

NUCLEAR TECHNIQUES IN RESEARCH FOR CULTURAL HERITAGE



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Kasztovszky and Zita Szikszai

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

FREDÉRIC
JOLIOT-CURIE
1900-1958

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 expert meetings to scientific excellence* develops your skills and diffuses knowledge through scientific and technical meetings

Joint research activities

Innovative methods & instrumentation for laboratory research establishes new methodologies for the study of artwork surfaces or of microsamples

Transnational access

ARQU
MOLAB
FIXLAB

Exp

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



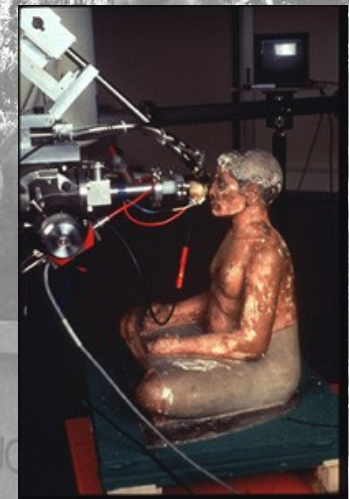
charisma
Cultural Heritage Advanced
Research Infrastructures:
Synergy for a Multidisciplinary
Approach to Conservation/Restoration



Open the archives of European Institutions

Collection of portable equipment for in-situ investigations

Access to large scale facilities for non-invasive techniques



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)

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

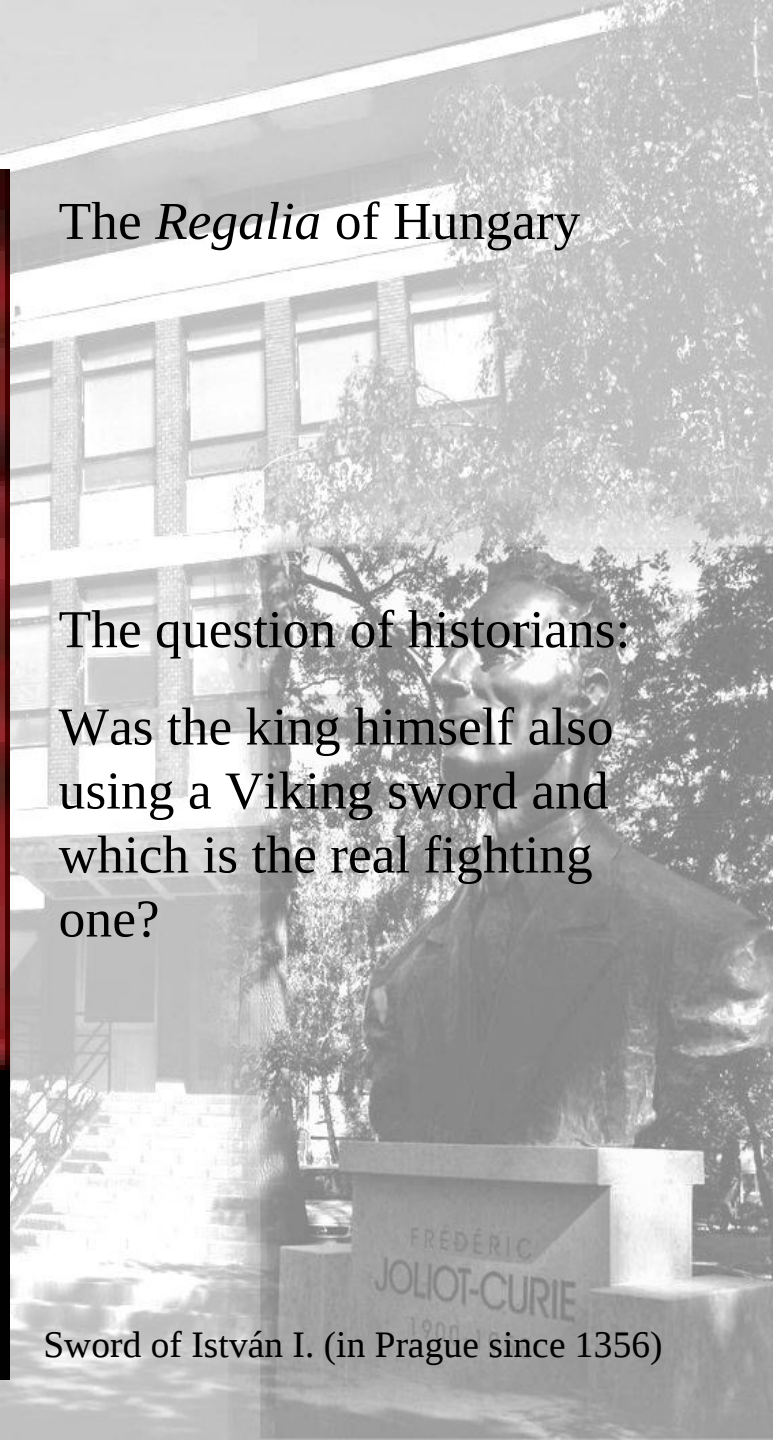


The *Regalia* of Hungary

The question of historians:
Was the king himself also
using a Viking sword and
which is the real fighting
one?

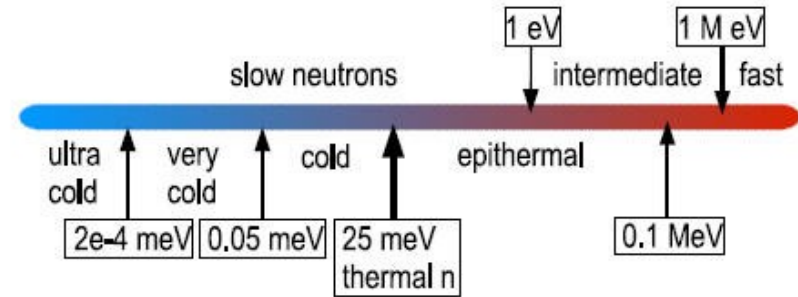


Sword of István I. (in Prague since 1356)



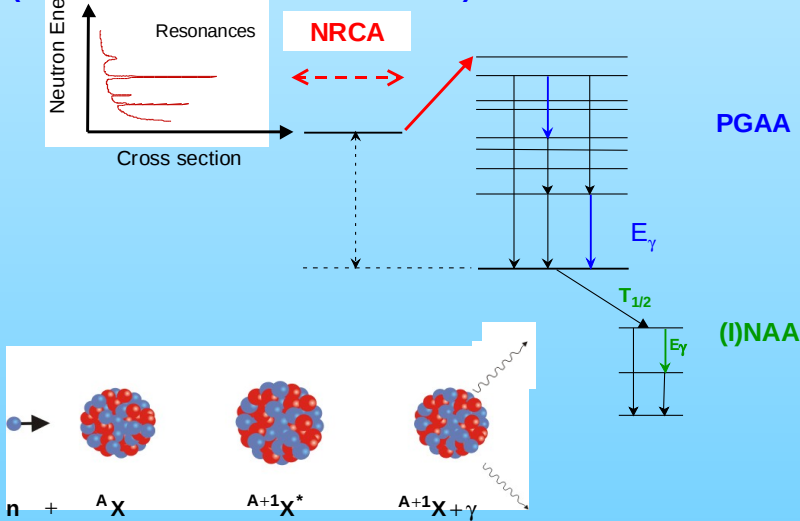
Neutron

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

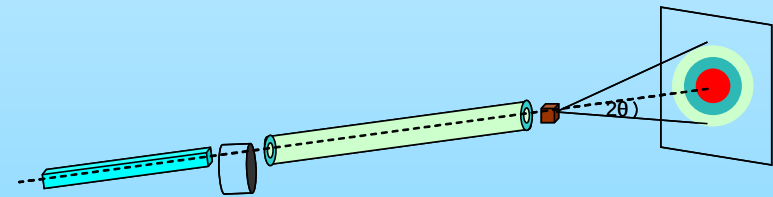


INTERACTIONS WITH MATTER

Radiative capture - (n,γ) reaction (elastic or inelastic)



Scattering



$$Q = \frac{k_1 - k_0}{\lambda}$$

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

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

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 ARCHAEOOMETRY

- 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

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

nmi3 **1**
... Access to 10 neutron and 2 muon facilities
... travel and subsistence support
Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy



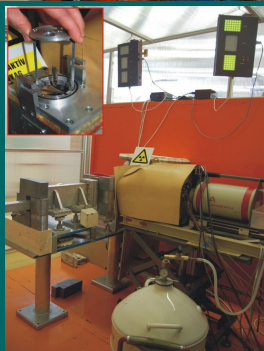
2000-2003



2004-2008



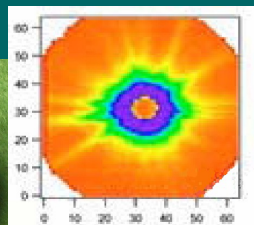
2009-2013



PGAA



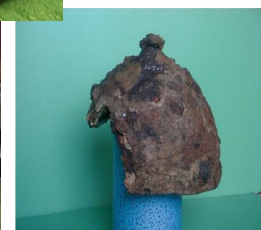
Silet fđv; ... C. / Eiblag Museum



TOF-ND



SANS



RADIOGRAPHY



Highlight 2008

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 mm² – 2X2 cm²)



APPROXIMATE DETECTION LIMITS FOR THE BUDAPEST PGAA

Element		Detection Limit [ppm]	
stable isotope		■ 0.01-1	■ 1-10
atomic weight		■ 10-100	■ 100-1000
σ - capture		■ >1000	□ no data
σ - scattering			
H 1 1.00794 0.3326 82.02 b			He 2 4.002602 0.007 b 1.34 b
Li 3 6.941 70.5 b 1.37 b	Be 4 9.0122 0.0076 b 7.63 b		B 5 10.811 767.2 26.7 b
Na 11 22.98977 0.530 b 3.26 b	Mg 12 24.305 0.0633 3.77 b		C 6 12.011 0.00350 b 5.551 b
K 19 39.0983 1.96 b	Ca 20 40.078 23.5 b	Al 13 26.9815 0.2311 1.503 b	N 7 14.00674 1.9 b 11.51 b
	Sc 21 44.9559 27.5 b 23.5 b	Si 14 28.0855 2.167 b	O 8 16.0000 15.9994 0.00019 b 4.232 b
	Ti 22 47.88 4.35 b	P 15 30.9738 0.172 b 3.312 b	F 9 18.9984 0.0096 b 4.018 b
	V 23 50.9415 5.08 b 5.10 b	S 16 32.066 0.53 b 1.026 b	Ne 10 20.1797 0.039 b 2.628 b
	Cr 24 51.9961 3.05 b 3.49 b	Cl 17 35.4527 33.5 b 10.8 b	Ar 18 39.948 0.675 b 0.683 b
	Mn 25 54.9380 2.15 b	Ar 18 39.948 0.675 b 0.683 b	Ne 10 20.1797 0.039 b 2.628 b
	Fe 26 55.845 11.62 b	Co 27 58.9332 37.18 b 5.6 b	Ne 10 20.1797 0.039 b 2.628 b
	Ni 28 58.6934 18.5 b	Cu 29 63.546 3.78 b 8.03 b	Ne 10 20.1797 0.039 b 2.628 b
	Cu 29 63.546 3.78 b 8.03 b	Zn 30 65.39 2.75 b 6.38 b	Ne 10 20.1797 0.039 b 2.628 b
	Zn 30 65.39 2.75 b 6.38 b	Ga 31 69.723 2.75 b 6.83 b	Ne 10 20.1797 0.039 b 2.628 b
	Ge 32 72.61 2.20 b 8.60 b	As 33 74.9216 4.6 b 5.50 b	Ne 10 20.1797 0.039 b 2.628 b
	As 33 74.9216 4.6 b 5.50 b	Se 34 78.96 11.7 b 8.30 b	Ne 10 20.1797 0.039 b 2.628 b
	Se 34 78.96 11.7 b 8.30 b	Br 35 79.904 6.9 b 5.90 b	Ne 10 20.1797 0.039 b 2.628 b
	Br 35 79.904 6.9 b 5.90 b	Kr 36 83.8 25 b 7.68 b	Ne 10 20.1797 0.039 b 2.628 b
Rb 37 85.4678 0.38 b 6.8 b	Sr 38 87.62 1.28 b 6.25 b	Y 39 88.90585 7.70 b	Ne 10 20.1797 0.039 b 2.628 b
	Zr 40 91.224 0.185 b 6.46 b	Nb 41 92.90638 1.15 b 6.255 b	Ne 10 20.1797 0.039 b 2.628 b
	Mo 42 95.94 2.48 b 5.71 b	(Tc) 43 20 b 6.3 b	Ne 10 20.1797 0.039 b 2.628 b
	Ru 44 101.07 2.56 b 6.6 b	Rh 45 102.9055 144.8 b 4.6 b	Ne 10 20.1797 0.039 b 2.628 b
	Pd 46 106.42 6.8 b 4.48 b	Aq 47 107.8682 63.3 b 4.99 b	Ne 10 20.1797 0.039 b 2.628 b
	Cd 48 112.411 2520 b 6.5 b	In 49 114.818 193.8 b 2.62 b	Ne 10 20.1797 0.039 b 2.628 b
	Sn 50 118.71 0.626 b 4.892 b	Sb 51 121.76 4.91 b 3.90 b	Ne 10 20.1797 0.039 b 2.628 b
	Te 52 127.6 4.7 b 4.32 b	I 53 126.90447 6.15 b 3.81 b	Ne 10 20.1797 0.039 b 2.628 b
	Xe 54 131.29 23.9 b		Ne 10 20.1797 0.039 b 2.628 b
Cs 55 132.90545 29.0 b 3.90 b	Ba 56 137.327 1.1 b 3.38 b	La 57 138.9055 8.97 b 9.66 b	Ne 10 20.1797 0.039 b 2.628 b
	Hf 72 178.49 104.1 b 10.2 b	Ta 73 180.9479 20.6 b 6.01 b	Ne 10 20.1797 0.039 b 2.628 b
	W 74 183.84 18.3 b 4.60 b	Re 75 186.207 89.7 b 11.5 b	Ne 10 20.1797 0.039 b 2.628 b
	Os 76 190.23 16.0 b 14.7 b	Ir 77 192.227 425 b 14 b	Ne 10 20.1797 0.039 b 2.628 b
	Pt 78 195.08 193.0 b 11.71 b	Au 79 196.96655 96.6 b 7.73 b	Ne 10 20.1797 0.039 b 2.628 b
	Hg 80 200.59 372.3 b 26.8 b	Tl 81 204.3833 3.43 b 9.89 b	Ne 10 20.1797 0.039 b 2.628 b
	Pb 82 207.2 0.171 b 11.12 b	Bi 83 208.98038 0.0338 b 9.156 b	Ne 10 20.1797 0.039 b 2.628 b
	(Po) 84 (209)	(At) 85 (210)	Ne 10 20.1797 0.039 b 2.628 b
	(Rn) 86 (222)		Ne 10 20.1797 0.039 b 2.628 b
(Fr) 87 (223)	(Ra) 88 (226)	(Ac) 89 (227)	Ne 10 20.1797 0.039 b 2.628 b
		104	Ne 10 20.1797 0.039 b 2.628 b
		105	Ne 10 20.1797 0.039 b 2.628 b
		106	Ne 10 20.1797 0.039 b 2.628 b
Ce 58 140.115 0.63 b 2.94 b	Pr 59 140.90765 11.5 b 2.66 b	Na 11 22.98977 0.530 b 3.26 b	Ne 10 20.1797 0.039 b 2.628 b
		Sm 62 150.36 5922 b	Ne 10 20.1797 0.039 b 2.628 b
		Eu 63 151.965 4530 b 9.2 b	Ne 10 20.1797 0.039 b 2.628 b
		Gd 64 157.25 6700 b	Ne 10 20.1797 0.039 b 2.628 b
		Tb 65 158.92534 6.84 b	Ne 10 20.1797 0.039 b 2.628 b
		Dy 66 162.5 994 b 90.3 b	Ne 10 20.1797 0.039 b 2.628 b
		Ho 67 164.93032 64.7 b 8.42 b	Ne 10 20.1797 0.039 b 2.628 b
		Er 68 167.259 170 b 159 b 8.7 b	Ne 10 20.1797 0.039 b 2.628 b
		Tm 69 168.93421 100 b 6.38 b	Ne 10 20.1797 0.039 b 2.628 b
		Yb 70 173.04 34.8 b 23.4 b	Ne 10 20.1797 0.039 b 2.628 b
		Lu 71 174.976 74 b 7.2 b	Ne 10 20.1797 0.039 b 2.628 b
Th 90 232.03805 7.37 b 13.36 b	(Pa) 91 (231)	U 92 238.02891 238.02891 8.9 b	Ne 10 20.1797 0.039 b 2.628 b
		(Np) 93 (237)	Ne 10 20.1797 0.039 b 2.628 b
		(Pu) 94 (244)	Ne 10 20.1797 0.039 b 2.628 b
		(Am) 95 (243)	Ne 10 20.1797 0.039 b 2.628 b
		(Cm) 96 (247)	Ne 10 20.1797 0.039 b 2.628 b
		(Bk) 97 (247)	Ne 10 20.1797 0.039 b 2.628 b
		(Cf) 98 (251)	Ne 10 20.1797 0.039 b 2.628 b
		(Es) 99 (252)	Ne 10 20.1797 0.039 b 2.628 b
		(Fm) 100 (257)	Ne 10 20.1797 0.039 b 2.628 b
		(Md) 101 (258)	Ne 10 20.1797 0.039 b 2.628 b
		(No) 102 (259)	Ne 10 20.1797 0.039 b 2.628 b
		(Lr) 103 (261)	Ne 10 20.1797 0.039 b 2.628 b

TIME OF FLIGHT NEUTRON DIFFRACTION - TOF- ND

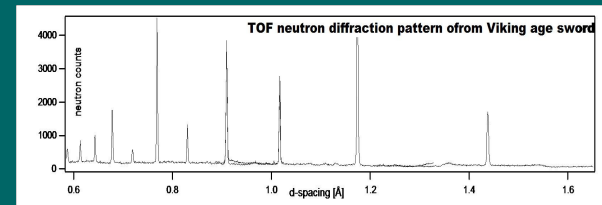


Applicable:

- To study monocrystal or polycrystal 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: $3 \text{ cm}^2 - 2,5 \times 10 \text{ cm}^2$)

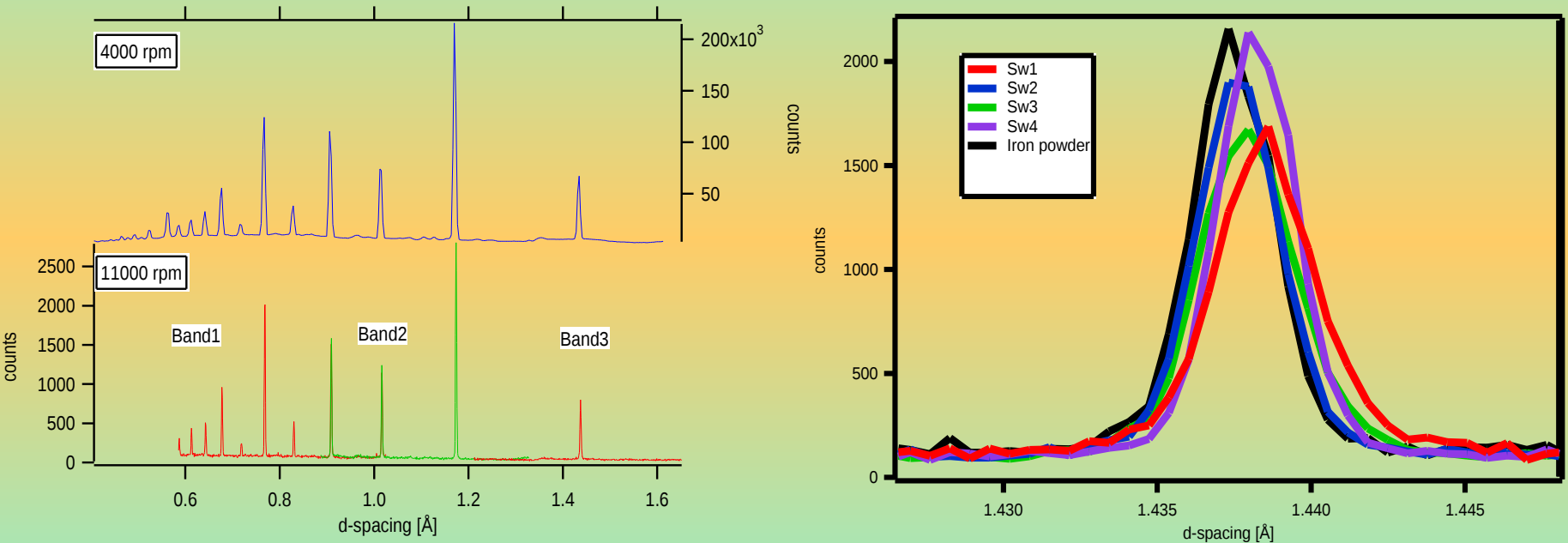


The secret of Viking arms

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

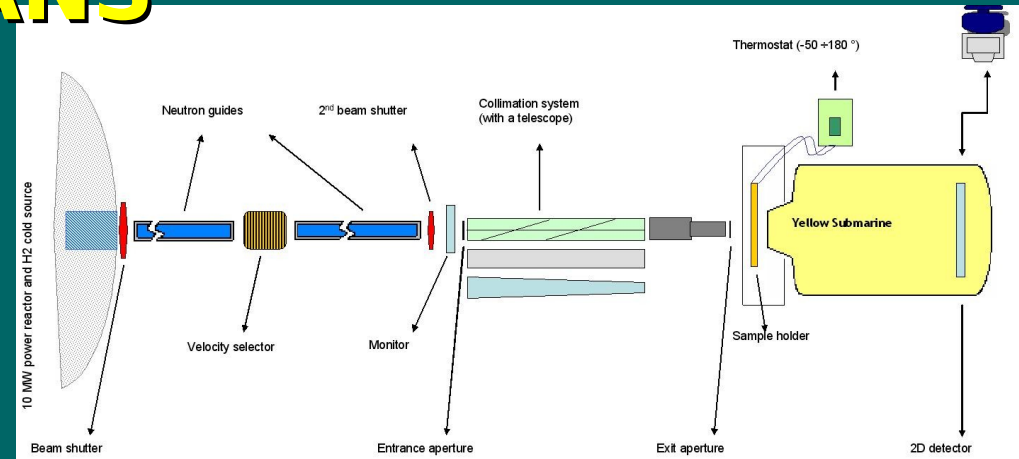


- Phase composition. (For steel phases as ferrite, cementite, martensite and non-steel phases).
- The degree of alloying of the main phase.
- The total carbon content (using the two previous information)
- Texture analyses (preferred orientations of the crystallites).
- Average internal stress and dislocation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

Some conclusions:

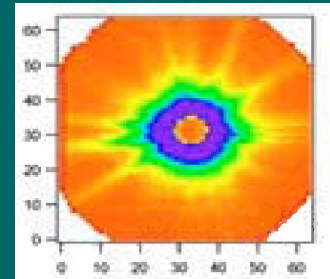
- Important and equal cementit content
- Inhomogeneous precipitate distribut.
- The tensile strength was nearly same
- *Except for 1 sword - decorated*

SMALL ANGLE NEUTRON SCATTERING - SANS



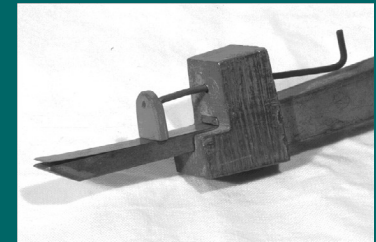
Applicable:

- 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 ceramics, stones

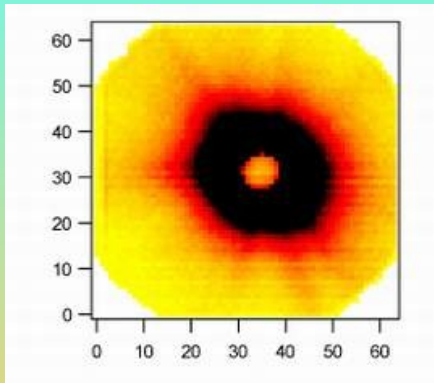


Advantages:

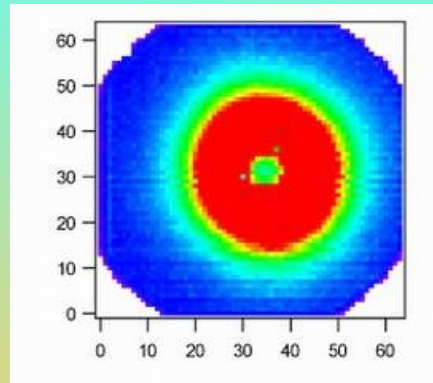
- Non-destructive
- Minimal sample preparation
- Average for the total irradiated volume
- Parts of large objects can be studied (beam size: mm² – 4X4 cm²)



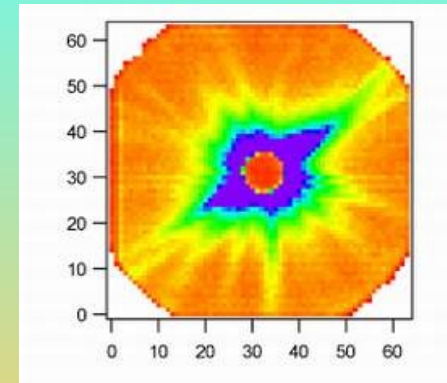
Marble samples from different mines



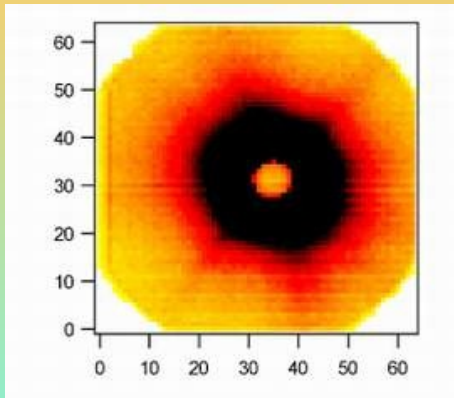
Rimski 2,
Hungary



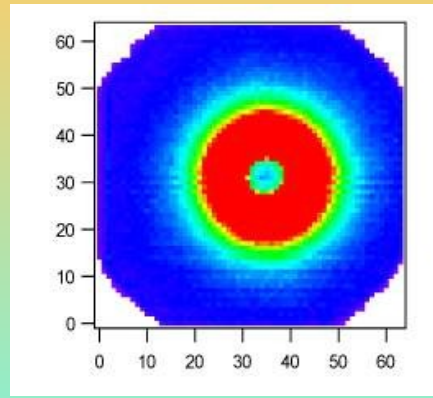
PK1,
Slovenia



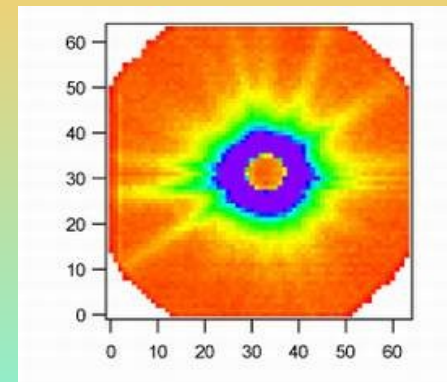
K7, Turkey



Rimski 3,
Hungary



PK3,
Slovenia



K9, Turkey

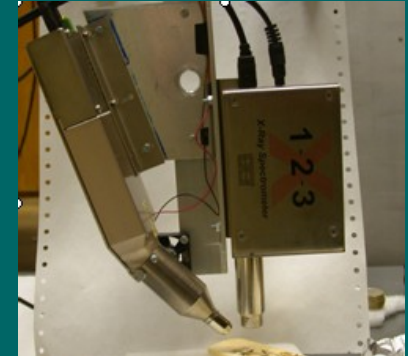
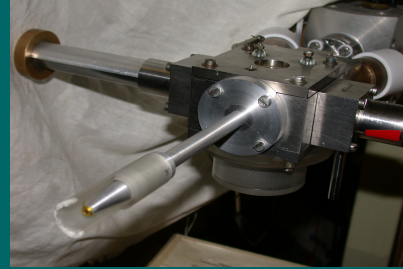
anisotropic distribution of nanoscale pores or precipitates

X-RAY SPECTROSCOPY - PIXE, XRF



Applicable:

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



Advantages:

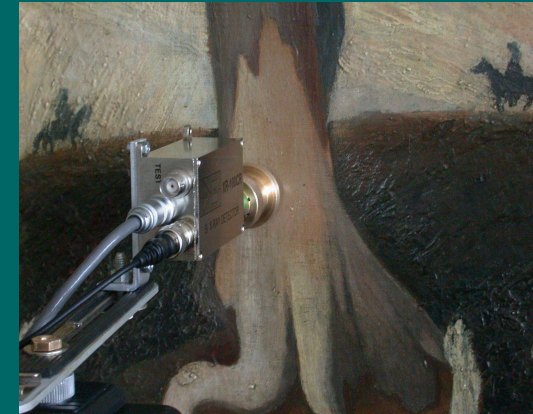
PIXE

- 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 contribution to the CHARISMA project

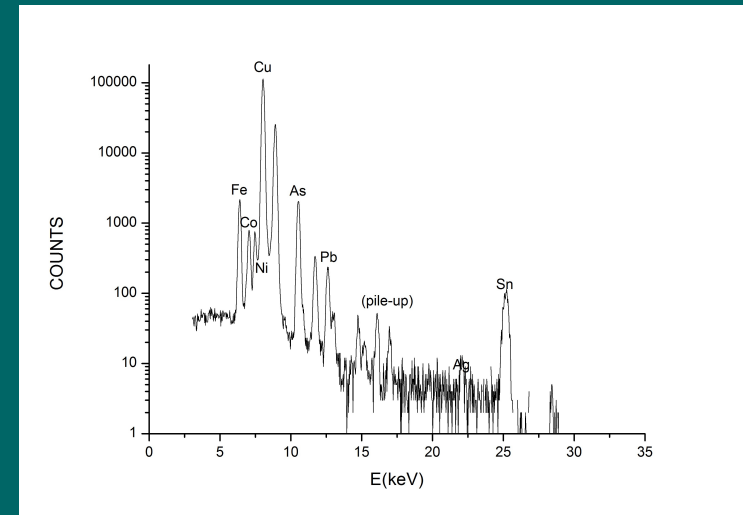


Bronze-Age Usage and Development of Defensive Armour in Eastern Europe

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	Nagytetény	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	Nagytetény	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: $1\mu\text{m} \times 1\mu\text{m}$

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 excavations
on 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

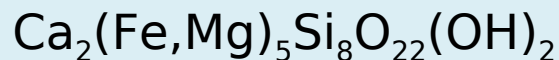
compared with modern reproductions to test
hypotheses about the tricks of ancient vase painters.



Ion beam analysis of Neolithic nephrite artefacts

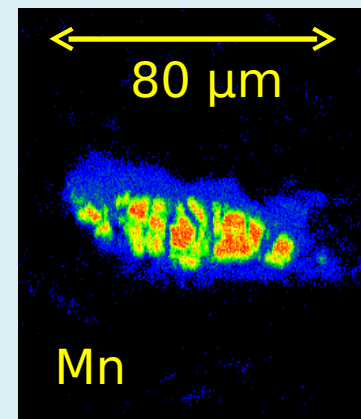
Project leader: Christo Protophristov
Country: Bulgaria
Measured objects: small axes and chisels
Date: 7000-6000 BC
 (the earliest nephrite culture)

Material: nephrite –



Techniques: PIXE, PIGE

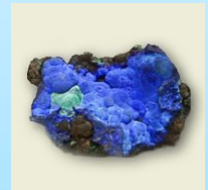
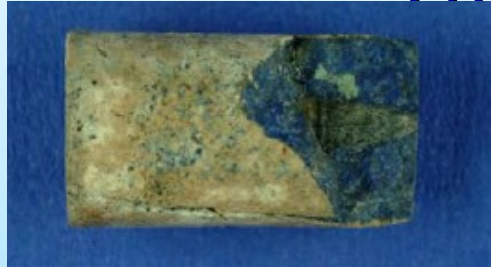
Achievements: The bulk composition and the composition of mineral inclusions were determined to get clues to the location of certain ultrabasic and its neighbouring outcrops in Bulgaria (Currently there is no nephrite deposit localized on the Balkans.)



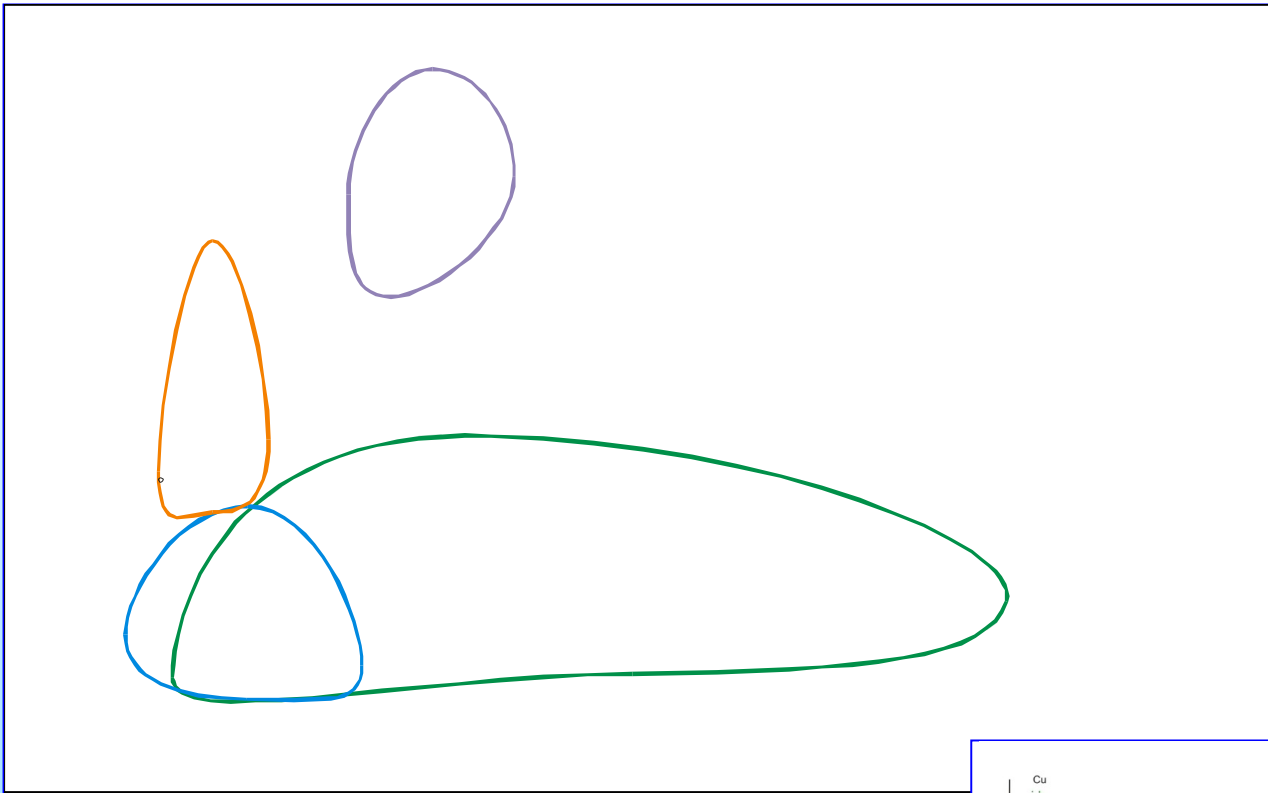
PROVENANCE STUDY OF LAPIS LAZULI BNC - ATOMKI - Tübingen University

Project

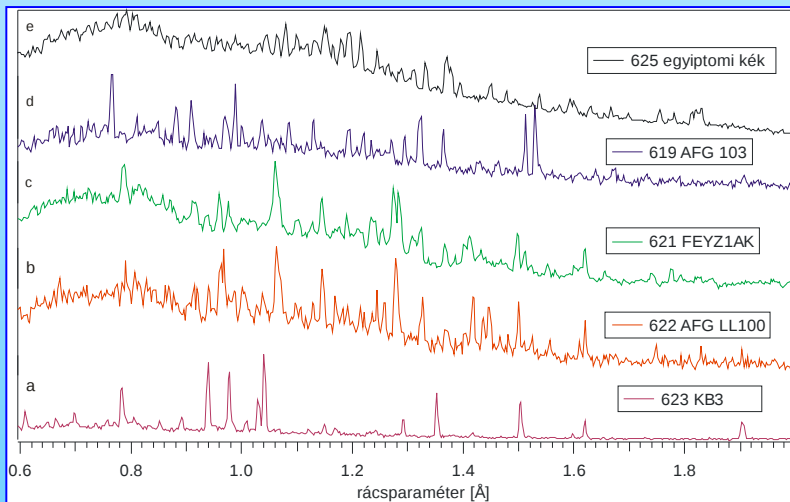
Zöldföldi



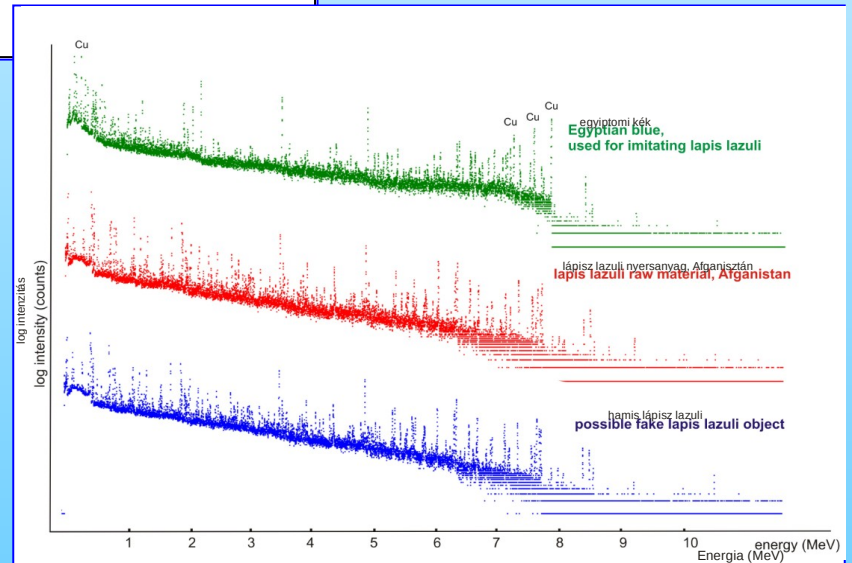
- A few geological occurrences in the World (Ural, Chile, Afghanistan, Lake Bajkal)
- **Main mineral:** Lazurit / $(\text{Na,Ca})_7\text{-}_8(\text{Al,Si})_{12}\text{O}_{24}[(\text{SO}_4)\text{Cl}_2(\text{OH})_2]$
- **AIM:** Identification of raw materials, provenance of art objects
- **PGAA:** H, Na, 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