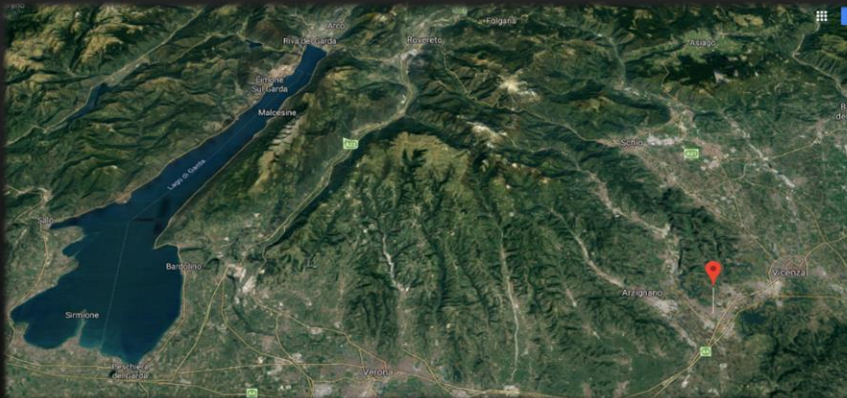


INFRARED  
REFLECTOGRAPHY

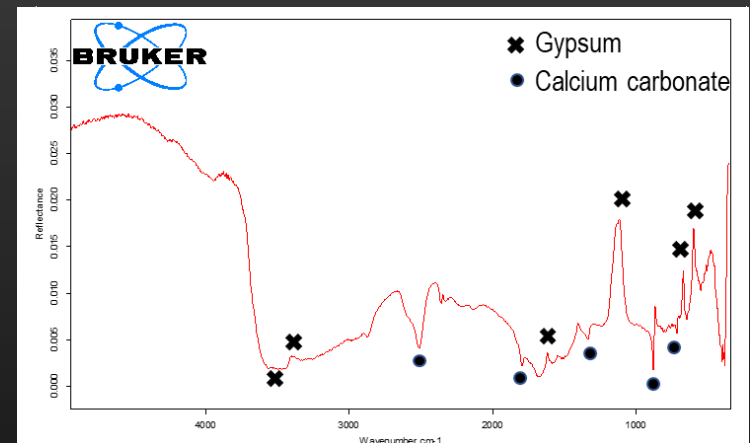
Different behavior of materials in the IR region → means different chemical composition

## Study of pigments provenience by XRF analyses

- Characterization of chemical elements of specific geographical areas
- Correlations
- Determination of provenience



## In situ Fourier Transform Infrared Spectroscopy (FT-IR).



Identification of Calcium Carbonate and Gypsum

Absence of organic protective materials characterized by a characteristic IR spectrum

Absence of degradation products: (oxalates)



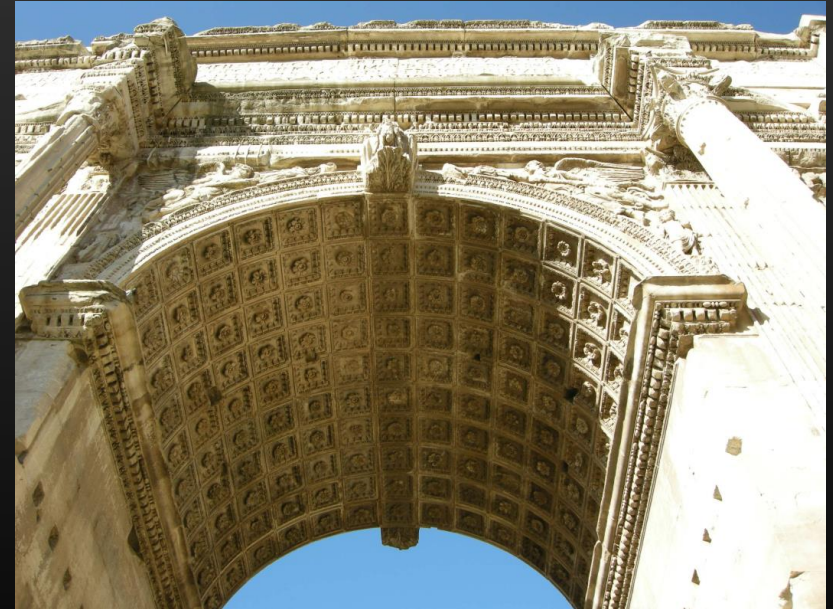
*Arch of Septimus Severus, III sec B.C.*

**PURPOSE:**

Characterization of degradation effects  
due to pollution of Rome



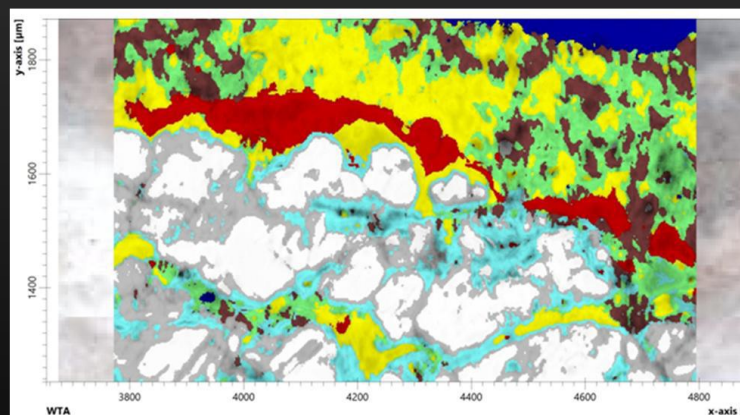
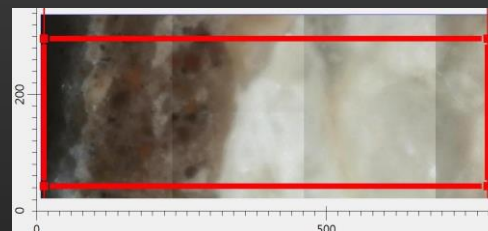
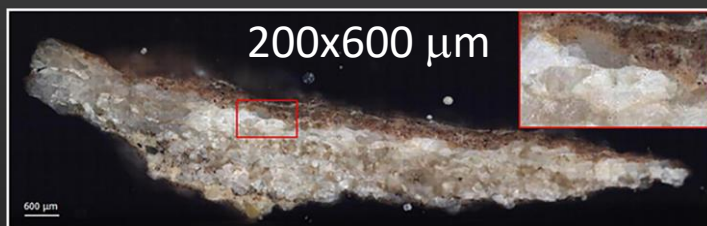
Establishing the distribution of materials and  
their degradation products in historical  
monuments is fundamental to  
understanding their state of preservation



# CASE STUDY: STUDY OF DEGRADATION PRODUCTS IN CROSS SECTION

## MICRO FT-IR chemical imaging

- FT-IR imaging: molecular composition of the material on a micrometer scale.
- Each colour correspond to a different chemical compound!



# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Mural Paintings in Hypogeus sites



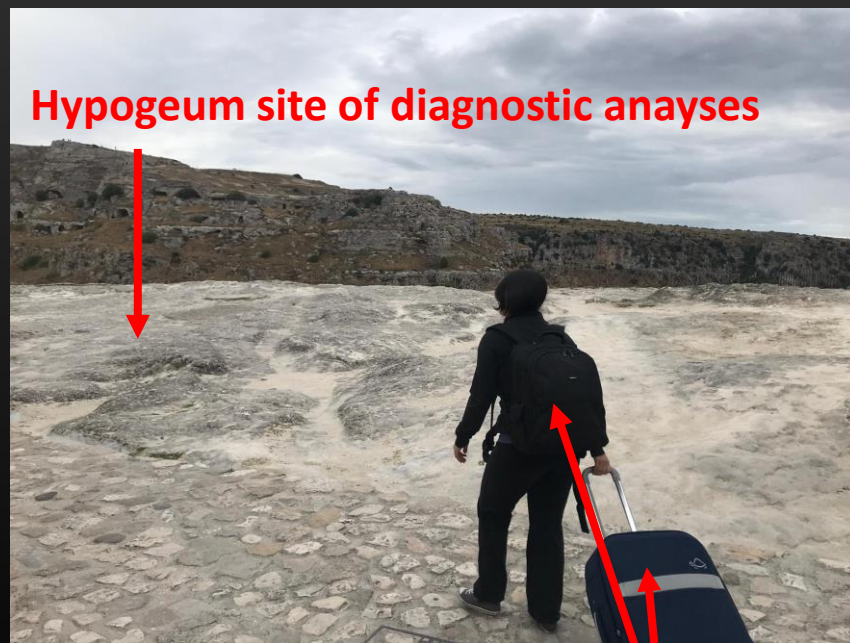
### *Mural Paintings in Hypogeus Sites*

#### PURPOSE:

Characterization of painting's materials



- Logistical difficulties related to the hypogeus sites
- Needs of compact and light instrumentation
- Microsampling for laboratory analyses



**Hypogeum site of diagnostic analyses**

**CHNet-mobile laboratory**



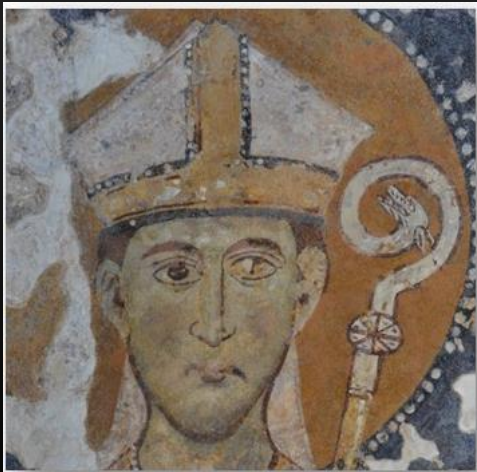
# CASE STUDY: IN SITU MEASUREMENTS IN HYPOGEUS SITES

Working at restoration site...

## 1. Imaging analysis



VISIBLE



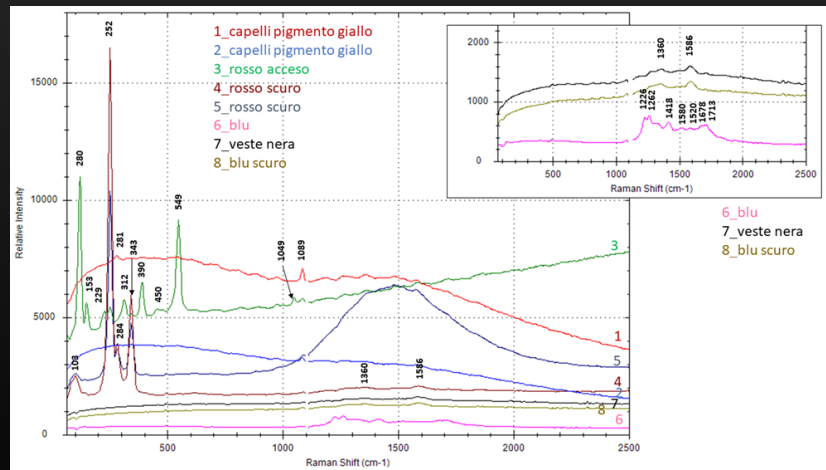
INFRARED  
REFLECTOGRAPHY



Characterization of previous  
restoration treatments

Working at restoration site...

## 2. Spectroscopic analyses

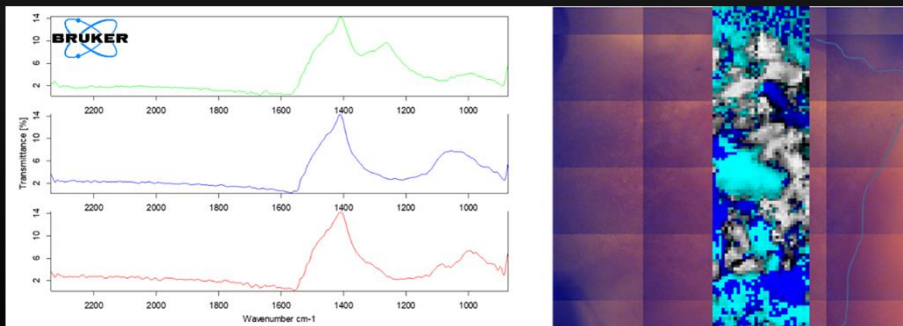
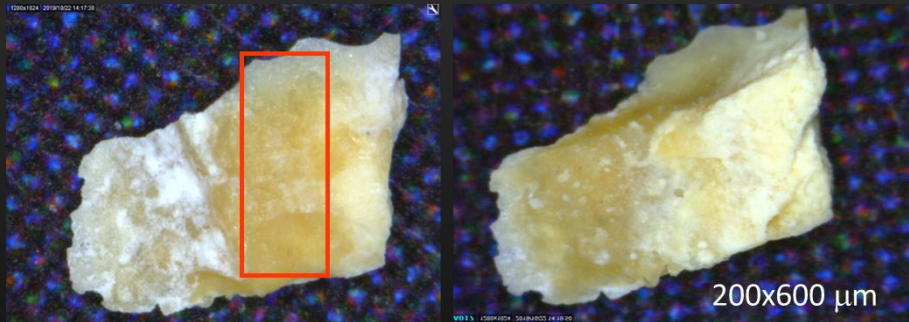


Pigments characterization by in situ Raman analyses



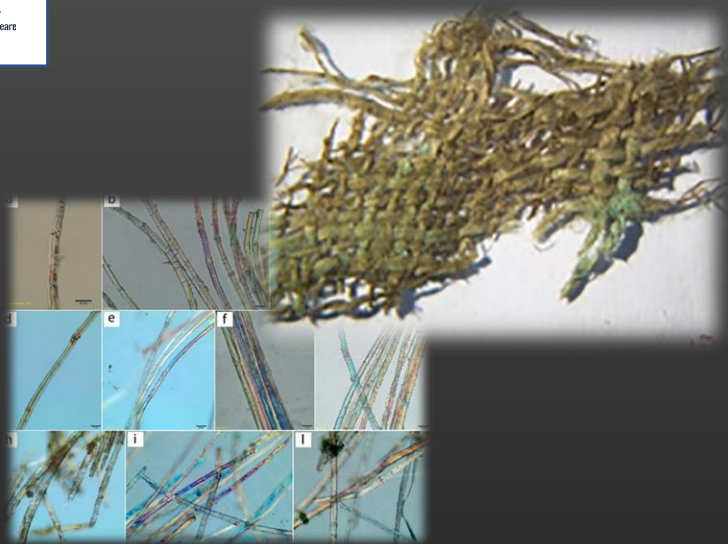
Working at restoration site...

3. Choice of areas of interest for microsampling

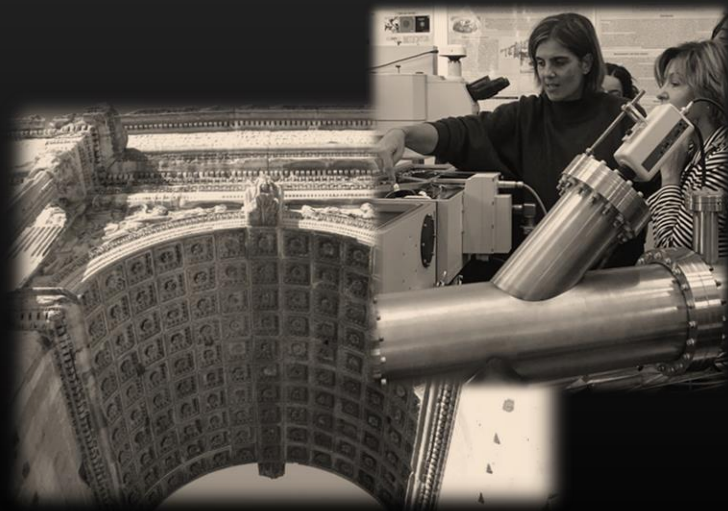


Laboratory analyses onto microsampling for stratigraphic characterization





# Ancient Textile Artefacts



# SCIENTIFIC INVESTIGATIONS OF CULTURAL HERITAGE

## Ancient Textile Artefacts



SAPIENZA  
UNIVERSITÀ DI ROMA



*Archeological Fibers of the Vesuvian Area, dated between the II century BC - I century AD characterized by a high historical value.*

### PURPOSE:

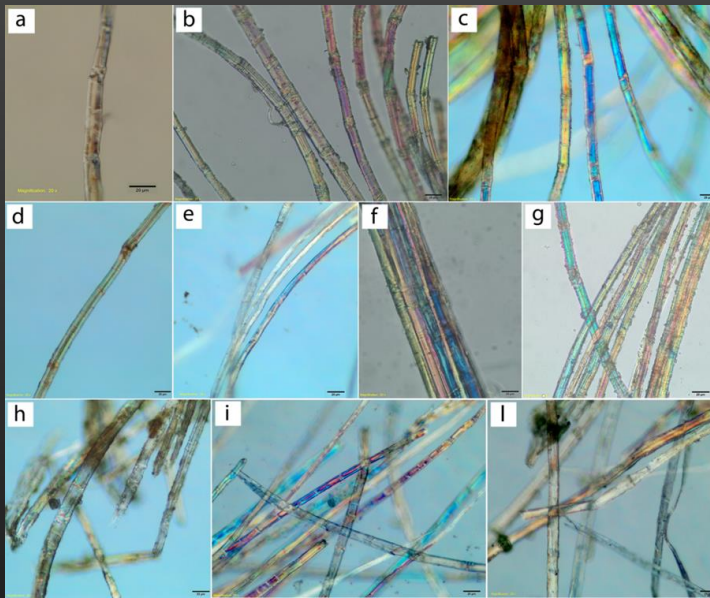
Characterization by ATR-FTIR spectroscopy of flax and hemp



- Flax and hemp are the most common fibers in the archaeological context of the Vesuvian Areas
- Problematic related to their conservation state

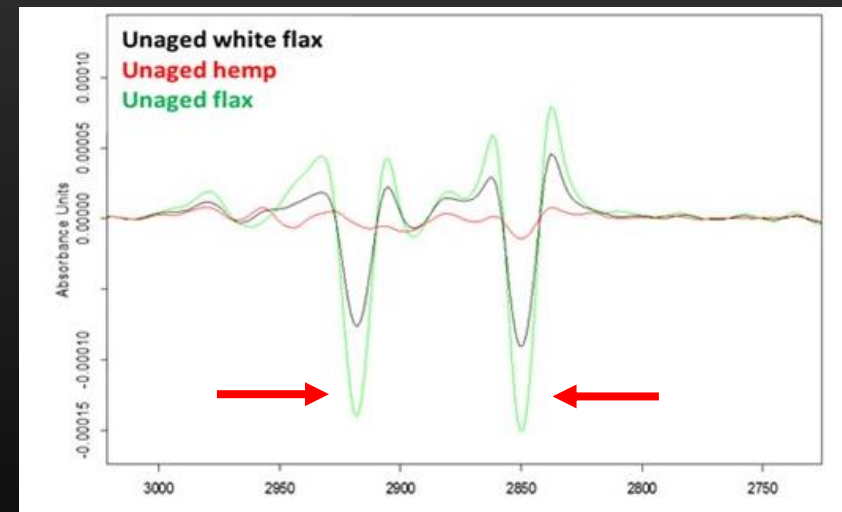


# CHARACTERIZATION OF ARCHEOLOGICAL FIBERS OF THE VESUVIAN AREA



Very difficult to distinguish by morphological analyses such as optical microscopy or SEM

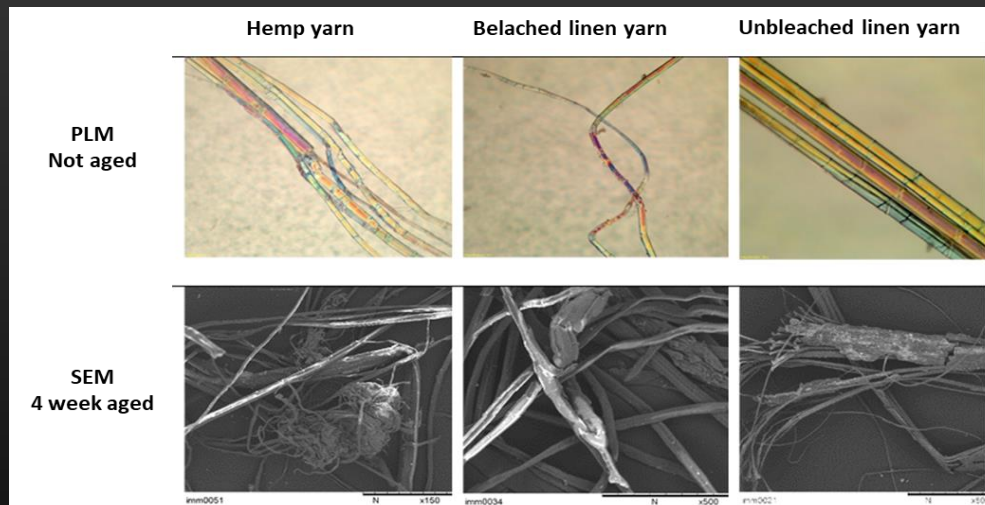
The FT-IR analysis allows the recognition of the two modern fibers thanks to the presence of the CH groups ...



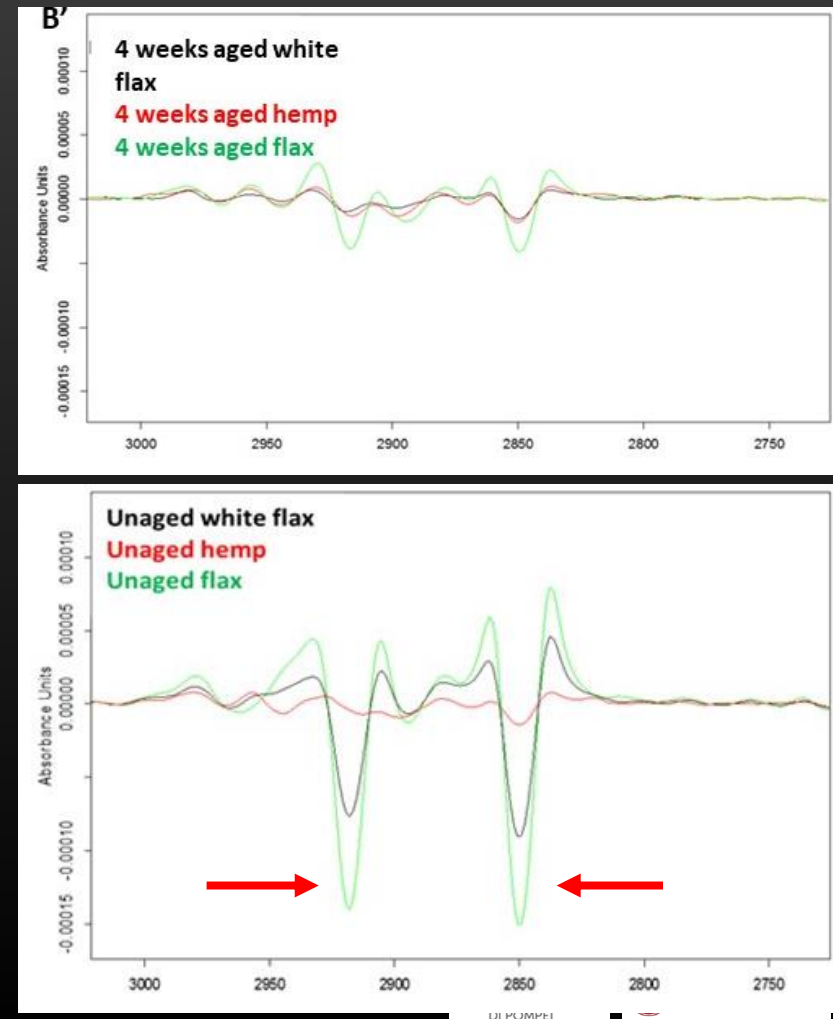
**But in archaeological contexts ???**

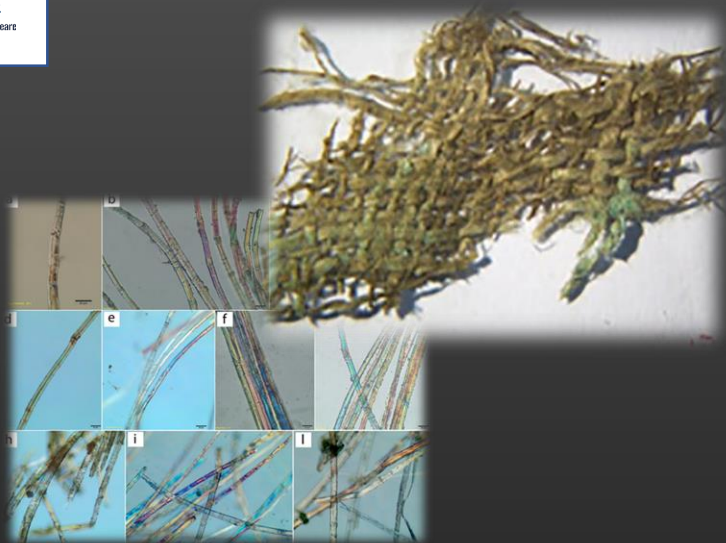


We decided to simulate artificial ageing by using a climatic chamber...in order to study how the ageing influenced the capability to recognize flax and hemp



After just four weeks of aging they become spectrally and morphologically indistinguishable!





**THANKS FOR YOUR ATTENTION**

