Accelerators and X-rays in cultural heritage studies

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- General introduction to accelerators
- Radiation in matter
- Examples
  - Trace analysis
  - Composition analysis
  - Glass and ceramics
- Perspectives

Introduction

Cultural heritage research:

As an alternative to modern laser techniques the application of x-rays (XFA, XRD) using x-ray tubes is quite well established.

Not so common are other sources like

- **„small“ accelerators for„museum“ studies**
- **large scale facilities for detailed studies**
- **mobile systems for „field studies“.**

Introduction

Accelerators:
Electron storage rings
Heavy ion accelerators and rings
Linacs
Small tandem

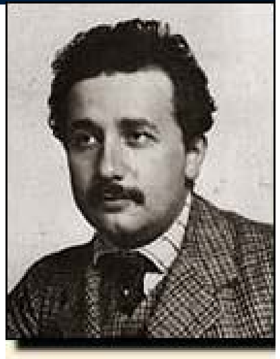
Accelerators

typical for	nuclear physics particle physics
New domains:	
Material science:	solid state physics analysis technical applications
Medical applications:	diagnostics, therapy
Cultural heritage:	analysis, archaeometry, imaging etc.

In CHARISMA, we have 3 accelerators participating.

Basis for fluorescence analysis

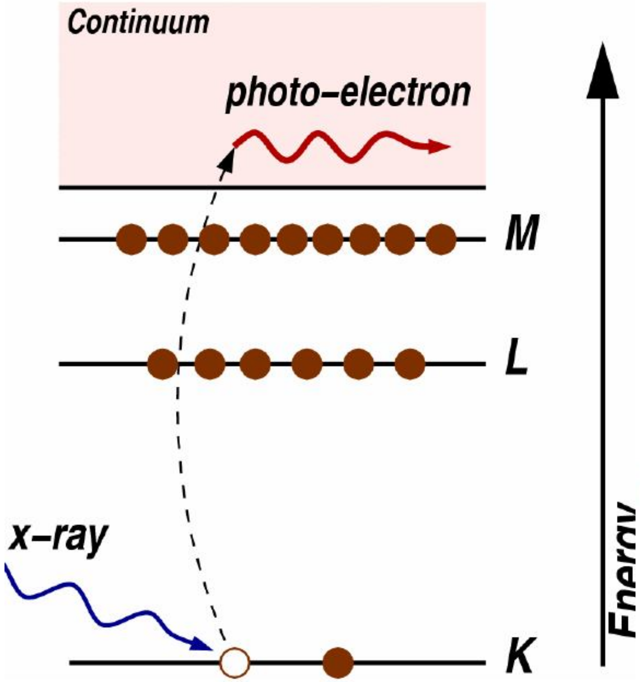
Photo electric effect



1905

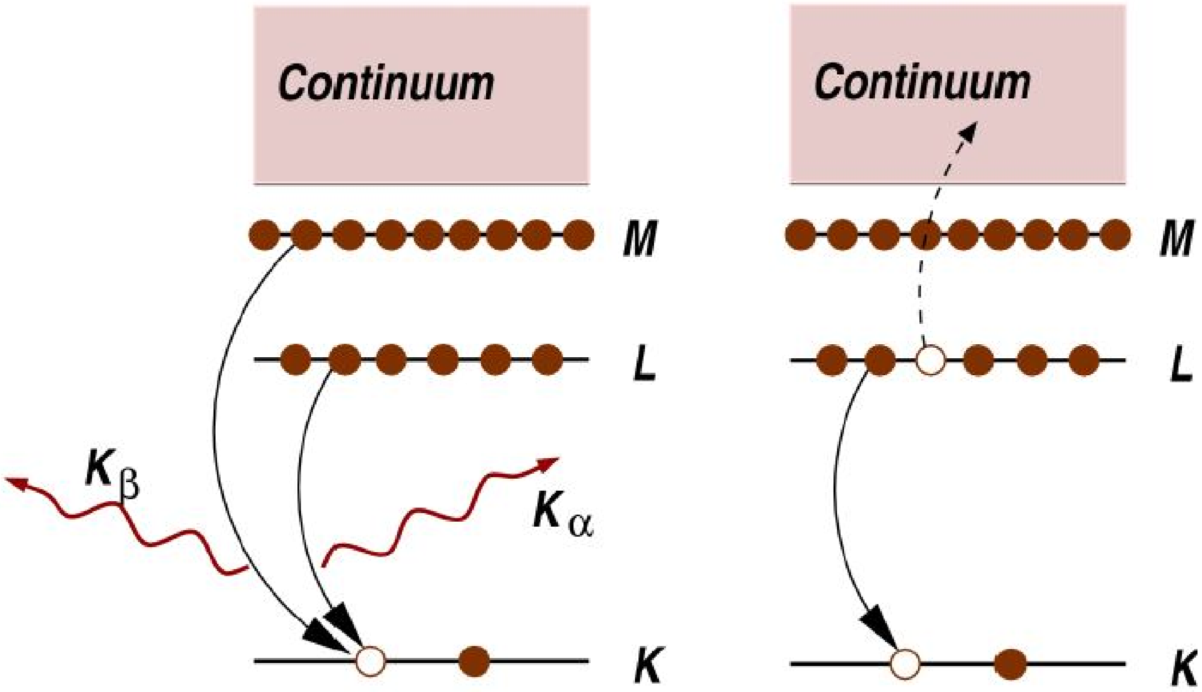
Absorption

an electron is kicked out by a photon or



by electron (EDX), proton (PIXE),..

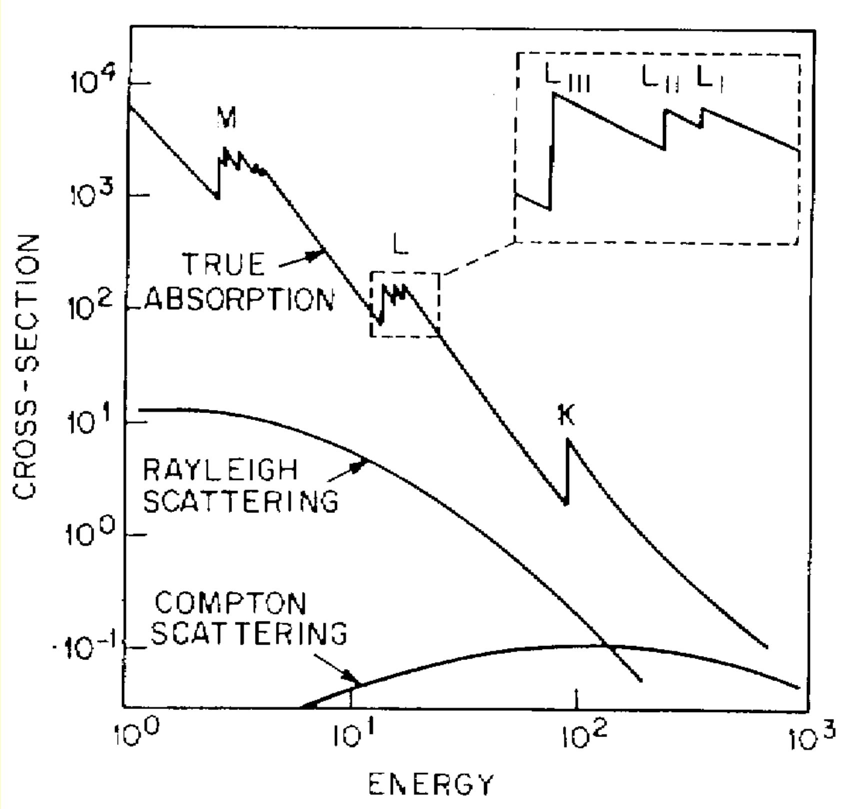
Emission

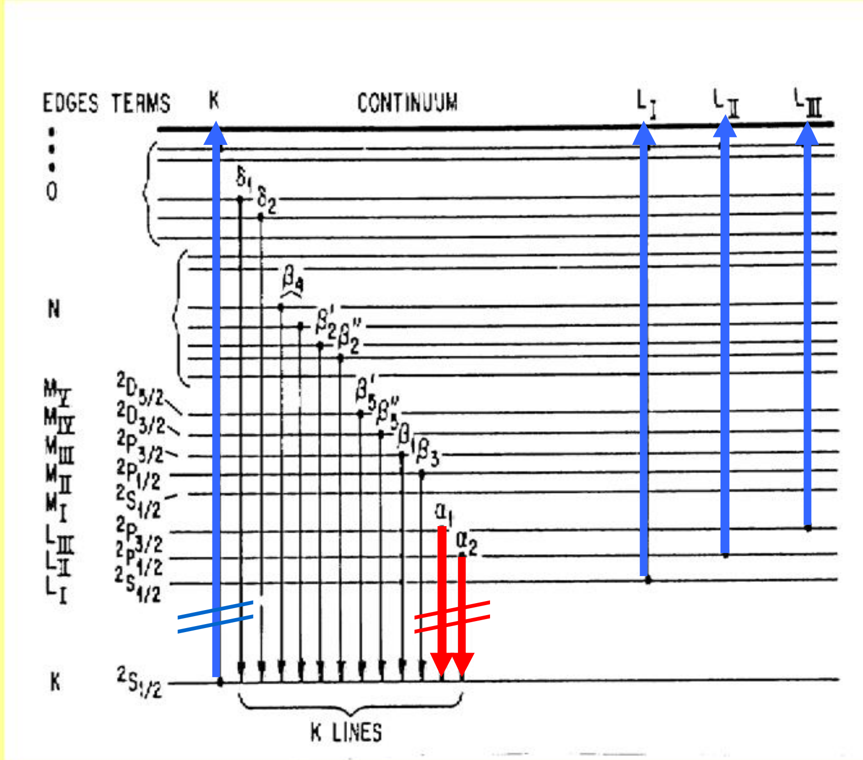


X-ray (fluorescence)

Auger electron

Absorption and Emission





cross-section

$h\nu \propto (Z - a)^2$ Moseley-law

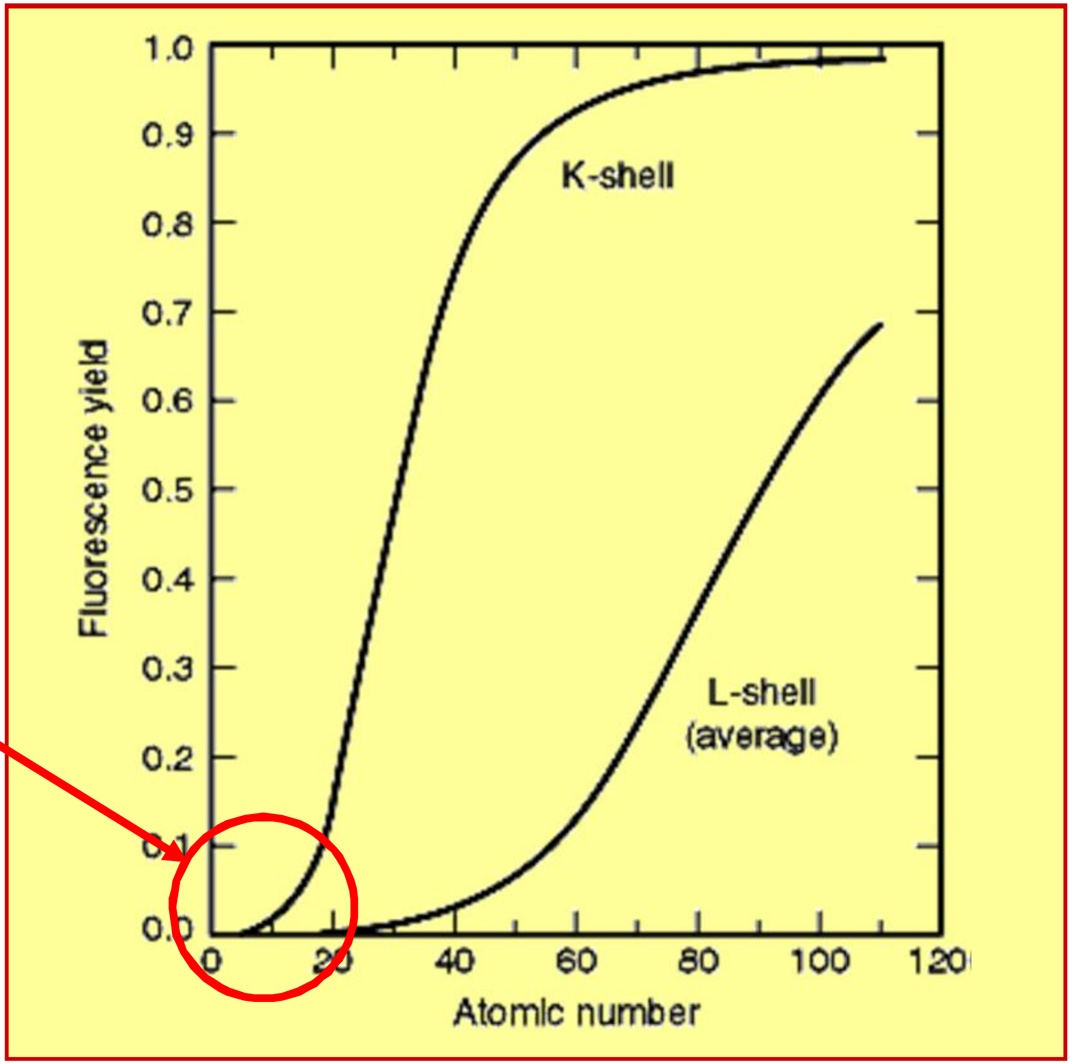
Elemental Sensitivity

from 13 eV (hydrogen) to 90 keV (uranium)

Basis for fluorescence analysis

Fluorescence yield

$I_{photon} / I_{electron}$

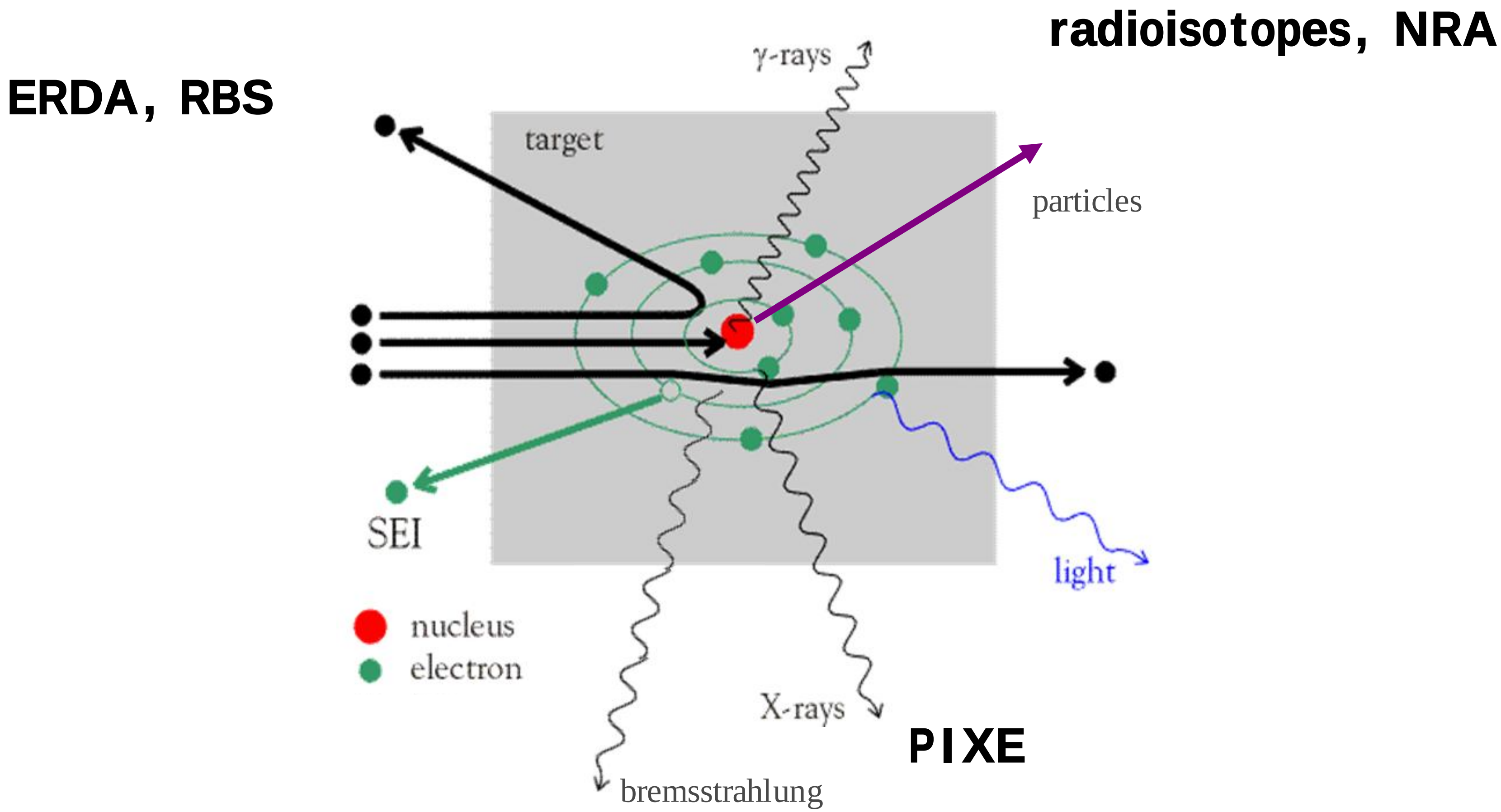


Low sensitivity for elements with Z<10

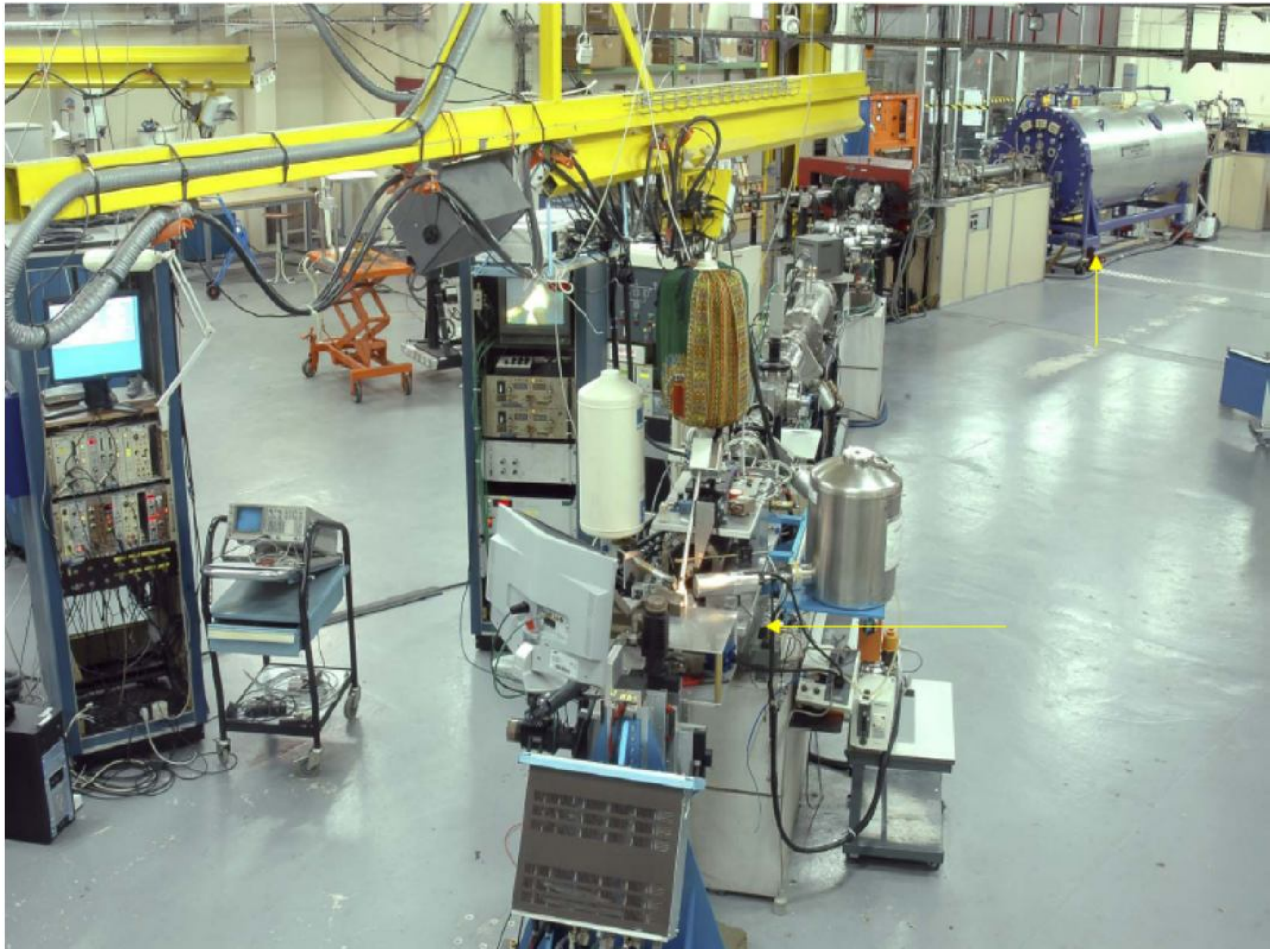
Ion-Matter Interaction

Ion-matter interaction:

Collision between charged particles – electrons and nuclei. Energy transfer ! Most of the energy will remain in the material, typically as ionisation and heat !



„Small“ accelerators



2 MV pelletron

microbeam

routinely proton, alpha.

Special feature:

external beam,

i.e. object in air (or flushed with He)

PIXE, RBS, PIGE

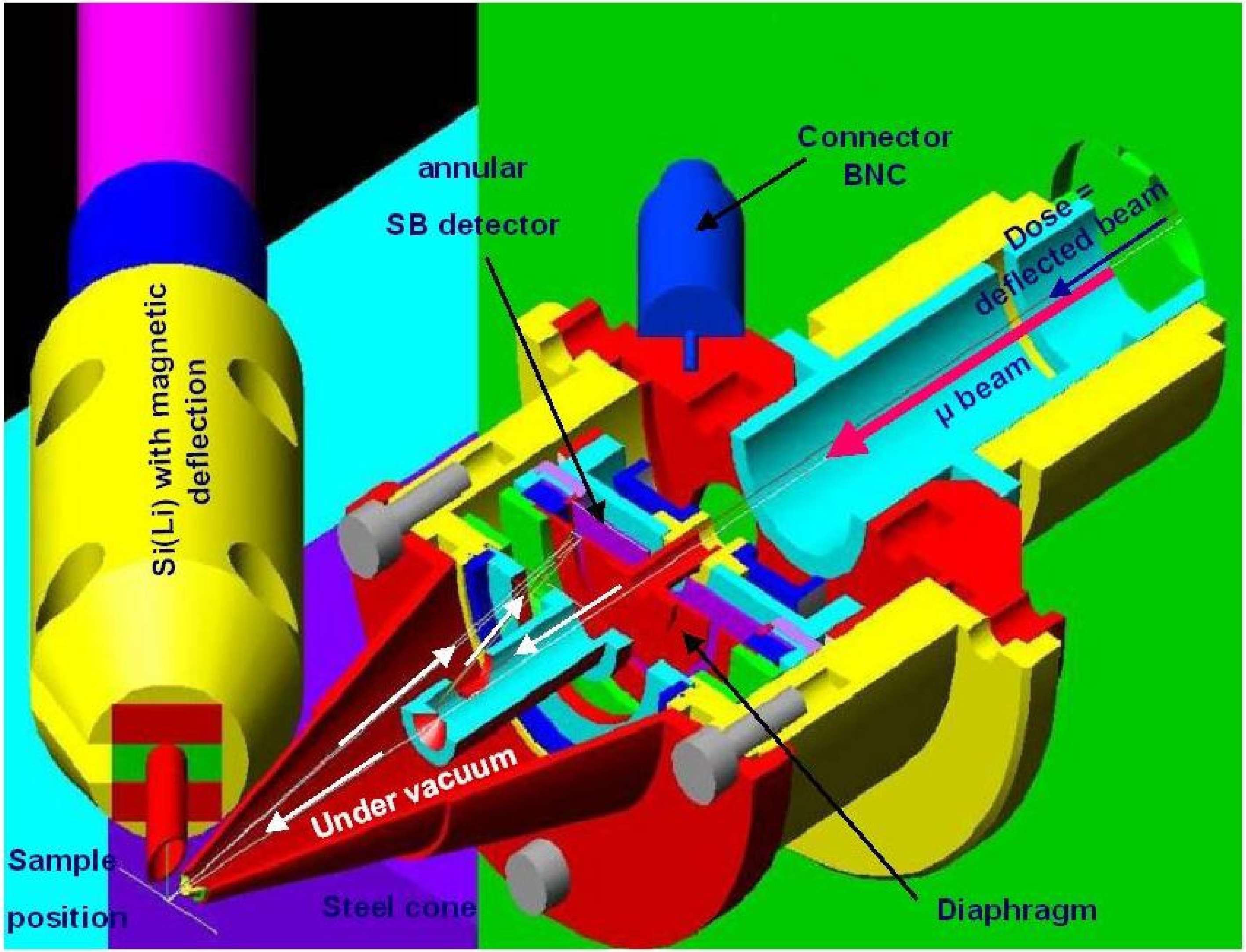
nA - µA

AGLAE (Accelerateur Grand Louvre d‘Analyse Elémentaire),

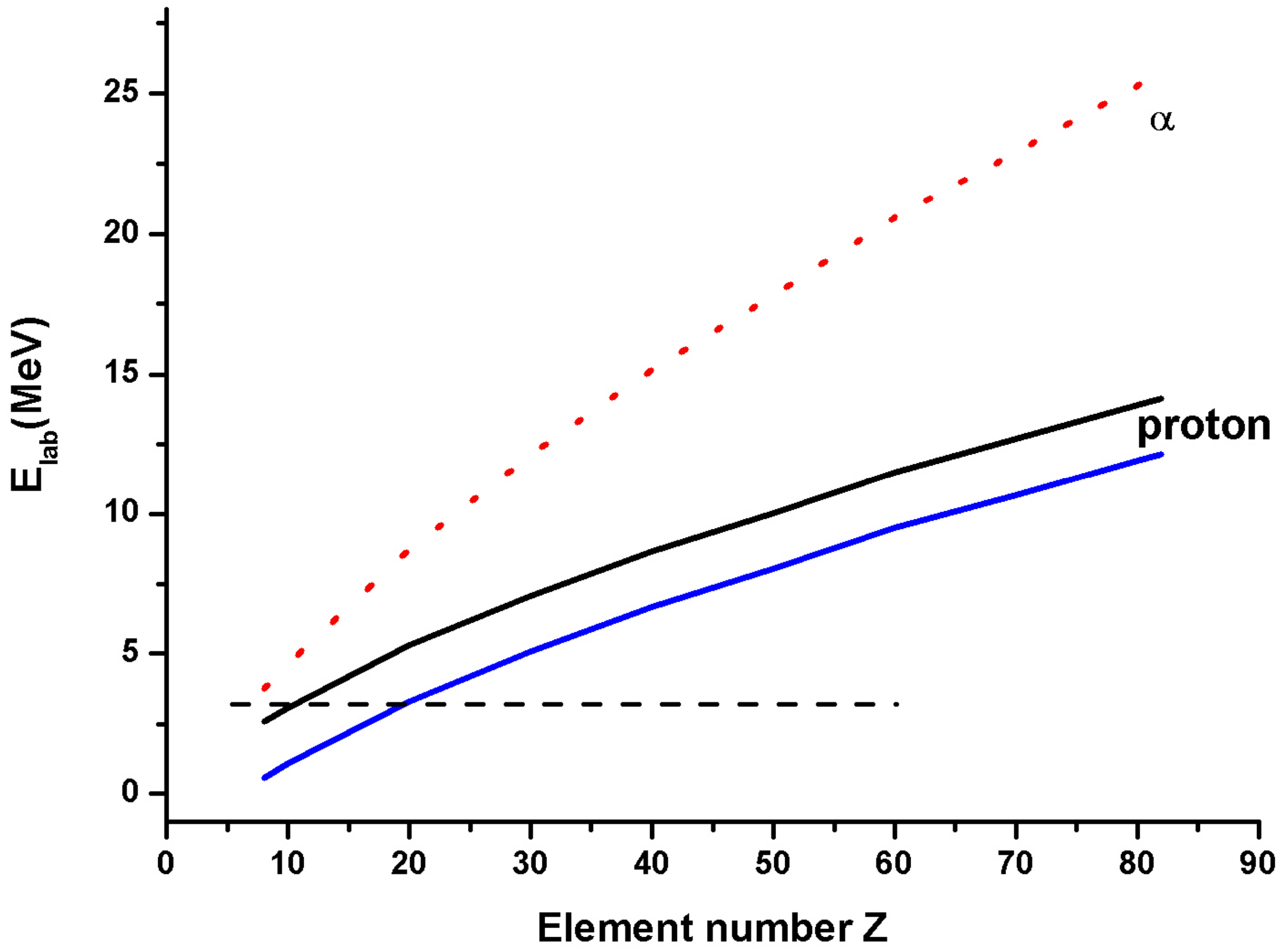
ongoing modernising program NewAGLAE.

Ion-beam analysis

Example: AGLAE



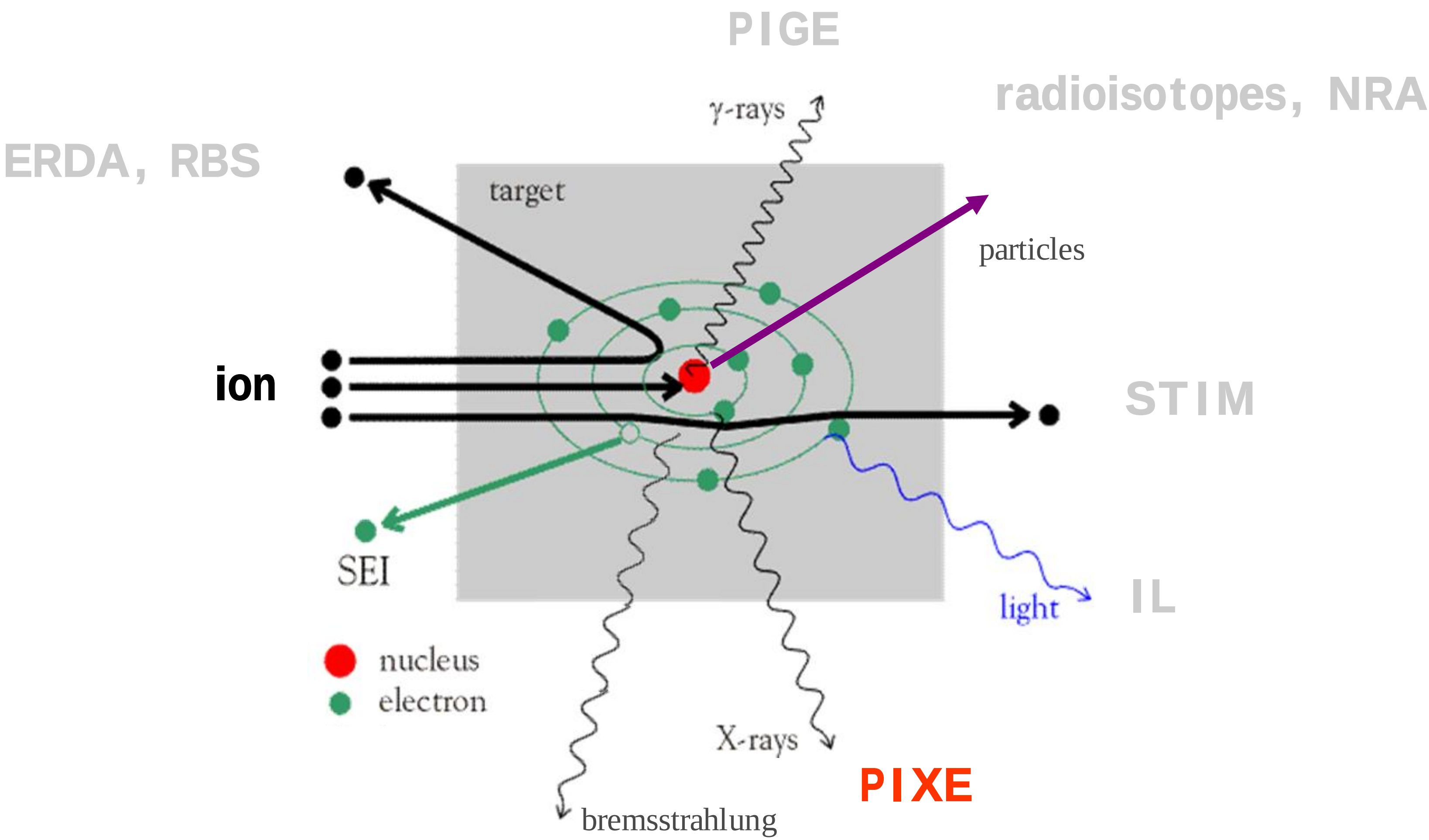
Coulomb - barrier



„no" nuclear reactions below the Coulomb barrier!

Ion-beam analysis

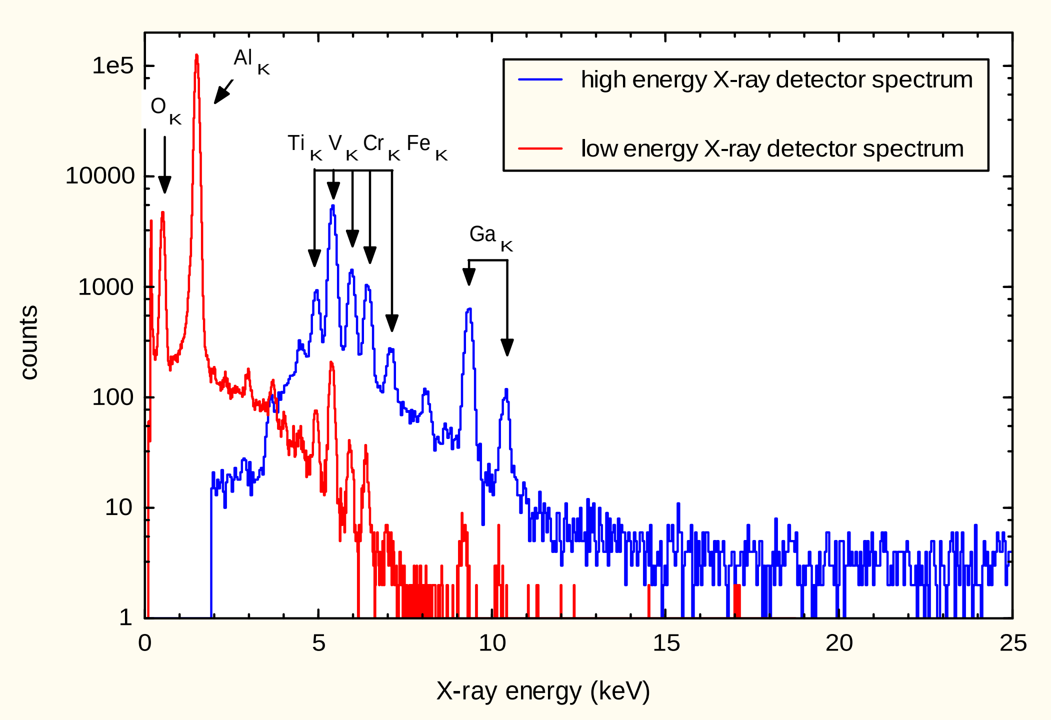
collision with electrons:
proton (particle) induced x-ray emission



!!! cross sections larger than nuclear cross sections !!!

Classical example: goddess Ishtar

trace element analysis of ruby (provenance)



Detailed comparison with rubies (no glass!) from different sources:

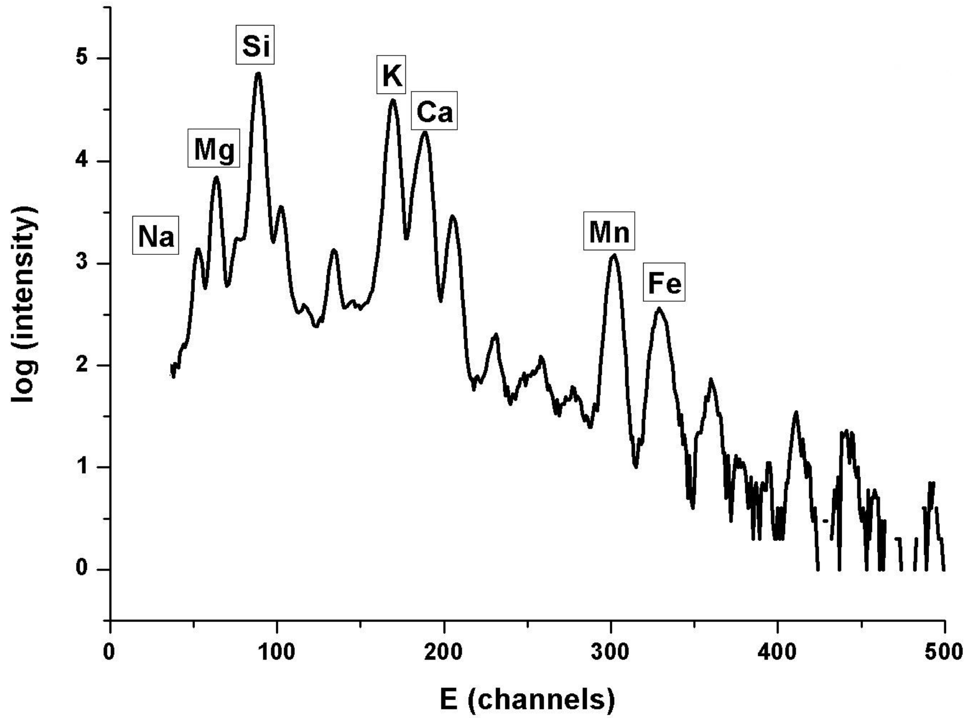
> Sri Lanka or Myanmar

(in accordance with a Sanskrit text).

T.Calligaro et al. NIMB 136-138 (1998)846

Ion-beam analysis

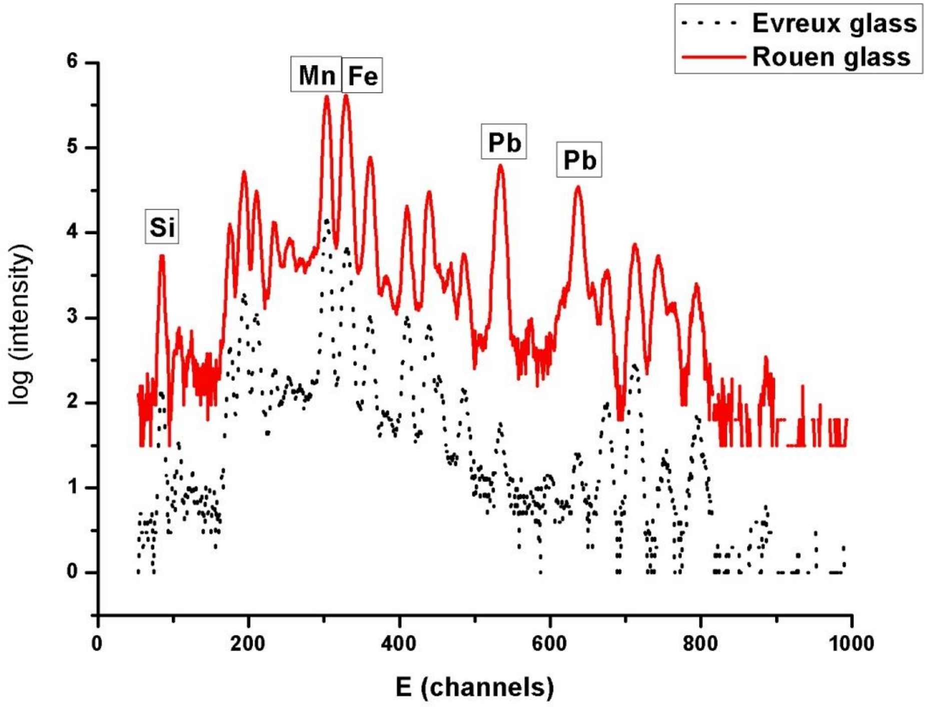
composition analysis for restoration purposes etc.

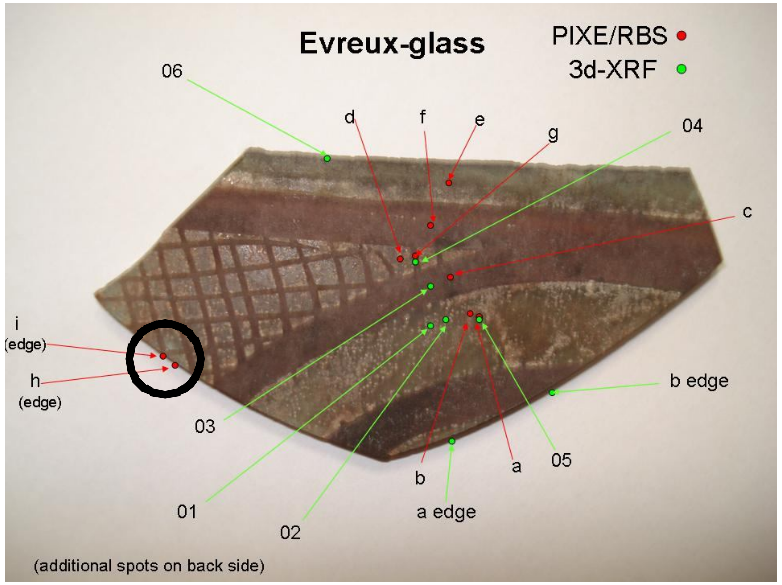


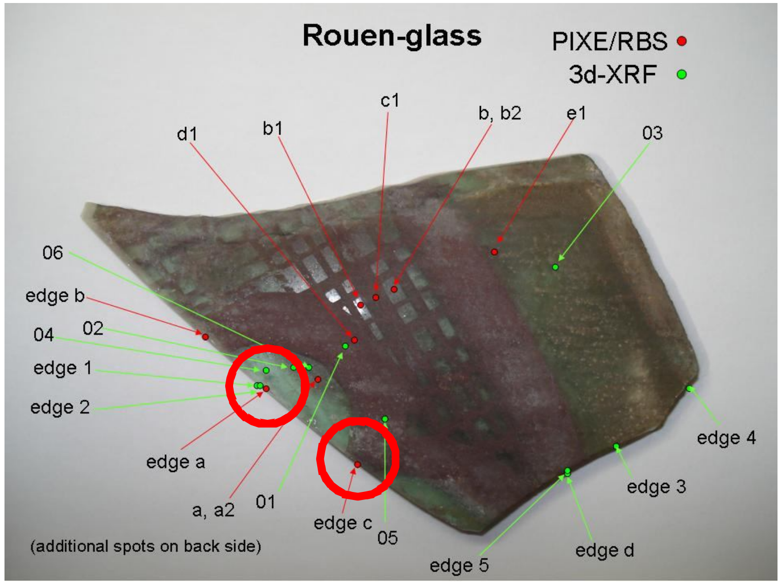
PIXE on a glass piece from the cathedral in Evreux

cooperation with C.Loisel LRMH

Analysis of stained glass windows - combine PIXE and RBS







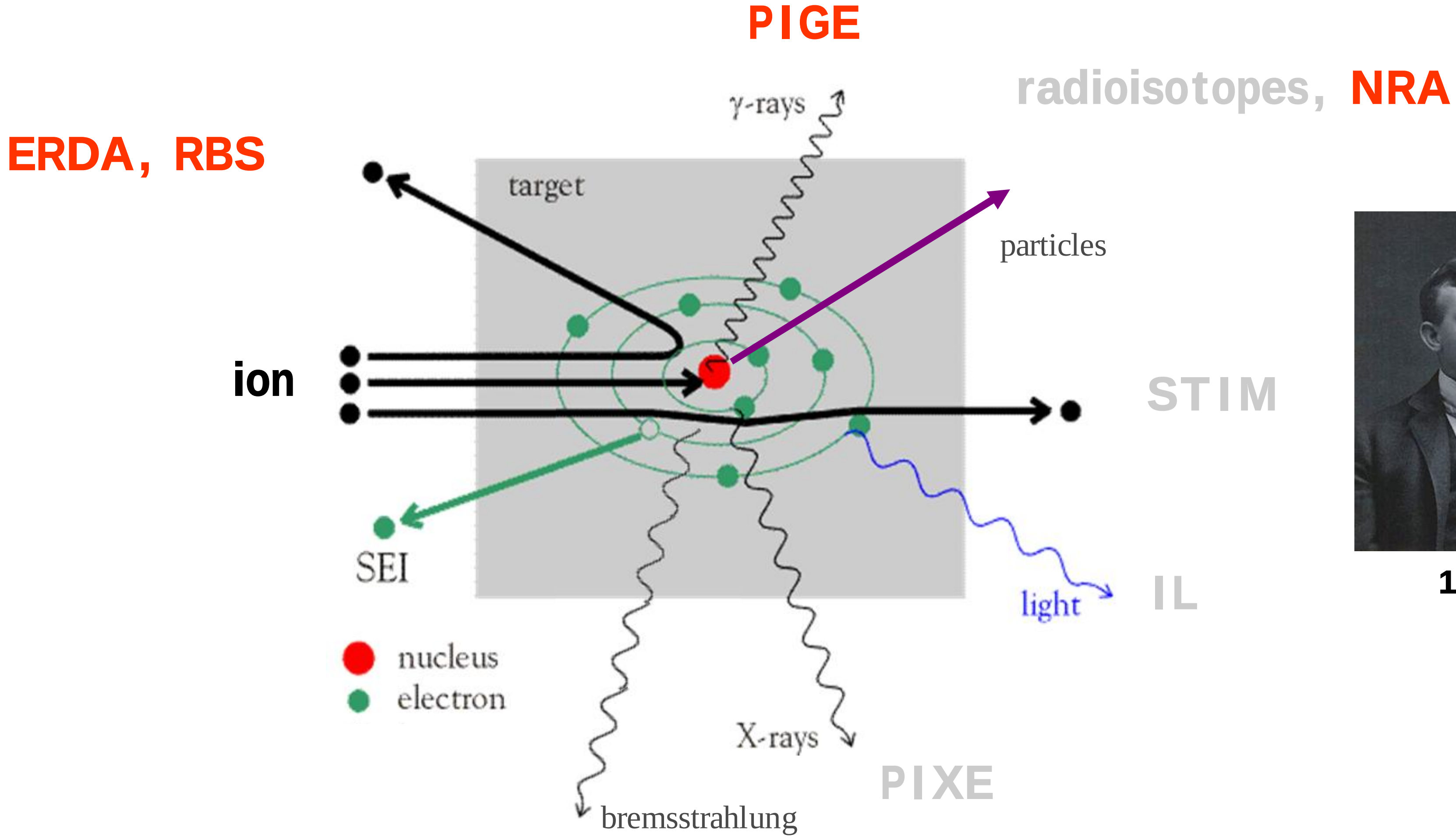
Pb in glass?
little depth information!

> Combine with RBS

Ion-beam analysis

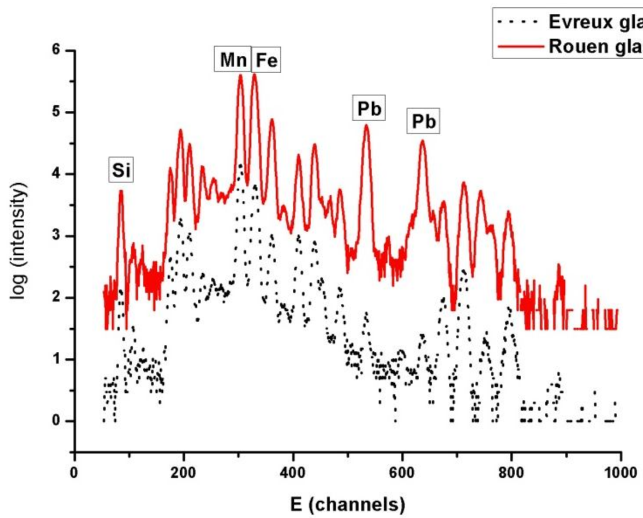
collision with nuclei:

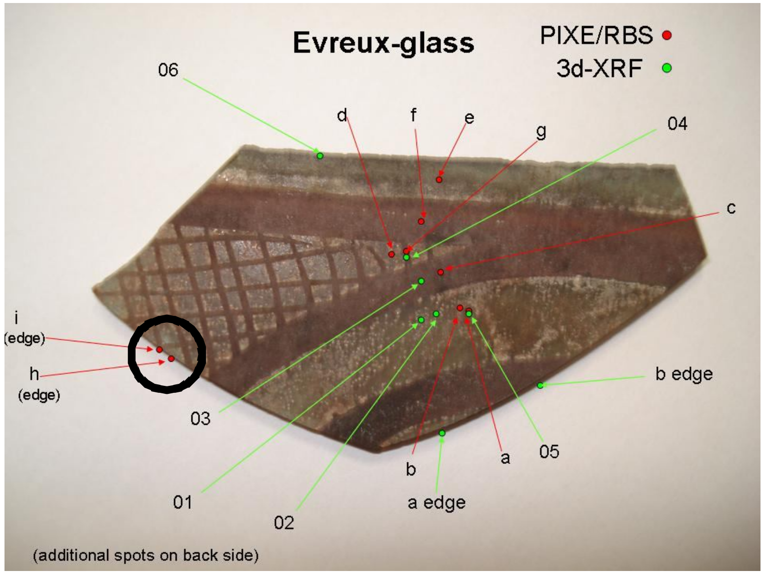
Rutherford backscattering spectroscopy, elastic recoil detection analysis, nuclear reaction analysis, proton induced γ-ray emission

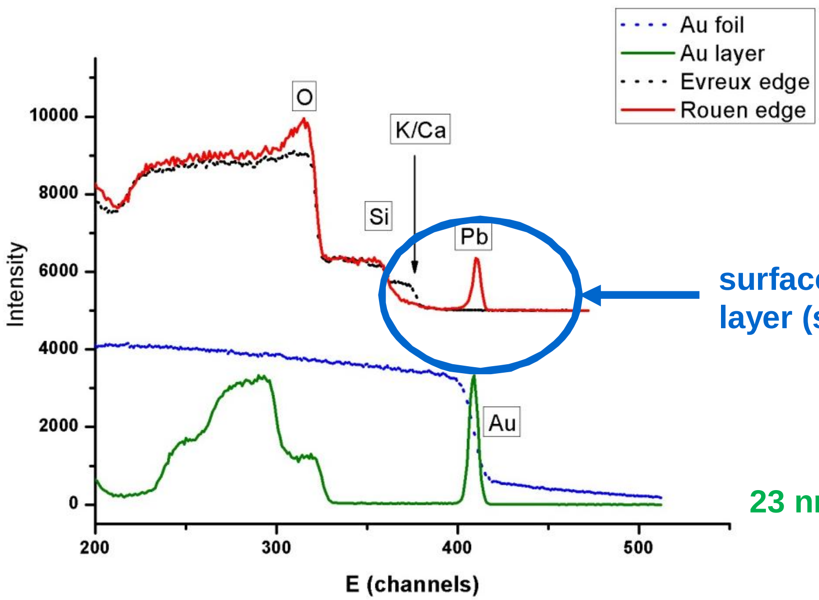


1911

Analysis of stained glass windows - combine PIXE and RBS

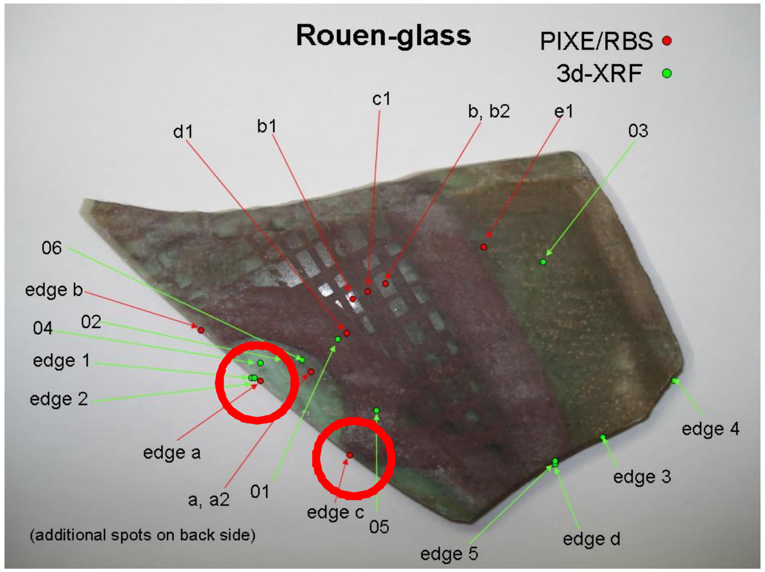






surface Pb-layer (sub-µm)

23 nm Au

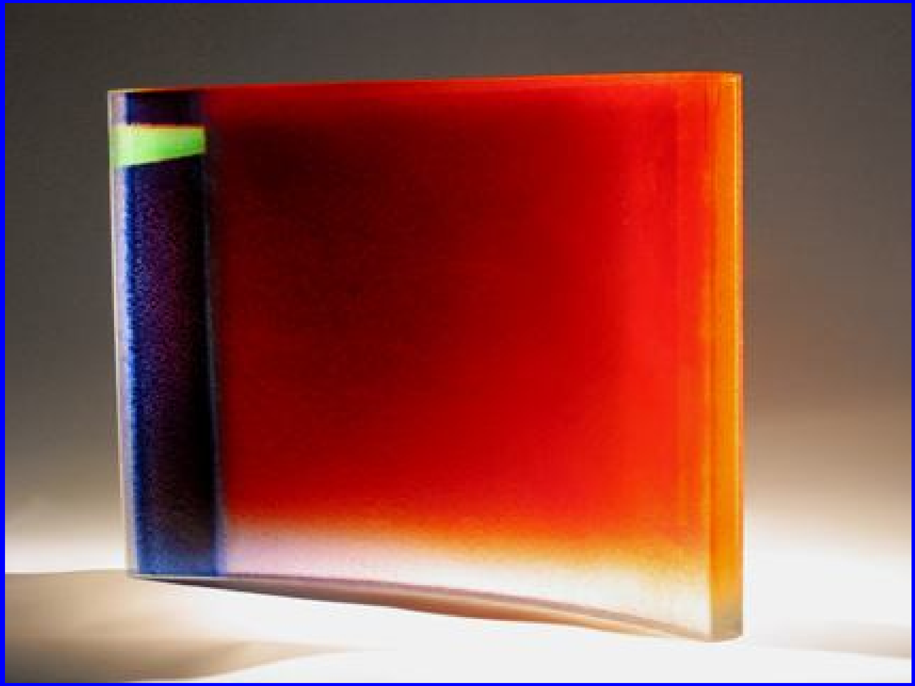


Metallic nanoclusters in glass

When illuminated from outside, the Lycurgus cup (4th century AD) appears green. When illuminated from within the cup, it glows red. The red color is due to nanometer-sized gold particles embedded in the glass, which have an absorption peak at around 520 nm.

Modern art work in glass and modern applications

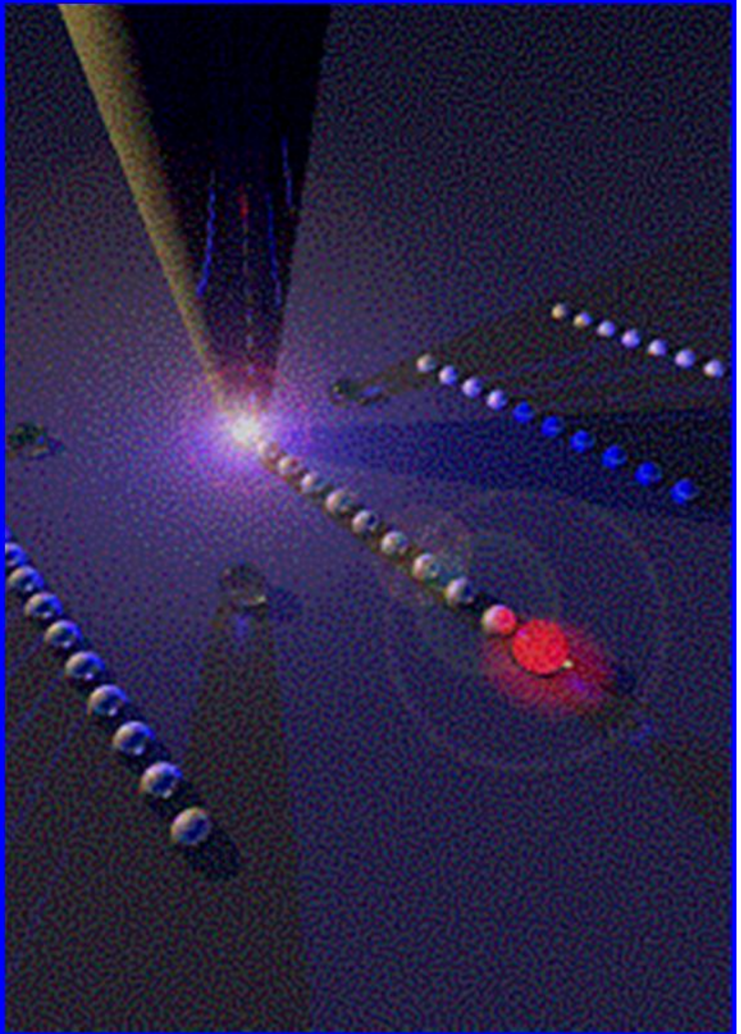
Udo Zembok: Colorfields 2006



Zembok regularly has exhibits, e.g. at the Centre International du Vitrail à Chartres

!!! Caution !!!
Qualitative difference between blue (ionic light emission) and red (light scattering and absorption on metallic nanoparticles)

Nanoparticle waveguides

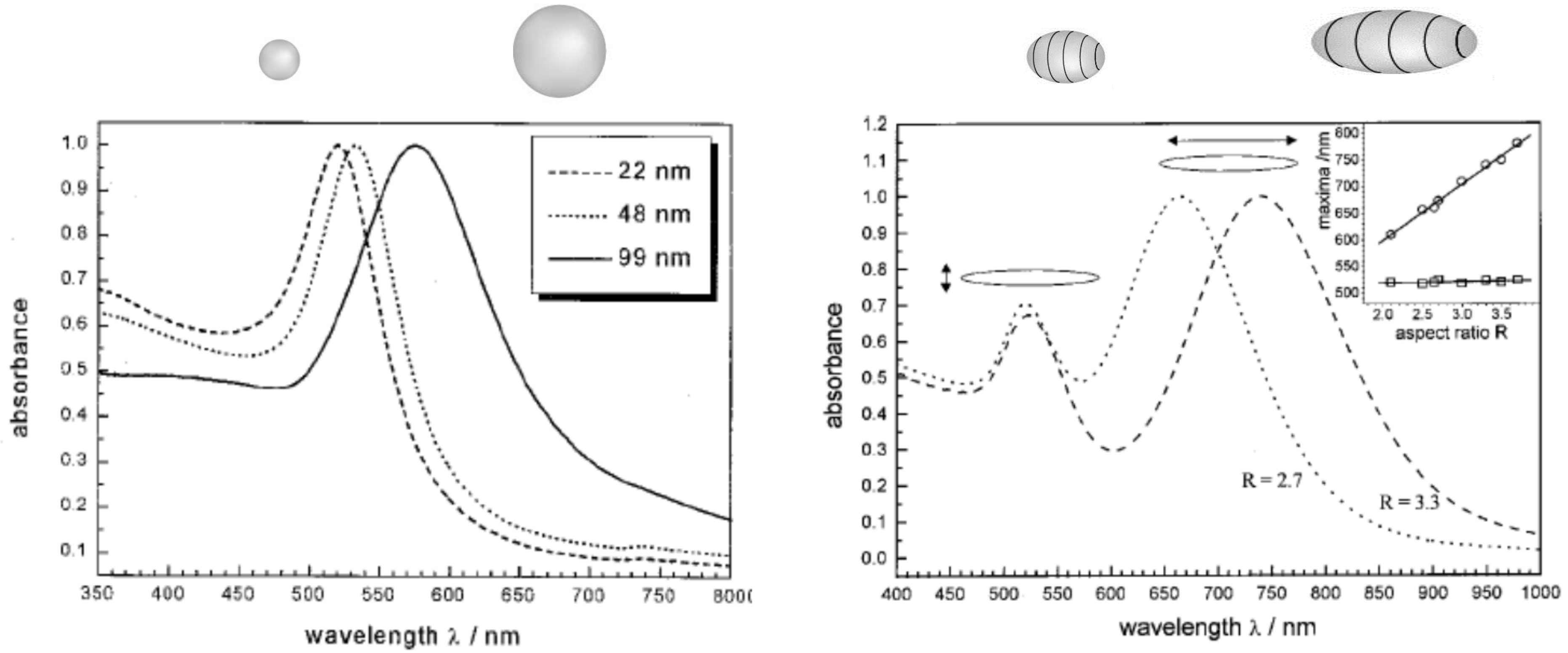


(cover Nature Materials 4/2003)

Surface plasmon resonances

Particle sizes between 1 and 100 nm

- Red shift with size
- shape-effect splitting
- red shift with size (anisotropy)

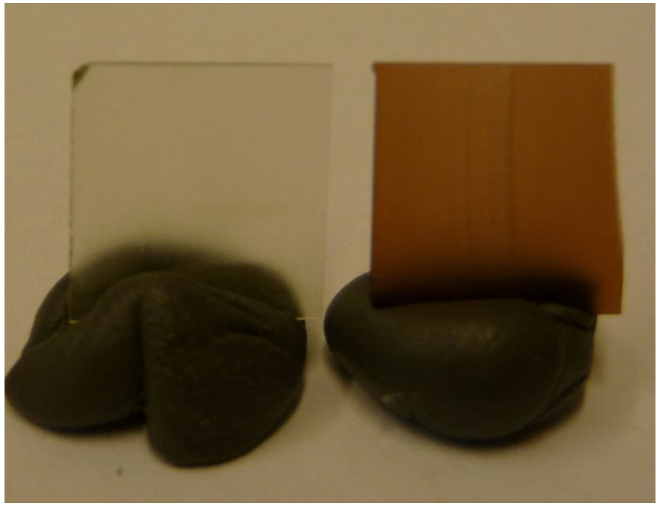


Link and El-Sayed, Int. Rev. Phys. Chem. 19(2000)409

EXAFS characterisation

Compare various glass pieces from the same base material:

Cu glass:
light and dark



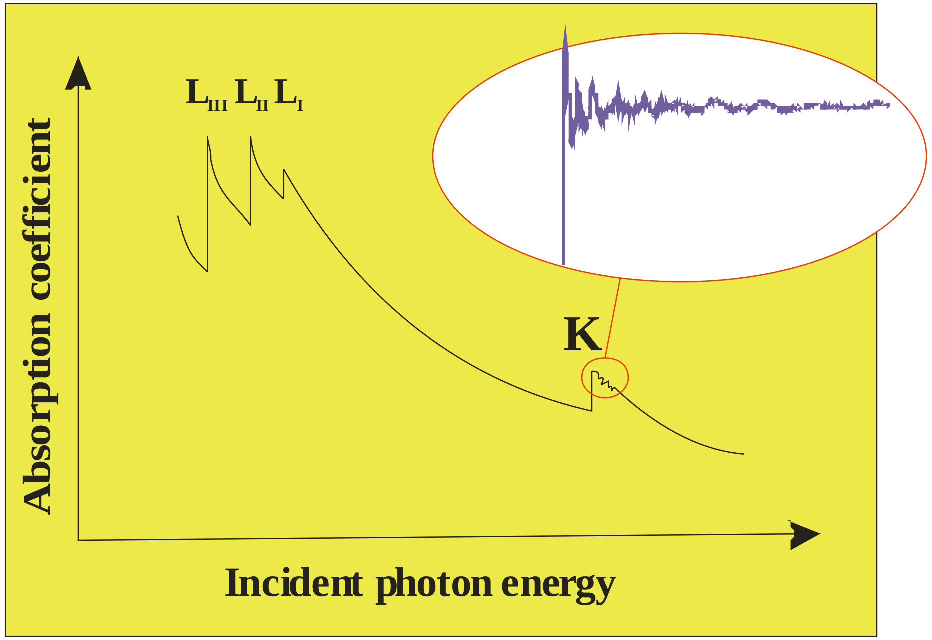
1 cm

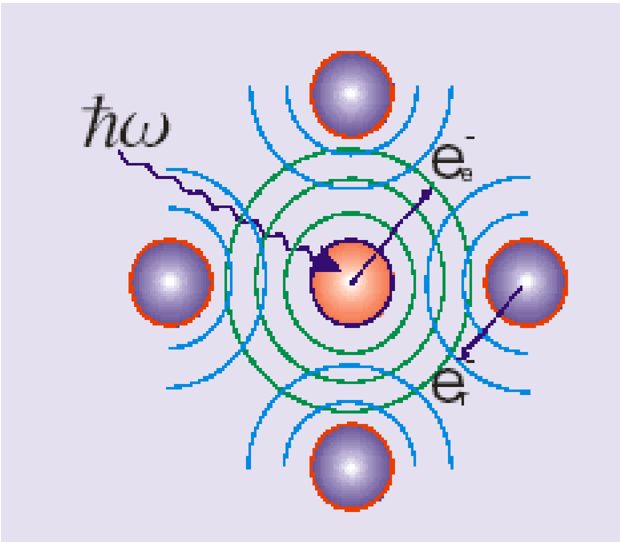
Elemental analysis shows the same composition

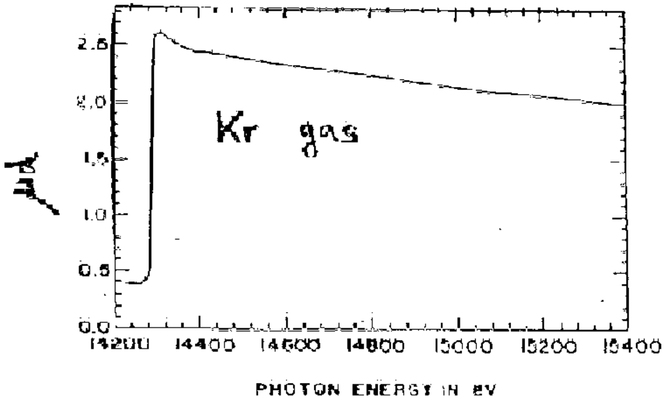
What is the difference?

Heat treatment.

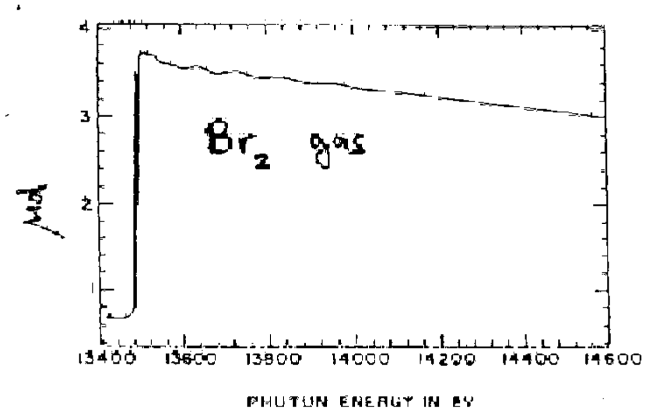
Absorption spectroscopy: basic principle



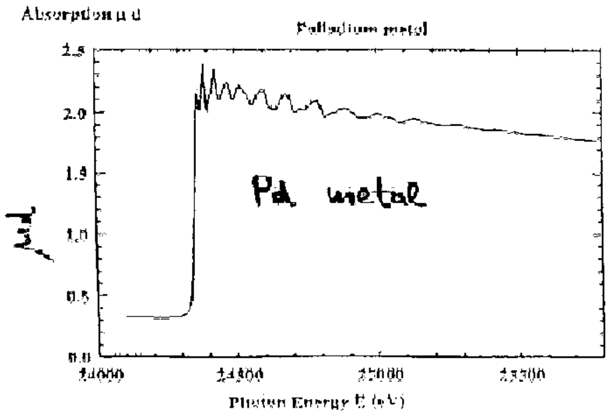




atom



molecule



solid

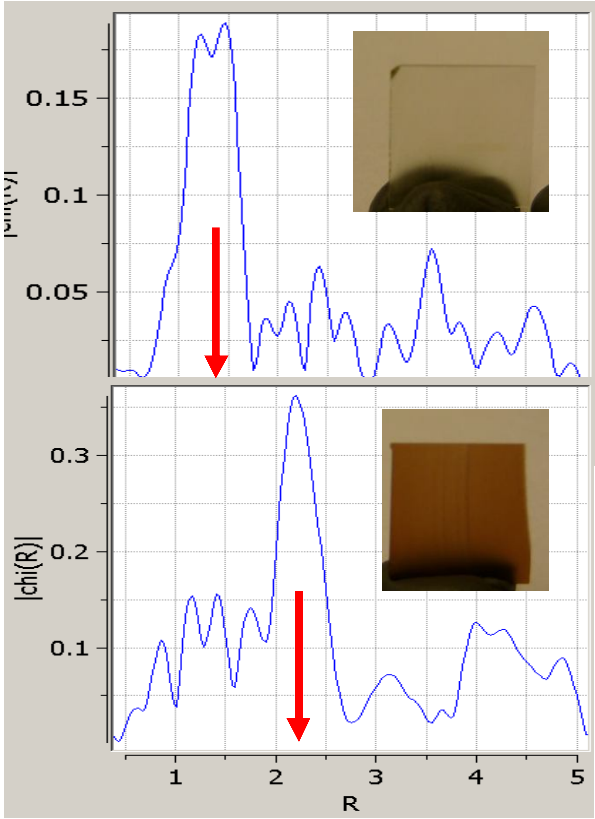
EXAFS characterisation

Cu glass – transparent and opaque (dark)

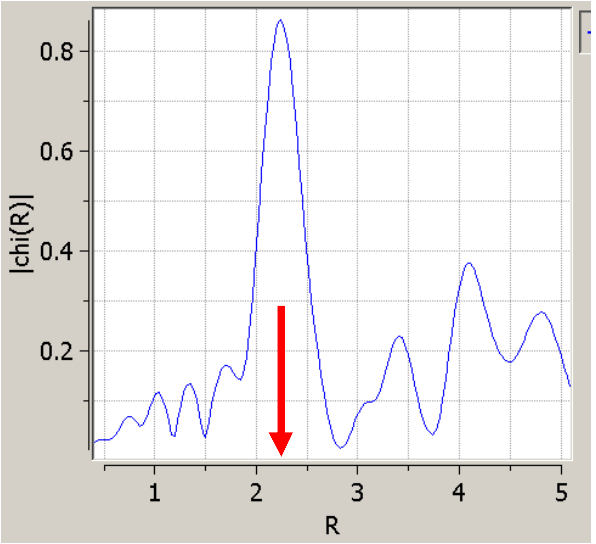
(differently heat treated – same concentration)

Transparent glass

Dark glass
(heat treatment)



Compare with pure Cu metal



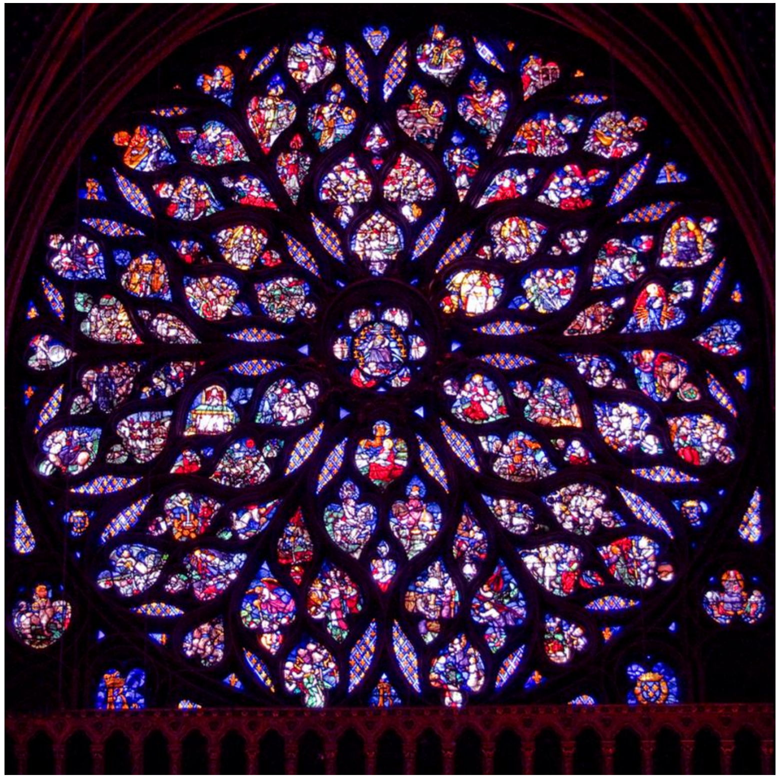
EXAFS signature for chemical form (phase) !!

Color results from metallic nanoclusters !!

(glass sample from Fa. Nachtmann)

Luster ceramics

Metallic Nanoparticles



Bulk, low density

Sainte Chapelle

near surface, high density

Abbasid, 9.c AC

(Louvre MAOS 657)

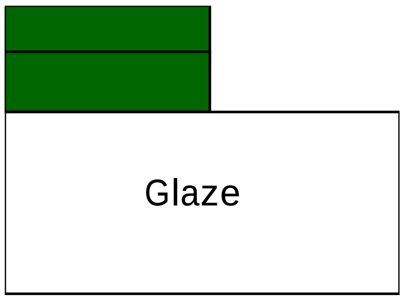
In luster ceramics, arrangement more complicated, complementary information necessary (electron microscopy, ion beam analysis etc.)

Luster ceramics

The luster process

Apply raw painting

Clay minerals, iron oxides, copper and/or silver compounds, sulfur–containing compounds



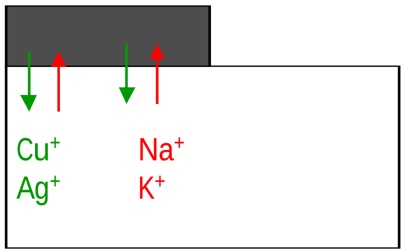
Cross sectional view

Top view

Heat in a neutral/ oxidizing ambient

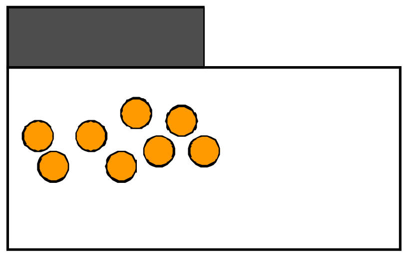
500 -600 ºC

Ion exchange!



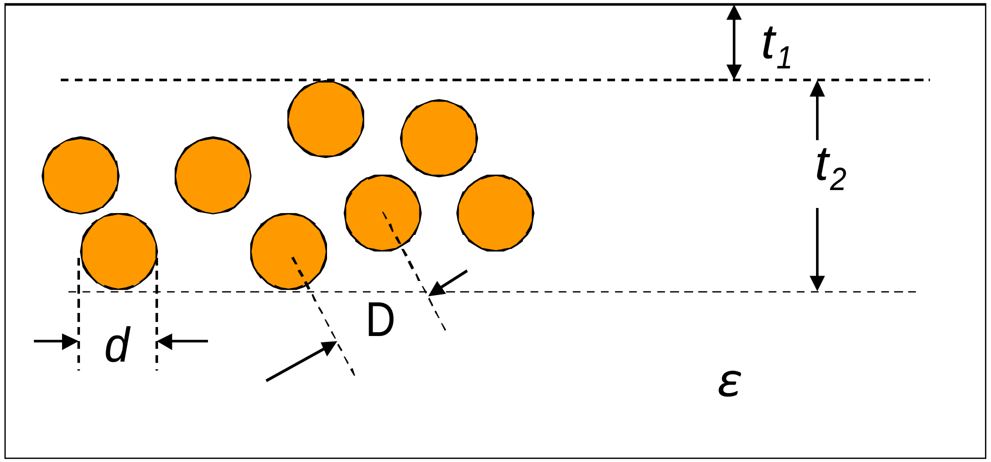
Change to a reducing Ambient

metallic nanoclusters are formed



Luster ceramics

Parameters of interest in the luster nanostructure



t_1 : thickness of the surface glaze several tens nm
t_2 : thickness of the luster layer *μm range*
***d*: 5 to 50 *nm* (Mie electrodynamics)**
***D*: *D*/*d* 1.14 - 1.7 (superposition – interference)**

Typical colors in the 9th century Abbasid lusters are:

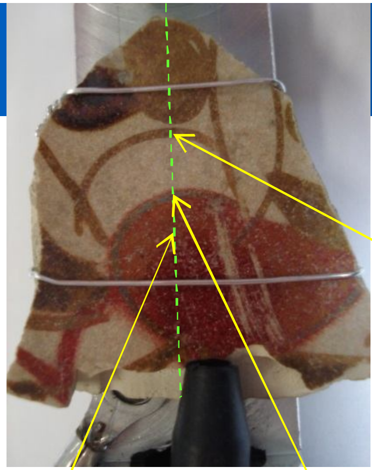
olive green, brown, amber (Ag rich)

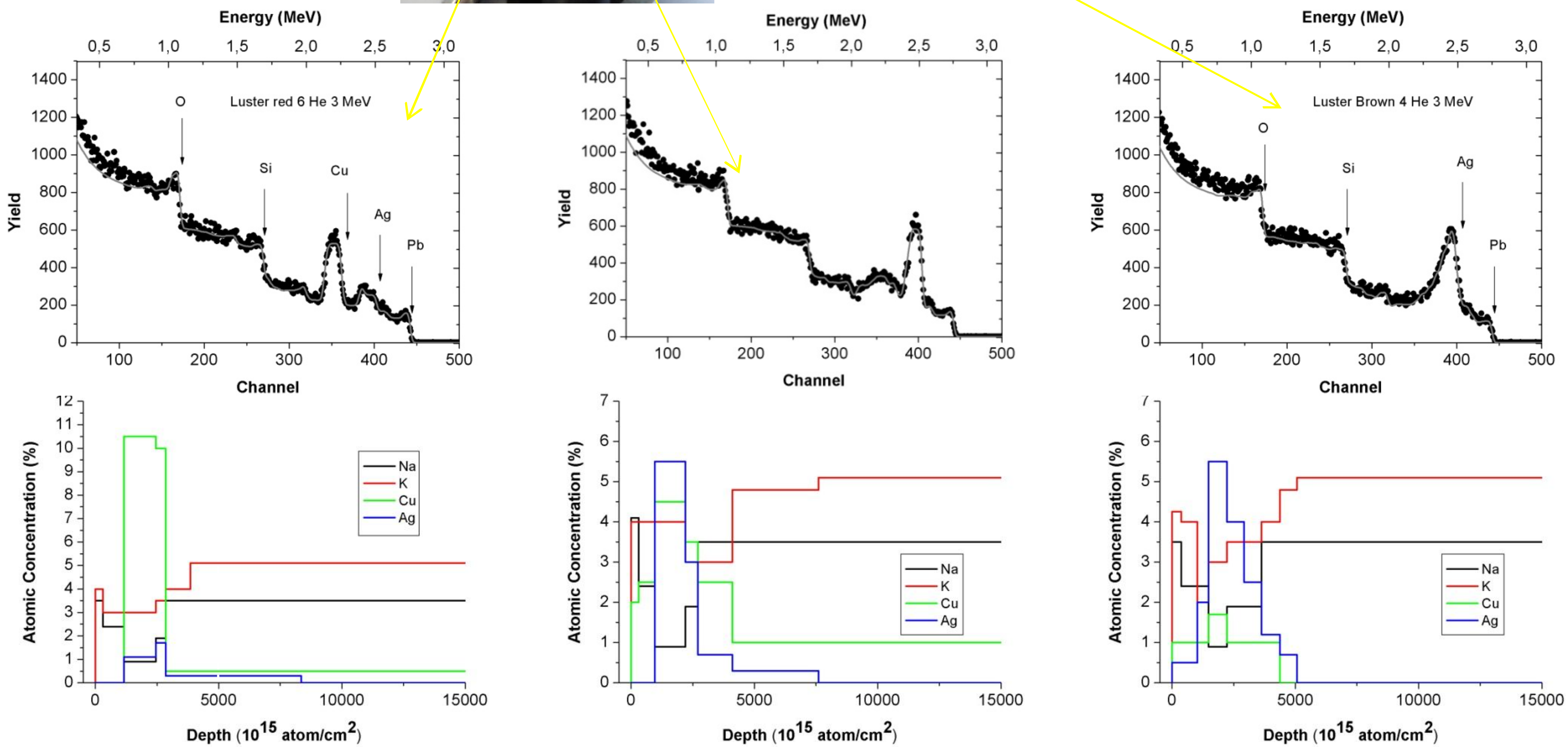
yellow, orange, crimson, and dark red (Cu rich)

Sometimes the artifacts show metallic shine.

RBS on the luster:

Concentration profiles



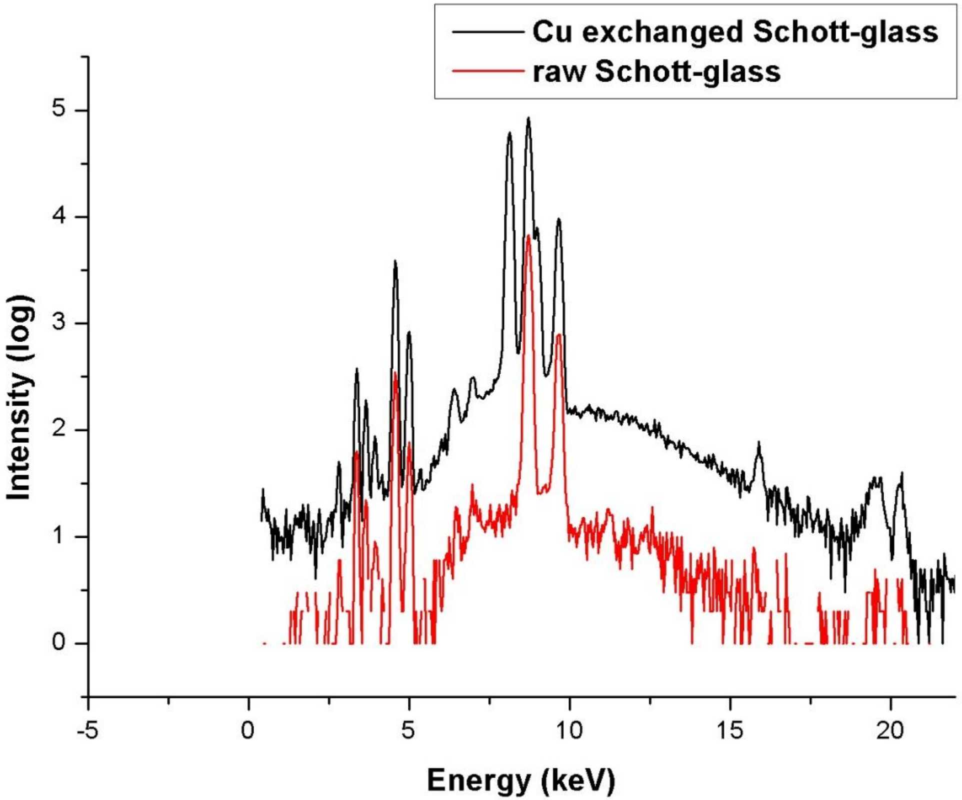


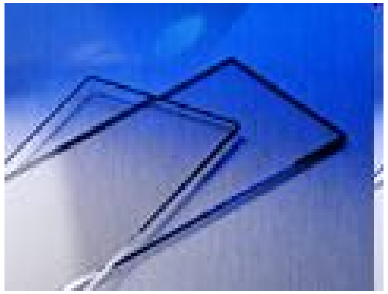
A.Climent-Font, M.Aucouturier, A.Deblonde, T.Dupuis, H.-E.Mahnke, J.Salomon, IBA 2011

Element analysis

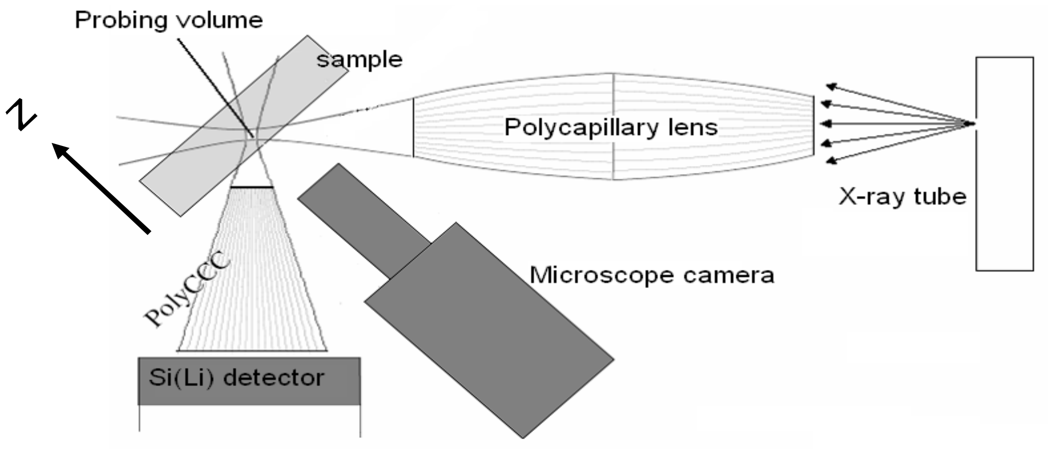
XRF

X-ray fluorescence analysis on simple Schott flat panel glass pieces (1cm x 1cm x 100µm), as purchased, and with Cu ion-exchange (from Cu(1)Cl melt at 510 °C for 10 min)





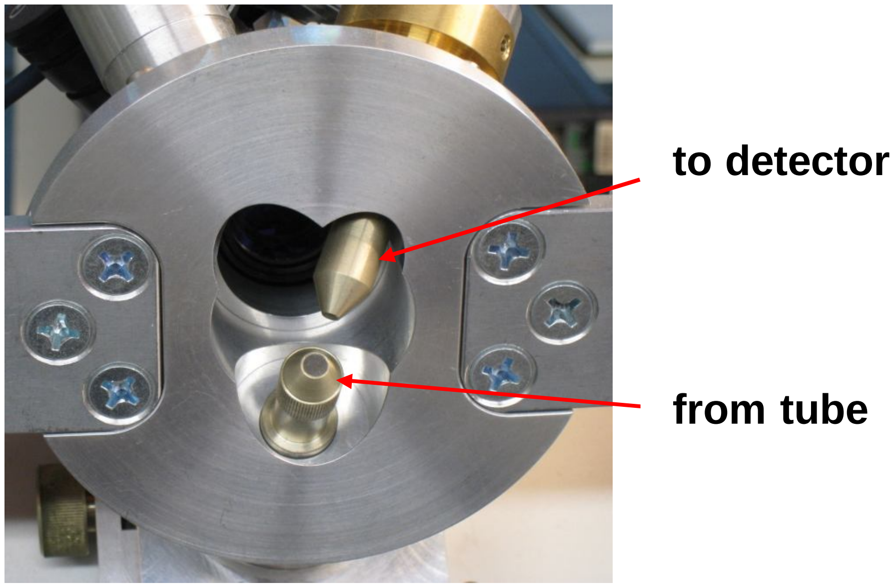
3D-microXRF

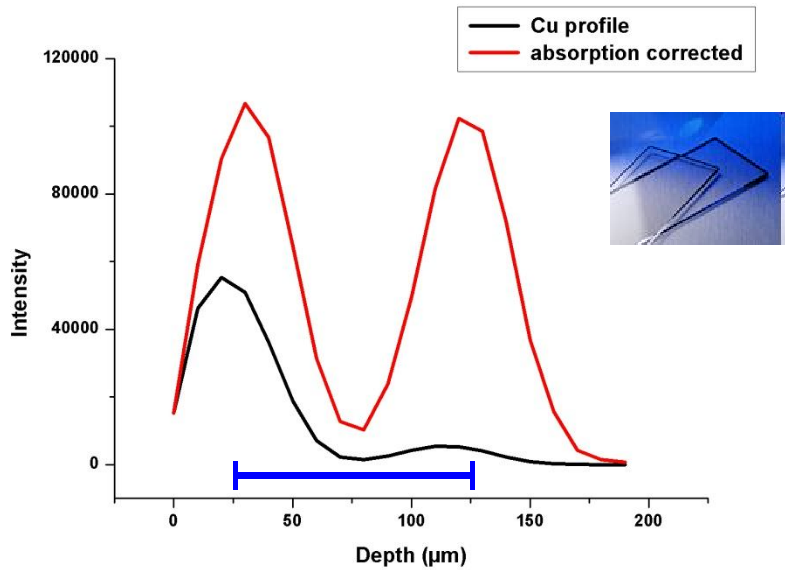


LouX^{3D}

Rh anode, 50 kV, about 50µm spot size, about 45 µm depth resolution, information depth less than 100 µm.

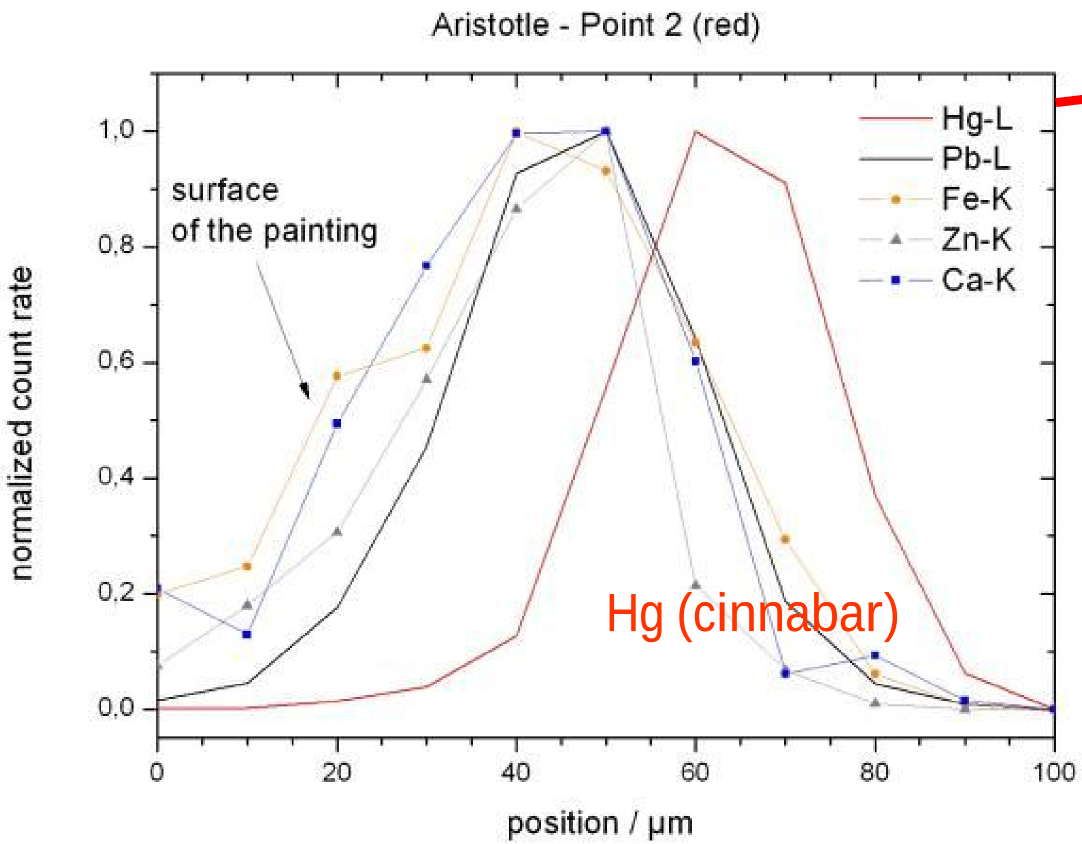
(coop. C2RMF, TU Berlin, IFG)





3D-microXRF

Overpaint in Renaissance paintings



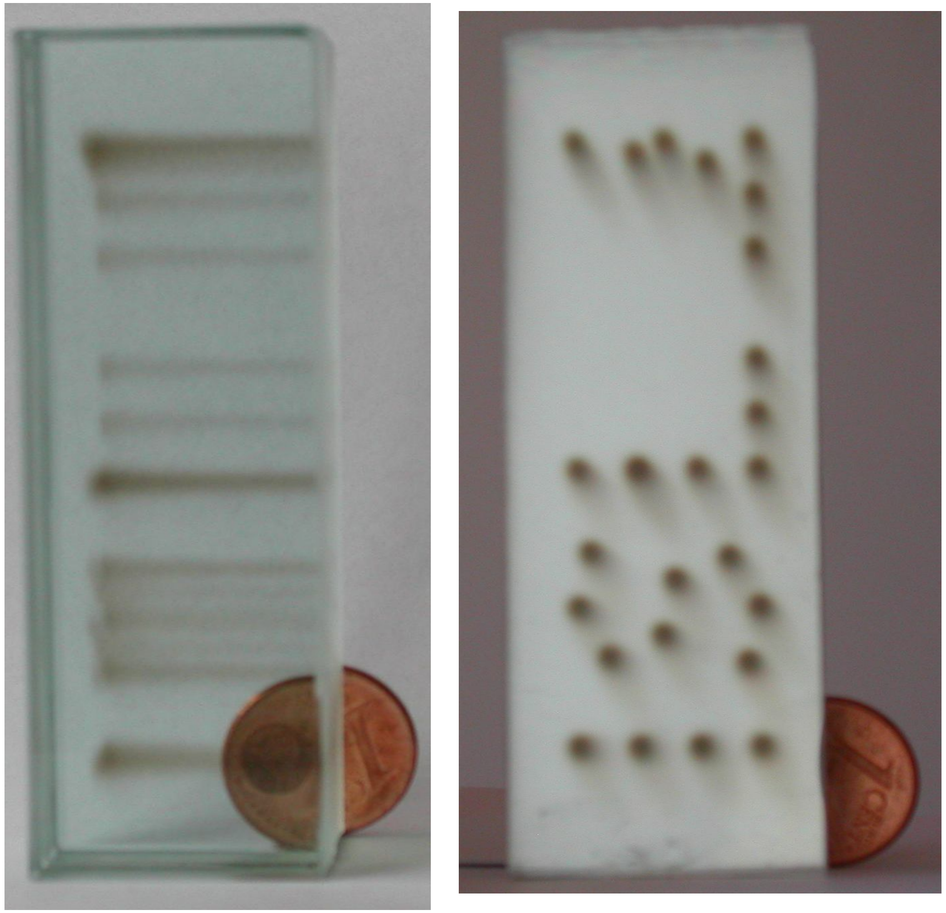
The "Famous Men" – Aristotle

I. Reiche, K. Müller, B. Kanngießer, E. Itié, M. Eveno, M. Menu, TechnArt 2011 Berlin

Ions for analysis

Why are there almost no studies on paintings with low-energy ion beam analysis?
Radiation damage!

Radiation damage!



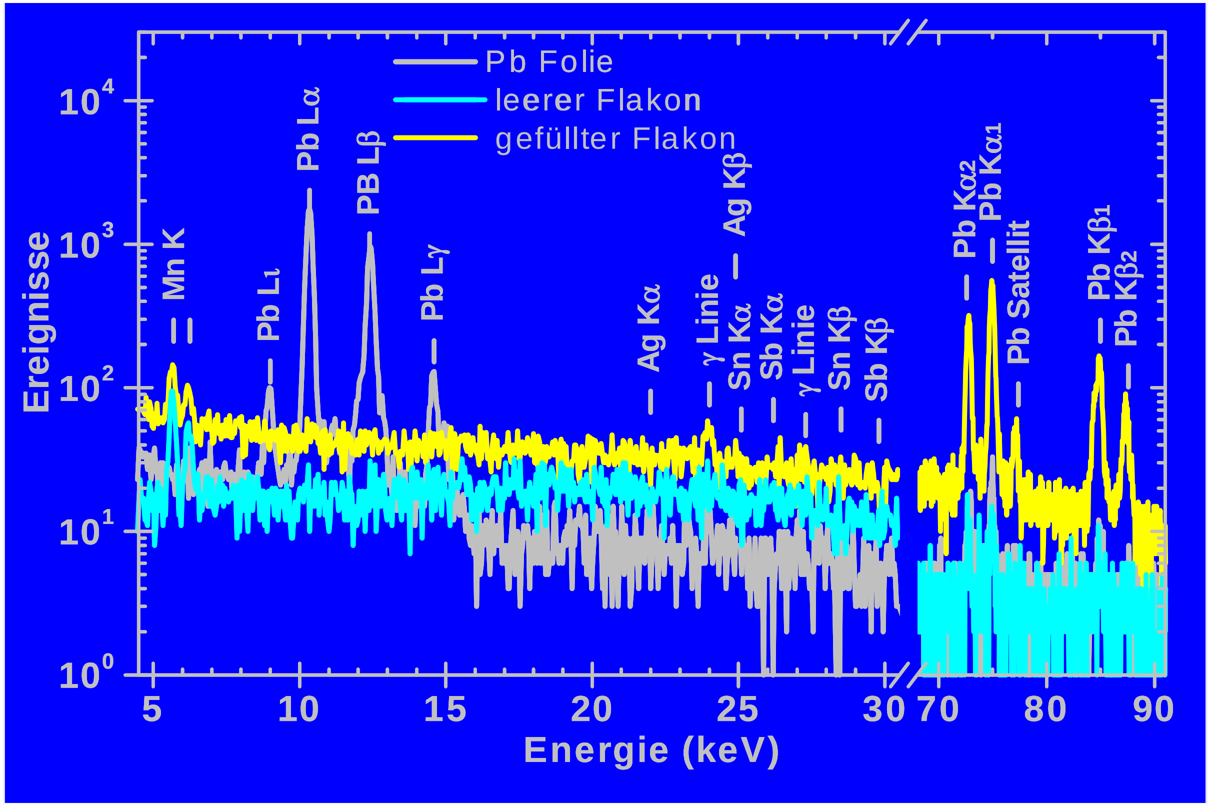
microscopy glass plates irradiated with 68-MeV p

High-energy-PIXE

Egyptian glass bottle (Mus. München):

- **filled with black powder**
- **Original seal ⇨ not to be broken**

(A. Denker et al.)

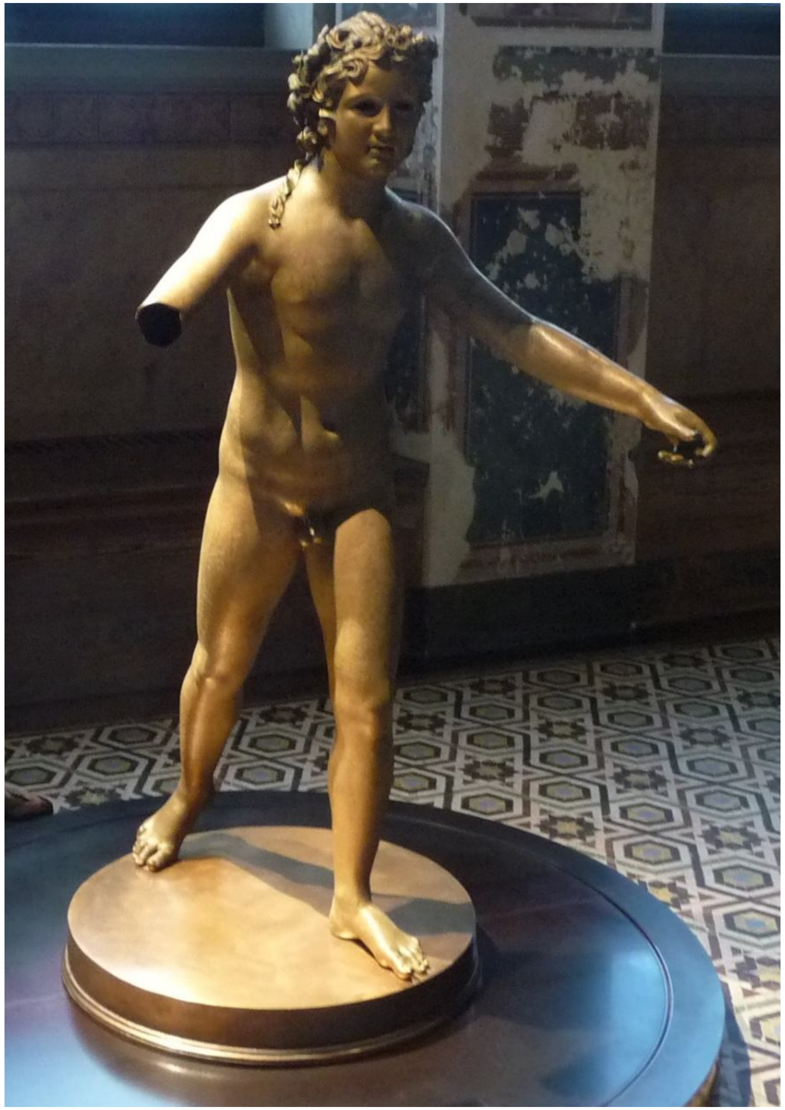


strong Pb K lines: lead compound

⇨ galena (for eye makeup – khol)?

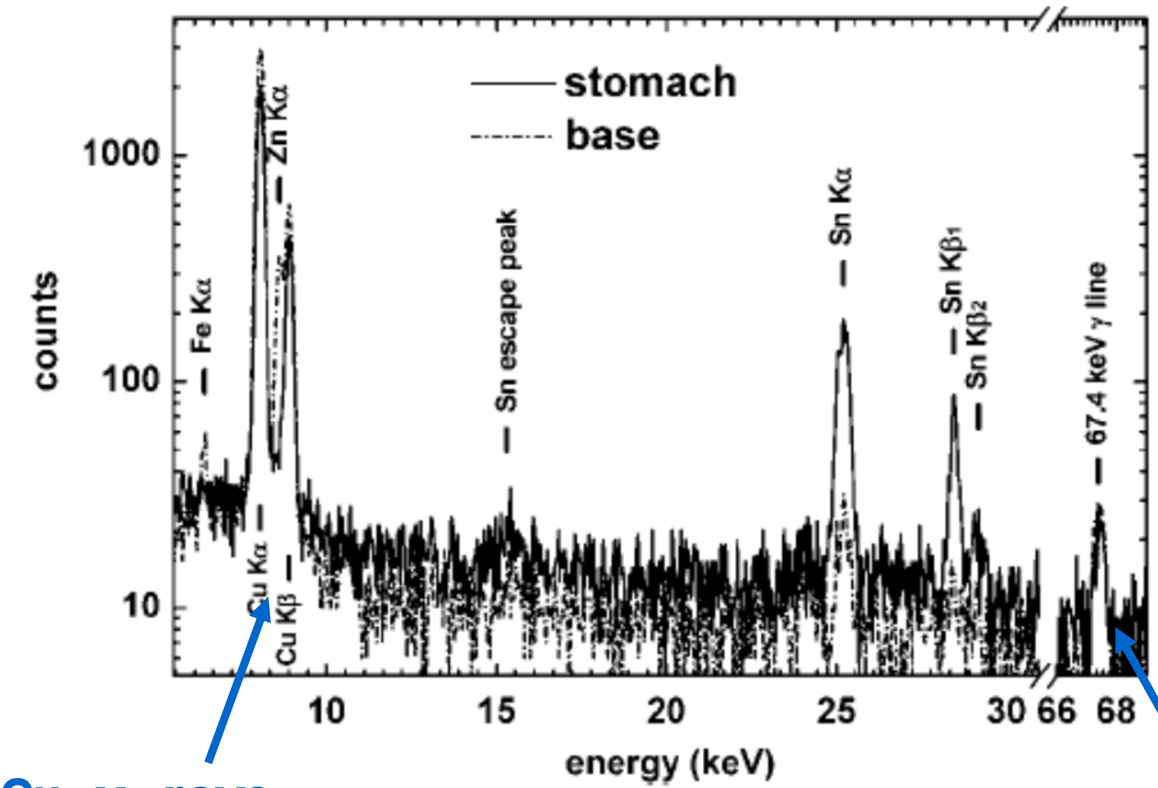
Xantener Knabe (boy of Xanten): Roman Bronze

A. Denker Z. Kertesz, U. Peltz, X-ray Spectr. 2011



Statue in „Neues Museum“

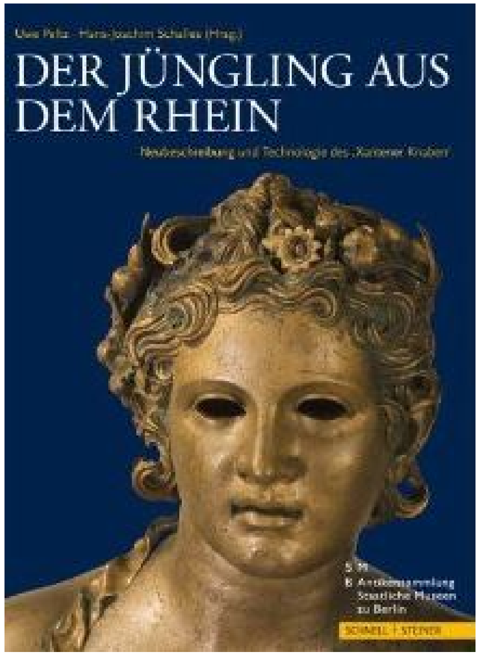
Over the whole statue a rather homogeneous bronze with 83% Cu and 17% Sn and no Pb was found, non-destructively, independent on the size and shape.



$^{63}Cu(p,3n)^{61}Zn$ > ^{61}Ni 67.4 keV γ -line

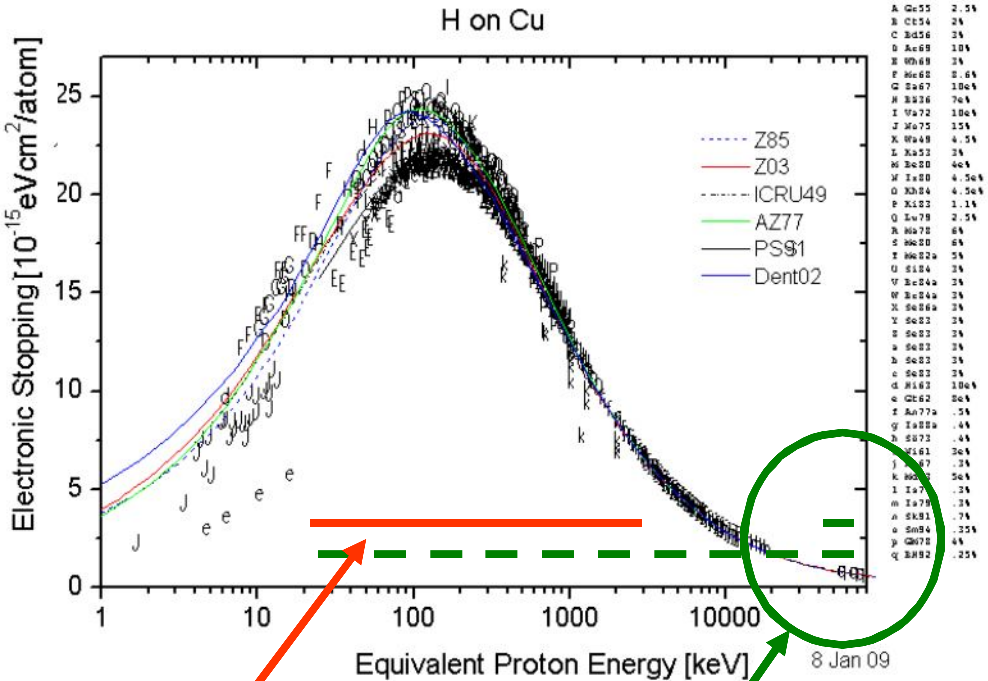
(half life 3.5 h)

U.Peltz, H.J.Schalles



Ions for analysis

Non-destructive?
Radiation damage!



PIXE (low energy):

-- **Maximum energy deposition within region of interest!!**
Be careful with paintings!!

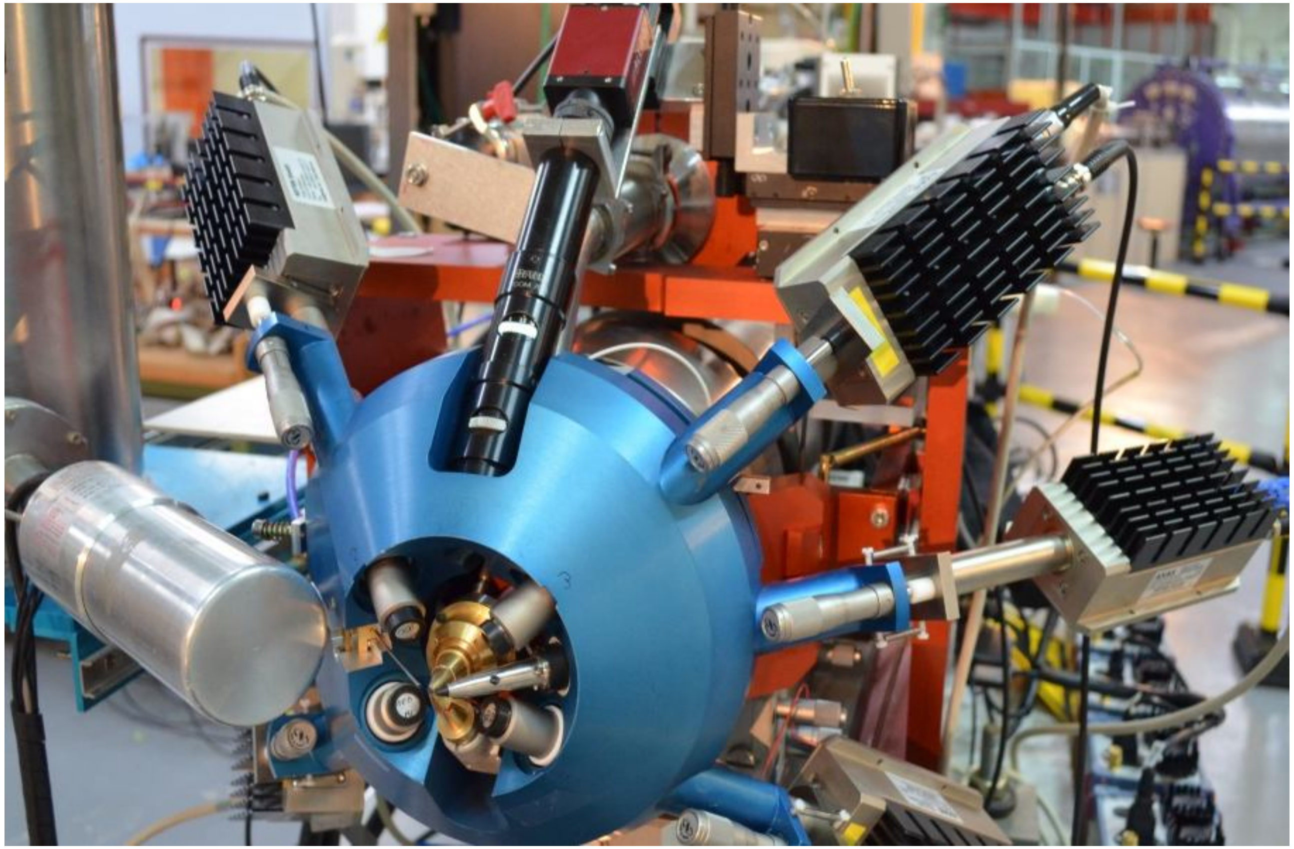
PIXE (high energy):

++ **Minimum energy deposition within region of interest.**
Paintings possible!

Ions for analysis: New developments

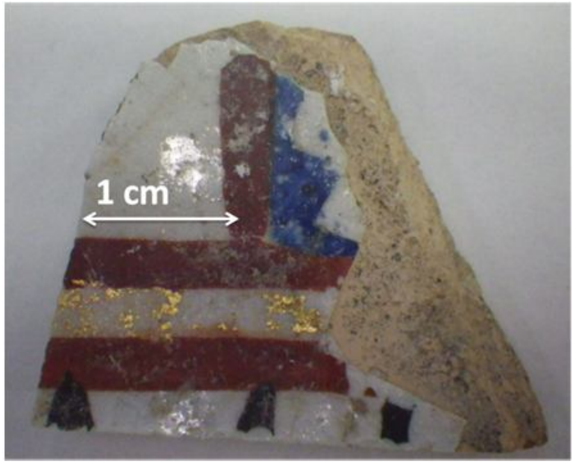
NewAGLAE: systematic elemental imaging and mapping

Increase detection efficiency, beam stability, automatization

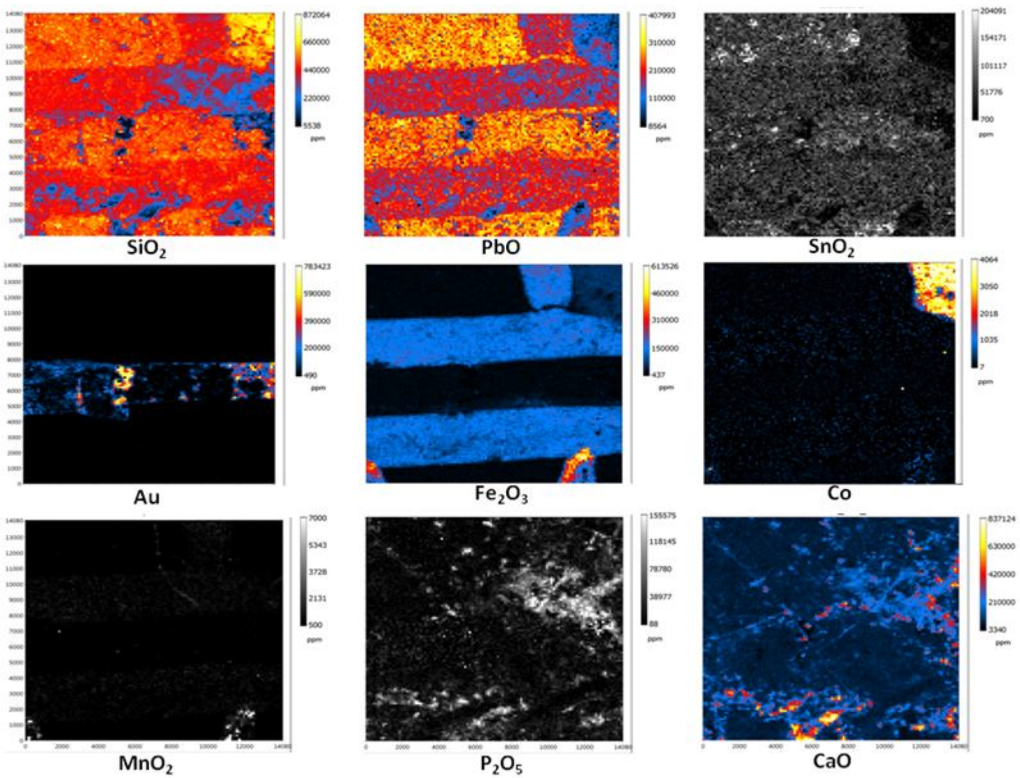


Q. Lemasson[1,2], C. Pacheco[1,2], B. Moignard[1,2], L. Pichon[1,2], Th. Guillou[2,3], Ph. Walter[2,3]
[1] C2RMF – Palais du Louvre – 14 quai F. Mitterrand 75001 Paris
[2] New AGLAE – FR3506 CNRS/Ministère de la Culture et de la Communication
[3] LAMS – UMR 8220 CNRS/UPMC 3 rue Galilée 94200 Ivry/Seine

Medieval ceramic (islamic, 14^{th} – 15^{th} century)



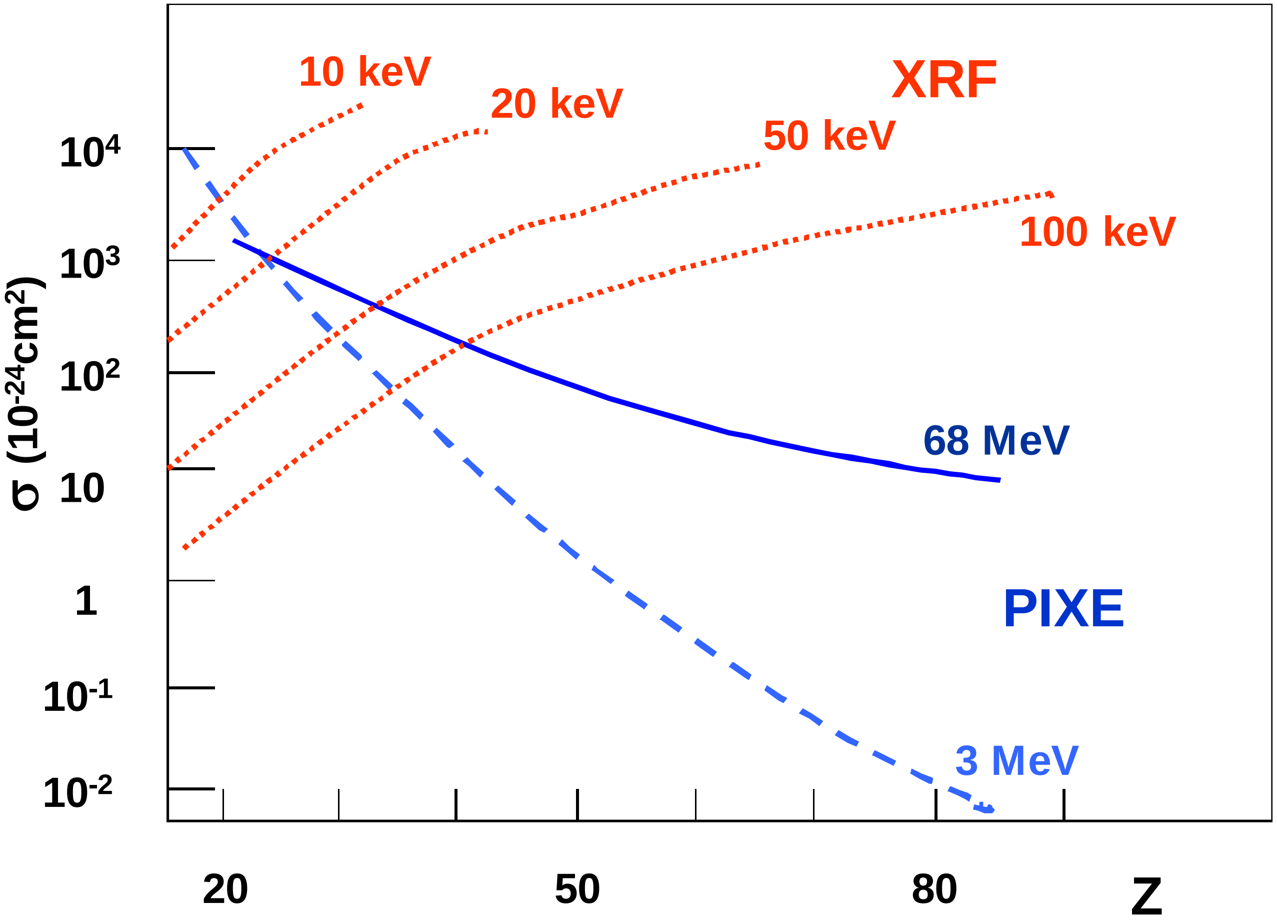
1,4x1,4 cm²



Ions and x-rays for analysis

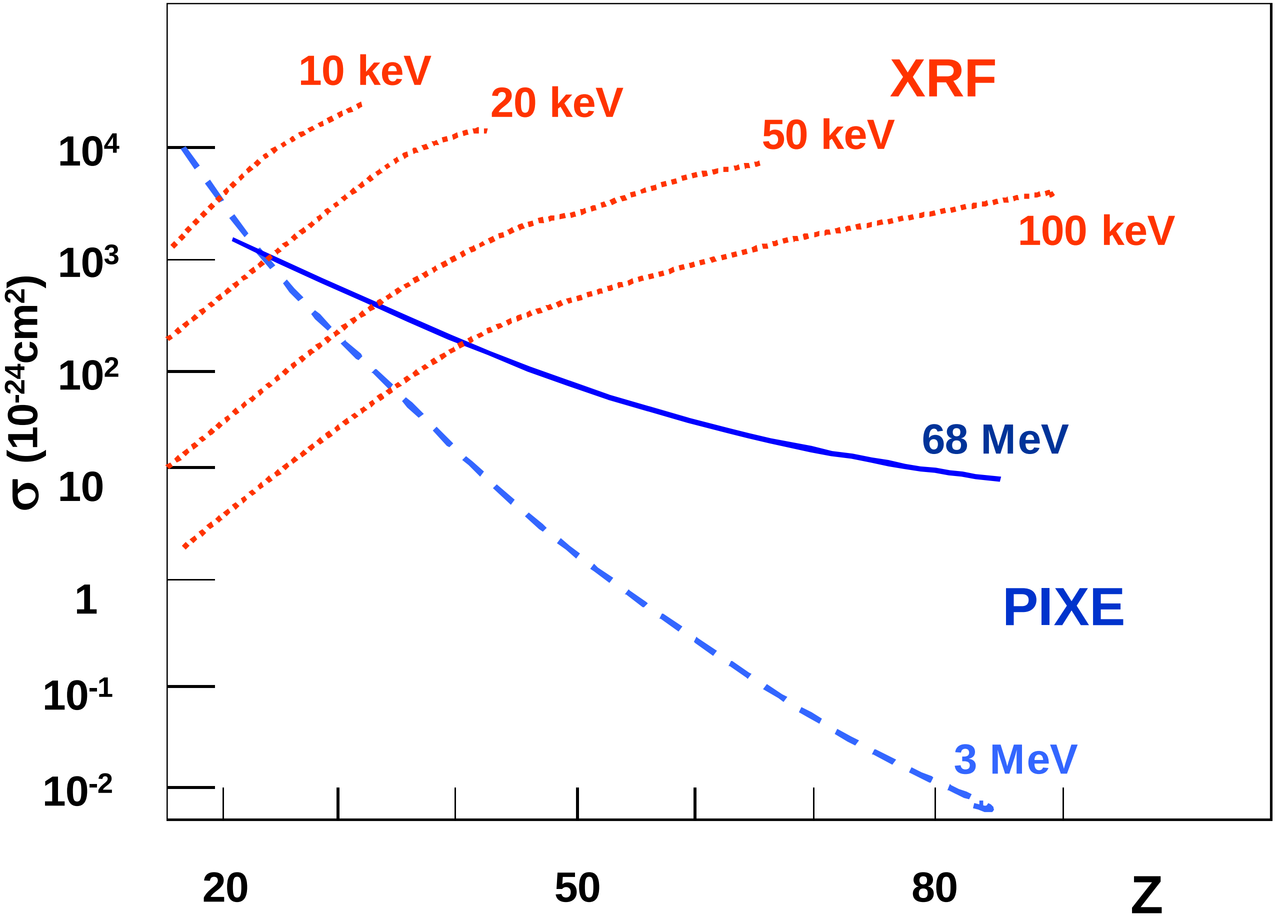
Excitation by x-rays (XRF) or by protons (PIXE)

- cross section for absorption and for ionization -



Perspectives for new x-ray sources

Argument for higher x-ray energies for (XRF)



for x-rays: absorption edges: switch on/off

for protons: global excitation with respect to Z

Synchrotron sources for « small » labs

New developments in the fields of

- femtosecond lasers and electron beams

- high-intensity femtosecond lasers

Sources for « small » labs

- femtosecond lasers and electron beams
  tomorrow (even today)

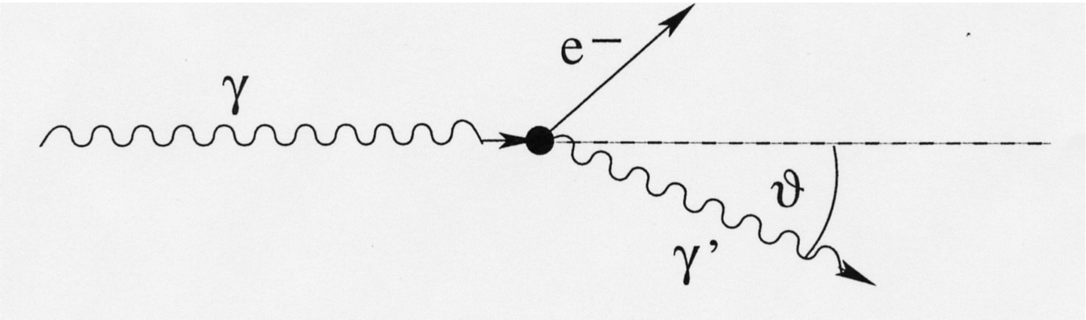
- high-intensity femtosecond lasers
  future

New x-ray sources – table top?

Standard Compton effect:

Electron almost at rest!

$$E_{photon}' = E_{photon} / \{1 + (E_{photon} / mc^2)(1 - \cos\delta)\}$$

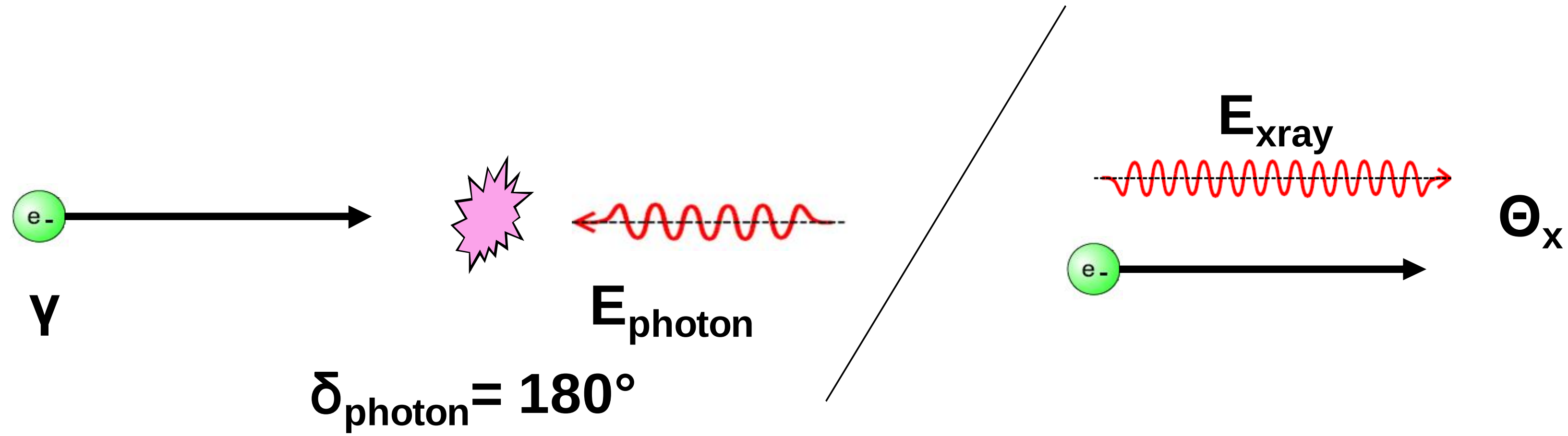


but, now:

Inverse Compton effect:

Collision between a fast electron γ and a photon results in an energy increase for the photon

$$E_{x\text{-}ray} \approx 2\,\gamma^2 E_{photon} (1 - \cos \delta_{photon}) \;/\; (1 + \gamma^2 \Theta_x^2)$$

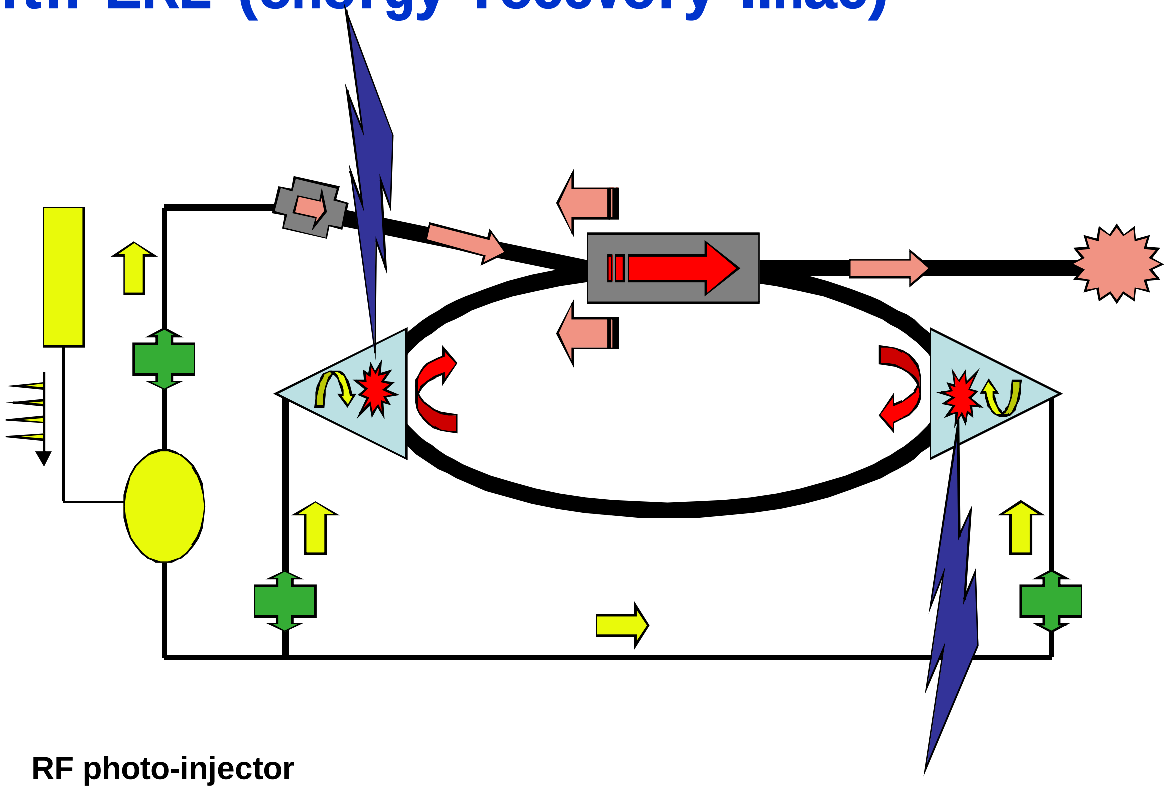


e.g. 70 MeV e, 1 eV photon → 80 keV x-ray

monoenergetic, energy variable, cone-like emission, coherent

New x-ray source

Possible design with ERL (energy recovery linac)



Legend

RF photo-injector
SC Linac (accel / deccel)
'Low' energy Beam dump
Seed laser
Light amplifier (main laser)
Time delay
Optical cavity (photon storage) + 'electron-photon' interaction point
X rays (energy upshifted photons by inverse Compton process)

New x-ray source

Specialties:

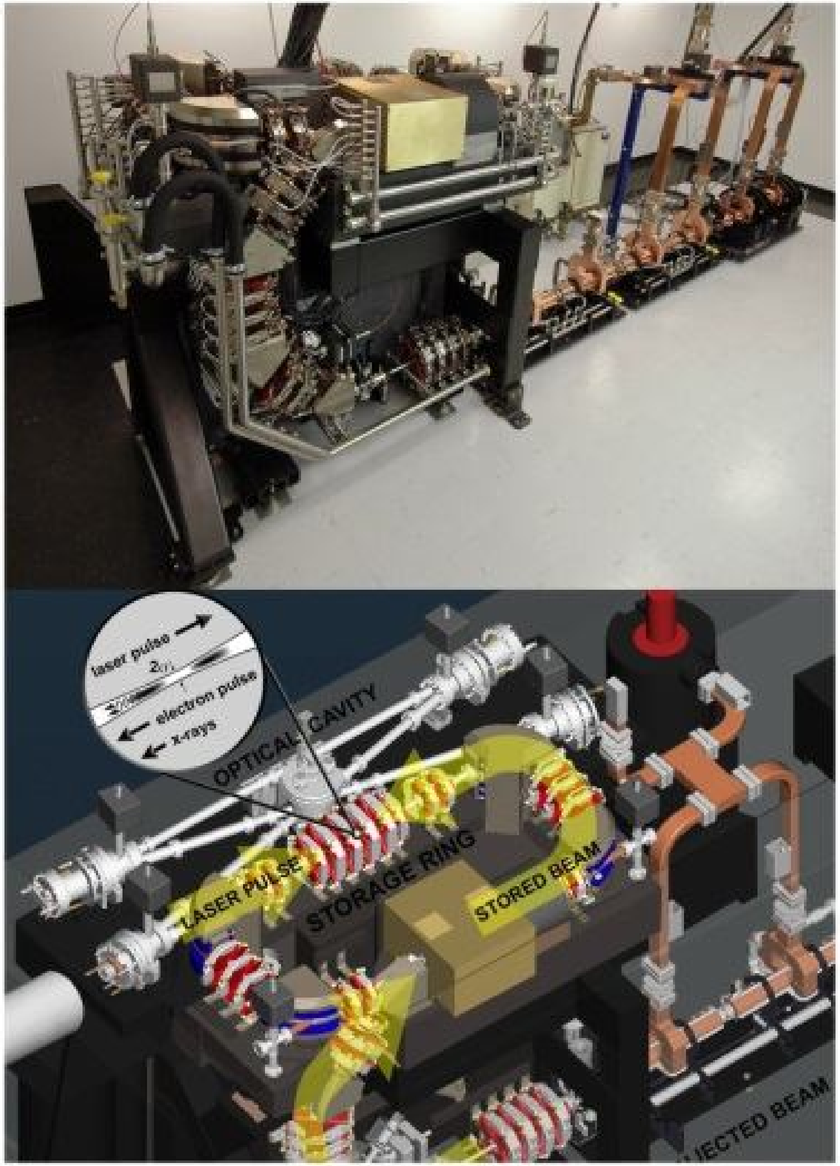
- Monochromatic x-rays: resolution depends on beam quality.
- Variable energy (in principle)
- High degree of coherence: increased contrast for imaging/tomography

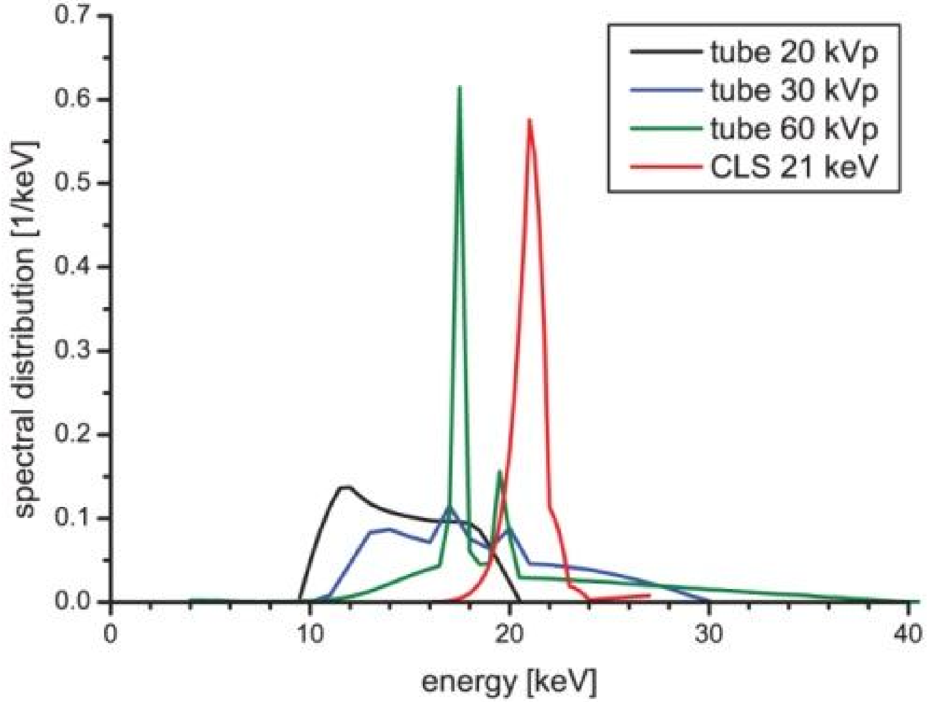
Realisation under way for archaeometry,

resp. cultural heritage research in general, by CNRS in Orsay as

ThomX

(A. Variola, Ph. Walter et al.)



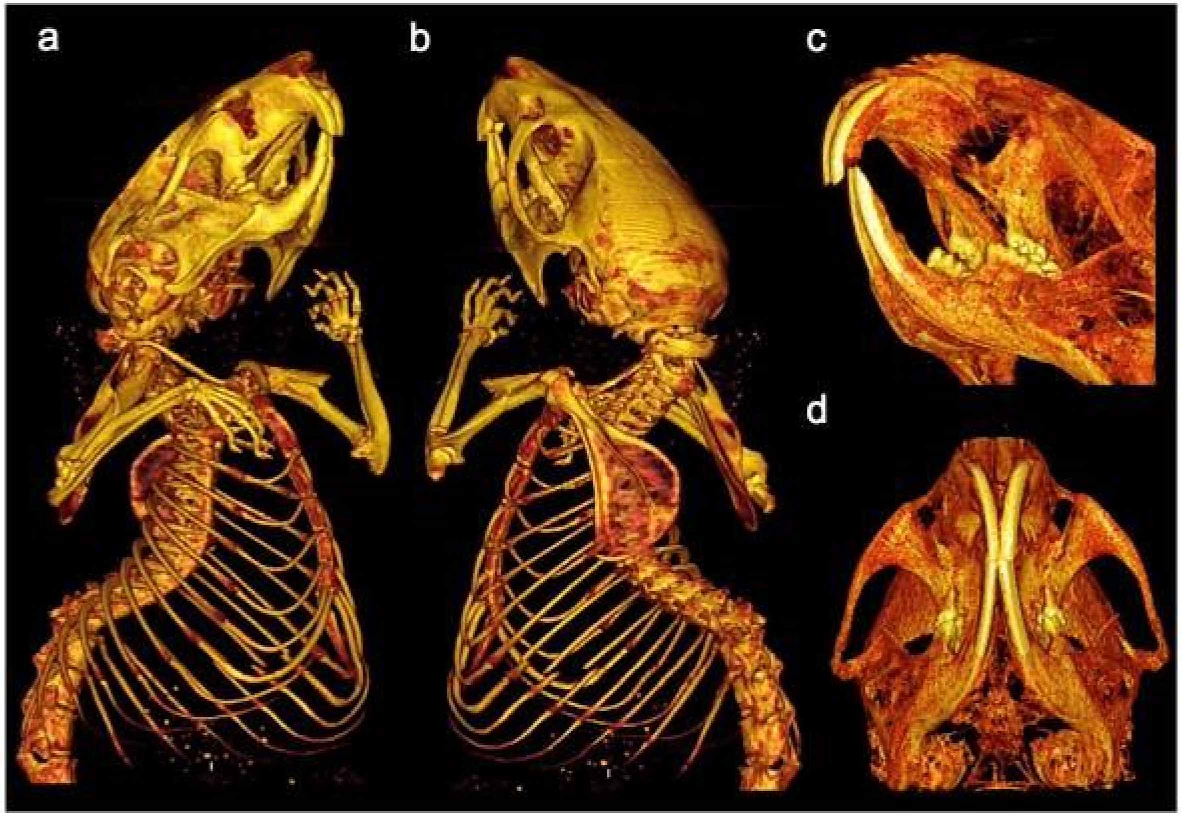


R.Ruth (Lyncean), F.Pfeiffer (TUM)

λ= 1064 nm, E=34 MeV)

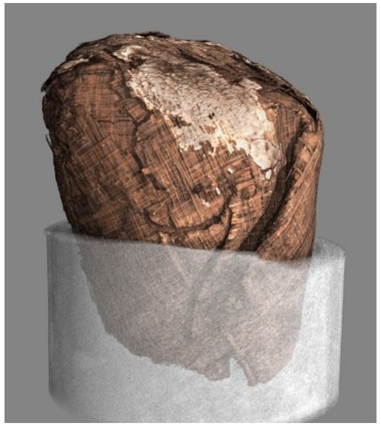
K.Achterhold et al, SREP-12-03112

Absorption tomography of a mouse

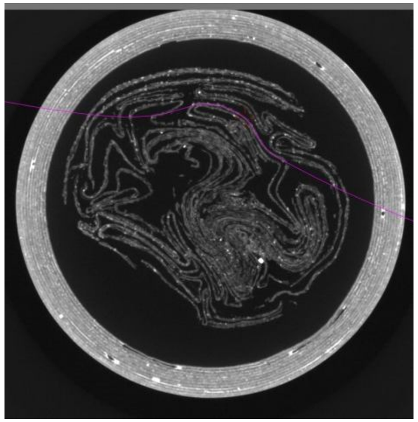


Perspective: reading of unfolded papyri

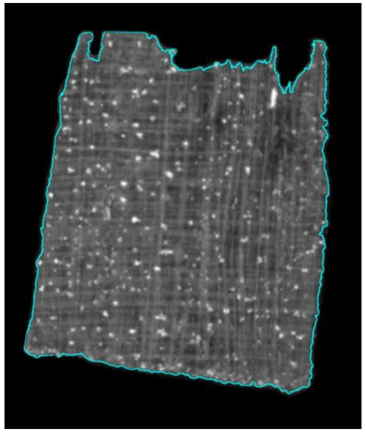
Photo



3D-reconstruction



Line for an unfolded 2D-part



segment- enhanced

No Fe ink!

with GE phoenix v|tome|x m

M.Krutzsch, H.-E.M., D.Neuber, H.Weber, G.Zacher 2012

Next step for metal ink: prescreening with portable XRF for Fe or Cu, then „standard“ CT with sub-micrometer resolution.

Beyond that for carbon ink: Inverse Compton source using phase contrast

Summary

I hope I have shown that ions and x-rays add complementary information when investigating cultural heritage objects.

And:

There is a built-in complementarity between large scale installations (like synchrotrons) and out-sourced mobile systems, the development and improvement on mobile system is not possible without the development on large scale instrumentation.

Thank you !

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ÄM	M. Krutzsch, V. Lepper, F. Seyfried

see H.-E.Mahnke, A. Denker, J. Salomon, CR Physique 10 (2009)660

Information

Gordon Research Conferences
frontiers of science

Next Gordon Research Conference on

Scientific methods in cultural heritage research

July 27 – August 1, 2014,
Sunday River Resort, Newry, Maine, USA,
Chair: Francesca Casadio, Philippe Walter

Preceding is a Gordon Research Seminar ("New")

Scientific methods in cultural heritage research
-Molecular and Material Analysis for Art, Archaeometry and Conservation-

July 26-27, 2014, Sunday River Resort, Newry, ME, USA
Chair: Stephanie Zaleski

see www.GRC.org.