Cultural heritage research with neutrons

presented by

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Outline

Introduction: why neutrons

Selected analysis techniques with examples

Typical archaeometry questions:

- How was it done? (technological knowledge and manufacturing techniques)
- When was it done? (dating)
- Where was it done? (geographical localization)
- How is the object conservation status?
- Is the artefact authentic?
- Where should we dig?

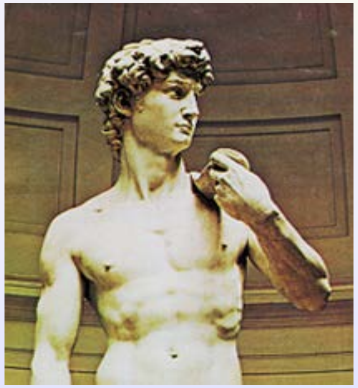
A fundamental request: non destructive techniques!

Artifacts investigated

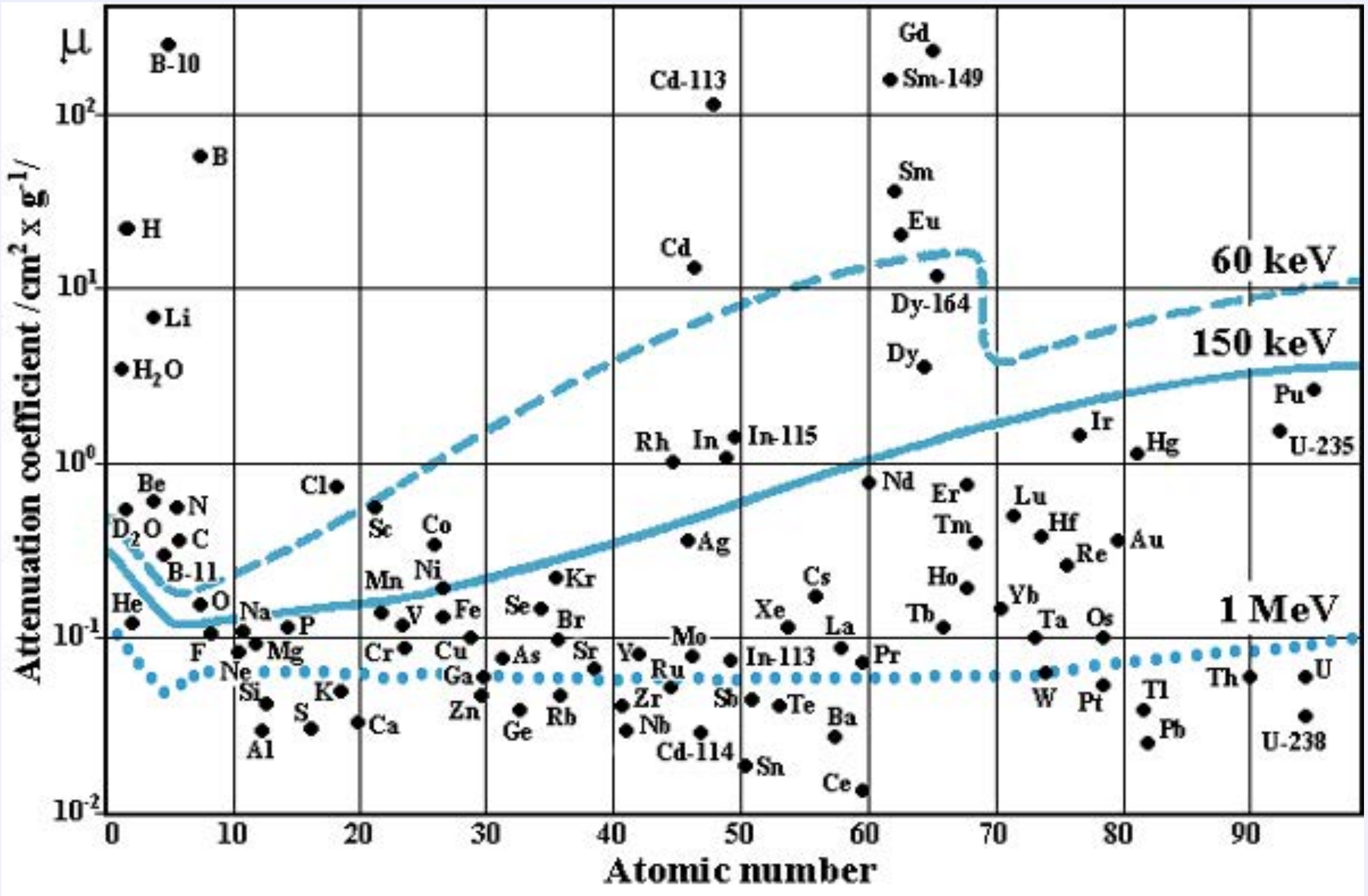
All kind of artifacts (dimensions from mm to meter): papers, ceramics, stones, marbles, glasses, metals, etc.

Neutron analysis provides information on:

- Elemental and phase Composition
- Making techniques
- Provenance Conservation and Restoration
- Genuine or fake



Neutrons vs X-rays



Attenuation coefficient (note the logarithmic scale) of elements for thermal neutrons (separate dots - black), for 1 MeV gamma-ray (dotted line), for 150 kV X-ray (solid line) and for 60 kV X-ray (dashed line)

Neutrons: advantages

- All crystalline material – metal, pigments, rock, ceramics – can be analysed e.g. by neutron diffraction. Archaeological object in most cases can be considered randomly oriented polycrystalline material

- Neutrons are an invaluable tool to analyse precious archaeological objects: they are non-destructive and can penetrate deep into the cultural artefact or beneath the surface of paintings, to reveal structures at the microscopic scale, phase composition or provide 3D images of the inner parts of the artefacts

- Whole artefacts can be placed in the neutron beam and analysed at room conditions, without sample preparation

Neutrons: weaknesses

- Neutrons are expensive and not easily available
- Objects need to be transported and stored safely
- Interaction of neutrons is weak therefore long measuring time (hours) needed
- Activation

Neutron-based techniques

Imaging: Neutron Radiography and Tomography

Including Energy selective tomography, Phase contrast tomography

Element analysis: Nuclear Analysis (and Imaging) Techniques

Neutron Activation Analysis (NAA)

Prompt Gamma Activation Analysis (PGAA) and Imaging (PGAI)

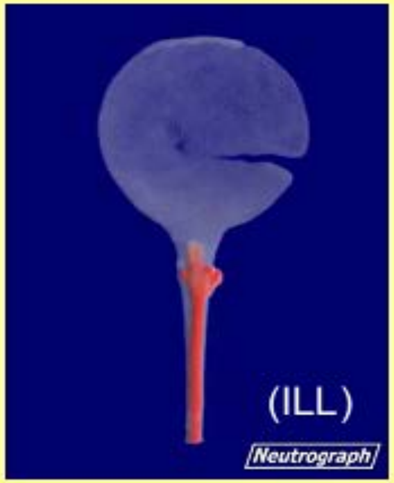
Neutron Resonance Capture Analysis (NRCA) Imaging (NRCI)

Crystallography: Scattering techniques

Neutron Diffraction

Small Angle Neutron Scattering (SANS) and Ultra SANS (USANS)

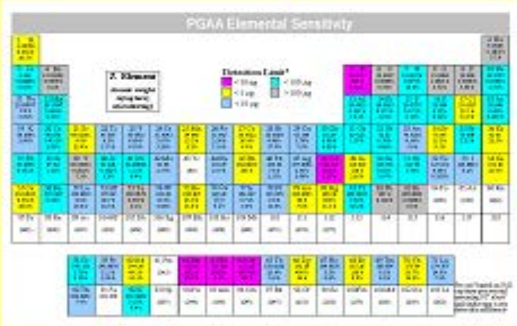
Imaging



By neutron attenuation

⇒ Making techniques

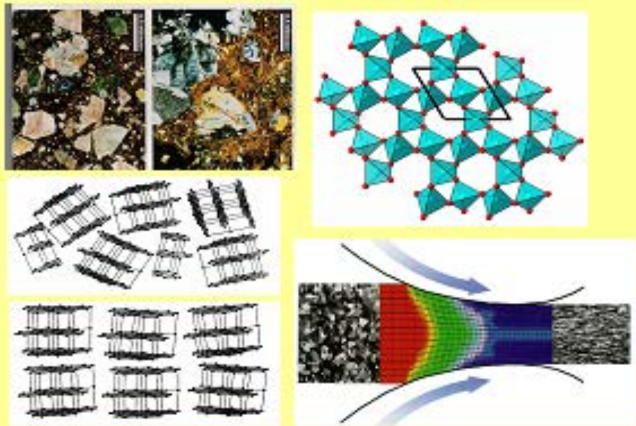
Element Analysis



By neutron activation analysis

⇒ Provenance

Crystallography

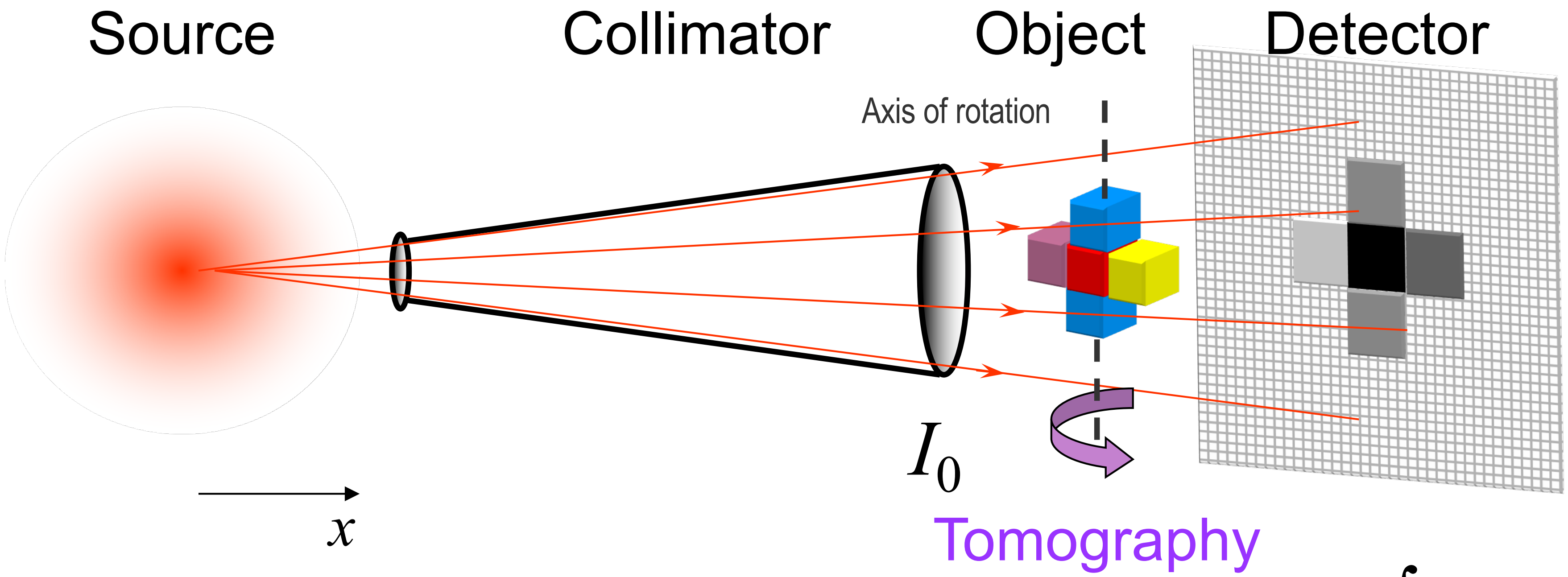


By neutron diffraction

⇒ Manufacturing techniques

Neutron Radiography and Tomography

Principle of conventional tomography



$$\sim I_0 e^{-\int \Sigma(x) dx}$$

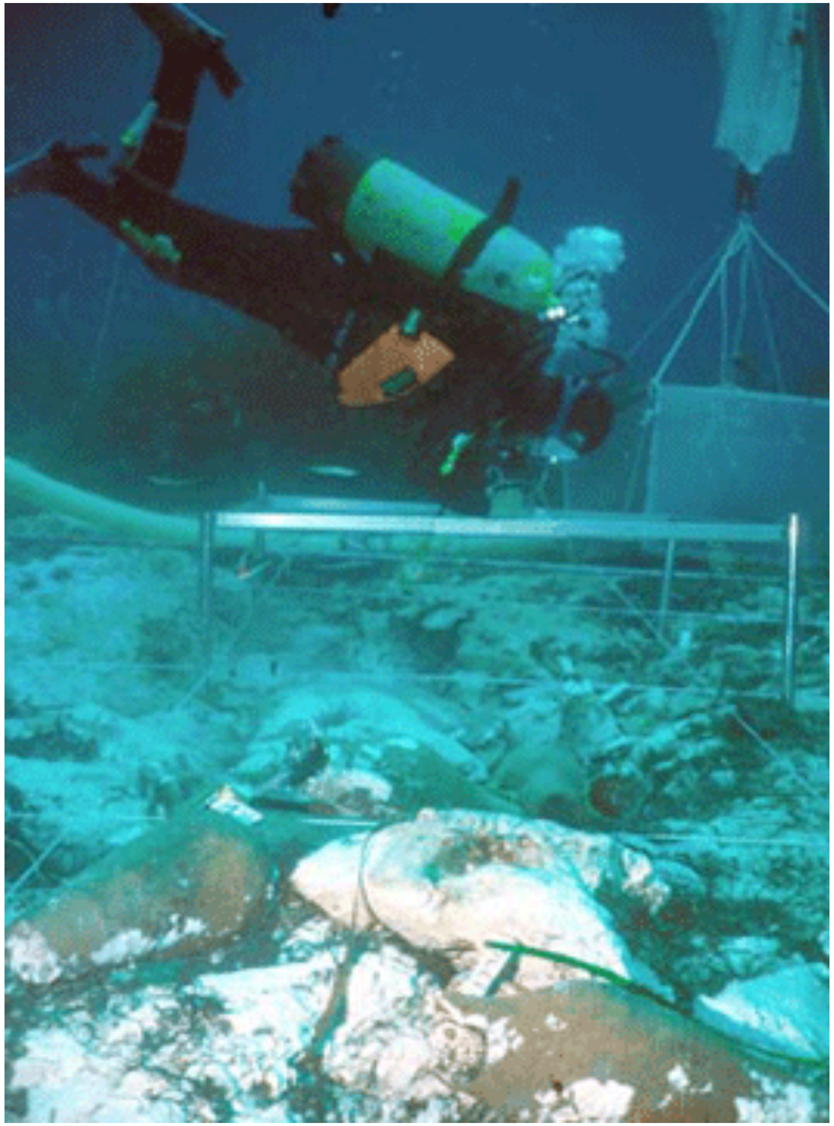
x – propagation direction

I_0 – primary beam

$\Sigma(x)$ – attenuation coefficient

Late Roman age findings (IV-V century A.D.) from ship wrecks near Sicily (Scoglio della Bottazza)

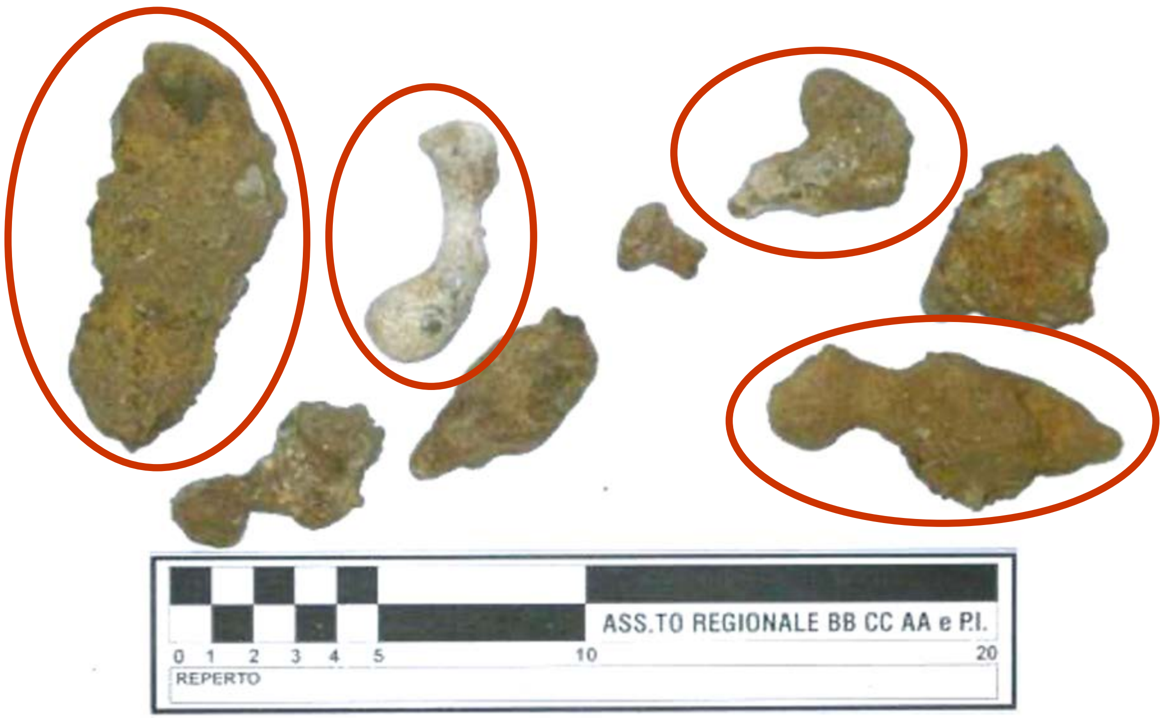
The corrosion process fully removed the metal part leaving only the calcareous matrix around the objects.



Research project in collaboration with *Soprintendenza del mare*, Sicily, Italy

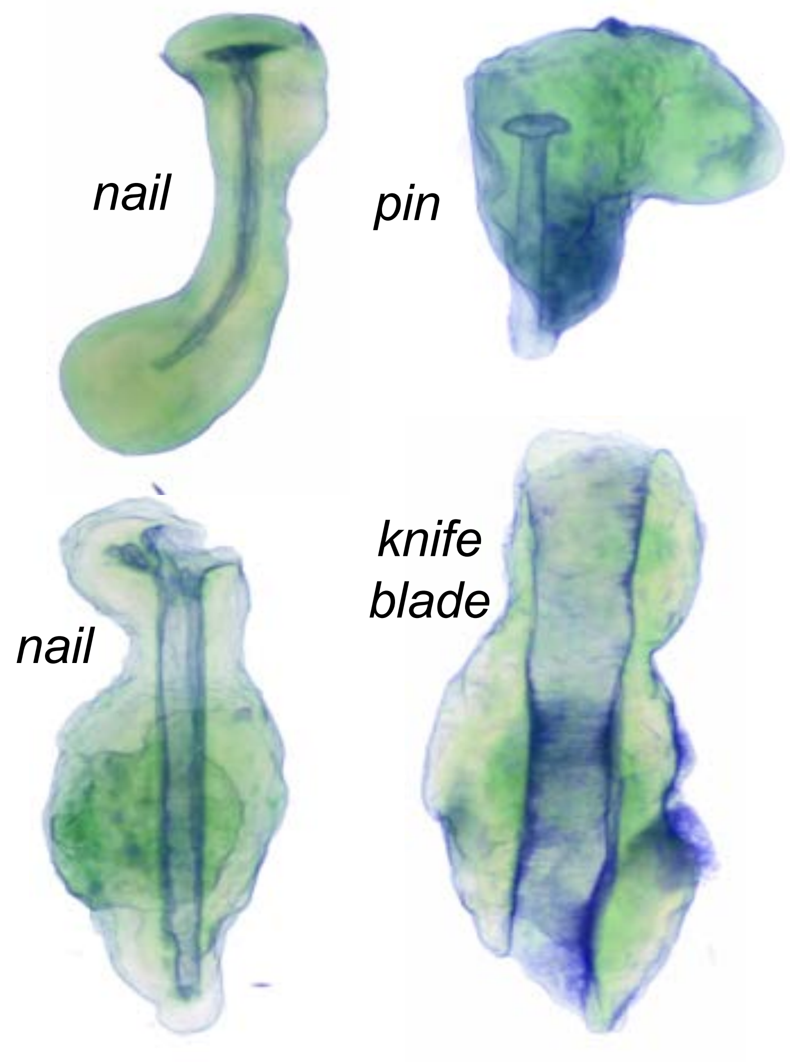
Neutron tomography

Late Roman age findings (IV-V century A.D.) from ship wrecks near Sicily (Scoglio della Bottazza)



The corrosion process fully removed the metal part leaving only the calcareous matrix around the objects.

Tomographic reconstruction



From tiny gold filigrees…

1 cm

…to large iron tie rods

80 cm

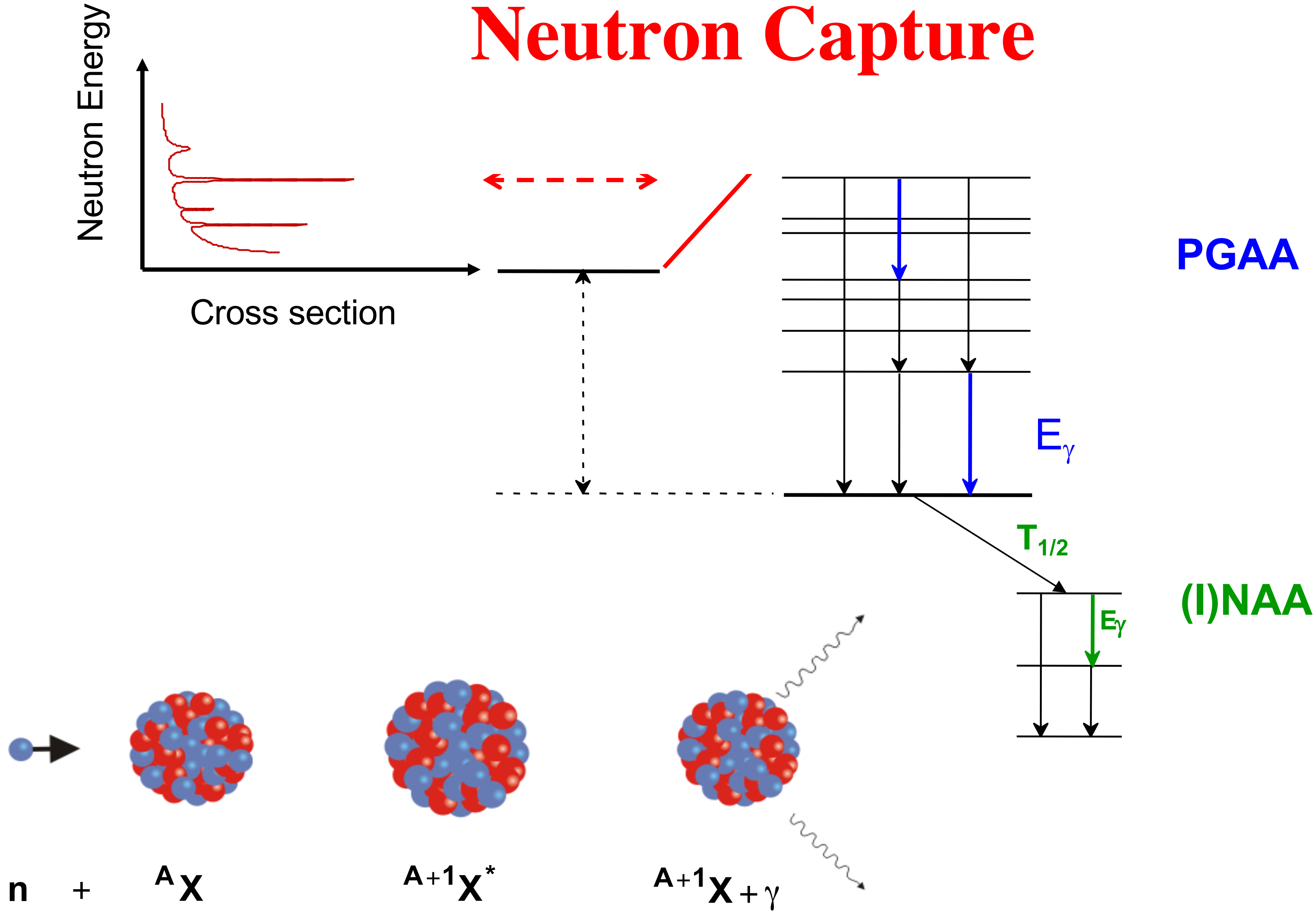
…and pearls too

End of first part of presentation

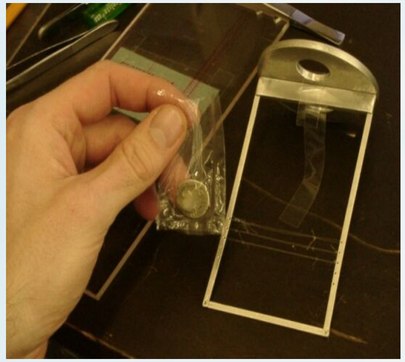
Nuclear Analysis / Imaging Techniques

Neutron Activation Analysis (NAA)
Prompt Gamma Activation Analysis (PGAA)
Neutron Resonance Capture Analysis (NRCA)
Neutron Resonance Transmission Imaging (NRT)

Neutron Capture



NAA vs. PGAA



	NAA	PGAA
•Sample	10 mg	100 mg - 1 g
•Sample preparation	Drying, glass	None/ PTFE bag, vial
•Irradiation	Reactor core	Guided beam of neutrons
•Detection	Separated in time and space	On-line, during the irradiation
•Spectrum	10-100 peaks, 3 MeV	100-5000 peaks, 12 MeV
•Result turnover time	weeks	Few hours
•Detection limits	ppm-ppb	>ppm, %
•Cooling time after irrad.	Several months	1-2 days

Periodic Table for PGAA

Element
stable isotope
atomic weight
σ - capture
σ - scattering

Detection Limit [ppm]

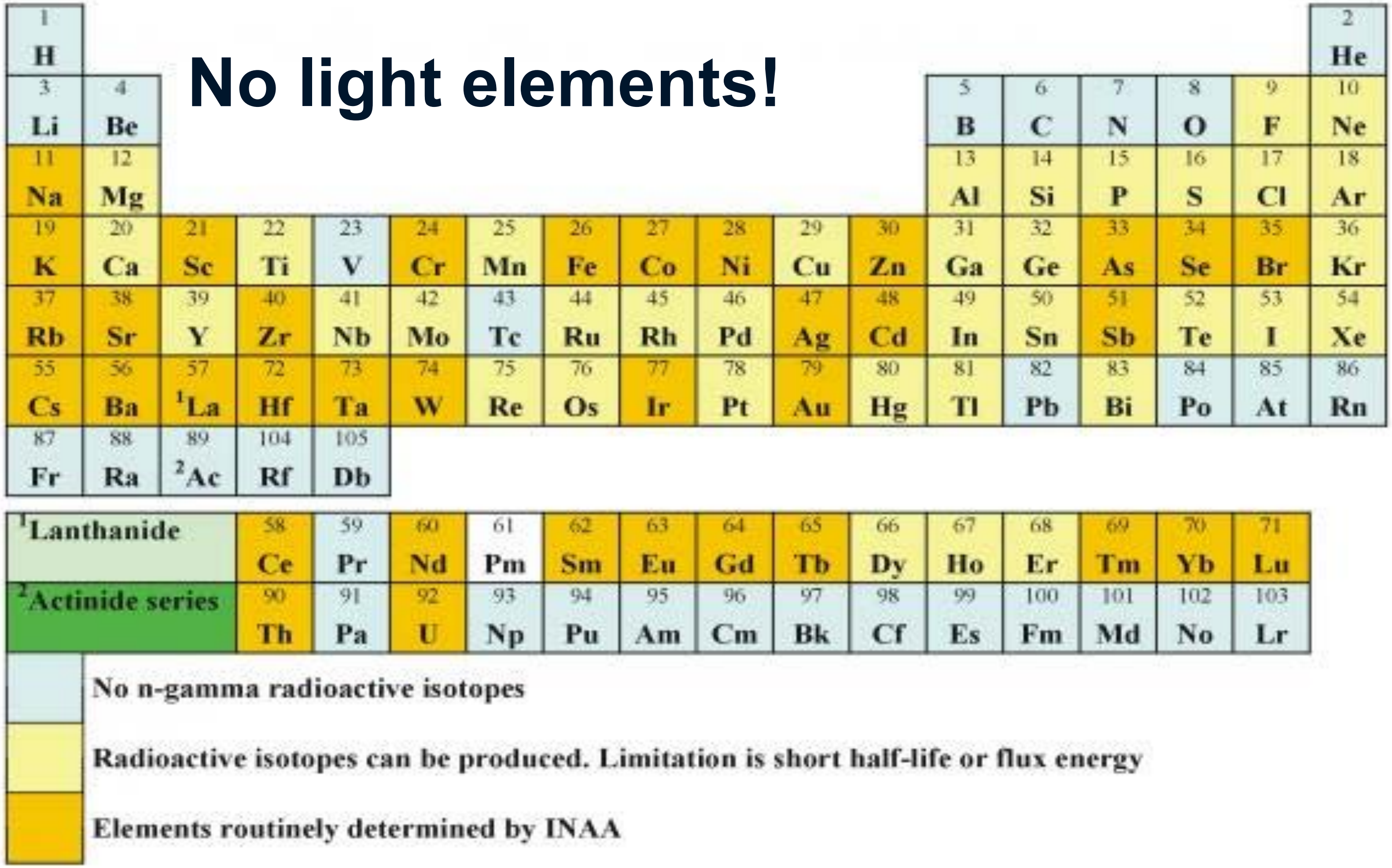
- 0.01-1 (red)
- 1-10 (yellow)
- 10-100 (green)
- 100-1000 (cyan)
- >1000 (black)
- no data (white)

H 1 1.00794 0.3326 b 82.02 b																	He $3^{0.00014}$ 4 4.002602 0.007 b 1.34 b
Li $6^{7.5}$ $7^{92.5}$ 6.941 70.5 b 1.37 b	Be 9 9.0122 0.0076 b 7.63 b											B 10^{20} 11^{80} 10.811 767 b 5.24 b	C 12^{99} $13^{1.1}$ 12.011 0.00350 b 5.551 b	N 14 $15^{.37}$ 14.00674 1.9 b 11.51 b	O 16 $17^{0.038}$ $18^{0.2}$ 15.9994 0.00019 b 4.232 b	F 19 18.998 0.0096 b 4.018 b	Ne 20^{91} $21^{0.26}$ 22^{9} 20.1797 0.039 b 2.628 b
Na 23 22.98977 0.530 b 3.28 b	Mg 24^{79} 25^{10} 26^{11} 24.305 0.063 b 3.71 b											Al 27 26.9815 0.231 b 1.503 b	Si 28^{92} $29^{4.7}$ $30^{3.1}$ 28.0855 0.171 b 2.167 b	P 31 30.9738 0.172 b 3.312 b	S 32^{95} 33 34^{4} 36 32.066 0.53 b 1.026 b	Cl 35^{76} 37^{24} 35.4527 33.5 b 16.8 b	Ar 36 38 $40^{99.6}$ 39.948 0.675 b 0.683 b
K 39^{93} 40 41^{7} 39.0983 2.1 b 1.96 b	Ca 40^{97} 42 43 44^{2} 46 48 40.078 27.5 b 23.5 b	Sc 45 44.9559 27.5 b 23.5 b	Ti 46^{8} 47^{7} 48^{74} 49^{5} 50^{5} 47.867 6.09 b 4.35 b	V $50^{0.25}$ 51 50.9415 5.08 b 5.10 b	Cr 50^{4} 52^{84} 53^{10} 54^{2} 51.9961 3.05 b 3.49 b	Mn 55 54.9380 13.3 b 2.15b	Fe 54^{6} 56^{92} 57^{2} 58 55.845 2.56 b 11.62 b	Co 59 58.9332 37.18 b 5.6 b	Ni 58^{68} 60^{26} $61^{1.1}$ $62^{3.6}$ $64^{0.9}$ 58.6934 4.49 b 18.5 b	Cu 63^{69} 65^{31} 63.546 3.78 b 8.03 b	Zn 64^{49} 66^{28} 67^{4} 68^{19} 70 65.39 2.75 b 6.38 b	Ga 69^{60} 71^{40} 69.723 2.75 b 6.83 b	Ge 70^{20} 72^{27} 73^{8} 74^{37} 76^{8} 72.61 2.20 b 8.60 b	As 75 74.9216 4.5 b 5.50 b	Se 74 76^{9} 77^{8} 78^{24} 80^{50} 82^{9} 78.96 11.7 b 8.30 b	Br 79^{51} 81^{49} 79.904 6.9 b 5.90 b	Kr 78 80^{2} 82^{12} 83^{12} 84^{54} 86^{17} 83.8 25 b 7.68 b
Rb 85^{72} 87^{28} 85.4678 0.38 b 6.8 b	Sr 84 86^{10} 87^{7} 88^{83} 87.62 1.28 b 6.25 b	Y 89 88.90585 1.28 b 7.70 b	Zr 90^{52} 91^{11} 92^{17} 94^{17} 96^{3} 91.224 0.185 b 6.46 b	Nb 93 92.90638 1.15 b 6.255 b	Mo 92^{15} 94^{9} 95^{16} 97^{10} 98^{24} 99^{10} 95.94 2.48 b 5.71 b	(Tc) (98) 20 b 6.3 b	Ru 96^{6} 98^{2} 99^{13} 100 101^{17} 102^{32} 104 101.07 2.56 b 6.6 b	Rh 103 102.9055 144.8 b 4.6 b	Pd 102^{1} 104^{11} 105^{22} 106^{27} 108^{27} 110^{12} 106.42 6.8 b 4.48 b	Ag 107^{52} 109^{48} 107.8682 63.3 b 4.99 b	Cd 106^{1} 108^{1} 110^{13} 111^{13} 112^{24} 113^{12} 114^{28} 116^{8} 112.411 2520 b 6.5 b	In 113^{4} 115^{96} 114.818 193.8 b 2.62 b	Sn 112^{1} 114 115 116^{15} 117^{8} 118^{24} 119^{9} 120^{32} 122^{5} 124^{6} 118.71 0.626 b 4.892 b	Sb 121^{57} 123^{43} 121.76 4.91 b 3.90 b	Te 120 122^{3} 123^{1} 124^{5} 125^{7} 126^{19} 128^{32} 130^{35} 127.6 4.7 b 4.32 b	I 127 126.90447 6.15 b 3.81 b	Xe 124 126 128^{2} 129^{27} 130^{4} 131^{21} 132^{27} 134^{10} 136^{9} 131.29 23.9 b -
Cs 133 132.90545 29.0 b 3.90 b	Ba 130 132 134^{2} 135^{7} 136^{8} 137^{11} 138^{72} 137.327 1.1 b 3.38 b	La 138 $139^{99.9}$ 138.9055 8.97 b 9.66 b	Hf 174 176^{5} 177^{19} 178^{27} 179^{14} 180^{35} 178.49 104.1 b 10.2 b	Ta 180 $181^{99.99}$ 180.9497 20.6 b 6.01 b	W 180 182^{26} 183^{14} 184^{31} 186^{29} 183.84 18.3 b 4.60 b	Re 185^{37} 187^{63} 186.207 89.7 b 11.5 b	Os 184 186^{2} 187^{2} 188^{13} 189^{16} 190^{26} 192^{41} 190.23 16.0 b 14.7 b	Ir 191^{37} 193^{63} 192.217 425 b 14 b	Pt 190 192^{1} 194^{33} 195^{34} 196^{25} 198^{7} 195.08 10.3 b 11.71 b	Au 197 196.96655 98.65 b 7.73 b	Hg 196 198^{10} 199^{17} 200^{23} 201^{13} 202^{30} 204^{7} 200.59 372.3 b 26.8 b	Tl 203^{30} 205^{70} 204.3833 3.43 b 9.89 b	Pb 204^{1} 206^{24} 207^{22} 208^{52} 207.2 0.171 b 11.12 b	Bi 209 208.98038 0.0338 b 9.156 b	(Po) (209) -	(At) (210) -	(Rn) (222) -
(Fr) (223) -	(Ra) (226) 12.8 b 13 b	(Ac) (227) -	104	105	106												

Ce 136 138 140^{89} 142^{11} 140.115 0.63 b 2.94b	Pr 141 140.90765 11.5 b 2.66 b	Nd 142^{27} 143^{12} 144^{24} 145^{8} 146^{17} 148^{6} 150^{6} 144.24 51 b 16.6b	(Pm) (145) 168.4 b 21.3 b	Sm 144^{3} 147^{15} 148^{11} 149^{14} 150^{7} 152^{27} 154^{23} 150.36 5922 b 39 b	Eu 151^{48} 153^{52} 151.965 4530 b 9.2 b	Gd 152 154^{2} 155^{15} 156^{20} 157^{16} 158^{25} 160^{22} 157.25 49700 b 180 b	Tb 159 158.92534 23.4 b 6.84 b	Dy 156 158 160^{2} 161^{19} 162^{26} 163^{25} 164^{28} 162.5 994 b 90.3 b	Ho 165 164.93032 64.7 b 8.42 b	Er 162 164^{2} 166^{33} 167^{23} 168^{27} 170^{15} 167.26 159 b 8.7 b	Tm 169 168.93421 100 b 6.38 b	Yb 168 170^{3} 171^{14} 172^{22} 173^{16} 174^{32} 176^{13} 173.04 34.8 b 23.4 b	Lu 175^{97} 176^{3} 174.976 74 b 7.2 b
Th 232 232.03805 7.37 b 13.36 b	(Pa) (231) 200.6 b 10.5 b	U $235^{0.72}$ $238^{99.3}$ 238.0289 7.57 b 8.9 b	(Np) (239) 175.9 b 14.5 b	(Pu) (244) 1017.3 b 7.7 b	(Am) (243)	(Cm) (247)	(Bk) (247)	(Cf) (251)	(Es) (252)	(Fm) (257)	(Md) (258)	(No) (259)	(Lr) (261)

Periodic Table for NAA

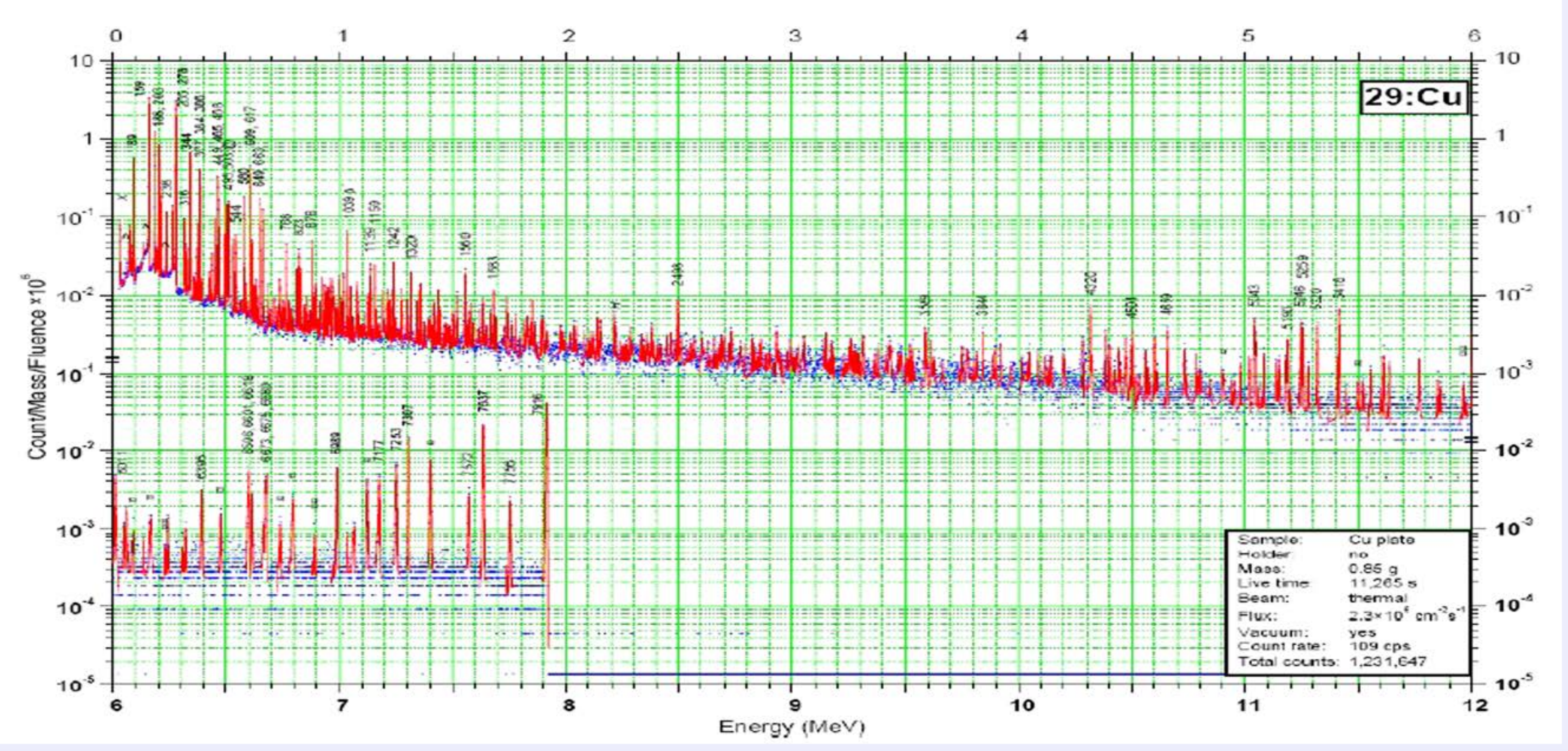
No light elements!



γ spectra:

characteristic for any element

used for elemental composition and isotope's identification



Elemental Analysis by PGAA

PGAA characteristics

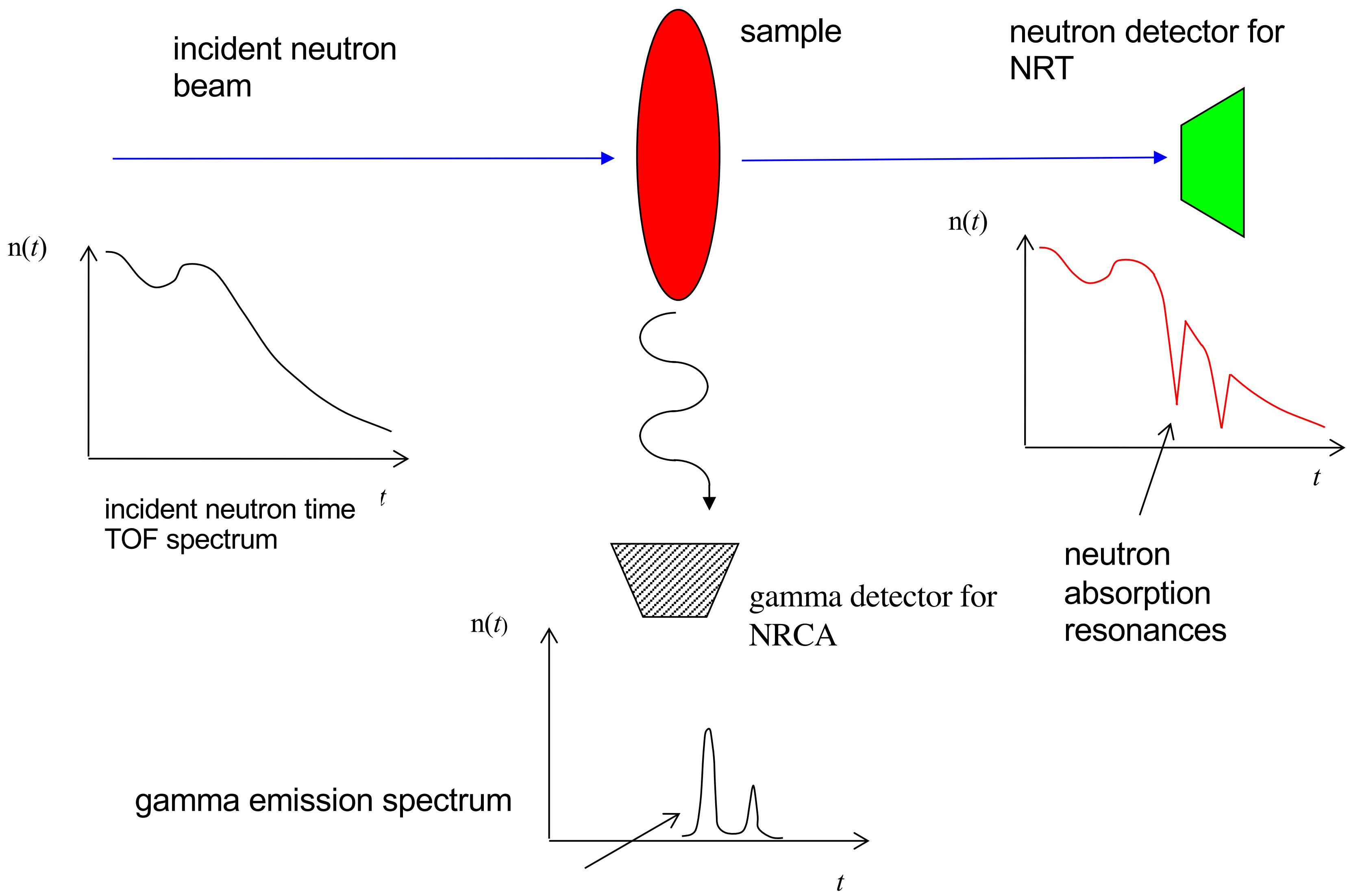
- Non-destructive, non invasive, no preparation
- Measurement in vacuum or in air
- Good sensitivity for **H, B**, **C**, N, P, S, Cl, Cd, Sm, Gd, Hg
- Quantitative

  detection limit down to ~ 10 ppb (element and object dependent)
- Acquisition time:

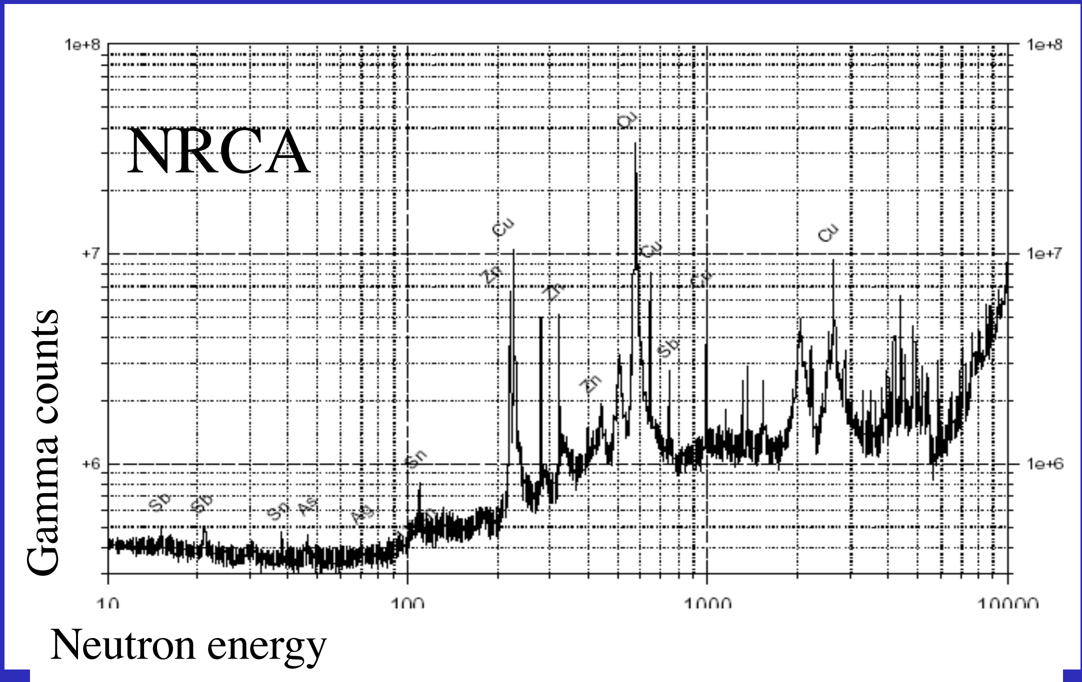
  few minutes (B, Gd, Sm, H) – few hours (C, N, Pb...)
- Zero spatial resolution (bulk analysis)
- Output = Averaged (relative) composition of the object
- Application: archaeometry, nuclear industry, medicine,

  material science, cosmo-chemistry, …

NRT/NRCA principle



NRCA on brass object, GELINA, Geel, Belgium



14/15th century
Cu/Zn Benin plaque
(private collection)

Element analysis

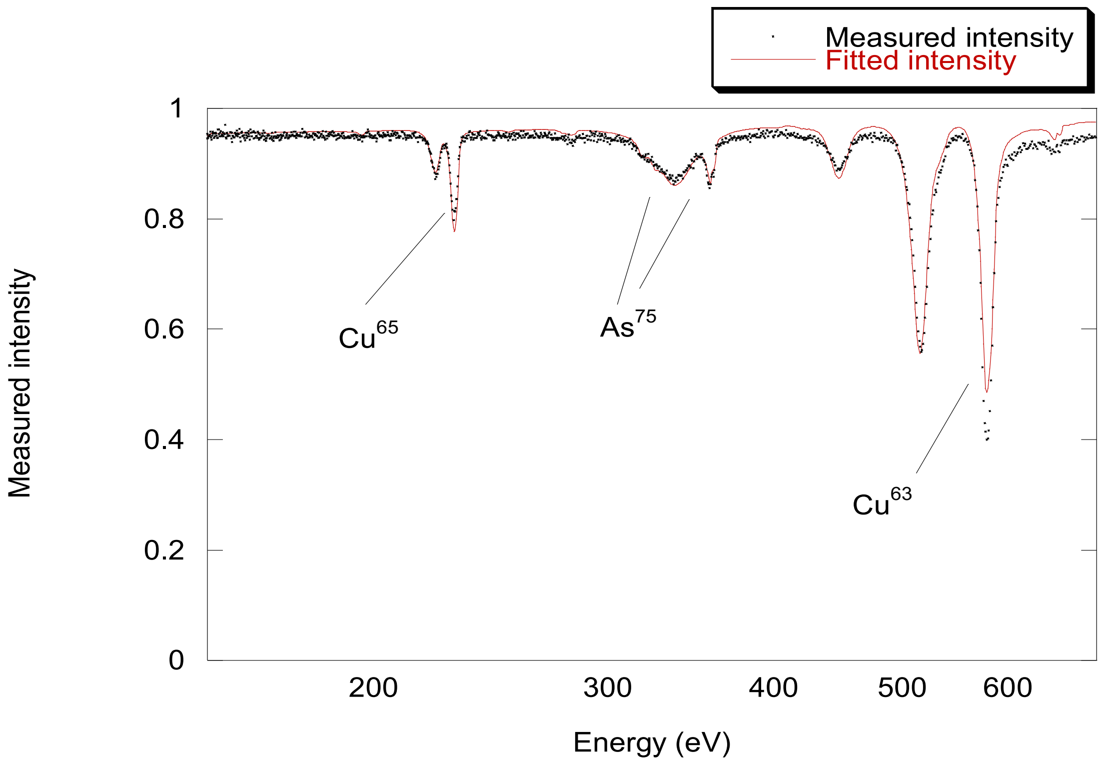
M. Blaauw, H. Postma, P. Mutti, (2002)

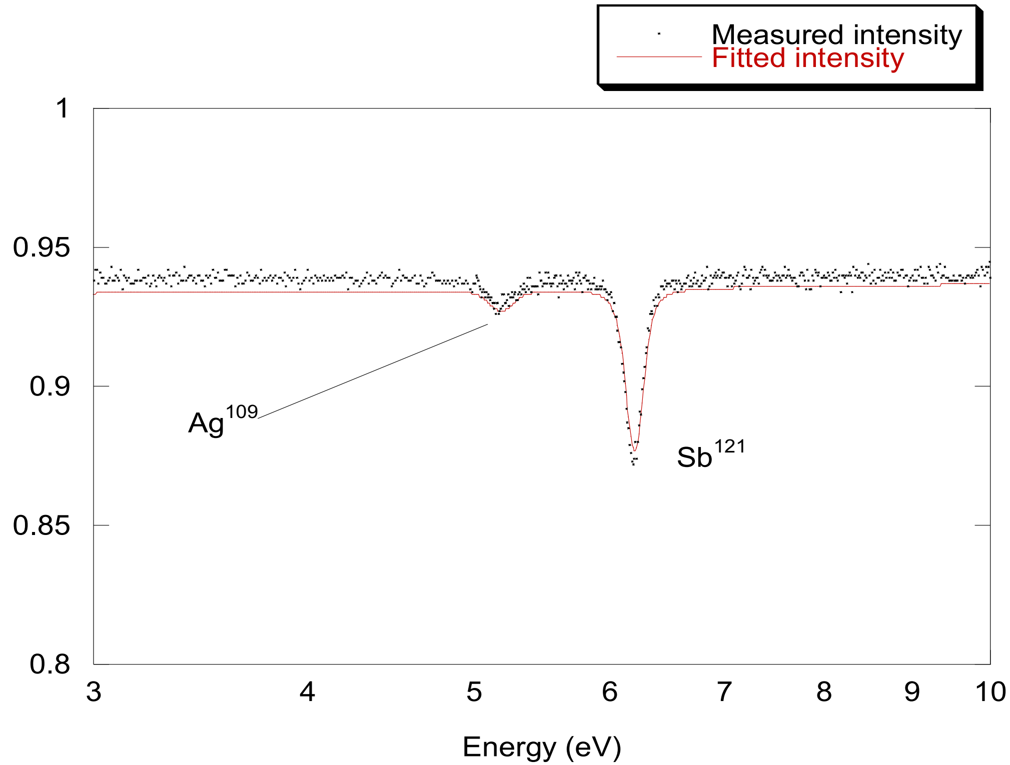
El.	energies used (eV)	plaque concentration (g/g and 95 % conf.)
Cu	230, 579, 650, 994	0.67 ± 0.02
Zn	282, 323	0.32 ± 0.01
Pb		< 0.08
Fe	1150	0.009 ± 0.005
Sn	111	0.0079 ± 0.0007
Sb	6.22, 21.4	$(3 \pm 1)\text{x}10^{-4}$
As	47	$(6.6 \pm 1.1)\text{x}10^{-4}$
Ag	5.19	$(4.3 \pm 0.2)\text{x}10^{-4}$

$$T(E) = \frac{C_{in}}{C_{out}} = e^{-\sum_x n_x \sigma_{tot}(E)} R(E)$$

NRT can be as sensitive as 0.01 % w/w for selected elements relevant for CH, like Ag, Au, and as 0.5% for Cu, Sn, As

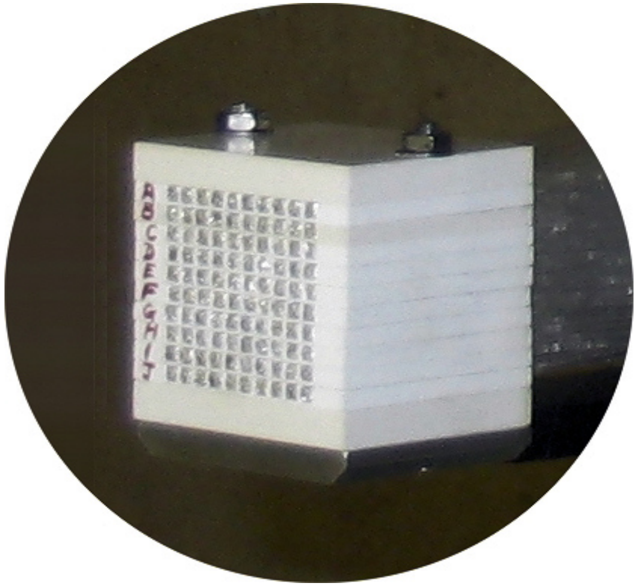
Ancient calcholitic axe blade from the near East.





E. M. Schooneveld and the ANCIENT CHARM collaboration, *J. Phys.* D 42 No. 15 152003 (2009)

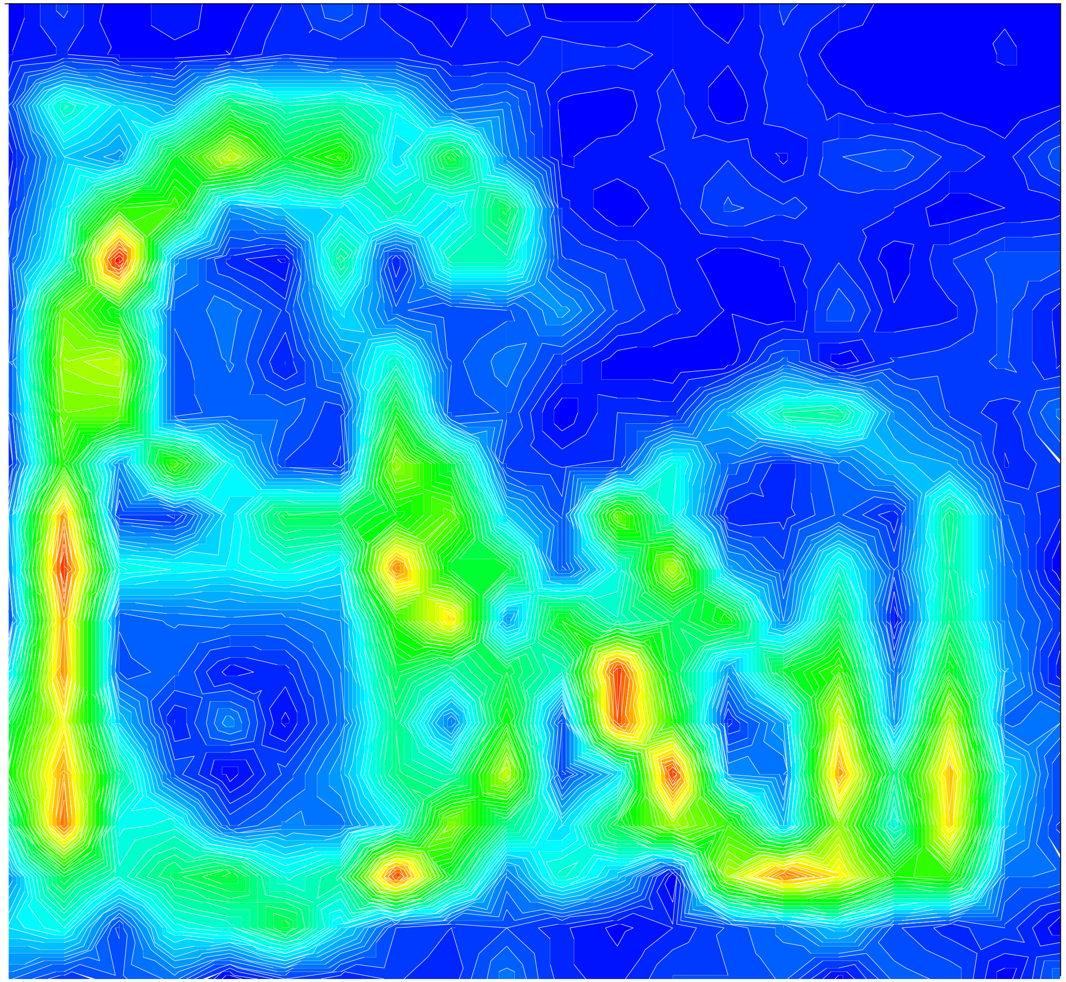
NRT detector



- 10 * 10 array of ^{6}Li-glass scintillators
- 1.8mm * 1.8mm * 9mm
- 2.5mm pitch
- Efficiency (1keV) = ~3%

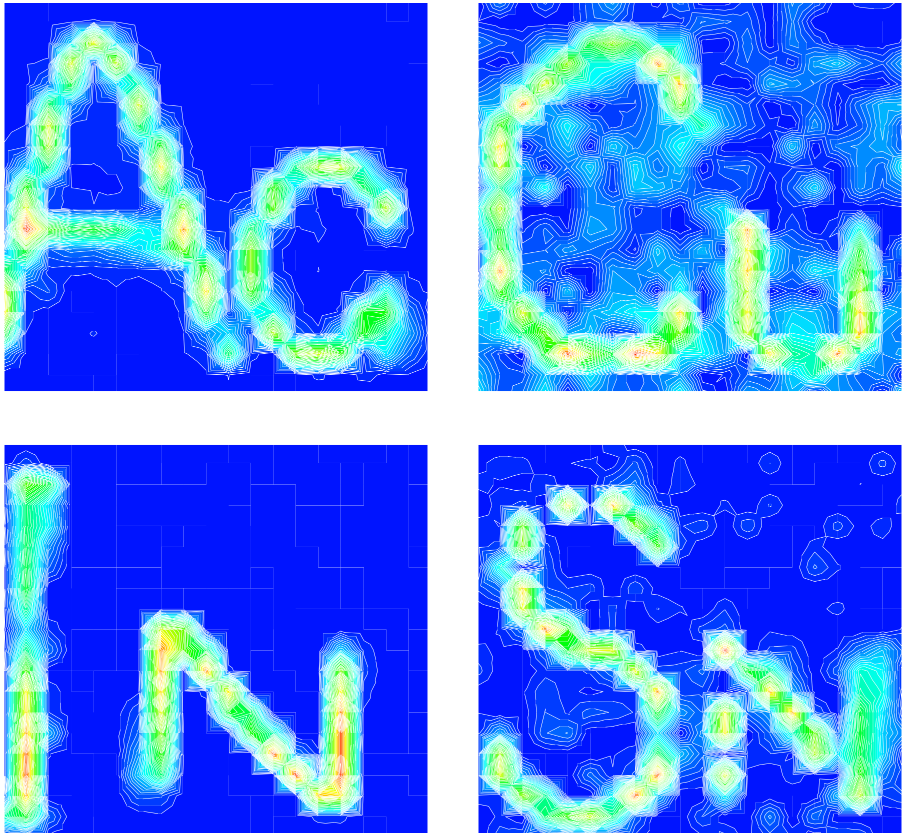
NRT test

- Mystery stack of 4 layers

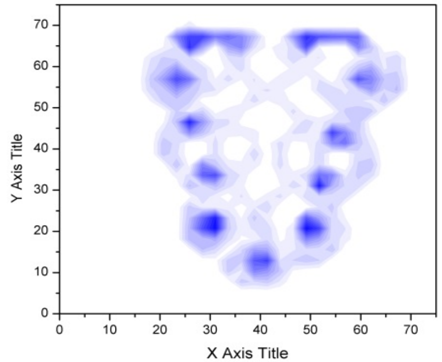
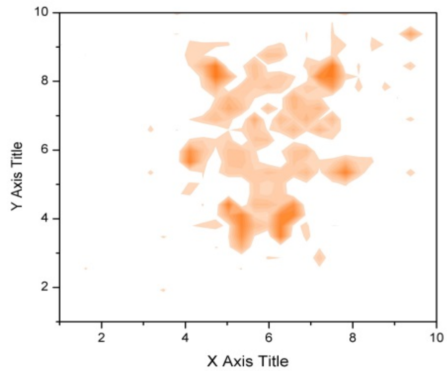
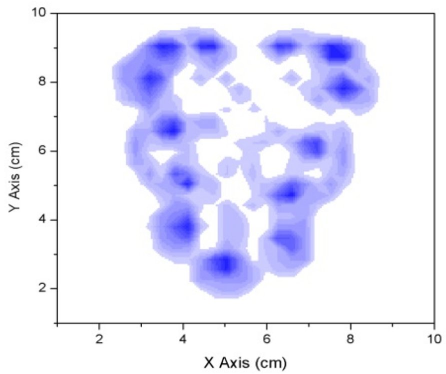
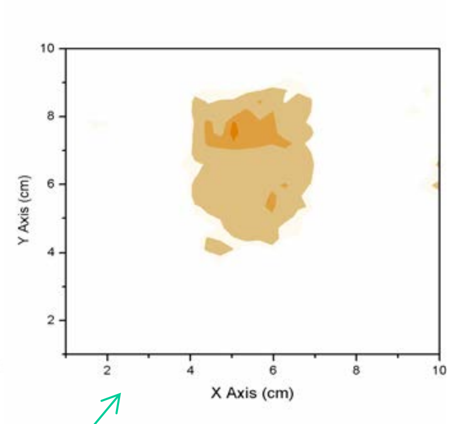


NRT test

- Thin wires of different materials



NRT Imaging (NRTI can reveal inner features in the bulk of metallic objects in a non-destructive way

	Image	Ag	Cu
Replica belt mount			
Real ancient belt mount (7° c. AD from Kronie, H)			

Trace of ancient fixing?

End of second part of presentation

Scattering techniques

Neutron Diffraction

Small Angle Neutron Scattering (SANS)

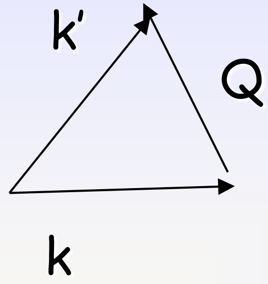
Ultra SANS (USANS)

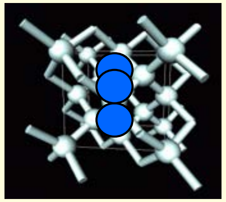
Where atoms 'are': Diffraction

Clifford G. Shull

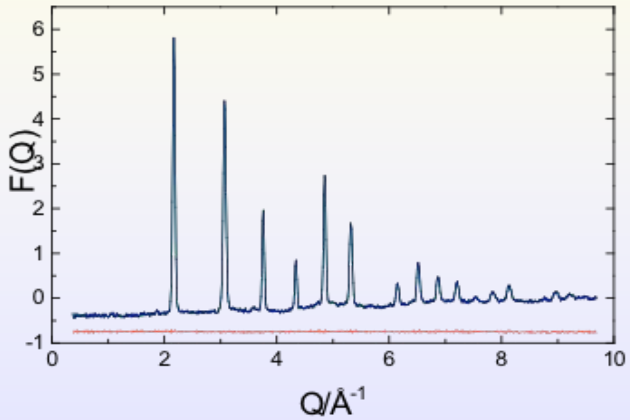
Premio Nobel 1994

Where atoms 'are'....

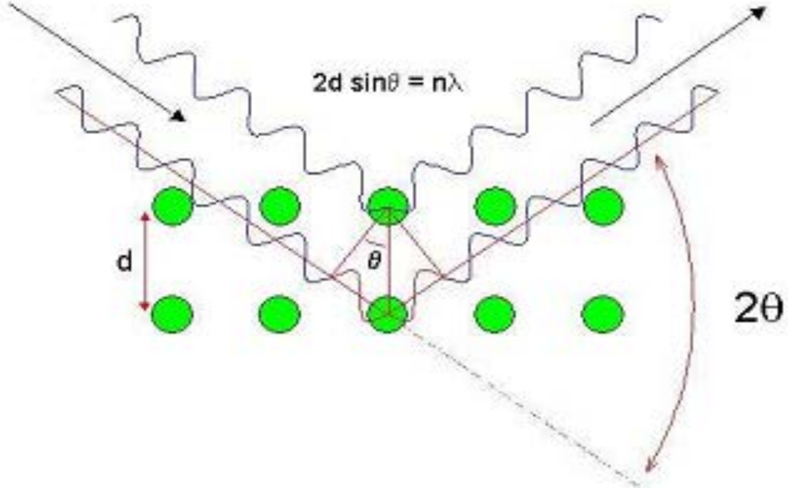




Neutron Diffraction

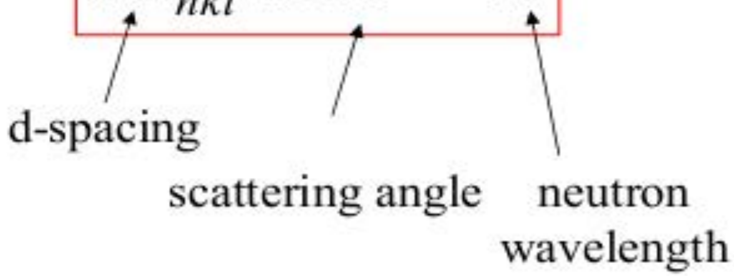


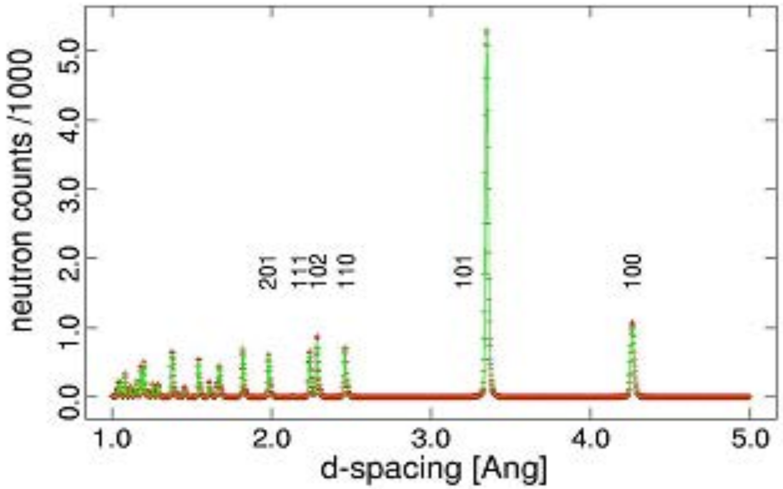
Fundamental equations of crystallography (1)



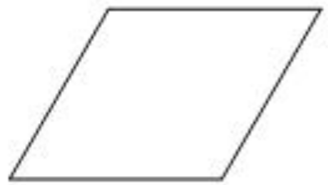
Bragg's law:

$$2d_{hkl}\sin\theta = \lambda$$

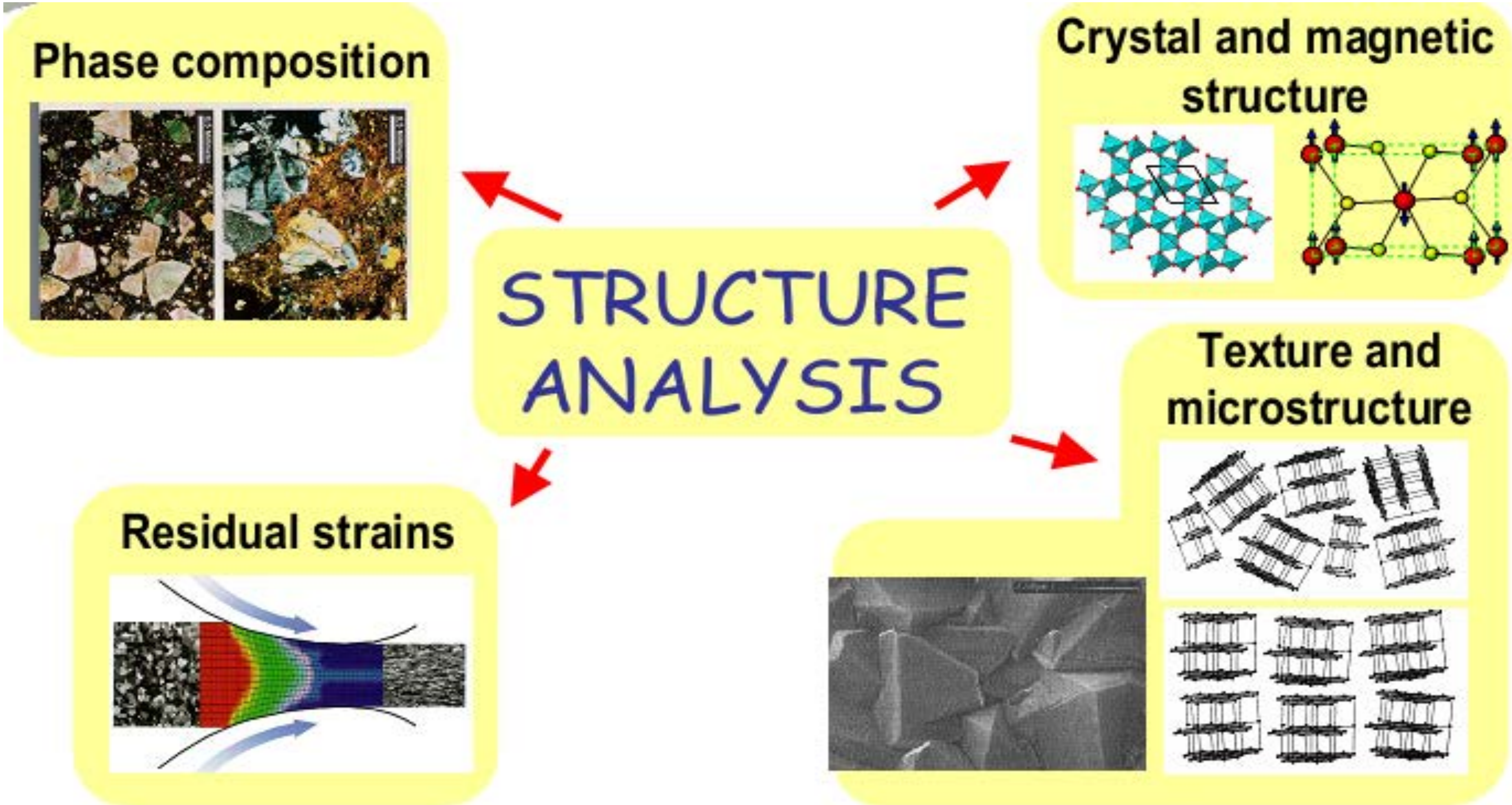




Measure reflections positions
⇨ interplanar spacings
⇨ size of unit cell in Å



Diffraction analysis of polycrystalline materials



Time of Flight Neutron Diffraction

- Powerful for investigating the crystal structure of the samples
- TOF: determination of neutron energy for a 'white beam' measuring their time of flight

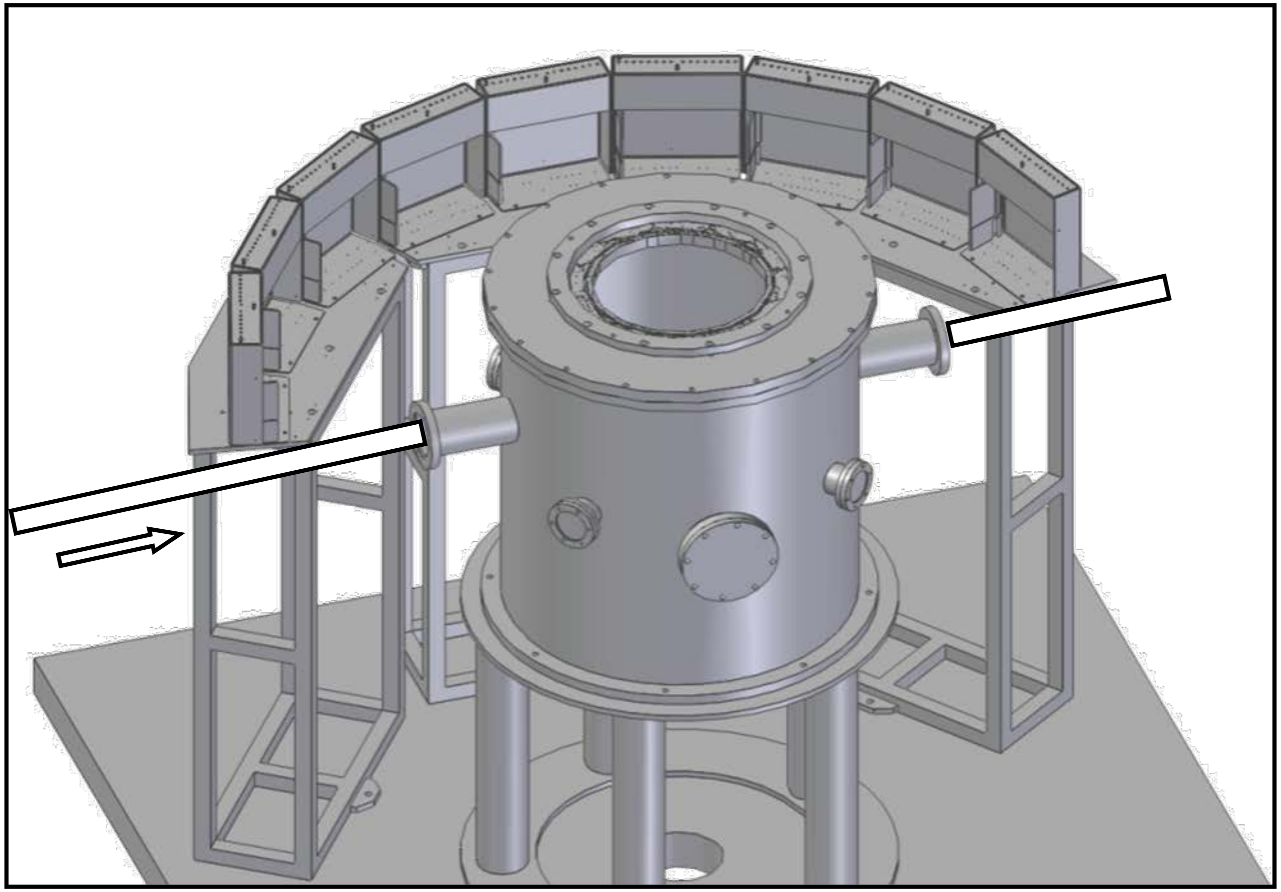
$$E = \frac{1}{2} m_n v^2 = \frac{1}{2} m_n \left(\frac{L}{TOF} \right)^2$$

Bragg's Law

$$(TOF)_{hkl} = \frac{2m_n}{h} L d_{hkl} sin\theta_0$$

m_n = neutron mass
L = flight length between the moderator to the sample
ToF = time employed to cover the distance L

Italian Neutron Experimental Station
INES@ISIS



Italian Neutron Experimental Station

- Large sample holder tank (1 m^3)
- 144 ^3He diffraction detectors
- 9 banks
- d-spacing: 0.4-12.0 Å
- High resolution: 0.10% backscattering
- Beam size: 30x30mm
- Jaws to shape the beam: min 2x2mm
- Laser pointer to align the sample
- Neutron Radiography apparatus to align and scan through the sample

ToF -ND for Archaeometry

What can be achieved in archaeometry by ToF – Neutron Diffraction measurement?

- **Determine the wt% of crystal phases present in the sample**
- **Alloys composition (elements wt%)**

Composition

- **Texture (preferred cristallites orientation)**
- **Cristallite size**
- **Residual stress**

Working techniques

Roman coins

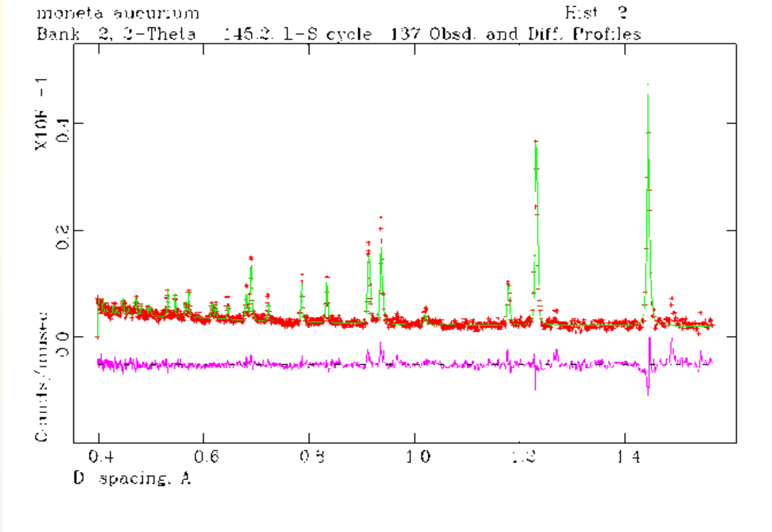
Authenticate the silver coins (264- 241 B.C. & 218-202 B.C.)

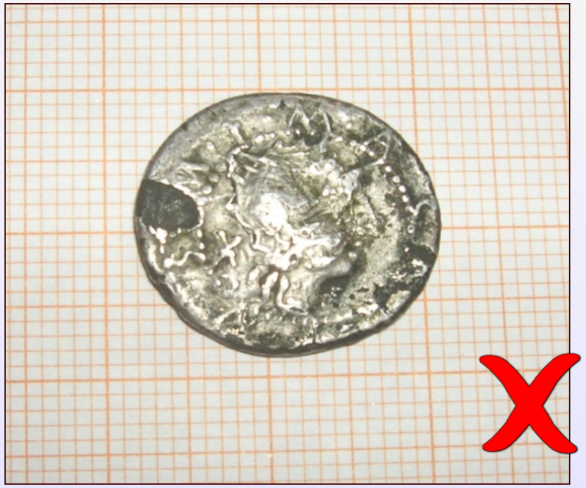
- During 2nd century BC large amount of counterfeit money was introduced

Aucurium

- 100% Silver

AUTHENTIC!

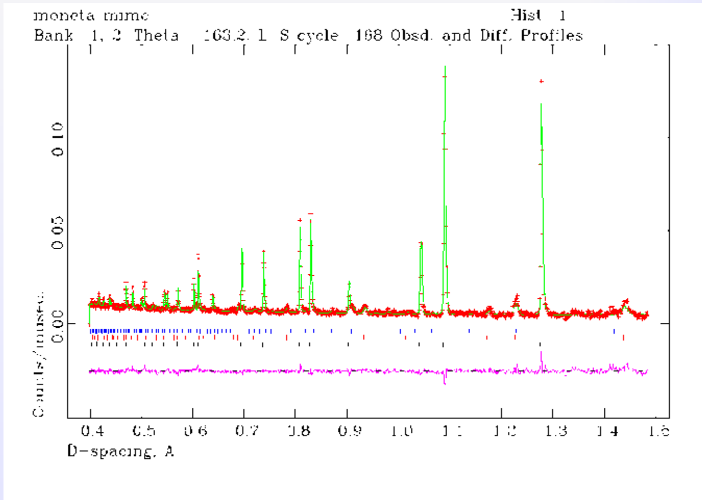




Mime

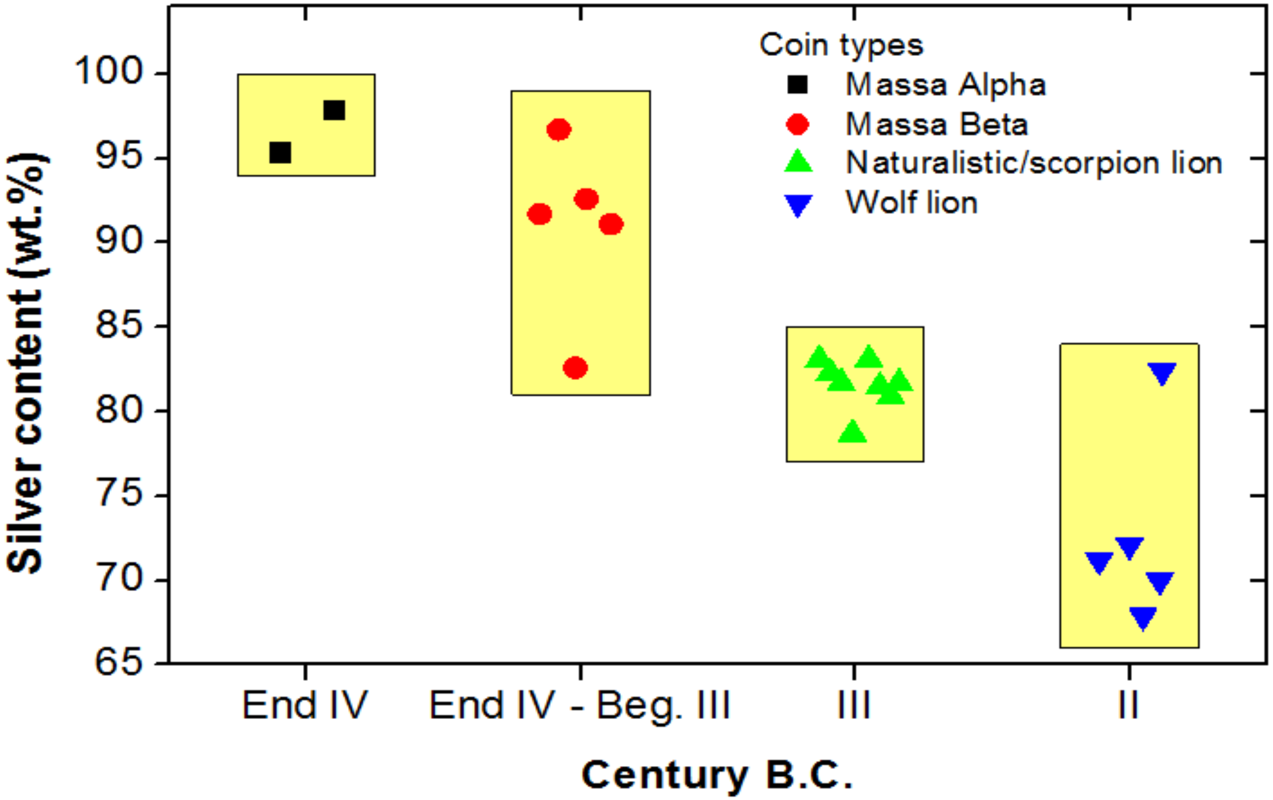
- Copper: 79.247 %
- Silver: 18.329 %
- Cuprite: 2.424 %

FAKE!



G. Festa and al. 2009

Celtic Silver coin from northern Italy



- The first imitation shows a Ag content similar to the original dracma
- Ag content allow us to establish a relative chronology
- We can now try to understand the comparison between celtic coins and the greek ones

J. Corsi *et al*, NINMACH, 9th–12th September 2013

Identification of the forging methods of Japanese swords from the Ancient Sword (Koto) Age to modern times (Gendaito). A non destructive study through neutron diffraction

Francesco Grazzi

Consiglio Nazionale delle Ricerche, Istituto Sistemi Complessi

Japanese sword: historical introduction

The Japanese style swordsmaking is historically divided in four periods:

Kotō (old sword) 987-1596

Shintō (new sword) 1596-1781
Shinshintō (new new sword) 1781-1876
Gendaitō (modern era sword) 1876-now

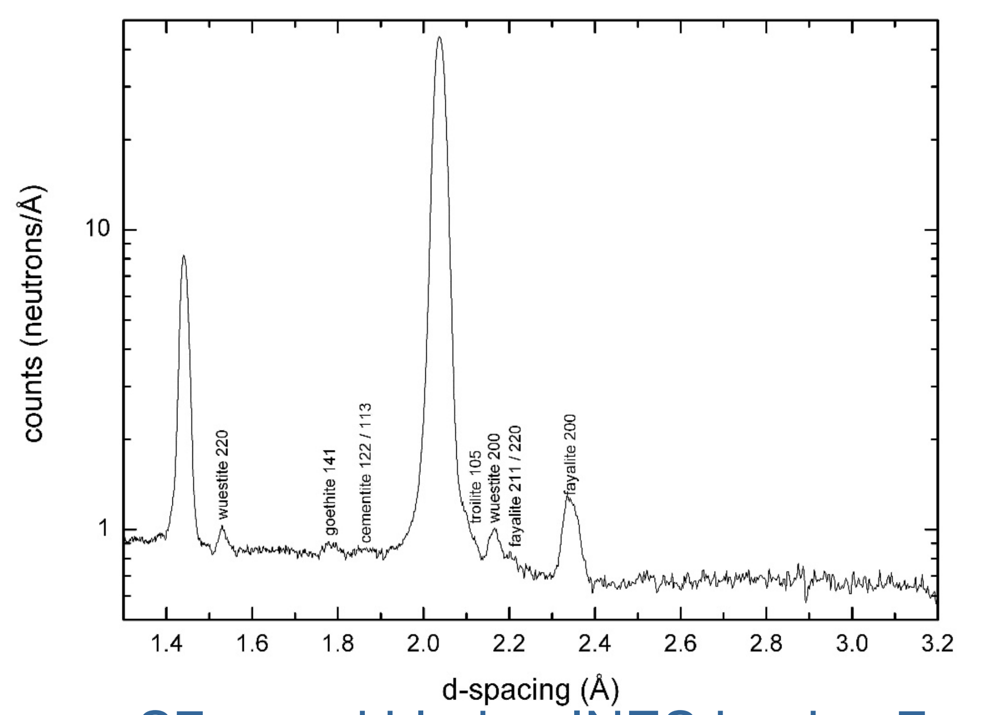
In Koto age five forging traditions were born and co-existed together
Different smelting and smithing procedures
Different forging techniques

Diffraction data

Sample group 1: broken swords

Quantitative multiphase analysis

3 cross sections
average



S7 sword blade - INES bank n.7

Searched phases:

- **ferrite, cementite:**
  stable metal phases;
- **martensite, austenite:**
  metastable metal phases
- **wuestite:**
  smelting;
- **goethite, magnetite:**
  mineralization;
- **hematite:**
  ore or mineralization;
- **fayalite:**
  smelting;
- **troilite:**
  carburization related

Results

Basic technological features of the five koto age sword forging traditions through neutron diffraction

Tradition	Type	Carbon level	Treatment after quenching	# samples
Yamato	Standard	Medium all	Quick or no tempering	2(1)
Yamashiro	Standard	High at edge and tip Very low at body	No tempering	2
Bizen	Mass production	Low at edge Wrought iron at body	No tempering	4
Bizen	High quality	High at edge Low at body	No tempering	1
Sohshu	Type a	Very high all	Long tempering	1
Sohshu	Type b	High at edge and tip Low at body	No tempering	2
Mino	Undetermined	Medium at edge Low at body	Short tempering	1

Final Remarks

Neutrons are a well suited tool in support of heritage science

Further developments:

Phase contrast / energy selective imaging

High resolution resonance neutron tomography

Integrated analysis: use of complementary techniques (e.g. n+X) is best