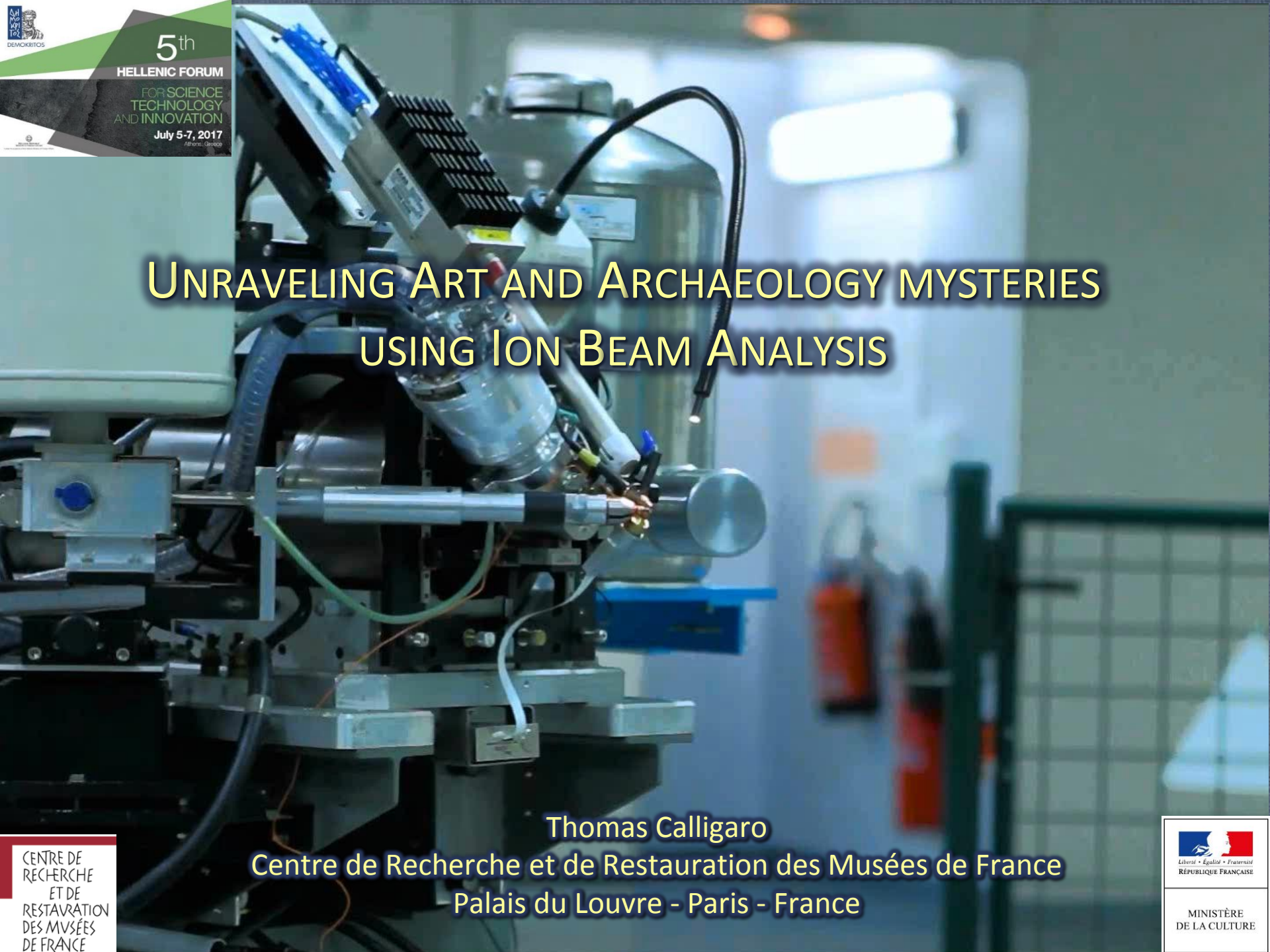

Unraveling Art and Archaeology mysteries using Ion Beam Analysis

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CENTRE DE RECHERCHE ET DE RESTAURATION DES MUSÉES DE FRANCE

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE
MINISTÈRE DE LA CULTURE

Great Issues in Heritage Studies

Archaeology Arts

- What is it ? ⇨ identification
- How was it made? ⇨ Man's knowledge
- Why? ⇨ motivation

Main Questions on Artworks and Archaeological Objects

- what are the materials composing the object?
- how was it made ?
- from where comes the materials ?
- is the object altered ?
- how old is it ?
- is the object authentic ?

SPECIFIC REQUIREMENTS

☞ Analytic capabilities

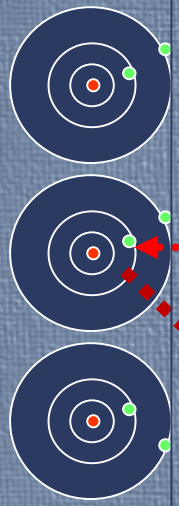
- identification ⇨ measurement of main elements
- provenancing ⇨ measurement of trace elements
- alteration process ⇨ sample surface characterisation

☞ Constrains

- precious items
  no sampling ⇨ non-invasive methods
  no damage ⇨ non-destructive methods
- unknown composition ⇨ wide range of measured elements
- non-homogeneous composition
  laterally ⇨ small probe diameter
  in-depth ⇨ depth profiling capabilities

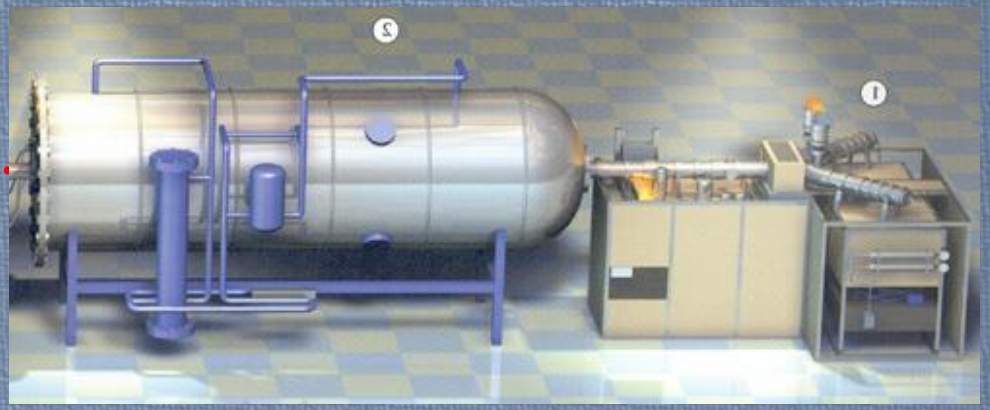
Principle of Ion Beam Analysis

target atoms



MeV ions

particle accelerator

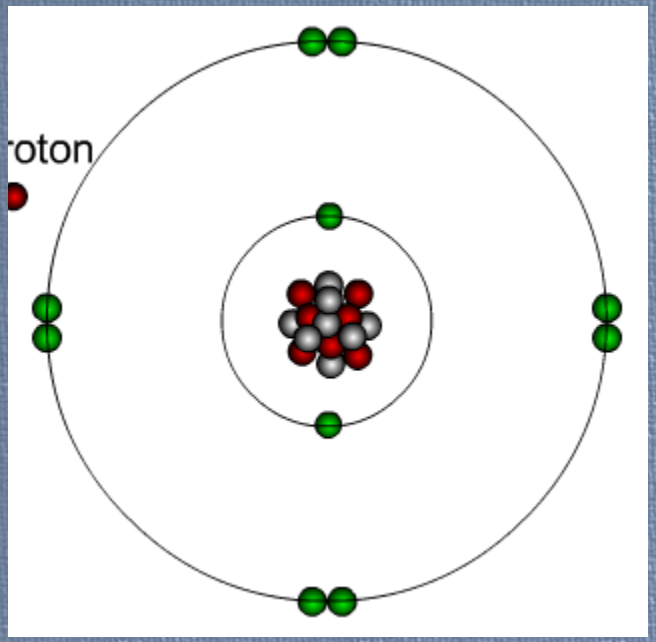


X-ray, γ-rays, charged particles

radiation detector

⇨ **N, E**

THE PIXE METHOD
PARTICLE INDUCED X-RAY EMISSION

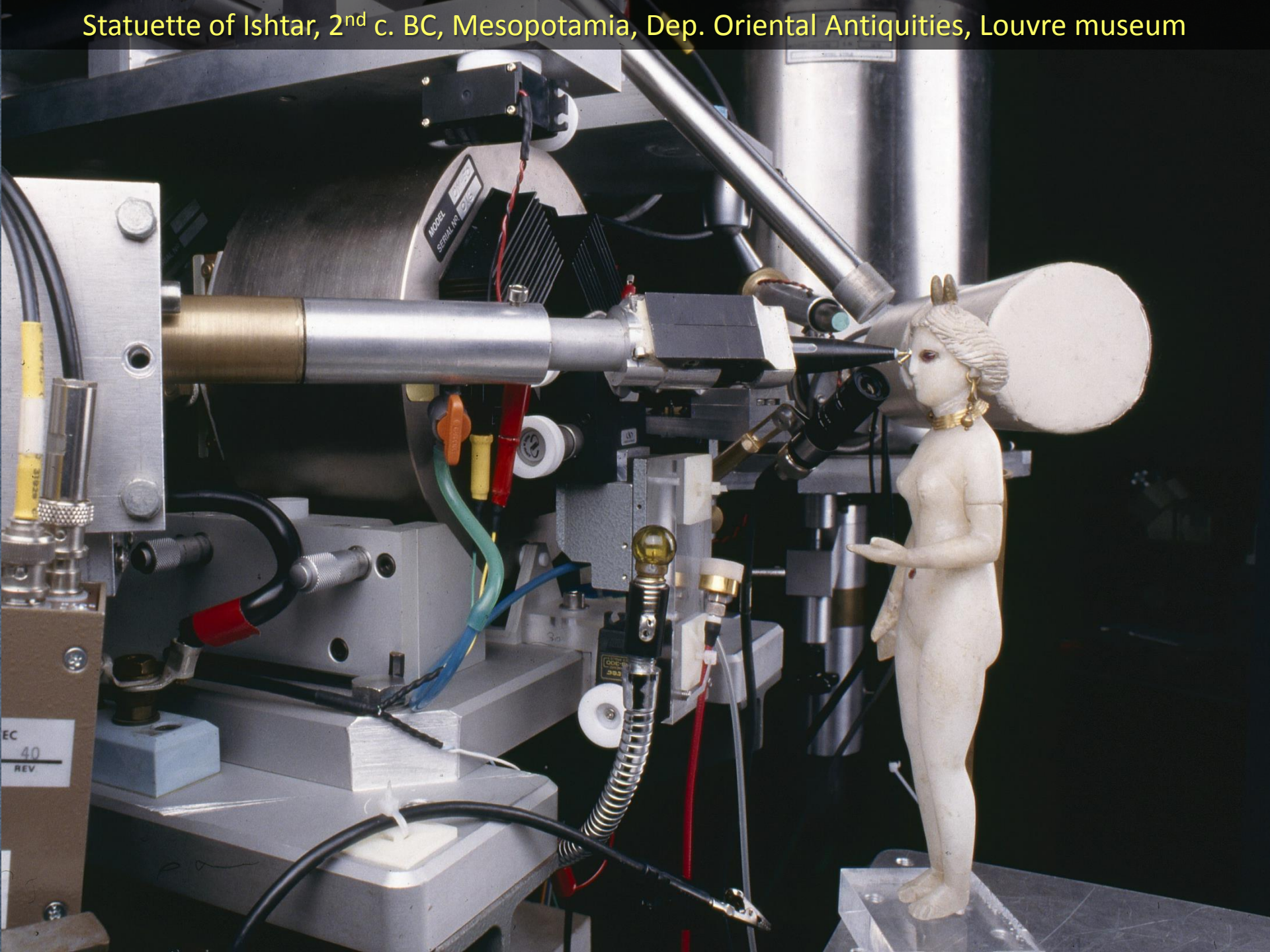


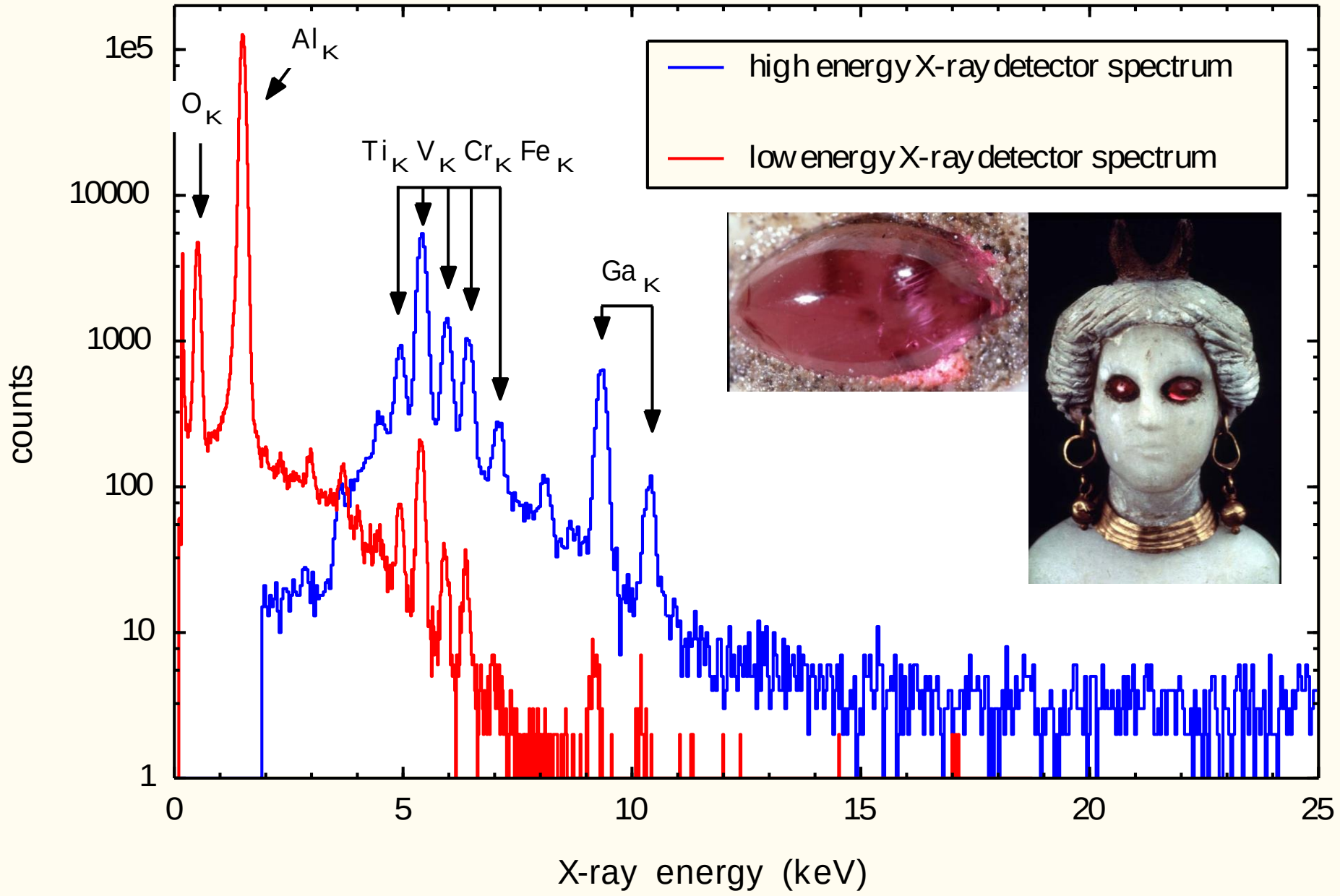
$E_x = k(Z-1)^2$ Henry Moseley' law (1913)

($k \approx 0.01$ keV for K-lines)

- Z range Z > 10
- incident beam 3-MeV protons
- low current ~1 nA ⇒ no damage
- high sensitivity ~ 1 µg/g
- probing depth 1-50 µm
- microprobe Ø 10-30 µm

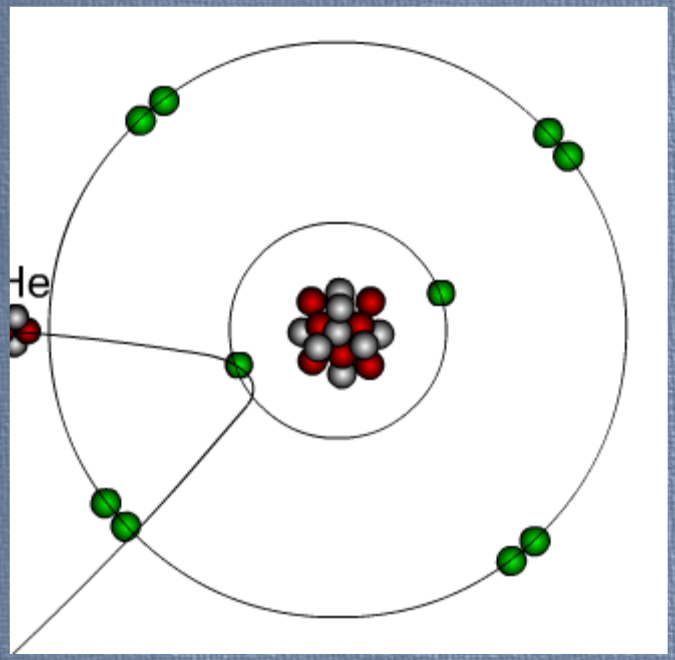
Applications
- bulk analysis of materials
- measurement of trace elements


Statuette of Ishtar, 2nd c. BC, Mesopotamia, Dep. Oriental Antiquities, Louvre museum


high energy X-ray detector spectrum
low energy X-ray detector spectrum
O K
Al K
Ti K V K Cr K Fe K
Ga K
counts
1e5
10000
1000
100
10
1
0
5
10
15
20
25
X-ray energy (keV)

Map of Middle East and Asia : sources of rubies

THE RBS METHOD
RUTHERFORD BACKSCATTERING SPECTROMETRY



purely electrostatic
elastic process

$K=E/E_0= f(M, depth)$ kinematic factor

$K = [(M_2^2-M_1^2 \sin^2 \theta)^{1/2}+M_1 \cos \theta]^2/[M_1+M_2]^2$

$\sigma \sim Z_1^2 Z_2^2 E^{-2} \sin^{-4} \theta/2$

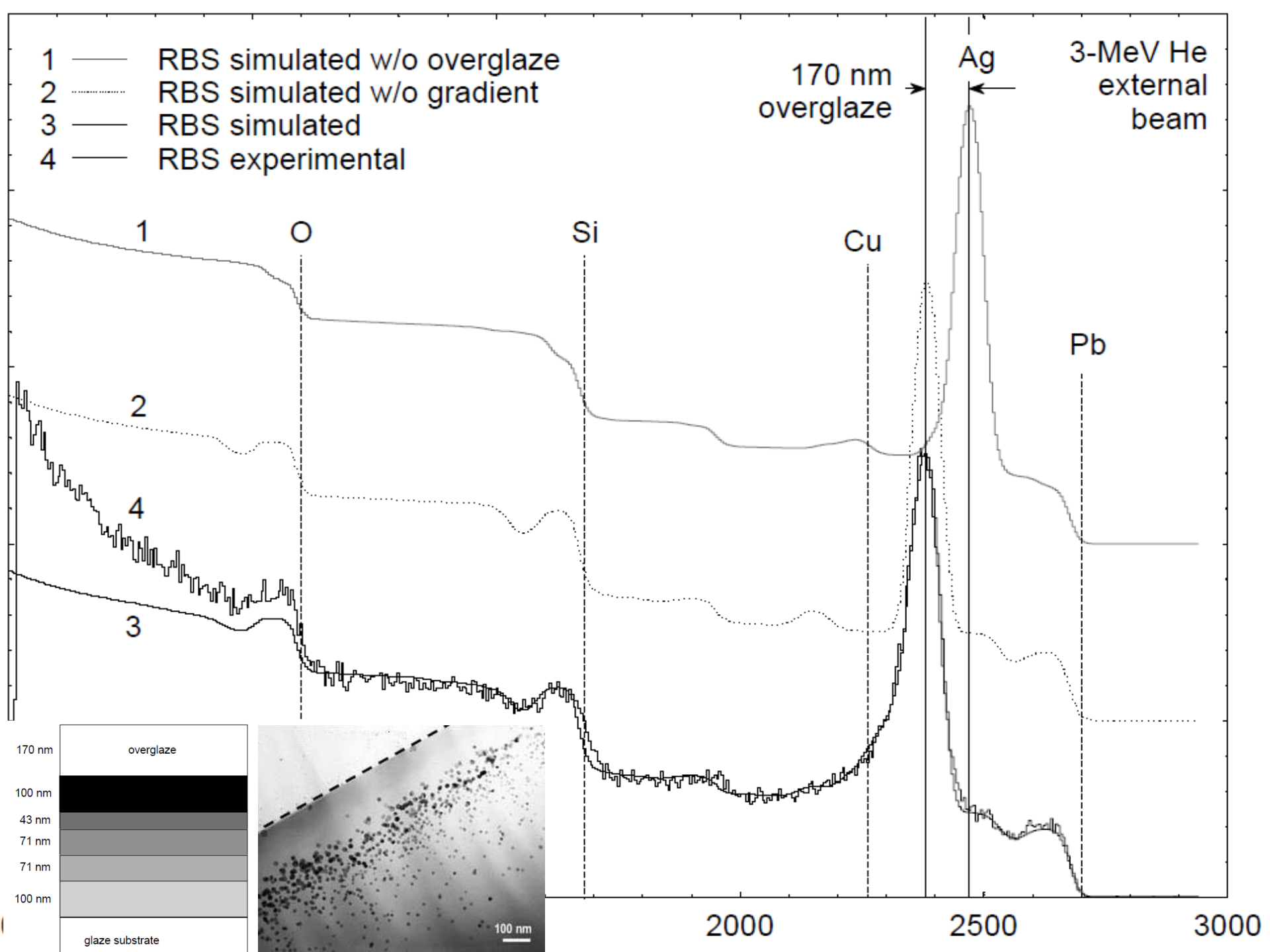
incident beam : 3-MeV ^{4}He or protons

- suitable for profiling
- high Z elements in a low Z matrix
- probing depth 1-10 µm

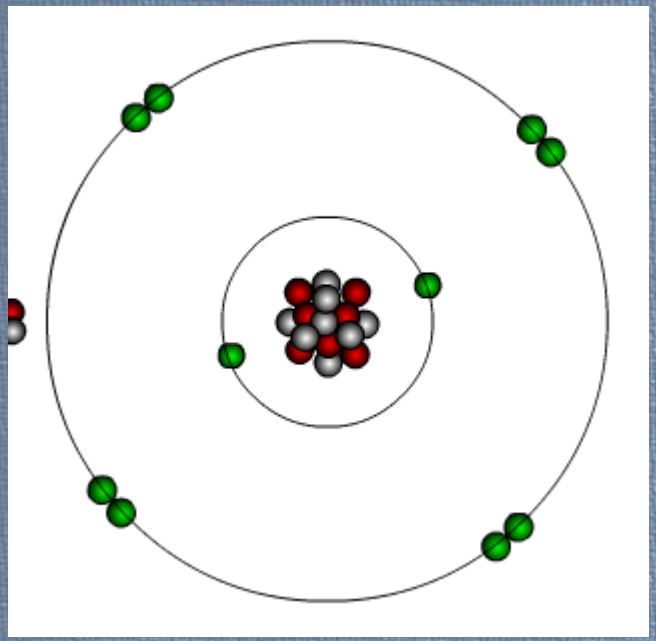
Applications

- layers of heavy elements on light matrices
- example : gilding of jewels

Lustre decorated plate representing Pâris judgement, 1520, Maestro Gorgio, Gubbio, Italy


1 RBS simulated w/o overglaze
2 RBS simulated w/o gradient
3 RBS simulated
4 RBS experimental
170 nm overglaze
Ag
3-MeV He external beam
1
O
Si
Cu
Pb
2
4
3
2000
2500
3000
170 nm
overglaze
100 nm
43 nm
71 nm
71 nm
100 nm
glaze substrate
100 nm

THE NRA METHOD
NUCLEAR REACTION ANALYSIS



beam of ^{1}H, ^{2}H or ^{3}He of a few MeV

PIGE : γ-ray detection

E_γ = f(isotope)

- bulk composition for 1<Z<11
- complementary to PIXE
- high sensitivity ~ ppm level

NRA : particle detection

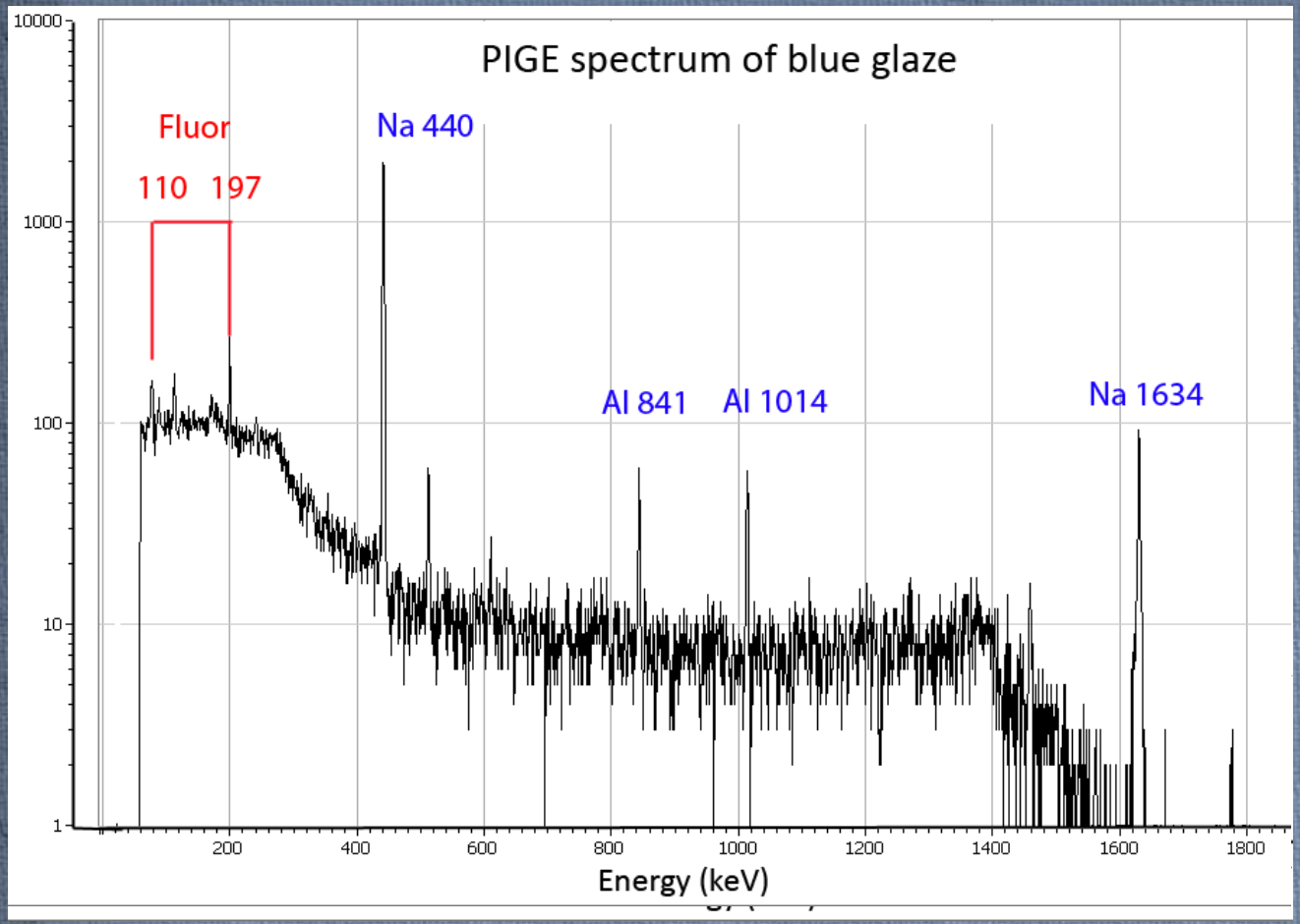
E_p = f(isotope, depth)

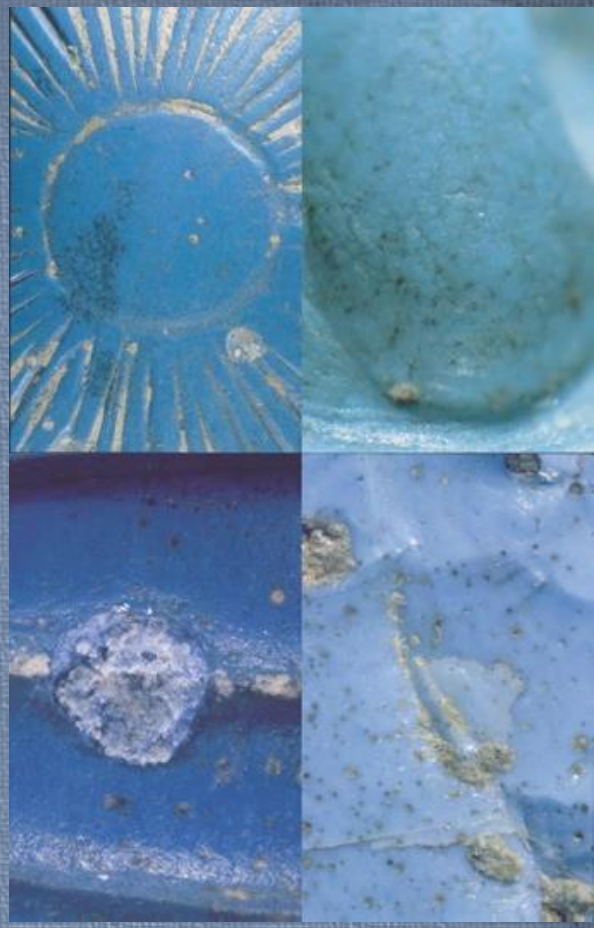
- profiling low Z elements in high Z matrix
- C,N,O composition of bronze patina
- weathering of glasses
- dating archaeological flint tools by F profiling

examples of nuclear reactions

- $^{1}H(^{19}F,\alpha\gamma)^{16}O$ fluorine profiling
- $^{19}F(^{1}H,\alpha\gamma)^{16}O$ hydrogen profiling
- $^{16}O(^{2}H, p)^{17}O$ oxygen profiling

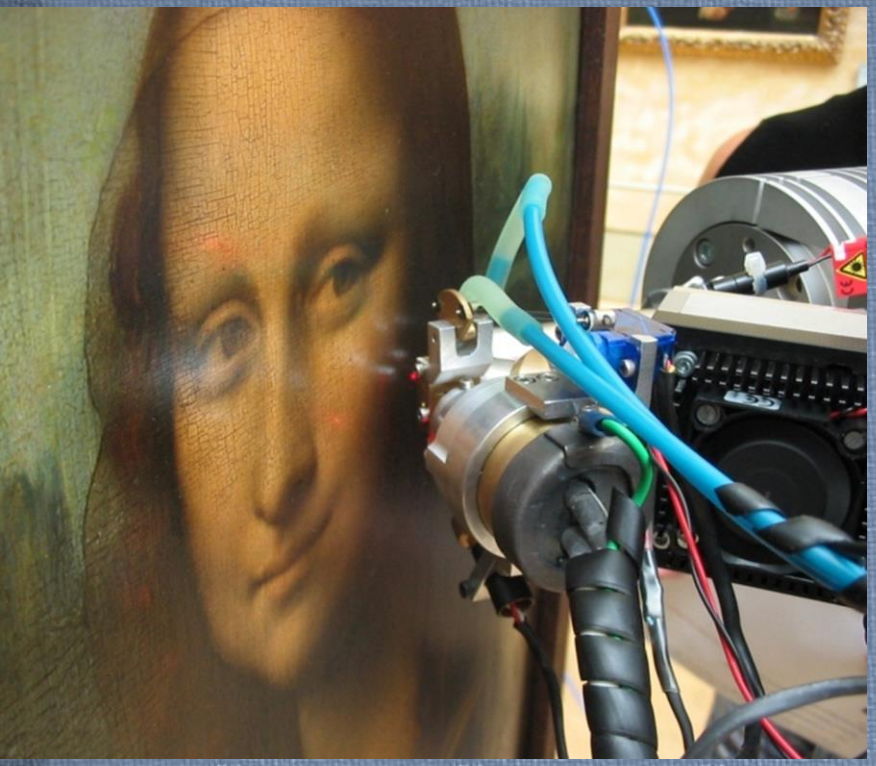
Glazed head, Middle Kingdom ?, Dep. Of Egyptian Antiquities, Louvre museum





- PIXE : lead arsenate opacifier $3Pb_3(As_2O_4)_2.PbO$ invented in the 13th c. AD
- PIGE : presence of fluor (artficial weathering with fluorhydric acid)
- ☹ demonstrated forgery, head removed from the Louvre displays in 2003

Benchmarking PIXE and XRF



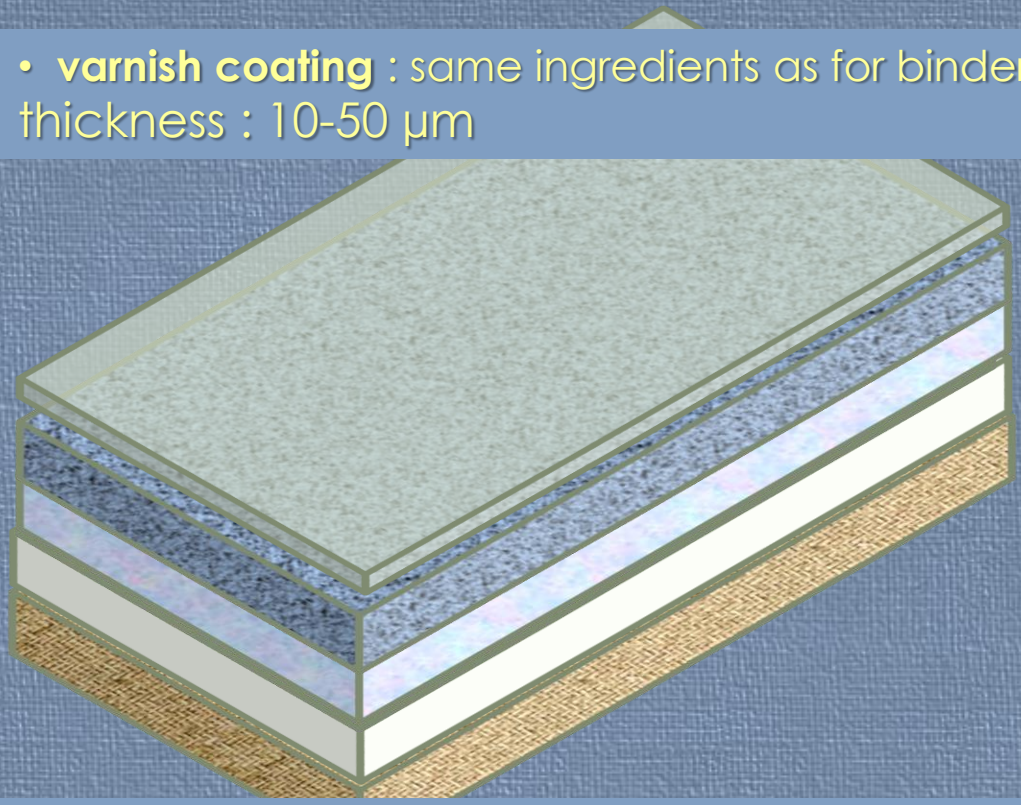
Analysis of old master paintings

Is PIXE better than XRF?

COMPOSITION AND STRUCTURE OF HISTORICAL PAINTINGS

- **varnish coating** : same ingredients as for binders

thickness : 10-50 µm

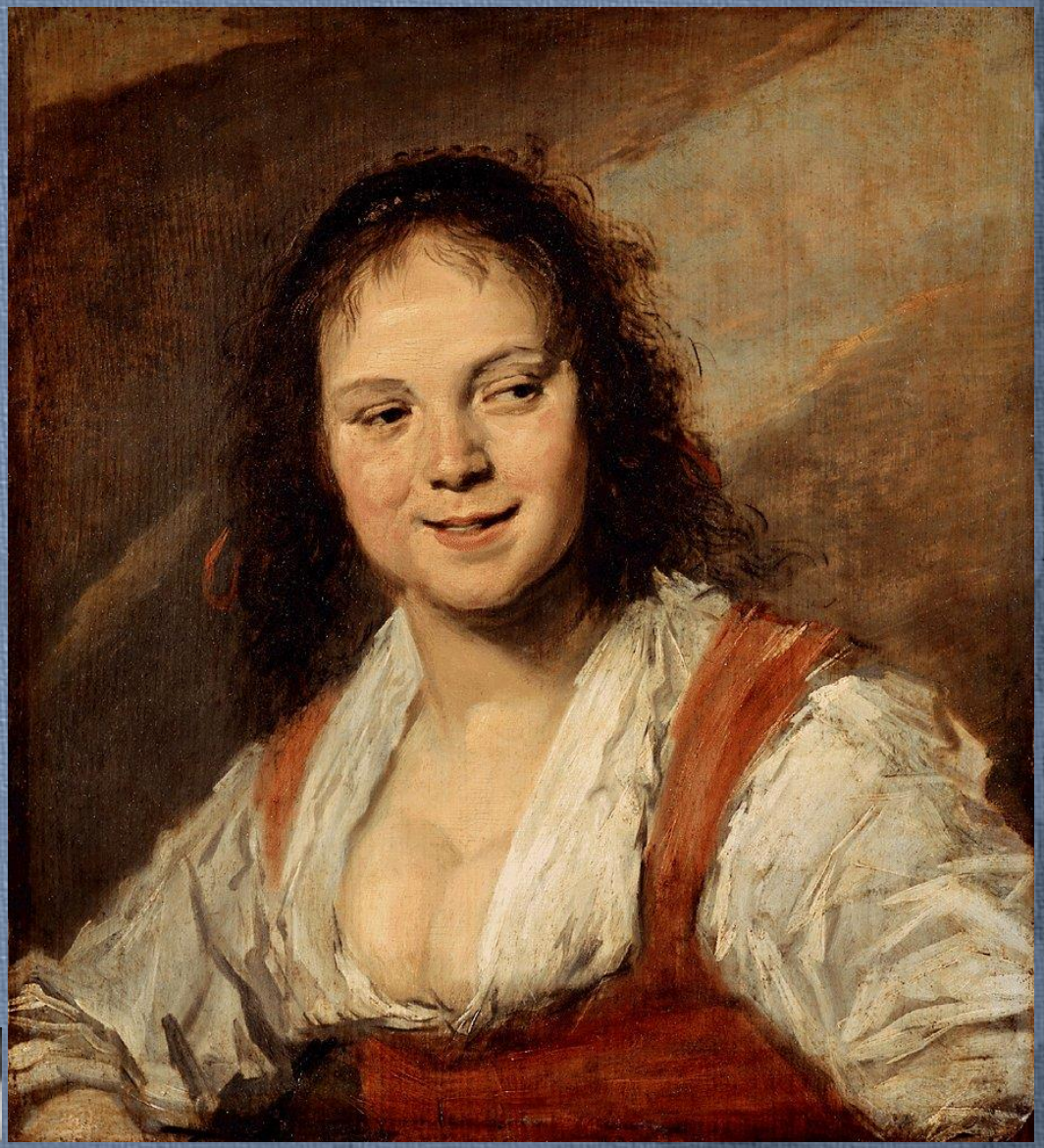


- **paint layer : binders**
  - **lipids : linseed, walnut, poppy seed oils, beeswax...**
  - **proteins : egg white, gelatine...**
  - **glucids : vegetal resin (dammar), gum, honey ...**

The Test Painting

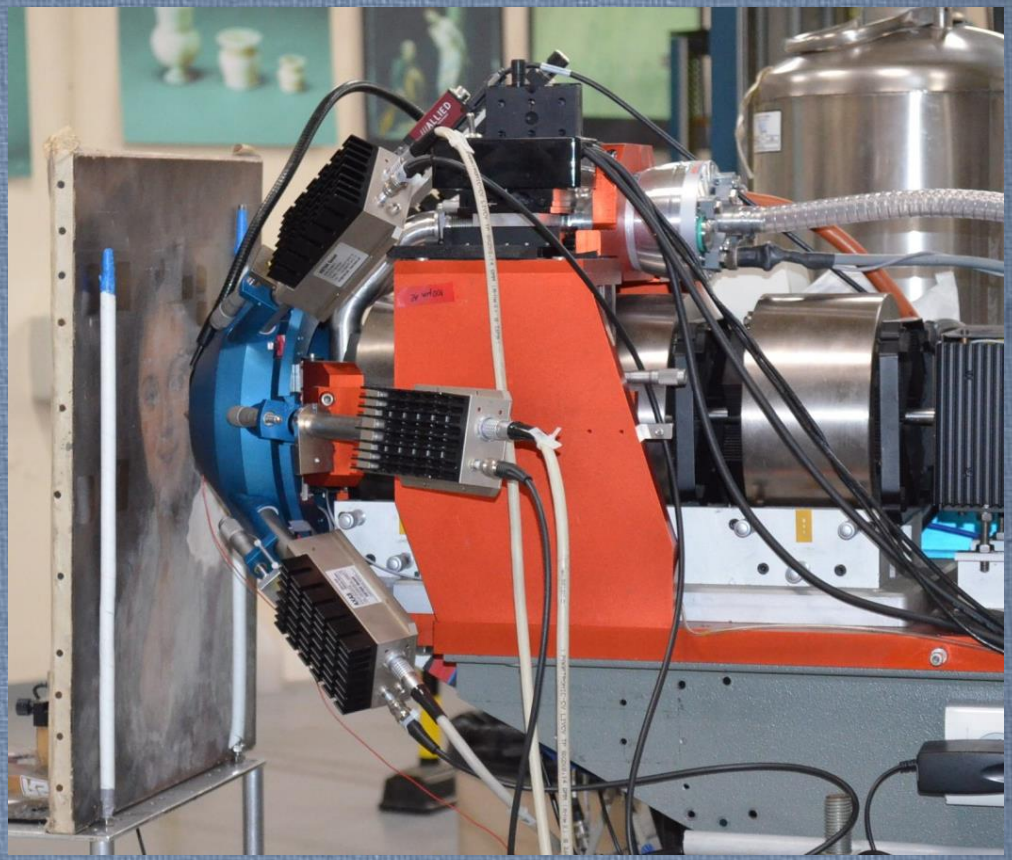
19th c. copy
acquired by C2RMF
for testing purposes

La Bohemienne
by Frans Hals 1630
Musée du Louvre



Equal Conditions

140 x 50 mm^2 area, 2 h scan



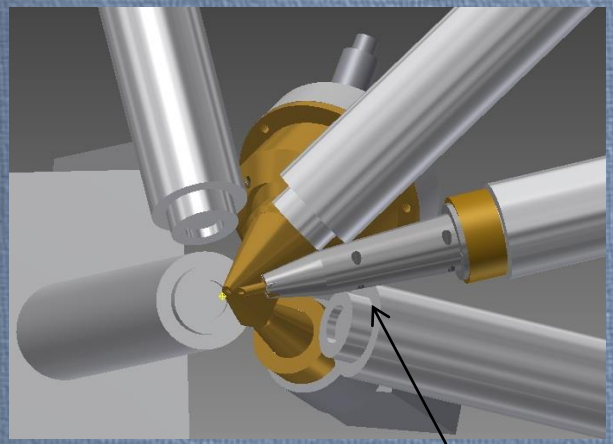
XRF : 40 kV 1 mA beam spot 0.7 mm
200 x 70 pixels, 500 msec/pixel
1 SDD 25 mm2, 40 kcps

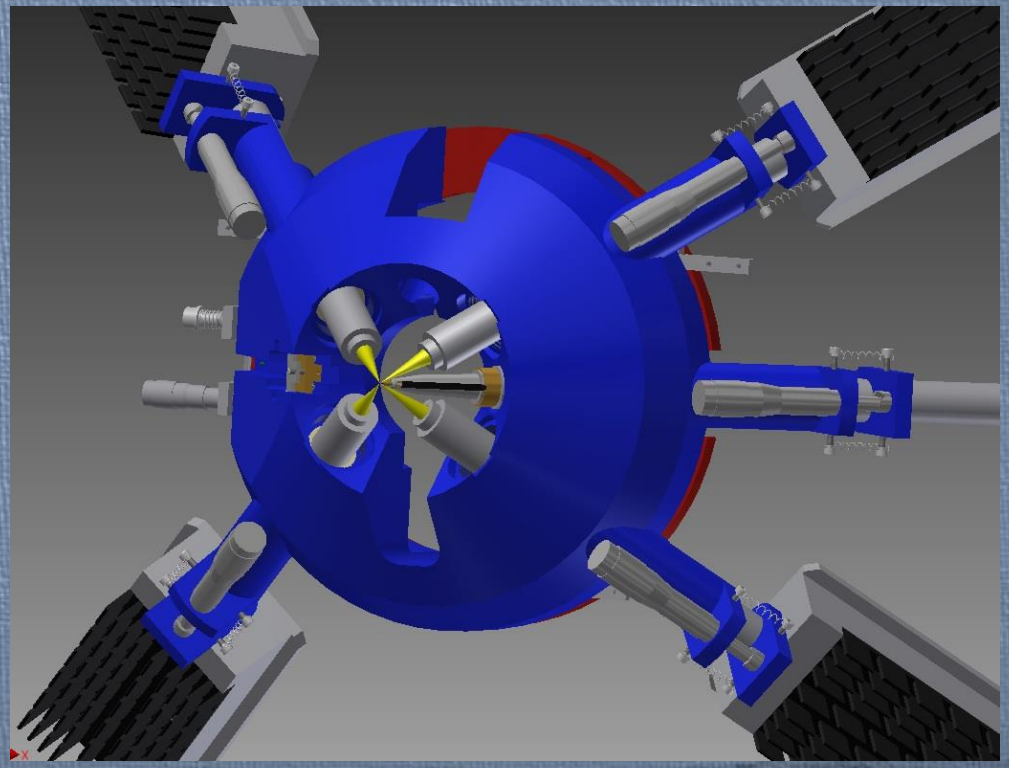
3 MeV p, beam spot 0.2 mm
700 x 200 pixels, 50 ms/pixel
0.5 µC/cm^2 0.3 x 10^{13} p/cm^2
3 x SDD 50 mm^2, 3 x 50 kcps, 100 µm Be filter

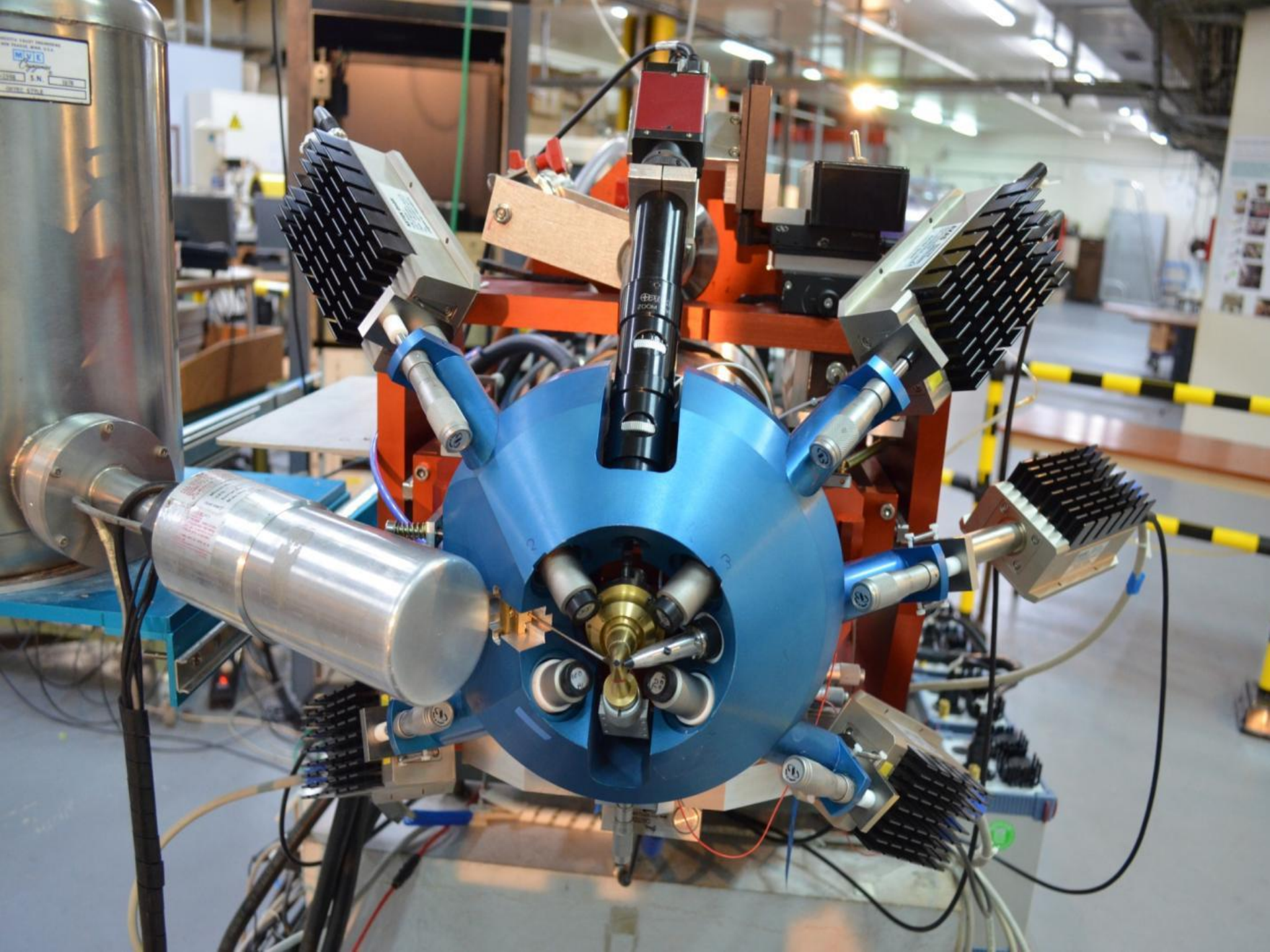
THE NEW AGLAE EXTERNAL BEAM END-STATION

- 4 x high energy detectors for trace elements : Ω = 500 mSr (x10 gain)
- 1 x low energy detector for major elements : Ω = 7m Sr (x3 gain)

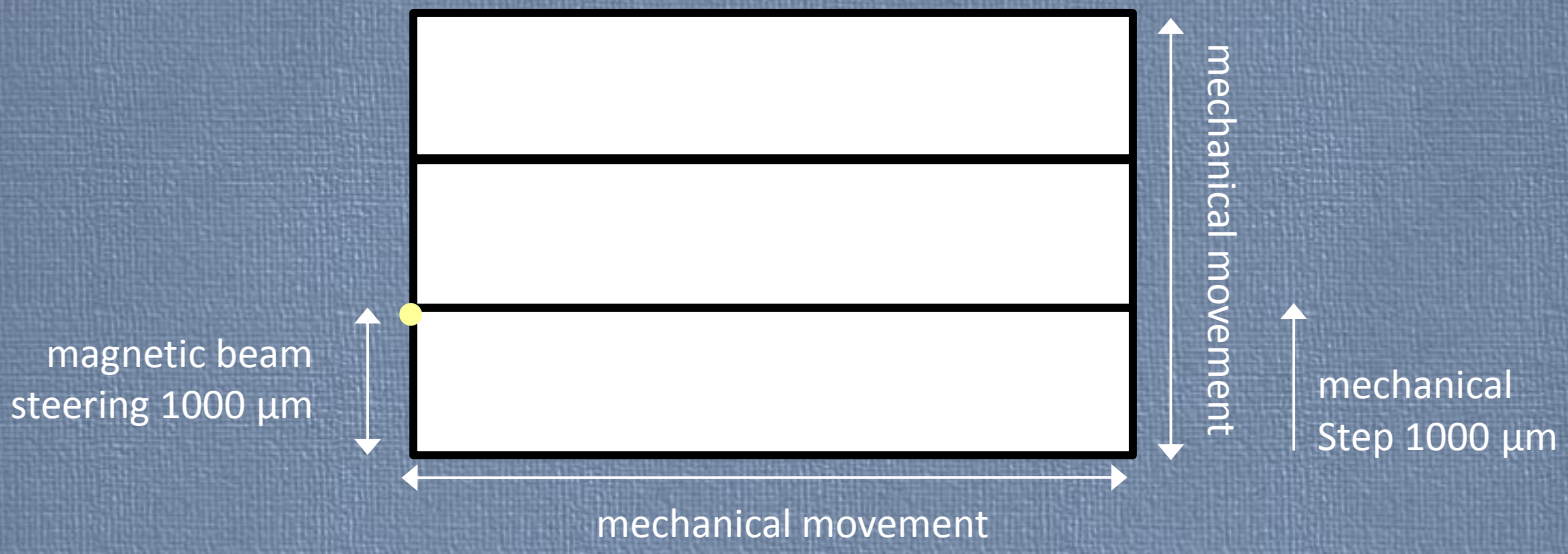
⇨ decrease incident beam intensity
⇨ high speed mapping



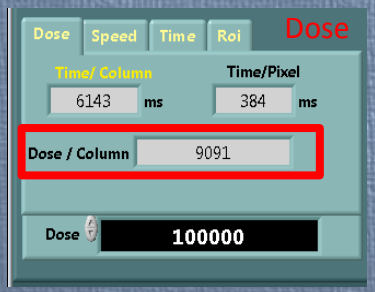




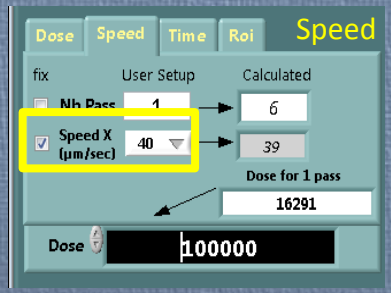
An innovative Ion Beam Scanning System



two ways to control beam scanning

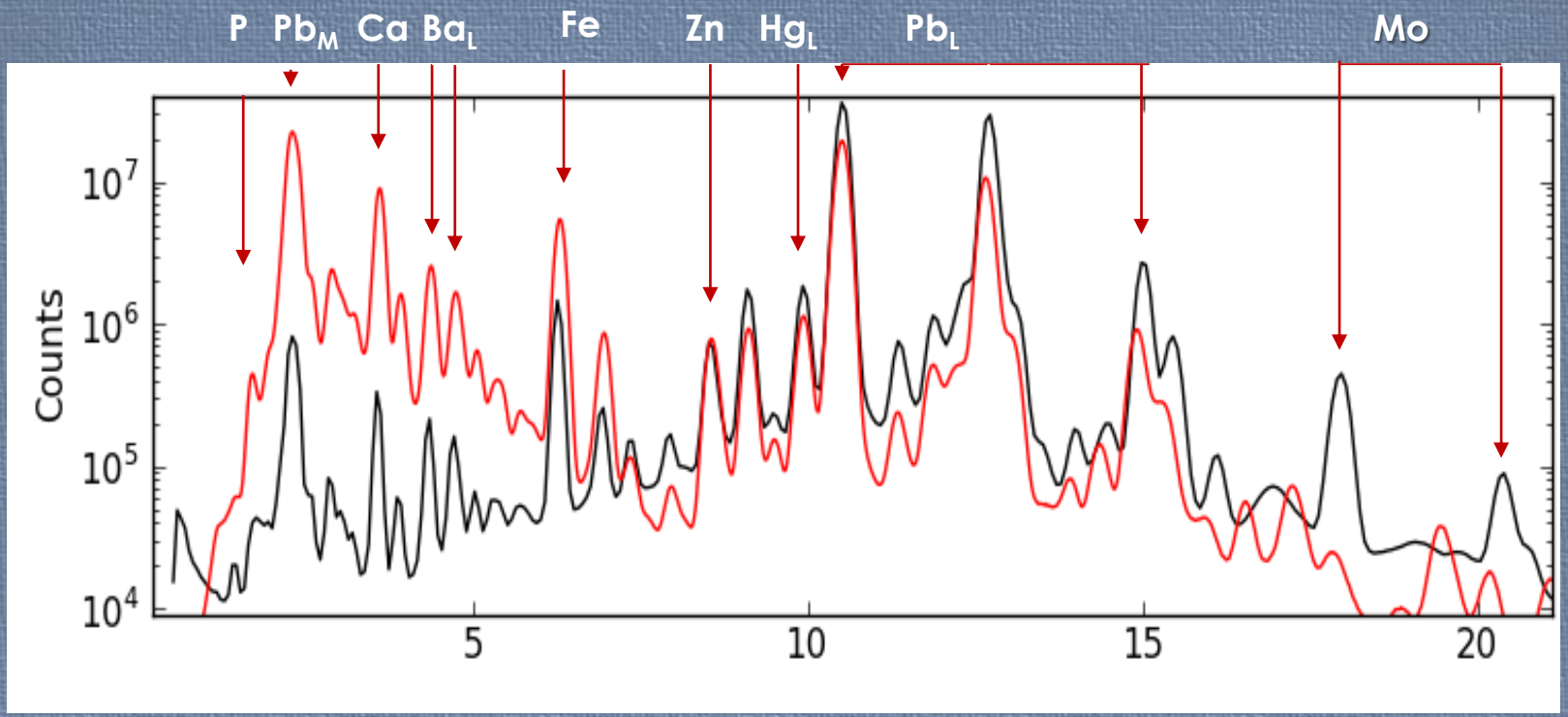


- beam monitoring
- slow mapping
- <50 µm/sec



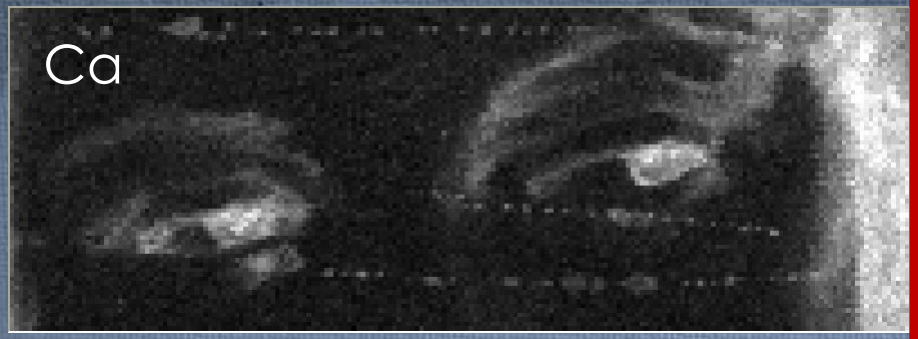
- no beam monitoring
- fast mapping (e.g. >500 µm/sec)

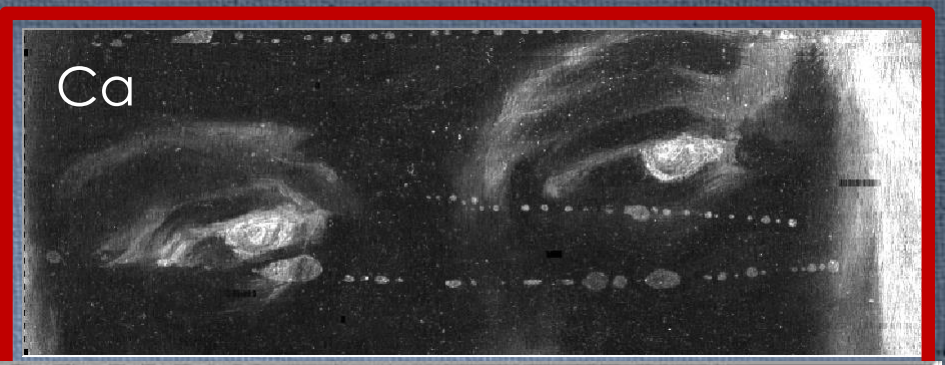
Comparison of global PIXE and XRF spectra

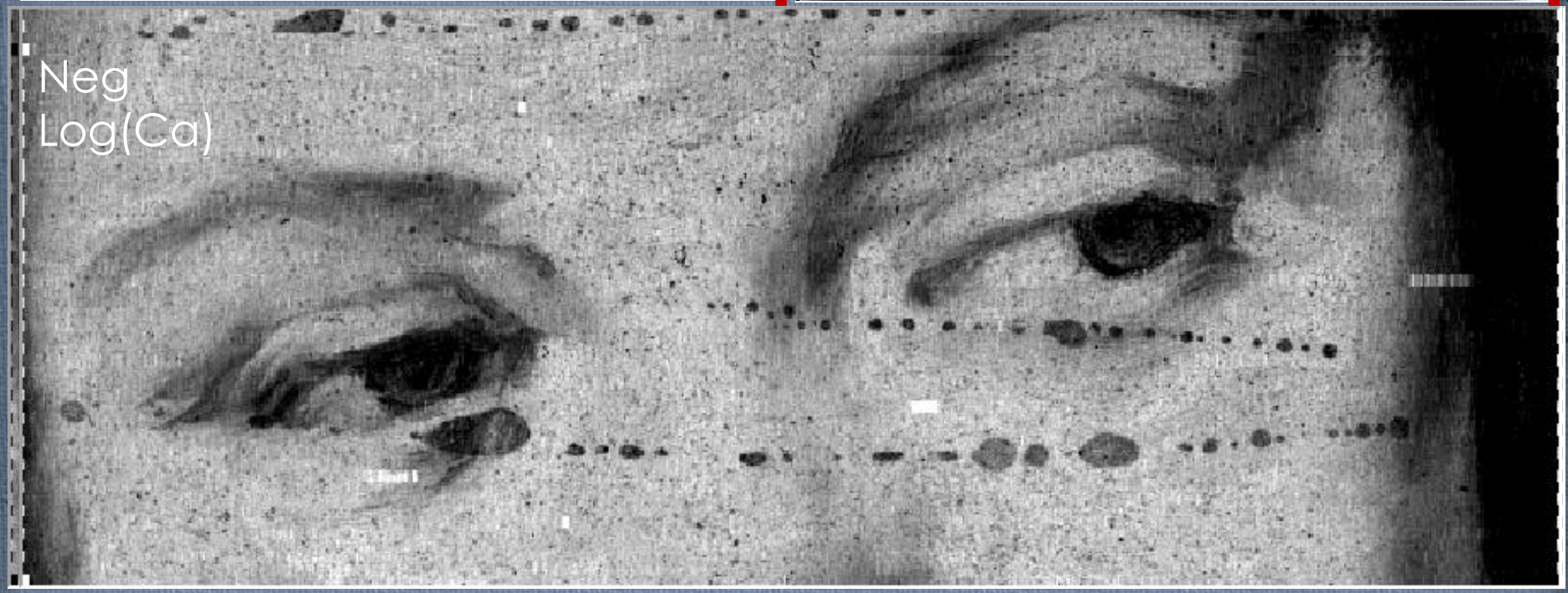


counts	PbM	Ca	Fe	PbL	Total
PIXE	2.5 x 10^8	6 x 10^7	2.5 x 10^7	2.2 x 10^8	1 x 10^9
XRF	2.5 x 10^6	6 x 10^5	3 x 10^6	1.2 x 10^8	3 x 10^8
Gain	**30 x**	**30 x**	**8 x**	**1 x**	**N/A**

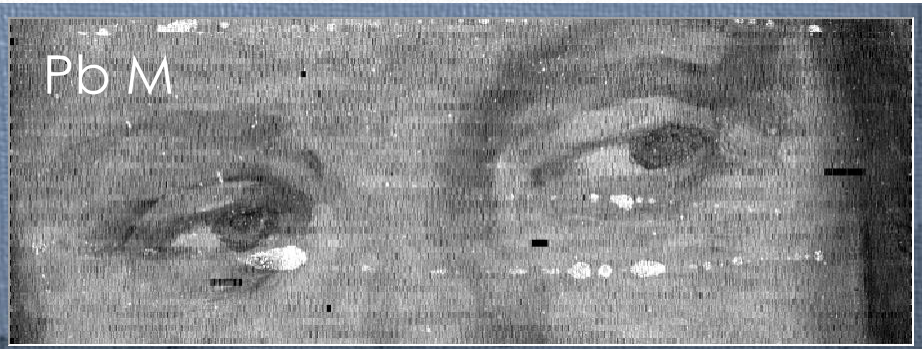
Lithopone $BaSO_4.ZnO$

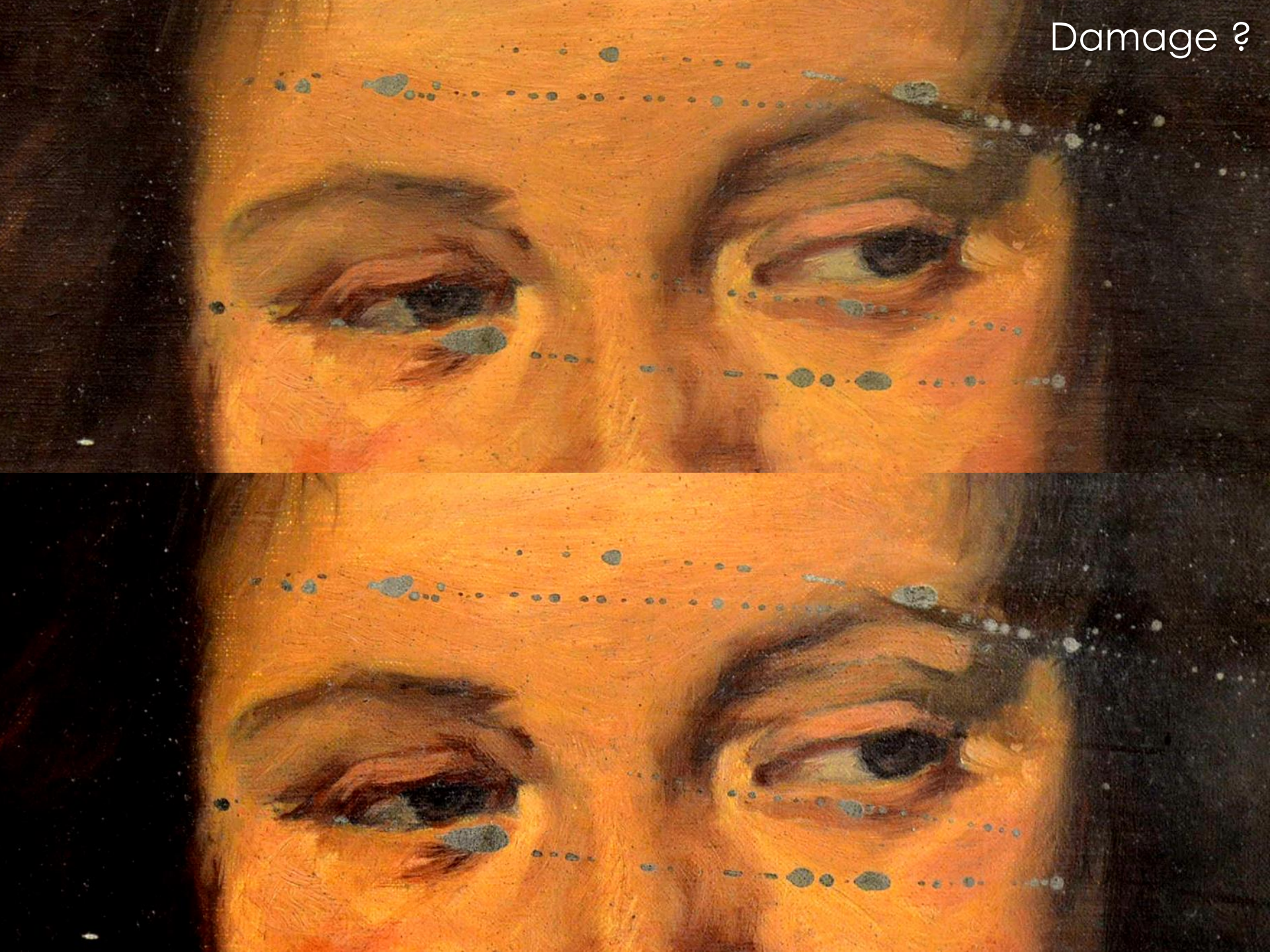

Ca


Ca


Neg
Log(Ca)


Pb M


Pb M


Damage ?

HANDS-ON EXPERIMENT!

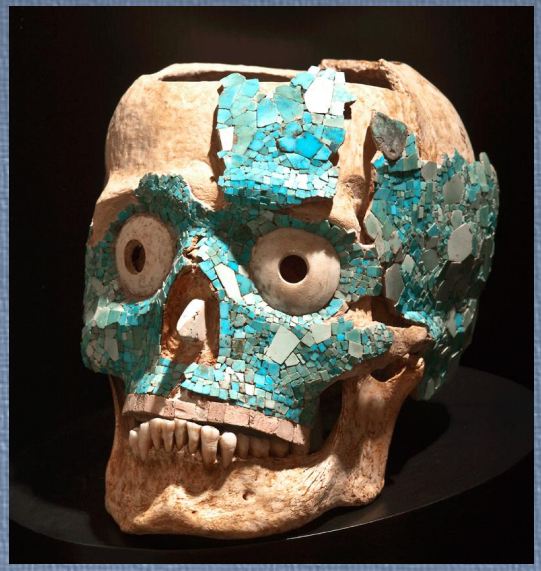
Decide by yourself the authenticity of an alledged PreColumbian human skull

Mosaic Decorated Skull

Purported Precolumbian object acquired in 1960

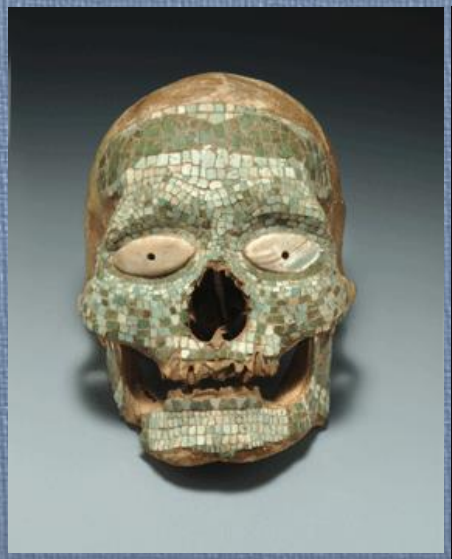
Other mosaic decorated skulls

British Museum, UK

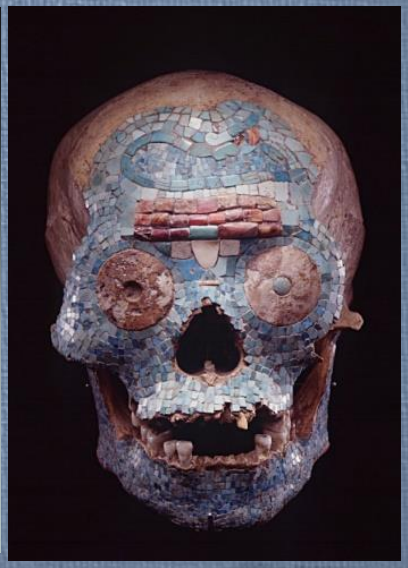


Monte Alban, Oaxaca, MX

Dumbarton Oaks museum, WA, USA

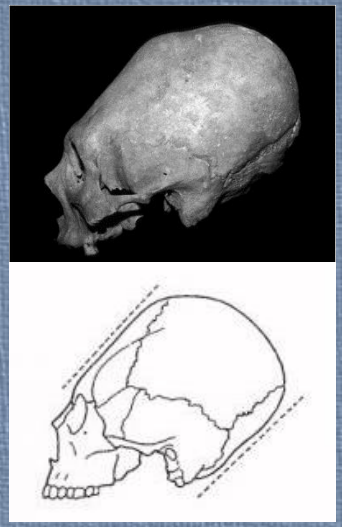


Leiden Museum, NL



Cranial Deformation Applied to Infants in Precolumbian Cultures

Figura 2. Deformación cefálica actual lograda con un aparato cefálico en un infante *shipibo conibo* en el Perú. (Foto del doctor Bruno Illius.)



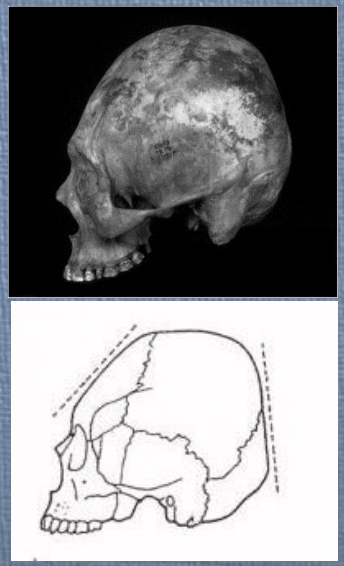
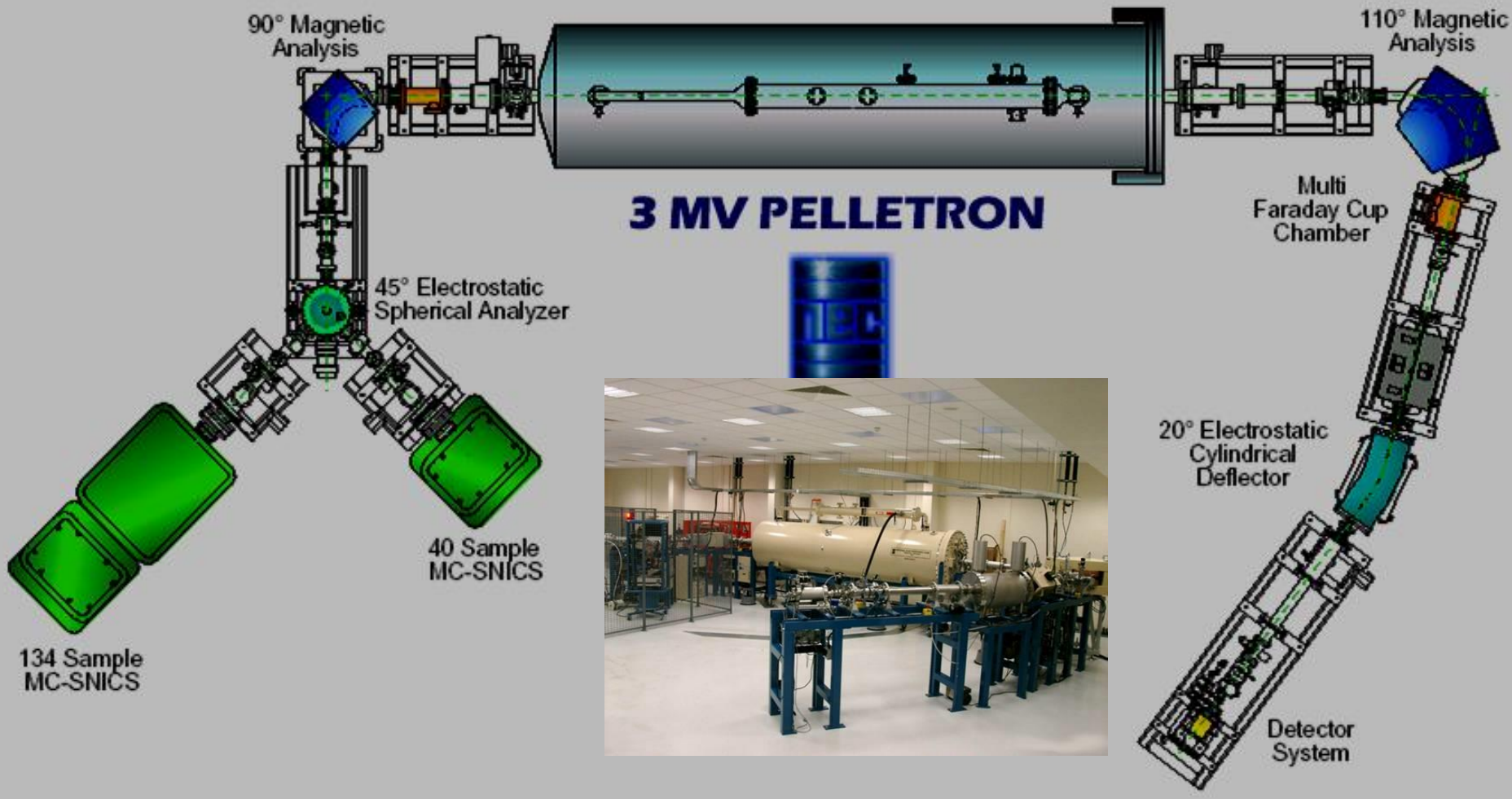


Figura 3. Acercamiento para apreciar la tablilla frontal, combinada con hilos y bandas compresoras, destinadas a distribuir la presión sobre la cabeza del infante. La tablilla está acolchonada.

DATING THE SKULL BY AMS 14C



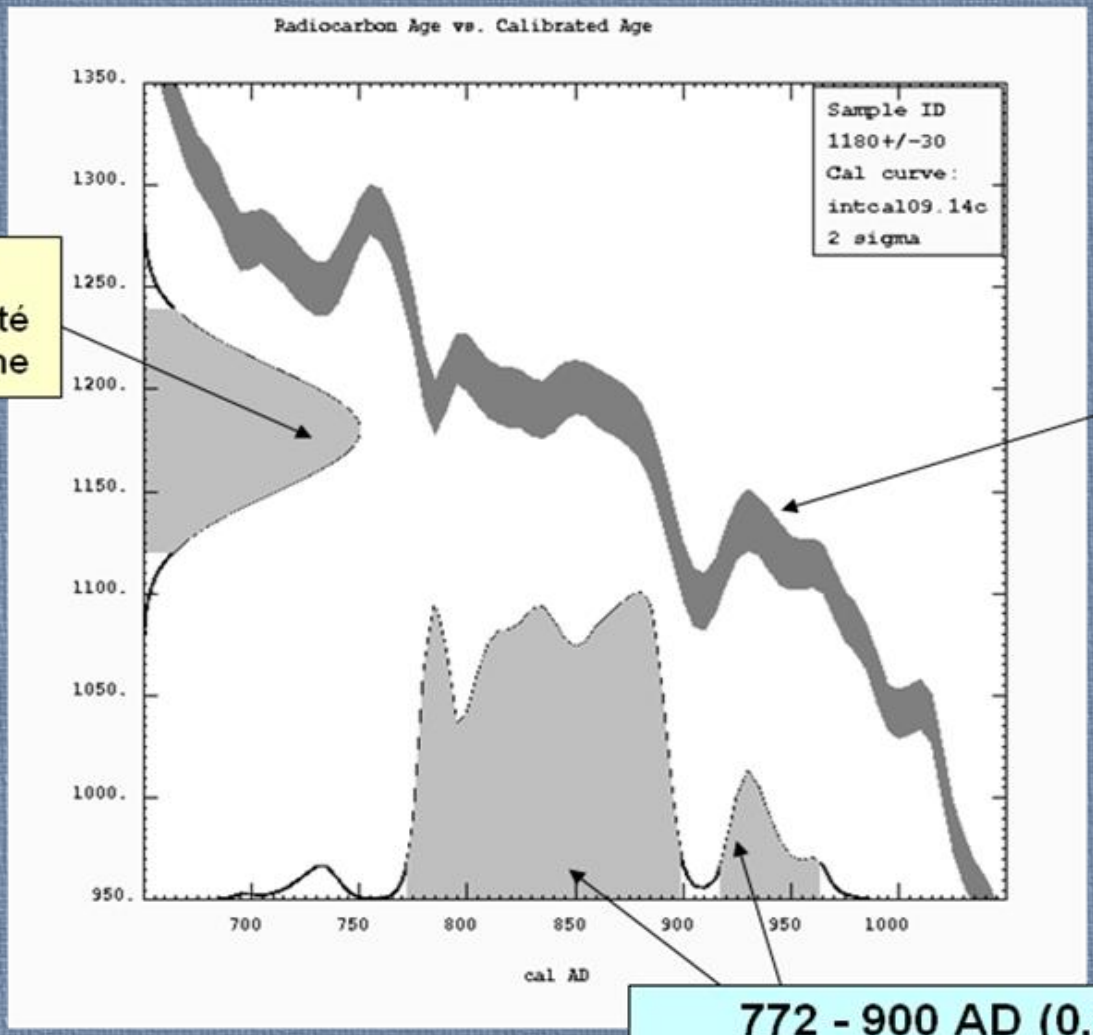
ARTEMIS NATIONAL LABORATORY

Sampling the Skull

300 mg of bone

The Age of the Skull

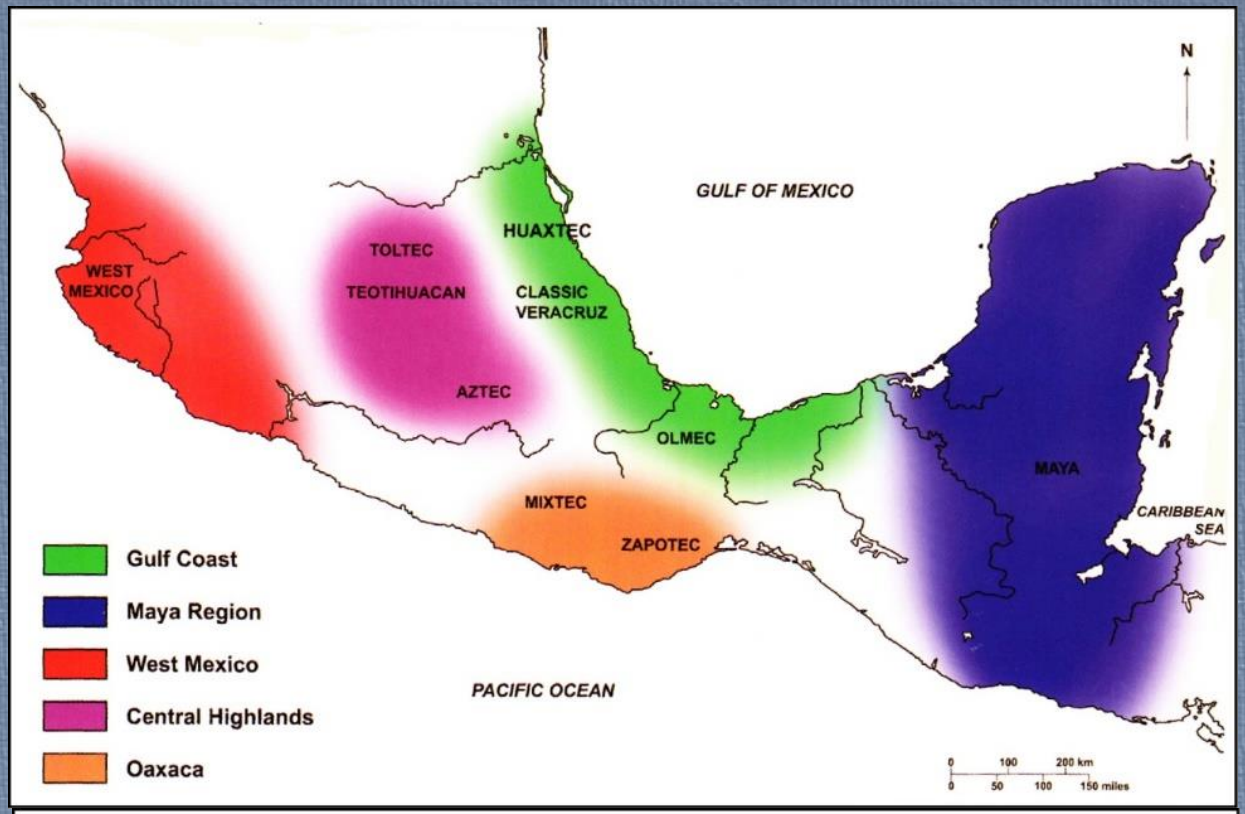
1180 ± 30 BP
Densité de probabilité de l'âge radiocarbone

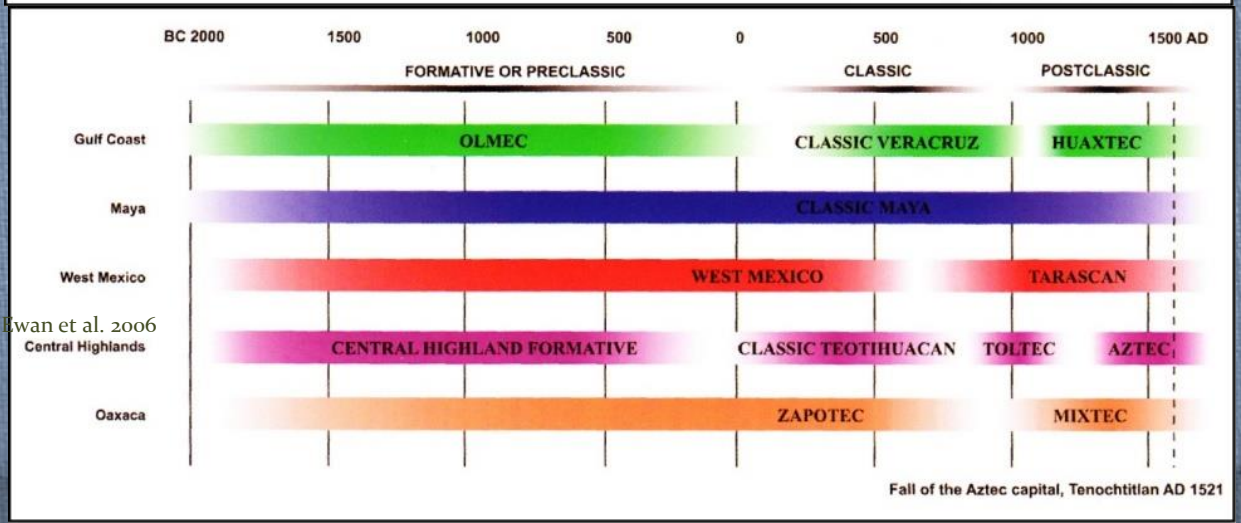


Courbe de calibration

772 - 900 AD (0,904)
918 - 963 AD (0,096)
Densité de probabilité de l'âge calendaire à 2σ

Precolumbian cultures in Mesoamerica



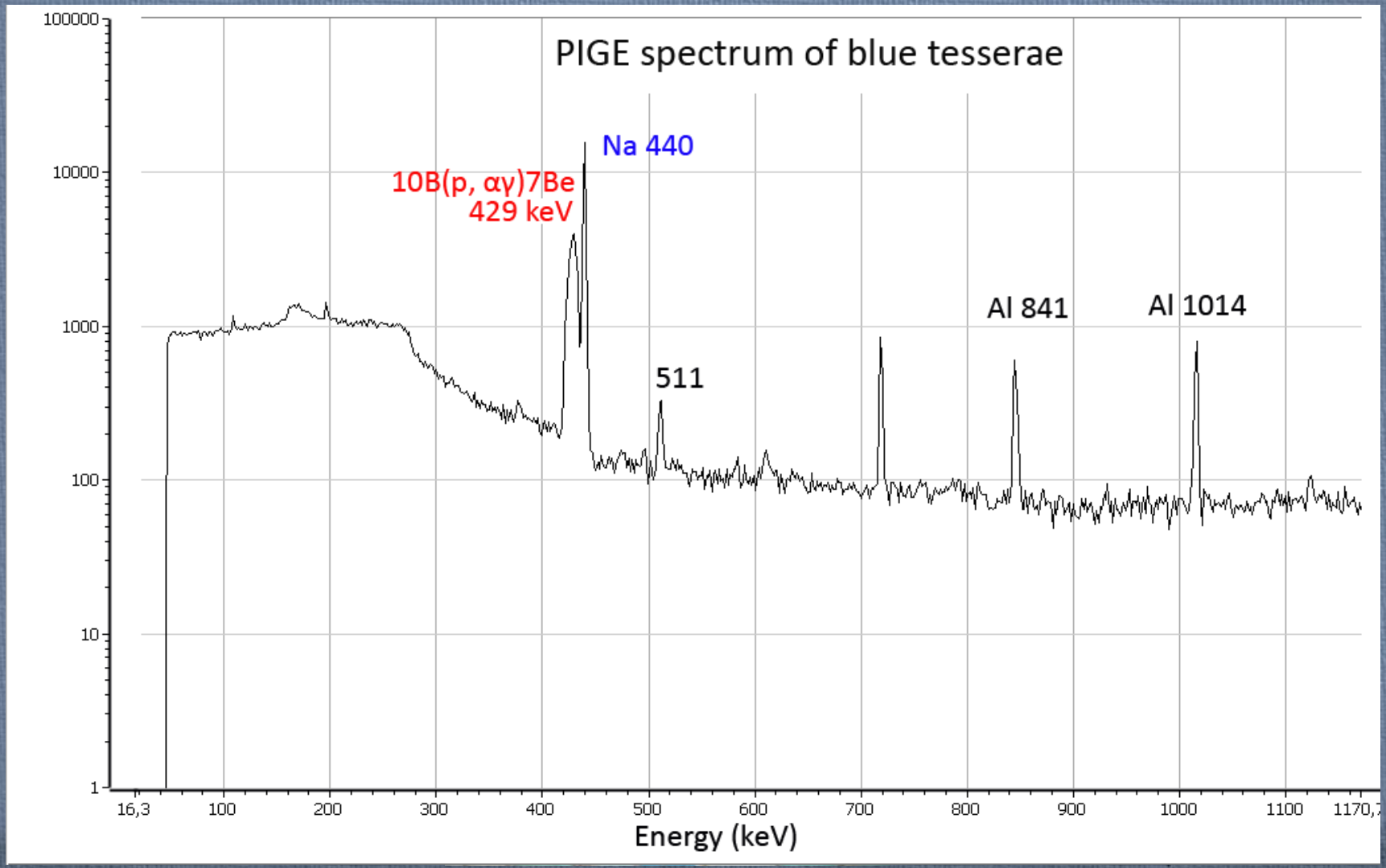


McEwan et al. 2006

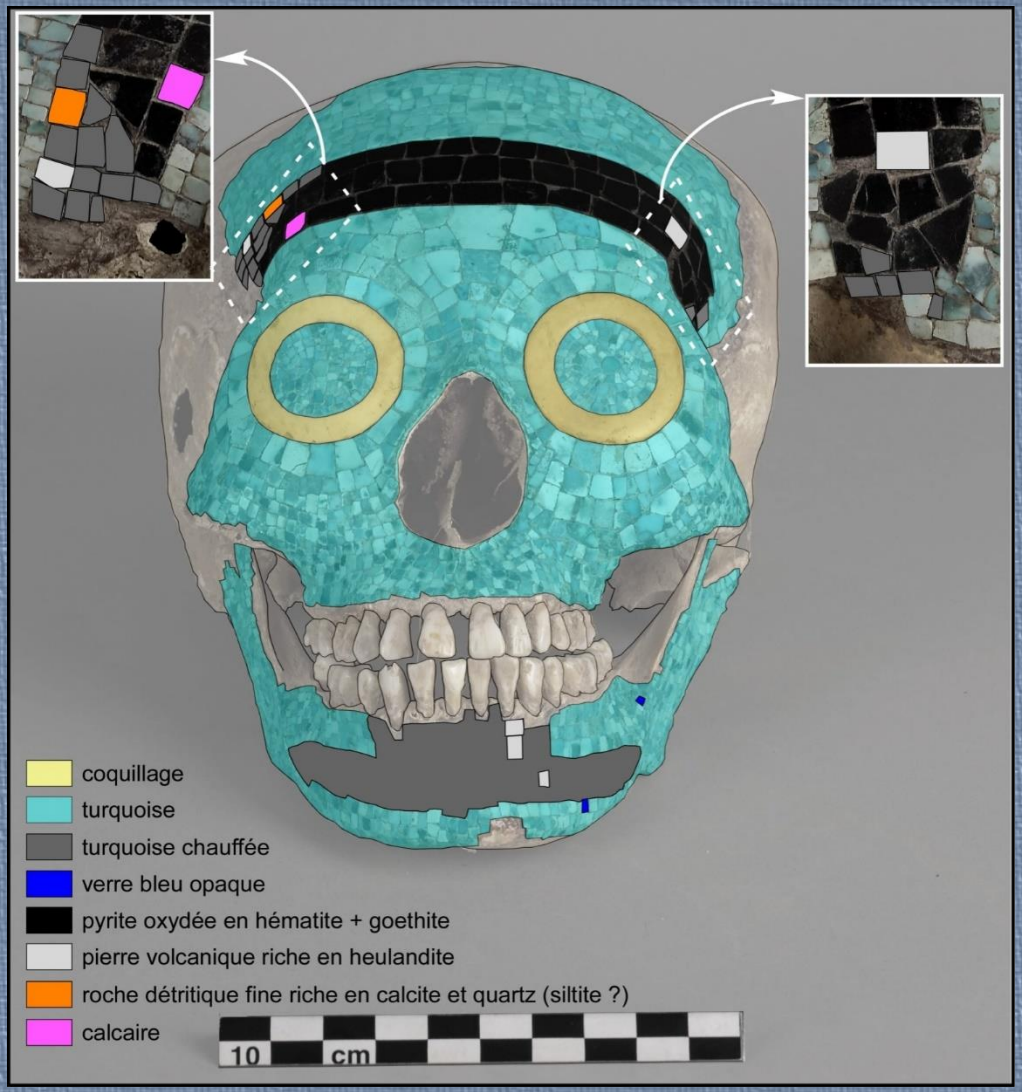

AGLAE 2 MV tandem accelerator

Anachronistic Materials

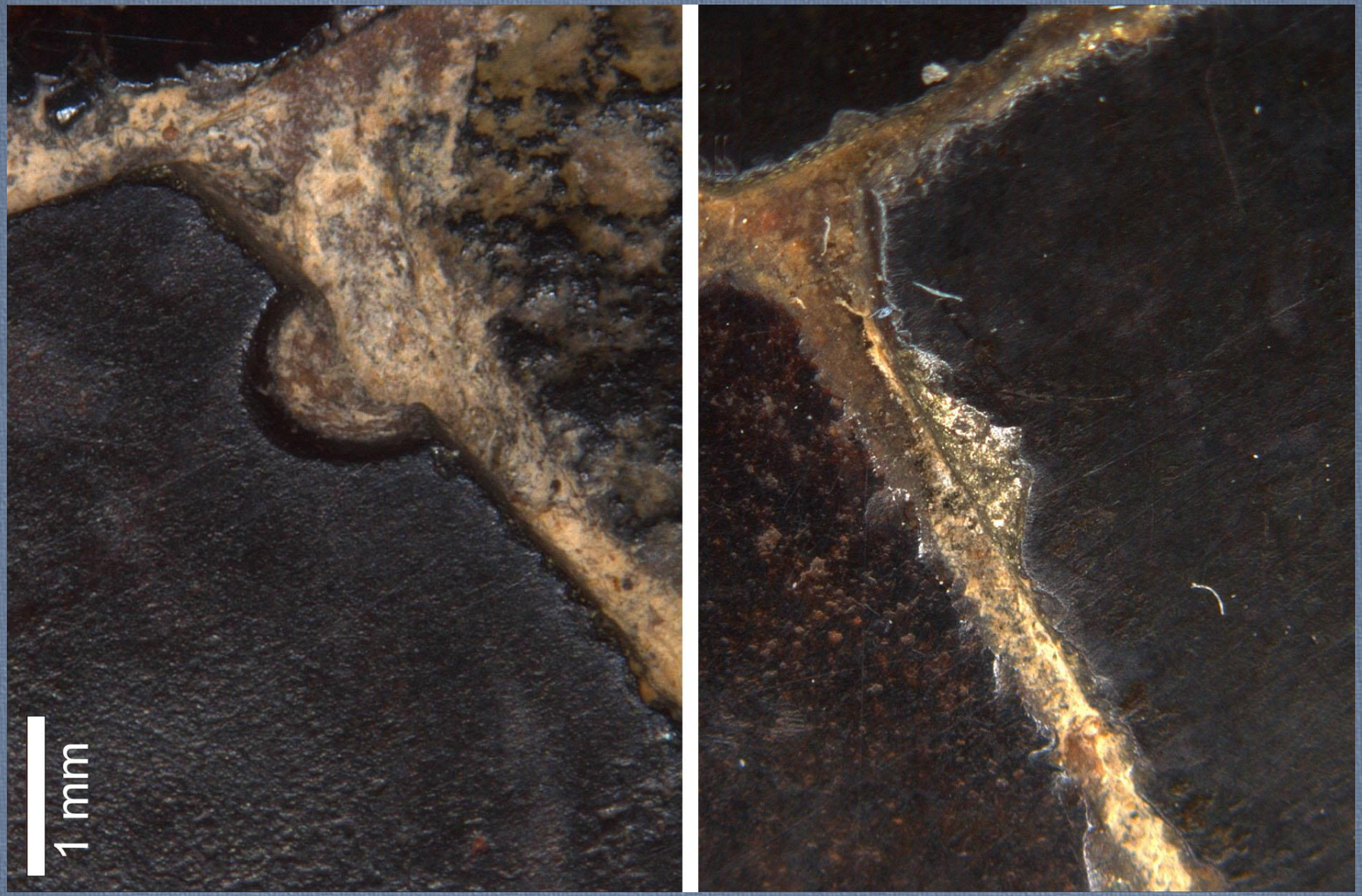
Two modern tesserea
glaze containing Boron as Flux and Antimony as opacifier



Pyrite
FeS_2



Turquoise
$CuAl_6P_4O_{28}H_{16}$



Re-use of pyrite platelets: drillings

Pyrite appearing under the alteration

Contrasted and Intriguing Results

- most materials are similar to those found on guenuine Aztec or Mixtec mosaics (shell, turquoise, pyrite)
- turquoise tesserea have the same composition as genuine mosaics
- black turquoise (unreported material)
- pyrite strongly alterated (ageing?)
- skull carbon-dated to the 10th century AD

- tesserae glued with shellac (cochineal) normaly from India

- two modern tesserae with boron glaze

FAKE OR GENUINE ?

Hypothesis

- globally genuine Precolumbian artefact + minor modern restorations
- genuine Precolumbian skull and mosaics recently put together
- fake made of a genuine Precolumbian skull and an artificially aged modern mosaic
- colonial curio manufactured after the conquest by Mexican artisans using traditional and european materials

… your guess ?

Impact of Ion Beam Analysis in Arts and Archaeology

- ARCHAEOLOGY : DOCUMENT MEN'S LIFE IN THE PAST

  raw materials procurement, manufacture technology, distribution networks

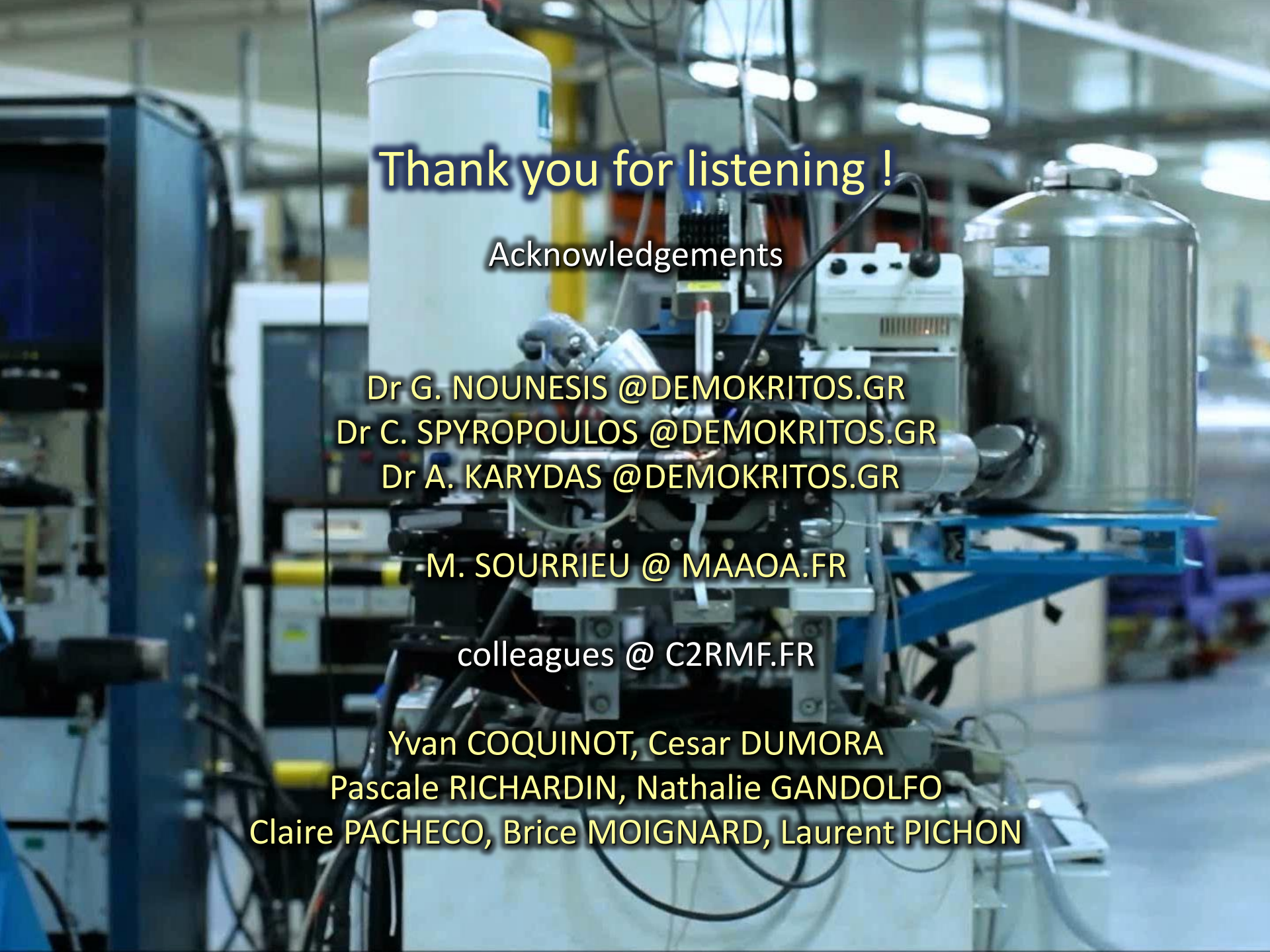
- ART HISTORY : HIGHLIGHT THE ARTIST'S CREATION

  Disclosing the artist's choice of materials and creative gesture

- SAFEGARDING our HERITAGE

  Help to preserve relics by understanding alteration

  preventing acquisition of fakes and unwanted objects



Thank you for listening !

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Pascale RICHARDIN, Nathalie GANDOLFO
Claire PACHECO, Brice MOIGNARD, Laurent PICHON