Accelerators in art and archaeology

Jean-Claude Dran

Centre de recherche et de restauration des Musées de France CNRS UMR 171 Paris

## Outline

#### ♦ Introduction

- Overview of scientific methods of examination and analysis of art works
- ♦ Ion beam analysis: physical principles, analytical capability and relevance to museum objects
- ◆ The IBA facility of the Louvre as an example
- ♦ Main applications
- ◆ <sup>14</sup>C dating with Accelerator Mass Spectrometry
- Conclusion and prospects

#### Scientific methods of examination

Visible light: photography optical microscopy
 Infrared: reflectography
 Ultraviolet: fluorescence
 Scanning electron microscope
 X-radiography, emissiography, betagraphy

## Scientific methods of analysis

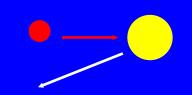
♦ Techniques of elemental analysis X-ray microanalysis coupled with SEM X-ray fluorescence Atomic emission spectrometry ICP-AES **IBA techniques (PIXE, RBS, NRA, PIGE)** ◆ Techniques of structural and molecular analysis X-ray diffraction Gas chromatography GCMS IR spectrometry Raman spectrometry ♦ Dating techniques <sup>14</sup>C radioactive counting and AMS **Thermoluminescence** 

4

## Physical principles of accelerator-based analytical techniques (IBA)

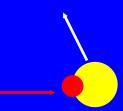
- $\bullet$ Interaction of light ions p, d,  $\alpha$  (energy ~MeV) with materials constituent atoms
- Energy of interaction product identifies the element (qualitative analysis)
- Signal intensity --> concentration (quantitative analysis)
   PIXE RBS NRA
- Emission of a characteristic X-ray

Ejection of an inner-shell electron



Backscattered ion

Secondary ion gamma ray



## Specificity of IBA techniques

♦ quantitative

multielemental including light elements

- non-destructive
- ♦ in-situ analysis with external beam without sampling
- ♦ high sensitivity (PIXE)
- ♦ possibility to combine several techniques
- ♦ concentration profiles (RBS, NRA)
- ◆ possibility of micro-beam for micro-mapping
- surface analysis (up to 15-20  $\mu$ m)
- ♦ no information on chemical state
- ♦ problems with insulators

#### The IBA facility of the Louvre

- 2 MV tandem Pelletron 6SDH-2 NEC
- Working voltage 0.35-2.15 MV
- Ion sources (negative):
  - Alphatross radiofrequency (Rb)
  - Duoplasmatron
- Dielectric gas :  $SF_6$  5 bars
- Stripper :  $N_2$
- Available beams : p, d, <sup>3</sup>He, <sup>4</sup>He, <sup>15</sup>N, <sup>16</sup>O
- **Radioprotection :**  $\mathbf{\Phi}$ deuteron beams allowed

Beam lines 

- Vacuum chamber
- External beam (microbeam)
- PIXE-induced X-ray fluorescence (in progress)
- IBA techniques : PIXE, PIGE, RBS, NRA, (ERDA)
- Acquisition system
  - multiple detection (3 channels)
  - dead time correction
  - pile-up rejection
- Detectors : X Si(Li);  $\gamma$  HPGe, BGO; particles 7

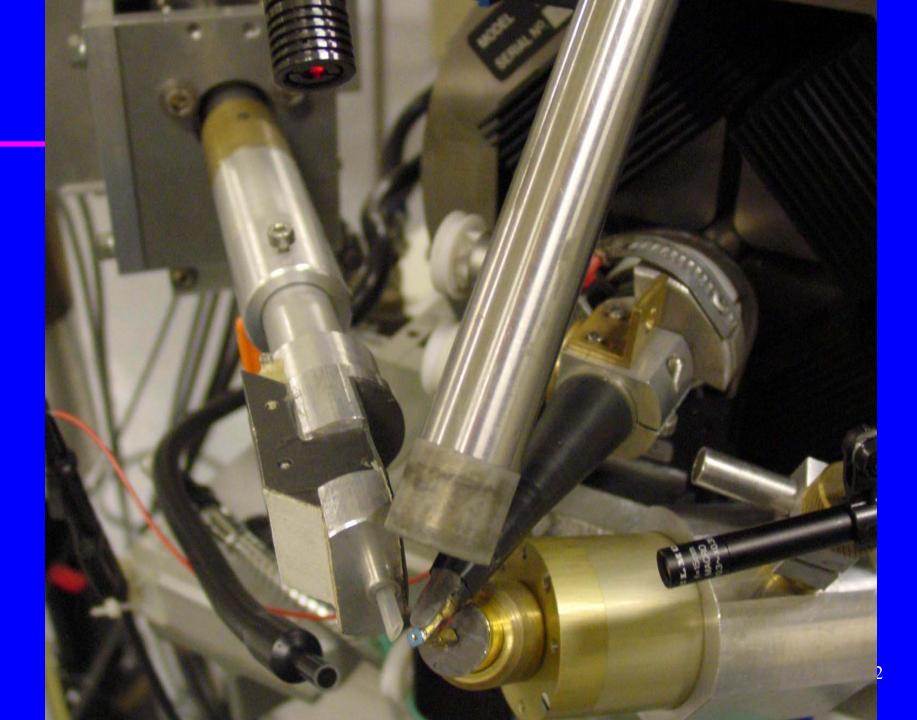


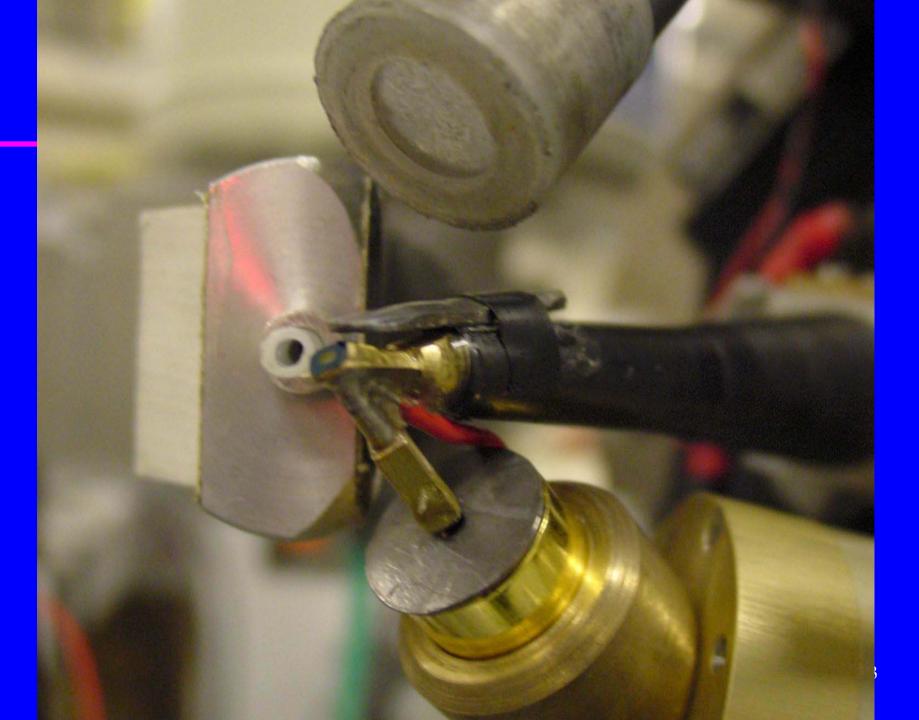


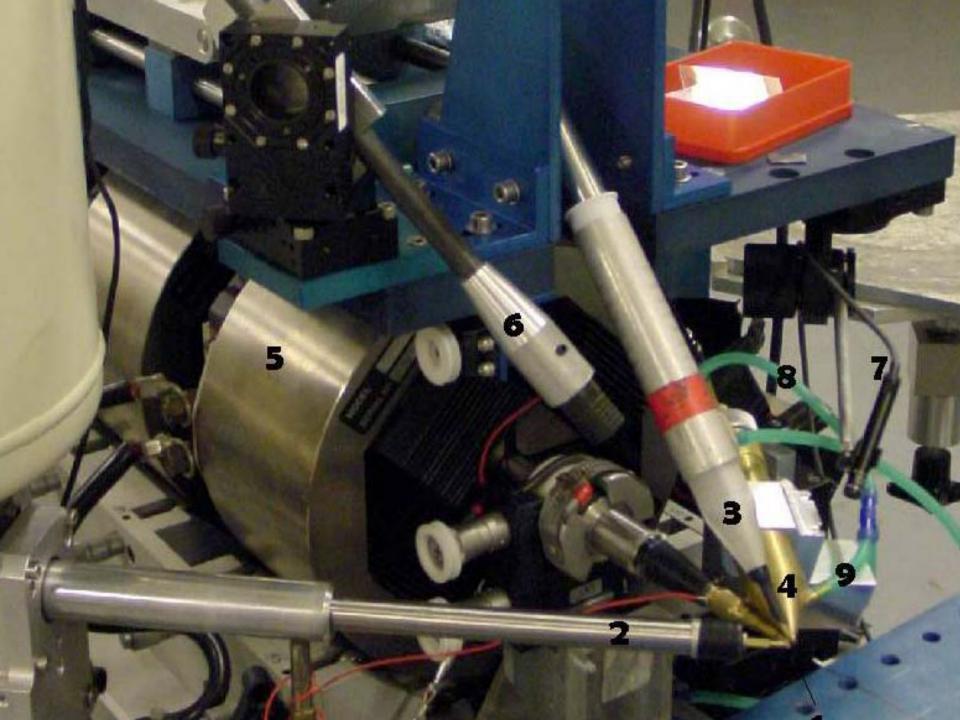


# Most useful experimental set-up : external beam

in-situ measurements---> no sampling
objects of large size or complex shape
ease of handling and moving of objects
no charging problem with insulators
reduced thermal effects ---> no damage
no dehydration problem
possibility of small-sized beam 10 μm







# Ion beam analysis applied to materials of cultural heritage (1)

Archaeometry (archaeological science)
 Materials identification
 *PIXE analysis of major elements* Materials provenance
 (sources of raw materials and trade routes)
 *PIXE analysis of trace elements* Artistic or fabrication technique
 Spatial distribution required: lateral uDIVE double

→ Spatial distribution required: lateral µPIXE, depth RBS

# Ion beam analysis applied to materials of cultural heritage (2)

Conservation science

Assessment of state of conservation of museum objects

- Study of alteration mechanisms with experimental materials submitted to accelerated ageing
- depth profiling by RBS and NRA
- Preventive conservation

Monitoring of museum environment

- PIXE analysis of collected dust
- BS analysis of monitors

#### Materials identification

- Artistic or archaeological object
- Renaissance drawings
  Antique jewels
  Antique statuette
  Antique papyrus
  Medieval miniatures
  Painted steles

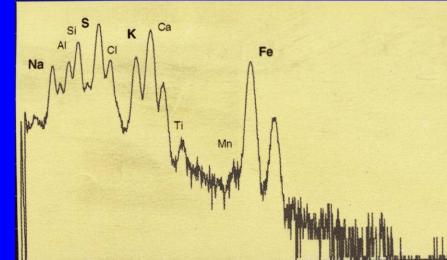
#### Material of interest

- Metal points
- Gemstones
- Gemstones
- Inks and pigments
- Pigments
- Pigments

## Materials identification by means of PIXE : nature of inks and pigments on manuscripts

- Micro-beam in PIXE mode with low beam current (50pA) well adapted :
  - very fragile material
  - need of good lateral resolution
  - easy quantitative measurements
  - easy discrimination between materials





## Drawing by Dürer



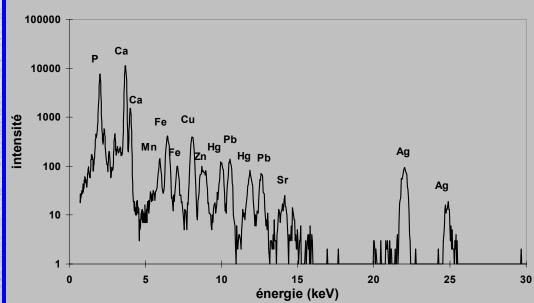
## Drawing by Pisanello

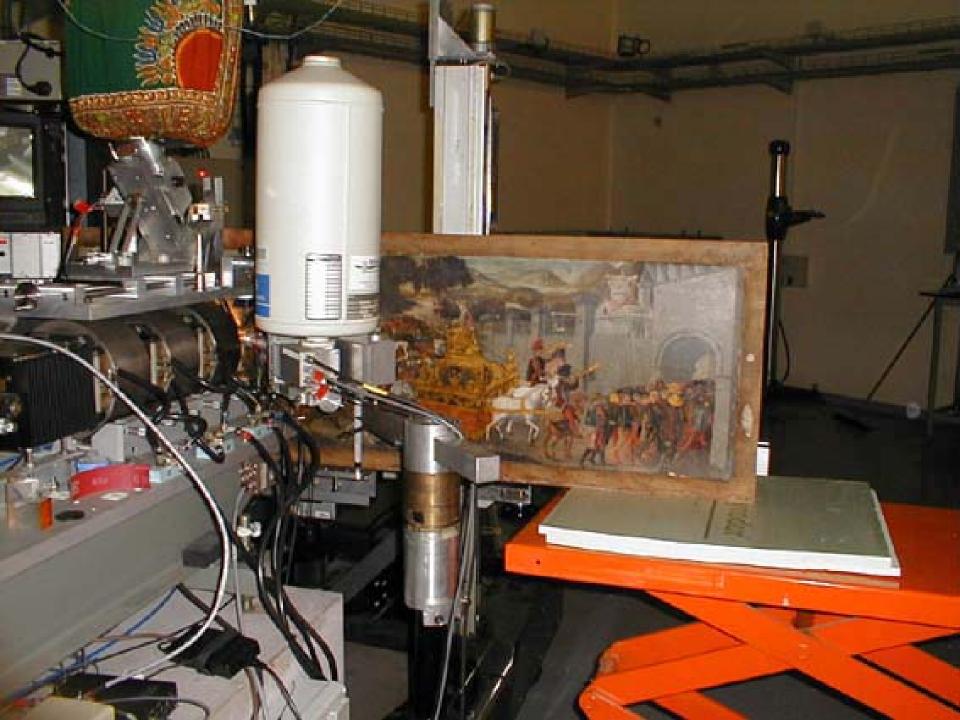
#### Mark of metal point





#### Drawing by Pisanello





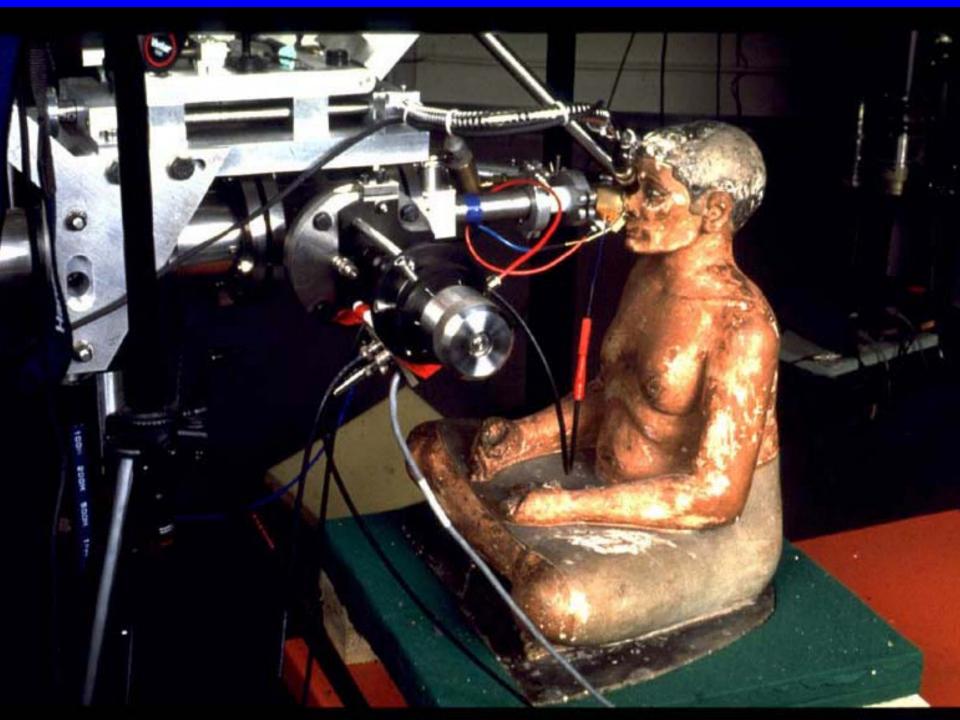


## Egyptian scribe: nature of eye components







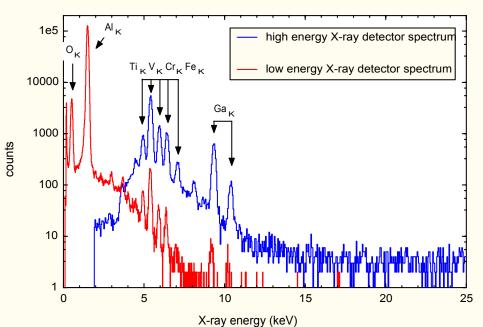


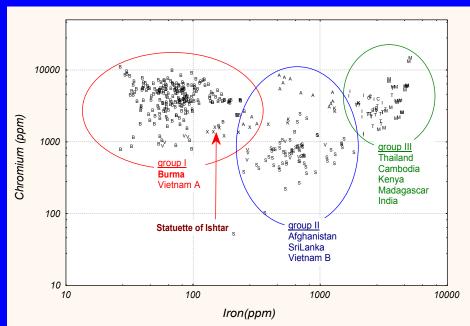
## Provenance studies using PIXE analysis of trace elements

- Trace element content currently used as a fingerprint in archaeology
  Comparison with geological materials
  Statistical processing of data
  Fields of application
  - Stones: obsidian, flint
  - Gemstones
  - Ceramics







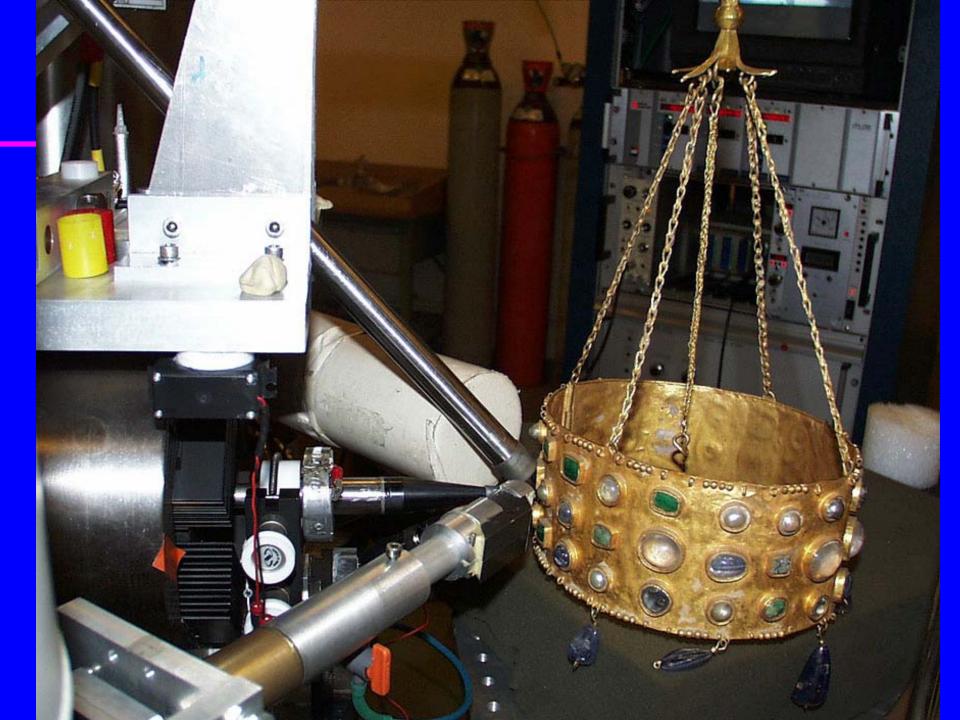


## Provenance of statuette rubies



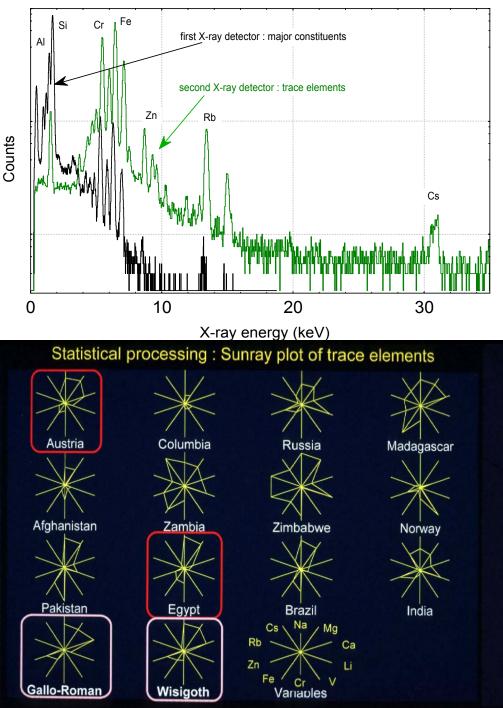
28

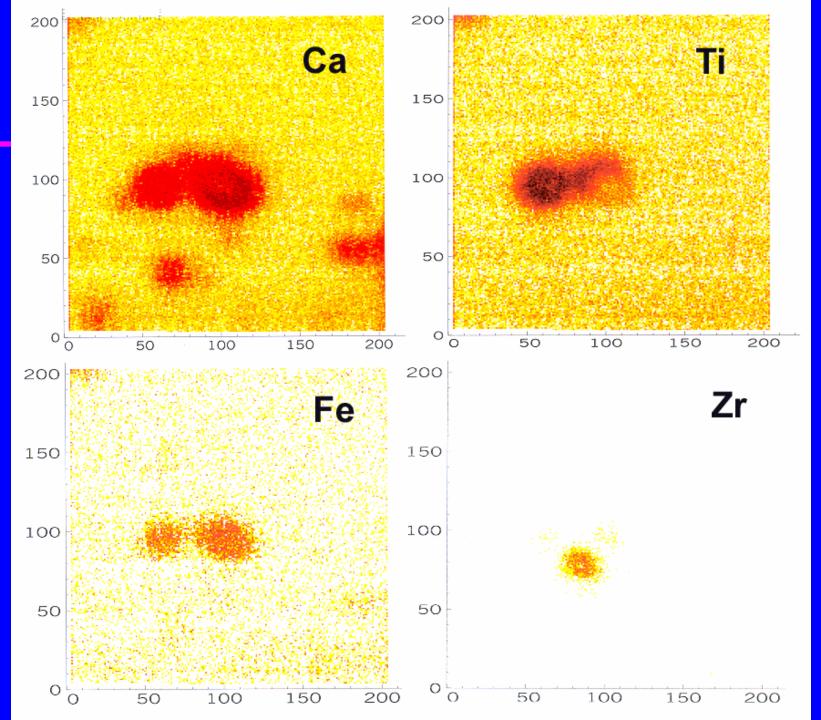


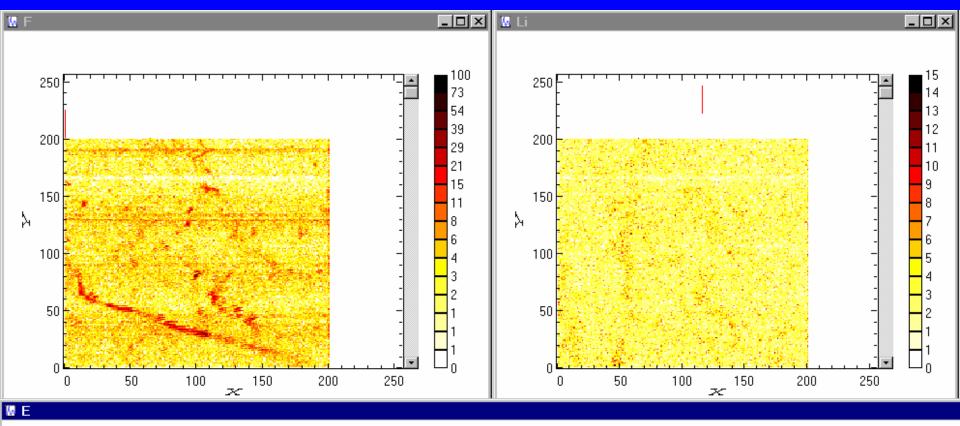


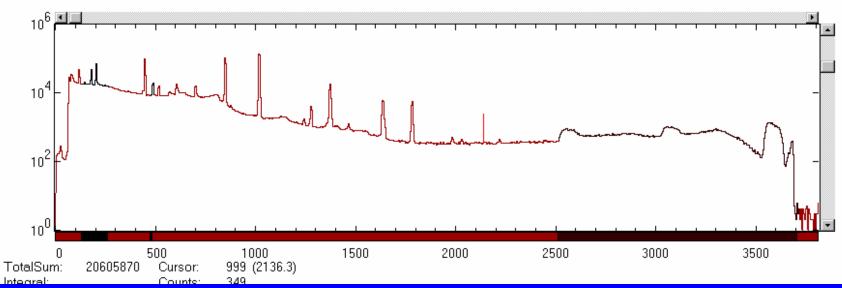
## Merovingian emerald







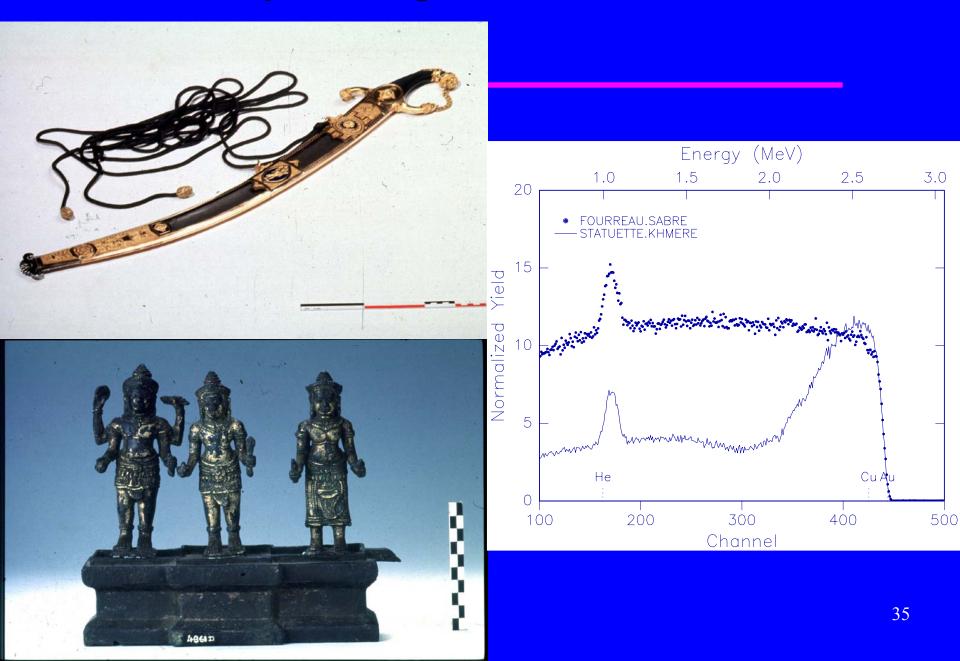




## Surface analysis using RBS and NRA

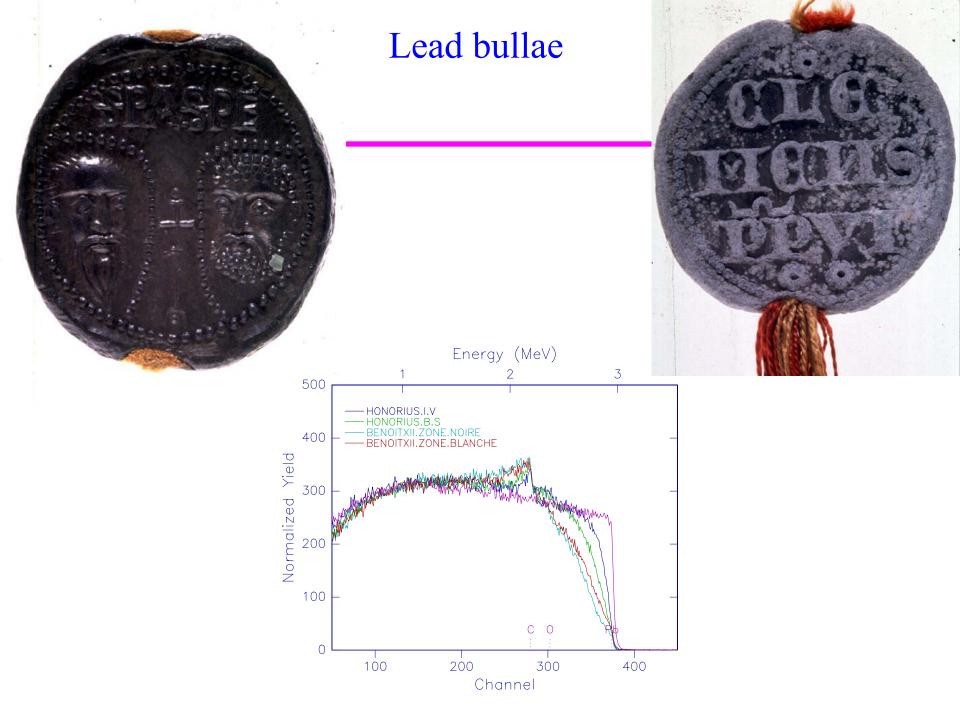
Structure of objects made of precious metals
Patina on bronzes

## Surface analysis using RBS and NRA



## Applications in conservation science

corroded lead bullae from National Archives
altered medieval enamels

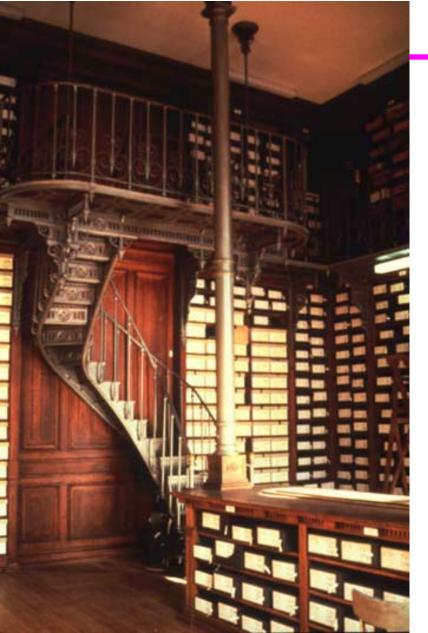


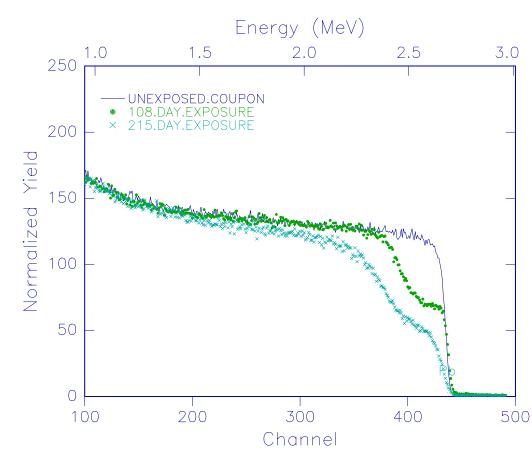


## Application in preventive conservation

 Control of museum environment by sampling atmosphere components and by monitoring risk of corrosion

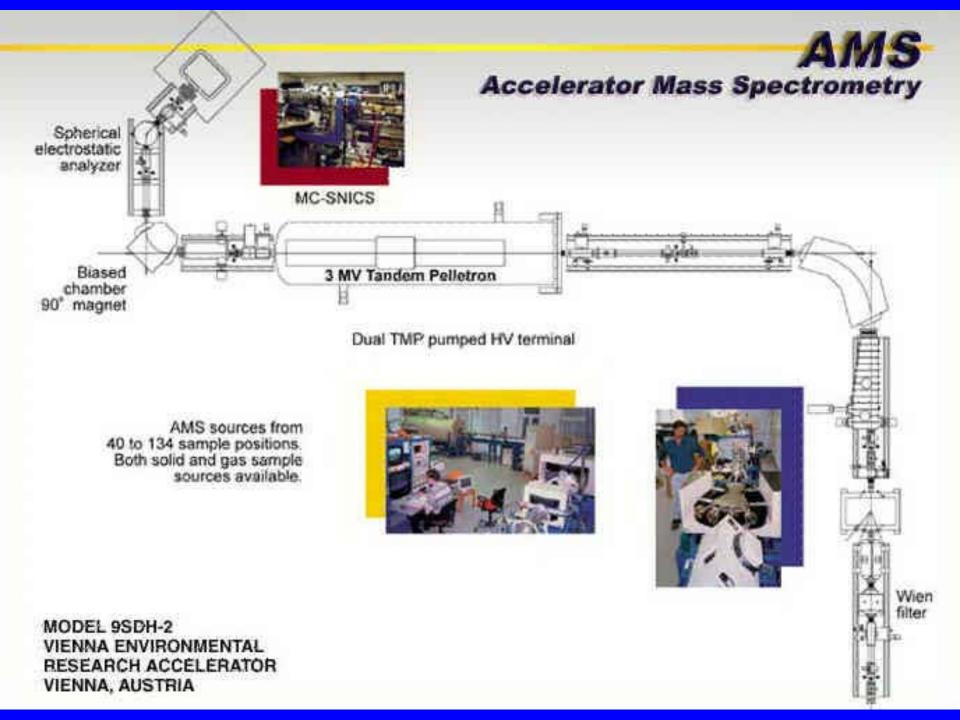
#### National Archives (seal department)





# <sup>14</sup>C dating with accelerator mass spectrometry (AMS)

- AMS applicable to cosmogenic nuclei <sup>10</sup>B, <sup>14</sup>C, <sup>26</sup>Al,...of extremely low isotopic abundance (10<sup>-15</sup> to 10<sup>-12</sup> for <sup>14</sup>C) and long half-life
- ◆ For <sup>14</sup>C direct measurement of amount of nuclei instead of radioactive counting → less material needed (1 mg vs 1 g) and reduced time of measurement
- C ions are accelerated up to 12 MeV to suppress isobaric molecular ions and use of nuclear detection systems (E-ΔE, TOF, SBD)



## Future AMS facility for <sup>14</sup>C dating



#### Future AMS facility for <sup>14</sup>C dating

- ♦ 3 MV tandem Pelletron 9SDH-2 from NEC
- Two multicathode negative ion sources (134 and 40 samples)
- ◆ Sequential injection of <sup>12</sup>C, <sup>13</sup>C, <sup>14</sup>C
- Precision 0.3% on modern C
- Fully automatic
- Expected to be operational in early 2003
- About 4000 measurements per year (1500-2000 for archaeology)

## Conclusion and prospects

- Usefulness of accelerator-based analytical techniques in the field of Art and Archaeology due to their performances and their non-destructive character
- Combination PIXE-PIGE mostly used
- ◆ Usefulness of external (micro-)beam
- Possibility of micro-mapping using the external microbeam
- Use of complementary methods based on RBS and NRA for elemental depth-profiling
- Possibility of kinetic studies in real time with external beam
- ◆ <sup>14</sup>C dating with AMS increasingly used