NUCLEAR TECHNIQUES IN RESEARCH FOR CULTURAL HERITAGE

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CHARISMA

Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme - GA FP7 228330

2009 - 2013

Partners (21)

- LOUVRE
- PRADO
- The National Gallery London
- The British Museum
- National Research Council, Italy
- Netherlands Cultural Heritage Agency
- Royal Institute for Cultural Heritage, Netherland
- Doerner Institute

- University of Perugia
- Foundation for Research and Technology, Hellas
- Soleil Synchrotron
- Nicolaus Copernicus University
- RWTH Aachen University
- ATOMKI, HAS
- Laboratoire de Recherche des Monuments Historiques
- Idryma Ormylia - Art Diagnosis Centre
- Opificio delle Pietre Dure
- BNC, HAS
- Alma Mater Studiorum, University of Bologna

Networking activities

- ***Towards European common standards*** leads to common strategies in analysis and assessment of best practices in conservation
- ***Workshops, training and expertmeetingsto scientific excellence*** develops your skills and diffuses knowledge through scientific and technical meetings

Transnational access

MOLAB

FIXLAB

Open the archives of European Institutions

Collection of portable equipment for in-situ investigations

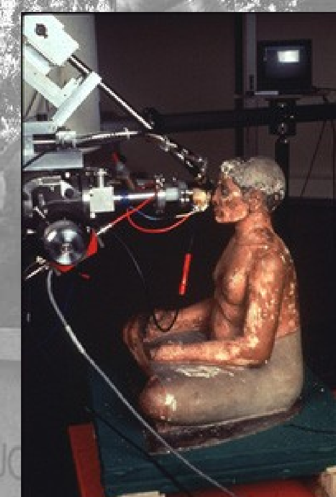
Access to large scale facilities for non-invasive techniques

Joint research activities

Innovative methods & instrumentation for laboratory research establishes newmethodologies for the study of artwork surfaces or of microsamples.

Exp

• *conservation-scientists* developing research on **materials** • *conservation-scientists* performing **provenance studies** • *conservation-scientists* that need to characterise **micro-details** and prevent further damages…



PIXE measurement in AGLAE

Expertise of the FIXLAB partners

- French platform
  - AGLAE @ C2RMF (external non-invasive, whole art object, elemental, high sensitivity including light elements, 20-µm lateral resolution, + µXRD…)
  - IPANEMA @ SOLEIL (mainly microsamples, elemental / speciation - molecular / structure - texture, µm lateral resolution)
- Hungarian platform
  - Budapest Neutron Center (non-invasive whole art object in bulk, elemental / structure – texture, + ion beam and XRF…)
  - ATOMKI Debrecen (in-vacuum milli- or microbeam, high lateral resolution elemental mapping, high sensitivity including light elements,
1-µm lateral resolution, surface topography and 2D tomography)

Budapest Neutron Centre
Budapest XII, Konkoly Thege út 29-33, KFKI H-1525 Budapest, Pf. 49. Hungary

charisma
Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration

SEVENTH FRAMEWORK PROGRAMME

Transnational access

FIXLAB_ *PLATFORM B*

BUDAPEST-DEBRECEN

ATOMKI-HAS, DEBRECEN

Single access & joint access service supported

Budapest Neutron Centre

contact: Dr. Kasztovszky Zsolt, kzsolt@iki.kfki.hu

http://www.bnc.hu/

Consortium:

HAS Atomic Energy Research Institute
HAS Research Institute for Solid States Physics and Optics
HAS Institute of Isotopes
HAS Research Institute for Particle and Nuclear Physics

Prompt gamma activation analysis (PGAA) facilities
Neutron scattering spectrometers
X-ray spectroscopy – PIXE, pXRF

ATOMKI - Institute of Nuclear Research (Debrecen)

contact: Dr. Zita Szikszai,
szikszai@namafia.atomki.hu

Accelerator based PIXE, PIGE, RBS with focused ion beams

The secret of Viking arms

This sword is supposed to be an arm of the Viking Guards of the first Hungarian king

István I. (1000-1038)

The secret of Viking arms

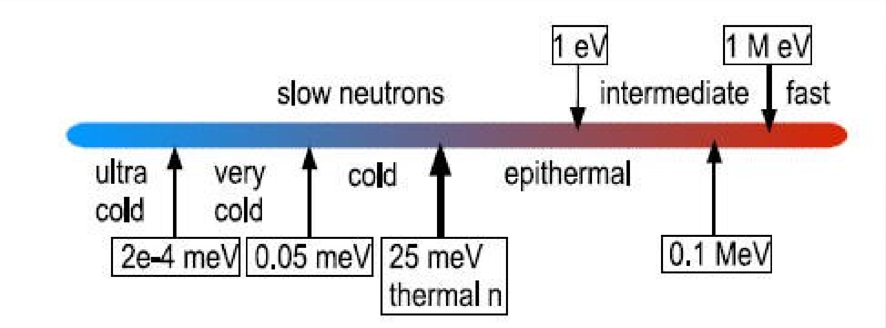
The *Regalia* of Hungary

The question of historians:

Was the king himself also using a Viking sword and which is the real fighting one?

Sword of István I. (in Prague since 1356)

Neutron

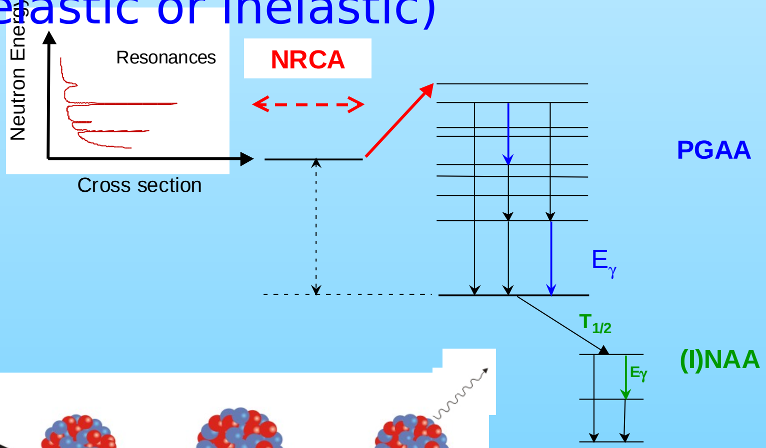


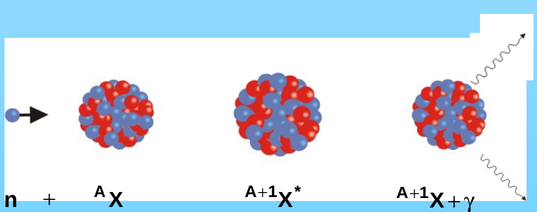
- Mass: m=939 MeV/c^2
- Electric charge: Q=0
- Magnetic momentum: $\mu = -1{,}9\ \mu_N$; Spin: 1/2

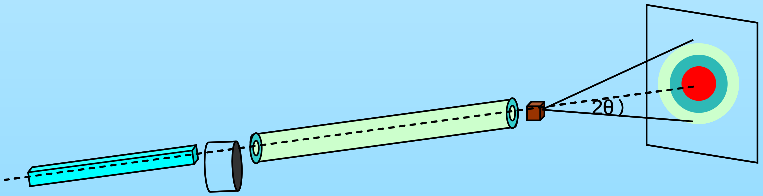
INTERACTIONS WITH MATTER

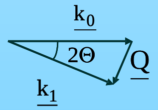
Radiative capture – (n,γ) reaction

Scattering (elastic or inelastic)









$$\underline{Q} = \underline{k}_1 - \underline{k}_0$$

$$|\underline{k}_1| = |\underline{k}_0|$$

$$Q = \frac{4\pi}{\lambda}\sin\Theta$$

$$k = \frac{2\pi}{\lambda}$$

Composition: NRCA, PGAA, INAA

Structure: SANS, TOF-ND

NEUTRONS FULFILL THE REQUIREMENT OF NON-DESTRUCTIVITY!

- As an electrically neutral particle, it can go deep into the sample
- Large objects can be placed in external beams – without sampling
- Induced radioactivity decays fast in most cases

TYPICAL TASKS IN ARCHAEOMETRY

- Provenance study – identification of raw material source(s) or workshop(s)
- Identification of fakes or imitations
- Survey of the art objects’ condition prior to restoration or conservation
- Dating - indirectly

Archaeometry applications at BNC

Budapest Neutron Centre

Budapest XII, Konkoly Thege út 29-33, KFKI H-1525 Budapest, Pf. 49. Hungary

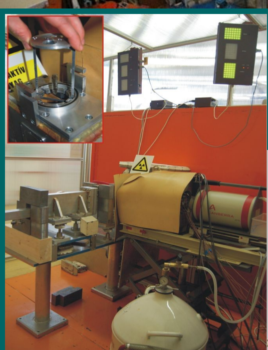
nmi3 — ... Access to 10 neutron and 2 muon facilities — ... travel and subsistence support — Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy

2000-2003

2004-2008

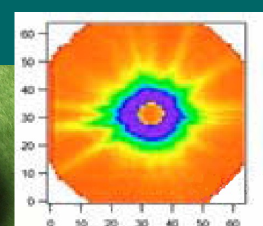
CAPACITIES

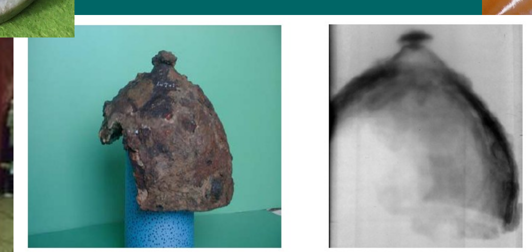
2009-2013



PGAA

Highlight 2008





RADIOGRAPHY

PROMPT GAMMA AKTIVATION ANALYSIS – PGAA

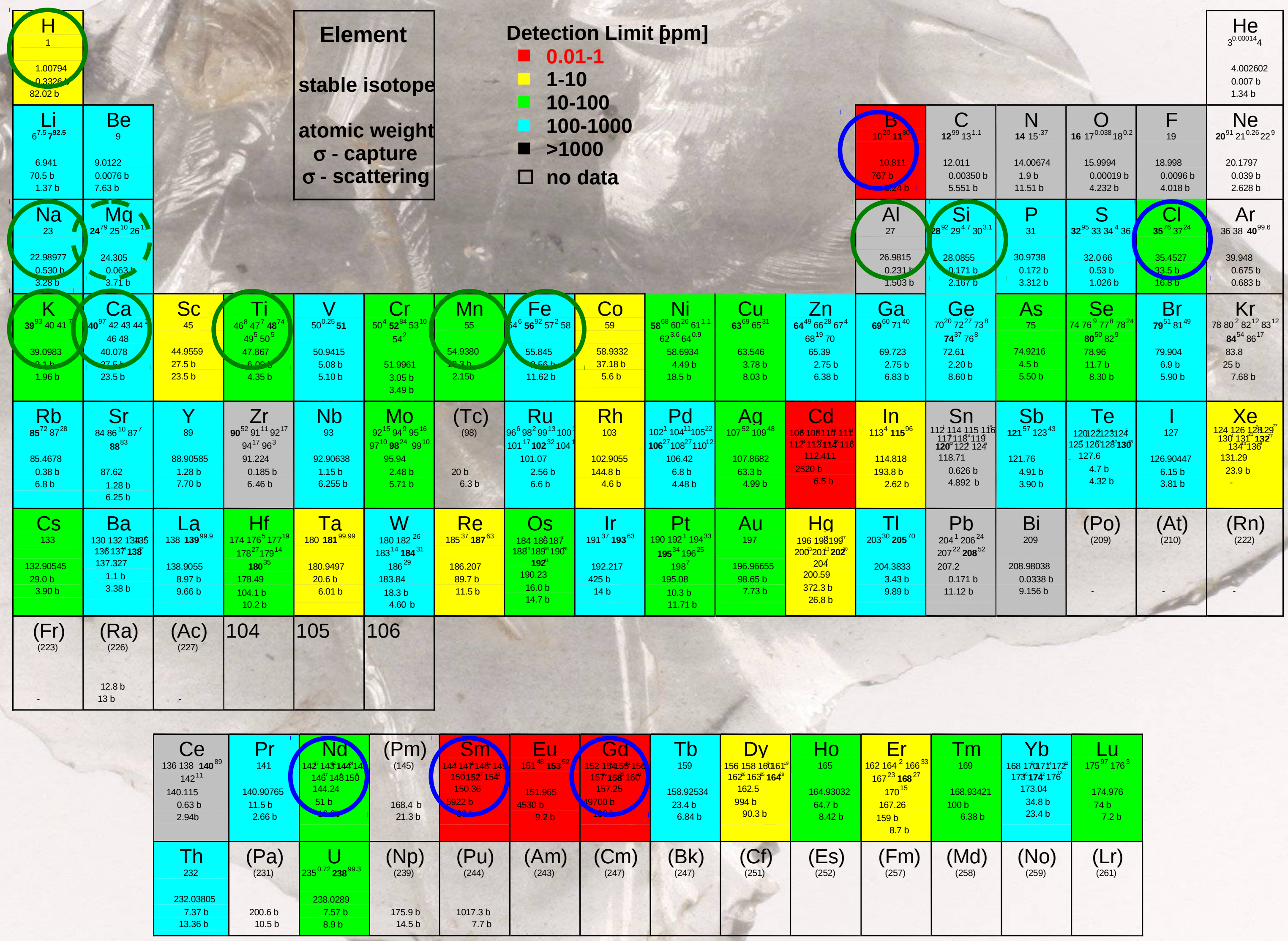
Applicable:

- Bulk composition of any (solid, liquid) sample
- Minimum sample mass ~ 0,1 g
- In principle all chemical elements
  Very sensitive: **H, B, Cl, Cd, Nd, Sm, Eu, Gd**
- Detection Limits 0,1 ppm – 1000 ppm

Advantages:

- Non-destructive
- Minimal sample preparation
- Average for the total irradiated volume
- Parts of large objects can be studied
  (beam size: 5 mm^2 – 2X2 cm^2)

APPROXIMATE DETECTION LIMITS FOR THE BUDAPEST PGAA



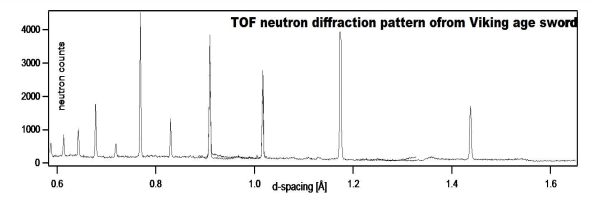
TIME OF FLIGHT NEUTRON DIFFRACTION – TOF-ND

Applicable:

- To study monochrystal or polychrystal structure
- Strain analysis
- Texture analysis
- To identify phases

Advantages:

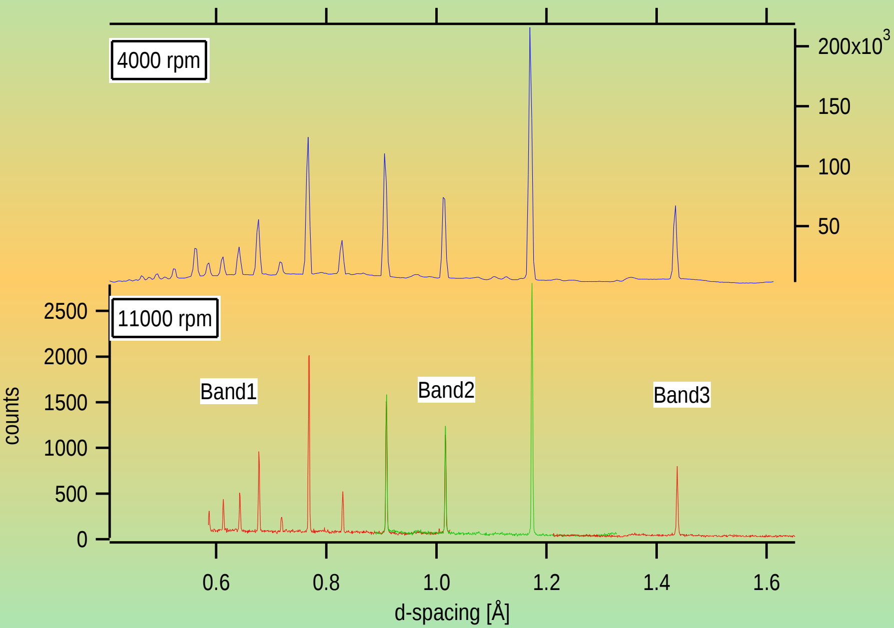
- Non-destructive
- Minimal sample preparation
- Average for the total irradiated volume
- Parts of large objects can be studied (beam size: 3 cm^2 – 2,5 X 10 cm^2)

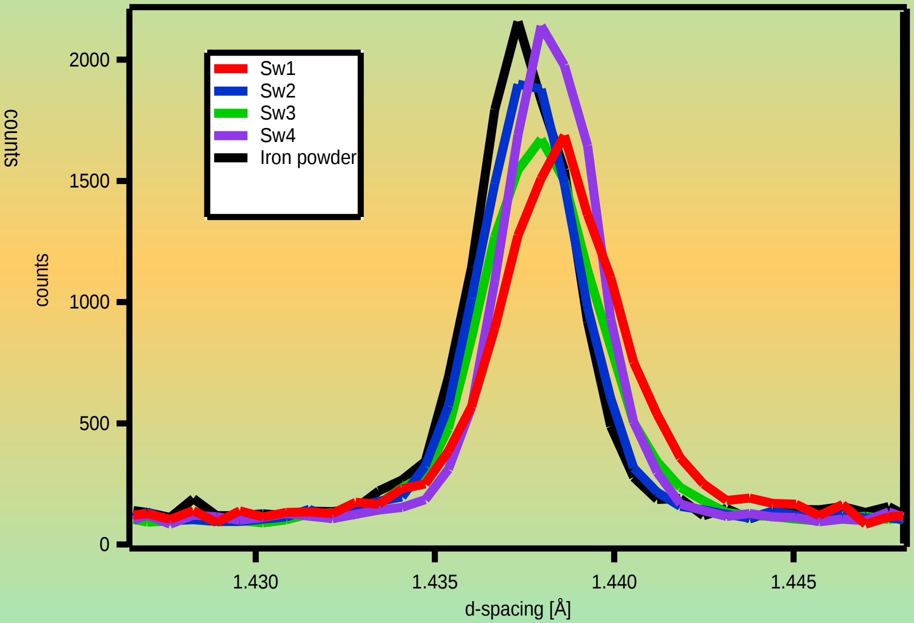


The secret of Viking arms

Four – believed – medieval swords had been studied.
Sword1 strongly corroded but together with **Sword2** were visibly Damascus blades, certificated archeological objects. **Sword3** and **Sword4** were in good state but not certificated.

High resolution TOF diffraction: 150 spectra



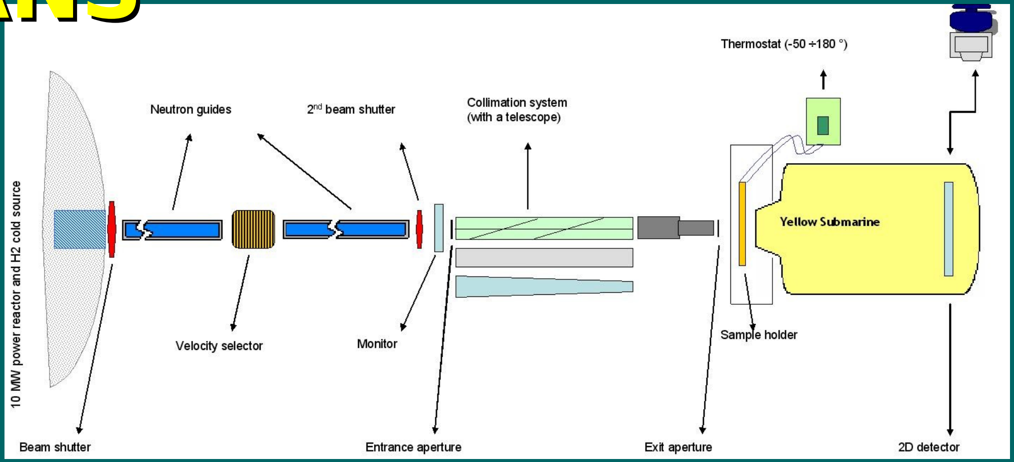


- Phase composition. (For steel phases as ferrite, cementite, martensite and non-steel phases).
- The degree of alloying of the main phase.
- The total carbon content (using the two previous information)
- Texture analyses (preferred orientations of the crystallites).
- Average internal stress and dislocation density.

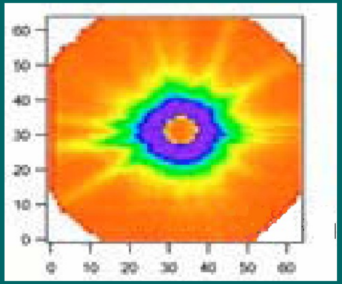
Some conclusions:

- Important and equal cementit content
- Inhomogeneous precipitate distribut.
- The tensile strength was nearly same
- ***Except for 1 sword - decorated***

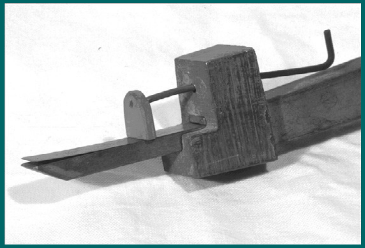
SMALL ANGLE NEUTRON SCATTERING – SANS



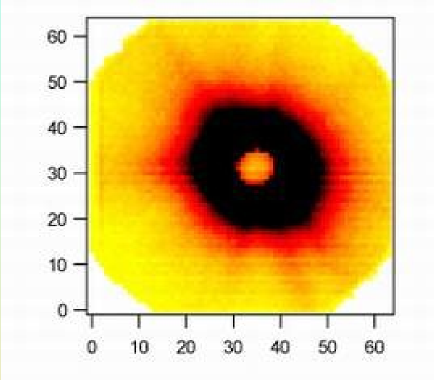
Applicable:
- To study inhomogeneities 1-100 nm scale
- To determine pore size
- To study anisotropy, precipitates in metals or in minerals
- To study inhomogeneities, porosity in cheramics, stones



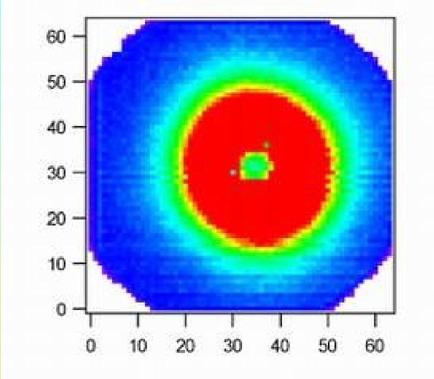
Advantages:
- Non-destructive
- Minimal sample preparation
- Average for the total irradiated volume
- Parts of large objects can be studied
  (beam size: mm^2 – 4X4 cm^2)



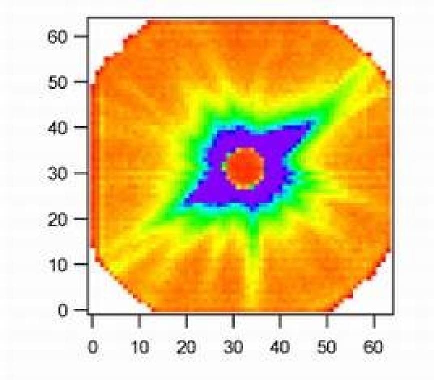
Marble samples from different mines



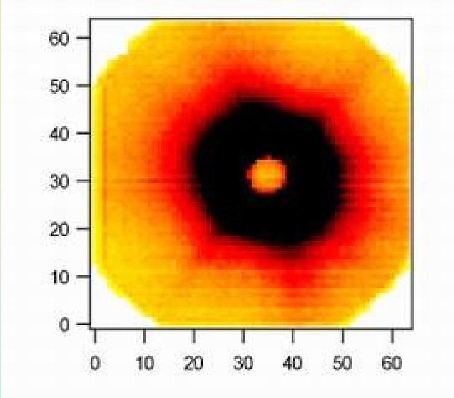
Rimski 2, Hungary



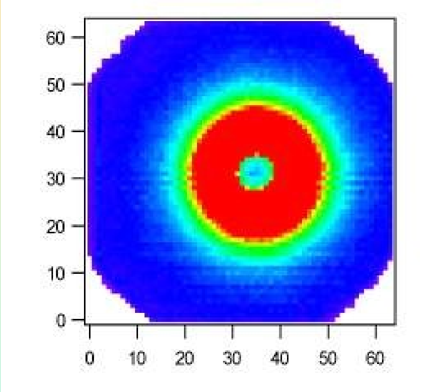
PK1, Slovenia



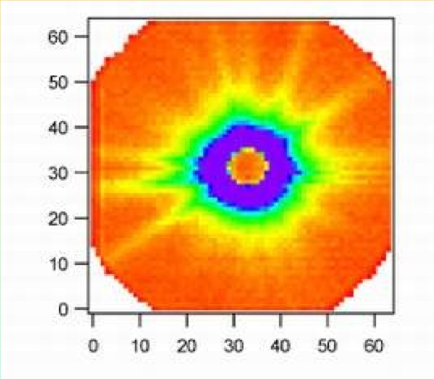
K7, Turkey



Rimski 3, Hungary



PK3, Slovenia



K9, Turkey

anisotropic distribution of nanoscale pores or precipitates

X-RAY SPECTROSCOPY – PIXE, XRF

Applicable:
- For near-surface analysis 10-500 µm
- Detection Limits 50-1000 ppm, Al-U

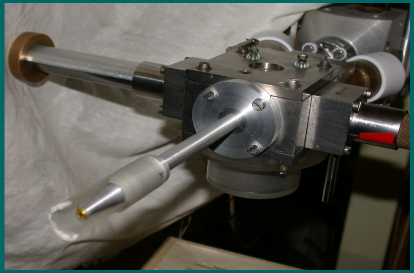
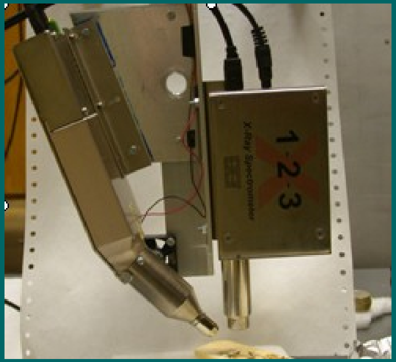
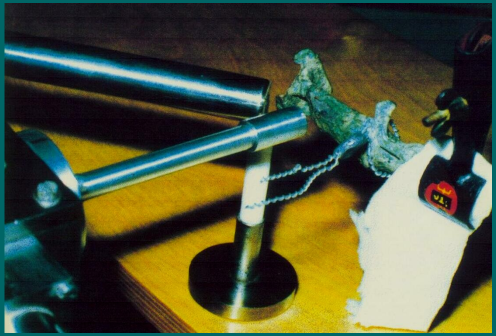
Advantages:

PIXE

- Non-destructive
- 3D positioning (even for large objects)
- Minimal sample preparation
- Penetration depth 8-20 µm
- Beam size: 1-2 mm^2

XRF

- Non-destructive
- Fast (in situ) analysis
- Penetration depth 20-170 µm
- Beam size : 25 mm^2

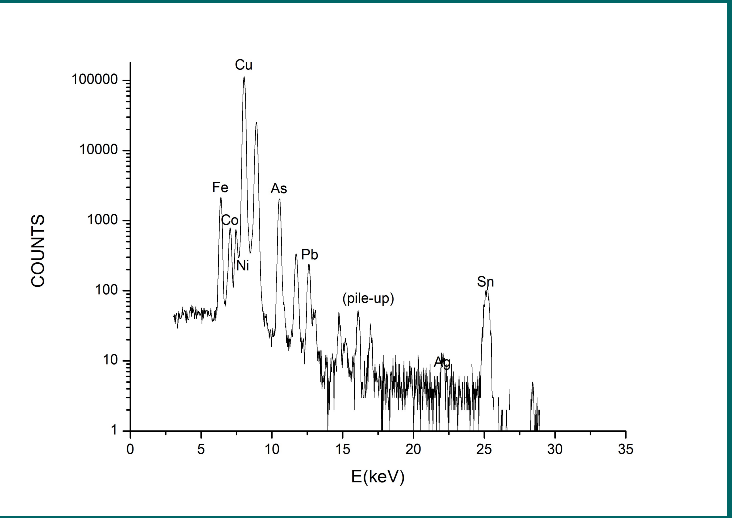





External beam PIXE contrubution to the CHARISMA project

Bronze-Age Usage and Development of Defensive Armour in Eastern Europe

Project leader: Marianne Mödlinger,
Landesmuseum Kärnten, Klagenfurt, Austria

A bronze helmet from Northern Hungary facing to the external proton beam



A typical PIXE spectrum

PIXE – results

	Object	Findspot	Measured part	H	S	Cl	Fe	Co	Ni	Cu	As	Ag	Sn	Pb	Sn% rel. unc.	Sn% abs. unc.
PGAA	greave (complete)	Várvölgy	sheat	0.06				0.04		83.60		0.12	8.89	7.28		
PIXE			sheat				0.51	0.01	0.00	83.60	1.35	0.62	16.46	1.51	4.23	0.70
			ring				0.10	0.00	0.02	71.35	0.32	0.19	28.81	0.65	5.90	1.70
			wire				0.06	0.01	0.07	99.71	0.00	0.00	0.52	0.03	85.98	0.45
PGAA	greave (complete)	Lengyeltóti	sheat	0.03				0.17	0.18	93.24	0.23	0.06	6.06			
PIXE			sheat				0.46	0.09	0.18	99.12	0.50	0.00	0.94	0.22	17.63	0.17
			rivet				0.38	0.00	0.09	99.39	0.15	0.05	0.68	0.26	18.38	0.13
			wire				0.36	0.04	0.16	99.43	0.46	0.04	0.62	0.24	23.59	0.15
PGAA	cap helmet with stars	Northern H.?	cap		0.40	0.02	0.28			90.76		0.00	6.32	2.17		
PIXE			cap				3.77		0.77	94.28	5.73	0.34	5.80	2.67	6.59	0.38
			cap				1.16		0.37	98.76	1.20	0.07	1.31	0.54	13.10	0.17
			rivet				0.84		0.42	93.35	3.25	0.12	6.75	1.62	12.01	0.81
PGAA	conical bell helmet	Dunaföldvár	cap	0.05				0.02		83.97		0.02	12.43	3.50		
PIXE			cap				1.02		0.07	91.78	0.13	0.03	8.31	0.26	8.50	0.71
		polished	cap				0.46		0.03	93.52	0.09	0.03	6.54	0.30	4.08	0.27
			cap				0.49		0.04	94.13	0.11	0.01	5.93	0.26	15.44	0.92
PGAA	cap helmet with stars	Paks	cap	0.03	0.22	0.01		0.01	0.35	89.56	0.11		9.71			
PIXE			cap				0.37	0.03	0.28	96.07	0.35		4.00	0.59	5.20	0.21
			knob	0.01	0.25	0.02		0.02		88.91		0.08	10.72			
			knob				0.49		0.23	93.84	0.32	0.00	6.24	0.31	4.20	0.26
PGAA	fragment; helmet	Jászkarajenő	cap	0.26	0.34	0.09		0.04	0.05	87.78		0.09	9.09	1.96		
PIXE			cap				0.92		0.07	96.20	0.75		3.86	0.11	7.24	0.28
			cap				0.81		0.13	96.67	0.76		3.79	0.00	10.86	0.41
			rivet				3.35		0.11	100.00	0.48		0.00	0.00		
PGAA	conical bell helmet	Keresztéte	cap	0.34	0.40	0.05				82.12		0.05	13.69	3.73		
PIXE							0.35	0.00	0.90	66.79	0.62	0.29	33.23	5.89	3.45	1.15
							0.25	0.01	0.56	88.19	0.40	0.05	11.84	1.77	4.98	0.59
PGAA	cuirass	Szentgáloskér	sheat	0.06	0.89	0.01		0.23	0.12	91.81	0.05		6.81			
PGAA	bell helmet	Nagytétény	cap	0.02	0.25	0.01		0.04		92.32	0.20	0.05	7.11			
PIXE			cap				0.42		0.14	99.40	0.33	0.03	0.68	0.80	20.51	0.14
PGAA	bell helmet	Nagytétény	knob	0.00				0.03		92.07		0.06	7.83			
PIXE			knob				0.40		0.19	99.06	0.33	0.08	1.02	1.36	15.63	0.16

PIXE – conclusions

→ unfortunately no analyses on the pure metal permitted; the penetration depth of 2.5 MeV protons is not large enough; no non-invasive possibility to check the thickness of the corrosion layer

→ with PIXE less amount Sn of was obtained in comparison with the PGAA, further studies are planned to find the reason

→ the quantitative results gave a good estimate of the alloy composition, and minor and trace element concentrations were also measured.

The CHARISMA TNA programme in ATOMKI

Scanning ion microprobe

Techniques:
PIXE, **PIGE**, **RBS** with **focused ion beams** (+XRF)

Trace element level composition and distribution

Beam size: 1µm x 1µm

PIXE is applied in all projects:
Elements: C-U (quantitative: O-U)
Typical det. limits: 10-100 ppm

Proton glances at classical Attic pottery

Project leader: Eleni Aloupi

Country: Greece

Measured objects: sherds from recent excavati… the slopes of the Acropolis and in the Kerameikos area

Date: 5th century BC

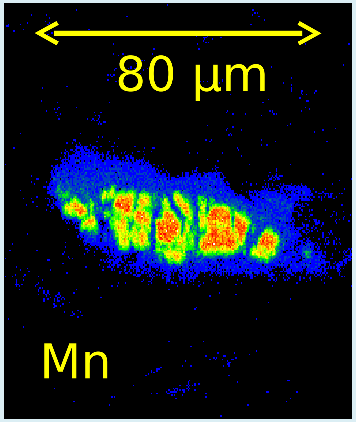
Material: ceramic decorated with clay based paints

Technique: PIXE

Achievements: The composition of specific decorative elements (relief lines, added colours, polychrome decoration) were determined and compared with modern reproductions to test hypotheses about the tricks of ancient vase painters.

Ion beam analysis of Neolithic nephrite artefacts

Project leader: Christo Protochristov
Country: Bulgaria
Measured objects: small axes and chisels
Date: 7000-6000 BC
(the earliest nephrite culture)
Material: nephrite – $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$
Techniques: PIXE, PIGE
Achievements: The bulk composition and the composition of mineral inclusions were determined to get clues to the location of certain ultrabasic outcrops in Bulgaria and its neighbouring countries.
(Currently there is no nephrite deposit localized on the Balkans.)

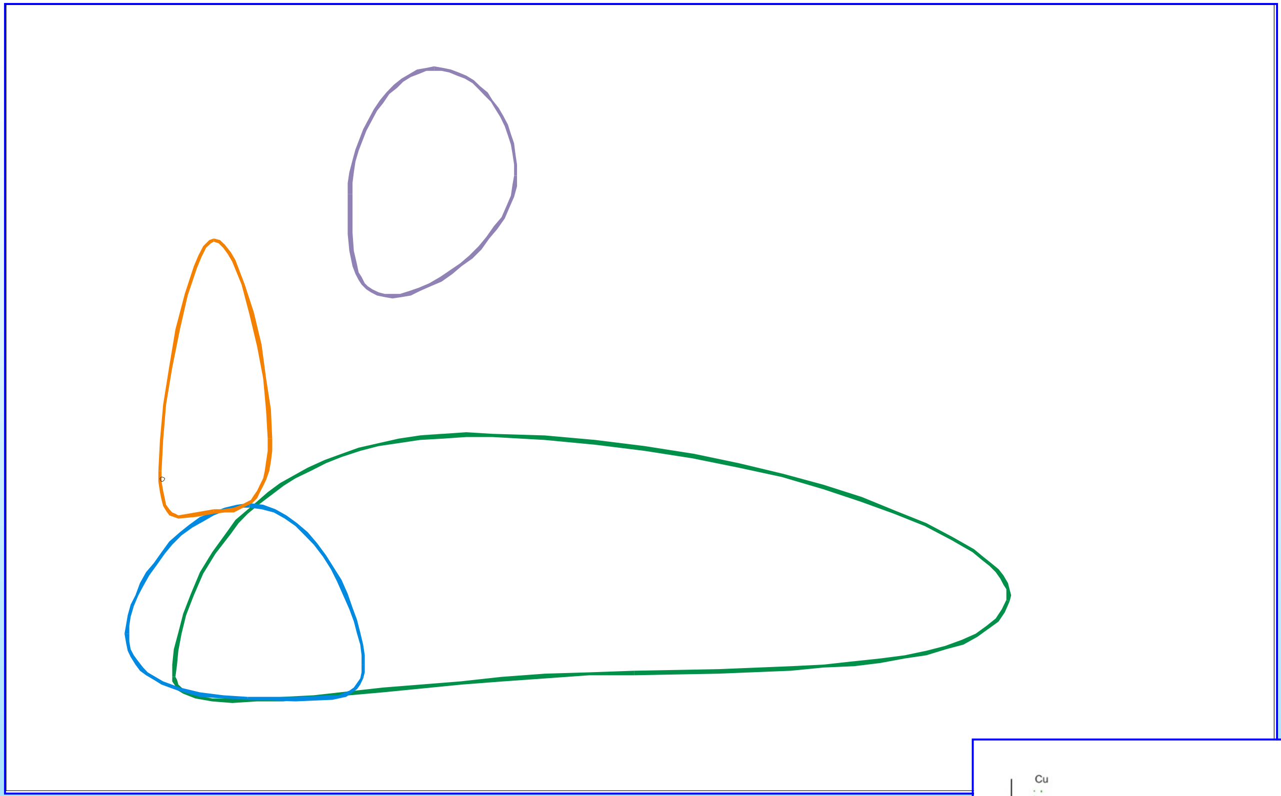


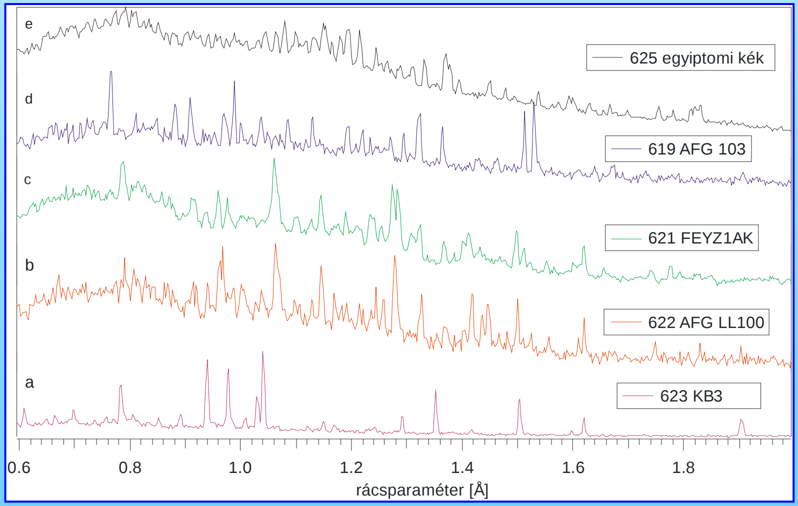
PROVENANCE STUDY OF LAPIS LAZULI
BNC – ATOMKI – Tübingen University

Project … Zöldföldi

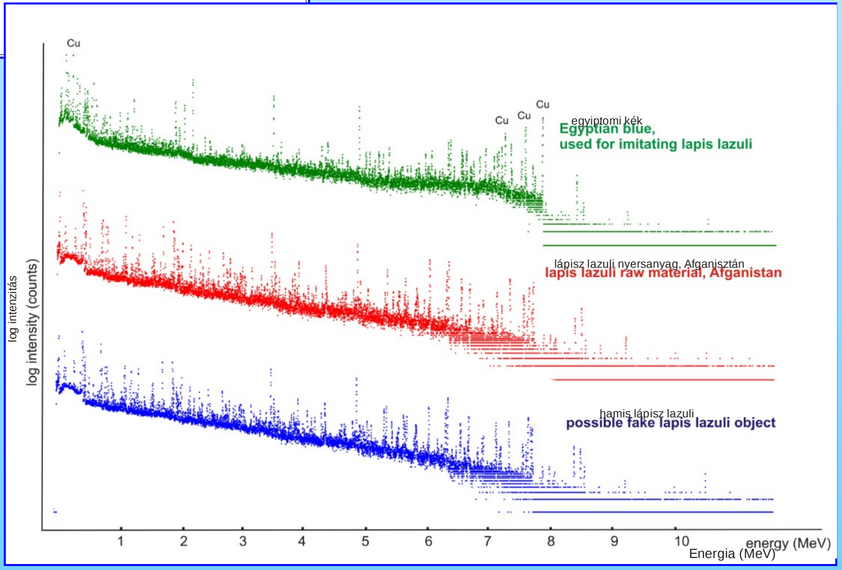
- A few geological occurances in the Worl… (Ural, Chile, Afghanistan, Lake Bajkal)
- **Main mineral**: Lazurit / $(Na,Ca)_{7-8}(Al,Si)_{12}O_{24}[(SO_4)Cl_2(OH)_2]$
- **AIM**: Identification of raw materials, provenance of art objects
- **PGAA**: H, Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, S, Cl

Characterisation of raw materials with PGAA





Fake identification with TOF-ND



Fake identification with PGAA

Thank you for your attention!

- KFKI Atomic Energy Research Institute, HAS
- Research Institute for Solid State Physics and Optics, HAS
- Institute of Isotopes, HAS
- Research Institute for Particle and Nuclear Physics, HAS
- Institute of Nuclear Research, HAS