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Materials Analysis Using Fast Ions

Introduction: Energy Loss

PIXE – Proton Induced X-ray Emission

RBS – Rutherford Back Scattering

ERDA – Elastic Recoil Detection Analysis

Introduction: Ion – Target Interaction

- elastic atomic collisions:

  very low energies
  typically below a few keV
  Ion Scattering Spectrometry (ISS)
  surface composition and structure

- inelastic atomic collisions:

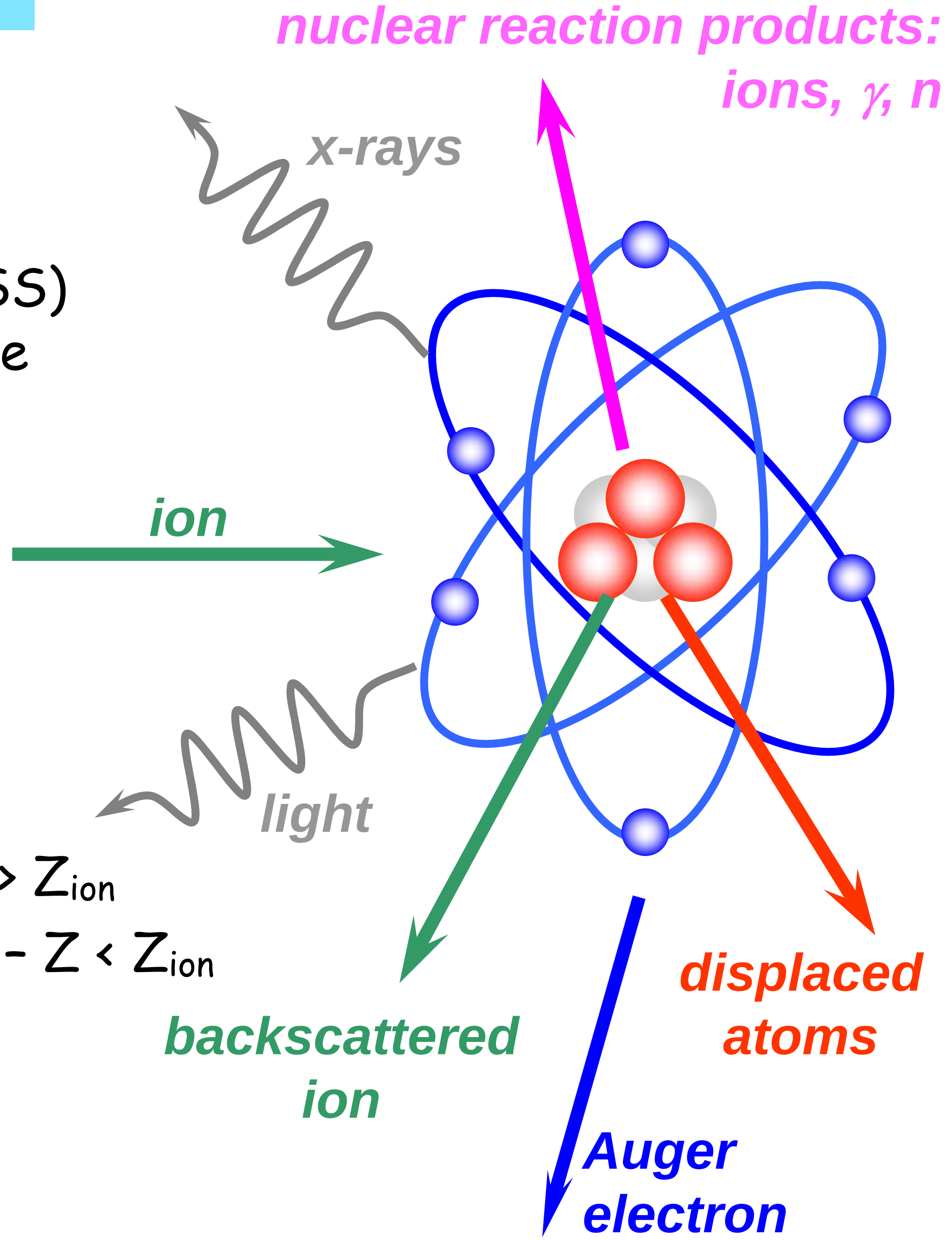
  ionisation of target atoms
  characteristic x-ray emission
  Particle Induced X-ray Emission,
  detection of elements with Z > 11

- elastic nuclear collisions:

  Rutherford-Back-Scattering – $Z > Z_{ion}$
  Elastic Recoil Detection Analysis – $Z < Z_{ion}$

- inelastic nuclear collisions:

  Nuclear Reaction Analysis



Introduction: Energy Loss

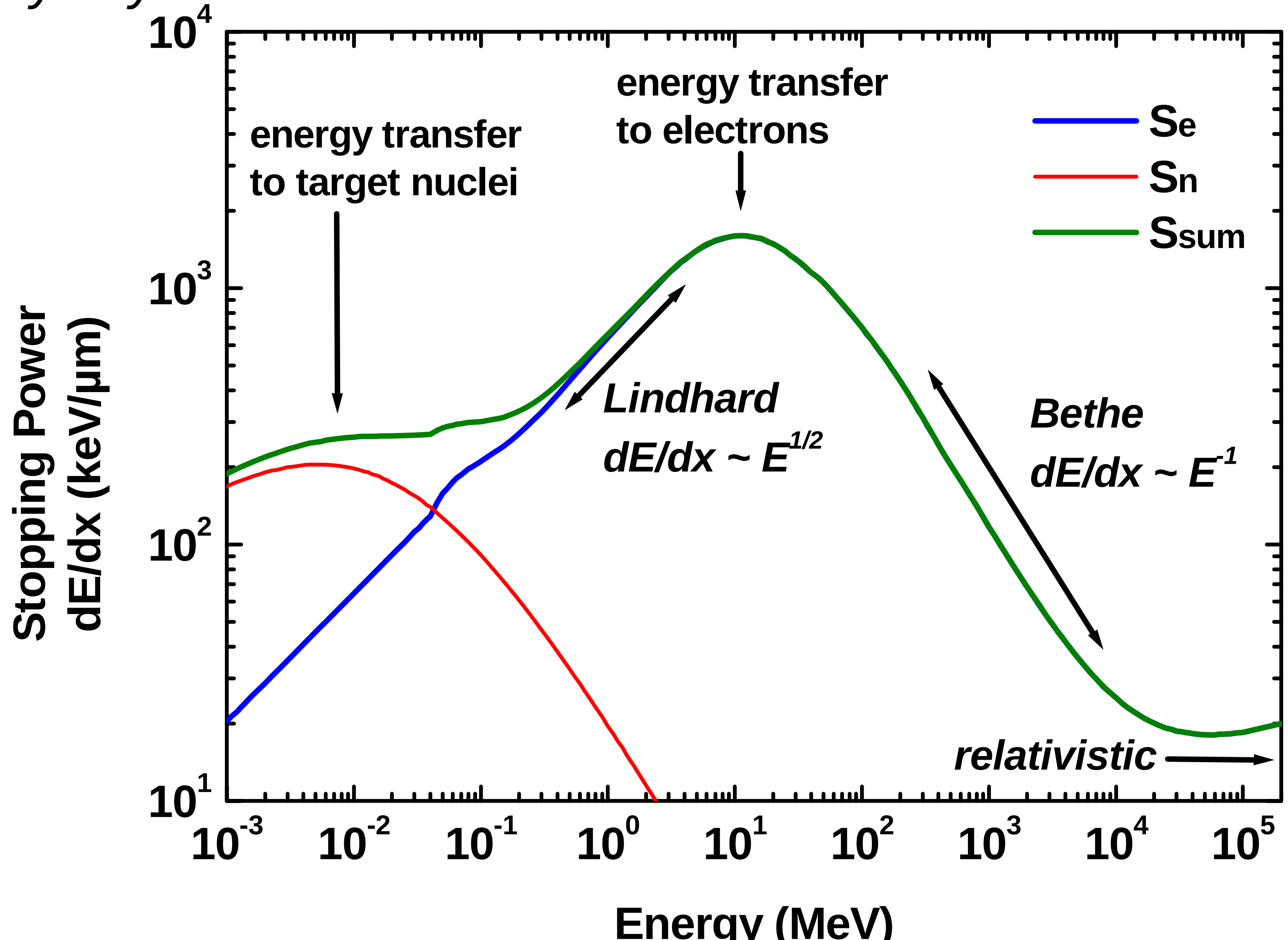
- interaction ion – target atoms:
  ⇒ slowing down of the projectile
- depends on
  - ion mass
  - ion energy
  - irradiated material

Experimental data, computer software, e.g. SRIM 2003

ion and energy	Sn (keV/µm)	Se (keV/µm)	range (µm)	lateral straggling (µm)
p, 3 MeV	0.01	20	92	4.1
p, 68 MeV	0.001	1.8	21000	860
He, 3 MeV	0.17	190	12	0.49
197Au, 350 MeV	90	19000	30	0.91

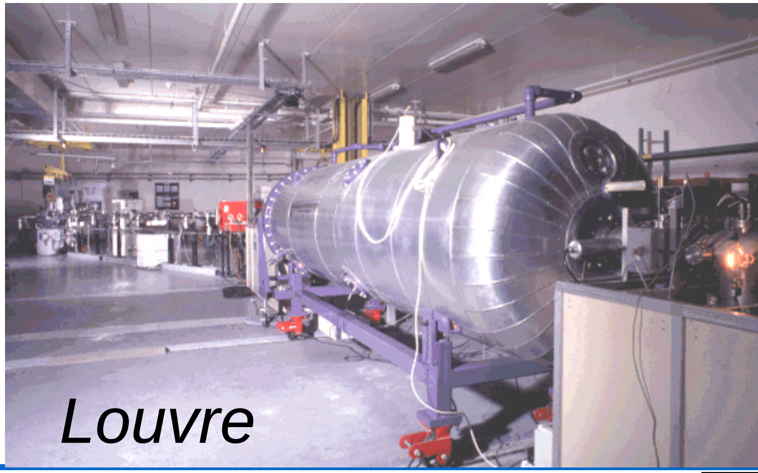
Introduction: Energy Loss

²⁰Ne on Polyethylene



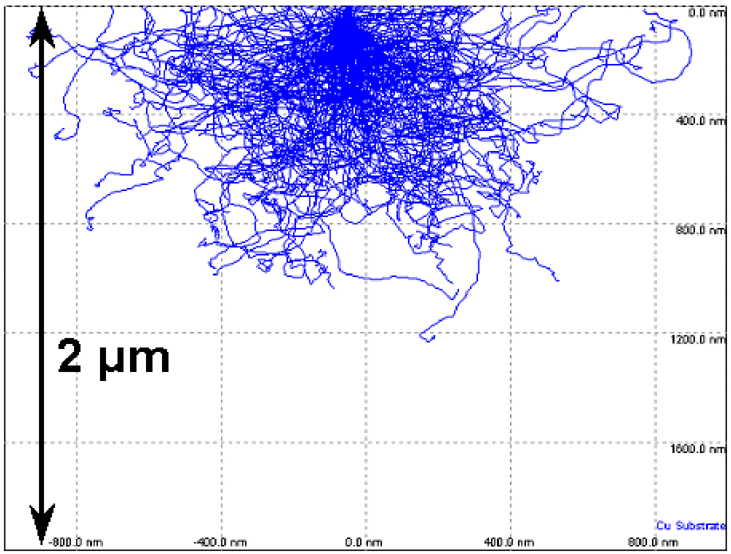
PIXE - Introduction: History

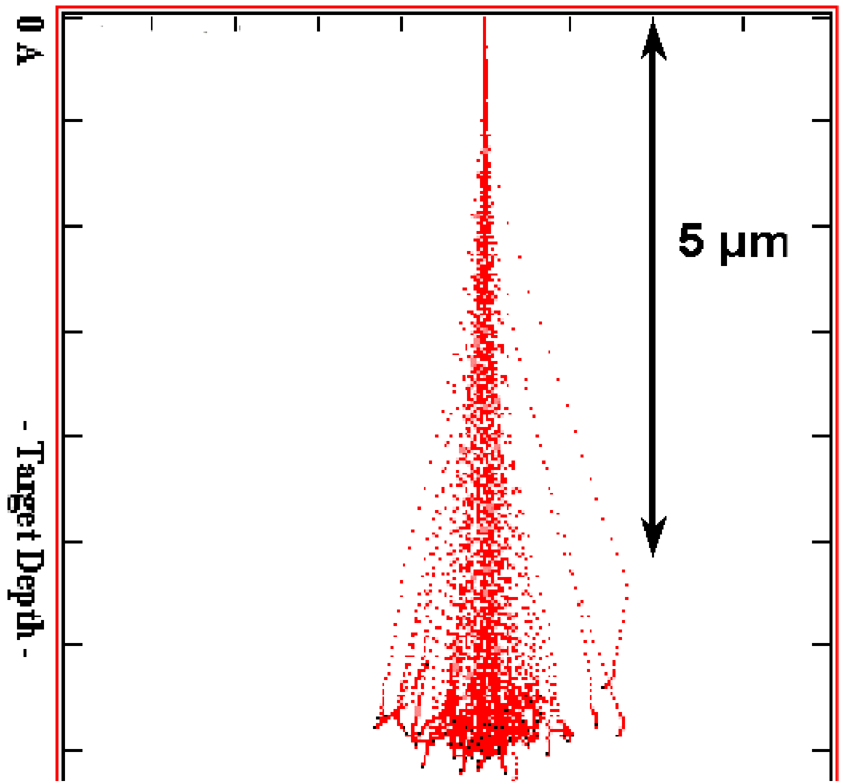
- PIXE = Particle Induced X-ray Emission
- first observation by Chadwick
  (Phil. Mag. 24 (1912) 54:
  x-ray emission induced by charged particles from a radioactive source
- Mosely 1913: the energy of the x-rays scales with Z^2
- first application as today:
  T.B. Johansson et al, Nucl. Instr. Meth. B 84 (1970) 141
- 2005: widely used technique in archaeology, biology, geology, environmental sciences.....
  Louvre Museum: dedicated accelerator for ion beam analysis



PIXE – Intro: Excitation Possibilities

- x-rays from x-ray tube or synchrotron
  - X-ray fluorescence analysis XRF
- electrons
  - electron microprobe, e.g. in scanning electron microscopes
- with ions





PIXE – Intro: Advantages

x-ray tube:

- larger background due to photon scattering
  ⇒ lower sensitivity

radioactive source, 1 Curie:

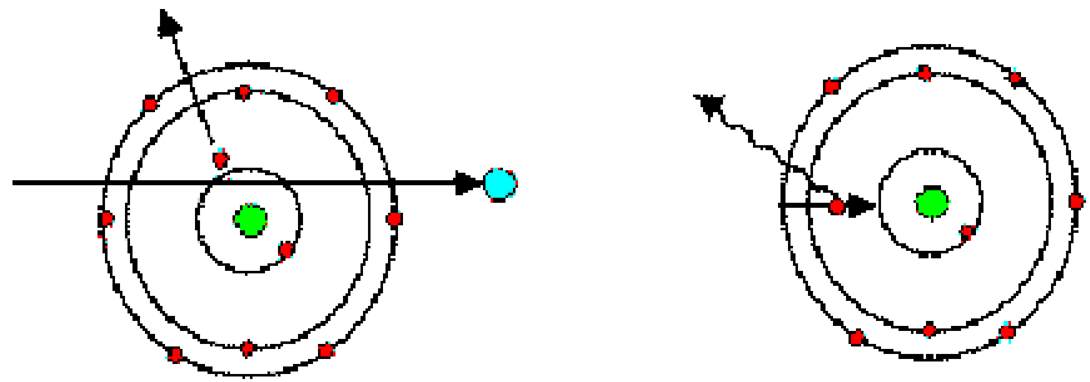
- 3×10^7 particles per 1 mm^2 per second
- range in Cu ~ 11 μm
- radio-safety, larger background

accelerator:

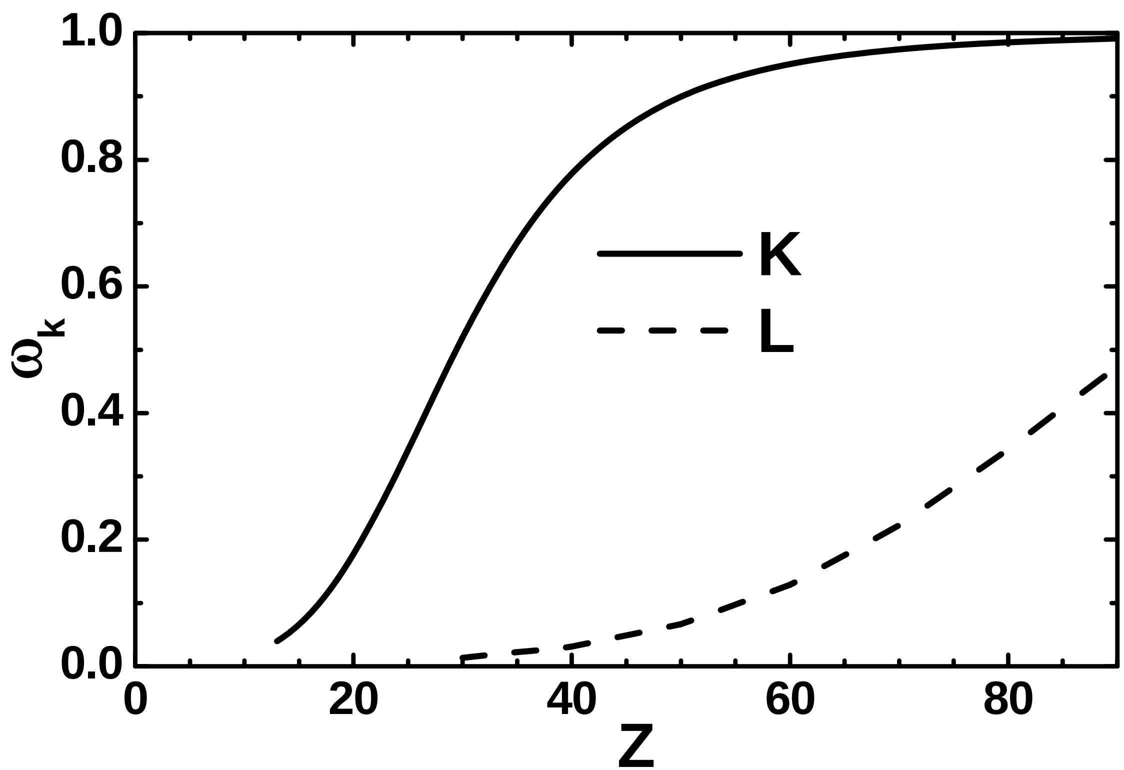
- 10^{13} particles per 1 mm^2 per second
- range in Cu for 3 MeV protons: ~ 34 μm
- beam can be focussed

PIXE - Basics: Fluorescence Coefficient

- hole in K- or L- shell
  $E_{kin} > E_B$

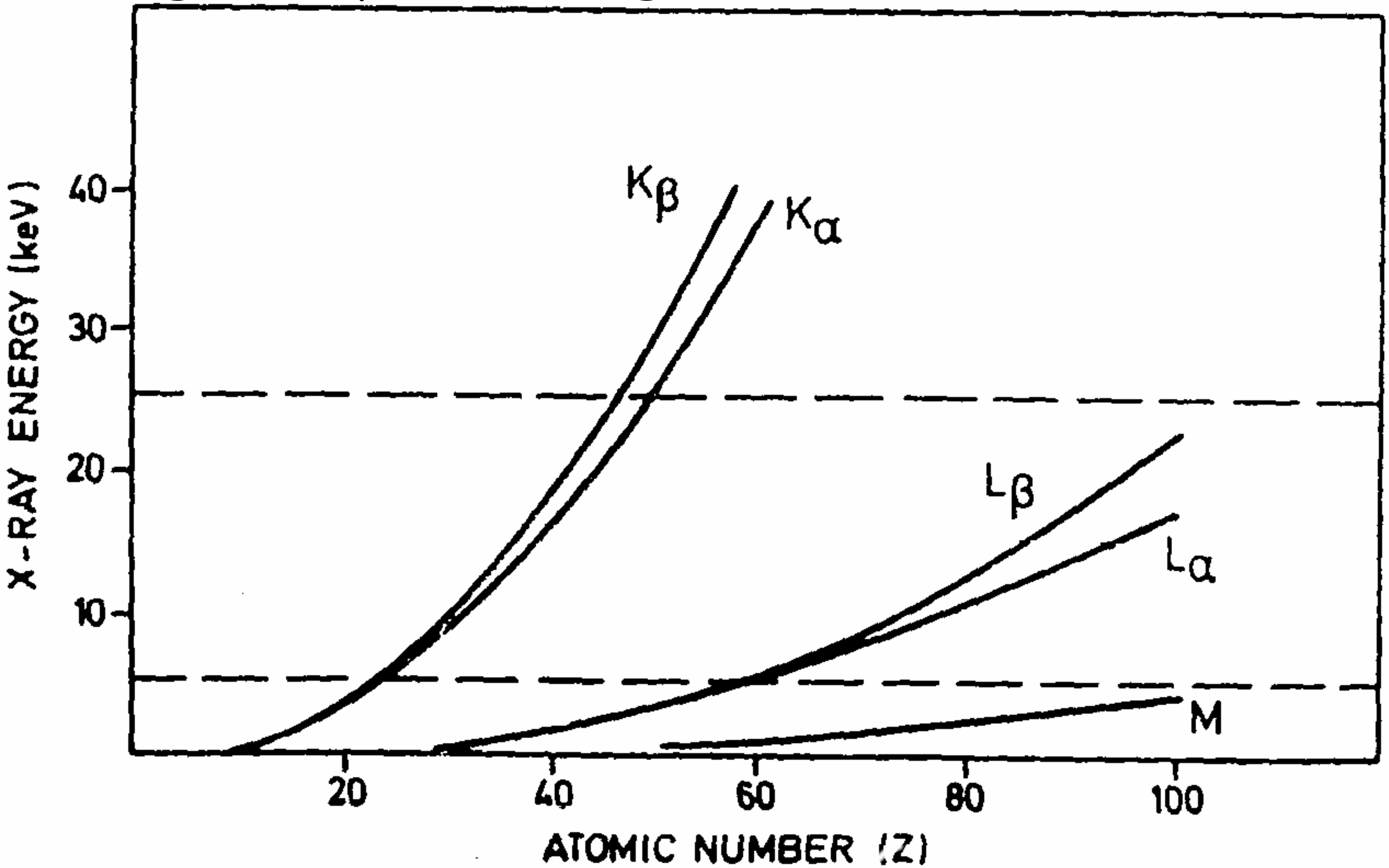


- recombination via
  X-ray or
  Auger electron:
  fluorescence yield

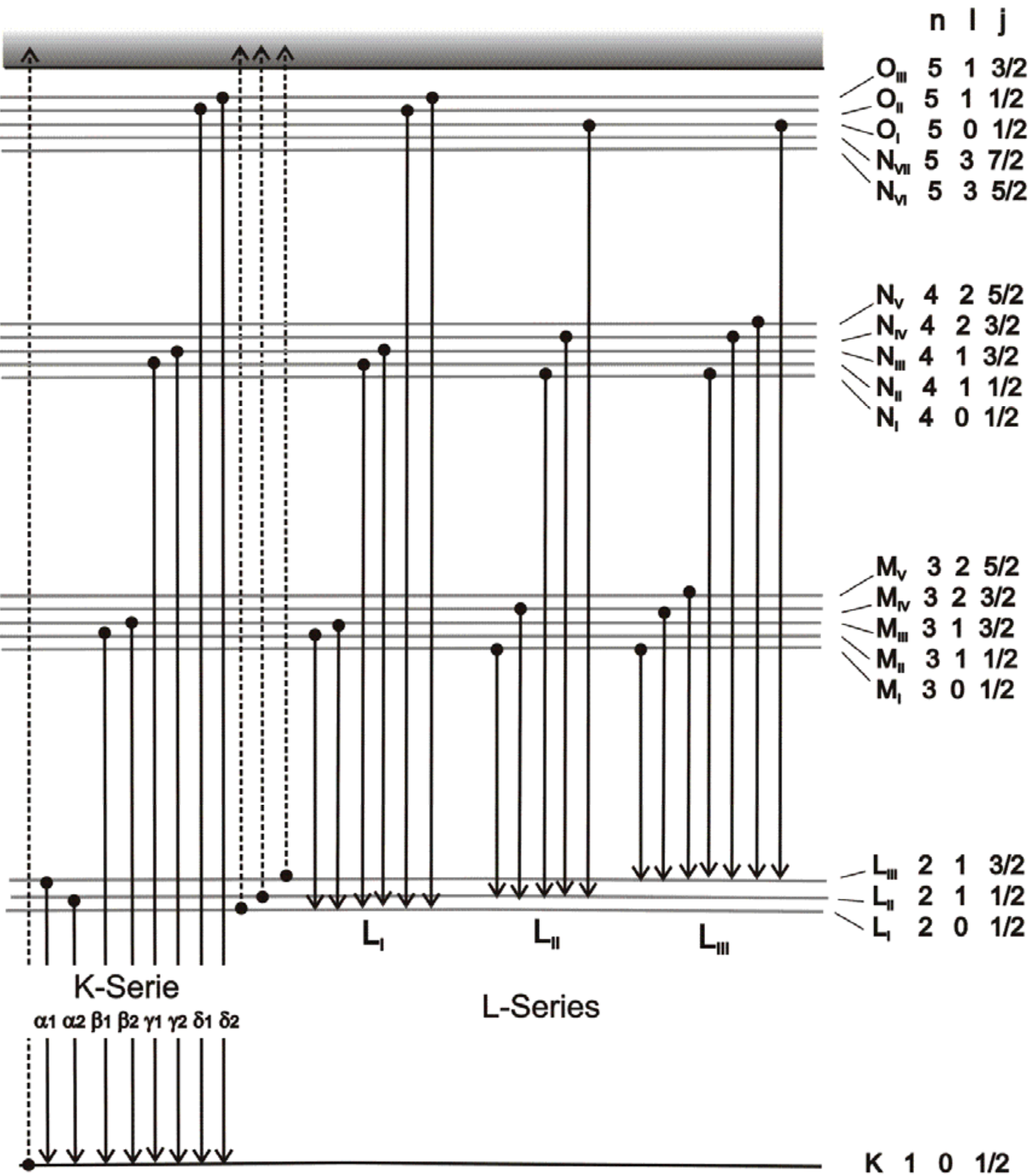


PIXE – Basics: Moseley Law

- frequency $\nu = c(Z-1)^2$ $c = 2.48 \times 10^{15}$ Hz
- ambiguities possible, e.g. Kα As - Lα Pb, both at 10.5 keV



PIXE - Basics: Fine Structure



selection rules:

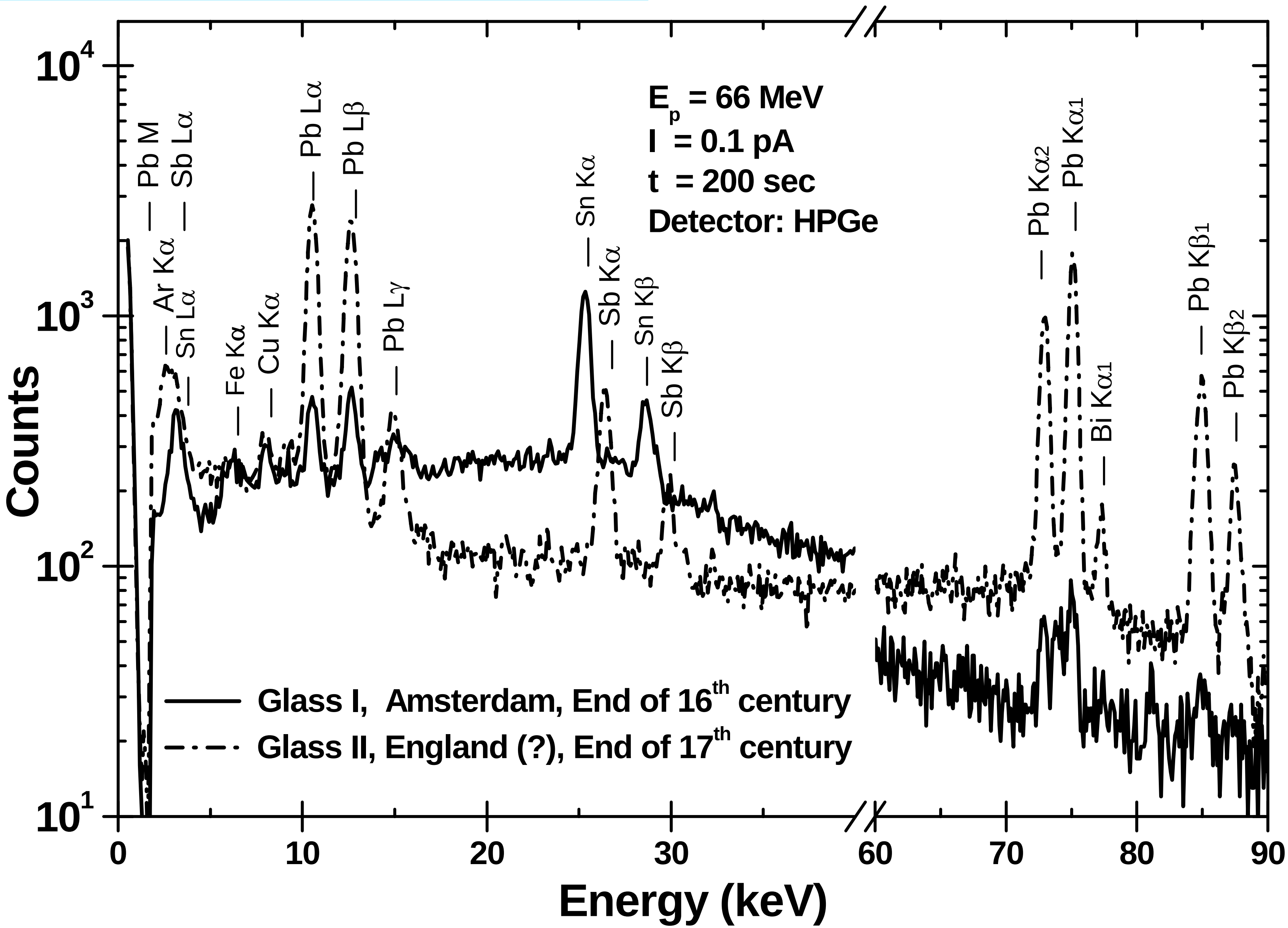
- $\Delta l = \pm 1$
- $\Delta j = 0, \pm 1$

vacancies in L-shell:

possibility of non-radiative transition before x-ray emission

(Coster-Kroning effect)

PIXE - Basics: Spectrum



PIXE – Basics: Cross Sections

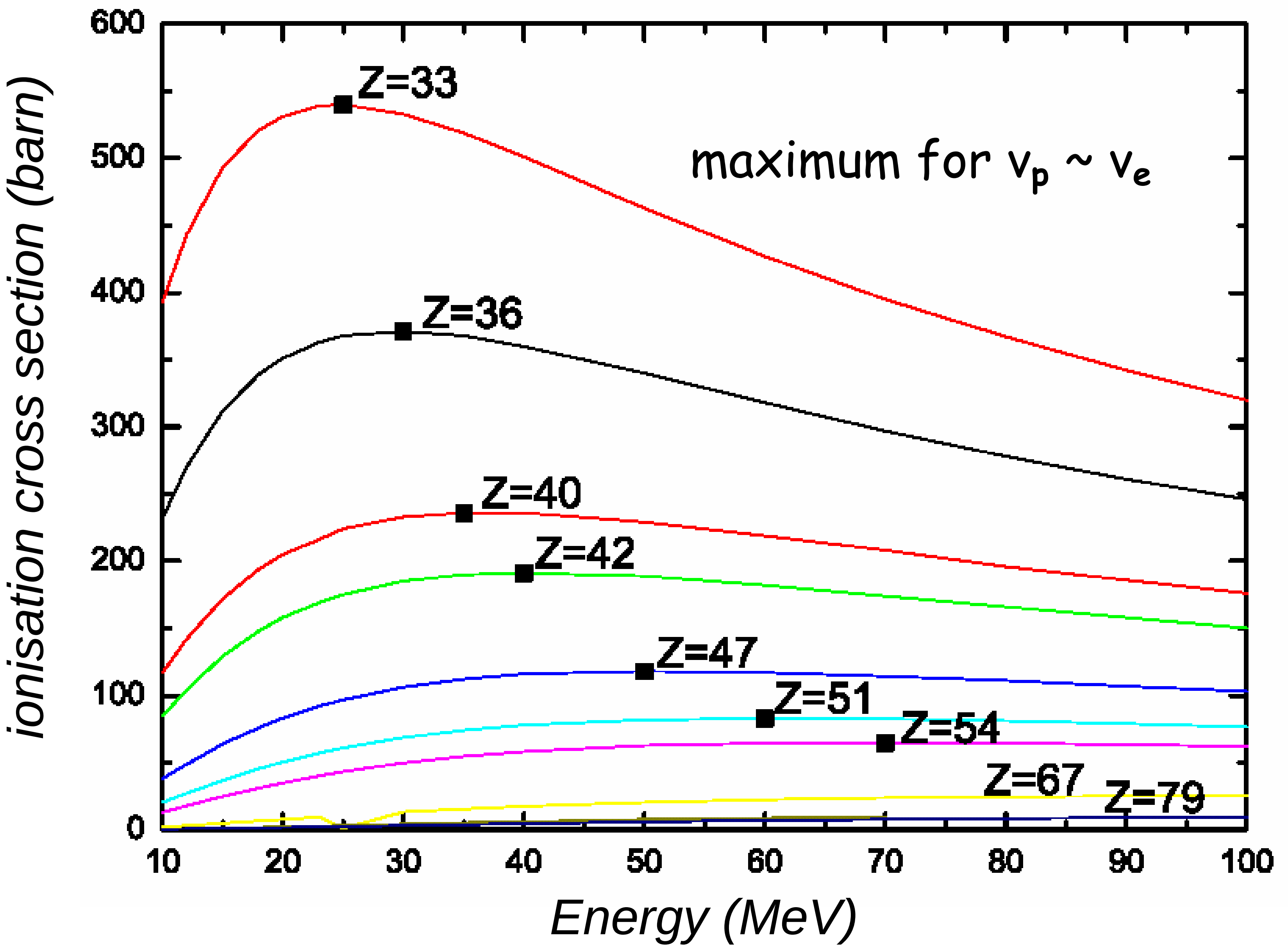
theoretical calculations:

PWBA (Plane Wave Born Approximation)

- application of perturbation theory on the transition between initial and final state
  - initial state:
    plane wave projectile and bound atomic electron
  - final state:
    plane wave projectile and electron in continuum

- enhanced: ECPSSR
  - E = energy loss
  - C= deviation/deceleration of projectile in Coulomb field
  - PSS = perturbation of stationary states of the atom by projectile
  - R = relativistic effects

PIXE – Basics: Cross Sections



PIXE – Basics: Cross Sections

$$\sigma_I = \frac{Y(Z)}{N_p\, M_a(Z)\, \omega_Z\, b_Z\, \varepsilon_{abs}\, a_\mu}$$

$Y(Z)$: x-ray yield (counts), peak area of K line

N_p: number of projectiles

$M_a(Z)$: target areal density (atoms/cm^2)

ω_Z: fluorescence-yield

b_z: part of x-rays in the line of interest

ε_{abs}: absolute detector efficiency

a_μ: absorption of x-rays in the material between place of x-ray production and detector crystal

PIXE – Practice: Quantitative Analysis

number of atoms/cm^2:

$$N_t = Y/(N_p\,\omega_z\,b_z\,\varepsilon_z \int_0^{xmax} \sigma_z(x)\exp(-a_\mu x/\sin\theta)dx)$$

Y measured x-ray yield
N_p number of projectiles
ε_z, θ angle and detection efficiency of detector

} experiment

σ_z ionisation cross section
ω_z fluorescence yield
b_z x-rays in line of interest
a_μ absorption coefficient
x range of protons

} literature/theory

de-convolution software, e.g. GUPIX, AXIL....

PIXE - Practice : Absorption and Ranges

- attenuation of x-rays in matter
  $I = I_0 \exp(-\mu d)$

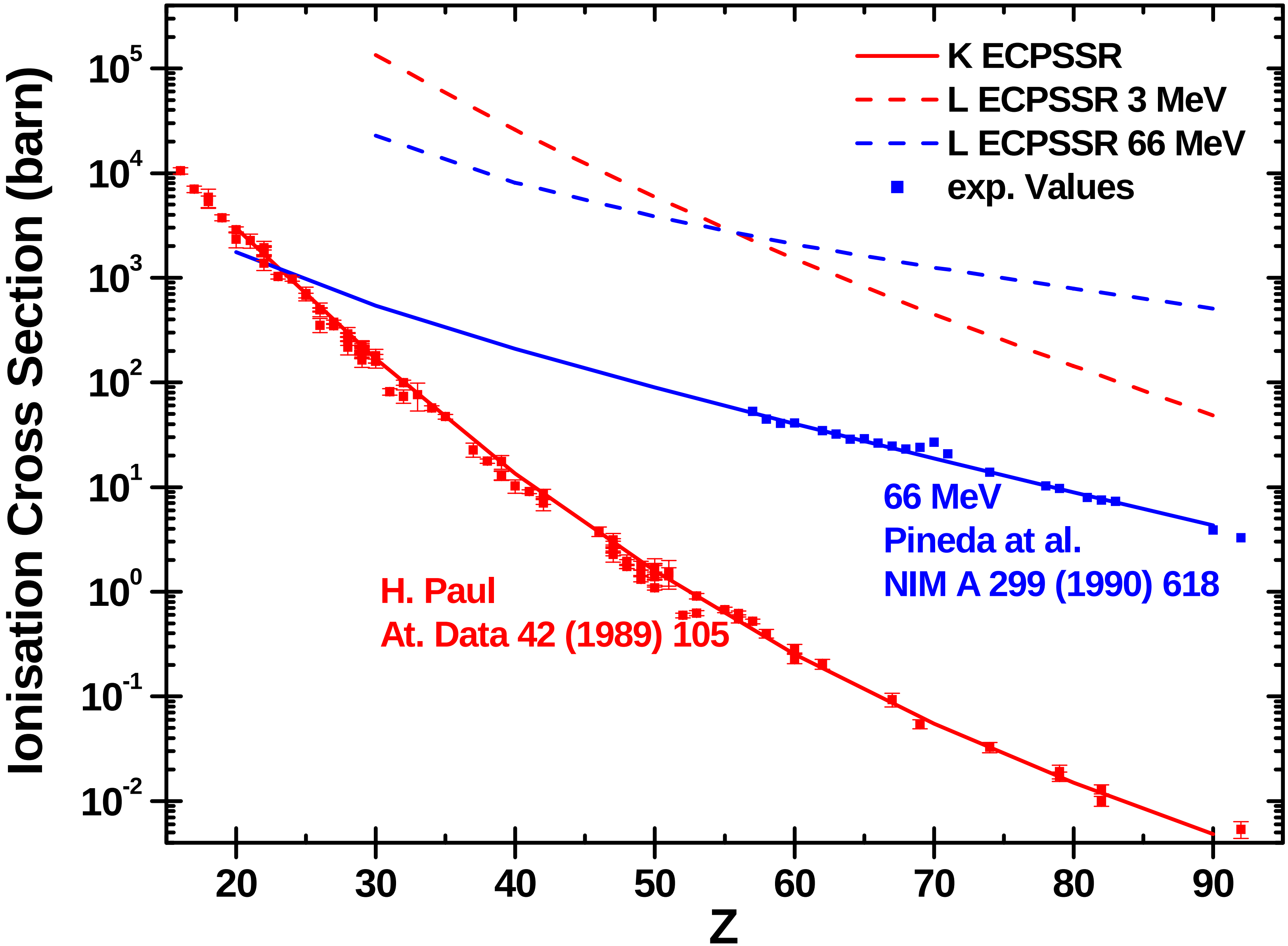
$d_{1/2}$ (μm)	Ca Kα 3.6 keV	Pb Lα 10.5 keV	Pb $K\alpha_1$ 75 keV
in C	78	2000	24000
in Cu	1.5	4.5	800

- ranges

	3 MeV	68 MeV
in air	140 mm	33 m
in C	0.75 mm	20 mm
in Cu	33 μm	7 mm

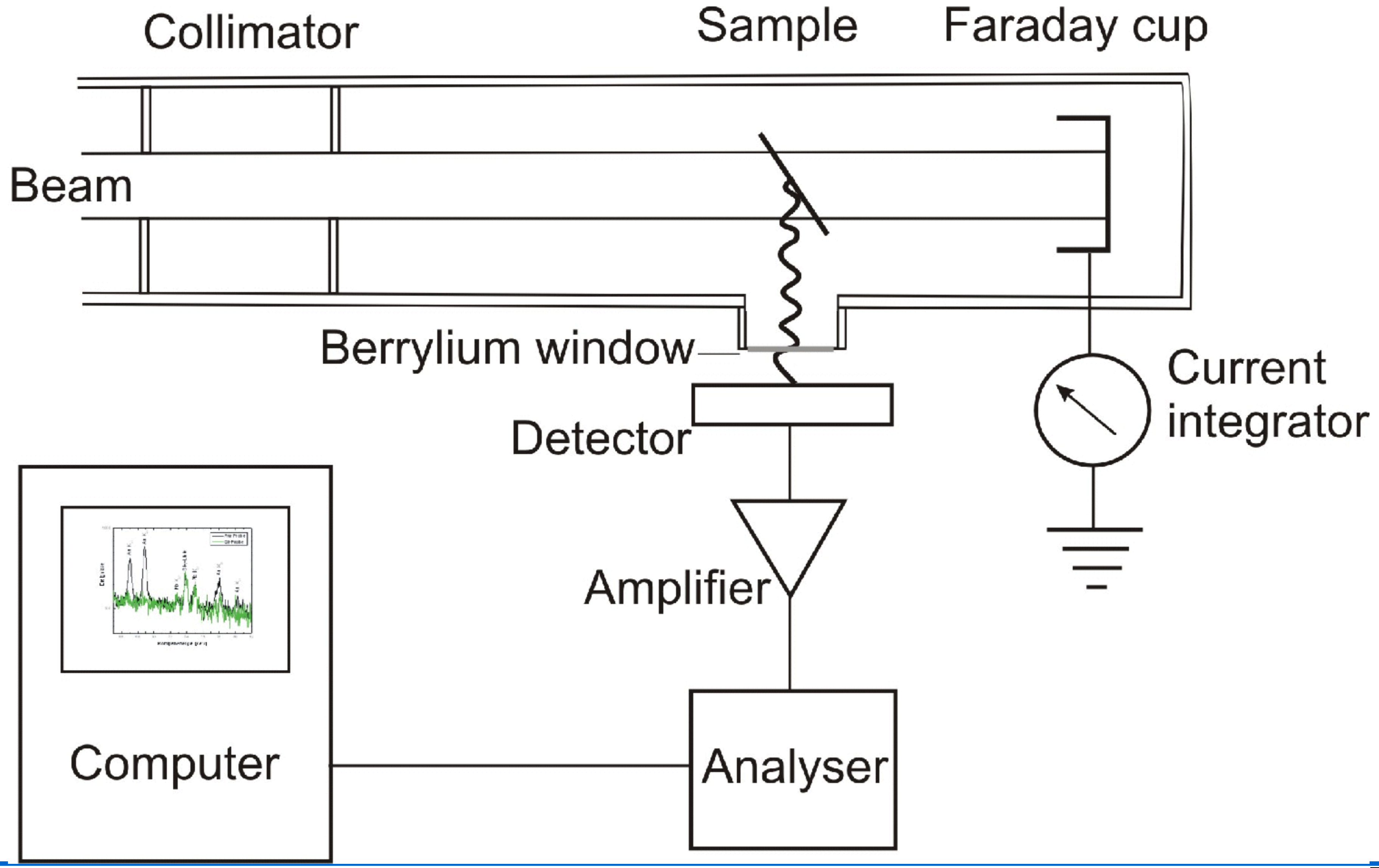
- maximum analytical depth depends on:
  - matrix
  - element (x-ray energy) looked for
  - proton energy

PIXE – Practice: Cross Sections



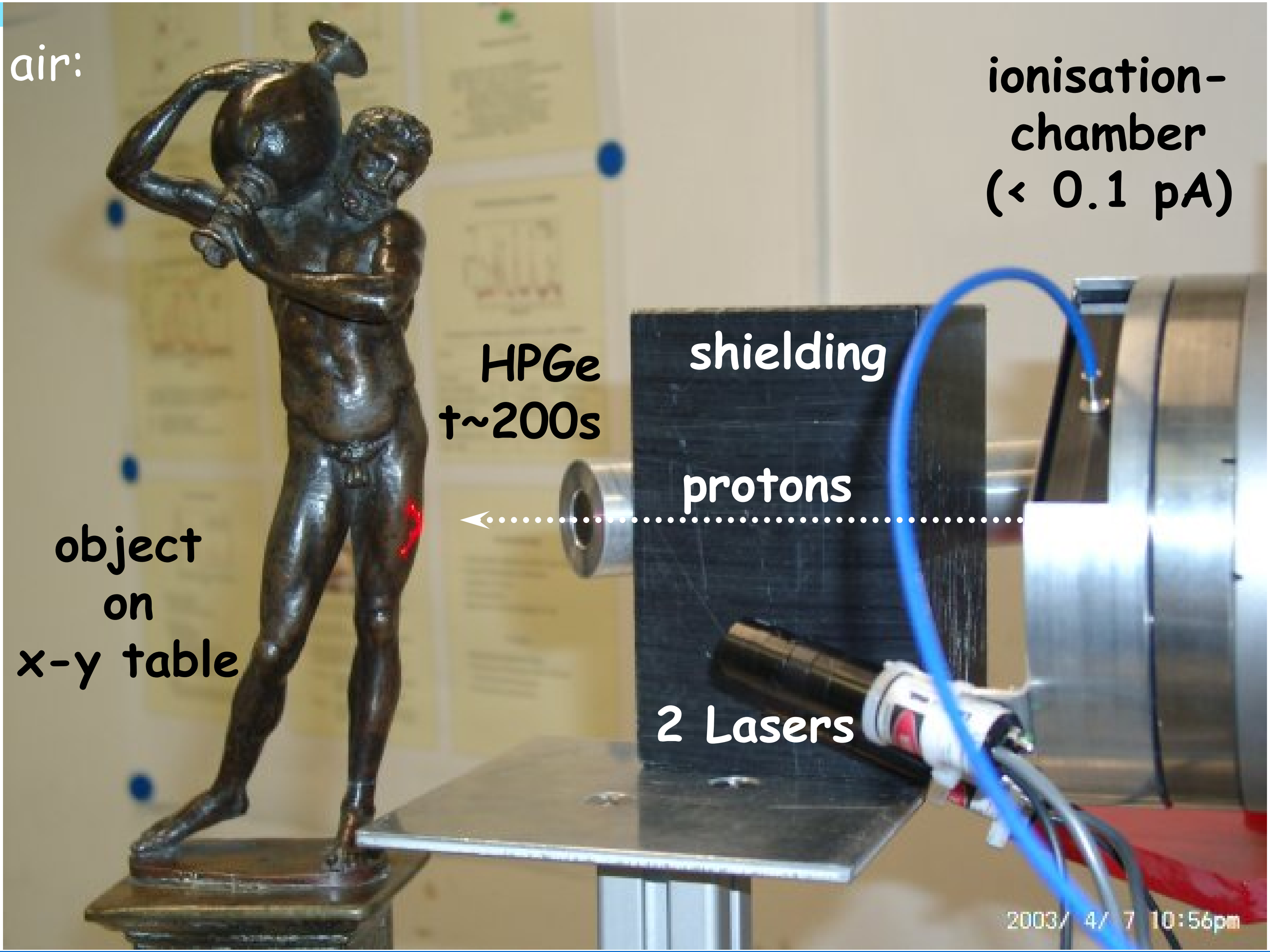
PIXE - Practice: Experimental Set-up

in vacuum:

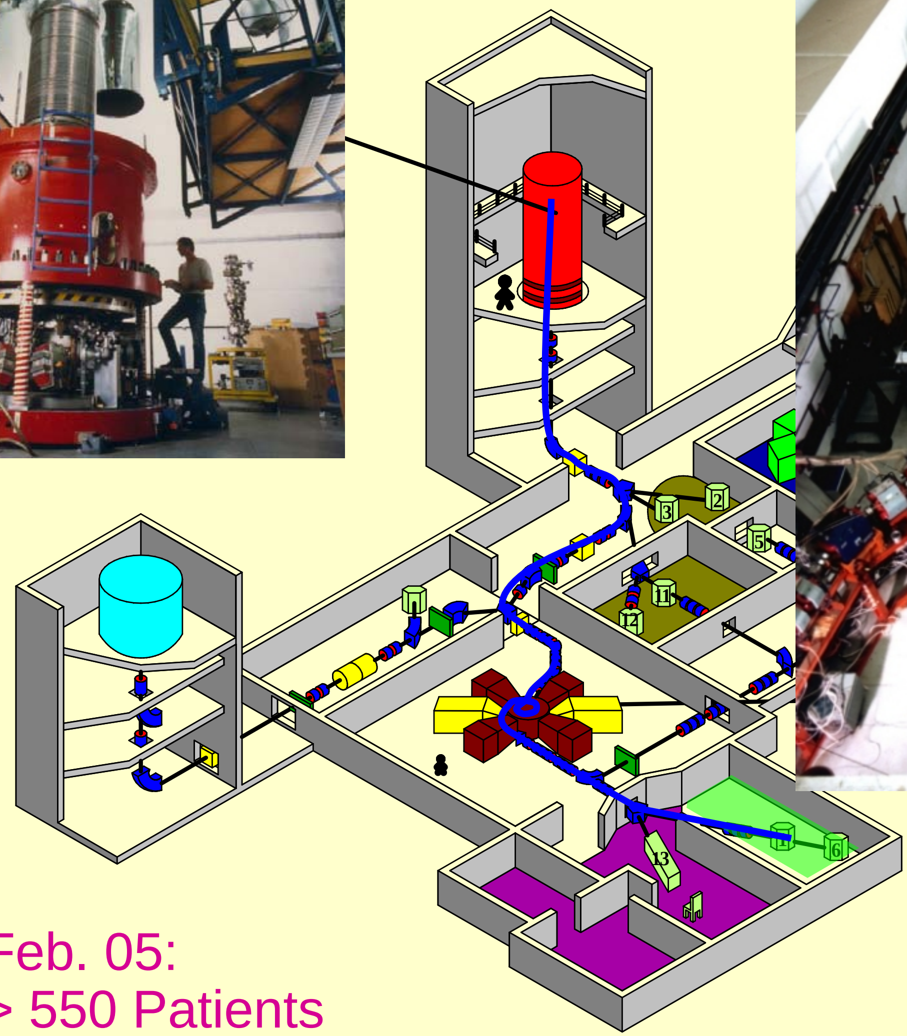


PIXE - Practice: Experimental Set-up

in air:



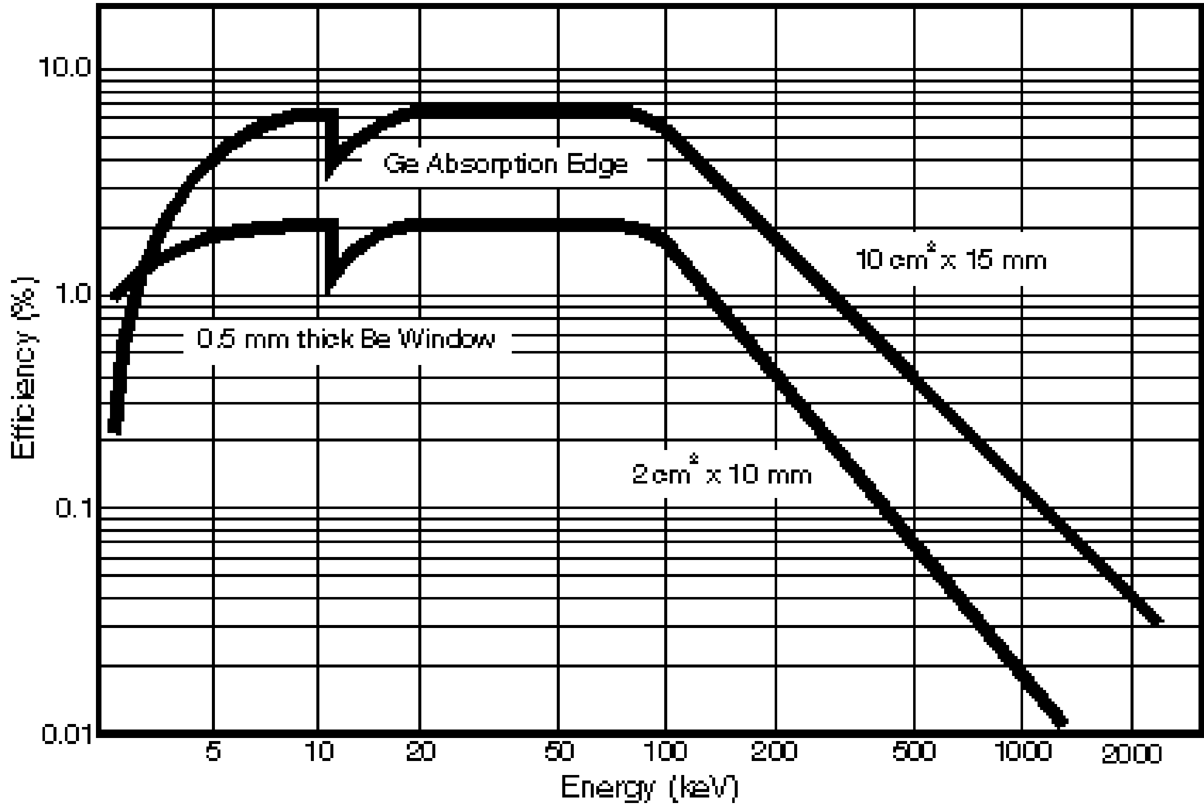
PIXE Practice: ISL- Accelerators and target areas



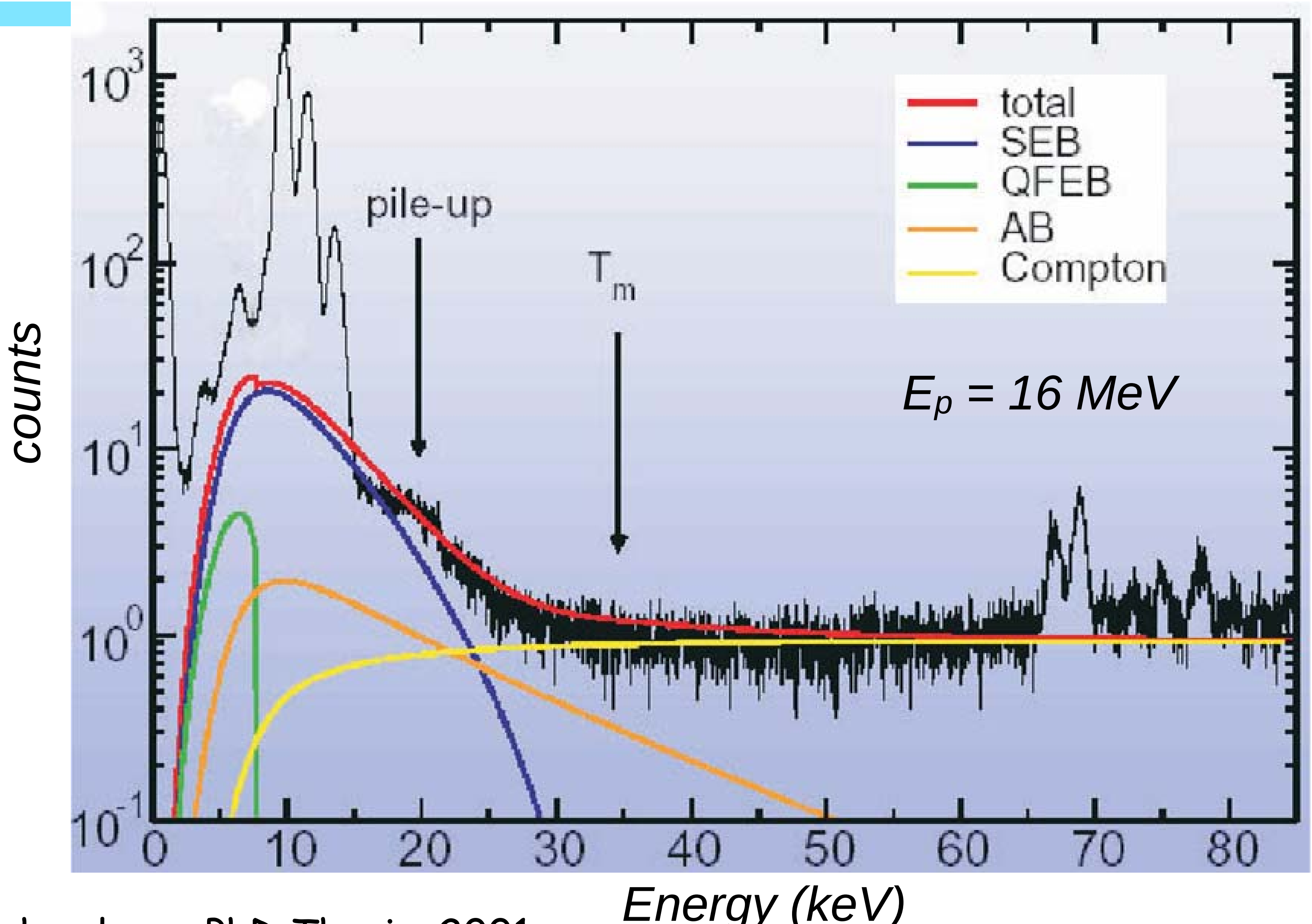
PIXE – Practice: Detector

Semiconductors

- Si(Li) = Li doted Si, up to E_X ~ 25keV, resolution 160eV at 5.9 keV price
- HPGe = high purity Ge, above E_X ~ 3 keV resolution 180 eV at 5.9 keV



PIXE – Practice: Spectrum



O. Schmelmer, PhD Thesis, 2001

PIXE – Practice: Spectrum Background

- AB:
  Atomic Bremsstrahlung = deceleration of bound target electrons in the Coulomb field of the projectile
- SEB:
  Secondary-Electron-Bremsstrahlung = Bremsstrahlung of electrons from ionisation processes
  $$E_{max} = 4m_e/M_p \times E_p$$
- QFEB:
  Quasi-free electron-Bremsstrahlung
  $$E_{max} = m_e/M_p \times E_p$$
- Compton:
  inelastic scattering of γ-rays from nuclear reactions with the electrons in the detector crystal

PIXE – Example: Chinese Bowl

report 1
(Japan):
500 years old
1 Mio. €

report 2
(Berlin):
100 years old
max. 25 000 €

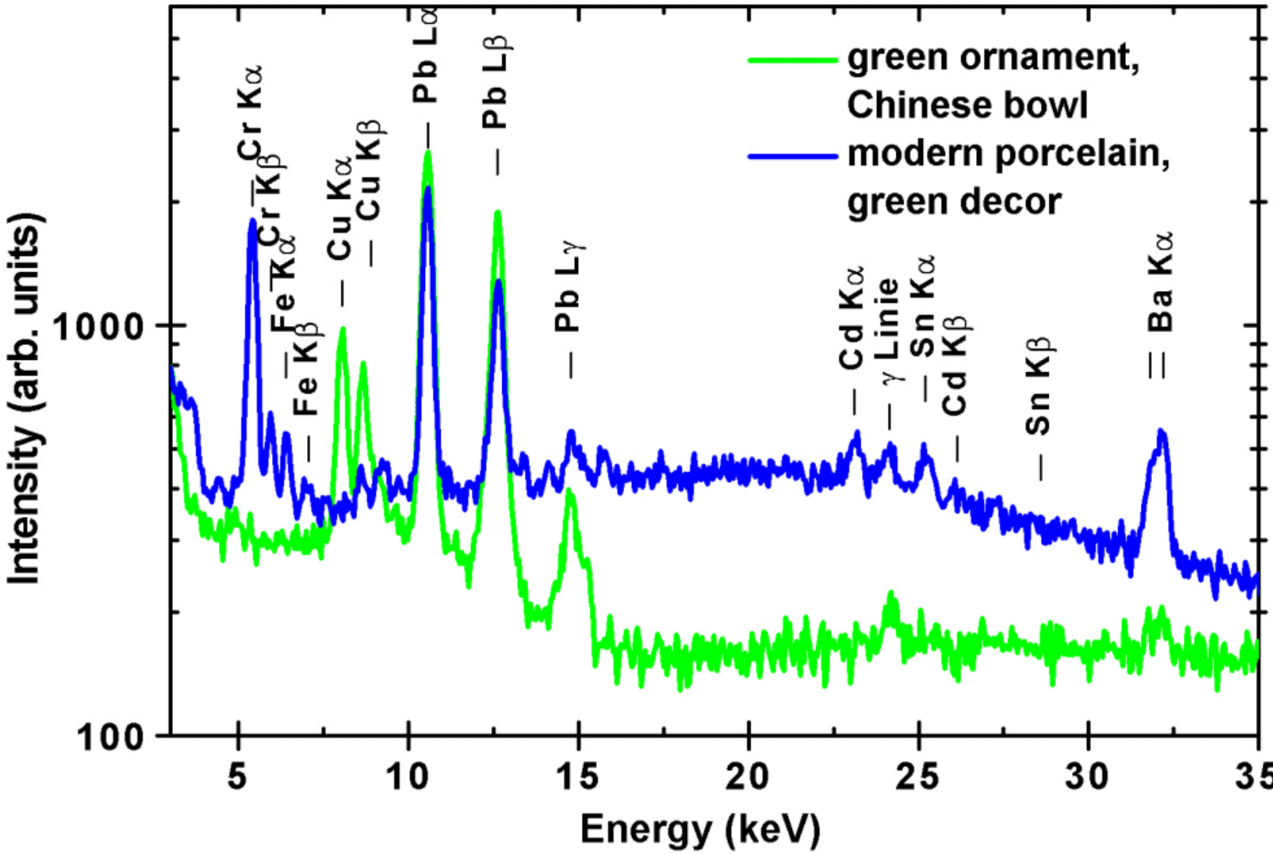
- both reports based on art historical expertise
- indirect dating: identification of pigments
  (Cr in green: after 1850)

PIXE – Example: Chinese Bowl

- porcelain extremely sensitive
- high-energy protons: small risk of damage due to low proton intensity and small dE/dx

- on bowl:
  - Pb (flux)
  - Cu (pigment)
  - no Cr

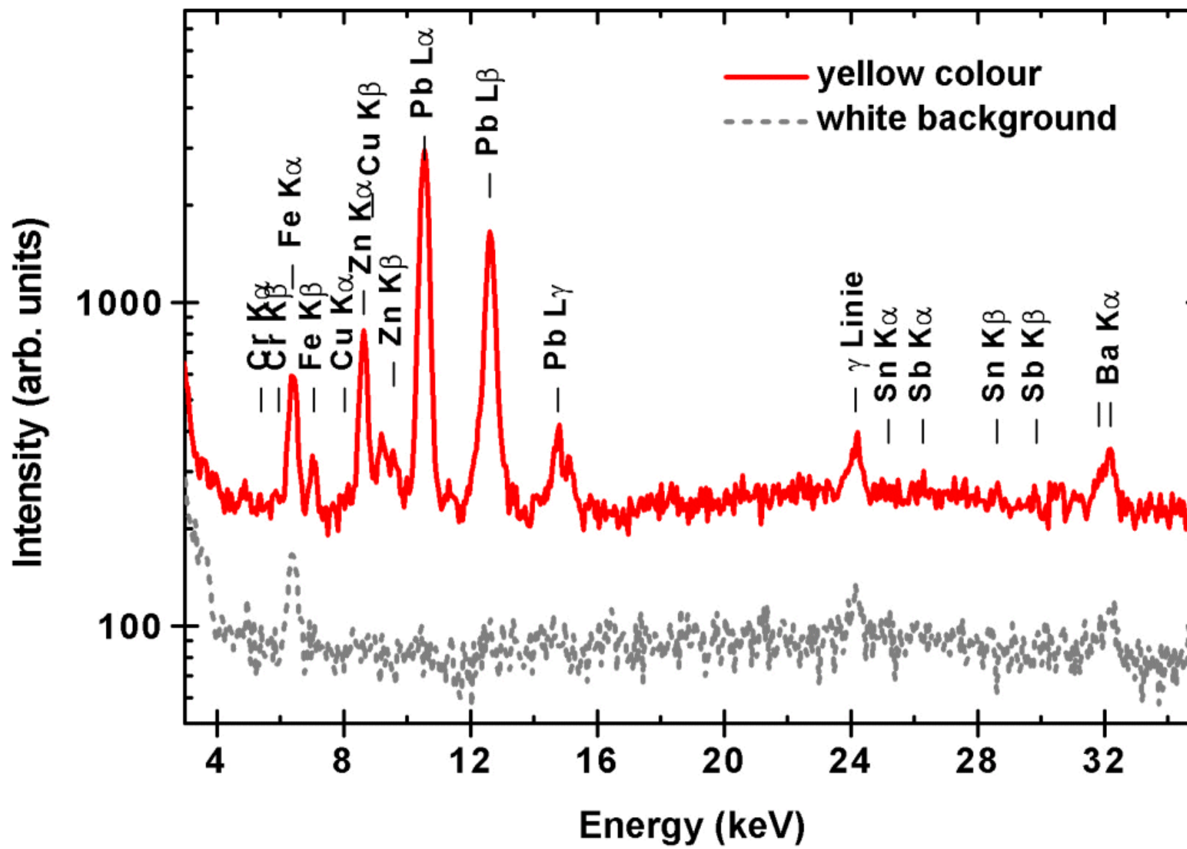
- modern porcelain:
  - Cr (pigment)



PIXE – Example: Chinese Bowl

- green colour no information
- yellow colour measured: Zn and Fe, no Sb
- absence of Sb is indication for age: after ~1850

⇒ report 2 could be confirmed

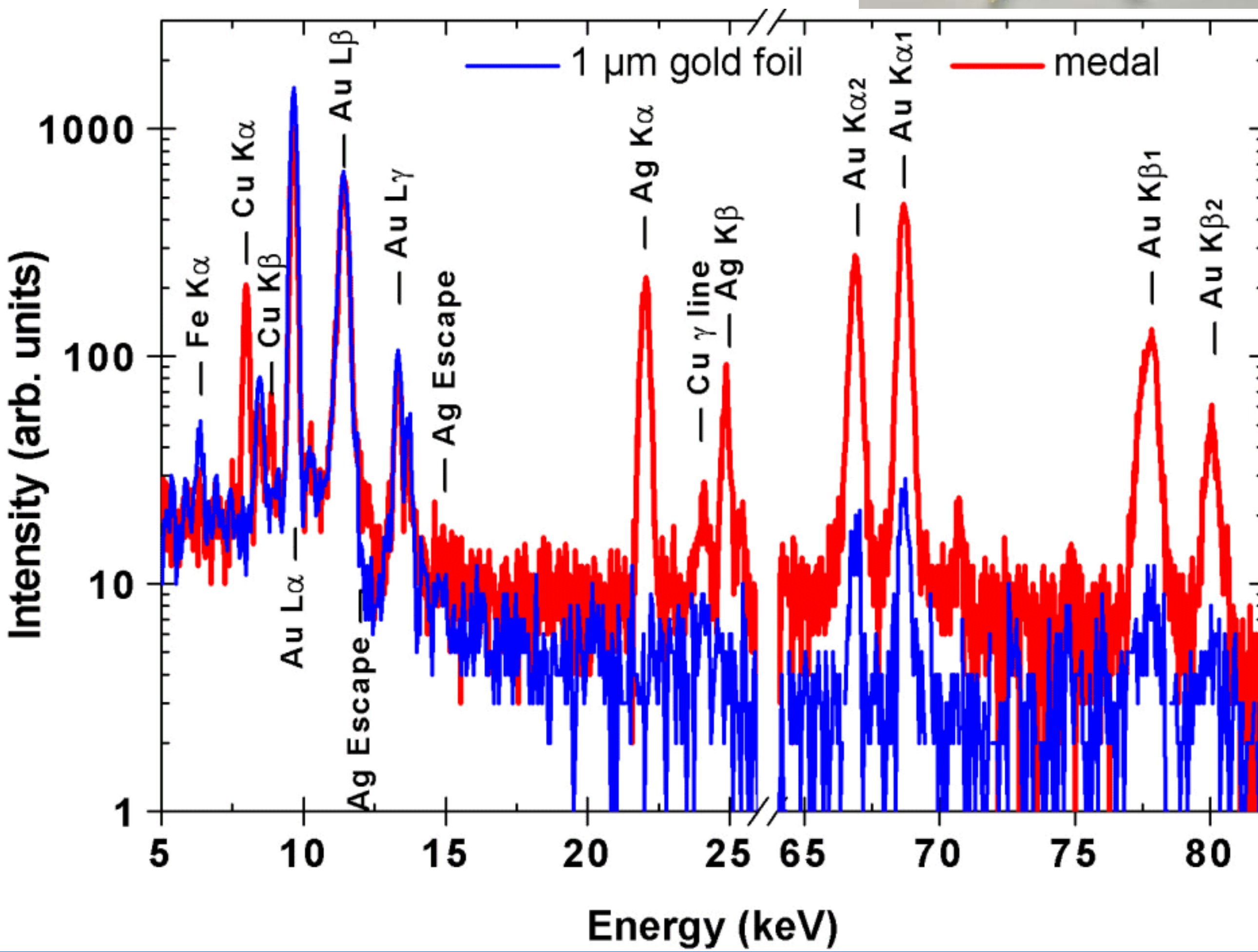


PIXE – Example: Prussian Medal

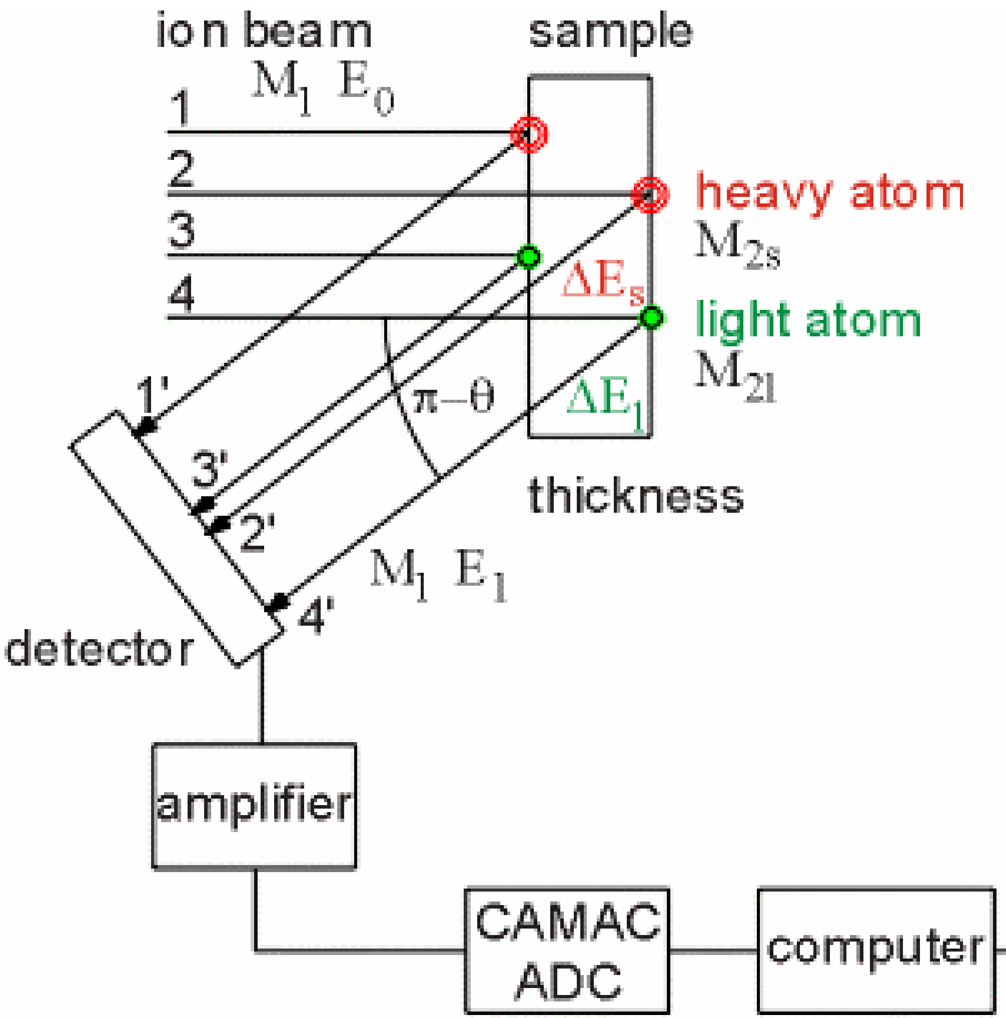
- Prussian Medal, about 1790
  Deutsches Historisches Museum, Berlin
- massive object?
  gilded?
- t = 200s,
  I_p ~0.1 pA
- result:
- medal:
  Lα/Kα = 1.09

  1 µm Au-foil:
  Lα/Kα ~ 40,

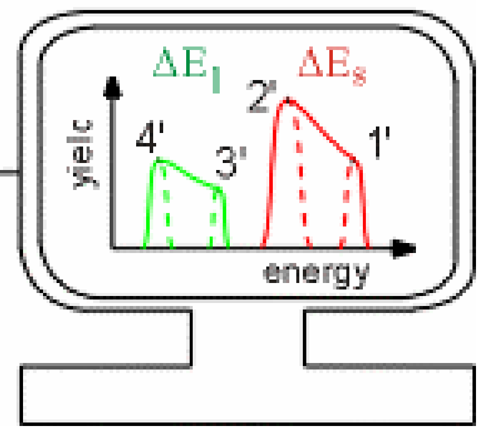
  ~ 75% Au
  ~ 15% Ag
  ~ 10% Cu



Rutherford Back Scattering - RBS: Principle



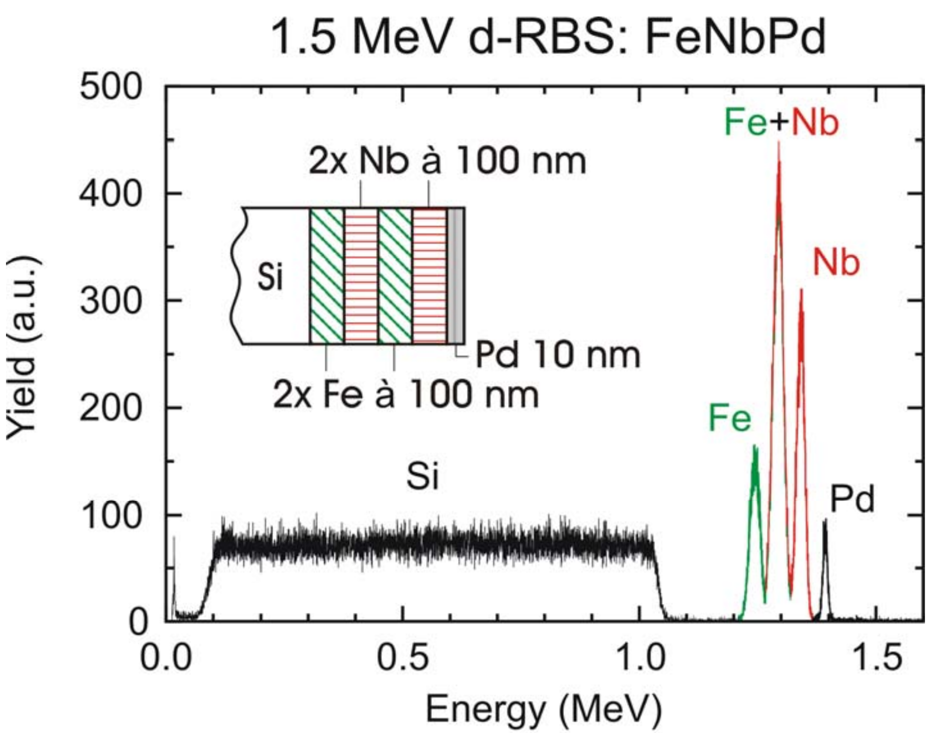
- conservation of energy and momentum
  $\Rightarrow$ univocal identification of target atom
  (thin samples)
- energy loss ΔE in target: thickness determination
- detectable elements:
  $Z > Z_{ion}$

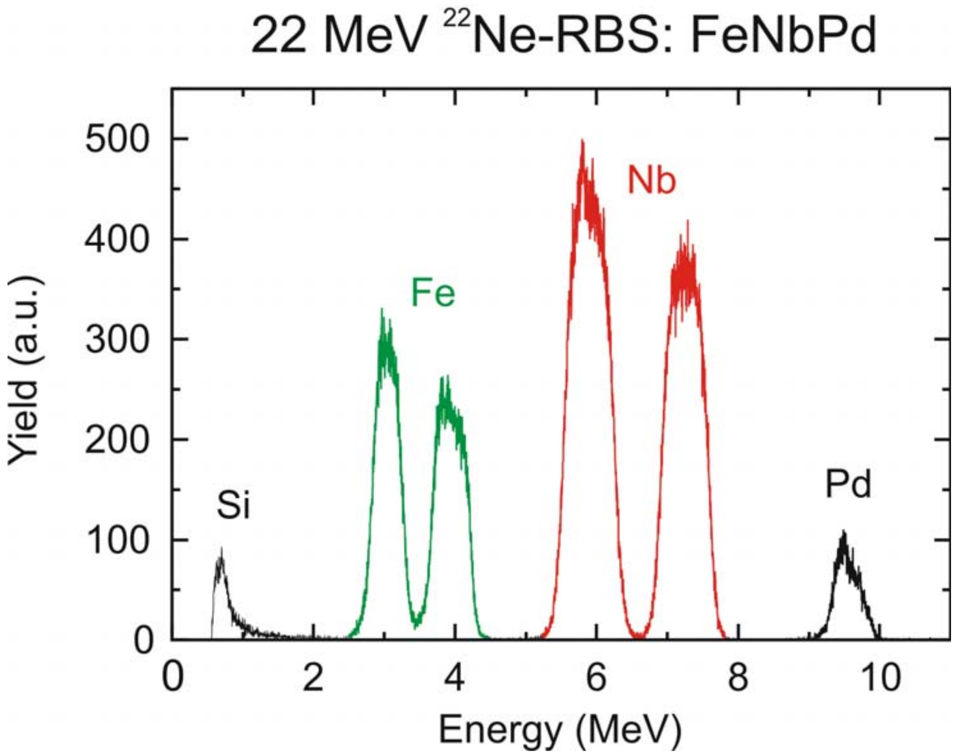


RBS - example: Light Ions contra Heavy Ions

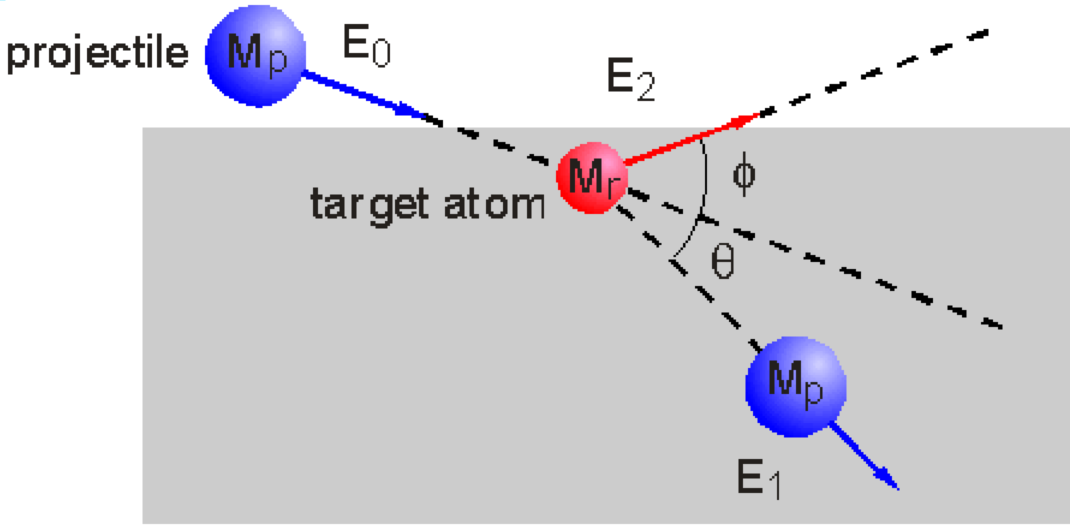
$$E_{ion} = k_p \, E_0$$

$$k_p = \left(\frac{M_p/M_r \cos\theta + \sqrt{1-\left(M_p/M_r\right)^2 \sin^2\theta}}{1+M_p/M_r} \right)^2$$





Elastic Recoil Detection Analysis - ERDA: Principle



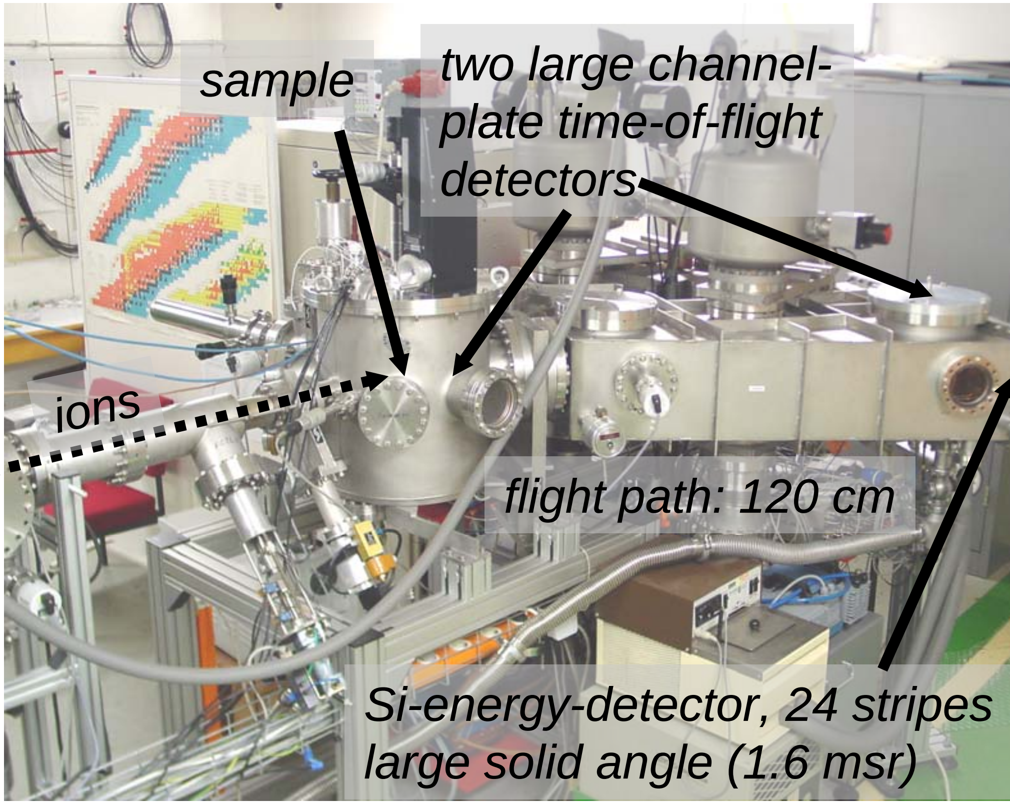
$$\frac{d\sigma_r}{d\Omega} = \left(\frac{Z_p Z_r e^2}{2E_0}\right)^2 \left(\frac{M_p + M_r}{M_r}\right)^2 \frac{1}{\cos^3\phi}$$

- detection of recoiled atoms
- identification by simultaneous measurement of energy and, e.g. time-of-flight
- comparable sensitivities for all elements (hydrogen enhanced by a factor of 4)

ERDA: Experimental Set-Up

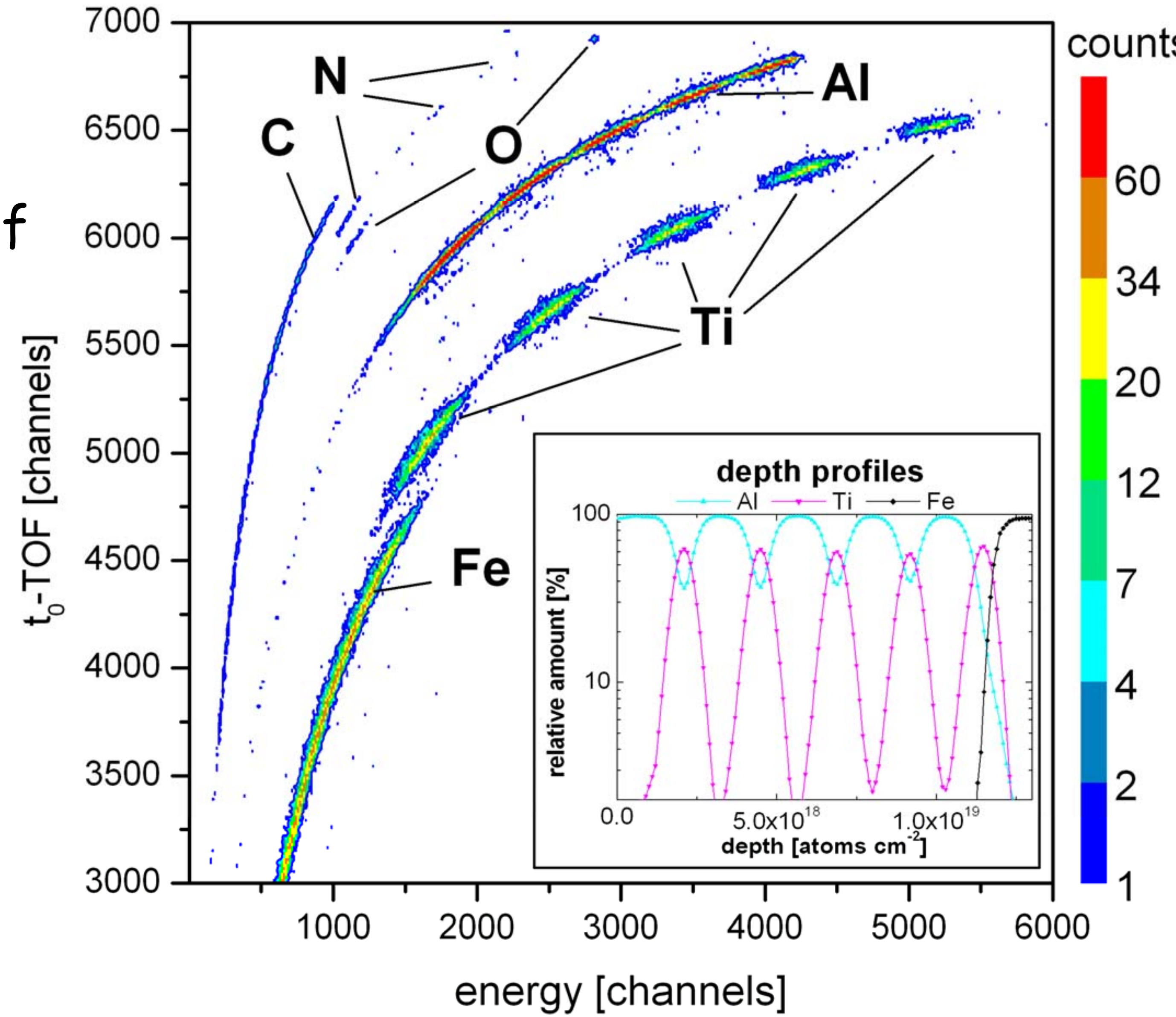
- only absolute, standard free method for the concentration of all elements in thin layers
- irradiation of the sample with heavy high energetic ions e.g. ^{197}Au 350MeV

- coincident measurement of energy + time-of-flight for the outscattered atoms of the sample (large dynamic range in energy (depth) due to TOF method)
- using cyclotrons: time structure of ion beam small emittance



ERDA: example

example:
Ti/Al multilayer
on steel
5 double layers of
150 nm Al and
100 nm Ti



Conclusion I

	ERDA	RBS	PIXE	NRA
sensitivity depends on matrix and element looked for	• ppm for H • 10 ppm for others	• ppm for heavy elements • 0.1% for light elements	ppm – 0.1%	100 ppm
depth resolution	10 nm close to surface	10 nm close to the surface	1 – 10 µm	5 nm close to surface
max. analytical depth	a few µm	a few µm	up to a few mm	a few µm
elements	all	$Z > Z_{ion}$	$Z > 11$	$^{15}N(H,\alpha)^{12}C$ ......

Conclusion II

- various ion – target interactions
  $\Rightarrow$ vast choice of different techniques
- each technique:
  specific advantages and drawbacks
- best answers to analytical problems:
  careful choice of analytical technique or
  combination of techniques, e.g. RBS + PIXE
- today: estimated 1000 accelerators world-wide used for ion beam analysis
- samples: