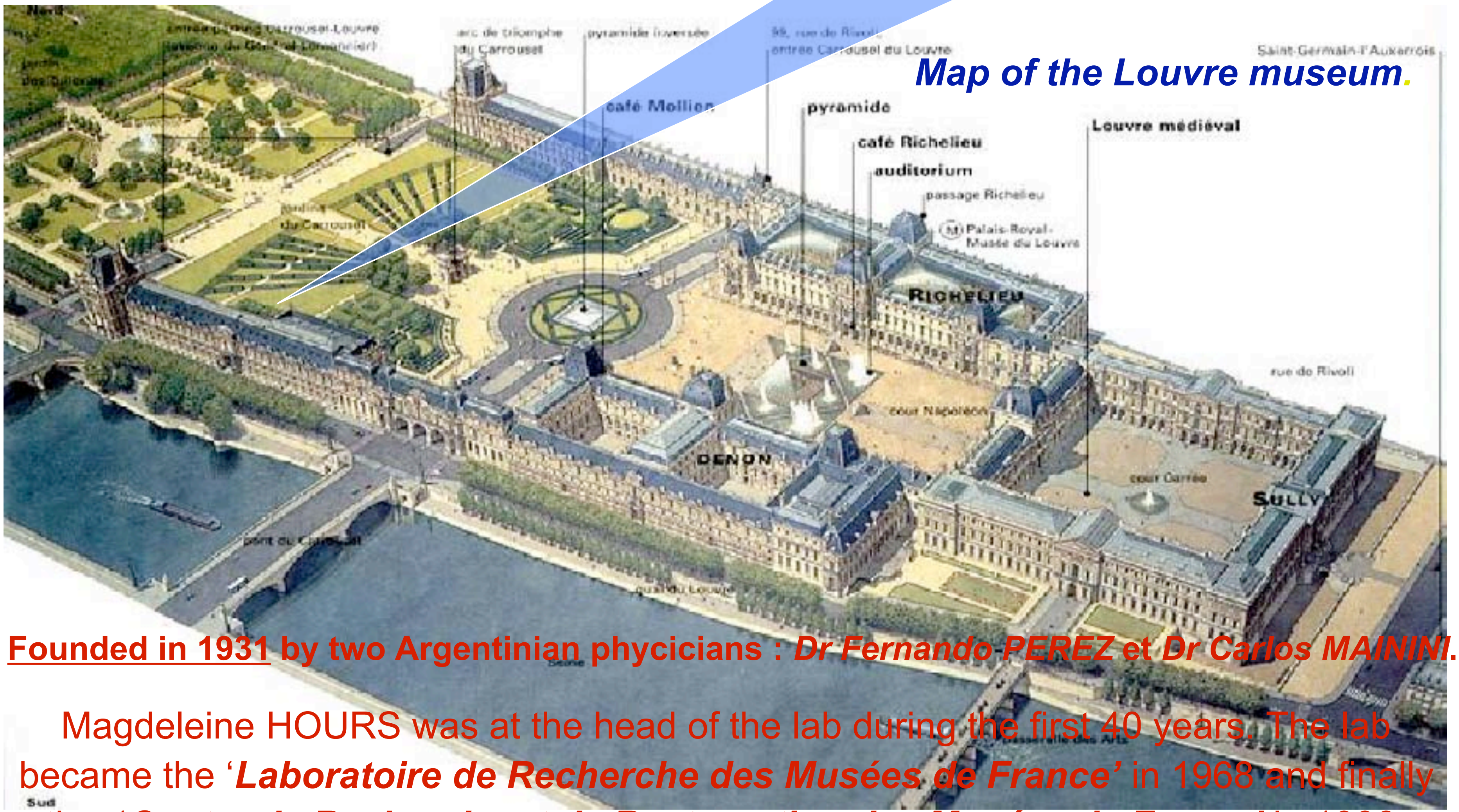

The AGLAE team:
Ph. Walter *
J. Castaing*
B. Moignard
Th. Guillou*
L. Pichon
J. Salomon
*= CNRS
C2RMF
Impact of the IBA techniques on the study of cultural heritage materials

The Louvre, palace of the French kings since 1190, became a museum in 1793.

Laboratory location,

underground, in the Louvre garden near the ‘Porte des Lions’.



<u>Founded in 1931</u> by two Argentinian phycicians : *Dr Fernando PEREZ et Dr Carlos MAININI*.

Magdeleine HOURS was at the head of the lab during the first 40 years. The lab became the ‘***Laboratoire de Recherche des Musées de France’*** in 1968 and finally the ‘***Centre de Recherche et de Restauration des Musées de France’*** in 1998.

Outline

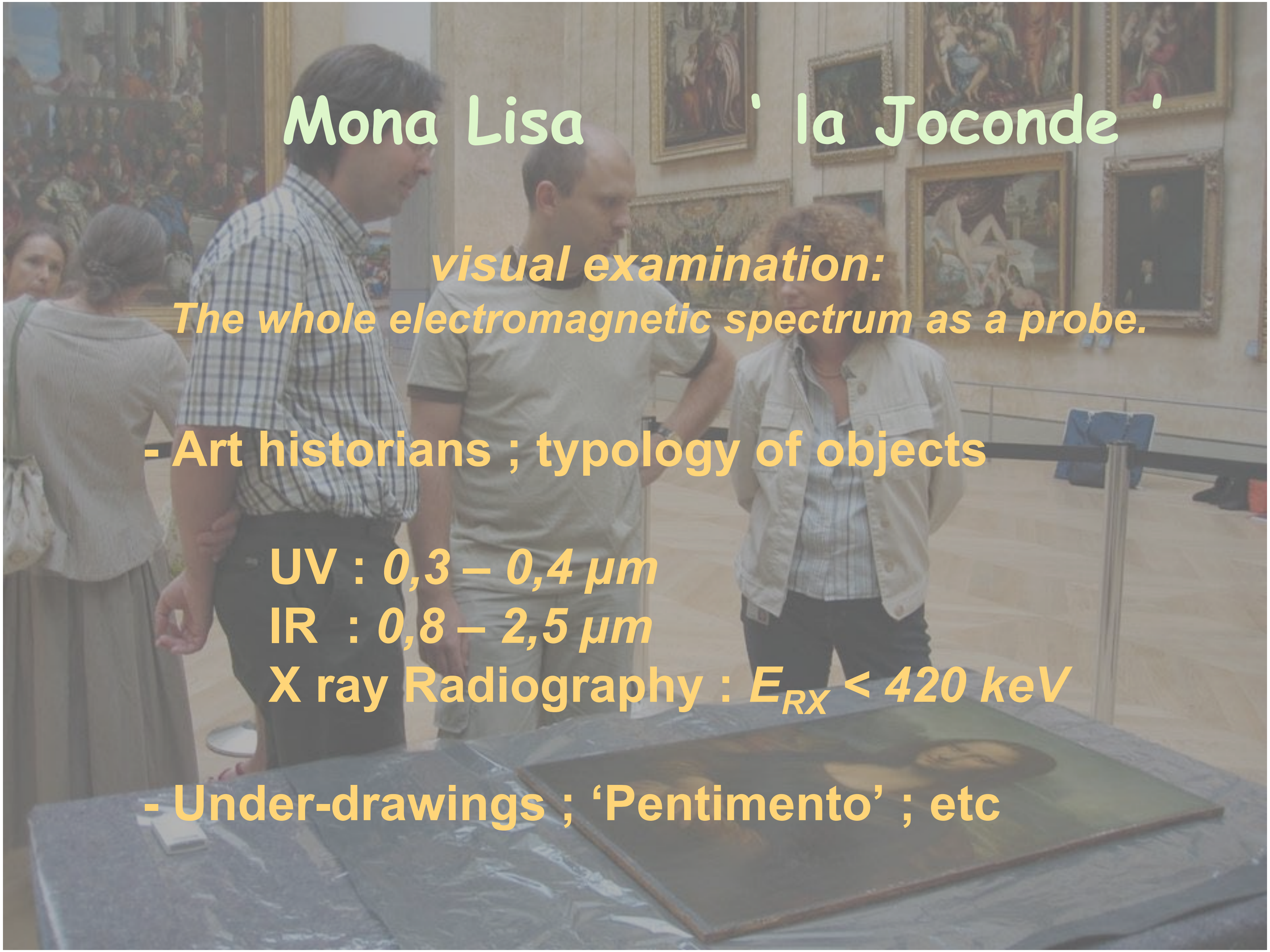
- **How to extract a particle beam to atmosphere**
- **Ion Beam Analysis**
- **Evolution of our external beam setup**
- Sequential PIXE/RBS with successive beams of protons and alphas:

    The analysis of lustered ceramics.
- Simultaneous PIXE/RBS with a single shot of α particles:

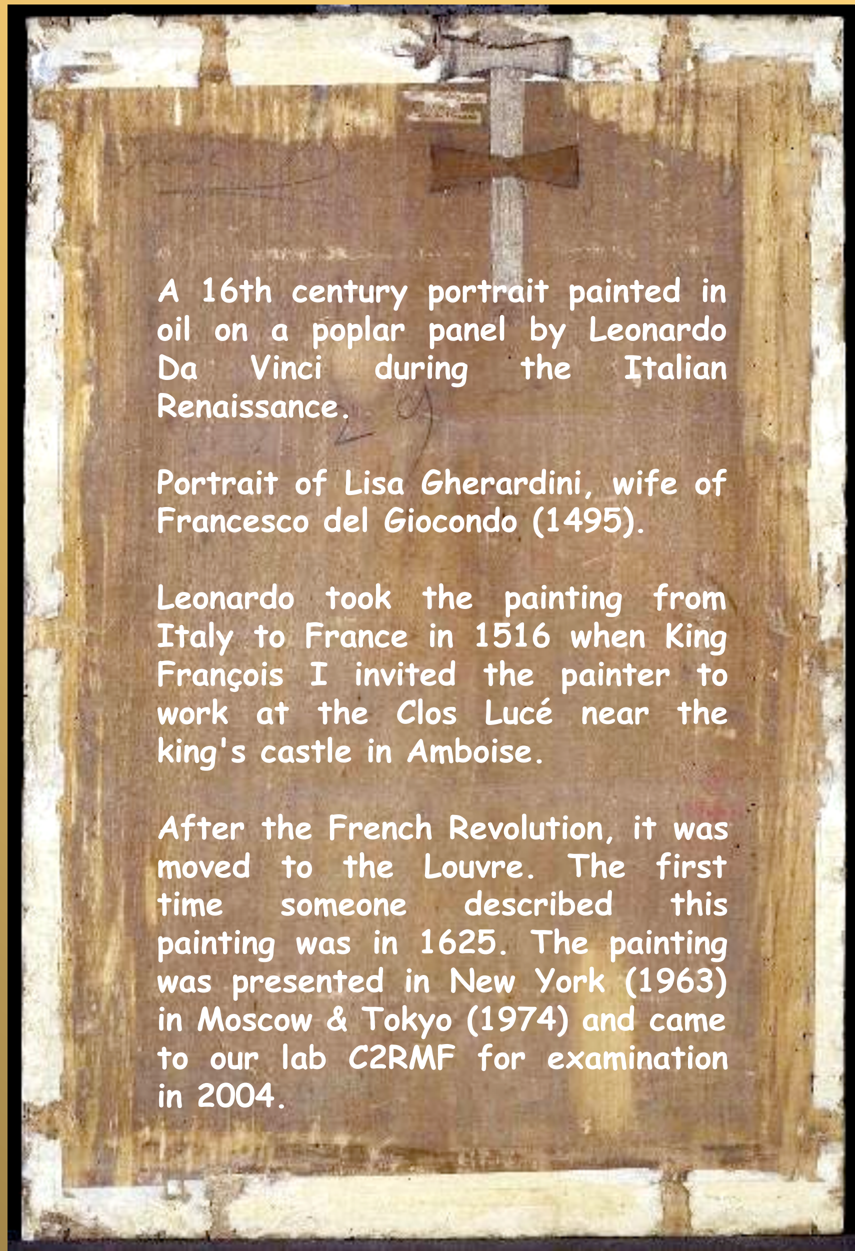
    The analysis of a patina.

    Usewear of tools.
- **Some new improvements**
- **Future prospects**

But before going to IBA I would like to present you a 500 year old lady: Mona Lisa


Mona Lisa ' la Joconde '
visual examination:
The whole electromagnetic spectrum as a probe.
- Art historians ; typology of objects
UV : 0,3 – 0,4 µm
IR : 0,8 – 2,5 µm
X ray Radiography : E_{RX} < 420 keV
- Under-drawings ; 'Pentimento' ; etc

79,4 cm x 53,4 cm x 13 mm; painting on a wooden poplar panel



A 16th century portrait painted in oil on a poplar panel by Leonardo Da Vinci during the Italian Renaissance.

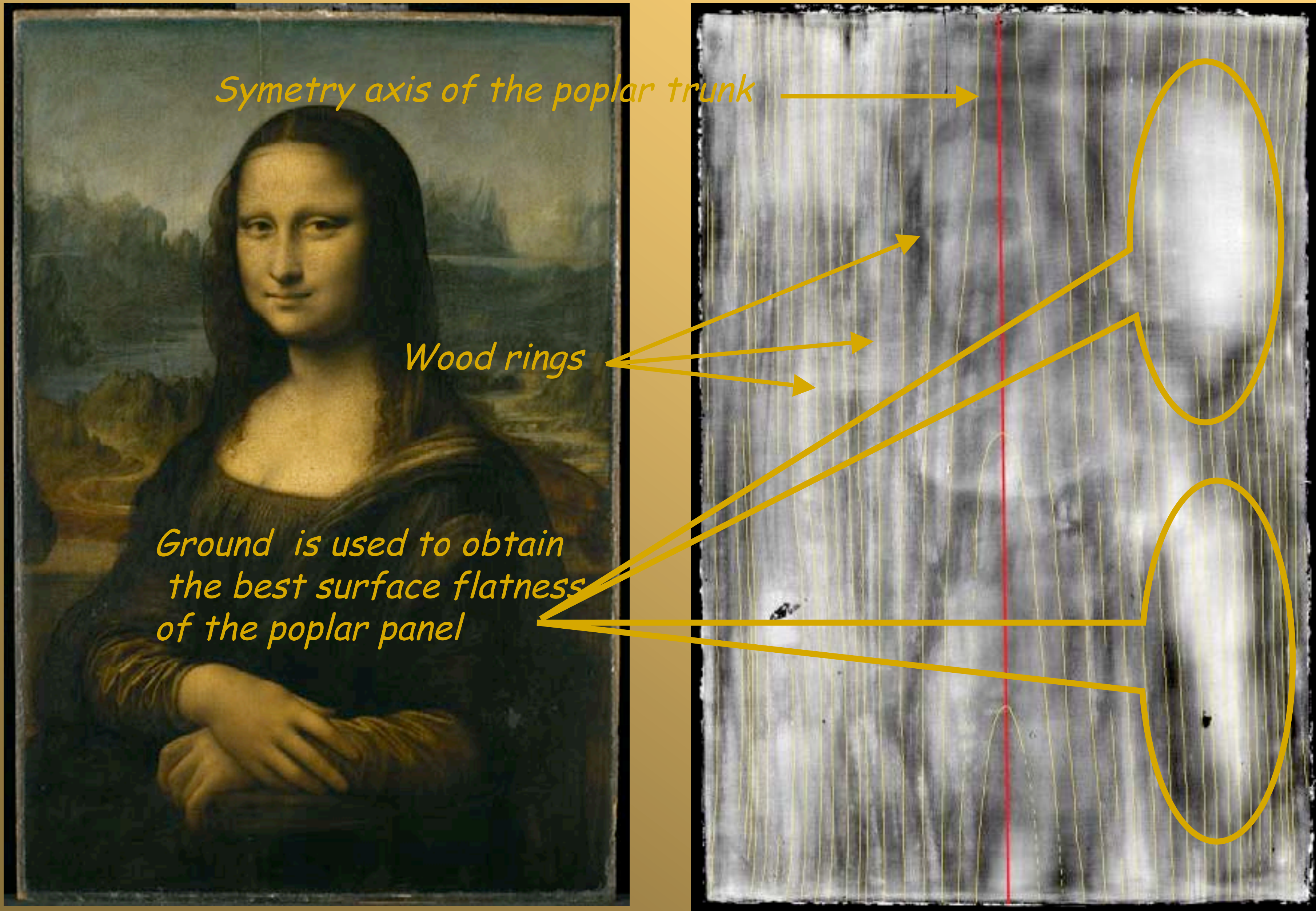
Portrait of Lisa Gherardini, wife of Francesco del Giocondo (1495).

Leonardo took the painting from Italy to France in 1516 when King François I invited the painter to work at the Clos Lucé near the king's castle in Amboise.

After the French Revolution, it was moved to the Louvre. The first time someone described this painting was in 1625. The painting was presented in New York (1963) in Moscow & Tokyo (1974) and came to our lab C2RMF for examination in 2004.

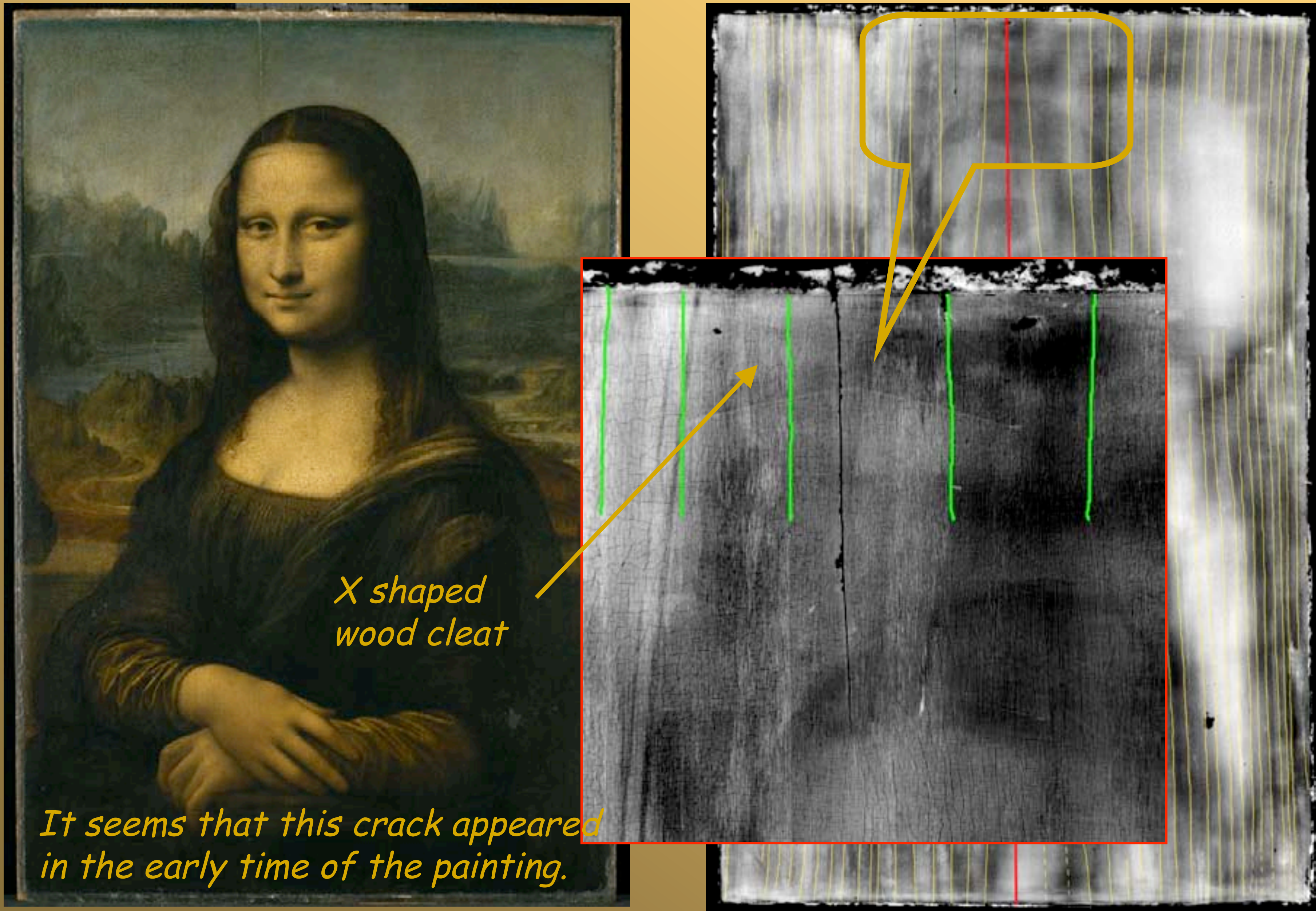
X-ray radiography

$E_{RX} = 45\ kV$



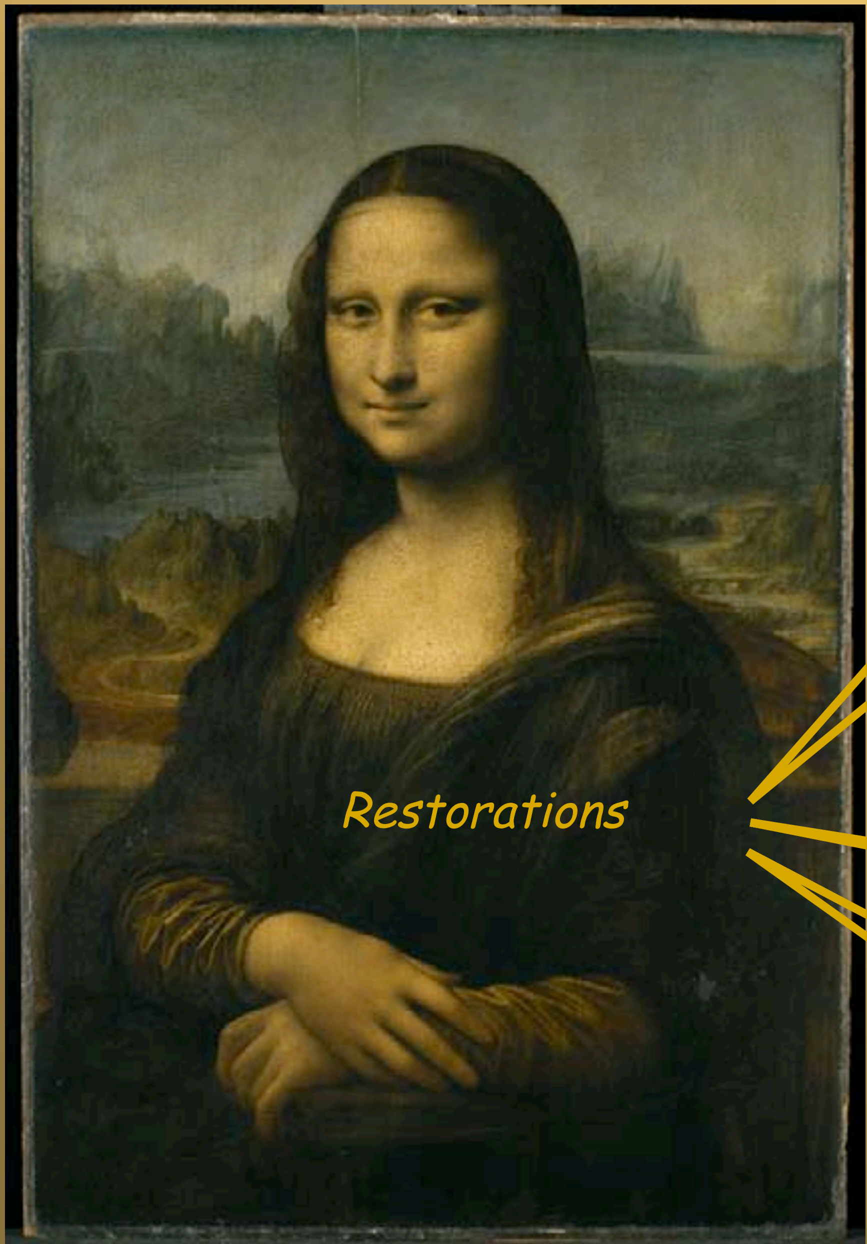
X-ray radiography

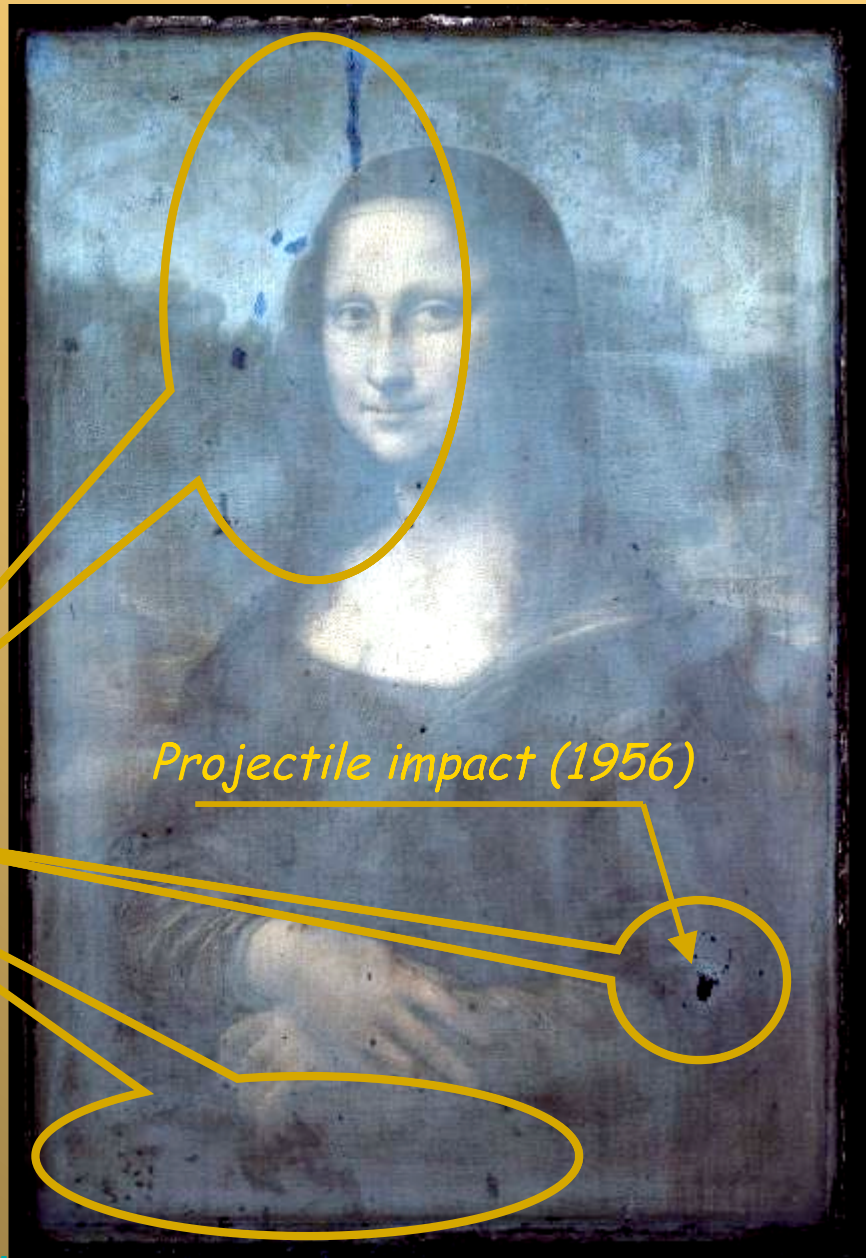
11,9 cm long crack stable since 1933 (first radiography)



UV fluorescence photography

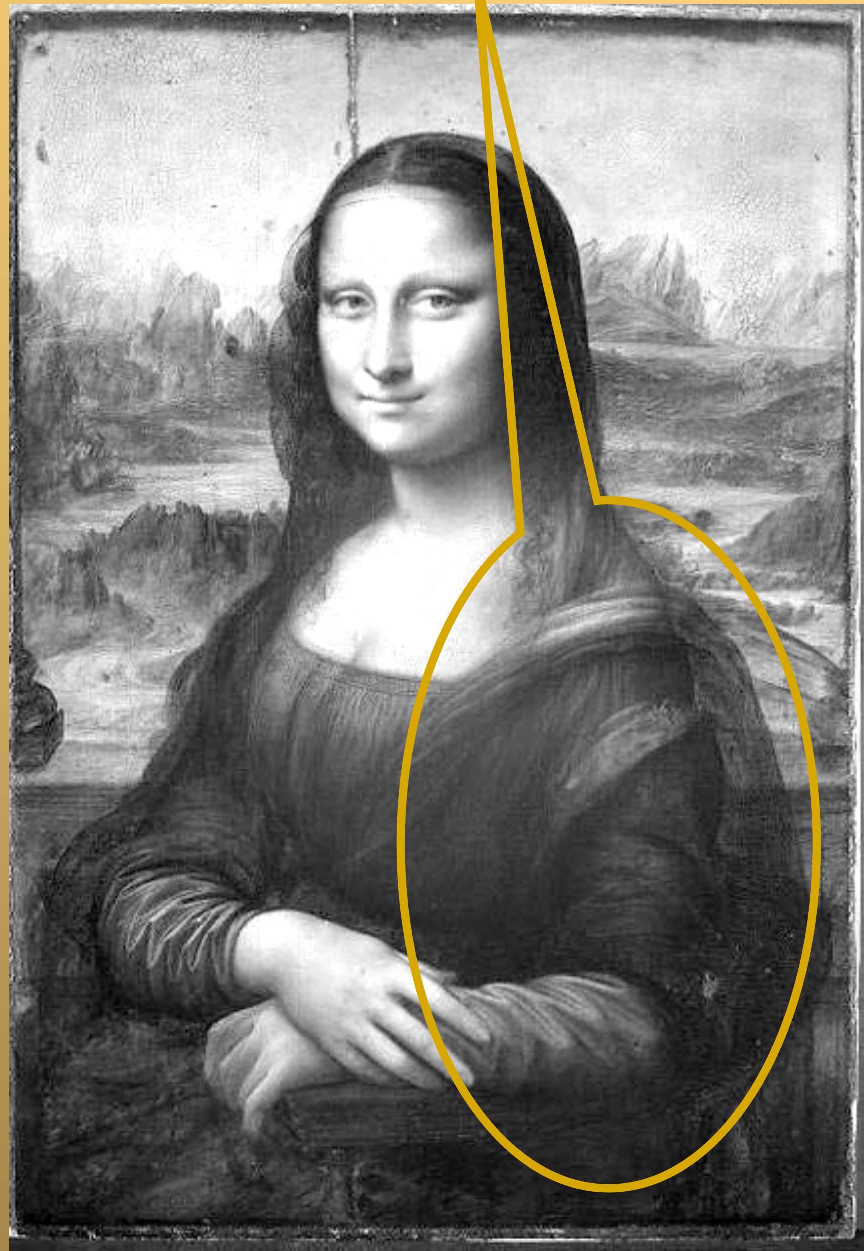
Shows the restorations





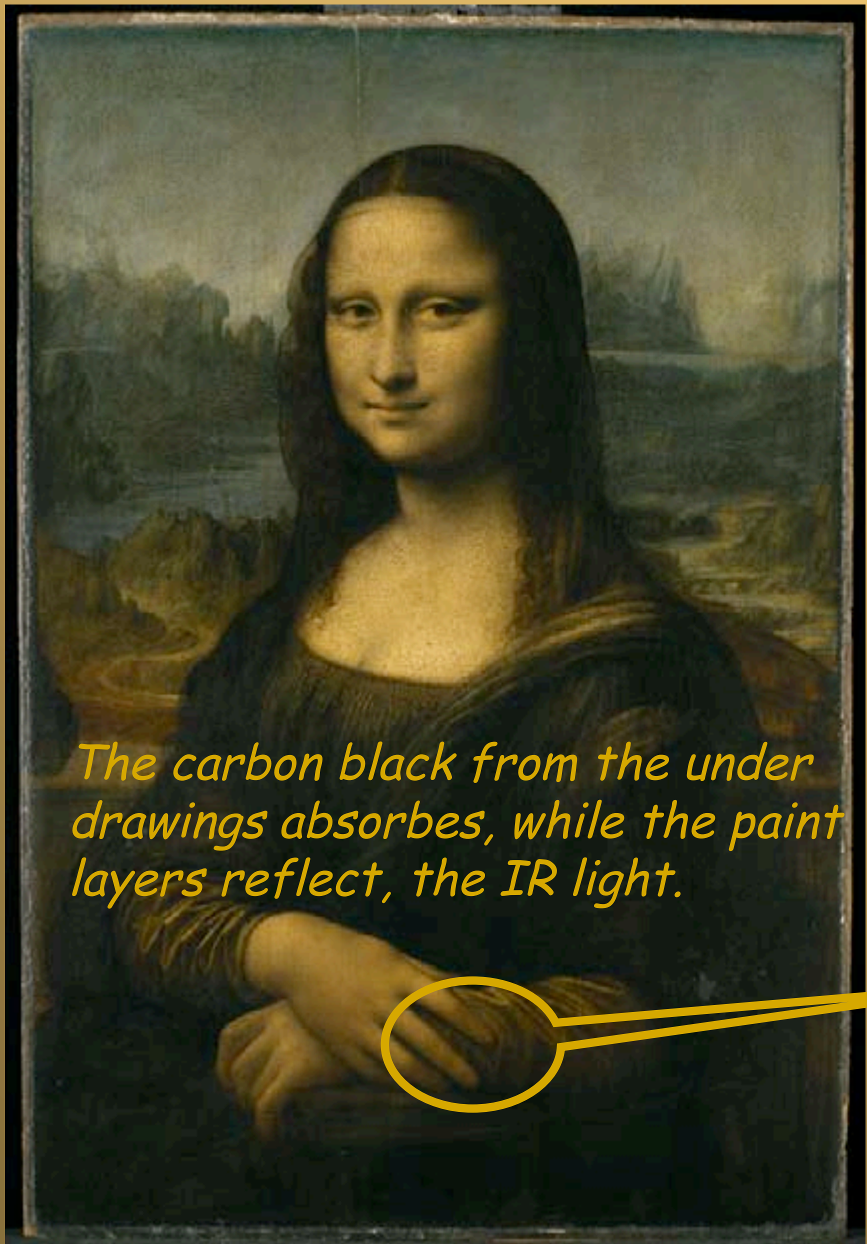
Infrared photography 900 nm

We start to penetrate inside the paint layer: more details are seen !

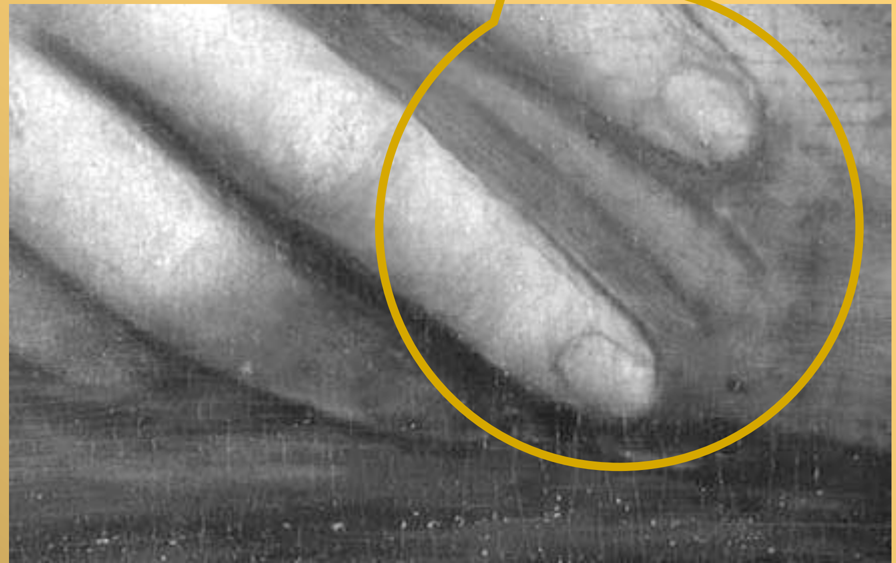


Infrared reflectography 1000 to 2200 nm

'Pentimento' of the painter



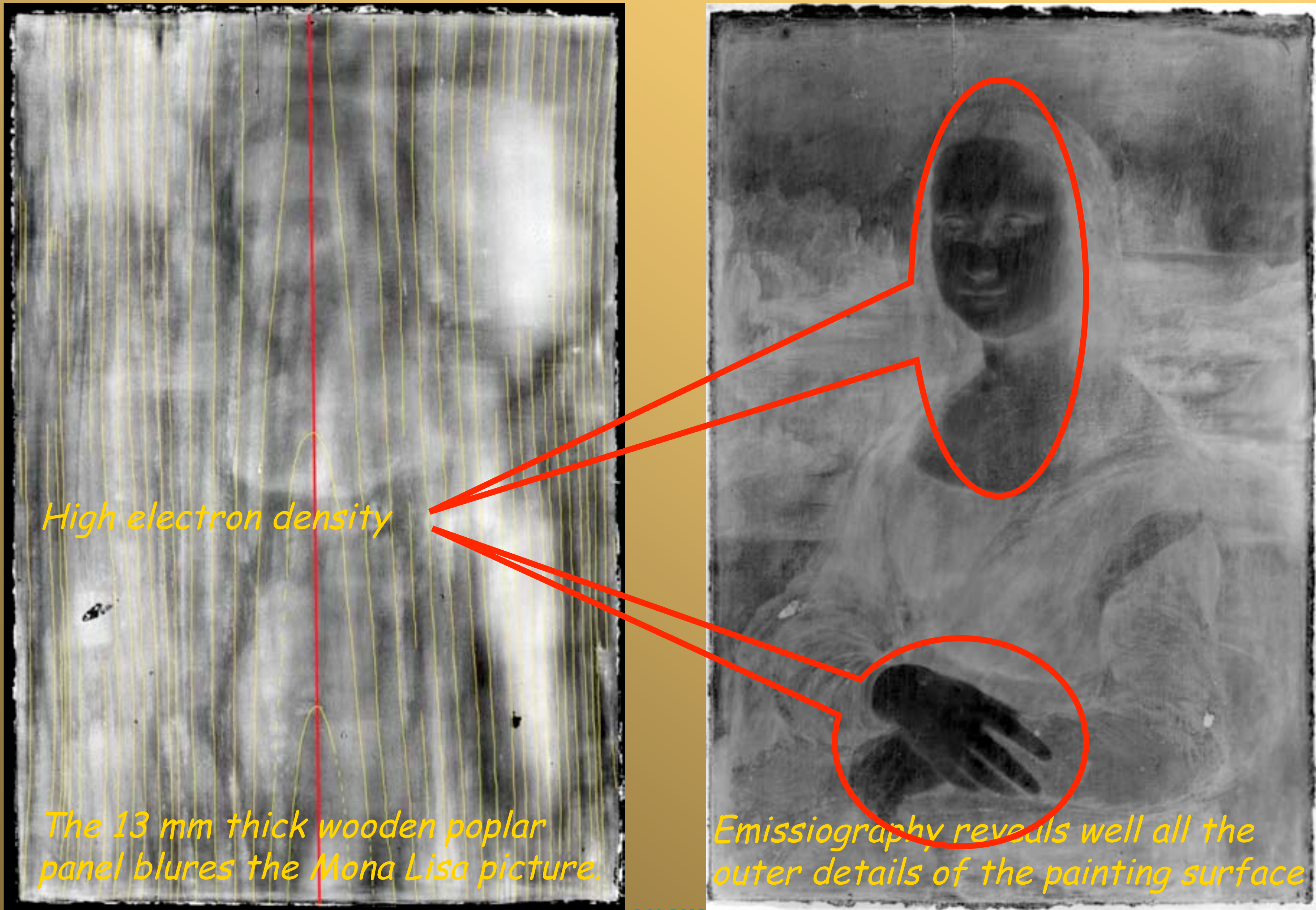
The carbon black from the under drawings absorbes, while the paint layers reflect, the IR light.



Pentimento

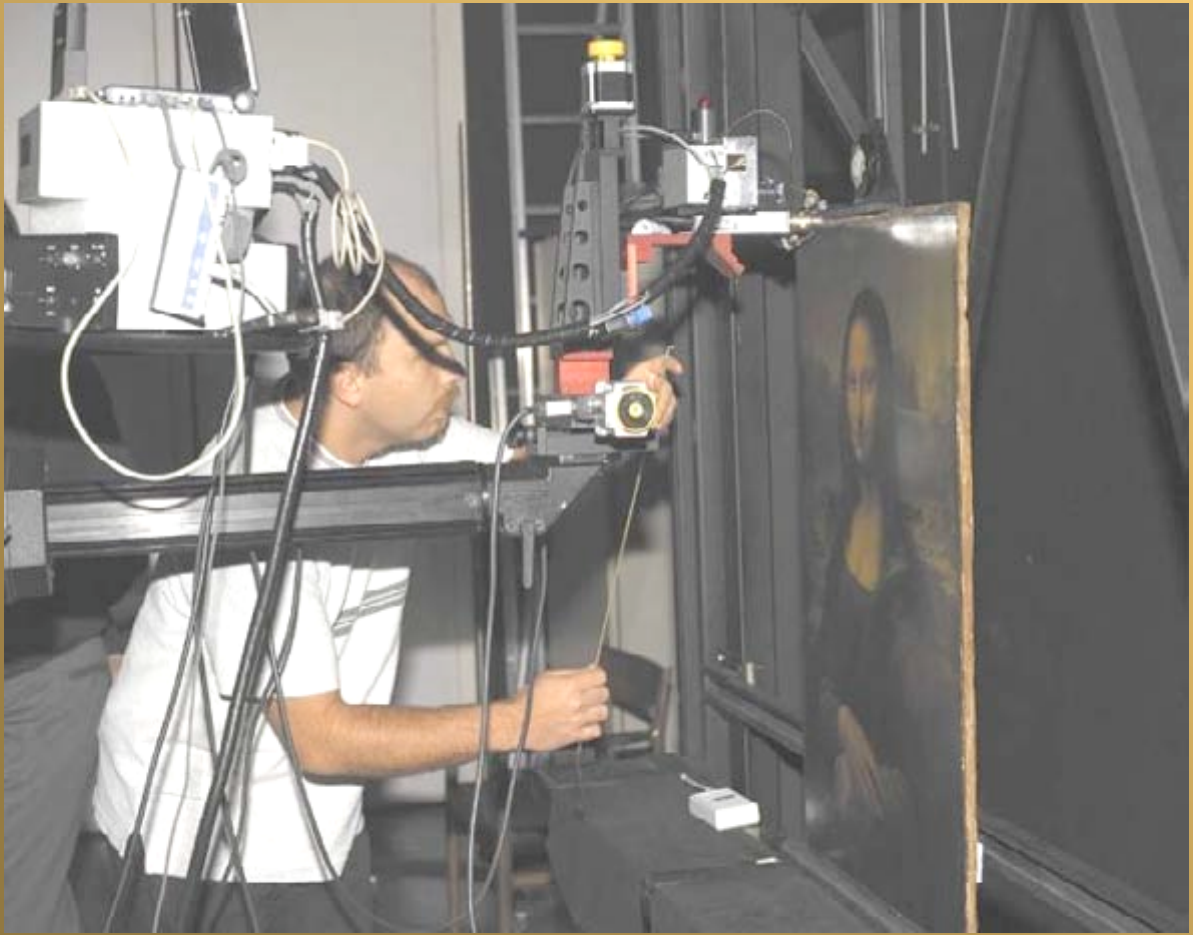
Emissiography polychromatic X-ray spectrum E_{RX} < 290 kV; 4 mA; 2 min

X-ray radiography versus Emissiography



XRF (X-Ray Fluorescence spectrometry) :

Portable X-ray fluorescence spectrometer for elemental analysis



X-ray tube from MOXTEK
Silver anode ; 3 W power
SDD from Röntec
with a resolution of 150 eV

XRF – Mona Lisa pigments:

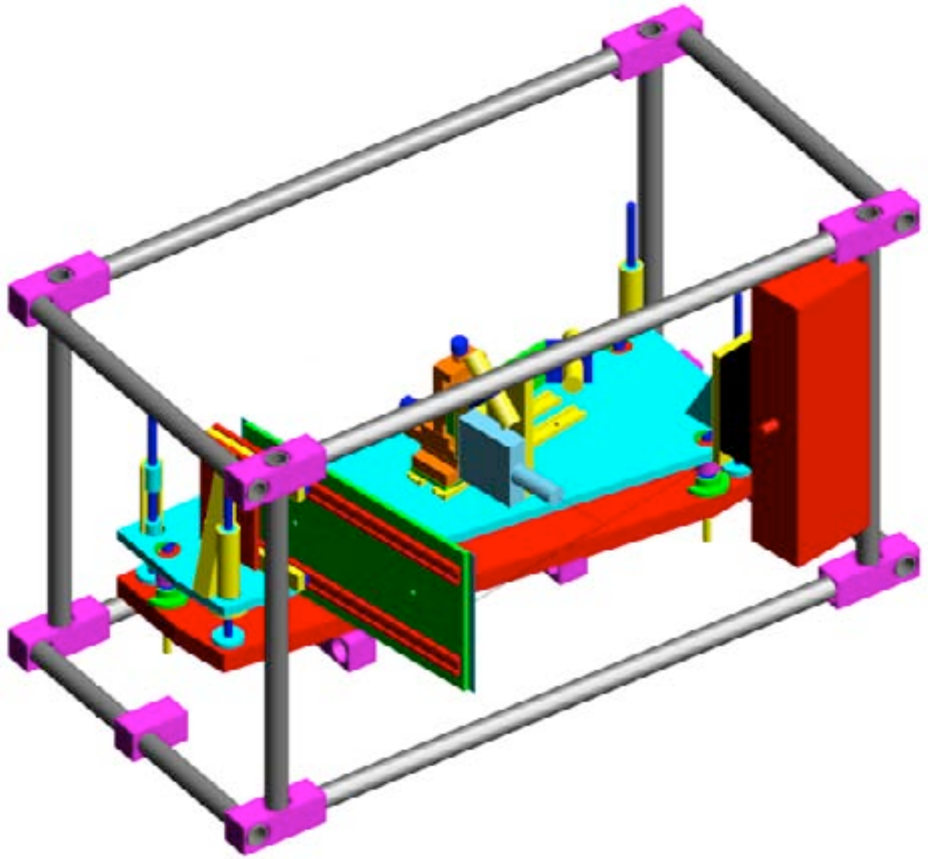
Lead white (carbonates ?)
Copper blue (azurite ?)
Copper green (malachite ?)
Yellow of lead and tin
Vermillon (cinnabar ?)
Black (carbon ?)
Brown (clays from Umbría: Fe; Mn; Ca)

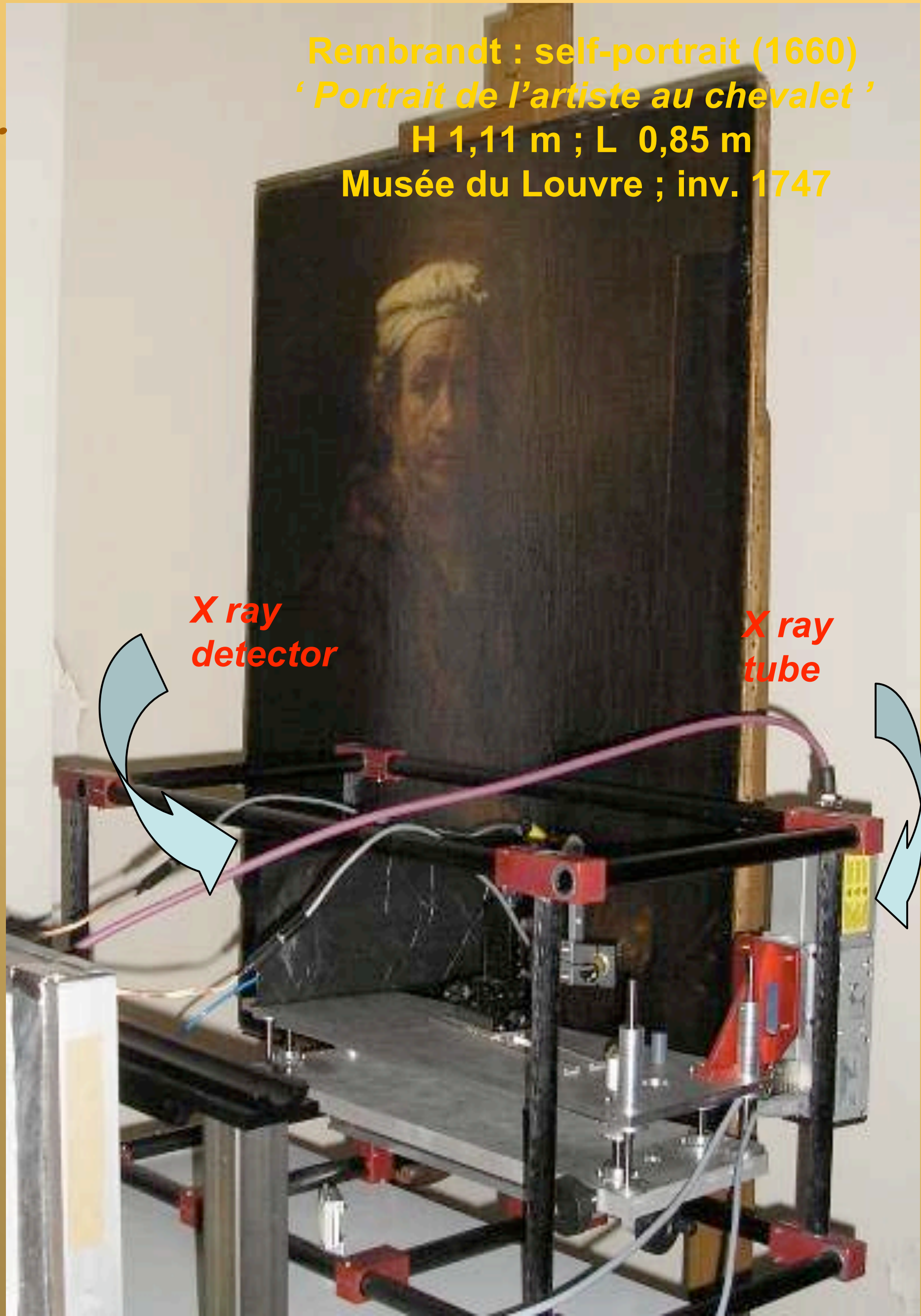
Due to absorption, below Si there is no XRF signal for low Z elements

Quantitative analysis of Della Robbia glazes with a portable XRFspectrometer and its comparison to PIXE methods.
A. Gianoncelli, J. Castaing, A. Bouquillon, A. Polvorinos, P. Walter.
X-ray Spectrometry, 2006, vol. 35, pp. 365 - 369

AU CŒUR DE « LA JOCONDE » : Léonard de Vinci décodé.
Ouvrage réalisé avec le C2RMF . Édition publiée sous la direction de
Michel Menu, Jean-Pierre Mohen et Bruno Mottin, 128 pages, 325 ill. Livres d'Art, Gallimard [2006]

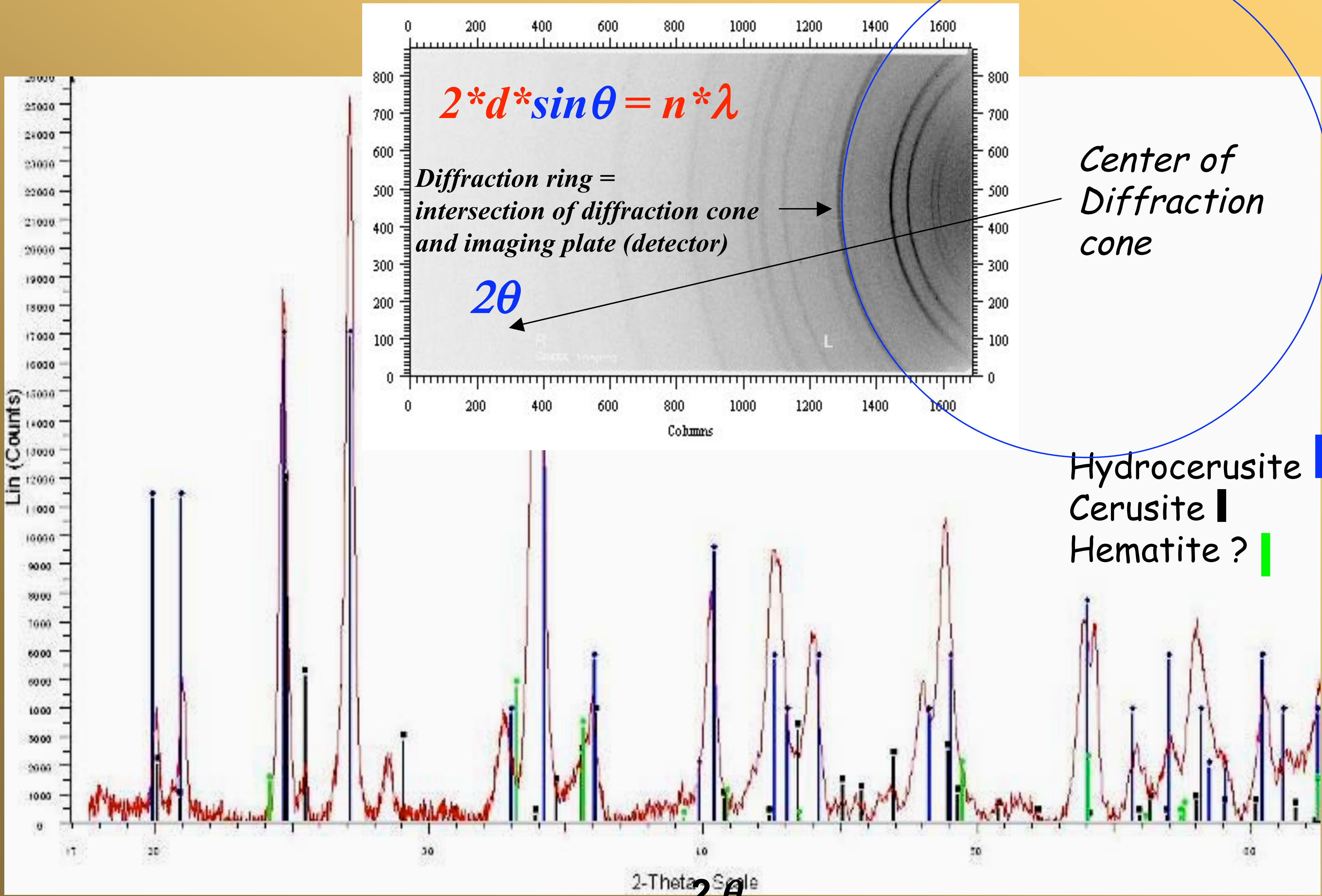
Portable combined XRD/XRF:
structural analysis of works of art.





X-ray tube from MOXTEK
Copper anode ; 3 W power
Equiped with a semi lens (// X-ray beam)
Detector: Imaging plate (XRD Cu Kα Kβ lines)
SDD from Röntec (XRF bremsstrhlung) with a resolution of 150 eV

Portable XRD: *structural analysis of works of art.*



Introduction => IBA

Applications of IBA to cultural heritage mostly rely on the use of **PIXE**:

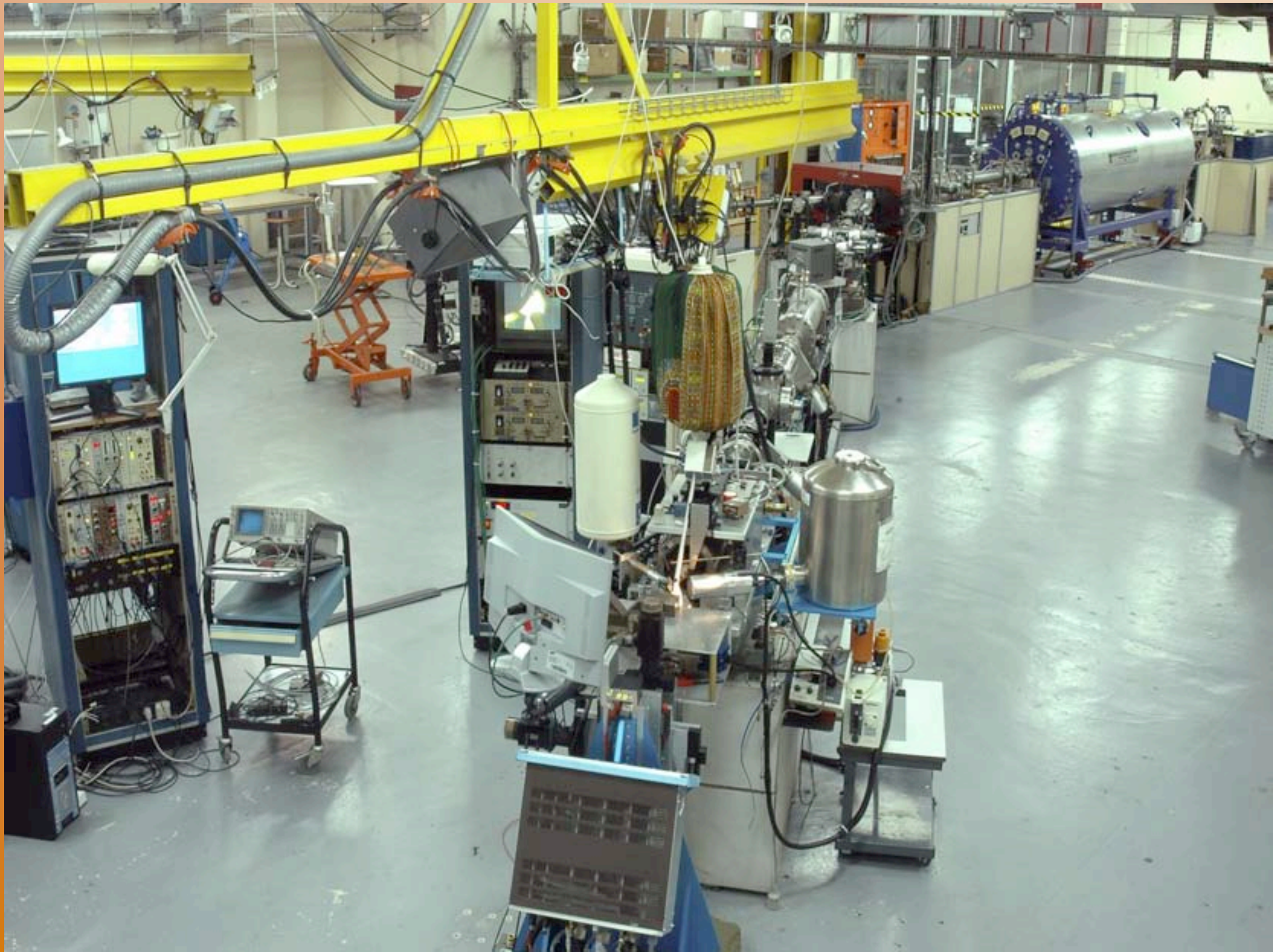
- high sensitivity down to trace elements
- ease of implementation at atmospheric pressure

However the poor depth information, of this technique, is a strong limitation frequently of primary importance in art works having multilayer structure like paintings, glazed ceramics, patinated bronzes, etc..

RBS can provide detailed depth information, but cannot readily be implemented in air due to potential beam deterioration by energy loss.

We have progressively developed setups that permit to combine PIXE and RBS / **NRA** under the best conditions with one / or two external beam(s).

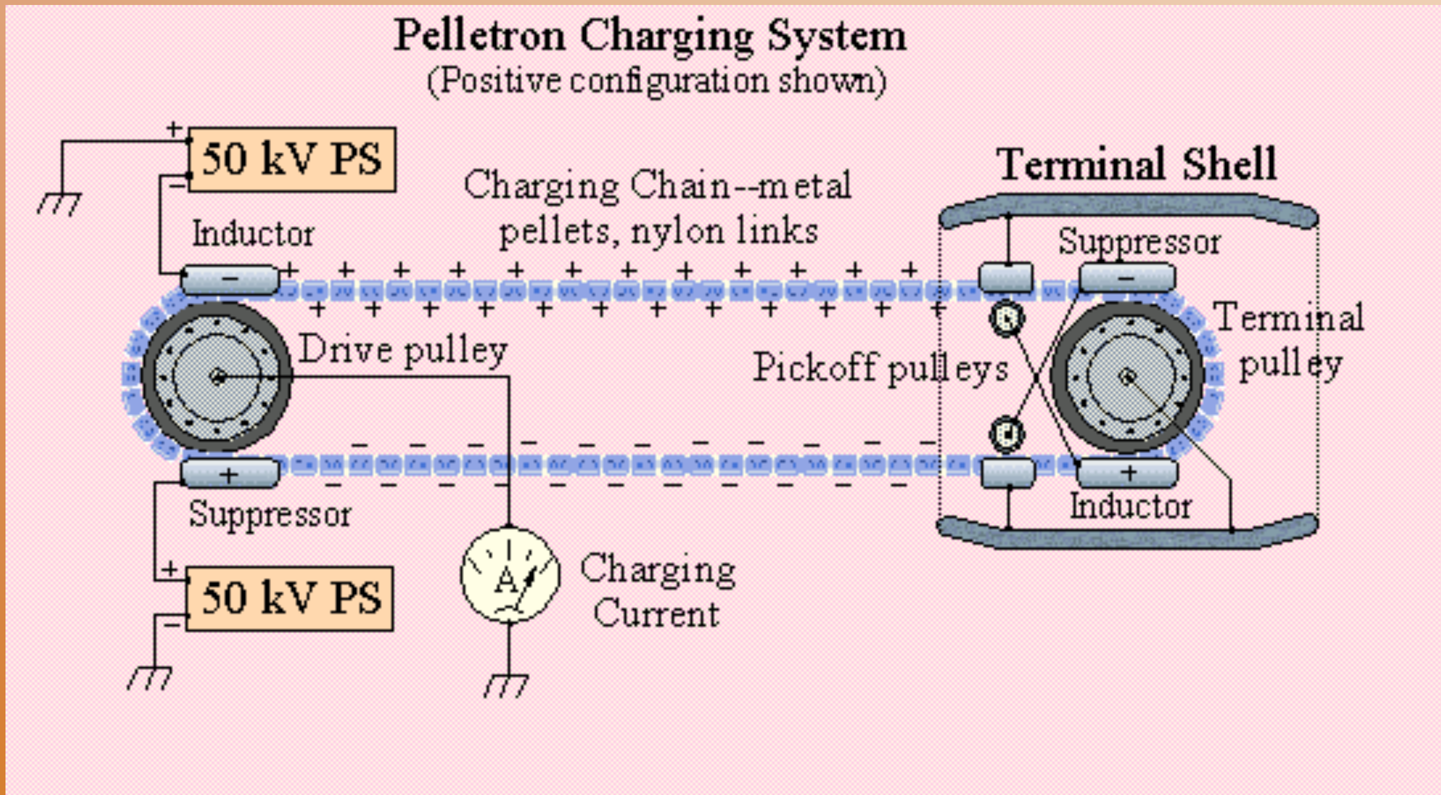
Overview of the AGLAE facility



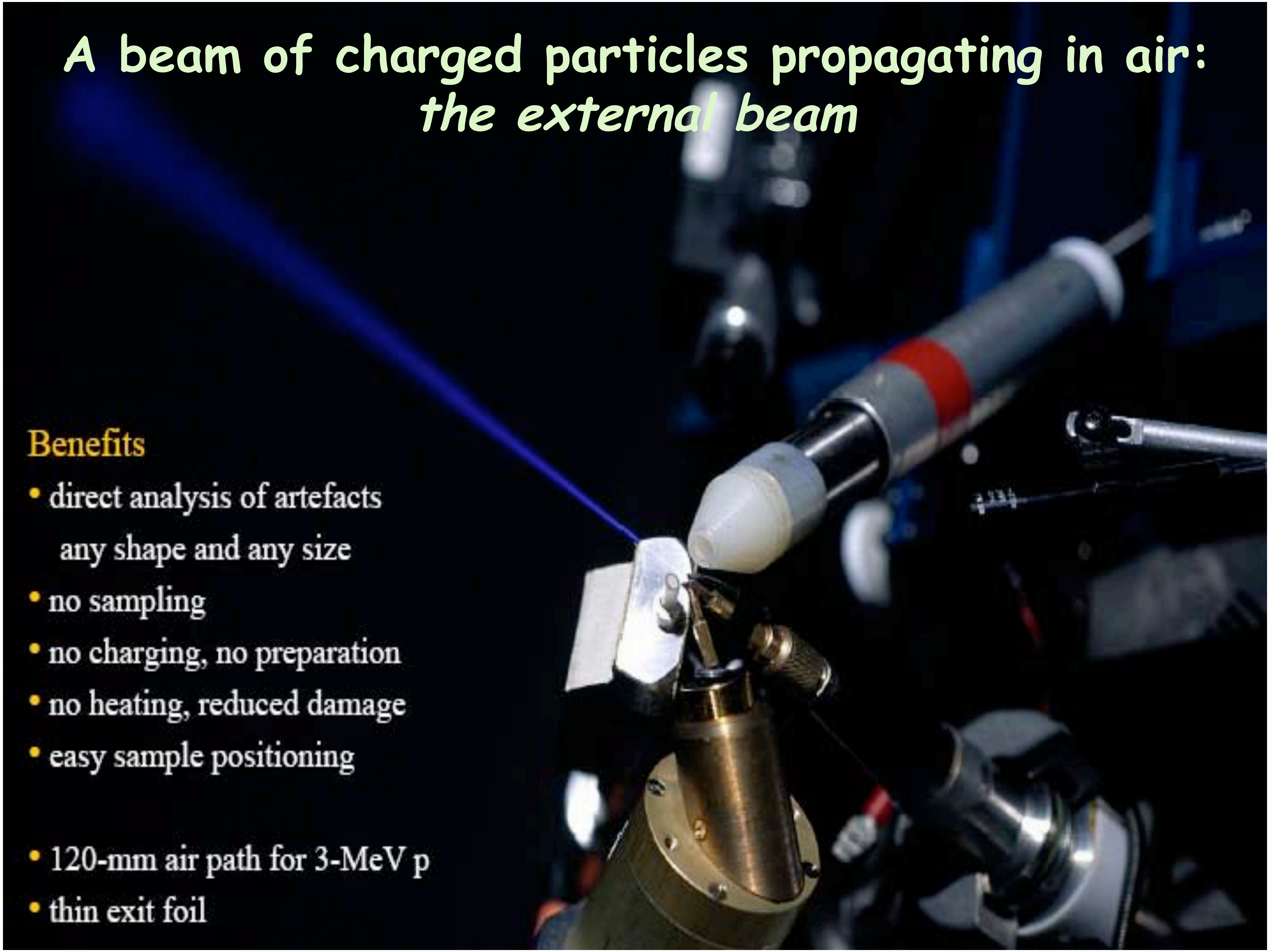
AGLAE

The high voltage generator

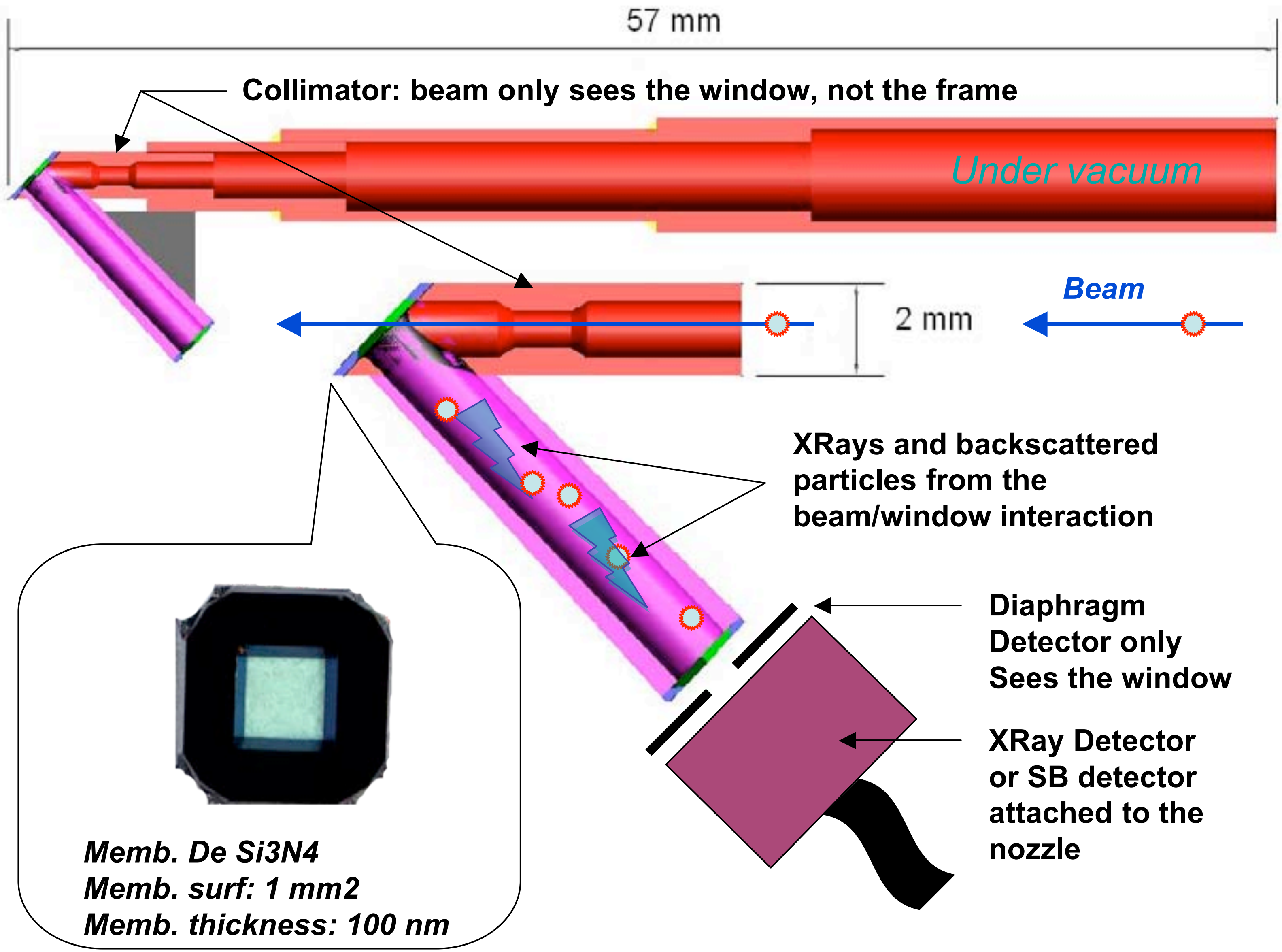
NEC machine (pelletron) :6SDH-2 tandem model
2 MV terminal voltage with a turbo pumped gas stripper



A beam of charged particles propagating in air: *the external beam*

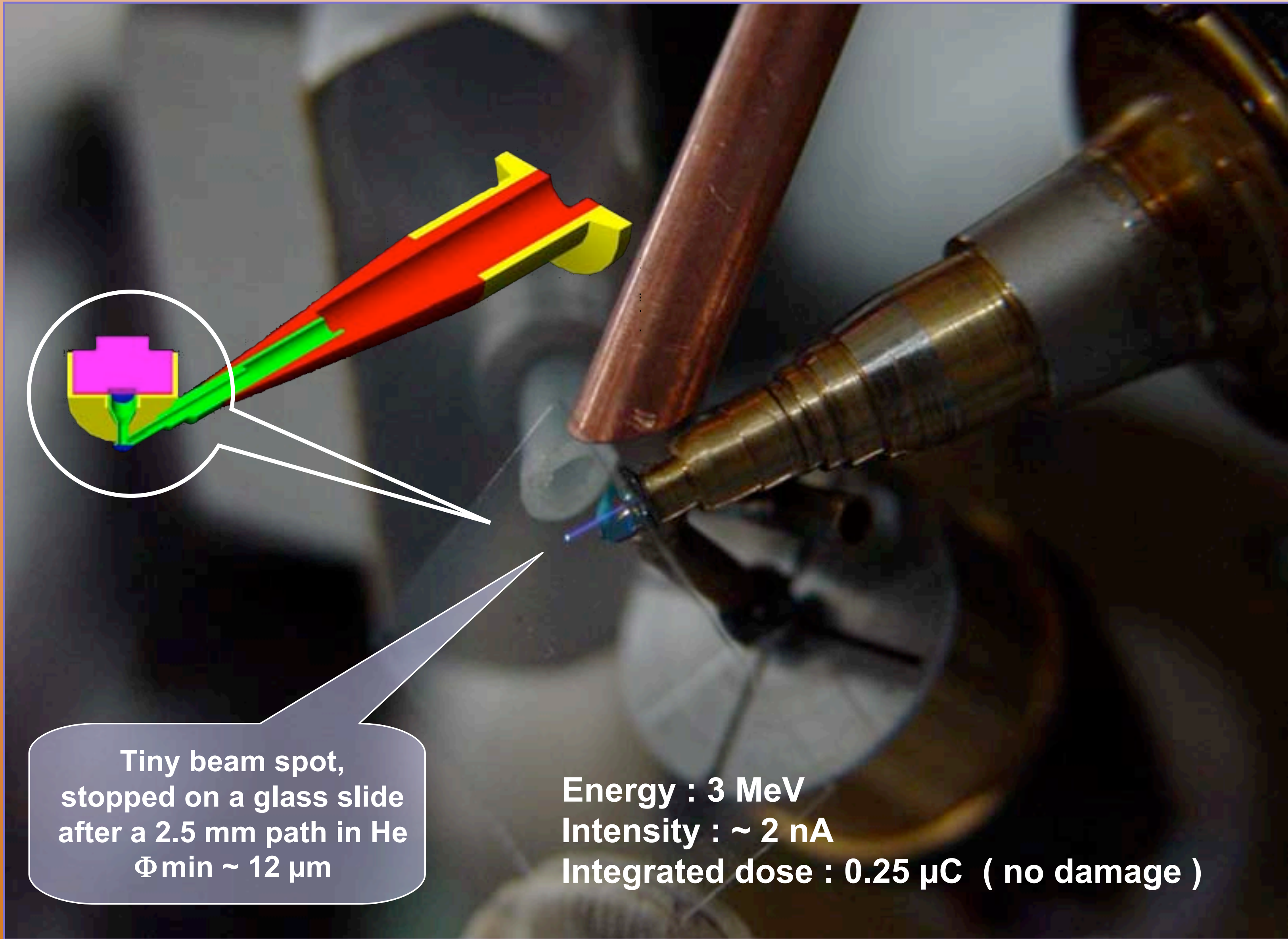


Detail of the extraction snout



beam extraction

beam extraction

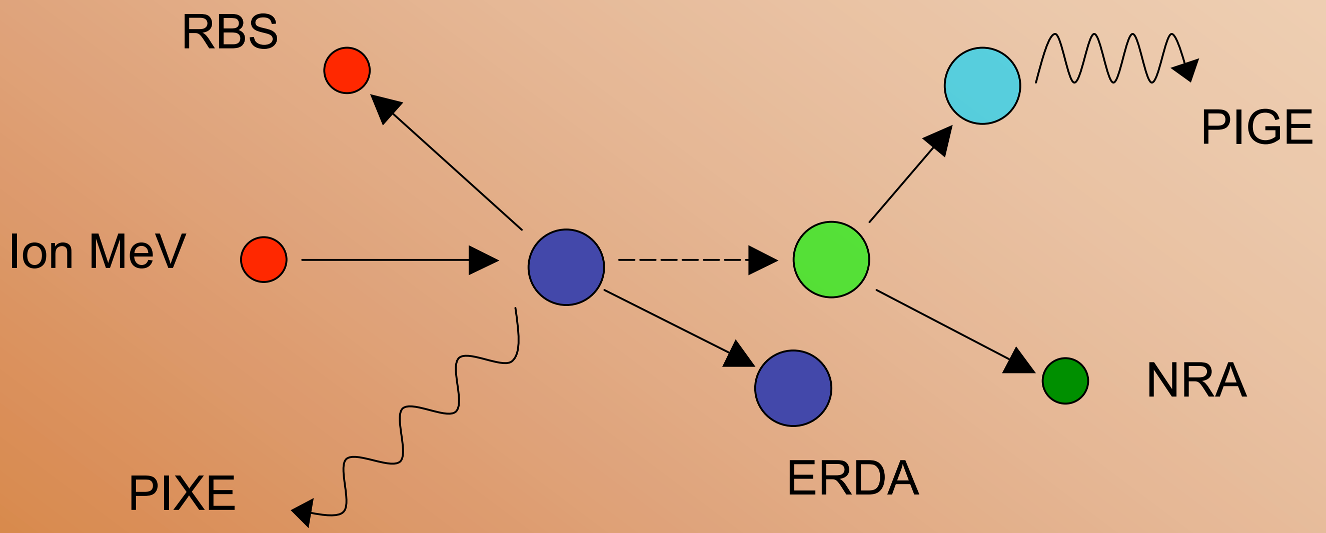


3 MeV proton µ-beam extracted to helium atmosphere through a silicon nitride membrane

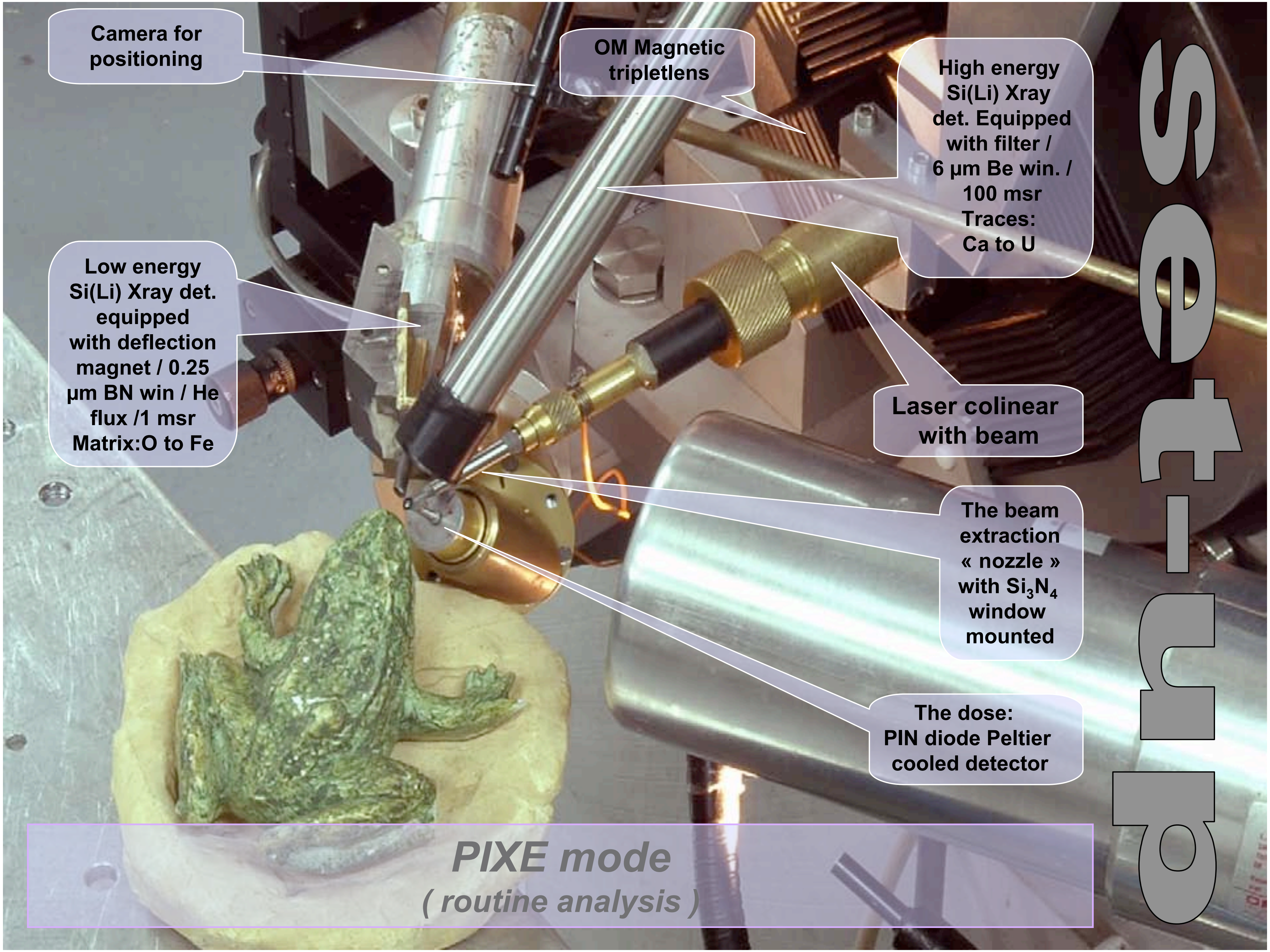
Memb. area: 1 mm2   Memb. thickness: 100 nm

Ion Beam Analysis

MeV ion beam based techniques constitute a powerful tool for the quantitative determination of the composition and structure of matter



Possibility of mapping with a spatial resolution of ~ 10 um


Camera for positioning
OM Magnetic tripletlens
High energy Si(Li) Xray det. Equipped with filter / 6 µm Be win. / 100 msr Traces: Ca to U
Low energy Si(Li) Xray det. equipped with deflection magnet / 0.25 µm BN win / He flux /1 msr Matrix:O to Fe
Laser colinear with beam
The beam extraction « nozzle » with Si_3N_4 window mounted
The dose: PIN diode Peltier cooled detector
set-up
PIXE mode
(routine analysis)

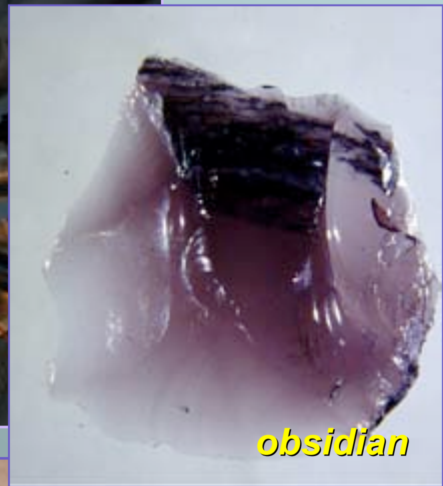
PIXE in art and archeology

PIXE is applied to the study of provenance and / or fabrication technique for major, minor and trace element analysis

(field of application)


drawings


Inks-illuminations


obsidian


alloys


gems


ceramics

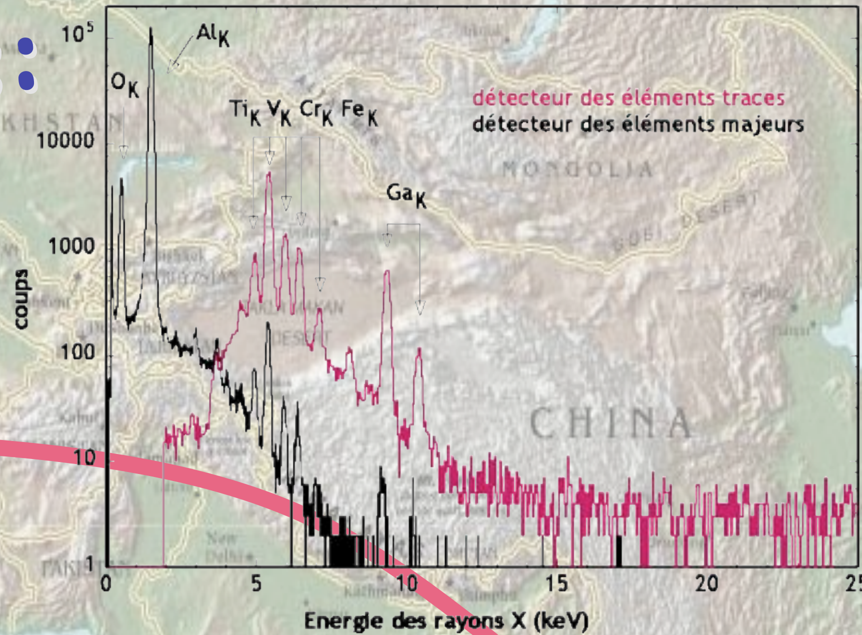

lustres

....

Provenance studies:

PIXE analysis of trace elements

(Th Calligaro, Ph Walter)

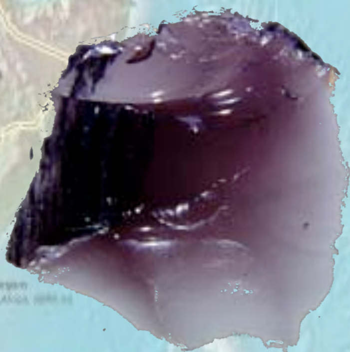


The method:

- We compare the object of interest with geological materials of the same nature *(sometimes old writings allow us to determine ancient deposits exploited by man)*
- The trace element content is currently used as a fingerprint in archaeology
- Statistical processing of data => sometimes allows us to conclude about provenance

Ishtar

fibules



Obsidian

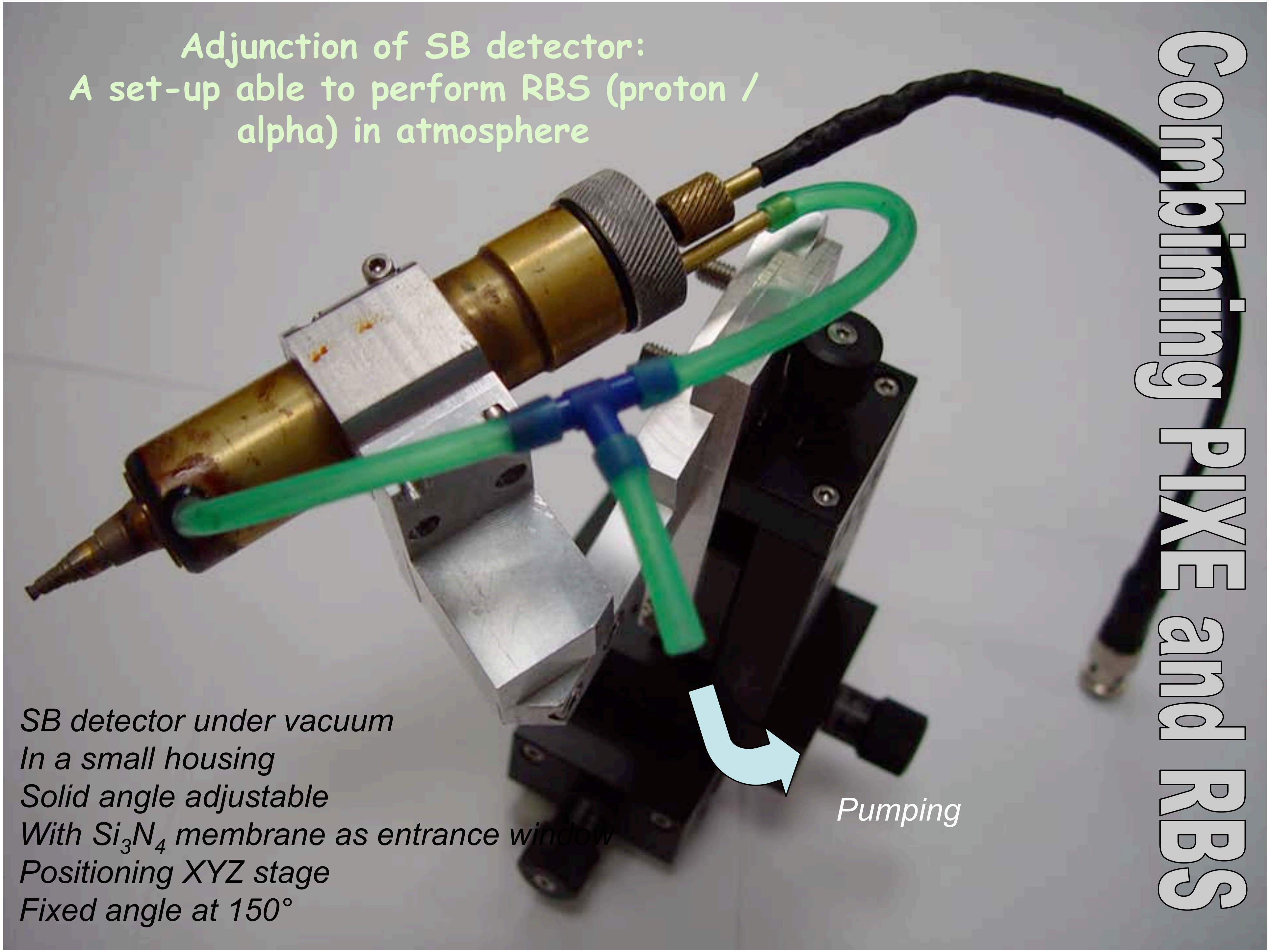
flints

gems


BABYLONE
du 14 mars au 2 juin 2008
> Flash version
> Html version

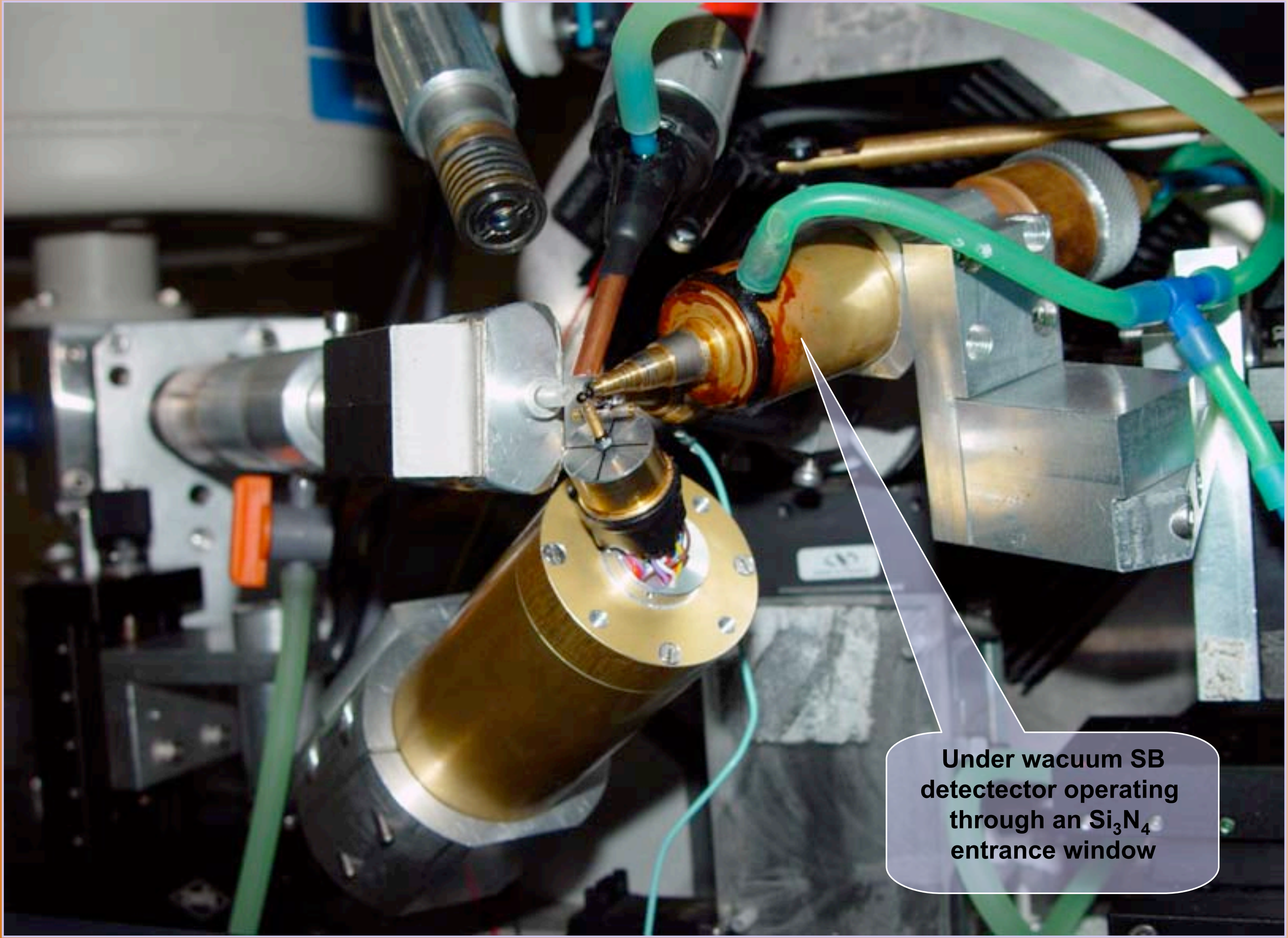
Combining PIXE and RBS

Adjunction of SB detector: A set-up able to perform RBS (proton / alpha) in atmosphere



SB detector under vacuum
In a small housing
Solid angle adjustable
With Si_3N_4 membrane as entrance window
Positioning XYZ stage
Fixed angle at 150°

set-up



Combined PIXE-RBS protons and/or alphas

(old version)

Sequential PIXE/RBS with successive beams of protons and alpha particles:

The analysis of lustered ceramics.

Experiments on ceramics

Study of lustered ceramics from Seville. ***A. Polverinos (University Seville, Spain).*** ***Lustered sherds from a Triana workshop, 15th century.***

Study of materials and techniques of lustered majolicas. ***G. Padeletti (ISMN-CNR, Italy) .*** ***Lustre from Gubbio, Italy*** **, Mastro Giorgio 16th century.**

Combination of PIXE (3 MeV p) and RBS (3 MeV He ions) to measure composition and thickness of glaze and lustre

What is lustre ?

- Decoration on top of the glaze with a metallic aspect
- It can have different colours
- It is made of a layer of metallic (Cu, Ag) nano particles

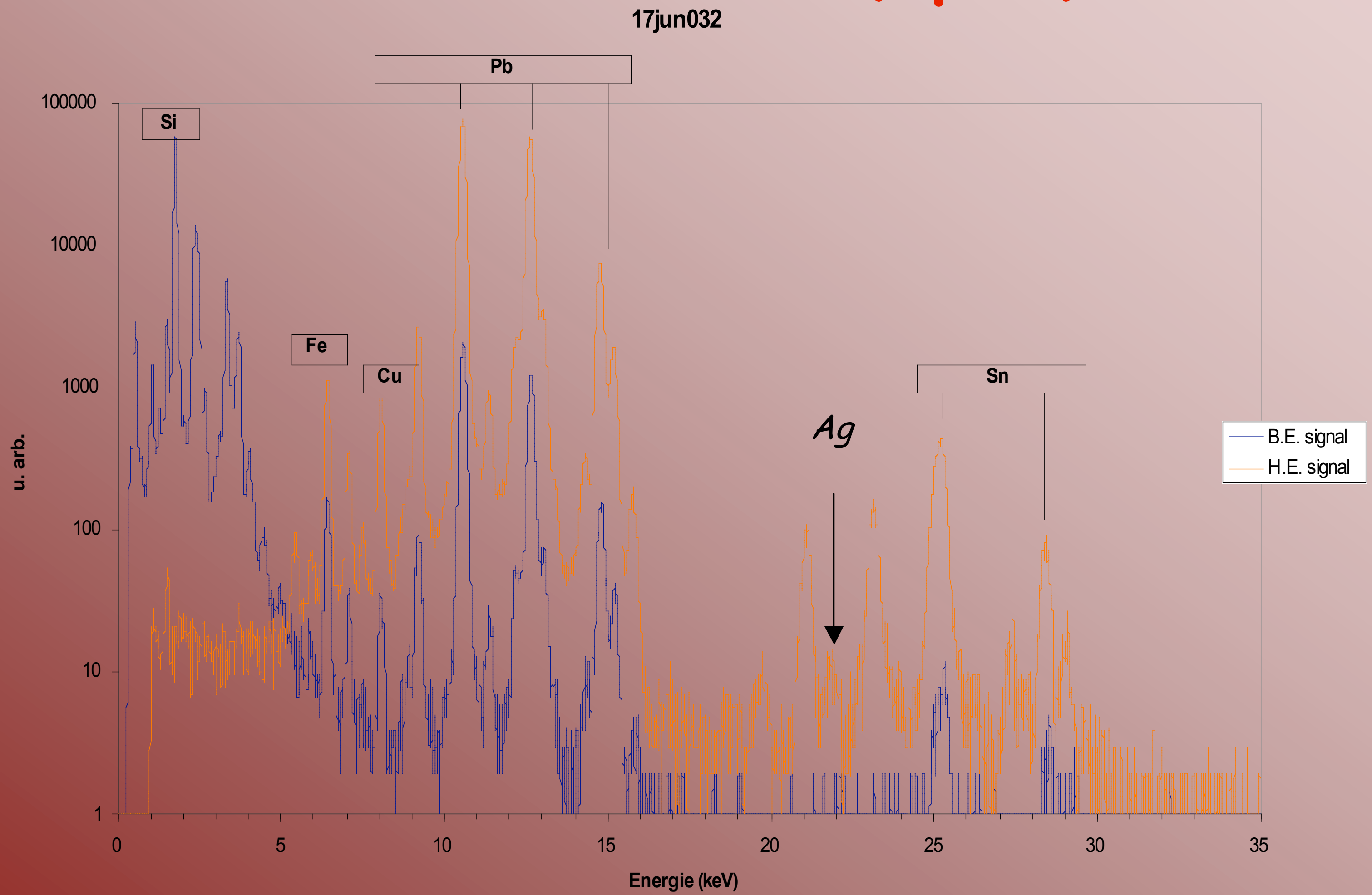
Lustre layer of Cu or Ag nano particles

Glaze (SnO_2 = opacity pigments)

Ceramic body

"metal salts* mixed with *a paste of clay are applied on top of a glazed object – the pottery is then fired again in a reducing atmosphere"

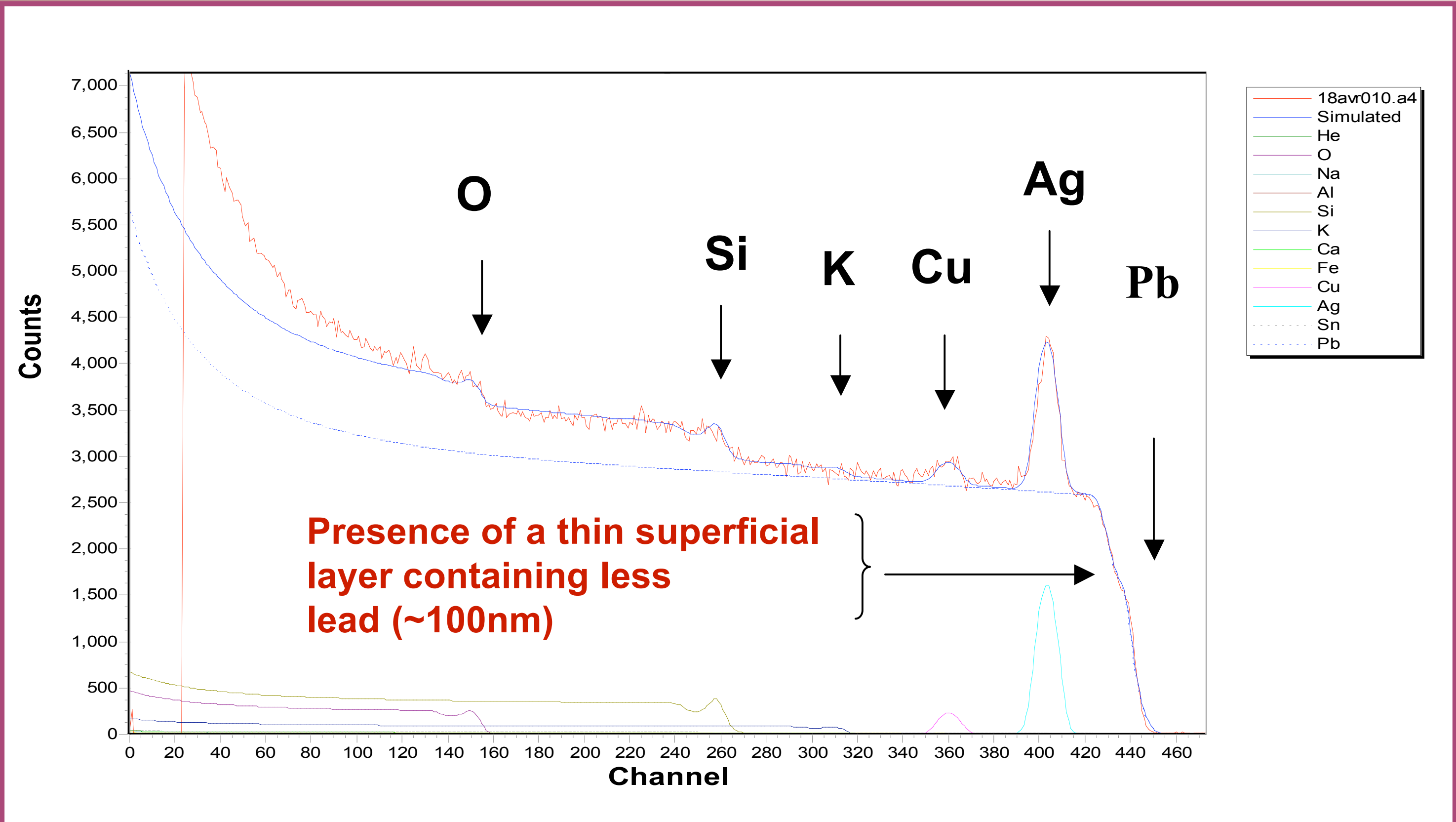
Typical proton PIXE spectrum from lustered ceramics (Spain)



-The glaze contains approximately 30% of PbO and 10% of SnO_2..

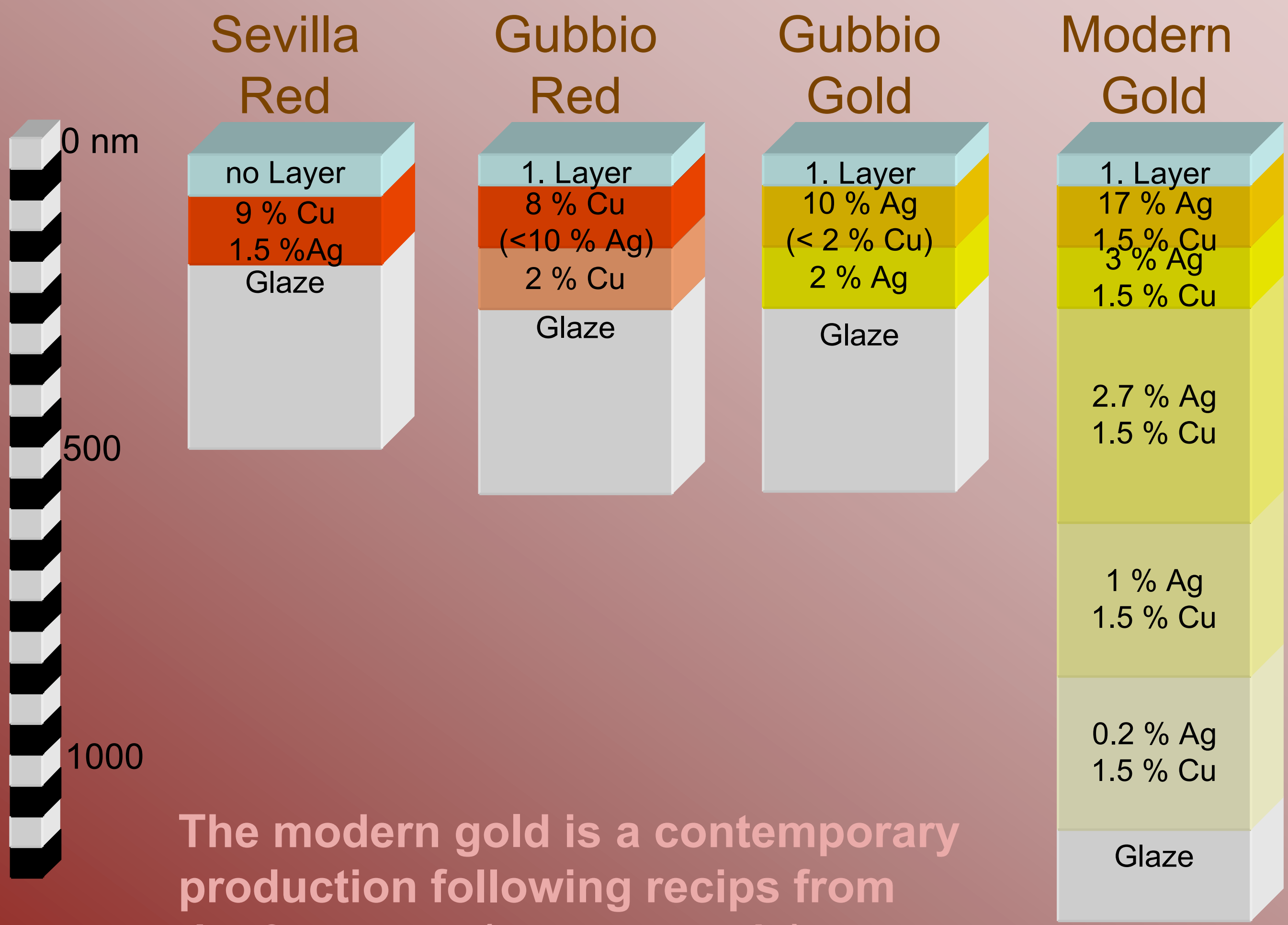
-Presence of Cu and some Ag responsible for red lustre.

Thickness evaluation from alpha RBS Spectra (Italy)



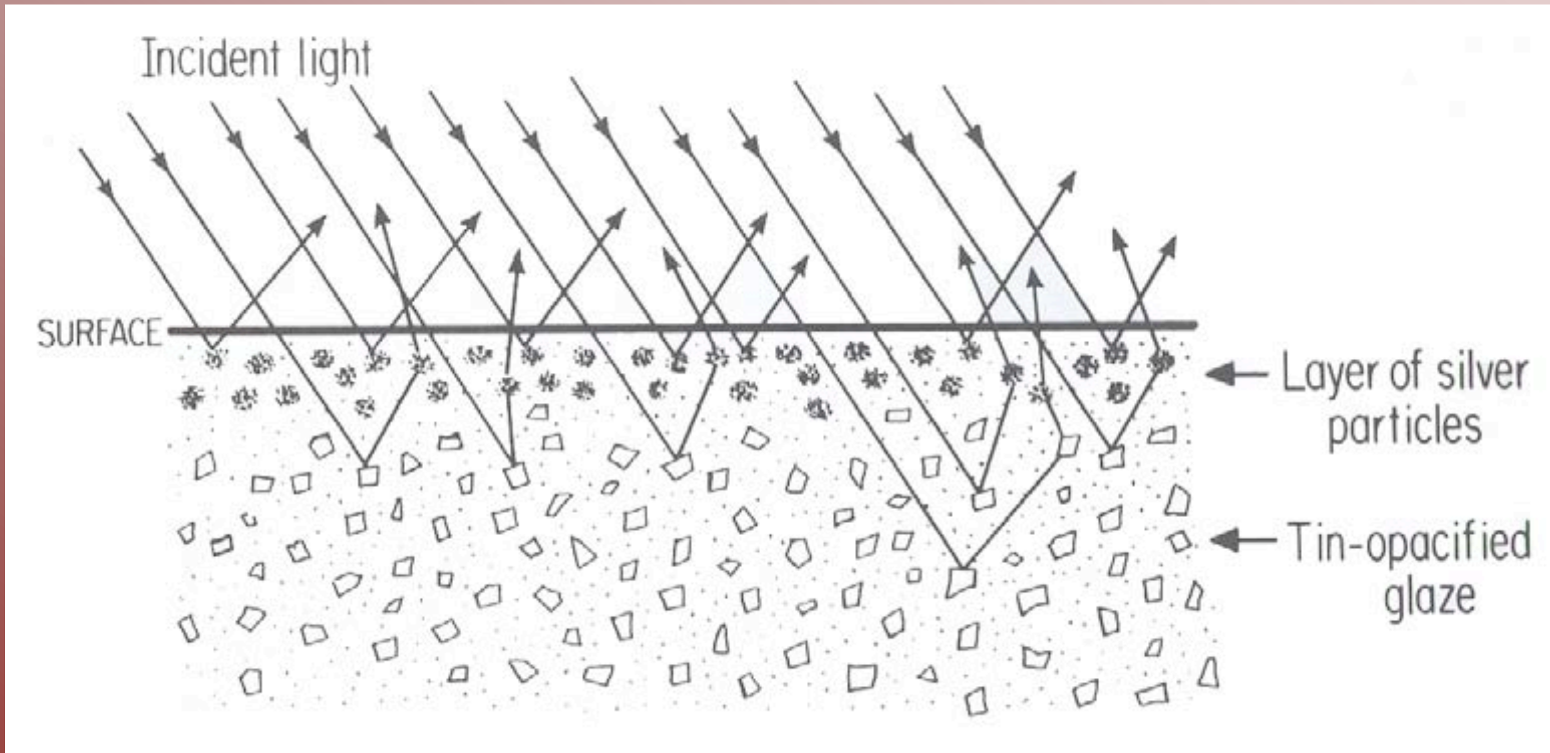
	O	Na	Al	Si	K	Ca	Cu	Ag	Pb	Thickness	
	at%	at%	at%	at%	at%	at%	at%	at%	at%	10^{15} at/cm?	nm
1. Layer	62.0	1.7	1.5	30.1	3.3	0.6	0.0	0.0	0.5	550	77
Luster	54.8	0.0	0.0	19.4	3.0	0.6	5.0	13.0	4.2	650	92
Glaze (PIXE)	62.0	1.7	1.5	25.1	3.3	0.6	0.0	0.0	5.5	inf.	inf.

RBS Lustre layer models:



The modern gold is a contemporary production following recips from the 9 century (mesopotamia).

Metallic reflection from the surface layer; light back-scattered from tin-opacified glaze.



From Kingery W.D. and Vandiver P.B. 1986

Main conclusions on lustres

- RBS provides the detailed description of the sub-surface region.
- RBS is a non destructif methode.
- Detailed structre of lustre is related to its origine
- Lustre effect is produced by a thin glaze (100-200 nm) layer containing Cu and Ag.
- Lustre layer from Spain is thinner and simpler than Italian one.
- Both technologies (Spain / Italy) seem to depart from original Islamic technology .

Simultaneous PIXE/RBS with a single shot of 3 MeV α particles:

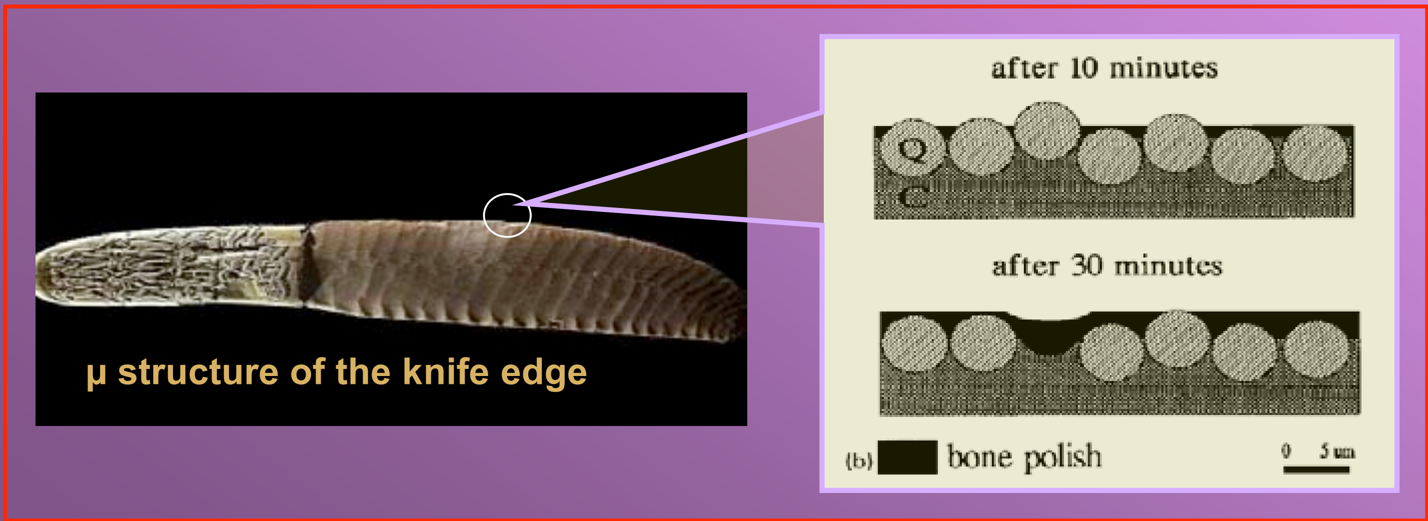
Usewear of tools.

Usewear on stone tools: traceology

- A discipline used to determine the function of stone tools. Our study concerns flint, which was the material of choice of prehistoric man.

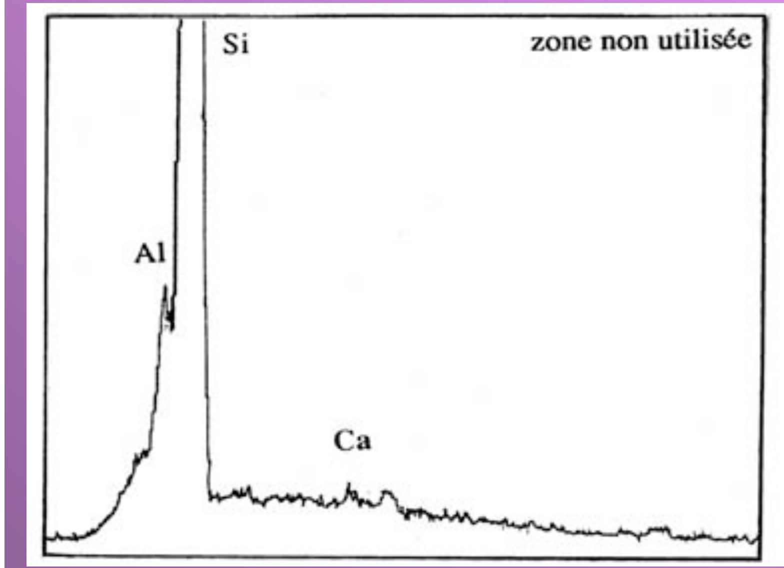
- If the tool is used for a relatively long period, a significant layer of residue can build up on the knife edge.

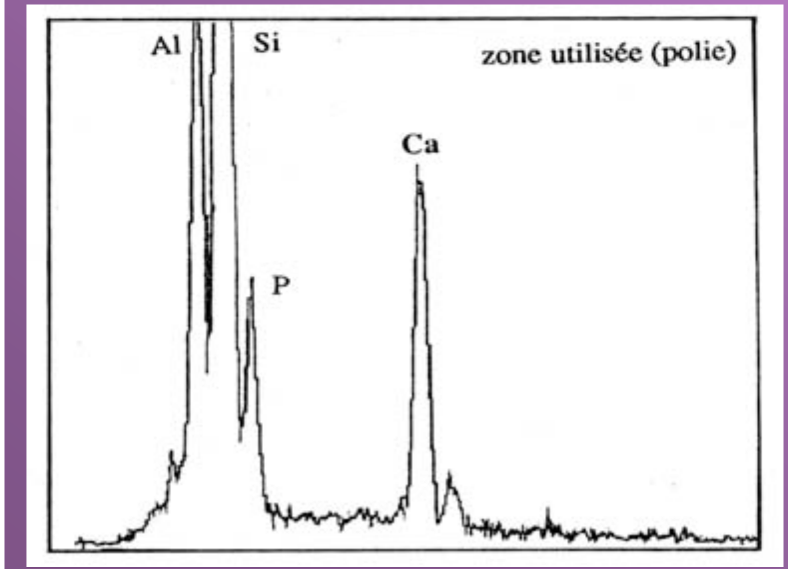
- Analysis of this layer can thus reveal the presence of elements that can identify the worked material. Thus, the presence of calcium and phosphorus indicates that the tool was used on animal material such as bone or horn.



Analysis of the knife edge

using alpha PIXE at 3 MeV

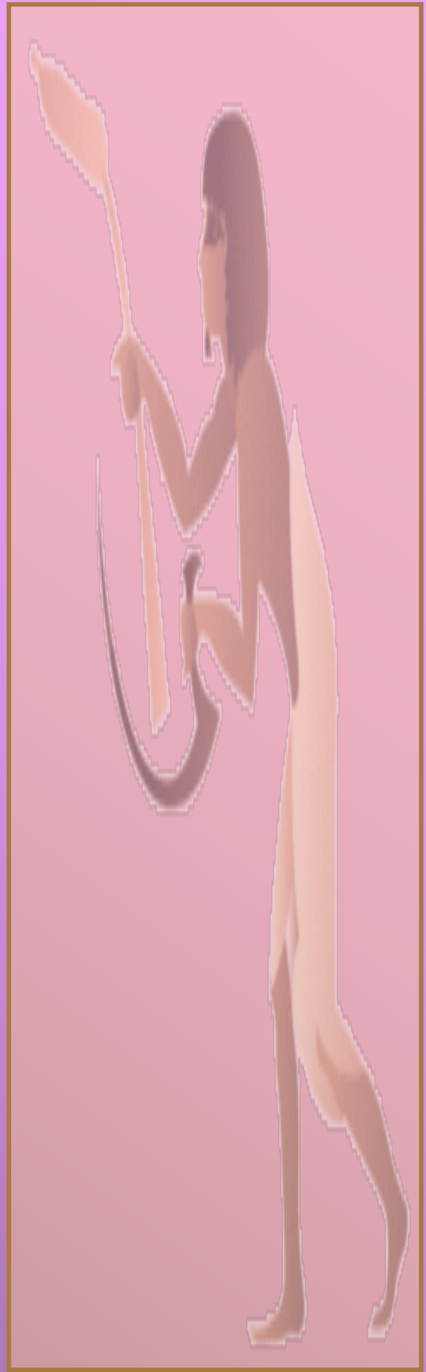




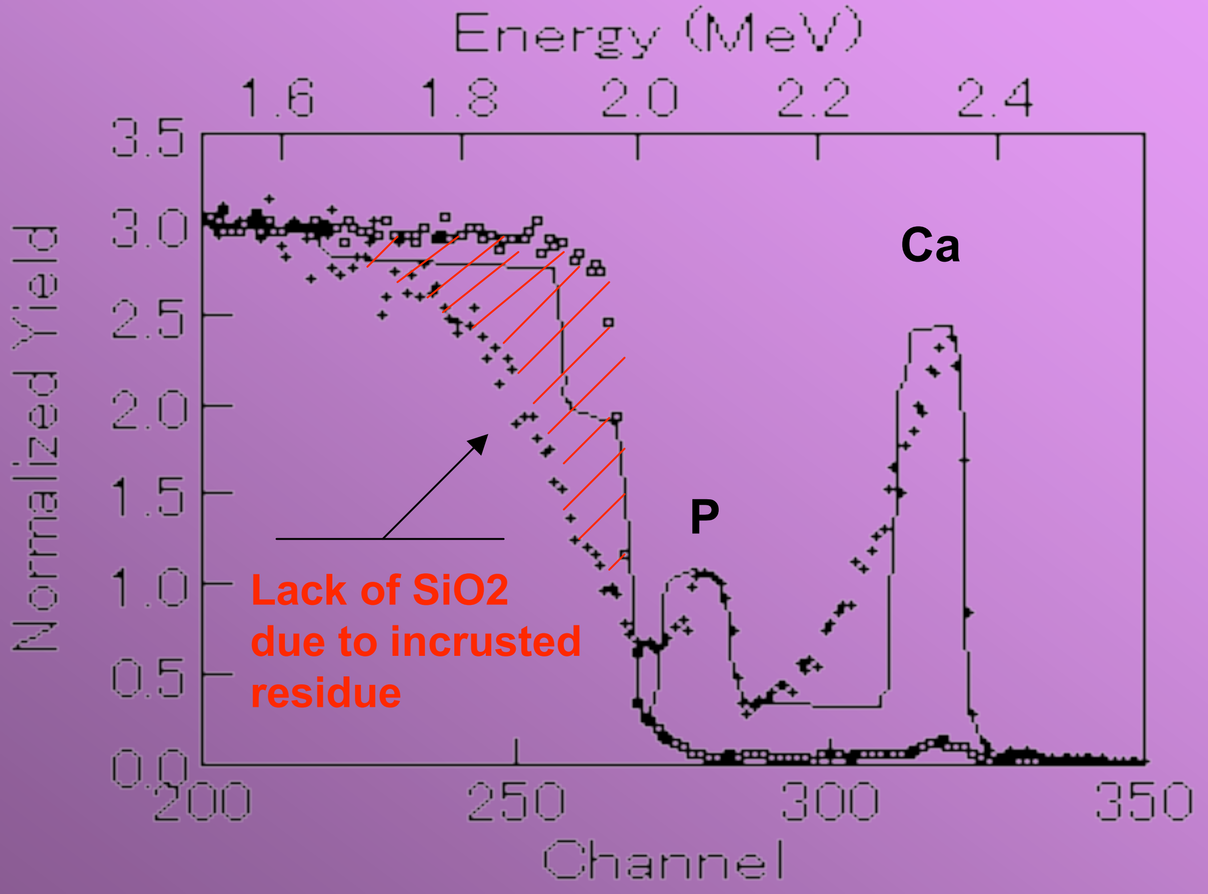
3 Mev alpha µ-beam (D=12 µm), was well adapted to the quantification of light elements …

Flint without and with polish.

Bone components (Ca and P) are found on the edge of the knife used for cutting bones.

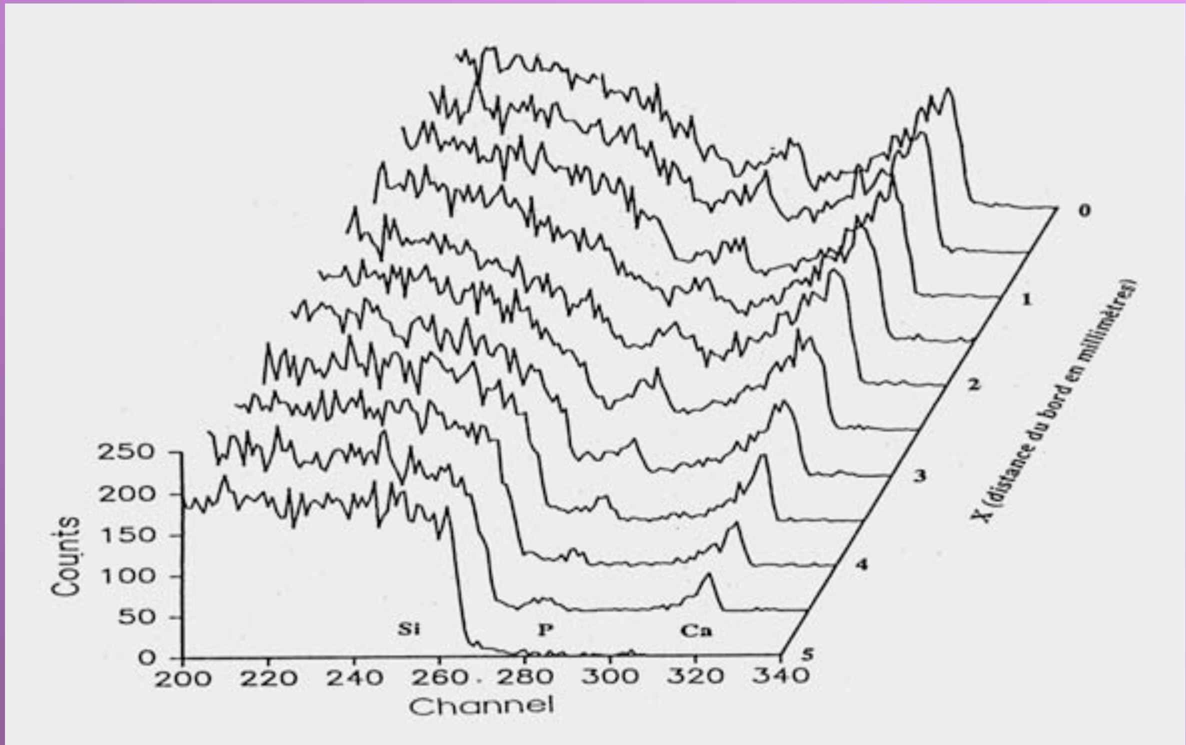


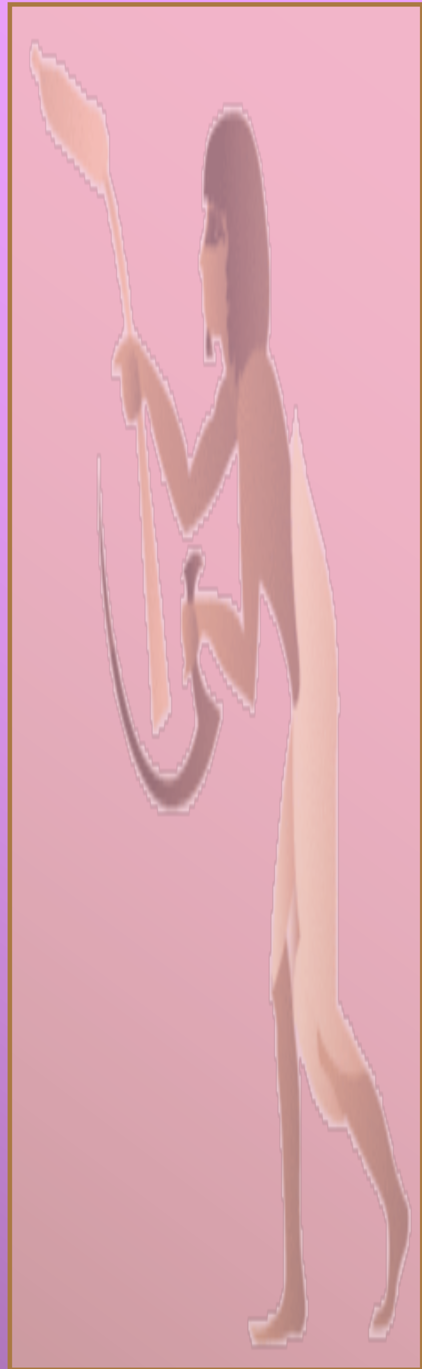
RBS analysis of the knife edge.



RBS spectrum of a tool with and without polish.
The tool was used to work fresh bone during 30 mn.
The simulation gives a 400 nm thick layer composed of 80% of apatite and 20% of calcium carbonate.

RBS profile on a knife edge





-Lateral scan of a bone polish. *(The sample was scanned in steps of 500 µm with a 3 MeV alpha beam)*
-We also measured the carbon profile on the knife edge using the nuclear reaction 12C(d,p)13C.
-The analysis of Egyptian Predynastic ceremonial knives showed that they have been used to cut plants like cereals …

Simultaneous PIXE/RBS with a single shot of 6 MeV α particles:

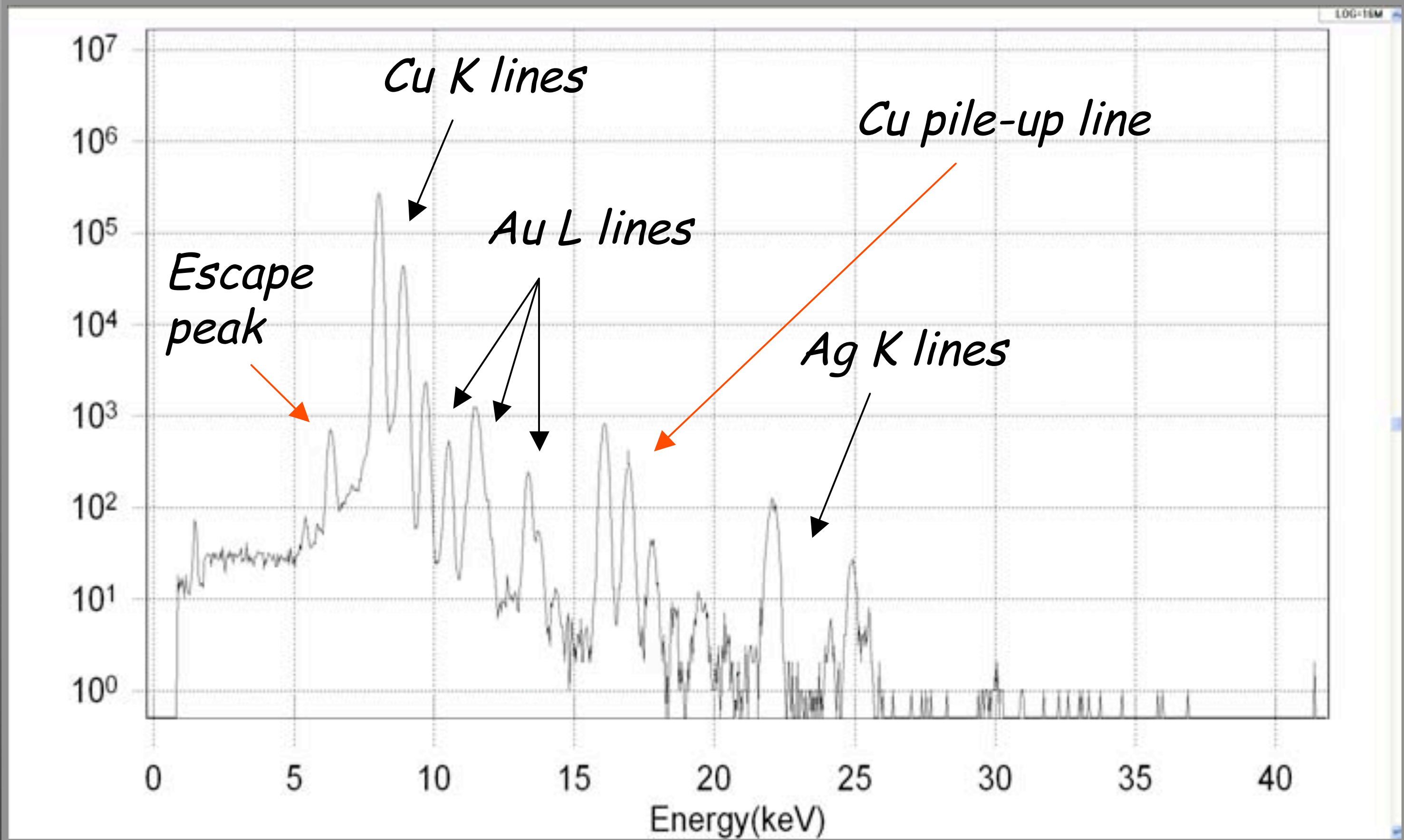
The analysis of a patina.

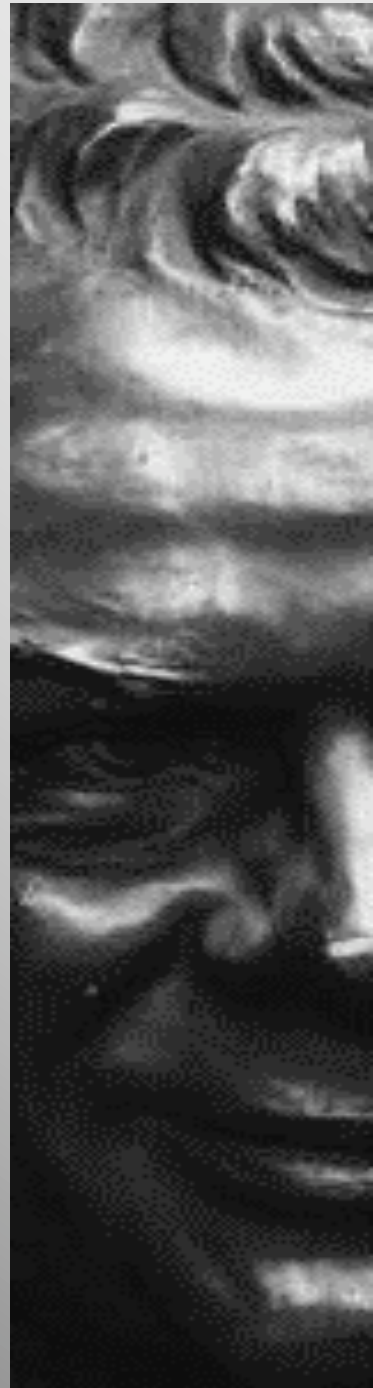
Combined PIXE / RBS on the patina of a drop dispenser

Japanese, shakudo decorated, drop dispenser (19 century)
first known black bronzes (patina): Egypt 2500 BC
first Japanese Shakudo (patina): 14 century

Due to their well adapted range, 6 MeV α particles are used to simultaneously profile (RBS) and quantify (PIXE) the artificial patina.

Combined PIXE / RBS on the patina of a drop dispenser

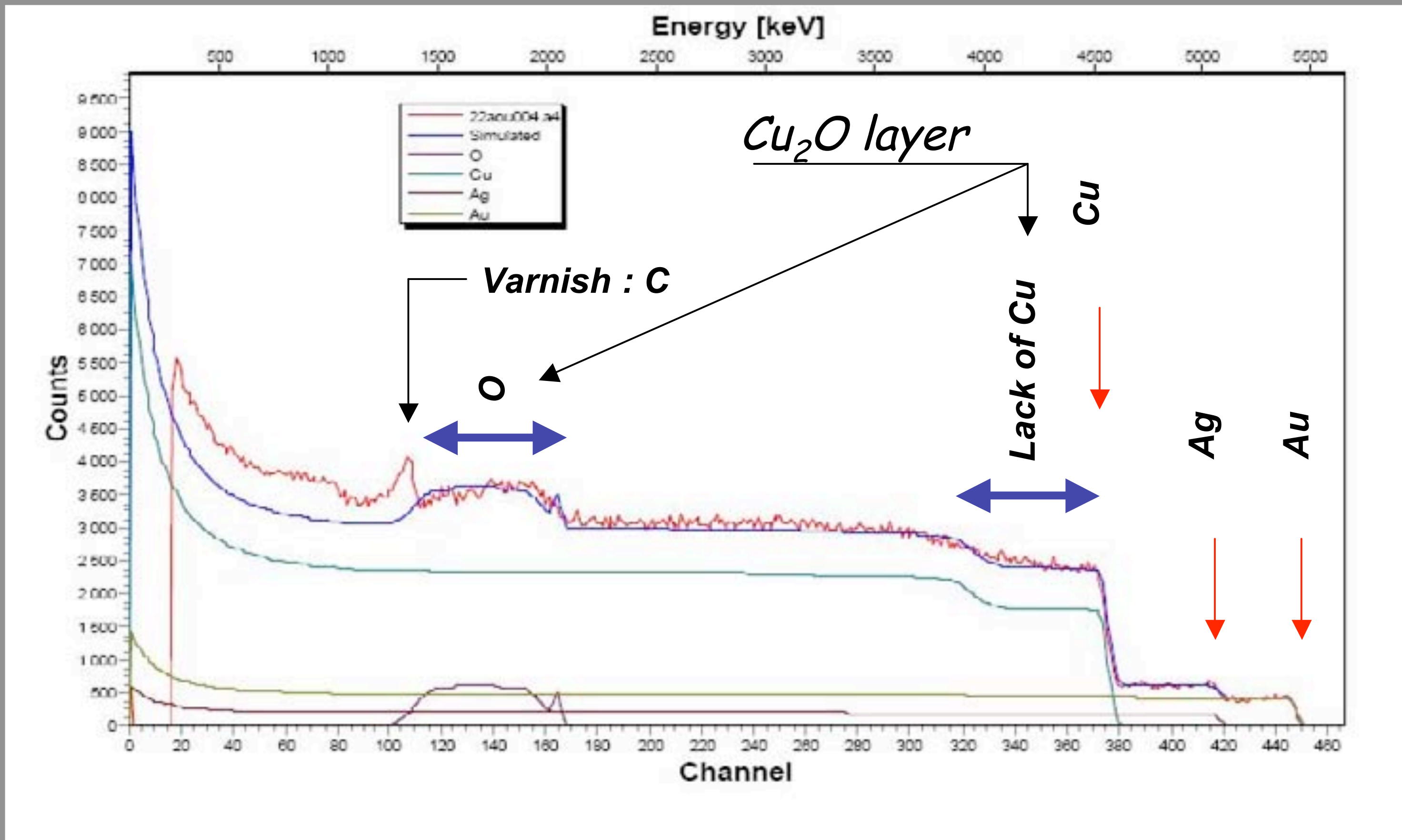




6 MeV α particle PIXE shows Cu content with a few % of Ag and Au

6 MeV α particles probe mostly the patina as well in Pixe mode as in RBS mode, 3 MeV protons probe mostly the bulk material.

Combined PIXE / RBS on the patina of a drop dispenser

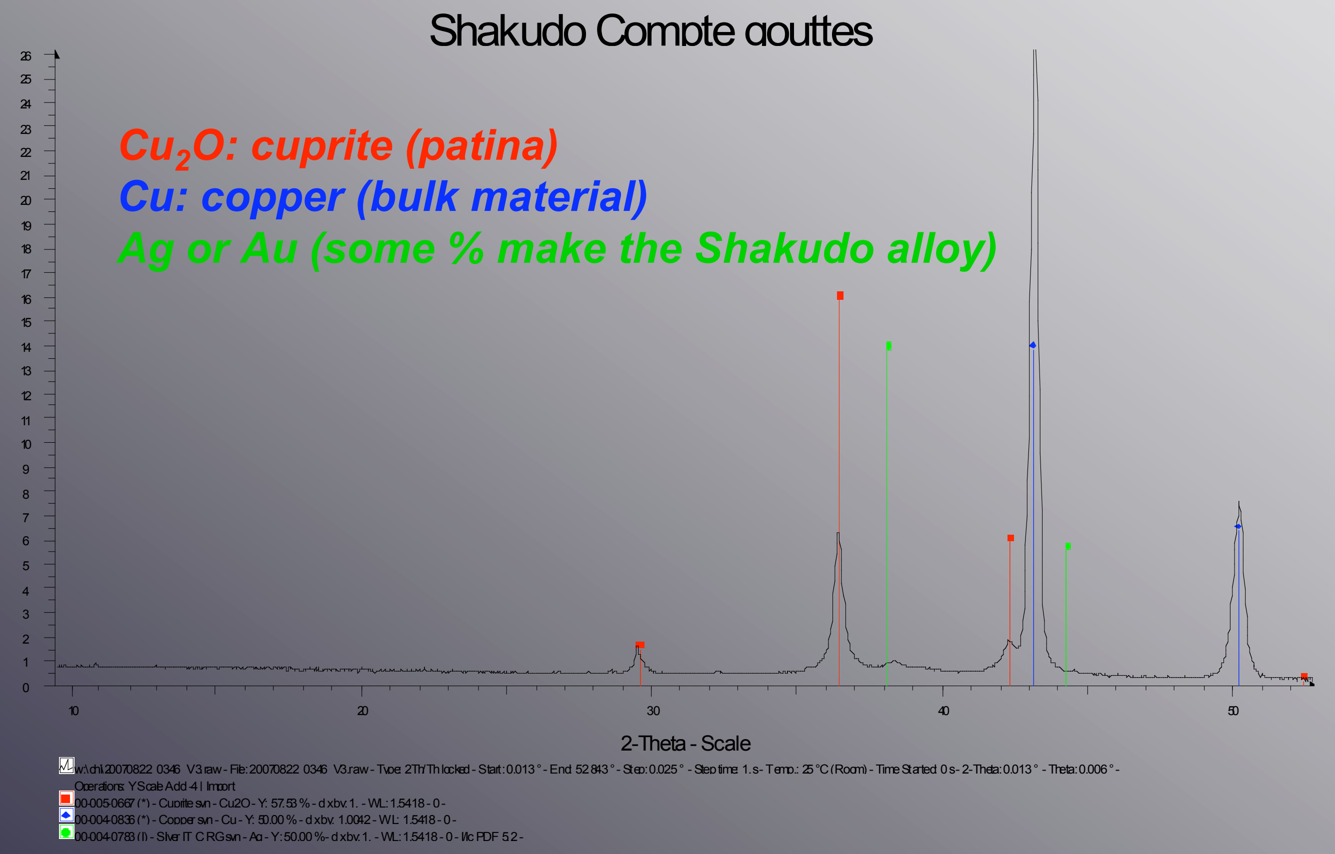


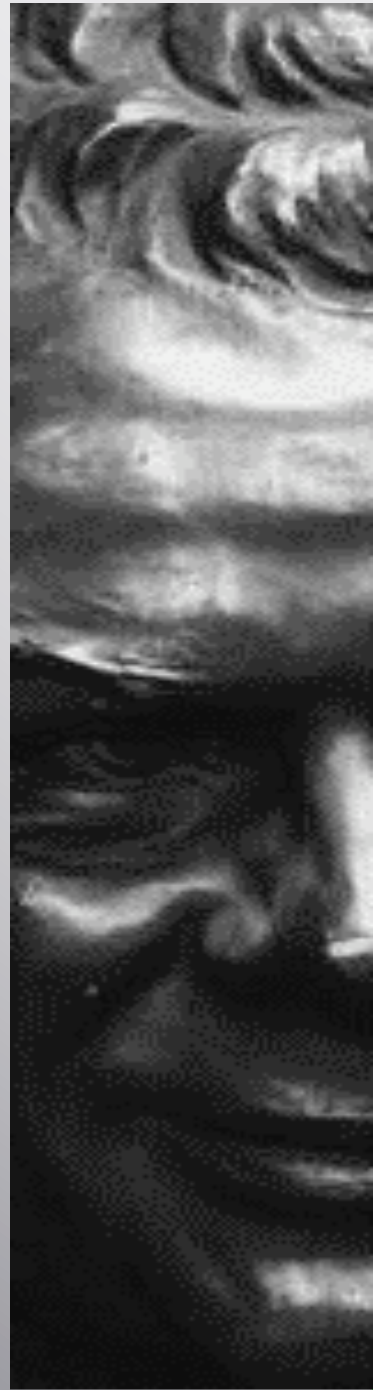
6 MeV α particle RBS shows Au , Ag , Cu and O content.

6 MeV α particles probe well the patina and show the altered copper surface (Cu_2O)

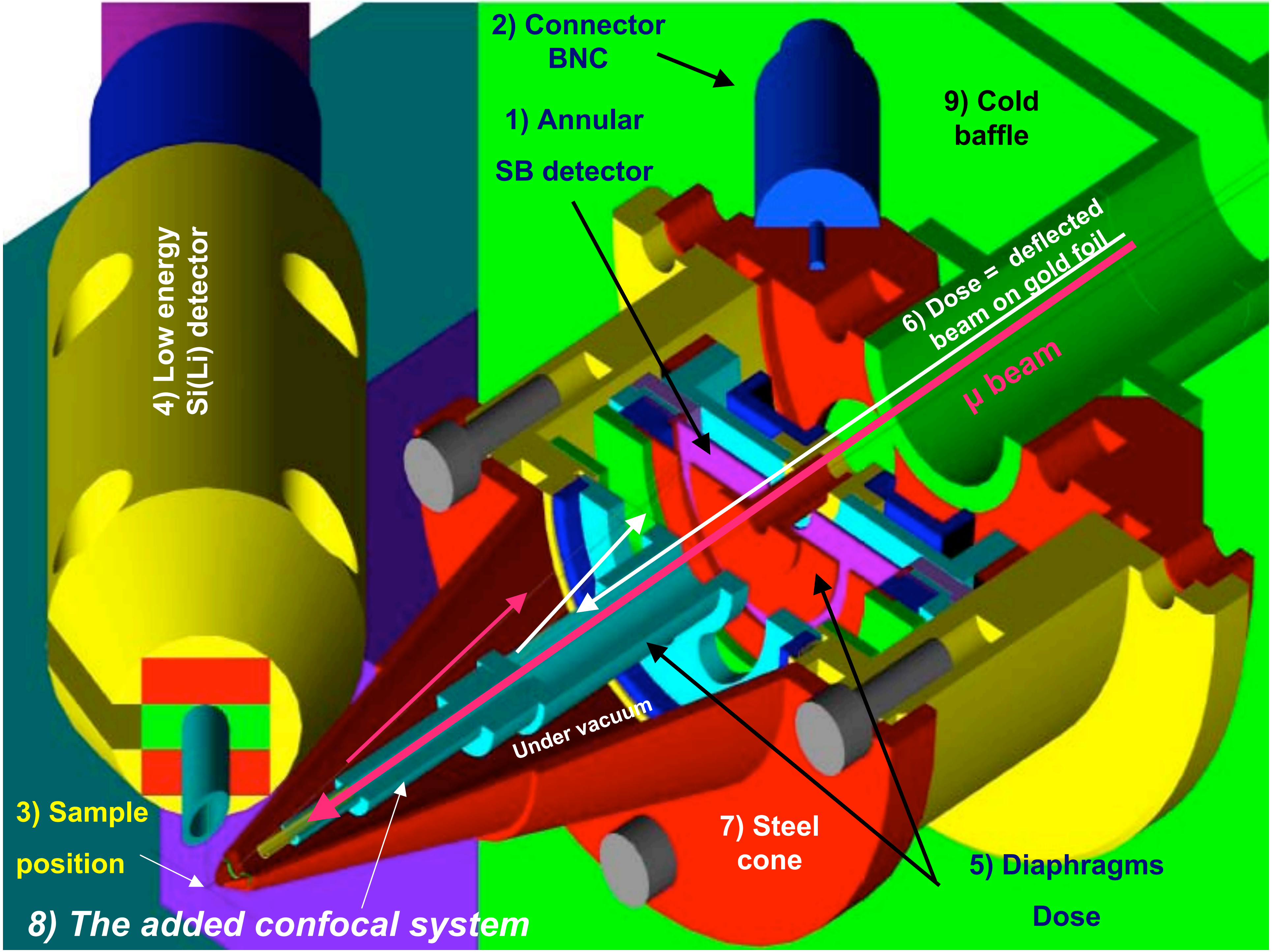
Diffraction diagram of the shakudo patina

Cu_2O is red but the presence in this oxide of some Au and or Ag (solution or nano crystals) changes the color to black ! => signature of a shakudo.



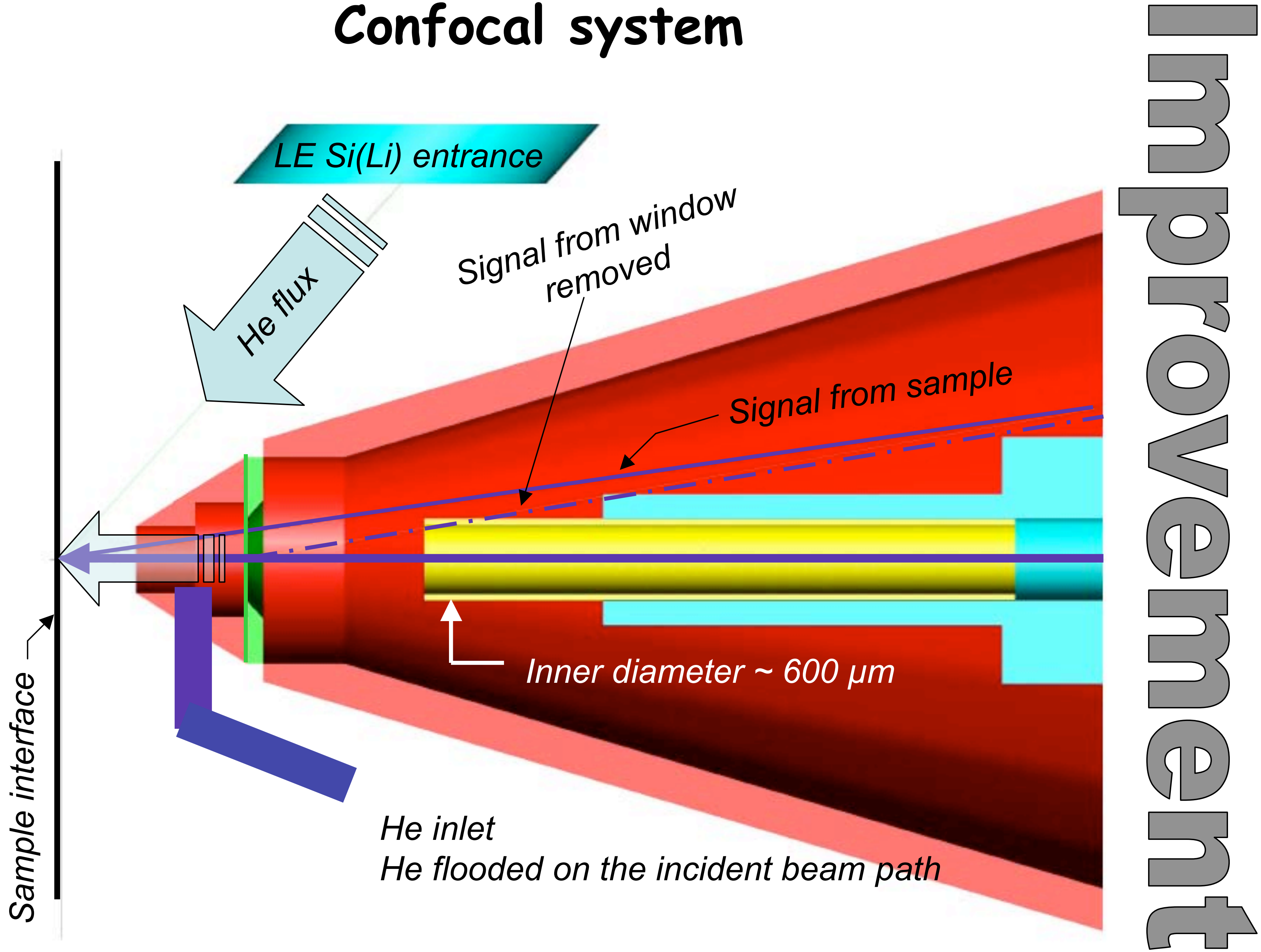


Technical improvements

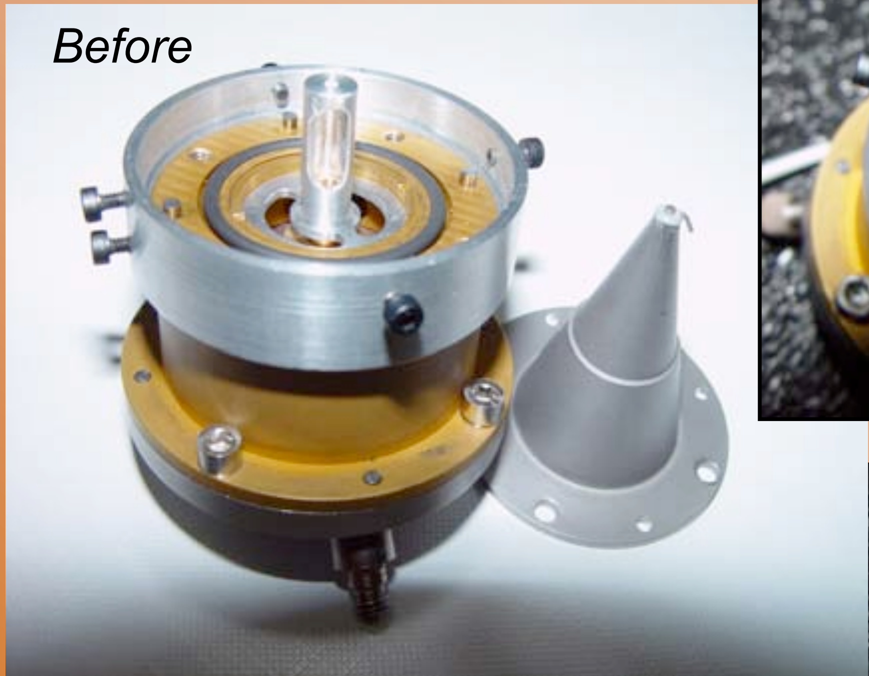


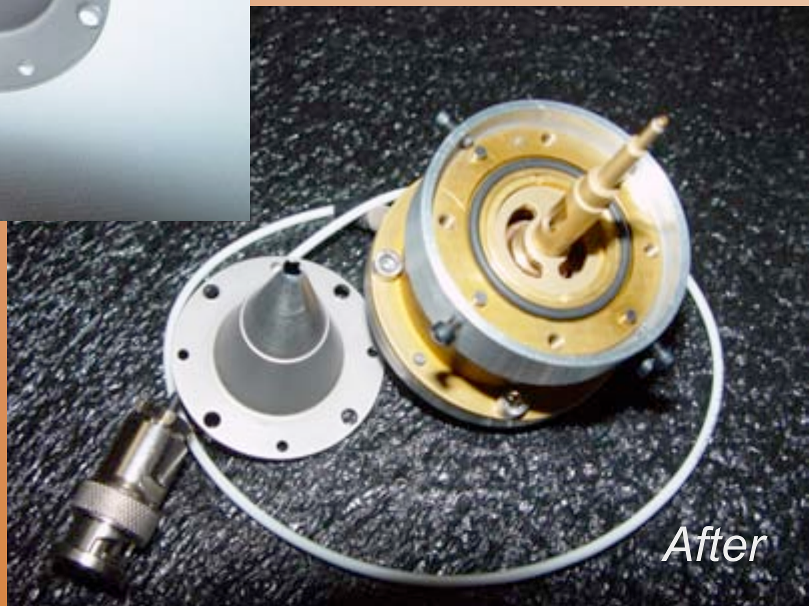
2) Connector BNC
1) Annular SB detector
9) Cold baffle
4) Low energy Si(Li) detector
6) Dose = deflected beam on gold foil
μ beam
Under vacuum
3) Sample position
7) Steel cone
5) Diaphragms Dose
8) The added confocal system

Confocal system



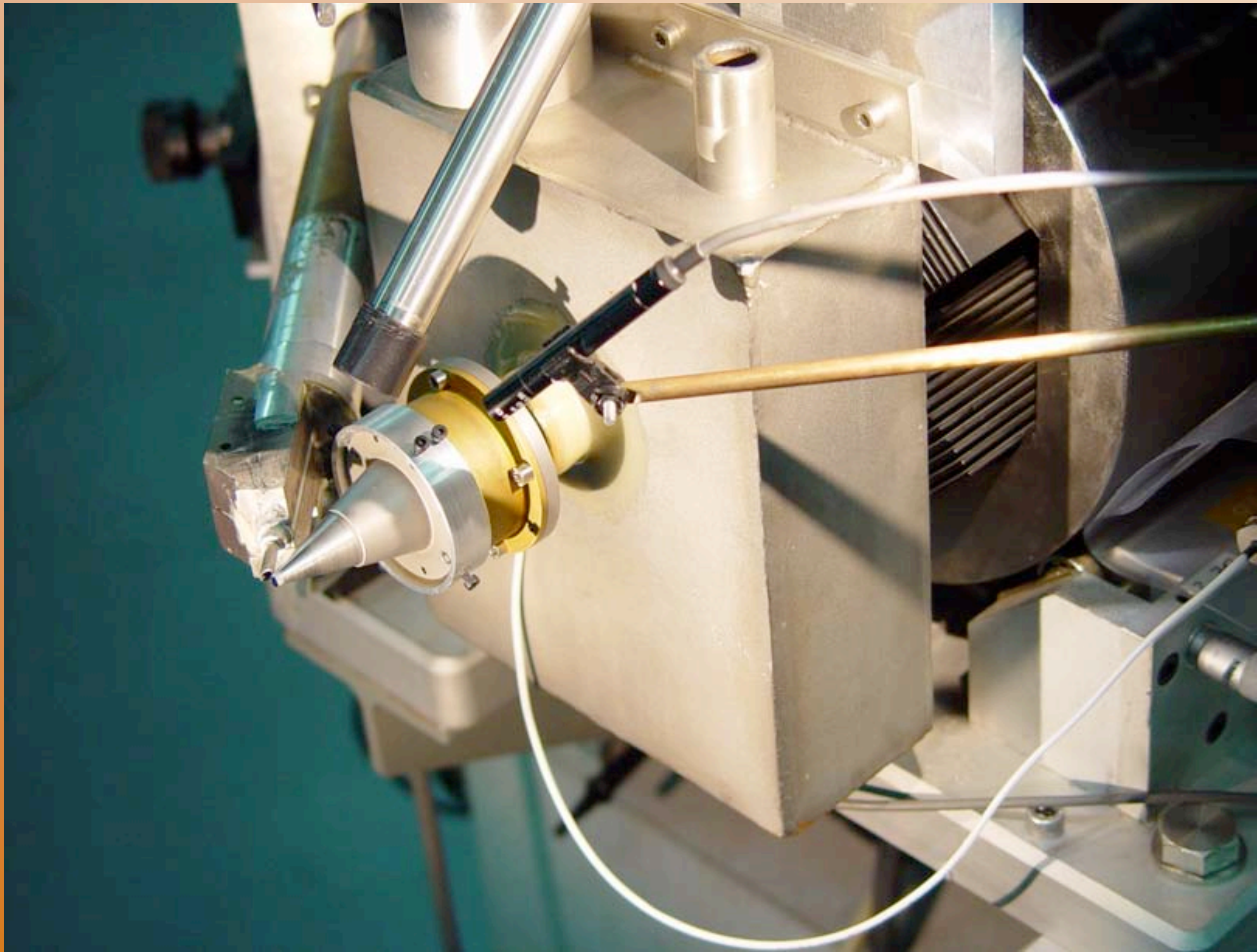
Technical details





Improvement

Improvment



Combined PIXE-RBS protons and/or alphas

Conclusion and prospects

-The development of a sophisticated external beam setup has permitted to implement simultaneously or sequentially PIXE(PIGE) and RBS.

-The setup is currently under improvement to permit simultaneous NRA measurement (depth profiles of light elements via d or 3He induced nuclear reactions) in addition to PIXE and RBS (by using a sectorised annular detector).

- 3He PIXE should even be more advantageous than 4He PIXE.

-The coupling of these techniques provides a wealth of information on cultural heritage objects, not easily attainable with any other single method.

-Although XRF (specially on synchrotron radiation facilities) can be subsituted to PIXE for trace element analysis, PIXE (and thus the whole set of IBA techniques) remains attractive because it can be complemented by PIGE for the measurements of light elements in the bulk material and RBS+NRA for depth profiling.


Thank you for your attention …