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

BNC

Bronze Age Usage and Development Of Defensive Armour in Hungary

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Archaeology

Fixlab
Budapest Neutron Centre

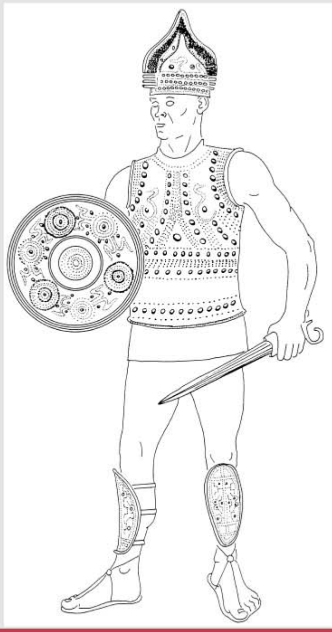
- Hungarian Armour was not allowed to be sampled nor taken out of the country
- Invasive sampling was prohibited
- non-invasive analyses in Hungary → PGAA, PIXE, ToF-ND

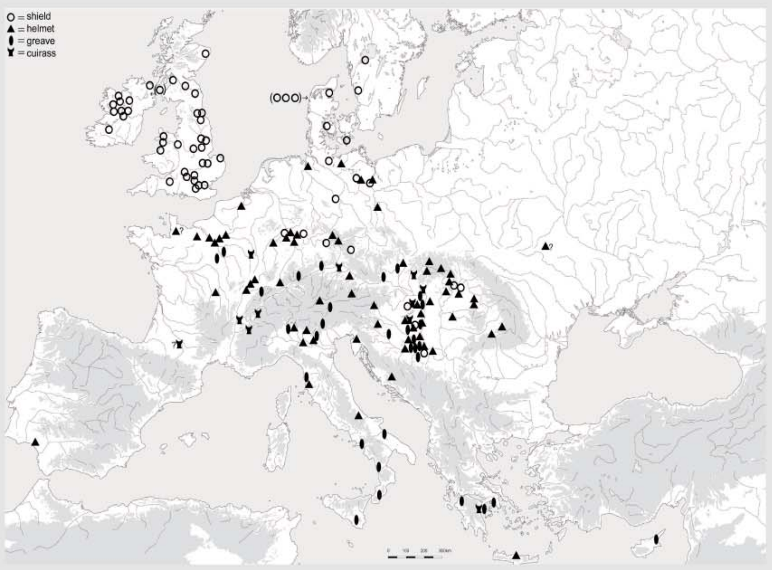
Defensive armour from the following museums

- Hungarian National Museum Budapest (5 helmets, 1 cuirass)
- Museum of Szekszárd (1 helmet)
- Museum of Kaposvár (1 helmet, 1 greave)
- Museum of Paks (1 helmet)
- Museum of Keszthely (2 (3?) Greaves)

Main Project

- Title: *Bronze Age Warfare in Eastern Europe: Development, Technology and Usage of Defensive Armour*
- 3-year project financed by the *Austrian Science Fund* (FWF) and *FP7-Marie Curie* (EU), 1.7.2011 - 31.6.2014
- Studying, documenting and sampling of approx. 120 pieces of armour in: Austria, Bosnia, Croatia, Czech Republic, Hungary, Serbia, Slovakia, Slovenia, Romania, …
- Place of research: *Dipartimento di Chimica e Chimica Industriale, Università di Genova*
- Archaeological documentation & analyses with SEM, XRF, Metallography, Raman, ToF-ND, PGAA, PIXE.





PGAA

- non-invasive!
- bulk composition
- main- and trace elements
- cold neutrons
- Higher flux
- higher reaction rate, shorter measurement time

Prompt Gamma Activation Analysis facility operates at one of the horizontal cold neutron beam of the 10 MW Budapest Research Reactor. The thermal equivalent intensity of the neutron beam is 10^8 $cm^{-2}s^{-1}$ at the sample position. PGAA is a non-destructive nuclear method capable to quantify elemental composition of bulk solid, liquid or gaseous samples. In principle, it can detect all the chemical elements (except He), but with very different sensitivities.

One of the most remarkable advantages of PGAA, is that the irradiation of a sample is performed by external guided neutrons, without limitations of the object's dimensions. Sampling from the object is not necessary, and the induced radioactivity due to irradiation is negligible.

The method is most applicable to measure all the major geochemical components and some trace elements in rocks, alloying components of bronzes, etc. It is unique in measuring some light elements, especially H and B.

	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

Results

- Alloy composition?
  - detected; tin-bronzes with 6-13.7% Sn and up to 7.3% Pb
    - trace elements (most important: Ni, As, Ag, Sb) are low
    - Change in the production technique or in the alloys used during time?
  - Yes! In Ha A2/B1 there seems to be a change; younger helmets contain clearly less tin, and not more lead. This is opposite to French helmets of the Atlantic Bronze Age.
- Different alloys for different types of helmets/objects?
  - Yes! Different alloys for different types of helmets; but this might be more due to the dating of the helmets
  - No! No different alloys for different weapon categories so far; more data for comparison needed (just 3 (4) greaves and one cuirass so far!).

Round circles for the elements typical in rocks (might be present as soil contamination?), elipses for components of bronzes.

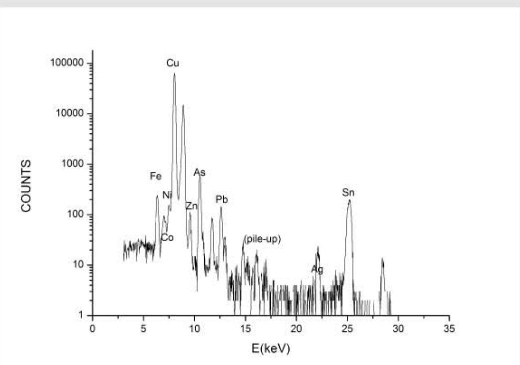
SENSITIVITY FOR BUDAPEST SYSTEM

PIXE

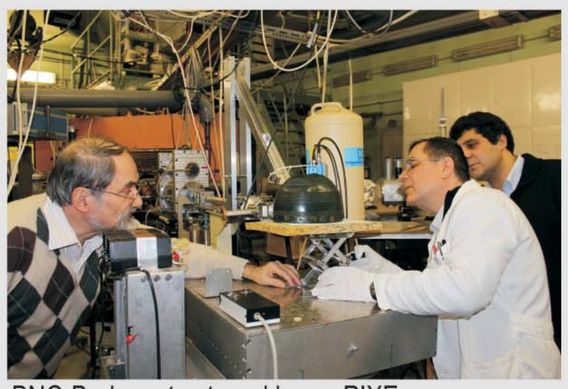
- Non-invasive! Analyses on corroded surfaces; or on the surface the corrosion is removed (invasive!).
- Elemental sensitivities: 5-100ppm range, depending on the element
- Depth of analysis for 2.5 MeV proton in bronze (micrometer):

Fe	8.6	As	7.5
Co	9.9	Ag	12.7
Ni	10.6	Sn	12.9
Cu	11.3	Pb	7.6
Zn	11.9		

- On several elements such as Ni, Au, Pb and Bi XRS-PIXE methods have a better sensitivity than PGAA.
- The analysis of Sn and Sb is more difficult, since the sensitivities of both PIXE and PGAA methods are poor, however the sensitivity of PIXE can be considerably improved by optimization of the experimental procedure.
- 90% of the X-ray counts are coming from the layer of thickness listed above.



Typical PIXE-spectrum setup



BNC-Budapest external beam PIXE

Results and challenges

- Corrosion on the surface: Unfortunately no analyses on the pure metal permitted; the penetration depth of 2.5 MeV protons is not large enough; no possibility to check the thickness of the corrosion layer non-invasive
- On the surface with PIXE less Sn was detected than with the PGAA in the bulk; further studies are planned to find the reasons
- The quantitative results were giving a good idea of the alloy composition, and in addition the minor and trace elements can also be analysed

ToF-ND

- non-invasive!
- phase analysis of composition
- texture analysis
- Elemental composition
- max. Illuminated surface: 25x100 mm².
  min. sample volume: a few cm²
- back scattering mode, ToF-ND resolution:
  Δd/d ~1x10^{-3} at λ=0.1 nm (200 Hz)
- In the case of inhomogeneous samples, the measured information is the average for the whole illuminated volume

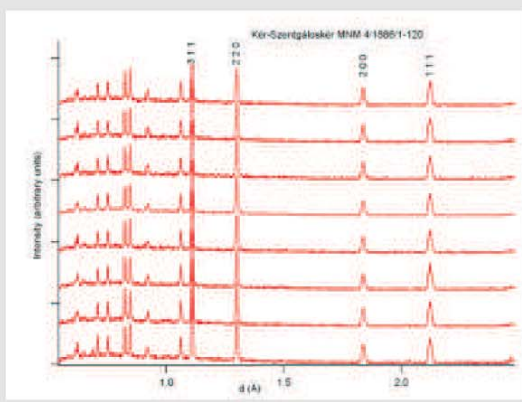
Object		H	S	Cl	Mn	Fe	Co	Ni	Cu	As	Ag	Cd	In	Sn	Pb	TOF-ND
greave (complete)	Várvölgy	0,058					0,037		83,6		0,121	1,0E-04	0,013	8,9	7,3	11,7
greave (complete)	Lengyeltóti	0,034					0,167	0,180	93,2	0,23	0,062	2,1E-05	0,015	6,1		9,26
cap helmet with stars	Northern H.?		0,40	0,023	0,045	0,28			90,8		0,004	1,2E-04	0,009	6,3	2,2	-
conical bell helmet	Dunaföldvár	0,053					0,022		84,0		0,022	3,1E-05		12,4	3,5	12,3
cap helmet with stars	Paks	0,030	0,22	0,014			0,012	0,346	89,6	0,11		8,5E-06		9,7		9,26
fragment; helmet	Jászkarajenő	0,262	0,34	0,089	0,035		0,038	0,047	87,8		0,087	1,8E-03	0,022	9,1	2,0	6,04
conical bell helmet	Keresztéte	0,339	0,40	0,054					82,1		0,055	3,8E-05	0,010	13,7	3,7	9,78
cap helmet with stars	Paks	0,014	0,25	0,018			0,016		88,9		0,076	4,0E-05		10,7		10,5
cuirass	Szentgáloskér	0,065	0,89	0,013			0,232	0,123	91,8	0,05		9,0E-05	0,009	6,8		10,4
bell helmet	Nagytétény	0,022	0,25	0,008			0,042		92,3	0,20	0,045	2,00E-05		7,1		7,87
bell helmet	Nagytétény	0,004					0,033		92,1		0,056	1,1E-04		7,8		8,51
	11% Sn Bronze standard	0,407							88,2					11,4		11
	11% Sn Bronze standard	0,004							88,5					11,5		-
	14% Sn Bronze standard	0,004							85,7					14,3		-

ToF-ND results

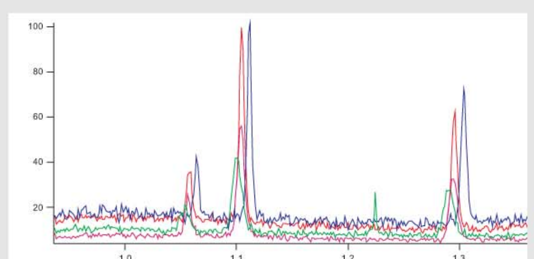
Elemental composition
The gained information in case of elemental composition is taken from all illuminated volume. In this way we can provide average information about the elemental composition of the sample. A good correlation was observed with PGAA data in case of two major components (Cu, Sn). In the case of three major components (Cu, Sn, Pb) the Vegard's law is not applicable.

Phase analysis
In all measures samples the CuSn α-phase was observed due to small Sn concentration (below 13,7w%). If the sample have lead content we suppose that a part of the tin makes a different phase with lead which is not observable in our spectra due to the small quantity of PbSn phase.

Texture
Texture analysis of three different type of objects were done. The Paks cap (knob part) and Várvölgy bronze greave shown weak texture. More remarkable texture was observed in case of Kér-Szentgáloskér bronze cuirass. Interpretation of preferred orientation (of crystallites) have to be supported by conventional metallography

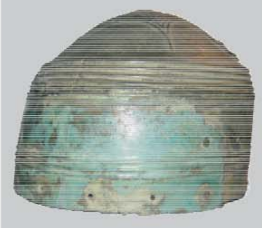


Diffraction spectra for one rotation setting measured on Kér-Szentgáloskér sample

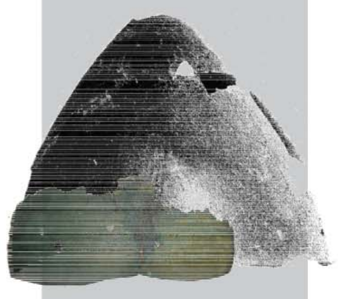


Diffraction pattern of measured sample

Cap helmets



Conical bell helmets



Bell helmets

Helmet fragment

Cuirass fragments

Applique

Greaves

Bronze Age metal defensive armour
Greave (leg protection)
Curiass
Helmet
Shield

Dating relative: Bz D Ha B3
Dating absolute:
(approx. 1300 800/750 BC)

Späte Bronzezeit	
Ha B2/3	800–950 v. Chr.
Ha B1	950–1050 v. Chr.
Ha A2	1050–1100 v. Chr.
Ha A1	1100–1200 v. Chr.
Bz D	1200–1300 v. Chr.
Mittlere Bronzezeit	
Bz C2	1300–1400 v. Chr.
Bz C1	1400–1500 v. Chr.
Bz B	1500–1600 v. Chr.
Frühe Bronzezeit	
Bz A2	1600–2000 v. Chr.
Bz A1	2000–2200 v. Chr.

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