

THE POSSIBILITIES AND LIMITATIONS OF MODERN SCIENTIFIC ANALYSIS OF BRONZE AGE ARTEFACTS IN HUNGARY*

LEHETŐSÉGEK ÉS KORLÁTOK A BRONZTÁRGYAK MODERN MŰSZERES VIZSGÁLATÁBAN MAGYARORSZÁGON

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Abstract

For a long while, the scope of scientific testing of bronze artefacts was limited, with studies focused primarily on the composition, the ratio of alloying agents and impurities, and the presence of trace elements in archaeological objects. From the 1960s, as the technique of spectral (Optical Emission Spectroscopy) analysis became widely available, tens of thousands of objects were sampled (Schubert & Schubert 1963, 1967), but metallographic analyses and the investigations concerning the microstructure were only carried out in a few cases (Szegedy 1954; 1957; Mozsolics & Hegedűs 1963). Despite this, by the direct application of measurements, serious historical and archaeological conclusions were drawn, in relation to raw material sources and metallurgical centres for Bronze Age Europe. As the metallographic thin-sections prepared from prehistoric bronze objects demonstrate, the majority of archaeological bronze artifacts are heterogenous in structure, or even inhomogenous. For this reason, the outcomes of scientific tests must be carried out with the understanding of microstructure in order to interpret the measurements within safe limits. Only scientifically accurate data can be used to draw archaeological-historical conclusions.

Kivonat

A bronztárgyak vizsgálata során a kutatás hosszú ideig csak a régészeti tárgyak anyagának összetételére, az ötvöző és szennyezőanyagok arányára, a különböző nyomelemek jelenlétére volt kíváncsi. Az 1960-as évektől széles körben elérhető spektrumanalízis (optikai emissziós spektrometria) elvégzéséhez tárgyak tízezeiből vettek mintát, de ehhez képest csak elenyésző esetben készítettek csiszolatokat, vizsgálták meg az anyagösszetétel mellett a szövetszerkezetet is. Ennek ellenére jellemzően a mérési eredmények közvetlen átvételével jelentős, történeti-régészeti szempontú következtetéseket vontak le pl. az európai bronzkori nyersanyaglelőhelyekkel, kohászati központokkal kapcsolatban. Az újabban vizsgált bronztárgyak csiszolati képéből látható, a régészeti bronztárgyak többségének szerkezete heterogén, sőt gyakran inhomogén is. Ezért a műszeres mérések adatait alapvetően a szövetszerkezet ismeretében lehet biztonsággal értelmezni, és a hitelesen vizsgált és értékelt adatokból lehet valós régészeti-történeti következtetéseket levonni.

KEYWORDS: BRONZE, BRONZE AGE, ARCHAOMETALLURGY, METHODS

KULCSSZAVAK: BRONZ, BRONZKOR, ARCHEOMETALLURGIA, MÓDSZERTAN

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The first decades of metal analysis

For a long while, the scope of scientific testing of bronze artefacts was limited, with studies focused primarily on the composition, the ratio of alloying agents and impurities, and the presence of trace elements in archaeological objects. From the 1960s, as the technique of spectral analysis became widely available, tens of thousands of objects were sampled (Schubert & Schubert 1963, 1967), but metallographic analyses and the investigations concerning the microstructure were only carried out in a few cases (Szegedy 1954; 1957; Mozsolics & Hegedűs 1963). Despite this, by the direct application of measurements, serious historical and archaeological conclusions were drawn, in relation to raw material sources and metallurgical centres for Bronze Age Europe.

By 1990s, a new situation began to emerge: the latest generation of instruments and techniques became available in Hungary too, such as the X-ray emission spectroscopy (Költő & Kis Varga 1992) or the neutron activation and laser micro-spectral

analysis (Bakos & Borszédi 1989). Some of these tests detected unusually high levels of alloys in archaeological materials for which it was impossible to provide a metallographic explanation (Költő 1996; Cseh 1997) (**Fig. 1.**).

Today we are aware that the problem stemmed from the fact that these artefacts were considered as homogenous entities, and that the surface measurements (which were only concerned with a particular surface area) were extended to the object as a whole. The characteristics of bronze objects, including the grain size, can be altered significantly not only by changing the ratio of alloys, but by cooling, cold or hot working (Kienlin 2010; Szabó 2013). These altered characteristics can then have an effect on the object's microstructure along with the metal surface and corrosion processes (Szabó 1998, 2001, 2010; Kienlin 2010). Therefore it is easy to see, how the increasingly modern scientific techniques – which require very small sample sizes – can produce results which can be misinterpreted, especially in the case of non-homogenous metal alloys with different compositional phases.

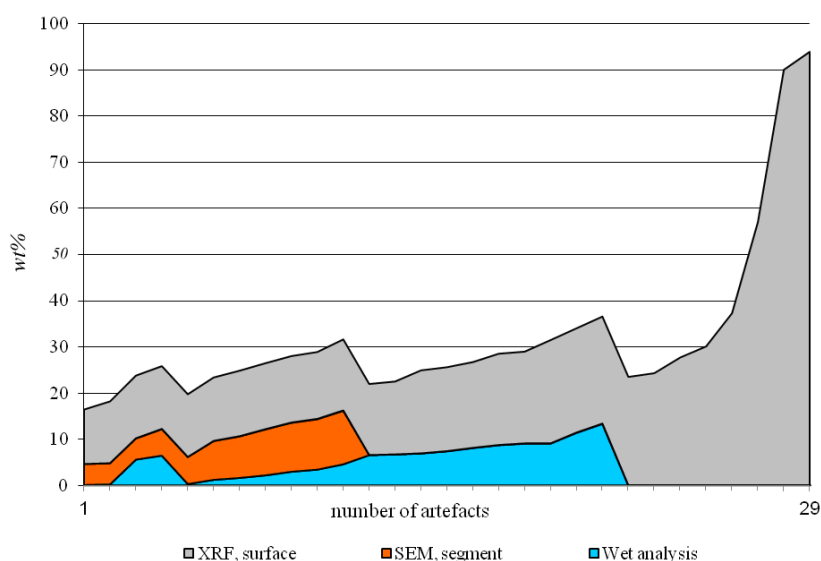


Fig. 1.:

Bronze Age artefacts from the Carpathian Basin tested for tin content by various approaches, both on the microstructural level and on samples taken from the objects' surface (after Szabó 2010, Fig. 1.)

1. ábra:

Kárpát-medencei bronztárgyak óntartalma eltérő módszerekkel, illetve felületen és csiszolaton végzett vizsgálatok alapján (Szabó 2010, 1. ábra nyomán)

Recent examinations: developing laboratory environment and increasing collaboration

In 1996, for the first time in Hungarian research, the composition and microstructure of metal artefacts were examined consistently and simultaneously on pieces of a bronze depot in the laboratory at the University of Bradford. The original objective of the examination was to understand the relationship between the raw material composition of bronze objects and their use. However, it soon became clear that the

measurements published during last decades were not suitable for this enquiry. At the same time, the results of current scientific tests (targeting the microstructure of objects) drew attention to the association between the sampling, the method of analysis and testing instruments, and the production and use of the artefacts, as well as the corrosion processes the object was exposed to (Szabó 1998; 1999; 2001). At this time, these associations only existed on the level of recognition, and no less than two decades had to pass in order to establish the theoretical grounds for these correlations; a process that is still continuing today.

Table 1.: Research facilities and relevant technologies available for the archaeometrical testing of artefacts in Hungary (listed by scientific technique)**1. táblázat:** Régészeti korú fém tárgyak archaeometriai vizsgálatának legfontosabb lehetőségei és helyszínei Magyarországon (módszerek szerint)

Method	Institution
microstructure analysis (thin section)	University of Miskolc, University of Debrecen
SEM-EDS, SEM-EDX (scanning electron microscopy - energy-dispersive X-ray spectroscopy) EMPA/EPMA (electron microprobe analysis)	University of Miskolc, University of Debrecen University of Debrecen, Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
microstructure analysis (thin sections, polished blocks embedded in Duracryl resin), optical emission spectrometer	Centre for Energy Research (HAS); Research Centre for Natural Sciences (HAS); Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
NR (neutron radiography, 2D)	Centre for Energy Research, Hungarian Academy of Sciences (HAS)
NT (neutron tomography, 3D)	Centre for Energy Research (HAS)
PGAA (prompt-gamma activation analysis)	Centre for Energy Research (HAS)
PGAI (prompt-gamma activation imaging)	Centre for Energy Research (HAS)
TOF-ND (Time-of-flight neutron diffraction, 2D)	Wigner Research Centre for Physics (HAS)
PIGE (proton-induced gamma emission analysis)	Institute for Nuclear Research (HAS)
PIXE (proton-induced X-ray emission analysis)	Institute for Nuclear Research (HAS)
micro-PIXE (proton-induced X-ray emission micrometry)	Institute for Nuclear Research (HAS)
ED-XRF (energy dispersive XRF analysis)	Budapest University of Technology and Economics
p-XRF (portable X-ray fluorescence analysis)	Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS) Centre for Energy Research (HAS) Budapest University of Technology and Economics
XRD, micro-XRD	Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
FTIR (Fourier-transform infrared spectroscopy)	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS) Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
UV-VIS (ultraviolet-visible) spectrometry	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS)
secondary neutral mass spectrometry (SNMS)	University of Debrecen, Institute of Physics

Table 2.: Research facilities and relevant technologies available for the archaeometrical testing of archaeological artefacts in Hungary (listed by institution)**2. táblázat:** Régészeti korú fém tárgyak archaeometriai vizsgálatának legfontosabb lehetőségei és helyszínei Magyarországon (intézmények szerint)

Location	Institution	Method	Research fellow
Budapest	Budapesti Neutron Centre (BNC)= Centre for Energy Research (HAS) Wigner Research Centre for Physics (HAS)	PGAA, PGAI, NR, NT, p-XRF TOF-ND	Zsolt Kasztovszky, Zoltán Kis, Boglárka Maróti, László Szentmiklósi, Ildikó Harsányi, Veronika Szilágyi György Káli
Budapest	Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences (HAS)	p-XRF	Zoltán May
Budapest	Budapest University of Technology and Economics	ED-XRF	Iván Gresits
Budapest	Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)	p-XRF EMPA/EPMA, XRD, micro-XRD FTIR	BernadettBajnóczi Viktória Mozgai Mária Tóth
Miskolc	University of Miskolc, Material Science Institute	XRD, SEM-EDX microstructure analysis (thin section)	Péter Barkóczy, Árpád Kovács
Debrecen	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS)	Vacuum & In-air PIXE, micro-PIXE), PIGE, XRF, FTIR, UV-VIS spectrometry	Zsófia Kertész, László Csedreki, Zita Szikszai, Zsófia Török, Imre Uzonyi
Debrecen	University of Debrecen, Institute of Physics	SEM-EDS misrostructure analysis, optical microscopy SNMS	Szilvia Gyöngyösi

However, since the outcomes of the Bradford examinations were made public, archaeological considerations have been taken into account – instead of the pure application of the results – not only during the interpretation of measurements but already at the stages of sampling, and during the planning of scientific testing. In this regard, since the early 2000s, a major step forward was the establishment of the modern laboratory environment with professional staff and cutting-

edge technology, where expert consultation taking place between scientists of different fields became the norm (**Table 1-2.**).

At the beginning, the scientific testing of metal artefacts in laboratories were generally carried out within the framework of particular projects targeting a single object or were brought about through the personal arrangements between individual scientists. However, there has been increasing collaboration between archaeologists and

natural scientists including the detailed overview and discussion of measurements. Such collaborations included the metallographic and metallurgical testing of a Copper Age hammer axe, a pair of Bronze Age arm ornaments from Borsodszentgyörgy and a disc-butted axe from Szendrőlád led by Klára P. Fischl, Péter Barkóczy and Árpád Kovács. The microstructure of the samples were examined by optical microscopy, while their average and local composition was tested by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) in the LISA laboratories at the University of Miskolc, where besides the composition of objects, experts were able to shed more light on their production technologies as well (Barkóczy et al. 2011; Török et al. 2013).

The bronze hoards of Hajdúsámson and Téglás were tested by using the technique of proton-induced X-ray emission (PIXE) in the laboratories of Atomki at Debrecen, Hungarian Academy of Sciences (HAS). The examinations took place in the MTA Atomki laboratory in Debrecen conducted by János Dani, Zsófia Török, László Csedreki, Zsófia Kertész and Zita Szikszai. The tests were to map the main components and trace elements, arsenic (As), antimony (Sb), silver (Ag), nickel (Ni), iron (Fe), gold (Au), zinc (Zn), manganese (Mn), chromium (Cr) and mercury (Hg, all in ppm) of tin bronzes which could provide clues for identifying differences of raw material and production centres (Dani et al. 2013; Török et al. 2015).

The testing of the hoard from Zalaszabar was also carried out in the LISA laboratories in collaboration with Viktória Kiss. Following the successful collaboration, the scope of the project broadened, and came to include the metallurgy of the Transdanubian Encrusted Pottery culture as a whole involving a series of sites and experts (Kiss et al. 2013). These newly established and successful protocols between archaeologists (particularly Bronze Age scholars) and natural scientists came to serve as benchmarks and led the way for Hungarian research, making it possible to extend the testing and evaluation even further by studying a diverse range of objects.

Further tests were carried out on a number of unique bronze artefacts in the Budapest Neutron Center (BNC) in order to determine production locales and the processes of crafting. The examinations included non-invasive 2D neutron radiography (NR), 3D neutron tomography (ND), while prompt-gamma activation analysis (PGAA) was conducted for the identification of raw materials. The changes induced to the microstructure of bronze objects during the production processes were clearly shown (even without the preparation of micrographs) by time-of-

flight neutron diffractometer (TOF-ND) measurements (Kiss et al. 2015). The establishment and dynamic operation of the Lendület/Momentum Mobility Research Group within the Institute of Archaeology of the Research Centre for the Humanities (HAS) marked a turning point in interdisciplinary collaborations (Kiss 2016). Provided its institutional background, social network and financial support, the Research Group was able to maximize its involvement in cutting-edge laboratory projects but was also able to recruit expert scholars from the fields of archaeology and natural sciences. The Group's primary objective is to interpret archaeological contradictions by the development of a range of theoretical frameworks, particularly to better understand phenomena that had previously been observed but were considered as exceptions to the norm. The first outcomes of this research have now been recognized internationally as well (Kulcsár et al. 2015). At the same time, the opportunity rose for the artefacts to be analysed in laboratories both in Hungary and abroad, making it possible to compare measurements taken in different research environments. Here we would like to present the flanged axe from Zalaszabar; an example through which the scientific methodologies, results and the issues around direct interpretation and the potential historical consequences will be illustrated. The Zalaszabar flanged axe was tested in the BNC in Budapest and in the Curt-Engelhorn-Centre for Archaeometry (CEZA) in Mannheim.

Results and questions: possible interpretations of metal analyses

The provenance of raw materials and the recycling of objects are among the pivotal questions of current prehistoric metallurgical enquiries (Radivojević et al. 2018). The main impurities and alloys detected in the composition of bronze objects (e.g. silver, arsenic, antimony, nickel and tin), as already mentioned, are generally regarded by current research as indices for classification and links to mining areas. A series of examinations carried out in the 1960s and 70s (*Studien zu den Anfängen der Metallurgie*, the so-called SAM project of Stuttgart) described 29 metal types (Fig. 2; cf. Junghans et al. 1968, Diagram 1. *Stuttgarter Stammbaum*) which were later re-grouped by Ernst Pernicka and Rüdiger Krause by using cluster-analysis (Fig. 2.; Krause 2003, Abb. 39; Kiss 2009a). The CEZA laboratory in Mannheim, led by Ernst Pernicka, is one of the leading centres of European research, focused on locating prehistoric mining areas by the application of composition analyses and lead-isotope measurements of metal artefacts. More recently the centre began testing for tin isotopes as well, in order to identify prehistoric tin sources.

Cluster no.	Copper type	No. of analyses	Trace elements (main elements printed bold)	Class
1	Classic 'Ösenringkupfer'	3804	As, Sb, Ag , (Bi), no Ni	Fahlore copper without Ni (IIa)
2	Purest copper	3329	no measurable trace elements	Pure copper (IIIa)
3	With occasional traces of Ag	2740	As , no Sb, Ni, Bi	Arsenic copper (Va)
4	Eastern alpine copper	6505	As, Ni , Sb, no Bi	Fahlore copper with Ni (Ib)
5		774	As, Ni , no Sb, Ag, Bi	Pure copper, low As and Ni content (IIIb)
6		1275	Sb, As, Ag, no Ni, Bi	Arsenic copper (Vb)
7	Copper with traces of Sb and Ag	522	Sb, Ag , no As, Ni, Bi	Antimony copper (IVa)
8	Singen copper	2882	As, Sb, Ni, Ag	Fahlore copper with Ni (Ia)
9		32	Sb, Ni , no As, Bi	Antimony copper (IVc)
10	Similar to 'Ösenringkupfer'	2929	As, Sb, Ni, Ag, no Bi	Fahlore copper without Ni (IIb)
11		375	Sb, Ag, Ni , no As, Bi	Antimony copper (IVb)
12	Fahlore copper without Ag	42	As, Sb , no Ag	Arsenic copper (Vc)
13		68	As, Bi , scarcely Ni, no As, low Sb	Pure copper (IIIc)
14	Possibly pure copper	82	Ni, Ag, scarcely Sb, no As, Bi	Pure copper (IIId)
15		42		Pure(st) copper (?)
16		2		Pure copper (?)
17	Arsenic copper with Ni, Bi	284	As, Sb, Ni, Bi	Fahlore copper with Ni (Ic)
18		10		?
19	White metal	16	As, Ni , Sb, scarcely Bi	Fahlore copper with Ni (Id)
20		110	As, Ni, Ag, Bi , no Sb	Arsenic copper (Vd)
21		26	As, Bi , scarcely Ag, no Sb, Ni	Arsenic copper (Ve)
22	Unalloyed copper with Ag	40	Ag, As, Ni, scarcely Sb, Bi	Fahlore copper with Ni (Ie)
23	Copper, low Sb and Ag content	20	Sb, Ni, no As, Ag, Bi	Antimony copper (IVd)
24		7		?
25		3		?
27		4		?
28	Copper, Sb and Ag high	7	Sb, Ag , Ni, Bi	Antimony copper (IVe)
30		4		?
31		3		?
32		4		?

Fig. 2.: Dendrogram showing the key copper types produced by the cluster analysis of the SAM project *Stammbaum*, based on their occurrence and composition (after Krause 2003, Abb. 39)

2. ábra: A stuttgarti törzsfák klaszteranalízissel csoportosított fő réztípusai gyakoriságuk és elemösszetételük alapján (Krause 2003, Abb. 39 nyomán)

However, there are still several issues to overcome as tin sources show large geographical overlaps making the archaeological interpretation problematic (Nessel et al. 2015, Fig. 5; Brüggemann et al. 2017, Abb. 1; Radivojević et al. 2018). Similarly to the cluster analysis of copper groups of the SAM project data (based on the presence or absence of impurities) the University of Oxford's FLAME metallurgy project established 16 metal categories (Fig. 3.; Bray et al. 2015, Fig. 1).

The series of tests carried out in Stuttgart on tens of thousand samples already indicated a paradigm-shift in the use of raw materials that had taken place during the 2nd Millennium BC (Schubert & Schubert 1967). In the broader region of Central Europe the artefacts dating to Early Bronze Age (between 2000/1900 and 1600 BC) can be classified into several groups: among these are the pure copper, arsenic copper, and the so-called

Ösenring copper objects (Fig. 2., Cluster No. 1-3, after Krause 2003) occur in the highest numbers. The latter (*Ösenring* copper) was coined after neck rings whose characteristic copper raw material contained high levels of silver, arsenic and antimony, while in the period after 1600 BC, the widespread usage of a copper type rich in arsenic and nickel, the so-called eastern Alpine copper type, is detected (Fig. 2, Cluster No. 4). Recent lead-isotope analyses aiming to refine the provenance of copper ore originate the raw material of *Ösenring* copper objects from the region of Slovakia, while the eastern Alpine type copper is suggested to be derived from the mines of Mitterberg (Salzburg region, Austria) (Radivojević et al. 2018, Fig. 7). However, it has to be noted here, that a technological change has also been considered among the explanations for this paradigm-shift (Melheim et al. 2018).

Copper Category	Copper with...	As	Sb	Ag	Ni
1	None	no	no	no	no
2	As	YES	no	no	no
3	Sb	no	YES	no	no
4	Ag	no	no	YES	no
5	Ni	no	no	no	YES
6	As+Sb	YES	YES	no	no
7	Sb+Ag	no	YES	YES	no
8	Ag+Ni	no	no	YES	YES
9	As+Ag	YES	no	YES	no
10	Sb+Ni	no	YES	no	YES
11	As+Ni	YES	no	no	YES
12	As+Sb+Ag	YES	YES	YES	no
13	Sb+Ag+Ni	no	YES	YES	YES
14	As+Sb+Ni	YES	YES	no	YES
15	As+Ag+Ni	YES	no	YES	YES
16	As+Sb+Ag+Ni	YES	YES	YES	YES

Fig. 3.:

The 16 ‘copper groups’ as defined by the presence/absence of four trace elements (presence is usually taken as greater than 0.1%; after Bray et al. 2015, Fig. 1)

3. ábra:

Négy nyomelem megléte/hiánya alapján meghatározott 16 cluster csoport (általában 0,1% fölött kimutatható nyomelemek; Bray et al. 2015, Fig. 1. nyomán)

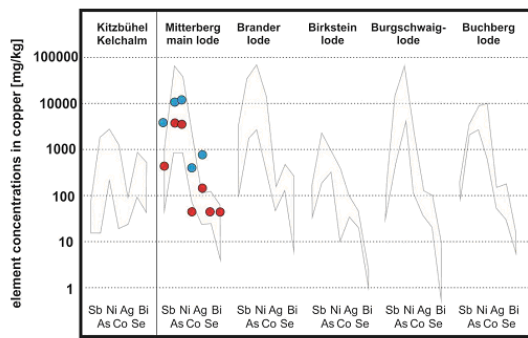


Fig. 4.: The elemental composition of the Hajdúsámson (in red) and the Téglás hoards (in blue) compared with the elemental composition of the eastern Alpine copper mining regions (Pernicka 2013, Fig. 4)

4. ábra: A hajdúsámsoni kincs (pirossal) és a téglási kincs (kékekkel jelezve) tárgyainak elemösszetétele a kelet-alpi bányák elemösszetételével összevetve (Pernicka 2013, Fig. 4)

The classification produced by the cluster analysis of the SAM project’s datacluster analysis has been accepted and applied by Hungarian research as well (Fig. 2.). According to analyses of a dagger and its rivets’ from burial no. 66 of the Early Bronze Age cemetery of Kiskundorozsma, measuring relatively high levels of nickel (4.27 and 5.88%), arsenic (2.16 and 2.45%) besides a low percentage of silver (0.17 and 0.21%), and iron (0.14 and 0.19%), Klára P. Fischl and Gabriella Kulcsár suggested that the raw material could also have contained fahlores with high levels of nickel and arsenic (P. Fischl & Kulcsár 2011).

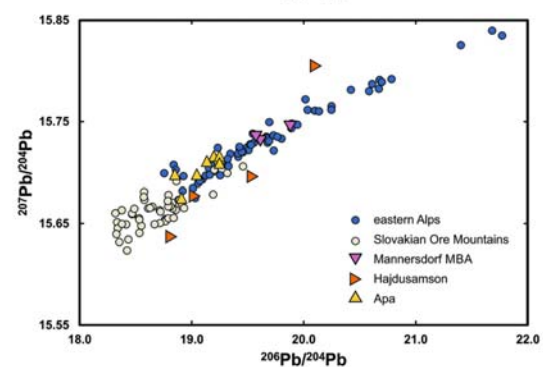


Fig. 5.: Lead isotope analyses of objects from the Hajdúsámson hoard compared with the analyses of assemblages from Austria, Romania, and eastern Alpine copper sources (Radivojević et al. 2018, Fig. 7)

5. ábra: A hajdúsámsoni kincs tárgyainak ólomizotóp elemzési eredménye (Radivojević et al. 2018, Fig. 7)

János Dani argues that the above mentioned swords from Téglás and the artefacts of the Hajdúsámson hoard are – based on trace elements – made of eastern Alpine fahlore copper (Krause 2003, Abb. 39, Cluster no. 4, *Fahlerzkupfer mit Nickel*). Following the system set up by David Liversage, he categorised the raw materials of the Hajdúsámson hoard to the ‘AsNi’ group and the sword from Téglás to the ‘ASN’ raw material cluster. Furthermore, while considering Ernst Pernicka’s examinations – based on element composition and complementary, the first published Hungarian lead-isotope analysis (Figs. 4-5.) – a direct, archaeological-historical link between certain mining regions and the raw material of the Téglás and Hajdúsámson swords has been drawn.

Table 3.: The elemental composition of the Zalaszarbar axe measured by ED-XRF analysis (Kiss et al. 2015, Table 2)**3. táblázat:** a zalaszarbari balta elemösszetétele az ED-XRF elemzés szerint (Kiss et al. 2015, Table 2)

Inv. nr	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Sn	Sb	Te	Au	Pb	Bi
2010.2.1.82	0.02	0.01	0.074	91	0.2	0.129	0.005	0.175	8	0.127	0.005	0.023	0.028	0.01

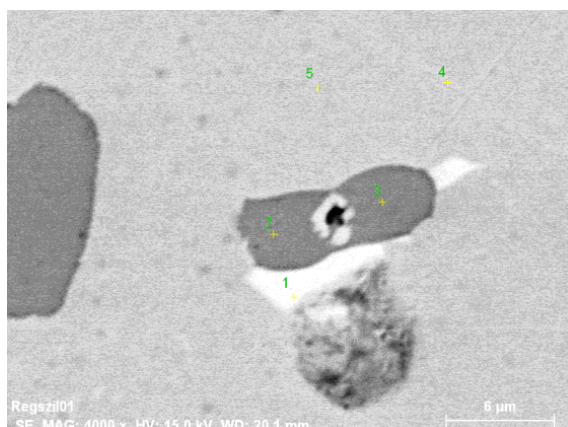
The axes of the Hajdúsámson hoard, the axe of Vámospércs (dating to the same period), along with the hilt of the Téglás sword were linked with the prehistoric mines of the Mitterberg region, south of Salzburg (Austria), that were exploited during the 16th–14th centuries BC. The ore used for the blade of the Téglás sword and an axe from the same hoard could have been mined in the Garam Valley region, Slovakia (Dani et al. 2013; Pernicka 2013).

The Middle Bronze Age hoard of Zalaszarbar containing over 80 artefacts was subject to a number of studies (Honti & Kiss 2013; Kiss et al. 2013). One of the artefacts, a flanged axe was made of, according to the ED-XRF analysis testing for 14 elements (**Table 3.**), an ore of high silver, antimony and arsenic content (Kiss et al. 2015). Based on these measurements, the axe was classified as an example of the classic tin bronzes (for more detail on the tin content, see below). Considering the axe's worked edge, the production-technological analysis made by TOF-ND concluded that – although similar objects are still being interpreted as bronze ingots – the Zalaszarbar piece was indeed an implement intended for use (see also Kienlin 2010).

Hungarian geologist experts, whose work focuses on the identification of raw materials, have long been drawing attention to fahlores (e.g. tetrahedrite, tennantite) which besides calcopyrite, are the second most frequently occurring minerals in copper deposits. These, however, do not contain nickel in their composition (Anthony et al. 2003; Czajlik 2012, 41, 87-91, 13. ábra). This also highlights the difficulties when it comes to the classification of copper ores based on impurities. The examination of the Zalaszarbar axe concluded that 'the raw material could have originated from a fahlore copper deposit given the presence of relatively high levels of arsenic, silver and antimony, where – as the higher iron levels detected in object 2010.2.1.71 demonstrate – calcopyrite minerals could also have occurred' (Kiss et al. 2013). This suggests that different types of ores either intentionally or unintentionally could have been combined during prehistoric metallurgical processes. In this way, ores containing nickel (or other) impurities could have made it into the raw material of prehistoric bronzes.

Our examinations show that artefacts containing nickel either in traces or in a low percentage occur among the Early Bronze Age Bell Beaker, Nagyrév, Kisapostag, and Early Transdanubian Encrusted Pottery assemblages and also among the finds of the Middle Bronze Age Füzesabony Culture (Endrődi et al. 2003; Kiss et al. 2013, Table 1). A range of tests carried out on the Zalaszarbar axe also indicated the presence of small amounts of nickel, which is not typical for the *Ösenring* raw material category, characteristic for the metallurgy of the Transdanubian Encrusted Pottery Culture. Furthermore, the results highlighted some issues around sampling and testing methodologies: the object-parts where the sample was taken from and the instruments involved in the examination produced – sometimes significantly – different results. The BNC's handheld XRF measured almost four times higher (45 %) tin content than the measurements by PGAA and time-of-flight neutrodiffraction (TOF-ND), and also by ED-XRF in the Mannheim laboratory. The difference was not so pronounced, when so-called bulk methods were being applied: samples taken from inside, the pure metal part of the object tested by ED-XRF measured 8% tin, while the prompt-gamma activation analysis (PGAA) indicated 90.2% copper, 9.6% tin, 0.18% silver, and 0.056 weight% H content for the axe's raw material. TOF-ND measurements resulted in 7.5±0.5 weight% for tin content. Both PGAA and ED-XRF tests measured corresponding values for copper and silver content, while the significant trace elements determined by the ED-XRF (Fe, Co, Ni, Zn, As, Se, Sb, Te, Au, Pb and Bi) were beyond the detection limit for the PGAA (Kiss et al. 2015). Most recently Boglárka Maróti studied the underlying causes for higher tin values occurring during PGAA tests and worked out a protocol for non-destructive PGAA tests to be carried out on archaeological objects (Maróti et al. 2018). With the validation of the method and according to the new protocol (and the relevant interference corrections) the tin content of the Zalaszarbar axe measured at 8,4 +/- 0,4 weight%.

The heterogenous measurements of the same object (i.e. the levels of nickel) raise the question whether the distinction between raw material categories, mining areas, and communication trajectories – often considered as archaeologically and historically conclusive – are truly well founded.



Regszil a						
Atomic percent (%)						
Spectrum	C	O	S	Ni	Cu	Sn
1	13.53	10.75	-	8.57	48.55	18.060
2	7.86	2.81	24.82	0.75	63.76	-
3	9.090	41.59	-	0.18	35.73	13.41
4	8.90	6.82	-	-	79.36	4.92
5	10.90	3.32	-	1.270	80.33	4.99

Fig. 6.: SEM-EDS analysis of the cauldron sample (Regszil 1a) discovered in the tumulus of Regöly Strupka-Magyar birtok

6. ábra: A Regöly Strupka-Magyar birtokon feltárt tumulusban talált bográcsperem Regszil 1a jelzésű mintájának SEM-EDS elemzése

In relation to the high percentage of tin and nickel, the long-ongoing discussion over when and how alloys entered the copper raw material has to be re-considered. Evidence for tin being used as a direct alloy appears only from the 7th century BC in the Carpathian Basin. More recently a sample taken from the cauldron found in the Early Iron Age tumulus of Regöly was tested by electron microscopy showing a basematrix of Cu-Sn solid solution (Gyöngyösi et al. 2017b). The ‘white areas’ appearing on the metallographic thin sections indicate a high nickel content, compared to the basematrix which contained a lower percentage of nickel. Nickel is not soluble in tin, it creates an intermetallic compound with a melting point of approx. 900 °C. Some of the SnNi content dissolves into the copper naturally, however the presence of nickel raises the copper’s melting point which in turn remains partially solid during the casting process (thus produces a ‘white area’ on the metallographic thin-sections). In sum, this indicates that the nickel entered the alloy along with the tin (Fig. 6.). Unfortunately, due to the lack of evidence so far, the question whether this reflects the appearance of a new technology or these particular objects were imported, cannot be answered at the moment (Gyöngyösi et al. 2017b, Fig. 6) The scientific examinations in relation to Early and Middle Bronze Age artefacts raise the possibility that differences in nickel content are not always associated with the composition of the copper raw material. Data so far suggests that during the Early and Middle Bronze Age, raw material ingots arrived in the Carpathian Basin in an alloyed form, therefore the alloying process must have taken place in the original mining region (Szabó 1996, 216; Kiss 2009b, 2012). Further research into this enquiry could provide evidence whether the above described paradigm-shift following the 17th century

BC was related to the change in exploitation of raw material sources or whether it was due to the introduction of a new technology.

Our examinations clearly show that a distinction has to be made between the amount of alloying agents and contaminants present in a given alloy and how much of these are actually measured. Scientific instruments do not map the object’s chemical composition but target and measure one particular physical characteristic which could be informative for the rest of the object’s composition. It is possible, in the case of a homogenous solid solutions and chemical compounds, that these two measurements overlap. However, as the metallographic thin-sections prepared from prehistoric bronze objects demonstrate, the majority of archaeological bronze artifacts are heterogenous in structure, or even inhomogenous. For this reason, the outcomes of scientific tests must be carried out with the understanding of microstructure in order to interpret the measurements within safe limits. Only scientifically accurate data can be used to draw archaeological–historical conclusions.

Although the topic of modern scientific instruments and their related protocols are hotly debated both nationally and internationally, this does not mean that there is no relevance or necessity for the testing of archaeological objects. On the contrary, modern scientific testing can provide more accurate and more complex answers to research enquiries. Thus a way forward could be the conceptualisation of more precise questions that are tailored to the abilities of scientific testing methods, and the development of standardised approaches for the testing of archaeological materials, as well as the establishment of wider collaboration for tackling more complex research enquiries would be

desirable (e.g. Gyöngyösi et al. 2017a,b; Kiss et al. 2017a,b; Király et al. 2017; Tarbay et al. 2018).

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DATA ON THE TECHNOLOGICAL CHANGE OF COPPER ALLOYING IN THE LIGHT OF FINDS EXCAVATED AT THE TUMULUS OF REGÖLY*

ADATOK A RÉZ ÖTVÖZÉSÉNEK TECHNOLÓGIÁVÁLTÁSÁHOZ A REGÖLYI TUMULUS LELETEINEK TÜKRÉBEN

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Abstract

We observed a Sn-Ni phase unnoticed earlier during the archaeometallurgical examinations even in several of the bronze objects of the tumulus of Regöly that can be linked to the early Ha D₁ period, showing substantial changes in its finds and traceable via Asia Minor to Central Asia in its interrelations. In examining and revealing the reasons for the unique phenomenon, focus was being shifted increasingly to the raw material, the way copper had been alloyed. The fundamental step of bronze workmanship in the prehistoric age that is alloying copper with tin still triggers a number of disputes. Making tin bronze has basically four options that we know: melting a mixture of metallic tin and copper; adding naturally occurring tin oxide (tin ore or cassiterite, SnO₂) to already molten copper; smelting an ore containing both copper and tin; reducing a mixture of copper ores and tin ores. Based on archaeological field observations, it is an overwhelming opinion on our continent that alloying to the raw material for the finds of the European Bronze Age was performed still in the smelting phase using a mixture of ores of the proper composition. At the same time, successful archaeological experiments demonstrate that it was possible to directly alloy pure metals, copper and tin, under the technical circumstances of the age in question. However, Europe shows no sign of having as intense production at significant archaeological sites of tin ores as at copper mines of the prehistoric age. Moreover, we are not aware of commerce of tin of any significant volume; the use of objects made from pure tin did not become widespread up to the end of the Bronze Age anywhere on our continent. The few tin objects known seem to be extremely low compared to the quantity of bronze produced in that age for the case of alloying pure copper even if we assume the melting of the majority of tin objects. Also, no proof of alloying pure-metallic tin has been shown as yet at archaeometallurgical sites in the area of Europe during archaeometallurgical examinations, to our knowledge. The data referring to the direct alloying of copper unknown earlier in the European material of the new Sn-Ni phase observed in the Regöly finds examined recently also proves that manufacturisation and the accompanying explosion-like technological advance is not the outcome of the internal development of the Hallstatt culture sphere. It had been a ready-implemented practice in Europe by masters of the last Ionian migration starting from Asia Minor in the last third of the 7th century BC in the Carpathian Basin just as had been the technology of alloying copper directly with metallic tin.

Kivonat

A Ha D₁ időszak kezdetéhez köthető, leleteiben gyökeres változásokat mutató, kapcsolatrendszerében Kis-Ázsián át Közép-Ázsiáig követhető regölyi tumulus bronztárgyainak archeometallurgiai vizsgálata során több tárgynál is egy korábban nem tapasztalt Sn-Ni fázist figyeltünk meg. A különös jelenség okainak vizsgálata és feltárása során egyre inkább az alapanyag, a réz ötvözésének módjára terelődött a figyelem. Az őskori bronzművesség alapvető lépése, a réz ónnal való ötvözésének módja még ma is sok vitát vált ki. Az ónbronozok előállításának alapvetően négy lehetősége ismert: fémes ón és réz keverékének megolvasztása; a természetben előforduló ón-oxid (ónkő vagy kassziterit, SnO₂) hozzáadása a már olvadt rézhez; rezet és ónt együttesen tartalmazó érc

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kohósítása; réz- és ónércek keverékének redukciója. A terepi régészeti megfigyelések alapján kontinensünkön az az általános vélemény, hogy az európai bronzkor leleteinek nyersanyagához az ötvözést még a kohósításkor, a megfelelő összetételű ércek keverékének felhasználásával végezték. Ugyanakkor eredményes régészeti kísérletek mutatnak arra, hogy az adott kor technikai lehetőségei mellett is lehetséges volt a színelemek, a réz és ón direkt ötvözése. Az ónércek jelentős lelőhelyein azonban Európában nincs nyoma az olyan intenzitású kitermelésnek, mint az őskori rézbányáknál. Ráadásul jelentős mennyiségű ón kereskedelmére utaló leleteket sem ismerünk; kontinensünkön a tiszta ónból készített tárgyak használata a bronzkor végéig sehol sem vált általánossá. A néhány ismert ón tárgy a korszakban gyártott bronz mennyiségéhez képest a tiszta réz ötvözése esetén rendkívül kevésnek tűnik még akkor is, ha feltételezzük az óntárgyak döntő többségének a beolvasztását. Ráadásul az eddigi archeometallurgiai vizsgálatok során tudomásunk szerint Európa területén az őskori lelőhelyeken még nem találtak bizonyítékot a fémtestre ónnal való ötvözésre. A most vizsgált regölyi leleteknél megfigyelt új Sn-Ni fázis az európai anyagban korábban eddig ismeretlen, a réz direkt ötvözésére utaló adata is megerősíti, hogy a manuakturalizálódás, és az azzal együtt járó robbanásszerű technológiai fejlődés nem a hallstatti kultúrkör belső fejlődésének eredménye. Az a Kárpát-medencébe a Kr. e. 7. század utolsó harmadában a Kis-Azsiából kiinduló utolsó ón vándorlás mesterei által Európába készen átültetett gyakorlat, miként a réz direkt módon, fémest ónnal való ötvözésének technológiája is.

KEYWORDS: CAULDRON, CHAIN, INCENSER, COPPER, TIN, NICKEL, LEAD, METAL-TO-METAL ALLOYING, MANUFACTURISATION, SERIAL PRODUCTION

KULCSSZAVAK: BOGRÁCS, FÜSTÖLŐ LÁNC, RÉZ, ÓN, NIKKEL, ÓLOM, FÉM-A-FÉMMEL ÖTVÖZÉS, MANUFAKTURIALIZÁLÓDÁS, SOROZATGYÁRTÁS

Introduction, archaeological background

The fundamental step of bronze workmanship in the prehistoric age that is alloying copper with tin still triggers a number of disputes. Making tin bronze has basically four options that we know: melting a mixture of metallic tin and copper; adding naturally occurring tin oxide (tin ore or cassiterite, SnO₂) to already molten copper; smelting an ore containing both copper and tin; melting a mixture of copper ores and tin ores (Heeb & Ottaway 2014, 178). Based on archaeological field observations, it is an overwhelming opinion on our continent that alloying to the raw material for the finds of the European Bronze Age was performed still in the smelting phase using a mixture of ores of the proper composition (Hauptmann 2014, 94). At the same time, successful archaeological experiments demonstrate that it was possible to directly alloy pure metals, copper and tin, under the technical circumstances of the age in question (Heeb & Ottaway 2014). This is also confirmed by the tin ingots found in the Uluburun and Salcombe ship finds, based on which the force of the question of tin commerce necessary for bronze production arises as well (Harding 2005; Harding 2013, 375). However, Europe shows no sign of having as intense production at significant archaeological sites of tin ores as at copper mines of the prehistoric age (Wang et al. 2016, 80). Moreover, we are not aware of commerce of tin of any significant volume; the use of objects made from pure tin did not become widespread until the end of the Bronze Age anywhere on our continent. Views without proper foundation are not considered in this study, such as tin pest causing the disappearance of a significant portion of Bronze Age ingots. Based on our results from the examinations we specifically

looked for parallelism in the direction of ore deposits with high nickel content. Their relative concentration has so far been observed on the territory of Switzerland alone where Margarita Primas collected Bronze Age tin finds that she dated them back to the late Bronze Age, the centuries 11th - 10th BC (Primas 1984). These objects mostly classified as small jewels have lately been supplemented by a tin ingot found at the Sursee-Gammainseli archaeological site (Nielsen 2014). However, these couple of objects seem to be extremely low compared to the quantity of bronze produced in that age for the case of alloying pure copper even if we assume the melting of the majority of tin objects. Also, no proof of alloying pure-metallic tin has been shown yet at archaeological prehistoric sites of Europe during archeometallurgical examinations, to our knowledge. Therefore, we handled the phenomena referring to the alloying in the age in question with priority when examining the samples from the mound of Regöly (Szabó & Fekete 2011; Fekete & Szabó 2017a).

The surroundings of the finds, the archaeological site at Regöly

The archaeological site is located in the Western half of the Carpathian Basin, in the Southern part of Transdanubia, at the confluence of the Kapos and Koppány rivers (**Fig. 1**). This site was a place of excavating of a tumulus in 2011 to 2012 whose material dates clearly back to the last third of the 7th century BC, the Iron Age, yet, but cannot match either the finds of the Scythian or that of the Hallstatt culture (Szabó & Fekete 2011, 49; Fekete & Szabó 2015).

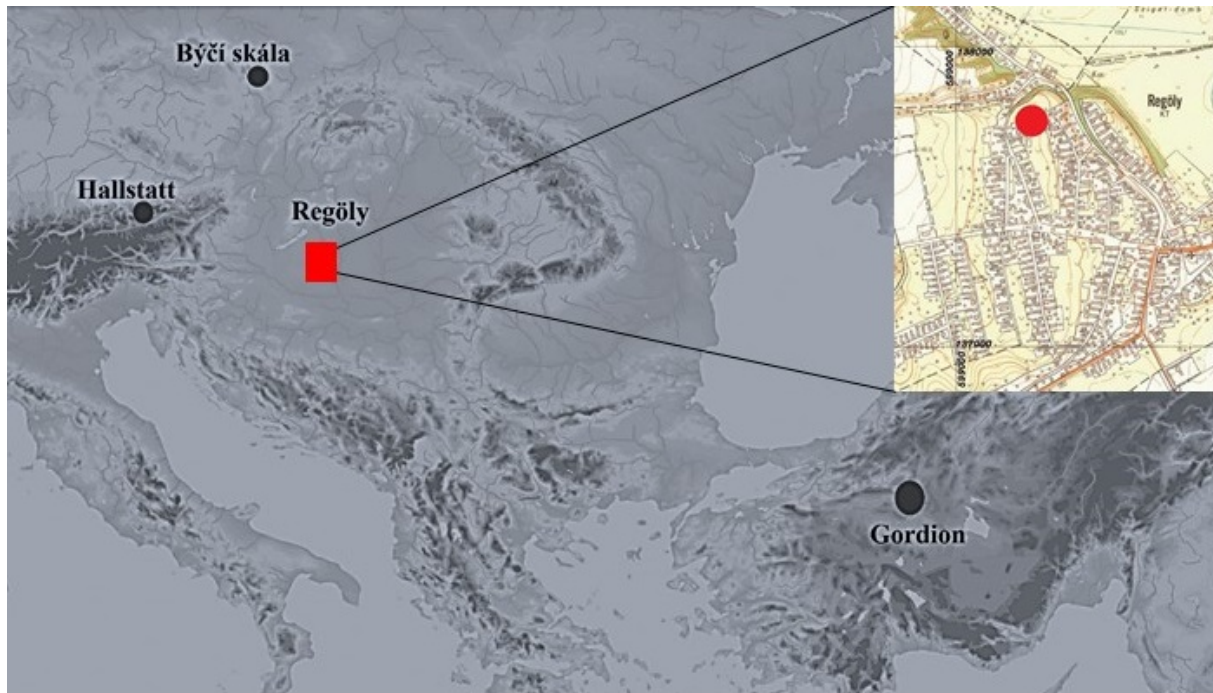


Fig. 1.: The location of Regöly in the Carpathian Basin. Regöly is in the Southern part of Transdanubia, at the confluence of the Kapos and Koppány rivers

1. ábra: Regöly elhelyezkedése a Kárpát-Medencében. Regöly a Dunántúl déli részén fekszik a Kapos és Koppány folyók összefolyásánál

Thus, it is of utmost importance even from this aspect that two contradicting positions have been established by the European and the Russian research in connection with the emergence of the Hallstatt culture. On the European side, according to the majority, the continuous internal development, transformation ongoing even after the late Bronze Age had been complemented by the commerce of Eastern objects and cultural influence (Metzner-Nebelsick 2002). On the part of Russian researchers, I. V. Bruyako, the appearance of Eastern horse harnesses and weapons in the West can be explained by mass migrations only (Bruyako 2005). As indicated by the latest finds at Regöly, however, an intermediary solution arises: the replacement of the ruling elite seems to be the most probable (Szabó & Fekete 2011, 49–50; Fekete & Szabó 2015; 2017b; Szabó 2015; Hansen 2011; 2017).

Those who excavated at the mound of Regöly, the objects revealed can be the legacy of the people called Sigynnii (sigynnoi) or later Pannoni who ruled the area of South Transdanubia southward from Lake Balaton from the second half of the 7th century to the beginning of the 4th century BC, almost 3 centuries (Szabó & Fekete 2011, 48–50). Objects or appearances orientating towards Asia Minor unknown so far on our territory can also be observed in the material of the mound showing close relations to the Hallstatt finds (Fekete &

Szabó 2015; Szabó et al. 2018). The mound structure itself built from stamped clay exhibits the utmost parallelism to one located in Gordion, Phrygia (Young 1981, 84. Fig. 52; Fekete & Szabó 2017 Fig. 8). We encountered a rare and special mineral (Cr-spinel) in the ceramic during the archaeometric examinations, which is unknown in the area of Europe but can also be found in the control sample from Gordion (Gyöngyösi et al. 2017; Kürthy et al. 2018). At the same time, the three-feathered bronze arrowheads, reptilian scale armour sheets (Horváth & Szabó 2015), the harnesses oriented towards Inner Asia (Szabó & Horváth 2016), the ceramic fragments, crockeries to be linked to both the Andronovo culture and the Ancient East (Kürthy et al. 2016) reveal, too, that a nation was reckoned with to be of Eastern roots who were, though, similar to Scythes of the steppe in their way of life but had bypassed the Black Sea not from the North but from the South, Asia Minor. Based on our current knowledge there was one and only such a nation in the period examined, the Cimmerians indicated in ancient sources who, in part, bypassed the Black Sea from North fleeing from the Scythes, while their other branch passing via the Caucasus fought on the territory of Urartu, Phrygia, and later Lydia already from the 8th century BC (Bruyako 2005, Fig. 31; Kohler 1995, 185–189). This is how the unique blend of objects of Eastern horse people and the advanced technology of the Ancient East becomes

understandable and interpretable in the legacy of those arriving from the former Median Empire to South Transdanubia via the Balkans in the last third of the 7th century BC according to ancient sources (Szabó & Czuppon 2014, 50–51. Fig. 1). As a result, tracing the historic background and connection system is exceptionally important to understand the complex data of these objects, showing radical technological changes in their forms and manufacturing methods due to the strong mixing of different traditions. It is considered crucial that the archaeometrical results of each object are carefully examined and evaluated together with the continuously developing historical and social connections before the disclosure of the full material on the excavation of Regöly.

When observing a part of the metal objects in a preliminary manner, we remarked technological phenomena that had gone undetected so far that is they refer to serial production and special technologies assembled from composite elements (Szabó 2013; Fekete & Szabó 2017a). We complemented the usual search for shape similarities and the determination of material composition of these archaeological objects by detailed metallographical examinations. We selected objects for these examinations that had been produced in a serial manner and their making had required special know-how of technology and a well-equipped workshop. Below we present the examination results of two object types closely linked to sacred activities from the line that is a cauldron used for offerings of food and drink as well as an incense burner. These exhibited results referring to the way of alloying unknown for the objects of the Carpathian Basin so far.

Preliminary results, examination of the cauldron found at Regöly in 1907

Up to now, a relatively intact bronze cauldron (**Fig. 2.**) was earlier excavated from Regöly, and fragments of at least another bronze cauldron has lately been excavated from the tumulus. The first one, fitted with doubled cross-shaped slings and pseudo-twisted ribs, slightly oval, with a flange diameter of 26 and 27.3 cm, cauldron with a missing bottom reached the museum of Szekszárd under unknown circumstances in 1907 (Patay 1990, 30). It can be well seen that two parallel lines run in two bands each under the flange on the external side on the old Regöly cauldron (Szabó 2009; 2012; 2013). The line design of the ornamentation is continuous, it seems to be carved. On the flange of a thickness of about 3 mm, in the proximity of the slings mounted with 4 cast-looking lens-shaped rivets on both sides, 2 slightly thickening parts protruding at 1.5 cm from the flange can be observed that shows uneven breakage surface in contrast to the smooth surface of the edge of the flange. Except for the corrosion phenomena, the external and internal sides of the cauldron is smooth in the upper third, whereas its side decreases to foil-thin towards its bottom. Signs of forging can be seen on both of its sides. (A considerable part of its bottom was missing that was complemented by restorer Mihály Nacsa using artificial resin.) We took sample from the part near the sling of the flange of the cauldron. The sample preparation and instrumental analysis of sample no. BrWMM63 were performed by support of G. McDonnell and M. Pollard, Head of Division at the Division of Archaeometallurgy. Embedded cold in resin and ground wet, we etched the carefully polished cross-section using an FeCl₃ solution.



Fig. 2.:

The intact bronze cauldron found at Regöly (1907)

2. ábra:

A Regölyben talált (1907) ép bronz bogrács

Almost nothing can be seen at low magnification on the cross-section image but the boundary of relatively large crystallites in the alpha structure is already silhouetted well at a magnification of 400, among them the twin-crystallites split along the straight limiting lines, hidden in some places. The cross-sectional image reveals copper sulphide inclusions in the spots located in a dispersed way, the distribution of tin is even, with a ratio of 8.89%. The annealed grain structure seen in the cross-sectional image with the twin-boundaries observed in some places refers to the fact that the object had been heat-treated after its plastic deformation. As few twin-boundaries can be observed, we can deduce from the grain structure that heat treatment had not been performed at high temperature and heat ramp-up had been slow and not shock-like. This results from the dimensions of the object as well. The dispersed appearance of the twin-crystallites refers in general more to the lattice stresses arising due to heat treatment than a raw material forged or carved during a post-processing. Considering the part referring to the place of mould pin, the enguss, which is protruding and slightly thickens, observed on the flange, as well as the forge marks polished surface and the composition, it can be determined that the than bronze workman made the cauldron from a semi-finished product of a raw material produced originally by casting and suitable for further processing (Szabó 2009, 348). Our earlier examinations also highlighted that the cauldron was made in a workshop where it was fitted with components produced in a serial manner (doubled cross-shaped sling, pseudo-twisted nibs) (Szabó 2012).

Metallographical examination of cauldron fragments and incenser chain links excavated in the Pannon tumulus at Regöly

During the excavation of the tumulus at Regöly (Kürthy et al. 2013), a half palm-sized flange fragment of a cauldron was dug out from the yellow loess layer marked RHQ20 containing many find fragments, between the burnt, stony layers of the chamber (Kürthy et al. 2013), that included the remainder of a rivet. (The layer mentioned contained several pseudo-twisted nib fragments, too, which, however, could have belonged to cysts.) Similarly, almost one and half dozens of intact and fragmented, more-or-less square-shaped chain links were excavated from this and the connected layers (Fig. 3).

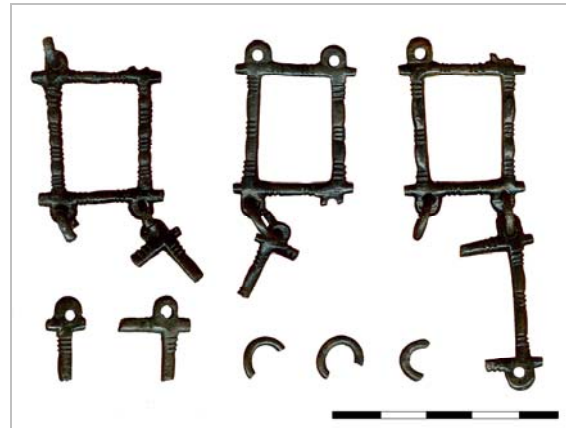


Fig. 3.: The excavated chain fragments from the Pannon tumulus of Regöly

3. ábra: A regölyi pannon sírhalomban feltárt lánc-tördelékek

Objects 8, 10, 14, 20, 22 and 45 of the fill-up of the tumulus at Regöly contained small-sized, cast, square-shaped, notched and formed from a stick-like shape, fragments of bronze chain (s) that were assembled from lugs fitted with 4 small nibs and rings bent from a bronze wire, posing apparently low-level technical challenge, unknown in the earlier finds material of the Carpathian Basin (Szabó & Fekete 2011, Table 20). Their function was clear to be determined at first sight: based on earlier, but of other design, of the same use, finds excavated also at Regöly (Fekete 1985b, Figure 1; 1986, Fig. 13). The appearance of incensers and the belonging chains can be regarded as almost massive in certain regions of the 7th – 6th centuries BC; parallel to a specific new cognitive-religious-ritual function (Fekete 2018).

The square-shaped cast chain links of the tumulus at Regöly exhibit many new technological processes. The jeweller removed all manufacture marks such that even the making is unclear whether it was through lost wax or some mould. That is, there are references uncertain and unclear to both procedures. There is a little burr at the nibs but it must be a worn-out, bulked-up part during use by the chain links. If it was a borehole, it had rather a mark only on the other side, but here it can be noticed on both sides of the hole. Small cross-directional notches can be seen in some places by the nibs. Such can be caused by gripping into a pair of pliers or a vice but they had had no such tools, as far as we know. It could be possibly a mark of carving or deformation but it seems to be completely unreasonable on such a small even surface where they appear.



Fig. 4.: Magnified photograph taken from a chain fragment. The photograph reveals some details of the processing technique and shows the ornamentation of the chain.

4. ábra: A lánc-töredékekről készült nagy nagyítású fotó. A fotó felfedi a készítés-technika pár részletét és a lánc díszítését.

One may think that these impressions may have possibly been generated by tiny differences of moulds. The linking rings had been clearly made using a wire processed by hammering. Their ornamentation is simple, small narrow 2 or 3 bean-pattern between groups of notches (**Fig. 4**).

The slightly trapezoid asymmetric shape of chain links of about 1.9×3.7 cm, the design of 4 nibs, the alternation of sophisticatedly divided beans and groups of notches are all workshop tricks that pop up not only in the direct neighbourhood (see Regöly hoard: Fekete 1995, Kemenczei 1996) but also in the bronze workmanship of the entire Transdanubia. In part (their elements) or in entirety, as copies, local version (s), including the metal working centres of paramount importance since centuries (Velem – Szentvid, Celldömölk – Ság-hegy, Keszthely – Apátdomb) where the new-style fibulas had been also made massively, as indicated by the semi-finished products and/or moulds (Fekete 1985b, Fig. 11-13; 1986, Fig. 8-10; 1995, 42., Fig. 1-5; 2006, 102., Table 61; Kemenczei 1996)

We selected a fragment of the cauldron from layer marked RHQ20 and that of an incenser chain link from the same object for complex archaeometallurgical examinations.

Examination methods

Description of sampling, the samples

During sampling, we cut off a slice to be examined in the full cross-section from the flange-side corner of the cauldron fragment (**Fig. 5**).

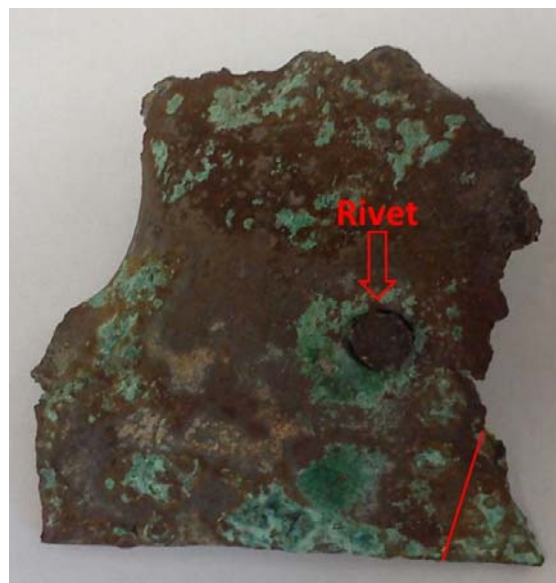


Fig. 5.: The fragment of a cauldron from Regöly. The positions of the examined samples are signed in the photograph. The material of the cauldron and the rivet were examined.

5. ábra: A Regölyben feltárt bogrács töredék. A fotón a vizsgált minta helyét jelöltük. A bogrács és a szegecs anyagát vizsgáltuk.

We removed the rivet located on the sheet piece and embedded it fully, the flat polished specimen was made at the bottom of the rivet. This way, it was possible to examine its entire cross-section. In the same manner, we added one of the nib fragments typically twisted and used frequently for cauldrons, the sample of whose end was examined in its cross-section, too.

In the case of the chain link, the longer side of the fragmented piece selected for examination remained intact, it contained even a ring. Its size made it suitable for embedding the entire chain without sampling and examining the cross-section of bars via the slight destruction of the object. The examination spot seemed suitable for examination of both the production technique and characteristics of the composition.

Goal and sequence of examinations

Our examinations focussed on the determination of the composition of alloy used, which is a relevant piece of information for the description of the characteristics of the making. The elemental composition of samples was determined by means of SEM-EDS (**Figs. 6-7, 9-10**). We made use of an optical microscope for the metallographical examination of the finds, to study the microstructure of the objects. Based on the features, description of the microstructure, we determined the technique and characteristics of making.



Fig. 6.: The microstructure of the cauldron-fragment. Recrystallized grains and intensive corrosion revealed by the optical micrograph. The corrosion can be discovered mainly at the grain boundaries. Zeiss Axio Scope.A1. Magnification.: 50x. Etching.: FeCl_3 , Bright Field

6. ábra: A bogrács töredék mikroszerkezete. Újrakristályosodott szemcséket és intenzív korrózió nyomait látjuk a mikroszkópi felvételen. A korrózió nyomai leginkább a szemcsehatárok mentén fedezhetők fel. A felvétel Zeiss Axio Scope A1 mikroszkóppal készült világos látótérben, 50x optikai nagyításban, FeCl_3 maratás után.

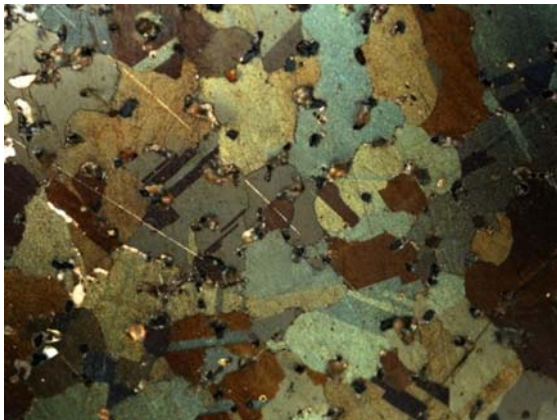


Fig. 7.: The grain structure of the cauldron in higher magnification. The colour etching reveals clearly the grains and the twin boundaries. The spots show the inclusions or corrosion products. Zeiss Axio Scope.A1. Magnification.: 100x. Etching.: K_2CrO_4 , Polarized.

7. ábra: A bogrács mikroszerkezete nagyobb nagyításban. A színes maratásban az iker határok jobban kivehetők. A fekete pontok zárványokat vagy korróziós terméket jelentenek. A felvétel Zeiss Axio Scope A1 mikroszkóppal készült polarizált megvilágításban, 100x optikai nagyításban, K_2CrO_4 maratás után.

The samples taken out from the selected archaeological finds were embedded in a cold-curing two-component resin. The samples were ground using grades 220, 600, 1200 for flat surface

specimen at 300 rpm, then polished using polishing tissue of 3 and 2 μ at 150 rpm. The samples prepared so were immersed in FeCl_2 and K_2CrO_4 etching agents for the analysis of grain structure. The goal of using two enchants was twofold. During etching with K_2CrO_4 , an optically active oxide layer is formed on specific grains with a thickness varying depending on their crystallographic orientation. The grains obtain differing colours in polarised light. By way of this, one obtains outstanding information about the grain structure (whether it is a cast, formed, annealed grained structure). By examining in bright field, the sample prepared with potassium chromate, the existing inclusions can be well seen (e.g. copper sulphide inclusions) as well. The analysis of inclusions also provides important information on the making of the specific object or even its use. However, etching with potassium chromate is sensitive to the combined etching of phases with different material grade. In such a case, etching with FeCl_2 makes grain structure optically sharper and more robust. Thus, it is less sensitive to enrichments and changes in composition caused by corrosion effects.

Samples examined recently

Fragment of the cauldron edge (Regszil1a)

Taking the average composition of the sample taken from the cauldron, it is a high tin-containing bronze. With consideration for the 11.3 w% of tin and 1.5 w% of nickel, a homogeneous solid solution phase is expected in the microstructure. As concerns its composition, this alloy has a high strength and hardness. It is still fit for cold-forming, with a high deformation resistance, though. For such an alloy, a high degree of plastic deformation, suggested by both the shape of the object and the hammer marks observed near the bottom of the cauldron excavated in 1907, cannot be imagined without annealing. The optical micrograph examinations revealed an annealed grain structure (**Fig. 6.**), just as did that of the cauldron found in the past. It is well visible in the micrographs taken in polarised light that the majority of sample is built by grains falling in the size range of 100 to 150 μm . In correspondence with earlier examinations, few but well distinguished twin-boundaries point out that the grain structure is annealed. A bent boundary surface can be observed in several places, which refers to the process of grain coarsening occurred due to increased temperature. The coarsening of the re-crystallised grains took place either during annealing or during use. This is a natural process but as was revealed by preparation using iron chloride, the grain size at the edges of the sample was well smaller (40 to 70 μm). Here, we need to consider two processes. The raw material is hard, difficult to form, thus, however

thick is the formed part, its transformation needs significant energy or power. If the transformation is not successful, the material near the surfaces in contact with the tool or counterpart undergoes stronger deformation than the internal parts. This gradient already present in the deformedness appears even during annealing, as tinier grains come to being near the surface than inside the sample volume. The degree of grain coarsening occurred in terms of the grain area does not depend on the original grain size but time and temperature. However, naturally due to constraints of geometry, one experiences other characteristic in the measured grain diameter. In addition, one can observe at the edge of sample in the microstructure revealed with iron chloride that the areas surrounding the surface are starkly corroded. Mostly corrosion along grain boundaries can be identified. The cauldron, in particular attention to its use, spent time in oxidising atmosphere at an elevated temperature. Oxygen tends to diffuse towards the internal volumes of the material along grain boundaries during the oxidation of copper alloys, and precipitate on the grain boundary as tiny phases of Cu_2O . If the object is subject to later corrosion effects, this phenomenon is able to promote corrosion along grain boundaries. Moreover, it can slow down grain coarsening process near the surface. All in all, it can be determined considering the circumstances of the excavation mentioned in the introduction to the finds, that both sides were subject to corrosion effects in the soil in most of the long period spent there. It can be well seen, however, that there is a noticeable difference for the degree of corrosion between the two sides. With a view to the circumstances of the excavation, the entire object can be regarded as to have been exposed to the identical corrosion effect, therefore the reason for the difference can be sought in the "history" of the sample. In the light of the composition of the material and the concluded properties, this can be the result of, on the one hand, the two different deformations on the two sides of the sheet. Considering the geometry of the object, this assumption can be backed by the fact that the shape and design carries this difference intrinsically. This is complemented by the technique of the period and the hardness of the metal. On the other hand, it is the use of the object. One side of the cauldron is in direct contact with the fire, so it is exposed to higher heat there. Depending on the fire, the oxidising effect can also be different, but we draw here attention to the fact

that we examine the flange where these differences are by all means of lower degree than in the case of the cauldron body. However, if we take this into account, we can expect a corrosion along boundaries with a different rate of corrosion due to the differing corrosion effect. In our present study, we see a more powerful effect in the forming technology based on our examinations. Our data indicate that the sheet was subject to an asymmetric formation (the formation was stronger from one side) and the transformation of the sheet had not taken place during the plastic deformation prior to the last annealing. Therefore, smaller-sized grains developed along this surface during the recrystallisation taking place in the annealing. The effects occurring during the mentioned oxidation, which slow down coarsening, could have intensified this difference during use. The differing rate of corrosion of the two sides could have been caused jointly by this difference and the two sides subjected to uneven oxidising effect. As mentioned, this coincides to what we may conclude from the shape and normal use of the object.

As was already mentioned, the analysis of the inclusion bears great importance, too. The presence of homogeneous solid solution can be expected, however, foreign phases can enter the metal both during smelting and making that can tell about the way of manufacture. As was shown by preliminary examinations, copper sulphide inclusions were found in the grain structure in the optical micrographs (Fig. 7). Their size is about $20\ \mu\text{m}$, their colour being dark grey on the optical micrograph. Their shape typically have a rounded boundary, mostly of globular nature. This make us conclude that the material spent an extended time at an elevated temperature after smelting. With consideration to the use of the object, we cannot draw any conclusion as to what technique was used for the making. Literature sources and earlier examinations point out that their origin derives back to smelting. SEM-EDS analyses revealed that the inclusions have measurable sulphur content in addition to copper, but no tin can be detected. Tin can be measured in metallic areas only. No nickel content can be detected even in some of the sulphide inclusions. In specific inclusions nickel can be detected but we note that copper is able to dissolve nickel in unlimited amounts, which is an important factor in this case. Phases with high tin and high nickel content can be mostly located in the proximity of sulphide phases (Fig. 8).

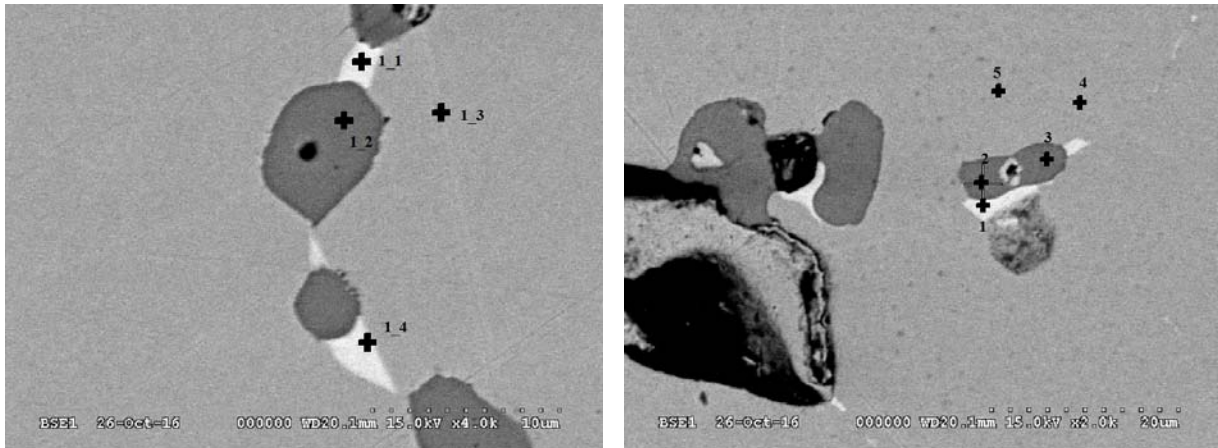


Fig. 8.: SEM micrographs taken from the cauldron. The micrograph shows the inclusions. The large phases are copper-sulphide inclusions, the small bright ones are SN-Ni rich phases.

8. ábra: A bogrács töredék éléből vett minta SEM felvételei. A felvételen a zárványok láthatók: a nagyméretű fázisok réz-szulfidok, a kisméretű világos fázisok az Sn-Ni gazdag fázisok.

Table 1.: Results of the local EDS analysis of cauldron edge

1. táblázat: A bogrács töredékből vett minta helyi SEM elemzéseinek eredményei

	Atomic percent (%)					
	C	O	S	Ni	Cu	Sn
Fig8a: 1_1				9.43	69.19	21.38
Fig8a: 1_2		1.93	30.19		67.89	
Fig8a: 1_3		3.57			90.66	5.77
Fig8a: 1_4				2.38	90.50	7.13
Fig8b: 1	13.53	10.75		8.57	48.55	18.60
Fig8b: 2	7.86	2.81	24.82	0.75	63.76	
Fig8b: 3	9.09	41.59		0.18	35.73	13.41
Fig8b: 4	8.90	6.82			79.36	4.92
Fig8b: 5	10.09	3.32		1.27	80.33	4.99

The SEM-EDS study provides only compositional data, whose evaluation requires the consideration that the examined phases are smaller than the excited volume, thus, the composition of the solid solution in the surrounding of the phase distorts its composition. However, it appears from the data that nickel content is about 9 w% and tin content is not lower than 18 w% (**Table 1.**). Copper dissolves tin both in liquid and solid state very well and dissolves nickel in unlimited amounts. (ASM

Handbook 1994, 318) Based on thermodynamic relations, a phase can remain in this state only if it is an intermetallic compound with a high melting temperature of the tin nickel alloy system. These are Ni_3Sn_2 and Ni_3Sn_4 . Although it cannot be supported by the presented examinations and is only a conclusion but it can be either of them based on the compositions, but Ni_3Sn_2 seems to be more probable, supported by its melting temperature. However, if copper and tin had been smelted together, the development probability of this compound based on the above dissolution tendencies is insignificant as the professional literature does not refer to this phase either. Yet, it develops easily in the tin nickel system. This leads to the assumption that metallic tin was alloyed into copper in this case. A part of the nickel content had been introduced in the alloy along with tin just as had been the mentioned compounds. Their tiny size is explained by the fact that these compounds dissolve slowly in copper and their tin and nickel content is transferred into a solid solution. However, the alloying and afterwards the crystallisation period had not been long enough to get dissolved all, the examined sample shows the remainder. This is backed also by the fact that the largest part is located near the copper sulphide. Copper sulphide is a phase with low melting temperature and solidifies in the last stage of crystallisation, thus, the inclusions with high melting temperature not able to dissolve in the melt shall be located here. These observations all point out that direct alloying had been applied for the making the material of the cauldron, the metal-state copper was molten together with metallic tin.

Fragment of the incenser chain link (Regszil_1)

Optical micrographs revealed a dendritic structure. This refers to the making of chain link by casting. Based on the large size of the dendrites and their radial arrangements in the cross-section, the melt had not been overheated much over its melting temperature. The fine structure of dendrite arms refers to high cooling rate, which arises from the dimensions of the object.

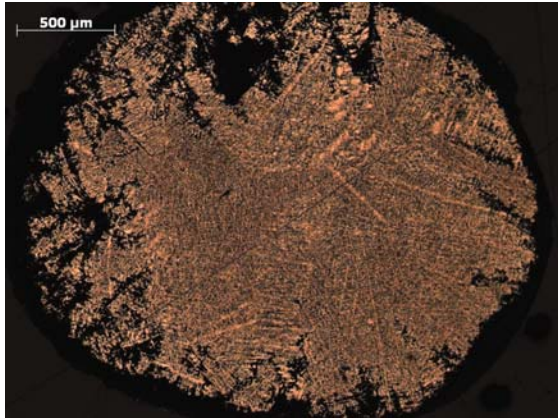


Fig. 9.: The microstructure of a chain fragment. Dendrites with fine secondary arms can be seen on the micrographs. Zeiss Axio Scope.A1. Magnification.: 50x. Etching: FeCl₃, Bright Field

9. ábra: A láncötredék mikroszerkezete. Kis szekunder ágtávolságú dendrites szerkezet látható a felvételen. A felvétel Zeiss Axio Scope A1 mikroszkóppal készült világos látótérben, 50x optikai nagyításban, FeCl₃ maratás után.

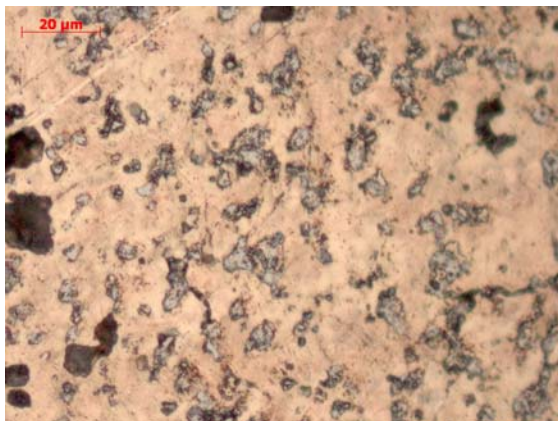


Fig. 10.: The microstructure of a chain fragment in higher magnification. A lot of inclusions can be seen on the micrographs. Zeiss Axio Scope.A1. Magnification.: 1000x. Etching: FeCl₃, Bright Field.

10. ábra: A láncötredék mikroszerkezete nagy nagyításban. A mikroszerkezetben sok zárvány fedezhető fel. A felvétel Zeiss Axio Scope A1 mikroszkóppal készült világos látótérben, 50x optikai nagyításban, FeCl₃ maratás után.

The raw material is bronze, which, in addition to its tin content above 5% contains a considerable amount of lead (14%). The addition of large amount of lead had been necessary for the sake of the high ability of the thin chain link to fill in the mould (**Fig. 9-10.**).

Electron microscopy reveals significantly heterogeneous structure where globular white phases are the drops of the metallic lead. Several studies highlight that copper dissolves lead neither in liquid nor solid state, thus, it creates separate globular phases. In addition, one can encounter here lower quantities of copper sulphide inclusions from smelting.

The material of the chain link similarly includes high tin- and nickel-containing phases just as in the case of the cauldron (**Fig. 11.**). The tin nickel ratio also in this case assumes the presence of the mentioned tin nickel intermetallic phases (**Table 2.**). Also here, these tiny phases can be found in small quantities, which supports that low nickel is present in the system and it had been incorporated in the raw material of the chain link as the contaminant of the lead during alloying.

The examination of the chain link exhibited the same material-specific features as also in the case of the object made by the other basic technique for making (casting) as was seen in the case of the object with larger weight formed by hammering, the cauldron. At the same time, the addition of lead is specific to the production technique. This is all supported by the fact that the presence of tin nickel intermetallic phases is the feature of the raw material for general use, the specialty of the bronze raw material. Also, this points out the metal-to-metal alloying.

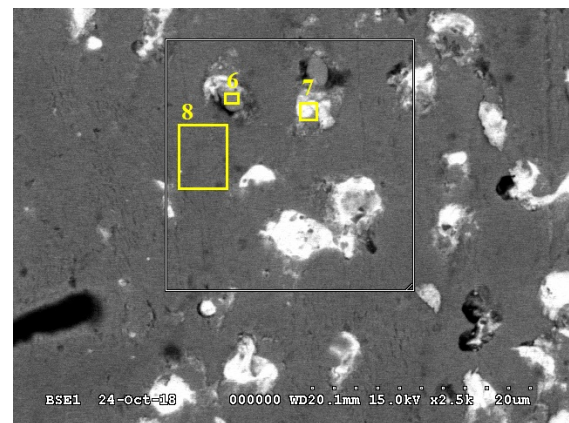


Fig. 11.: SEM analysis of the chain fragment reveals that the majority of the inclusions are lead drops (white phases)

11. ábra: A láncötredék SEM vizsgálata rámutatott, hogy a zárványok jelentős része ólom csepp (fehér színű fázis)

Table 2.: Results of EDS analysis of different phases in chain link**2. táblázat:** A láncötredék különböző fázisainak EDS elemzése

Chemical composition. wt %						
	C	O	Ni	Cu	Sn	Pb
Spectrum 6	4.10	2.41	7.24	50.96	25.26	10.03
Spectrum 7	12.03	5.55		10.44		71.98
Spectrum 8	1.14	1.73		86.35	10.78	

Evaluation of the results of metallographical examinations

We carried out metal analyses in the case of the cauldron found in Regöly, on the material of the cauldron, the rivet holding the nib and the nib itself. The goal of the analyses was to determine the raw material and the way of making. Therefore, we performed optical microscopy (OM) and electron microscopy (SEM) analyses on the flat polish specimens of the samples taken from the objects. It was determined that the cauldron was made of a high lead-containing raw material, which had presumably been required to increase strength and this is supported by the wall thickness of the cauldron. The cauldron had been formed by hammering and made by an intermediate annealing. This is shown by both the dimensions and design of the cauldron. Due to high tin content, the raw material is hard and still can be cold-formed though, but the large deformation necessary for achieving the wall thickness of the cauldron by applying annealing, whose traces are reflected in the microstructure as well. The analysis of the corrosion effects highlighted that one side of the cauldron had undergone a stronger deformation-formation. This is also supported by the shape of the cauldron as the base plate had to be deepened. We measured a significant quantity of nickel in the raw material composition besides tin. This should not be a surprise based on parallelisms, but we encountered tiny tin nickel inclusions in addition to the copper sulphide inclusions usual of origin of smelting. Considering the thermodynamic behaviour of the alloy, this phase can be found only if the tin nickel is an intermetallic compound with high melting temperature. This is backed by its measured composition, too. This intermetallic compound can, however, be included in the copper raw material by direct alloying during adding lead if the intermetallic phases had been developed in the tin prior to alloying. This clearly indicates direct alloying of the raw material of the cauldron and requires re-thinking about the source for the ores used. The high nickel content provides a safe

fingerprint for the search of the tin source (**Fig 8., 11., Tables 1-2.**).

Archaeological parallels, historical background of the cauldrons of Regöly

The research grouped cauldrons, similar in form to the ones from Regöly, as type C for decades, or created local groups based on that one. (Merhart 1952, 61; Egg & Kramer 2013, 243-255, Abb. 104; Patay 1990, 25-30; Jereb 2016, 105). Today it is clear however, that the traditional grouping method is not sensible for cauldrons produced in serial manufacturing, sometimes even made from different parts. Studies had been written on the subject earlier, presenting the actual significant parallelism (Szabó 2009, 348; 2012, 86; 2013, 296; Fekete & Szabó 2017a). Therefore, these categorizations are not considered in these examinations with a technological aspect. The passage from Bronze Age to Iron Age refers to a historical, ethnical changeover underlying in the background of the serial production appearing in the second half of the 7th century BC in the Carpathian Basin that these products and the histories of technologies used for their production show orientation towards Asia Minor. Thanks to those arriving from there in several waves, Europe had been invaded by an elite belonging in part relative nations/cultural medium and their armed escorts via the Carpathians, Balkans, Italy and the Western Mediterranean Basin (Horváth & Szabó 2017). At the time of the first Eastern waves, the Urnfield culture and the early Hallstatt culture, a dispersed appearance of the new object types is typical (Fekete & Szabó 2015; Szabó 2017b). In the light of newer direct Regöly finds showing relations with Asia Minor, not to be explained by commercial relations, it can be well seen that metal workmanship based on workshop practices and technological know-how of the Ancient East had been radically transforming the local sheet industry of Bronze Age origin from the second half of the 7th century BC and it had been already producing its products locally as well. At this time, it not only concerned copying object shapes to be observed in the Urnfield period but an exact knowledge and application of new technological processes and work organisation. This indicates that those arriving in this age in recurrent waves via various paths and with different destinations had brought their craftsmen as well, as it was shown in other fields by technological changes occurring explosively at almost at the same time across Europe such as in iron making or pottery. One important element of these changes was the phenomenon observed first on Regöly cauldron and chain link fragment that they had already begun to alloy copper with metallic tin during bronze making. According to Lloyd Weeks, the metallurgy and commerce of tin is one of the most disputed issues of the

manufacture of bronze (Weeks 2004; 2012, 303). After some smaller objects appearing from the middle of 3rd millennium BC, the commerce of metallic tin appears only in the second half of the 2nd century BC in Assyrian texts. At this time, an already considerable amount could have been in circulation as was shown by the ship of Uluburun sunken around 1300 BC where over a ton of metallic tin ingots was found (Weeks 2012, 303-305). It appeared in minor quantities in Europe at around this time as was indicated by the Swiss finds (Primas 1984). Mária Fekete drew the attention to its application in the early Iron Age of the Carpathian Basin, the ornamentation of clay vessels with tin foil (Fekete 1981, 151-152; 1985a, 61-63; 2007, 61). However, we had no data for the use in its metallic state for alloying similarly pure metallic copper in Europe so far.

The way copper is alloyed in the HaD₁ period in the case of examined cauldrons and chain links

According to our measurements, the difference between the cast sling of cauldron excavated from Regöly, Hallstatt burial site no. 696 and Býčí skála Cave is lower than 5% at each point, which indicates the use of identical matrice or mould (Szabó 2013, Pl. 6. 1). The serial production is just as a relevant issue in the finds material as the separation of products made in the same workshop provides an opportunity to shed light more exactly on relations in history and time-scale. The use of bronze casting, matrices and moulds itself carries intrinsically the opportunity of the serial production from earliest times and the craftsmen of the period made use of this for smaller serial production mainly for local use. From the early Iron Age, however, in part parallel to the Greek colonisation, extremely similar objects appear across Europe, among which often only just some small parts show a great extent of similarity (Kimmig 1983). Exactly in the era of changeover from bronze to iron, a new phenomenon can be encountered: certain objects are assembled from components produced in serial production. This is already a higher level of workshop activities and shows towards the manufacturisation, whose origins can be found in the Ancient East and may refer in its background to the societal structure different from the state of Europe at the end of Bronze Age. The data referring to the direct alloying of copper unknown earlier in the European material of the current archaeometallurgical examination of the cauldron fragment of Regöly and the serially produced censer chain link based on a similar work organisation also proves the earlier observations (Fekete & Szabó 2015, 2017a; Kürthy et al 2016; 2018), that manufacturisation and the accompanying explosion-like technological advance are not the outcome of the internal

development of the Hallstatt culture sphere. It had been a ready-implemented practice in Europe by masters of the last Ionian migration starting from Asia Minor in the last third of the 7th century BC into the Carpathian Basin just as had been the technology of alloying copper directly with metallic tin, one of whose main proofs is the Sn-Ni phase observed on our objects recently in their raw material.

Table 3.: Chemical analysis and identification of the Ni-Sn phases by its composition and the data from the equilibrium phase diagram

3. táblázat: A Ni-Sn intermetallikus fázisok kémiai elemzése és azonosítása az egyensúlyi fázisdiagram összetételi adatai alapján

measure	Sn (solid solution)	Ni	Sn	Sn (phase)	Sn/Ni	phase
weight %	11.3	8.66	37.44	26.14	1.49	Ni ₃ Sn ₂ (1.35)
weight %	11.3	9.56	37.47	26.17	1.35	Ni ₃ Sn ₂ (1.35)
atomic %	5.77	9.43	21.38	15.61	1.66	Ni ₃ Sn ₄ (1.33)
atomic %	4.92	8.57	18.6	13.68	1.60	Ni ₃ Sn ₄ (1.33)
atomic %	4.99	2.33	7.13	2.14	0.92	Ni ₂ Sn ₂ (0.67)

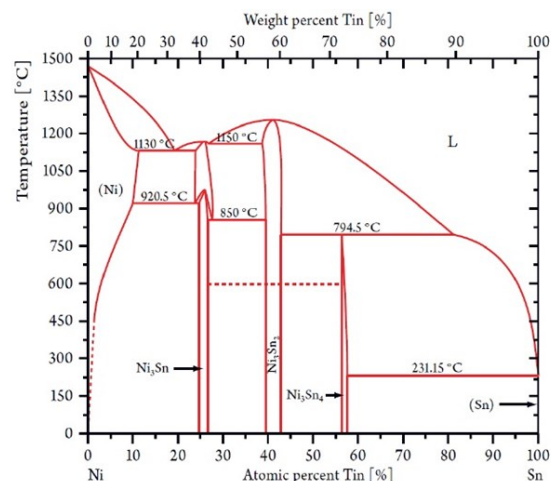


Fig. 12.: Sn-Ni Phase Diagram

12. ábra: Az Sn-Ni egyensúlyi fázisdiagram

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APPLICATION OF A LABORATORY MICRO-X-RAY DIFFRACTOMETER (RIGAKU DMAX RAPID II) IN THE ARCHAOMETRIC ANALYSIS OF ARCHAEOLOGICAL ARTEFACTS – CASE STUDIES OF METAL OBJECTS*

LABORATÓRIUMI MIKRO-RÖNTGENDIFFRAKTOMÉTER (RIGAKU DMAX RAPID II) ALKALMAZÁSA RÉGÉSZETI LELETEK ARCHEOMETRIAI VIZSGÁLATÁBAN FÉMTÁRGYAK PÉLDÁJÁN

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Abstract

X-ray diffraction (XRD) is a widely used method to specify the mineralogical composition of archaeological artefacts, e.g. the material of inlays or corrosion products of metal objects. Laboratory micro-XRD instruments, like the RIGAKU DMAX RAPID II micro-X-ray diffractometer (μ -XRD), can be used instead of conventional X-ray (powder) diffraction analysis if sampling is not or just limitedly allowed due to e.g. the high value of the archaeological object. In these cases, in situ non-destructive measurements directly on the object or on the detached, small-sized samples are preferred. The possible application of this laboratory micro-XRD instrument in the analysis of archaeological metal objects is demonstrated on the example of three case studies.

In order to reconstruct the manufacturing technique of Roman-period niello (black metal sulphide), niello inlays of a late Roman silver augur staff were analysed. Due to the uniqueness and high value of the well-dated and intact object, only non-destructive analytical methods were permitted. Based on the SEM-EDS and μ -XRD results, five niello types were found on the object: pure silver sulphide and different silver-copper sulphides (with silver/copper ratio from 3:1 to 1:1). The object was originally decorated with these diverse niello inlays indicating that silver-copper sulphide niello, even stromeyerite (AgCuS), was used by the Roman craftsmen two-hundred years earlier (last third of 3rd century AD) than the previous studies indicated (end of 5th century AD).

Corrosion products of a large-sized, late Roman copper cauldron were examined in order to characterise the burial environment. The corroded metal samples taken from the cauldron were analysed in cross section, layer-by-layer, using electron microprobe and μ -XRD analyses. Different corrosion products were identified: copper oxide (cuprite) and copper carbonate (malachite) are the products of passive corrosion indicating burial in a well-aerated, calcareous soil environment, whereas copper chloride (nantokite), copper hydrochloride (paratacamite/atacamite) and copper sulphate (brochantite) are the products of active corrosion forming after excavation.

Material and corrosion products of gold and gilded silver objects of the Hunnic Period were analysed by using electron microprobe and μ -XRD analyses. The surface of the high-purity gold objects is covered by a very thin reddish layer, which is a tarnish composed of mixture of gold-silver sulphide corrosion products. The silver objects were completely mineralised into silver sulphobromide and bromian silver chloride (embolite), typical corrosion products of silver alloys buried in soil environment (rich in organic matter). No copper corrosion products were detected indicating that the silver objects were most probably manufactured from high-purity silver alloy.

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Kivonat

A röntgendiffrakció (XRD) széles körben alkalmazott módszer régészeti leletek, pl. különböző berakások vagy korróziós termékek ásványos összetételének meghatározásában. Laboratóriumi mikro-XRD készülékek, mint a RIGAKU DMAX RAPID II mikro-röntgendiffraktométer (μ -XRD), jól használhatók a hagyományos, porpreparátumot igénylő röntgendiffraktométerek helyett, ha a mintavétel nem vagy csak korlátozott mértékben engedélyezett, például a régészeti tárgyak nagy értéke miatt. Ezekben az esetekben *in situ* roncsolásmentes méréseket részesítik előnyben közvetlenül a tárgyak felületén, vagy a kivett, kisméretű mintákon. A fent említett készülék régészeti fém tárgyak vizsgálatában való alkalmazhatóságát három esettanulmányban mutatjuk be.

A római korban alkalmazott niello (fekete fém-szulfid berakás) készítése technikájának rekonstrukciójához egy késő római ezüst augurbot nielloberakásait elemeztük. A jól datált és érintetlen állapotban talált tárgy egyedisége és nagy értéke miatt csak roncsolásmentes vizsgálati módszereket alkalmazhattunk. A SEM-EDS és μ -XRD eredmények alapján a tárgyat ötféle nielloberakás díszíti: tiszta ezüst-szulfid és különböző ezüst-réz-szulfidok (ezüst/réz arány 3:1-től 1:1-ig). A tárgyat már a készítése során ezzel a változatos összetételű nielloberakással díszítették, ami arra utal, hogy már a római mesterek használták az ezüst-réz-szulfid niellót, még a stromeyeritet is (AgCuS), kétszáz évvel korábban (3. század utolsó harmada), mint ahogy a korábbi tanulmányok feltételezték (5. század vége).

Egy nagyméretű, késő római rézüst korróziós termékeit vizsgáltuk az eltemetési környezet jellemzéséhez. Az üstből levett korrodált rézmintákat keresztmetszetben, rétegről rétegre elemeztük elektron-mikroszondával és mikro-röntgendiffraktométerrel. Különböző korróziós termékeket különítettünk el: a réz-oxid (kuprit) és réz-karbonát (malachit) passzív korróziós termékek, amelyek jól átszellőzött, meszes talajkörnyezetben való eltemetés során alakultak ki, míg a réz-klorid (nantokit), réz-hidroklorid (paratacamit/atacamit) és réz-szulfát (brochantit) aktív korróziós termékek, amelyek a megtalálás után képződtek.

Hun kori arany- és aranyozott ezüstitárgyak anyagát és korróziós termékeit vizsgáltuk elektron-mikroszondával és mikro-röntgendiffraktométerrel. A nagy tisztaságú aranyból készült tárgyak felületét nagyon vékony vöröses bevonat borítja, ami korróziós termékek, arany-ezüst-szulfidok keverékéből álló réteg. Az ezüstitárgyak anyaga teljesen átalakult ezüst-szulfobromiddá és brómtartalmú ezüst-kloriddá (embolit), melyek (szerves anyagban gazdag) talajokban eltemetett ezüstitárgyak tipikus korróziós termékei. A rézkorróziós termékek hiánya arra utal, hogy a tárgyakat feltehetőleg nagy tisztaságú ezüstből készítették.

KEYWORDS: MICRO-X-RAY DIFFRACTION, NIELLO, CORROSION, SILVER, COPPER, GOLD

KULCSSZAVAK: MIKRO-RÖNTGENDIFFRAKCIÓ, NIELLÓ, KORRÓZIÓ, EZÜST, RÉZ, ARANY

Introduction

Material analysis of archaeological metal artefacts, especially their decorations, inlays or corrosion products, involves not only the study of microstructure and chemical composition, but in several cases the determination of mineralogical composition as well. X-ray diffraction (XRD) is a widely used method to specify the mineralogical composition (phase identification) of natural as well as artificial materials. However, when sampling is not or just limitedly allowed due to e.g. the high value of the archaeological object, the conventional X-ray diffraction analysis performed on powdered specimens can hardly be used. Laboratory micro-XRD instruments provide good alternatives, like the RIGAKU DMAX RAPID II micro-X-ray diffractometer (μ -XRD). One of the main advantages of laboratory μ -XRD over traditional (powder) XRD is its non-destructiveness (non-invasiveness). In most cases, no sampling or special specimen preparation is needed. Objects and small-sized, non-flat or non-smooth samples, in addition polished blocks and thin sections prepared for other, e.g. scanning electron microscope

(SEM)/electron microprobe (EMP) and petrographic studies, can directly be analysed *in situ* without any further preparation. Besides non-destructiveness, with the RIGAKU DMAX RAPID II instrument an area as small as 10 μ m in diameter can be analysed on the object/sample. However, some limits should be taken into consideration during data processing and evaluation. Due to the geometry of the instrument, the object/sample may cover certain areas of the imaging plate detector depending on its actual position in the diffraction geometry; therefore, some higher d_{hkl} values could not be detected. The areas, where measurements take place, neither are single crystals, nor represent an ideal powder. Measured peak intensities are increased or decreased in specific hkl crystallographic directions compared to that of powdered specimens due to preferred orientations; therefore, during data evaluation peak intensities cannot be taken into consideration, only peak positions are used. Another important issue is that the smaller collimator is used, the longer measurement time is needed in order to obtain adequate intensities.

The RIGAKU DMAX RAPID II micro-X-ray diffractometer has already been used in the archaeometric investigation of cultural heritage materials, e.g. mortars, glazes, glasses, pigments, stones (e.g. Benedetti et al. 2004; Bontempi et al. 2008; Swider 2010; Abbe et al. 2012; Kingery-Schwartz et al. 2013; Takumi & Maeyama 2015; Bajnóczi et al. 2016; Howe et al. 2018; Osváth et al. 2018). In this paper, we present three case studies showing how this laboratory micro-XRD instrument can be used in the investigation of archaeological (and historic) metal objects, where in most cases no or only very limited sampling is permitted due to the high value of the objects.

Methodology

Prior to micro-XRD analysis the microstructure and chemical composition of the analysed objects/samples were studied using a scanning electron microscope (SEM) or an electron microprobe (EMP).

A large chamber door (width 290 mm) AMRAY 1830i type scanning electron microscope equipped with EDAX PV 9800 energy-dispersive X-ray spectrometer (EDS) was used for large objects (*case study 1*). Analytical conditions: 20 kV acceleration voltage, 1 nA beam current, net counting time of 100 sec for the point and area analyses. The results were normalised to 100 wt%.

A JEOL Superprobe-733 type electron microprobe equipped with an Oxford Instruments INCA Energy 200 type energy-dispersive X-ray spectrometer (EDS) was used for small artefacts (maximum 5 cm in diameter, *case study 3*) or small-sized layered samples detached from corroded metal objects and embedded in epoxy resin (*case study 2*). Analytical conditions: 20 kV accelerating voltage, 6 nA beam current, 40–90 sec and 5–10 min acquisition time

for point and area analyses, respectively. Natural and artificial materials of the Taylor Co. (Stanford, California) were used as standards during quantitative analyses, specifically gold (Au), chalcopyrite (CuFeS_2) and acanthite (Ag_2S) in *case study 3*. For considering sufficient amount of data, totals between 95 wt% and 105 wt% were evaluated (*case study 3*).

For the analysis of the largest buckle in *case study 3*, a ZEISS EVO 40XVP scanning electron microscope equipped with Oxford Instruments INCA ISIS energy-dispersive spectrometer (EDS) was used. Analytical conditions: 20 kV accelerating voltage, 6 nA beam current and 30 sec acquisition time. The results were normalised to 100 wt%.

The mineralogical composition of the samples presumed on account of the SEM-EDS/EPMA results was verified with the use of RIGAKU D/MAX RAPID II micro-X-ray diffractometer (μ -XRD), which is a unique combination of a MicroMax-003 third generation microfocus, sealed tube X-ray generator and a curved imaging plate detector (**Fig. 1a**, for analytical conditions in each case study see **Table 1**). The diffractometer was operated with $\text{CuK}\alpha$ radiation generated at 50 kV and 0.6 mA. Different types of collimators can be used (10 μm , 30 μm , 50 μm , 100 μm , 300 μm , 500 μm , 800 μm) depending on the size of the measured area. A built-in CCD camera was used to select the measurement areas. A laser scanning readout system reads the imaging plate detector in about 1 min. RIGAKU 2D Data Processing software 2DP was used to record the diffraction image from the laser readout. For each XRD pattern the interpretable 2θ region was selected manually. RIGAKU PDXL 1.8 integrated X-ray powder diffraction software was used for data processing.

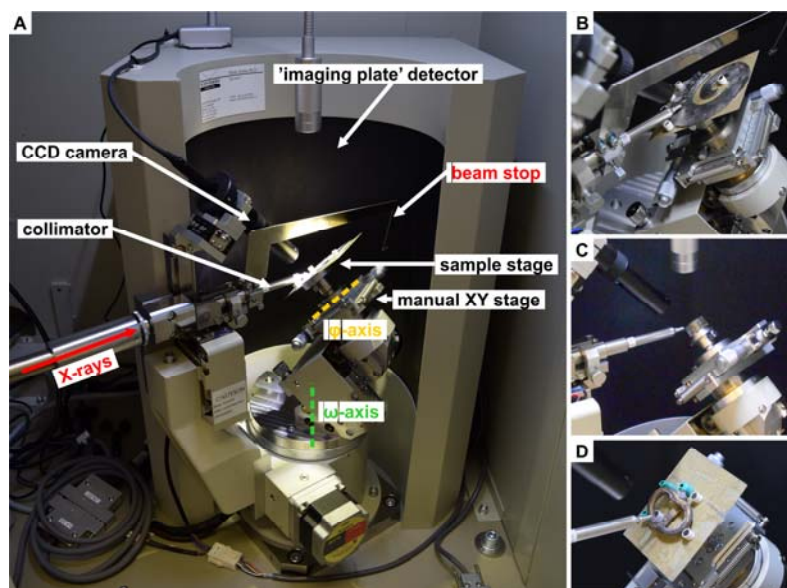


Fig. 1.:

A: The setup of the RIGAKU DMAX RAPID II micro-X-ray diffractometer. B–D: objects/samples of the case studies mounted onto the sample holder.

1. ábra:

A: A RIGAKU DMAX RAPID II mikro-röntgendiffraktométer felépítése. B–D: az esettanulmányokban vizsgált tárgyak/minták elhelyezkedése a mintatartón.

Table 1.: Analytical conditions of μ -XRD measurements in the case studies discussed in the paper**1. táblázat:** A három esettanulmány μ -XRD vizsgálatának mérési körülményei

	CASE STUDY 1	CASE STUDY 2	CASE STUDY 3
Sample preparation	-	polished cross sections	-
Collimator	100 μm	10–100 μm	50–800 μm
Measurement time	5–20 min	10–40 min	1–60 min
ω -axis	20–30°	0–25°	0–35°
φ -axis	0–25°	20–115°	0–15°

Case study 1: Niello inlays of a late Roman silver augur staff

Niello is a bluish black inlaying material, which was widely used to decorate metal objects from the 1st century AD and is still used today. Its composition has changed through times depending on the metal it decorates. As no written sources are available for niello manufacturing from the Roman period, our knowledge about the contemporary technique is very sparse. Based on previous studies, it has been widely accepted that Roman niello was

generally composed of one metal sulphide, the same as it decorates e.g. silver sulphide (acanthite, Ag_2S) was used for silver objects (Moss 1953; Dennis 1979; Newman et al. 1982; La Niece 1983; Oddy et al. 1983; Schweizer 1993; Northover & La Niece 2009). Binary silver-copper sulphide niello (stromeyerite, AgCuS) was apparently used intentionally only from the end of 5th century AD (Dennis 1979; Newman et al. 1982; La Niece 1983; Oddy et al. 1983; Schweizer 1993; Northover & La Niece 2009).

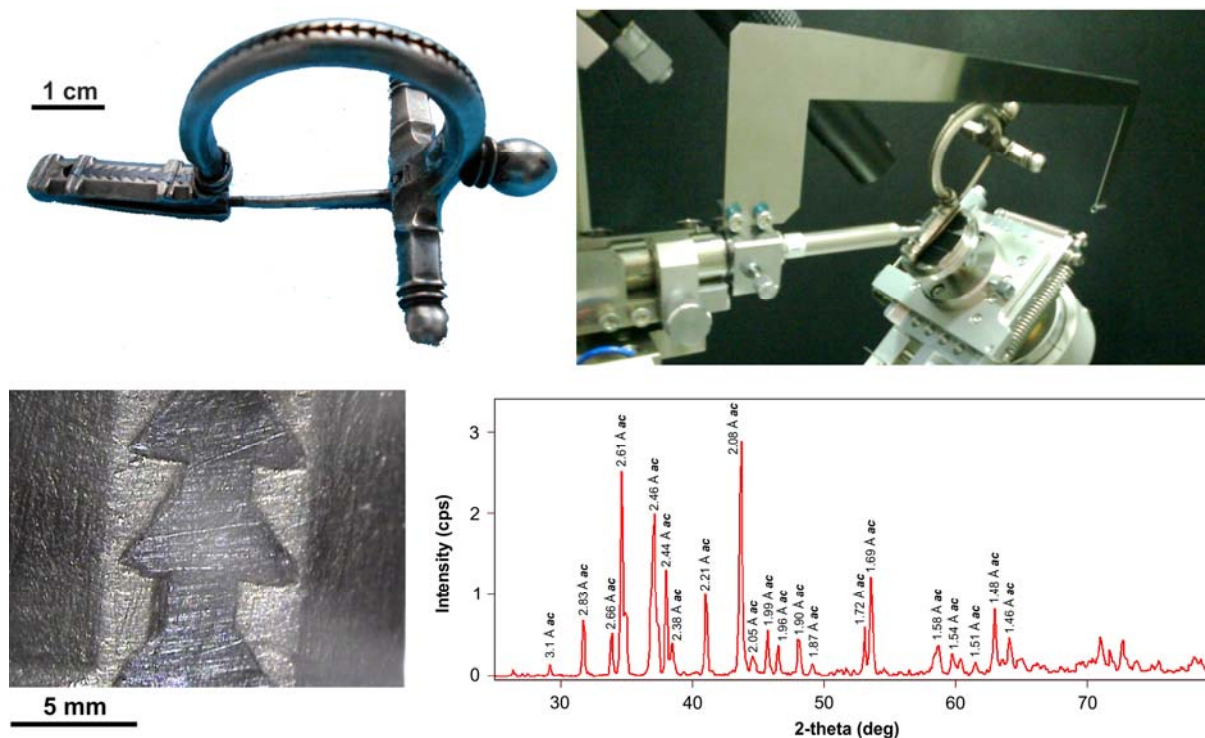


Fig. 2.: A late Roman niello-inlaid silver fibula (photo: A. Dabasi, Hungarian National Museum) and its position in the micro-X-ray diffractometer. Binocular microscopic image and μ -XRD pattern of the niello inlay of the fibula. Abbreviation: ac = acanthite (Ag_2S) (PDF 00-014-0072).

2. ábra: Késő római niellóberakásos ezüstfibula (fotó: Dabasi A., Magyar Nemzeti Múzeum) és rögzítése a mikro-röntgendiffraktométerben. A niellóberakás sztereomikroszkópos képe és diffraktogramja. Rövidítés: ac = akantit (Ag_2S) (PDF 00-014-0072).

In order to better understand the late Roman niello technique, several niello-inlaid objects (Mráv 2010a, 2010b, 2011), found in the Pannonian provinces and preserved now in the Hungarian National Museum, were analysed by using handheld X-ray fluorescence spectrometry (hXRF) and proton-induced X-ray emission spectrometry (PIXE) (Mozgai et al. 2016). Most of the analysed objects were decorated with one metal sulphide niello confirming the previous studies, as in the case of a silver fibula dated to the second half of the 3rd century, for which micro-XRD measurements verified the only presence of silver sulphide (acanthite, Ag_2S) (Fig. 2.). However, the niello inlays of a silver augur staff (*lituus*) (Fig. 3.) showed elevated and inhomogeneous copper content (up to 30 wt% based on PIXE analysis). The object was excavated from an undisturbed grave in *Brigetio* (Komárom-Szöny in Hungary) in the 1960s and it is the only known silver augur staff from the territory of the Roman Empire (Barkóczy 1965, Tóth 2017). A more detailed examination regarding the microstructure and the mineralogical composition of niello inlays was performed non-destructively due to the high value of the object by using SEM-EDS and μ -XRD (Fig. 1b).

Five niello types were identified, their chemical compositions range from silver sulphide (acanthite) to binary silver-copper sulphide of Ag:Cu ratio 1:1 (stromeyerite). Type 1 niello is homogeneous polycrystalline silver sulphide (acanthite, Ag_2S); Type 2 niello is inhomogeneous silver-copper sulphide (exsolution of acanthite, Ag_2S and jalpaite, Ag_3CuS_2); Type 3 niello is homogeneous polycrystalline silver-copper sulphide (jalpaite, Ag_3CuS_2); Type 4 niello is inhomogeneous silver-copper sulphide (exsolution of jalpaite, Ag_3CuS_2 and mckinstryite, $\text{Ag}_5\text{Cu}_3\text{S}_4$); and Type 5 niello is homogeneous polycrystalline silver-copper sulphide (stromeyerite, AgCuS) (Figs. 4-5.) (Mozgai et al. 2019).



Fig. 3.: The late Roman silver augur staff (*lituus*) decorated with niello inlays (photo: A. Dabasi, Hungarian National Museum)

3. ábra: A niellóberakásokkal díszített késő római ezüst augurbot (*lituus*) (fotó: Dabasi A., Magyar Nemzeti Múzeum)

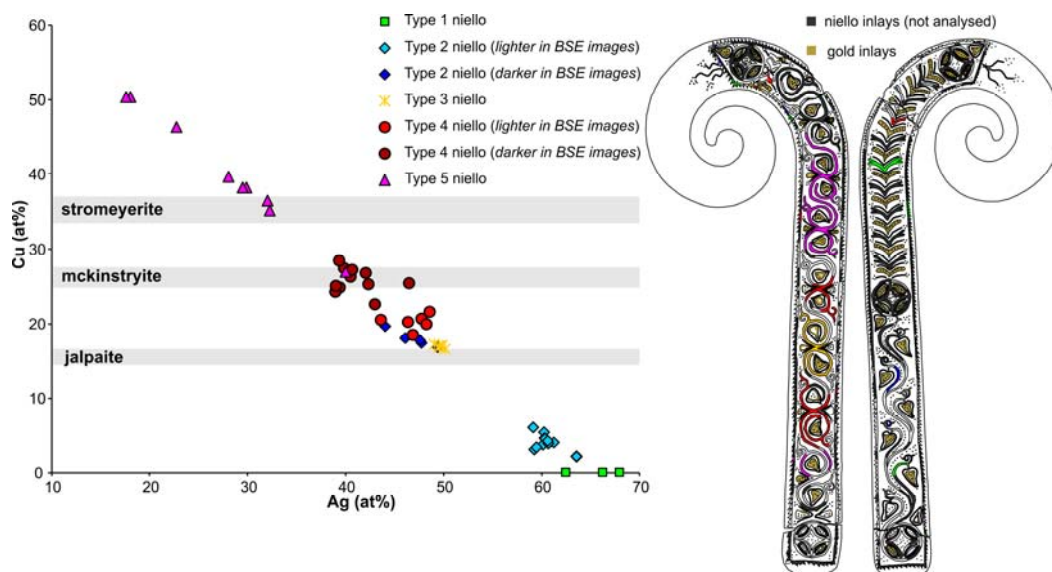


Fig. 4.: Chemical composition of the different niello types of the augur staff based on SEM-EDS measurements and the distribution of different types of niello inlays on the augur staff based on the SEM-EDS and μ -XRD results. Chemical ranges for silver-copper sulphides are based on Grybeck & Finney (1968) for jalpaite ($\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ – $\text{Ag}_{1.5}\text{Cu}_{0.5}\text{S}$); Skinner et al. (1966) and Kolitsch (2010) for mckinstryite ($\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$ – $\text{Ag}_{1.25}\text{Cu}_{0.75}\text{S}$) and Frueh (1955) and Tokuhara et al. (2009) for stromeyerite ($\text{Ag}_{0.9}\text{Cu}_{1.1}\text{S}$ – $\text{Ag}_{1.0}\text{Cu}_{1.0}\text{S}$), respectively. Note that Type 5 niello exhibits higher copper concentrations than ideal stromeyerite due to the presence of surface corrosion products.

4. ábra: A különböző niellótípusok kémiai összetétele a SEM-EDS elemzések alapján és a különböző niellótípusok eloszlása az augurboton a SEM-EDS és μ -XRD eredmények alapján. Az ezüst-réz-szulfidok kémiai tartománya: jalpaite ($\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ – $\text{Ag}_{1.5}\text{Cu}_{0.5}\text{S}$) Grybeck & Finney (1968) alapján; mckinstryit ($\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$ – $\text{Ag}_{1.25}\text{Cu}_{0.75}\text{S}$) Skinner et al. (1966) és Kolitsch (2010) alapján és stromeyerit ($\text{Ag}_{0.9}\text{Cu}_{1.1}\text{S}$ – $\text{Ag}_{1.0}\text{Cu}_{1.0}\text{S}$) Frueh (1955) és Tokuhara et al. (2009) alapján. Az 5. típusú niellóban az ideális stromeyeritnél nagyobb réztartalom oka a felületen jelenlévő korróziós termékek.

The augur staff decorated with such heterogeneous niello inlays is the first object ever analysed in this manner. Based on archaeological arguments the augur staff is well-dated to 260–280s AD and was presumably buried with the last augur of *Brigetio* in the early decades of the 4th century AD (Barkóczy 1965; Mráv 2010a; 2010b). Both mineralogical and archaeological arguments link niello heterogeneity to the primary production of the object rather than to any post-production repair or post-burial corrosion processes (Mozgai et al. 2019). The variable copper content of the niello decorations of the augur staff indicates no technological innovation. The silversmith simply employed not only silver but in order to make up for the shortage of silver also differently debased silver, possibly scrap materials of the workshop for producing niello (Mozgai et al. 2019). The elevated copper content of niello inlays shows that silver-copper sulphide niello, even stromeyerite (AgCuS), was used by the Roman craftsmen two-hundred years earlier (last third of 3rd century AD) than the previous studies indicated (end of 5th century AD).

Case study 2: Corrosion products of a late Roman copper cauldron

Corrosion products of a large-sized late Roman copper cauldron (**Fig. 6.**), with uncertain provenance (finding location) and now stored in the Hungarian National Museum, were examined. The cauldron is part of the Seuso Treasure, and fourteen large silver vessels were hidden in it; the imprints of the rim of the platters were detected on the inner side of the cauldron (Nagy & Tóth 1990; Bennett 1994; Nagy 2012; Visy 2012). The object is rather large-sized: 83 cm in diameter and 32.5 cm in height, 150 litres capacity. This cylindrical cauldron with an originally convex bottom has stepped wall made of two separate hammered copper sheets joined together with hammering, riveting and soldering. The wall is joined to the bottom with crenelated seam. The cauldron was most probably manufactured in the 3rd or 4th century AD. Based on its shape and manufacturing techniques, it belongs to a type widespread in the Rhine and Danube regions of the Roman Empire in the 2nd–4th centuries AD. The southernmost examples of this type of object were unearthed in the Transdanubian region of Pannonia around Lake Balaton in Hungary (Nagy & Tóth 1990; Nagy 2012).



Fig. 6.: Late Roman copper cauldron (photo: A. Dabasi, Hungarian National Museum) and one of the corroded metal samples taken from the cauldron.

6. ábra: Késő római rézüst (fotó: Dabasi A., Magyar Nemzeti Múzeum) és az üstből kivett, korrodált fémminták egyike.

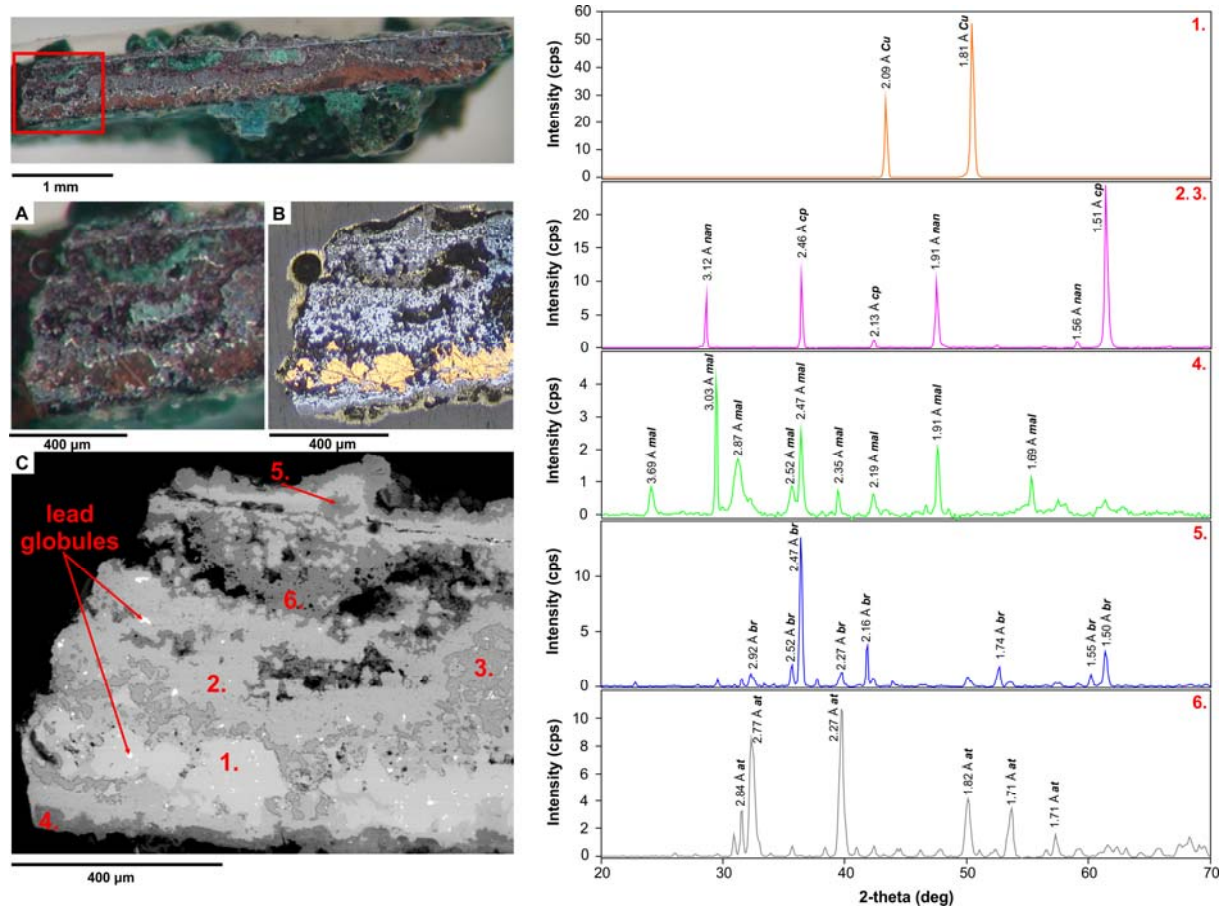


Fig. 7.: Binocular (A), reflected light microscopy (B) and back-scattered electron (BSE) (C) images of the cross section of a small corroded metal sample detached from the cauldron. Bright patches in BSE image are lead globules dispersed in the metal. μ -XRD patterns of the layers of the corroded metal: 1. uncorroded copper, 2. copper oxide (cuprite), 3. copper chloride (nantokite), 4. copper carbonate (malachite), 5. copper sulphate (brochantite), 6. copper hydroxychloride (atacamite/paratacamite). Abbreviations: Cu = copper metal (PDF 01-085-1326); cp = cuprite (Cu_2O) (PDF 01-078-2076); nan = nantokite (CuCl) (PDF 00-006-0344); mal = malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (PDF 01-076-0660); br = brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) (PDF 01-087-0454); at = atacamite/paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) (PDF 01-077-0116).

7. ábra: Az üstből levett korrodált fémminta keresztmetszetének sztereomikroszkópos (A), rásófényes polarizációs mikroszkópos (B) és visszászórtelektron-képe (C). Az ólom világos zárványok formájában elkülönült a réztől. A különböző korróziós rétegek diffraktogramjai: 1. vörösréz, 2. réz-oxid (kuprit), 3. réz-klorid (nantokit), 4. réz-karbonát (malachit), 5. réz-szulfát (brochantit), 6. réz-hidroklorid (atacamit/paratacamit). Rövidítések: Cu = vörösréz (PDF 01-085-1326); cp = kuprit (Cu_2O) (PDF 01-078-2076); nan = nantokit (CuCl) (PDF 00-006-0344); mal = malachit ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (PDF 01-076-0660); br = brochantit ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) (PDF 01-087-0454); at = atacamit/paratacamit ($\text{Cu}_2\text{Cl}(\text{OH})_3$) (PDF 01-077-0116).

The appearance of the cauldron, the extent of corrosion, and its overall preservation state indicates that it was kept in a protected environment. Thick calcareous encrustations and soil remnants on the surface implies that the cauldron was probably buried in soil for a long time. Our aim was to determine and characterise the burial environment and the corrosion processes with the characterisation of the different corrosion products found on the cauldron, since they may hold clues about the burial conditions (Eh, pH, etc.) of the object.

An *in situ*, layer-by-layer analysis was performed on polished cross sections of small corroded metal samples detached from the cauldron by using EPMA and μ -XRD (Fig. 1c). Only the latter method enables to determine the mineralogical composition of the different corrosion products forming layers separately. The cauldron is made of unalloyed copper, small (few micrometer-sized) lead globules are dispersed in the metal. Two corrosion zones are present: (1) the original (internal) surface zone of the metallic copper was replaced by copper oxide (cuprite, Cu_2O), whereas (2) basic copper carbonate (malachite,

$\text{Cu}_2\text{CO}_3(\text{OH})_2$ was deposited (externally) on the original surface along with calcium carbonate (calcite, CaCO_3) incorporating some soil minerals (e.g. quartz, feldspars) (Fig. 7). These copper minerals were formed during long-time burial (passive corrosion) and protected the cauldron from further severe corrosion, therefore, their appearance corresponds well with a well-aerated, calcareous soil burial environment with moderate pH and Eh (Fig. 8.) (Tylecote 1979; Miller et al. 1981; McNeil & Little 1992; Schweizer 1994; Scott 2002). Based on the absence of copper sulphides, anoxic and waterlogged environment as burial site can be

excluded (Tylecote 1979; Miller et al. 1981; McNeil & Little 1992; Schweizer 1994; Scott 2002). Rarely copper chloride (nantokite, CuCl), basic copper trihydroxychloride (paratacamite / atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$) and basic copper sulphate (brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$) were also identified in the two corrosion zones (Fig. 7.). Their uneven distribution on the cauldron and their formation conditions (typically formed on air, in outdoor environments, not in soil environments) indicate that these minerals may be the results of active corrosion, forming most possibly after excavation (Fig. 8.) (Tylecote 1979; Scott 2002).

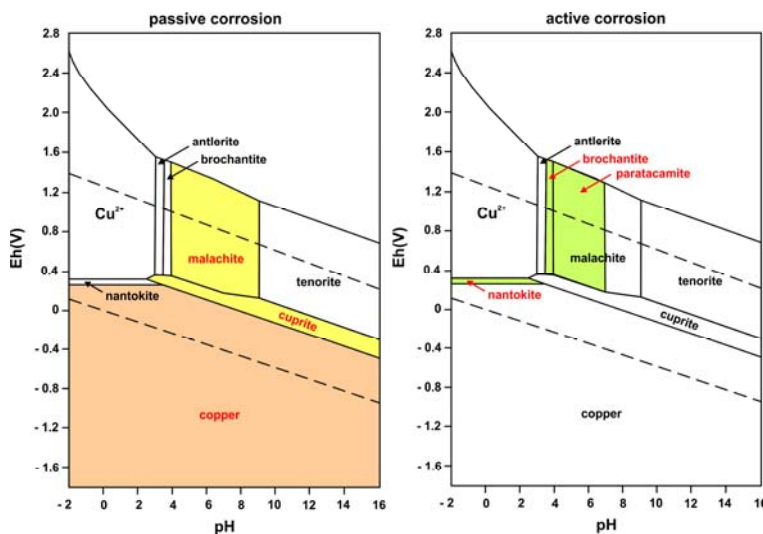


Fig. 8.: Pourbaix diagrams of the $\text{Cu-CO}_3\text{-SO}_4\text{-Cl-H}_2\text{O}$ system indicating the stability field of the different copper corrosion products for solutions containing 229 ppm CO_2 and 46 ppm SO_3 (after Pourbaix 1977). Passive corrosion products (cuprite, malachite) were formed in moderate pH and Eh conditions, whereas active corrosion products (nantokite, paratacamite/atacamite, brochantite) indicate a more oxidative and/or acidic environment.

8. ábra: A különböző rézkorróziós termékek stabilitási mezeje a $\text{Cu-CO}_3\text{-SO}_4\text{-Cl-H}_2\text{O}$ rendszer Pourbaix diagramjain (229 ppm CO_2 , 46 ppm SO_3) (Pourbaix 1977 nyomán). A passzív korróziós termékek (kuprit, malachit) közepes Eh-pH viszonyok közt keletkeztek, míg az aktív korrózió termékei (nantokit, paratacamit/atacamit, brochantit) savasabb és/vagy oxidatívabb környezetet jelölnek.

Case study 3: Corrosion products of Hunnic-period gold and gilded silver objects

A lonely grave (SNR 2785) of an 18–20-year-old man was discovered during the preventive excavation of the Mercedes factory in Kecskemét-Mindszenti-dűlő in 2017. Based on the attire items (gold hair ring, knife with a gold sheath-decorated handle, different buckles covered with gold foil) and the sword buried with the deceased, the grave can be dated to the Hunnic period. The sword also indicates his high social status, who supposed to be a noble member of the society. Both the finds and the rite of this burial differs from the traditions of the Sarmatians, who lived in this area during this period. This may prove that after the arrival of the Huns into the Carpathian Basin, they chose one of their nobility to be the leader of the Sarmatians, who lived this area of the Danube-Tisza Interfluve for hundreds of years. The deceased can be this nobility or one of his relatives.



Fig. 9.: The analysed objects from Kecskemét-Mindszenti-dűlő: a gold hair ring, a ribbed gold sheet and four gilded silver buckles (photo: B. Kiss, Katona József Museum of Kecskemét).

9. ábra: Kecskemét-Mindszenti-dűlőn előkerült és elemzett tárgyak: arany hajkarika, bordázott aranylemez és négy aranyozott ezüstsat (fotó: Kiss B., Kecskeméti Katona József Múzeum).

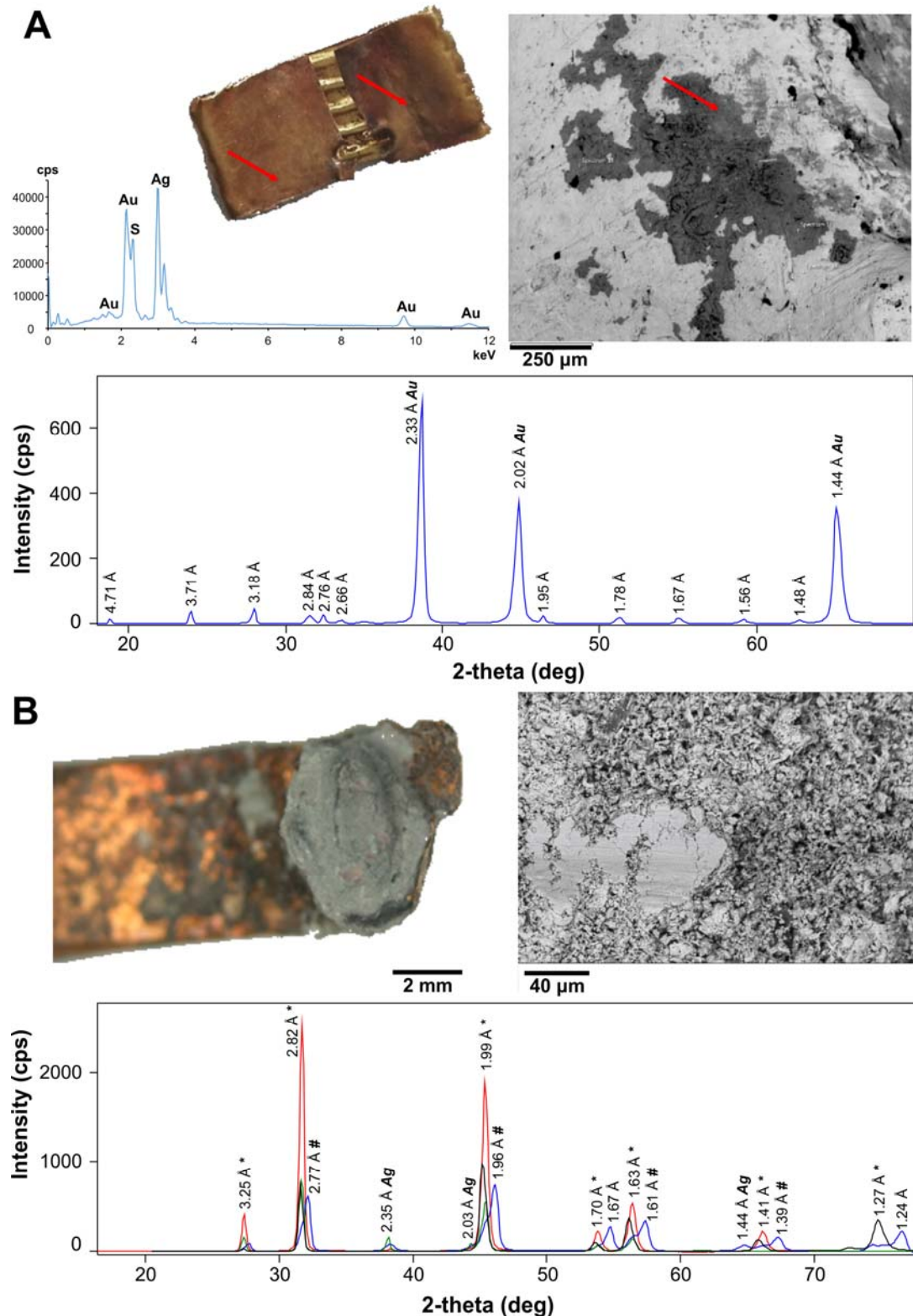


Fig. 10.: A: Macroscopic and back-scattered electron (BSE) images, energy-dispersive X-ray spectrum and μ -XRD pattern of the thin reddish layer (red arrows) on the surface of the ribbed gold sheet. B: Binocular microscopic and back-scattered electron (BSE) images and μ -XRD patterns of the corroded silver alloy of the buckles. Symbols and abbreviations: Au = gold (JCPDS 04-0784); Ag = silver (JCPDS 87-0720); * = Ag(Cl,Br) (JCPDS 14-0255); # = Ag₃SBr (JCPDS 18-1189).

10. ábra: A: A bordázott aranylemezt felületén megjelenő vékony, vörös színű réteg (piros nyilak) makroszkópos és visszashórteléktron-képe (BSE), energiadiszerzív röntgenspektruma és diffraktogramja. B: A korrodált ezüstesatok sztereomikroszkópos és visszashórteléktron-képe, és μ -XRD diffraktogramjai. Szimbólumok és rövidítések: Au = arany (JCPDS 04-0784); Ag = ezüst (JCPDS 87-0720); * = Ag(Cl,Br) (JCPDS 14-0255); # = Ag₃SBr (JCPDS 18-1189).

The material and the corrosion products of gold and gilded silver objects, namely a gold hair ring, a ribbed gold sheet and four gilded silver buckles found in the grave (**Fig. 9**), were analysed non-destructively by using EPMA and μ -XRD (**Fig. 1d**). The silver objects are heavily corroded; therefore, the original composition of the used alloy can barely be determined.

The gold hair ring and the ribbed gold sheet were both manufactured from a high-quality gold alloy (gold hair ring (n=4): 91.9 \pm 2.4 wt% Au, 6.0 \pm 1.2 wt% Ag, 0.7 \pm 0.1 wt% Cu; ribbed gold sheet (n=4): 96.1 \pm 2.8 wt% Au, 3.4 \pm 0.2 wt% Ag, 0.6 \pm 0.3 wt% Cu, 0.2 \pm 0.1 wt% Fe). The surface of the ribbed gold sheet is covered with a very thin reddish layer (**Fig. 10a**). The reddish coloration of gold objects is a well-known and studied phenomena, and can be related to (1) addition of red materials onto the surface (coating with cinnabar (HgS) or with iron oxides) (Shimada & Griffin 2005; Rastrelli et al. 2009), (2) specific composition of alloy (gold alloys with high copper content) (Lucas 1962; Troalen et al. 2009), or (3) surface corrosion (presence of silver-gold sulphides, e.g. petrovskaita (AgAuS), uytenbogaardtite (Ag₃AuS₂), in addition, acanthite (Ag₂S), silver sulphate (Ag₂SO₄) and chalcocite (Cu₂S)) (Lucas 1962; Frantz & Schorsch 1990; Randin et al. 1992; Gusmano et al. 2004; Selwyn 2004; Griesser et al. 2005; Mayerhofer et al. 2005; Bastidas et al. 2008; Tissot et al. 2009; Liang et al. 2011; Guerra & Tissot 2013; Tissot et al. 2015). It is difficult to identify the mineralogical composition of the corrosion tarnish, due to its few hundred Å thickness (Ankersmit et al. 2005; Bastidas et al. 2008; Guerra & Tissot 2013). Based on the EPMA and μ -XRD measurements, the reddish layer is a tarnish most probably composed of the mixtures of gold-silver sulphides (and other corrosion products) (**Fig. 10a**). Since the tarnish layer is very thin and μ -XRD intensities are not relevant, we could not determine its exact mineralogical composition merely taking into consideration the peak positions.

The buckles were manufactured from a silver alloy covered with approx. 0.05–0.1 mm thick gold foil ('foil-gilding'). The gold foils were produced from high-quality gold: three of the buckles were decorated with foils of 94.8–96.4 wt% gold content, whereas one of the buckles was covered with leaf of 88.0 wt% gold content. The original silver alloy has completely mineralised during corrosion processes (**Fig. 10b**). The EPMA and μ -XRD measurements proved the presence of silver, sulphur, chloride and bromide in the form of silver sulphobromide (Ag₃SBr) and bromian chlorargyrite (embolite, Ag(Cl,Br)) (**Fig. 10b**). Copper corrosion products were not determined; therefore, the objects were most probably manufactured from a high-purity silver alloy. The silver sulphides and

chlorides are the typical corrosion products of silver objects buried in soils, whereas silver bromides are characteristic only of soils with high organic matter content (Hedges 1976; McNeil & Little 1992; Martina et al. 2012; Marchand et al. 2014). The presence of silver chloride indicates shallow burial in soil (McNeil & Little 1992).

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**PURE GOLD WITH POOR WORKMANSHIP
– SOME UNUSUAL PIECES OF POLYCHROME METALWORK
FROM THE 5TH-CENTURY CARPATHIAN BASIN***

**AZ ARANY TESZI AZ EMBERT – GYENGE KIDOLGOZÁSÚ POLIKRÓM
ARANYTÁRGYAK AZ 5. SZÁZADI KÁRPÁT-MEDENCÉBŐL**

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Abstract

Jewellery, dress accessories and other personal ornaments made of precious metal and decorated with gemstones were representative elements (prestige objects) of Migration-period supra-regional fashion in Europe. Due to their valuable materials and impressive appearance, these polychrome artefacts are highlighted items in art albums and exhibition catalogues as the key objects of the period. Their vast majority represents high standard of workmanship even from a modern perspective. A small minority comprises, however, objects of lower or even poor quality, falling below the standard. This paper focuses on these exceptions. Dozen finds showing low-quality workmanship are collected, analysed and interpreted below, with special attention to their technical features, material compositions as well as their functions as status indicator.

Our results indicated that the poorly-made objects were produced in workshops of local significance following and imitating high-standard models. The observed technological features pointed out that their makers were inexperienced in techniques requiring meticulous work and precision. The analytical data revealed, however, that they were dominantly made of high purity gold with a composition of partly or wholly identical to that of the technically outstanding items. Apparently, the high social status was not so demanding on the workmanship, rather the quality of the processed gold.

Kivonat

A színes ékkövekkel berakott, nemesfém-ből készült ékszerek, viseleti tárgyak és egyéb díszítmények a népvándorlás kori divat meghatározó elemei (presztízstárgyai) voltak Európában. Ezek a polikróm ötvösmunkák, értékes alapanyagaik és látványos megjelenésük miatt a korszak leleteit bemutató művészeti albumok és kiállítási katalógusok elmaradhatatlan elemei. Döntő többségük technikai kidolgozása modern szemmel nézve is kiemelkedő színvonalú, de szűk kisebbséget képezve vannak közöttük olyan darabok is, melyek (jóval) alulmúlják a sztenderd minőséget. Jelen írásban ezekről a kivételekről lesz szó, összesen tizenkét tárgyról. Elemzésünk és értelmezésünk során főként technikai jellemzőikre, anyagösszetételükre, valamint státuszjelző szerepükre került hangsúly.

Eredményeink azt támasztják alá, hogy a gyengébb kivitelű tárgyak lokális jelentőségű műhelyekben, minőségi előképe(ke)t követve és imitálva készültek el. A megfigyelt technológiai jegyek azt a benyomást keltik, hogy készítőiknek nem volt elegendő tapasztalata az aprólékos munkát és precizitást igénylő eljárásokban. A vizsgálatok ugyanakkor rávilágítottak, hogy anyagösszetételük részben vagy egészében megegyezik a technikailag kiemelkedő darabokéval, ebben a minőségükben tehát nem, vagy csak pontszerűen mutatkozik éles különbség. Mindez arra utal, hogy a tárgyak viselőinek társadalmi megítélése függetlenedett a technikai színvonalától, és inkább a feldolgozott alapanyagok minőségén, abszolút értelemben vett értékén múlt.

KEYWORDS: 5TH-CENTURY ELITE, POLYCHROME METALWORK, HIGH PURITY GOLD, WORKMANSHIP, IMITATION

KULCSSZAVAK: 5. SZÁZADI ELIT, POLIKRÓM ÖTVÖSSÉG, NAGY TISZTASÁGÚ ARANY, KIVITELEZÉS, IMITÁCIÓ

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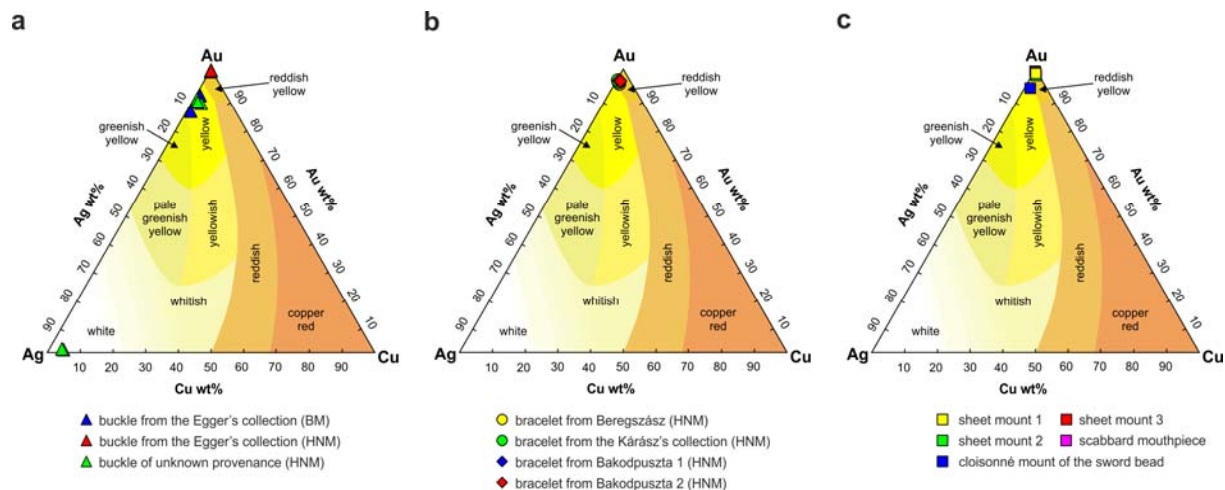


Fig. 1.: Chemical composition of the objects discussed in the paper, plotted in the gold–silver–copper ternary diagram: a) shoe buckles, b) bracelets with animal-head terminals, c) sword accessories. The colouring indicates the colours of various gold–silver–copper alloys (after Leuser 1949). Diagram: Viktória Mozgai

1. ábra: A cikkben említett tárgyak kémiai összetétele az arany–ezüst–réz háromszög diagramon ábrázolva: a) cipőcsatok, b) állatfejben végződő karperecek, c) kard szerelések. A színezés a különféle arany–ezüst–réz ötvözetek színét jelzi (Leuser 1949 nyomán). Diagram: Mozgai Viktória

Introduction

In the Carpathian Basin, the first bloom of the polychrome metalwork can be dated to the late 4th and 5th centuries AD, which corresponds to the Hunnic period and the subsequent decades. This group of goldsmiths' works – unearthed mainly from aristocratic burials, hoards and ritual deposits – are generally interpreted as the legacy of the elite members of the barbarian communities of these times, primarily as markers of prestige (e.g. Tejral 1999; Schmauder 2002; Quast 2009). Their owners – chiefly military or political officials in alliance with the Roman Empire and their relatives – were in a privileged position. They could afford to display their wealth, authority, and power through valuable objects with special decoration and workmanship (Hardt 2004, 60-96.). Their sources were diplomatic gifts accepted from the Empire, as well as the golden tribute (*tributum*) received annual in terms of the alliance (Kiss 1986, 108-110; Hardt 2004, 187-190.)

Although most of the 5th-century polychrome goldsmiths' works were made for the needs of the elite, the sites and organisational framework of their production are little known. There are only indirect evidence derived from the analysis of the finished products. Based on the previous studies (Horváth 2012; 2013), some the objects were made in the Barbaricum and some in the Roman Empire, either in a local or central workshop – actually, there are examples for any combinations of these categories. The manufacturing process involved at least two craftsmen – specialised in the gem-processing and the metal-working. Cooperation between them was not usual but rather

occasional. The phases of workflow were characterised by low degree of standardisation. Gold of high purity even up to a fineness of 99 wt% was often used as raw material of the objects. In these cases, Roman *solidi*, available in large quantities due to the *tributum*, could have been directly processed (Hawkes et al. 1966, 99; Kovrig 1985, 129; Giunlia-Maír 2013, 27.). Among the coloured inlays, red garnets originating from India and Sri Lanka were dominant, obtained in sets, ready for setting or in pre-cut form, which still needed to be shaped and sized (Horváth & Bendó 2011; Horváth 2013, 290-291.). Their acquisition required the maintenance of long-distance trade relationships with the sites where their extraction and/or preparation was carried out.

The vast majority of the objects represents high standard of workmanship even from a modern perspective. They comprise simpler artefacts rich in identical details and more complex, unique masterpieces. Gold items are outstanding even in this context: their shaping and decorating phases of production usually relies on meticulous, time-consuming techniques. Normally, they were crafted of a large number of components – pieces of sheet metal and small elements of filigree and granulation – which were fixed to each other by precision soldering. All of these indicate experienced and skilful makers. The polychrome jewellery is however far from being uniform in quality. In contrast to the splendid exemplars some items are of lower or even poor quality, falling below the standard described above from one or more aspects. The present paper focuses on these exceptions.

Table 1.: Short catalogue of the low-standard objects discussed in the paper.**1. táblázat:** A cikkben tárgyalt gyenge kivitelű tárgyak rövid katalógusa.

Ref. nr.	Provenance site	Country	County/Raion	Context	Object type	Museum	Inventory number	Dating	Materials	Metalworking techniques	References
1	Egger's collection	H	Szeged?	unknown	shoe buckle	British Museum (BM)	1900,0714.2	5 th c. 1/2	Au	hammering	Kiss 1970, 123, Pl. 1.5
2				unknown	shoe buckle	Hungarian National Museum (HNM)	107/1893.4	5 th c. 1/2	Au	hammering	Alföldi 1932, 86, Pl. 34.4; Bóna 1993, 256, Fig. 93.5.
3	unknown provenance	H	unknown	unknown	shoe buckle	Hungarian National Museum (HNM)	235/1870.III.12	5 th c. 1/2	Au, Ag	hammering, casting, granulation	Alföldi 1932, 86, Pl. 34.3; Bóna 1993, 256, Fig. 93.2.
4	Miskolc-Sajópart	H	Borsod-Abaúj-Zemplén	unknown	earring with polyhedral bead	Herman Ottó Museum (HOM)	R.3913.	5 th c. 1/2	Au	hammering, beaded wire	Lovász 1999, 258.
5-6	Békéscsaba-Téglagyár	H	Békés	unknown	pair of earrings with polyhedral bead	Móra Ferenc Museum (MFM)	A.53.146.1.	5 th c.	Au	hammering, twisted wire	Csallány 1961, 121, Taf. 188.14-15.
7	Kárász's collection	H	unknown	unknown	bracelet with animal head terminals	Hungarian National Museum (HNM)	107/1893.3.	5 th c. 2/3	Au	casting, punching	Hampel 1905, 418, Taf. 42.1.
8	Bátaszék-Iskola	H	Tolna	ritual deposit	scabbard mouthpiece	Wosinsky Mór Museum (WMM)	65.1.8.	5 th c. 1/2	Au	hammering	Kovrig 1985, 129, Abb. 9.3; Bóna 1993, 249-250, Fig. 53.
9					sheet mounts of the handle and the scabbard of a <i>spatha</i>		65.1.13.		Au	hammering	Kovrig 1985, 129, Abb. 9.4; Bóna 1993, 249-250, Fig. 53.
10							65.1.13.		Au	hammering	Kovrig 1985, 129; Bóna 1993, 249-250.
11							65.1.13.		Au	hammering	
12							65.1.13.		Au	hammering	

Presentation of the objects

The finds representing low-quality workmanship form a small minority of polychrome fine metalwork pieces. Although further items may later be added to the list, from the currently known nearly 250 late 4th-5th-century gold objects (Horváth 2012, Table 4.1), only twelve belong here. These artefacts involve a pair of buckles from the Egger's collection preserved in Budapest and London, another buckle of an unknown provenance, three earrings with polyhedral beads from Miskolc and Békéscsaba, a bracelet with animal-head terminals from the Kárász's collection without any indication of the provenance, as well as five sheet mounts decorating the double-edged sword (*spatha*) of the ritual deposit from Bátaszék (Table 1.).

With the exception of the Bátaszék finds, all of them are stray items – there is no information about the context of their discovery or their owners. In terms of their function, the artefacts show a mixed picture: they can be identified as jewellery, dress accessories, or ornaments of weaponry. Qualitative differences are most discernible with respect to their object types. Accordingly, the examples are described in four groups: 1) shoe buckles; 2) earrings with polyhedral beads; 3) bracelets with animal-head terminals; 4) sheet mounts.

The following descriptions are based on our technological and material analyses extended with available previous data. The technological

characteristics were observed by optical microscope at the accessible finds. In those cases where no previous analyses were performed, the chemical composition of the objects (their metals) was determined non-destructively by handheld X-ray fluorescence analysis (hXRF) (Fig. 1, Table 2)

Shoe buckles

The first examples belong to a notable object type of the Hunnic period, a distinctive form of buckle with a stumpy plate and a long tongue bent onto a massive loop, made in gold. The small and medium-sized items of this type form a significant part of 5th-century polychrome gold finds in the Carpathian Basin (Fig. 2d). Their characteristic feature is the golden cellwork executed in standard *cloisonné* technique on the plate (Horváth 2012b, 215, Fig. 2b). This was the most time-consuming phase of the workflow, which required special attention because of the multiple joining and soldering. From the nearly thirty gold buckles preserved in Hungarian museums, only two items have their surface decorated with simpler bezel settings instead of cellwork. One of them has a pair currently found in the collection of the British Museum. Their sizes indicate that all three pieces were used to decorate the straps of footwear. In their appearance, they are far below the average level of Hunnic-period polychrome metalwork (Fig. 2, Table 1.1-3.).

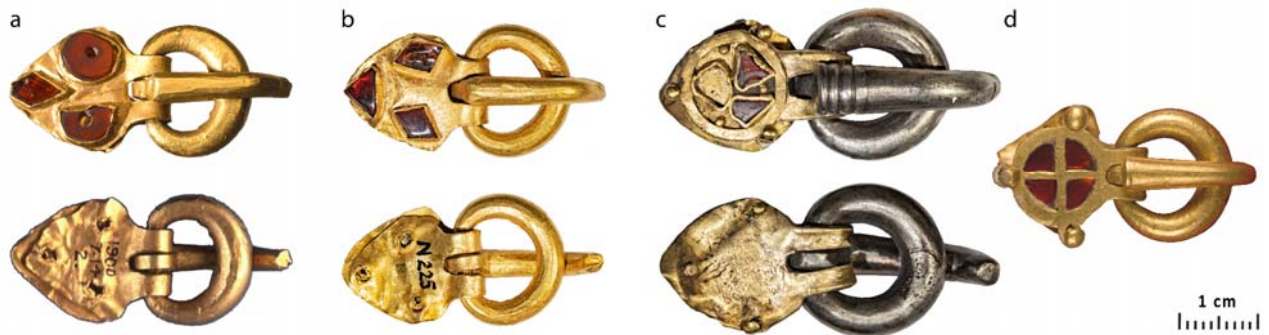


Fig. 2.: Hunnic-period shoe buckles of the Egger's collection from the British Museum (a) and from the Hungarian National Museum (b), of unknown provenance (c) and from Bátaszék (d). Photo: Trustees of the British Museum (a), Eszter Horváth (b-d)

2. ábra: Hun kori cipőcsatok az Egger gyűjteményből, a British Museumból (a), és a Magyar Nemzeti Múzeumból (b), ismeretlen lelőhelyről (c) és Bátaszékről (d). Fotó: Trustees of the British Museum (a), Horváth Eszter (b-d)

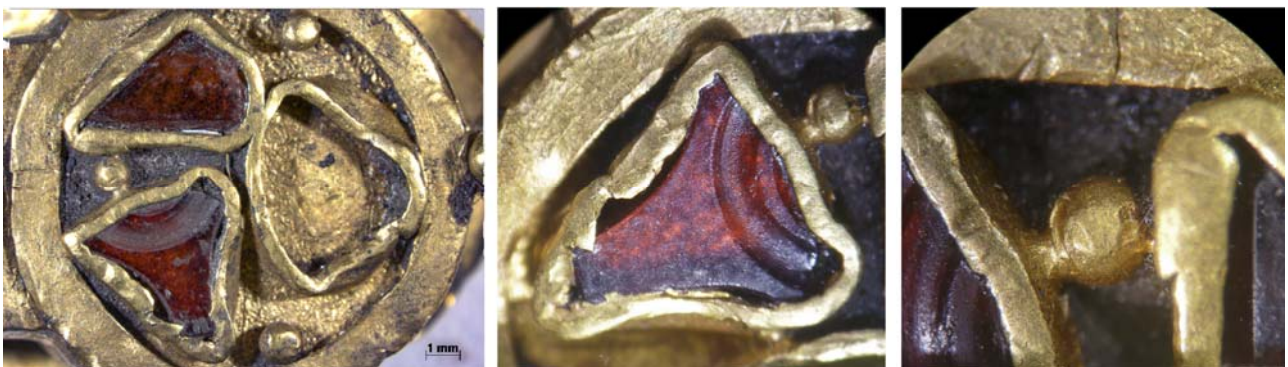


Fig. 3.: Garnet inlays and granulation on the shoe buckle of unknown provenance. Photo: Eszter Horváth

3. ábra: Az ismeretlen lelőhelyű cipőcsat gránátberakásai és granulációs díszítése. Fotó: Horváth Eszter

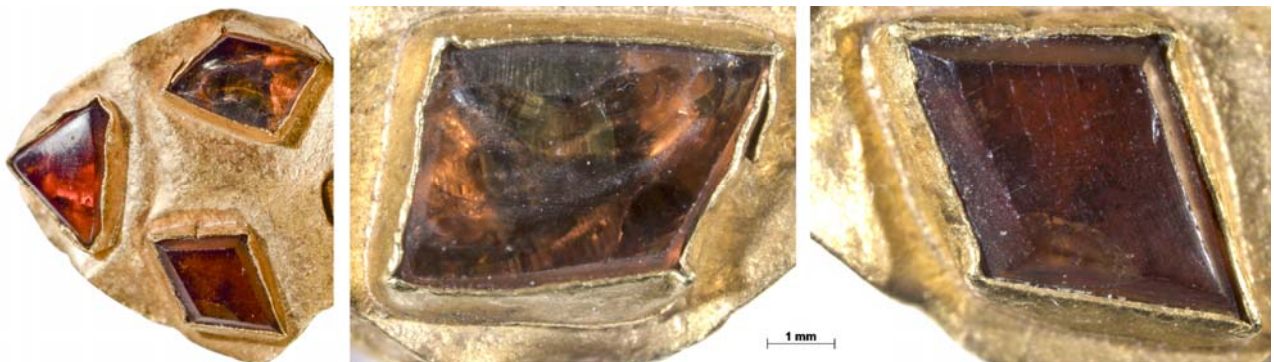


Fig. 4.: Garnet inlays on the shoe buckle of the Egger's collection from the Hungarian National Museum. Photo: Eszter Horváth

4. ábra: A Magyar Nemzeti Múzeumban őrzött Egger-féle cipőcsat gránátberakásai. Fotó: Horváth Eszter

Two of the buckles survived thanks to the collecting activity of the Egger brothers, who were influential goldsmiths and antiques dealers during the dual monarchy of Austria-Hungary (Kemenczei 2011). The buckles originating from the region of Szeged (Csongrád) (erroneously noted Tolna by Kiss 1969-70) had different fates after the private collectors died in the late 19th century. Following a brief interlude, one

was purchased by the Hungarian National Museum, and the other by the British Museum (Bóna 1993, 256, Fig. 93.5). The unity of the two finds, their identification as a pair has never been questioned in scholarship. Their technical execution is surprisingly unhandy and negligent. Their plates are unusually plain constructions made of folded sheet metals shaped as irregular triangles.

Table 2.: Chemical composition of the objects discussed in the paper. ¹SEM-EDS data from Craddock et al. 2010; ²new hXRF data, not published yet; ³hXRF data from Horváth 2012; ⁴AES data from Vorsatz 1985. (< LOD=below limit of detection) Elements deriving from surface contamination or corrosion (e.g. Si, Fe, S) were not taken into account during data evaluation.

2. táblázat: A cikkben említett tárgyak kémiai összetétele. ¹SEM-EDS adatok Craddock et al. 2010 alapján; ²új, közöletlen hXRF adatok; ³hXRF adatok Horváth 2012 alapján; ⁴AES adatok Vorsatz 1985 alapján. (< LOD=kimutatási határ alatt) Az adatok kiértékelésénél a felületi szennyeződésből, illetve korrózióból származó elemeket (pl. Si, Fe, S) figyelmen kívül hagytuk.

Ref. nr.	Measurement points	Chemical composition (weight %)				
		Au	Ag	Cu	Pb	Bi
1 shoe buckle from the Egger's collection (British Museum)¹						
1.1	plate	99.3	0.7	0.2	< LOD	< LOD
1.2	loop	90.7	8.1	1.2	< LOD	< LOD
1.3	tongue	85.1	13.8	1.1	< LOD	< LOD
2 shoe buckle from the Egger's collection (Hungarian National Museum)²						
2.1	plate	99.5	0.4	0.1	< LOD	< LOD
2.2	loop	99.7	0.3	0.0	< LOD	< LOD
2.3	tongue	99.5	0.4	0.1	< LOD	< LOD
3 shoe buckle of unknown provenance²						
3.1	plate (back)	89.5	9.6	0.9	< LOD	< LOD
3.2	plate (side)	87.8	9.1	3.0	< LOD	< LOD
3.3	plate (front)	88.0	9.9	1.6	< LOD	< LOD
3.4	loop	1.1	93.9	3.7	0.6	0.1
3.5	tongue	0.9	93.6	4.3	0.6	0.1
7 bracelet from the Kárász's collection²						
7.1	ring	93.7	3.5	0.2	< LOD	< LOD
7.2	bezel	95.3	3.8	0.8	< LOD	< LOD
A bracelet from Bereaszás²						
A.1	ring	94.7	3.8	1.4	< LOD	< LOD
B bracelet from Bakodpuszta (1)²						
B.1	ring 1	95.0	3.3	0.6	< LOD	< LOD
B.2	ring 2	94.9	3.2	0.7	< LOD	< LOD
C bracelet from Bakodpuszta (2)²						
C.1	ring 1	96.2	3.0	0.7	< LOD	< LOD
C.2	ring 2	95.7	3.0	1.3	< LOD	< LOD
8-11 sheet mounts from Bátaszék³						
8	scabbard mouthpiece	98.7	0.6	< LOD	< LOD	< LOD
9	sheet mount 1	97.0	1.1	1.0	< LOD	< LOD
10	sheet mount 2	98.7	0.7	0.1	< LOD	< LOD
11	sheet mount 3	97.8	0.8	0.6	< LOD	< LOD
D sword-bead from Bátaszék⁴						
D.1	cloisonné mount	95.0	4.0	1.0	< LOD	< LOD
D.2	rivet	0.4	99.4	< LOD	< LOD	< LOD

Note to **Table 2.:**

1: New hXRF data were acquired by a SPECTRO xSORT Combi type handheld X-ray fluorescence spectrometer (Peltier cooling, Rh anode X-ray tube, energy-dispersive, SDD detector, 15–50 kV, 30–120 µA, 'Light Elements' built-in calibration, 3 mm measured area in diameter, 30 sec acquisition time).

According to the results of material analysis, the buckle kept in the British Museum was made up of parts of extremely different quality, which were certainly used secondarily (**Fig. 2a**). The material of the plate is pure gold (99.3 wt% Au, 0.7 wt% Ag, 0.2 wt% Cu), like Roman *solidi*, whereas the loop and the tongue are alloys containing more silver and copper, (loop: 90.7 wt% Au, 8.1 wt% Ag, 1.2 wt% Cu; tongue: 85.1 wt% Au, 13.8 wt% Ag, 1.1 wt% Cu) (**Table 2.1.**) (Craddock et al. 2010, 57-59, Table 1). Similarly, the surface of the buckle was decorated with re-used inlays. The settings enclose two flat beads (one of which is broken in half) and a flat-cut, lozenge-shaped, chipped slab, with bevelled edges. Thus, the buckle comprises the remains of three or four individual objects.

The other piece of the pair, kept in the Hungarian National Museum, is much more homogenous in general (**Fig. 2b**). Its components were all made of gold of great fineness (99.5–99.7 wt% Au, 0.3–0.4 wt% Ag, 0.03–0.1 wt% Cu) (**Table 2.2, Fig. 1a**). It is inlaid with regular-shaped garnet slabs, however one of the lozenge-shaped slabs has a rough or chipped surface, which indicates that still not only carefully processed gemstones were selected for the decoration of this item (**Fig. 3.**).

The third buckle, which is of unknown provenance, was also acquired by the Hungarian National Museum towards the end of the 19th century (**Fig. 2c**). It can be connected to the previous pair of buckles since its maker was also inexperienced and had little artistic sense. Among the three examples it represents the lowest material quality. Based on the results of the metal analysis, its plate was made of less pure gold (87.8–89.5 wt% Au, 9.1–9.9 wt% Ag, 0.9–3.0 wt% Cu) (**Table 2.3.1-3, Fig. 1a**). The low purity is even reflected by the dull colour of gold (**Fig. 2c**). In contrast with the plate, the loop and the tongue were made of a silver-copper alloy (loop: 93.9 wt% Ag, 3.7 wt% Cu; tongue: 93.6 wt% Ag, 4.3 wt% Cu). The chemical composition of the two parts is quite similar, even in minor and trace element composition (loop: 1.1 wt% Au, 0.6 wt% Pb, 0.1 wt% Bi; tongue: 0.9 wt% Au, 0.6 wt% Pb, 0.1 wt% Bi) (**Table 2.3.4-5, Fig. 1a**). Apparently, the object was patched together from elements of different origins. Similarly to the examples above, the plate of this buckle is decorated with secondarily used garnet inlays enclosed by poorly made, irregular bezel settings, accompanied by three awkwardly arranged granules (**Fig. 4.**). One bezel contains the broken angle of a concave, triangular slab decorated with concentric circles, while the other contains another chipped triangle. The third inlay of the buckle is missing, but the shape of its setting suggests that it was again irregular.

Earrings with polyhedral bead

The next three examples represent another characteristic type of 4th- and 5th-century polychrome

jewellery, the earring with polyhedral bead. The appearance of the earrings is greatly unified in the discussed period, which is primarily due to the same material and construction they have, as well as their distinctive form that resembles rhombic dodecahedron garnet crystals. They were made from relatively plain elements, with a simple workflow. Normally, their hoop is a single undecorated wire most often made of gold, occasionally of gold-plated copper alloy. Seldom, it was made by twisting three or four fine round wires (for the examples see Horváth 2012). Their ornament – the bead – was crafted of a single hammered sheet of gold, cut-out for the inlays, which was then folded serving as the edges of a polyhedron, soldered at its vertices (**Fig. 5a-b**).

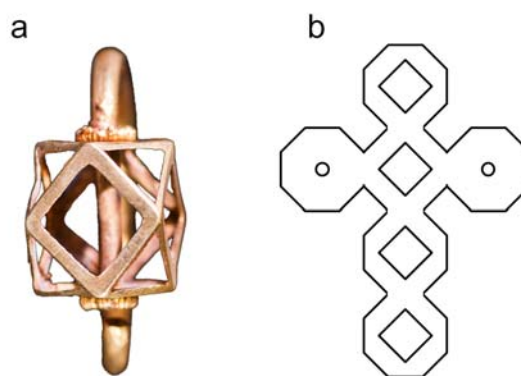


Fig. 5.: Earring with polyhedral bead from Bakodpuszta (a), polyhedral bead fold-out (b). Photo: Eszter Horváth

5. ábra: Poliédergombos fülbevaló Bakodpusztáról (a), a poliédergomb kiterített rajza (b). Fotó: Horváth Eszter

Inside, the bead was filled with backing paste, in which the garnet slabs of matching size and shape were set. There are only minimal differences in the design of the openwork settings – occasional enrichment or division of the central settings or alternative shapes of inlay on the triangular faces of the beads (Horváth 2012).

Among the multitude of uniform pieces in the collections of Hungarian museums there are only two stray finds that stand out. One was found in Miskolc, on the bank of River Sajó (Borsod-Abaúj-Zemplén), and the other (a pair) was discovered in the area of a brick factory in Békéscsaba (Békés) (**Fig. 6., Table 1.4-6.**). Similarly to other items, these earrings were made of gold sheets (unfortunately, chemical analysis was not yet performed on them) and garnet slabs, but with unusual technical and geometric solutions. All three lack the characteristic network structure. The real openwork settings were replaced by an alternative.



Fig. 6.: Earrings with polyhedral bead from Miskolc (a) and Békéscsaba (b). Photo: Eszter Horváth

6. ábra: Poliédergombos fülbevalók Miskolcraól (a) és Békéscsabaról (b). Fotó: Horváth Eszter

The earring from Miskolc more or less resembles the other items in shape. As a significant difference from the standard, its polyhedral bead is formed from two four-pronged sheets, folded and soldered to each other on their vertices (**Fig. 6a, 7a**). The sheets enclose four rectangular holes, but no additional shapes (round or triangular) were cut out. As a consequence, the earring could be set only with four inlays instead of the usual twelve pieces. The maker of the pair from Békéscsaba was apparently unaware of even the basic steps of producing a polyhedral bead. The basis of the ornaments is a rectangular prism, onto which the bezel settings of the lozenge-shaped, rectangular and round inlays were soldered (**Fig. 6b, 8a**). Both of the beads could be set with altogether five inlays.

In addition to the structural differences, the hoops of the earrings were also produced and adorned in an unusual way. While in the case of the Miskolc example, the maker tried to prepare beaded wire using a single-bladed tool (**Fig. 7b**), in the case of the pair from Békéscsaba, twisting was employed to a simple wire of square cross-section (**Fig. 8b**).

Finally, the objects are also outliers as their technical execution falls below the standard. In the case of the item from Miskolc, the jagged edges of the gold sheets, the uneven and unfinished character of the beaded wire, whereas at the pair from Békéscsaba, the irregular twisting of the wire and the unaligned beads of unequal size and shape suggest careless, negligent work.



Fig. 7.: Details of the earring from Miskolc, a) polyhedral bead, b) hook, c) garnet inlay. Photo: Eszter Horváth

7. ábra: A miskolci fülbevaló részletei, a) poliédergomb, b) karika, c) gránátberakás. Fotó: Horváth Eszter



Fig. 8.: Details of the earring from Békéscsaba, a) polyhedral bead, b) hook, c) garnet inlay. Photo: Eszter Horváth

8. ábra: A békécsabai fülbevaló részletei, a) poliédergomb, b) karika, c) gránátberakás. Fotó: Horváth Eszter

The irregular shape and the uneven edges of the majority of the garnets, which might have been shaped by breaking, convey an even more clumsy impression (**Fig. 7c, 8c**).

Bracelets with animal-head terminals

Our next example leads to the golden bracelets terminating in animal heads. The earliest examples of this jewellery type – combining Greek Hellenistic and Early Roman elements with the Sarmatian polychrome animal style – is dated as early as the 1st century AD (Schiltz 2006, 173, 272, Cat. 58; Mordvinceva & Treister 2007). These are particular items produced in relatively small quantities – only six whole examples are known from the 5th-century Carpathian Basin. Compared to the buckles and earrings discussed above, they are more diverse in manufacturing technique, construction and ornamentation.

Four bracelets are solid casts with a simple, open ring construction, ending in robust or plane heads.



Fig. 9.: Bracelets with animal-head terminals from Bakodpuszta (a, d), Beregszász (Berehove/Beregovo, Ukraine) (b, e), and from the Kárász's collection (c, f). Photo: Eszter Horváth

9. ábra: Állatfejben végződő karperecek Bakodpusztáról (a, d), Beregszászról (b, e), és a Kárász gyűjteményből (c, f). Fotó: Horváth Eszter

Examples with robust heads are from Beregszász (today: Berehove/Beregovo, Ukraine) (Hampel 1905, 418.), and from the Kárász's collection (**Fig. 9b-c, Table 1.7, 1.A**), whereas pieces with plate heads are from Diósjenő (unpublished material). In contrast with them, the pair of bracelets discovered in grave No. 1 at Bakodpuszta (today: Dunapataj-Bödpuszta, Bács-Kiskun) (Fettich 1951, 22-23, 82.) represents a special technical solution with hollow structure, hinged construction and screw-clasp (**Fig. 9a**). In addition to its exact parallel from the Kiev treasure (Merowingerzeit 2007, 363, Cat. III.18.1.), analogues are known only among the early Byzantine goldsmiths' works, such as the extraordinary pieces from the princely grave at Malaya Pereschepina, dated to around 600 (Werner 1984, 19, Taf. 25; Deppert-Lippitz & Krause 1995, 171-172, Abb. 134).

Despite the decisive structural differences, the bracelets from Beregszász and the Kárász's collection show similarities with the Bakodpuszta pair in terms of the decorative techniques and ornamentation. Their settings played essential role in the design of the animal heads. While the eyes and ears were highlighted by bezel settings, the collars were formed by cellworks executed in standard *cloisonné* technique

(**Fig. 9d-f**). This latter ornamentation – being unusual on polychrome bracelets, occurring rather on other object types of the period (Nagy 2007, 31) – is of key importance.

With regard to the quality of workmanship, different levels including extremities can be discerned. While the highest level is shown by the Bakodpuszta pair, which can be considered as a kind of prototype, the example from the Kárász's collection represents the lowest standard. This latter one is even the most robust, with a weight of over 150 grams. Comparing with the Beregszász item, the quality of its casting process shows a significant decline from technical and aesthetical aspects. This can be observed especially on its surface; the simplified workflow lacked the post-casting treatment. The bezels and the cell walls forming the eyes, ears and collars were clumsily set to the raw cast (**Fig. 10a**). They are almost completely empty now, only one single backing foil has remained as a possible evidence to the former inlays (**Fig. 10b**). The rough edges and the lack of inlays suggest that it is an unfinished object. Nevertheless, it must have been in use, as the round bezels are fragmented, and the central part of the ring is broken (**Fig. 10c-d**).

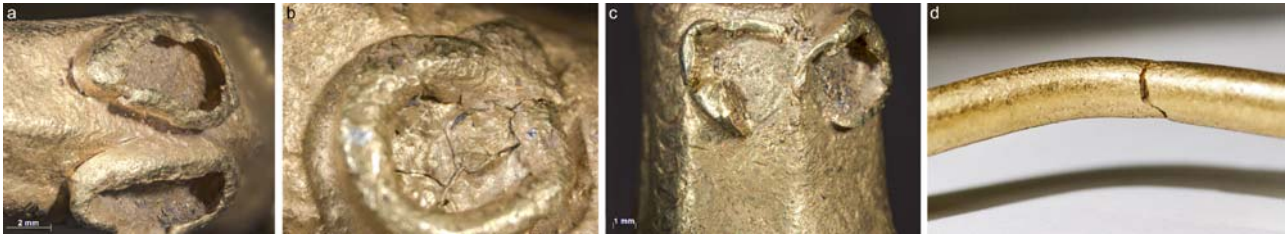


Fig. 10.: The raw cast surface (a), a backing foil (b), fragmented round bezels (c), and the broken ring (d) of the bracelet from the Kárász's collection. Photo: Eszter Horváth

10. ábra: A Kárász-féle karperec nyers öntvény felülete (a), megmaradt fólia alátéte (b), töredékes állapotú pántfogalatai (c), és megpedt karikája (d). Fotó: Horváth Eszter

The technical and quality differences are not reflected by the material composition. Based on the performed analyses, the four bracelets with *cloisonné* cellwork were made of high purity (but not pure) gold, without significant differences in the fineness (93.7–96.2 wt% Au, 3.0–3.8 wt% Ag, 0.6–1.4 wt% Cu) (Table 2.7, 2.A-C; Fig. 1b). The measured silver and copper amount can suggest conscious alloying and primary natural gold-silver alloy as well (Craddock 1995, 111; Mozgai 2017, 232-233.).

Sheet mounts

Qualitative difference can be observed among items of the same find assemblage or even among ornaments of a particular artefact. An example of this is the ritual deposit from Bátaszék (Tolna), and within that, those pieces of polychrome metalwork, which decorated the accessories of the *spatha* i.e. the handle, the scabbard as well as the sword-bead (Fig. 11., Table 1.8-12, 1.D). These gold ornaments with garnet inlays do not represent the same technological standard in spite of that they were set together during the ritual. Their common origin and workshop affinity can be clearly excluded, as Ilona Kovrig had already deduced in her detailed analysis of the finds (Kovrig 1985, 129).

The sword-bead is adorned with a cellwork (standard *cloisonné*) of high technical quality: the appearance of the wing-shaped inlays is uniform and regular, the finishing of the upper rims of the cell walls was carried out with great care, the cells enclose patterned backing foils, and the beaded wire frame is evenly distributed (Fig. 12a). As opposed to this, the mounts of the handle and scabbard – one wider and four narrower sheets – show extremely poor workmanship. The edges of the sheets are uneven, the length of the bezel settings does not correspond to the circumference of the inlays, and the size and shape of the garnet slabs are not uniform, either. The latter is particularly true for the widest sheet, which is decorated with slabs of mixed size and irregular shape – including a flat bead broken in half (Fig. 12b). Besides, one of the narrower sheets was also inlaid with secondarily used garnet slabs (Fig. 12c).

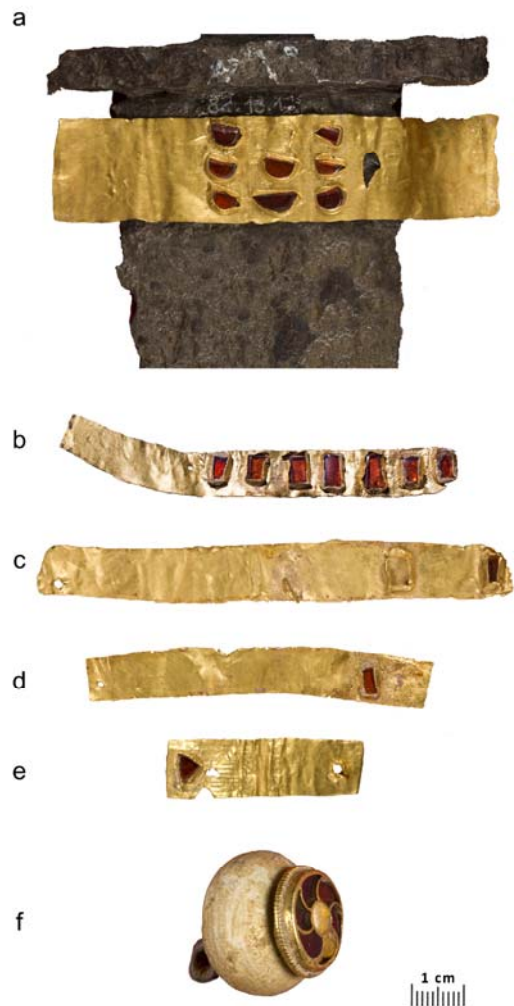


Fig. 11.: Sword accessories from the ritual deposit from Bátaszék, a) scabbard mouthpiece, b-e) various sheet mounts, f) sword-bead. Photo: Wosinsky Mór Museum (a, c-d), Eszter Horváth (b)

11. ábra: Kard szerelékek a bátaszéki áldozati együttesből, a) tokszájveret, b-e) különféle lemezveretek, f) kardfüggesztő gomb. Fotó: Wosinsky Mór Múzeum (a, c-d), Horváth Eszter (b)

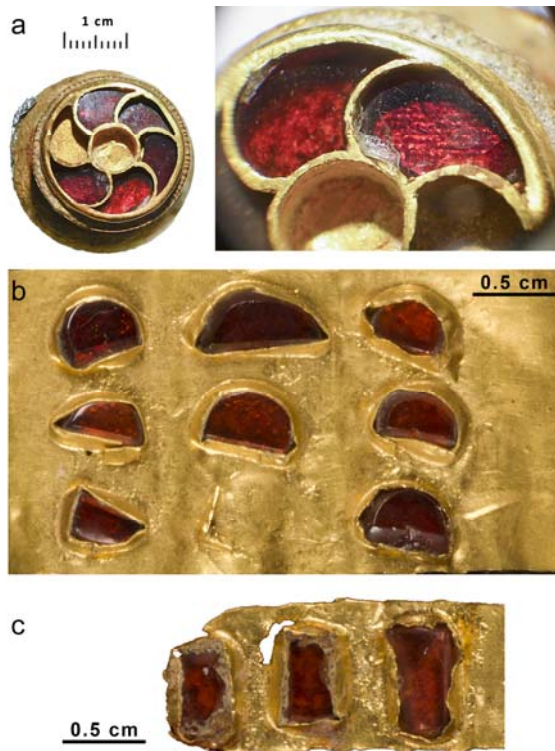


Fig. 12.: Details of the garnet inlays and their settings on the sword-bead (a), scabbard mouthpiece (b) and one of the sheet mounts (c) from Bátaszék. Photo: Eszter Horváth (a), Wosinsky Mór Museum (b-c)

12. ábra: Gránátberakások és foglalásuk részletei a bátaszéki kardfüggesztő gombon (a), tokszájvereten (b) és az egyik lemezvereten (c). Fotó: Horváth Eszter (a), Wosinsky Mór Múzeum (b-c)

Based on the results of the previous material analysis, even the metal composition of the ornaments is diverse (Vorsatz 1985, 146-147, Table 1. nr. 3, 12; Horváth 2012, Table 6.2.). The mounts of the handle and scabbard were made of unalloyed gold (97.0–98.7 wt% Au, 0.6–1.1 wt% Ag, 0–1.0 wt% Cu) (Table 2.8-11; Fig. 1c), most probably obtained directly by the melting of *solidi*. However, the *cloisonné* mount of the sword-bead was made of less fine gold (95.0 wt%), containing considerable amount of silver and copper (4.0 wt% Ag, 1.0 wt% Cu) (Table 2.D.1; Fig. 1c). The fineness of gold and the delicacy of workmanship are in inverse relation. A similar phenomenon occurs in case of analogous gold mounts from Nagyszéksós (Giumlíá-Mair 2013, 29-35).

The differences above can partly be explained by the different purposes of the objects. The decorated sword-bead – including both the magnesite bead and the mounted cellwork – clearly bear the signs of use. The sheet mounts, on the other hand, – which are damaged but not worn – were obviously designed for a single use. The simpler design, and the less elaborate details are generally typical of the garnet inlaid sheet gold ornaments belonging to Hunnic-period ritual deposits.



Fig. 13.: Bow brooch with spiral ornamentation from Szilágysomlyó (Șimleu Silvaniei, Romania) (a), details of the irregularly arranged filigree ornaments and inlays. Photo: Eszter Horváth

13. ábra: Spiráldíszes kengyelfibula Szilágysomlyóról (a), a szabálytalanul elrendezett rátétdíszek és berakások részletei (b). Fotó: Horváth Eszter

The pieces from Bátaszék represent the lowest quality even among them. Analogues of extremely poor quality are known only from outside the Carpathian Basin, from Jakuszowice (Poland) (Kürti 1987, 180, Taf. 8. Kat. III.49.d; Bóna 1993, 233). The scabbard mount from Pécsüszög reflects a barely better workmanship, whereas the horse harness ornaments from Pécsüszög and Nagyszéksós bear more adornments, and their inlays are in greater harmony in terms of shape and size (Alföldi 1932, 65, 67; Fettich 1953, 21.). Furthermore, the cross-guards of the *spathae* discovered in Pannonhalma (Tomka 1986, 438-441, Fig. 18; Bóna 1993, 250, Fig. 58.) and Katzelsdorf (Austria) (Müller & Nowotny 2018, 955-956, Abb. 3.) as well as the dagger mouthpiece from Telki (Szenthe et al. 2019, Fig. 10.) were decorated with more massive and compact *cloisonné* cellworks.

The twelve examples presented here were dominantly made of high purity gold with poor workmanship. Their special position is manifested in the selection of the ornaments and related goldsmiths' techniques, as well as the quality of execution of the latter. These products must have been made by craftsmen, who did not reach up to the general outstanding level of the period, either in terms of their knowledge (i.e. "know-

how?) or their skills in practice. The organisational framework and infrastructure of production – reconstructed indirectly – also point out more primitive conditions.

In case of the objects normally rich in identical features, the distinctive forms and techniques are missing, as if the standard design had not been known to the makers. Some ornaments and mounts were carried out in a specifically amateur manner or poorly. This is shown by the clumsy use of tools, the uneven and irregular features, as well as the imprecise joining and soldering. There is a lack of consistency in size and design. Further common phenomena are the secondary use of items or their remnants that became unsuitable for wearing, the shortening of workflow, and the replacing of certain procedures with simpler techniques (such as employing casting instead of hammering and soldering). The result gives the impression that the makers were inexperienced in techniques requiring meticulous work and precision.

The metallic raw material of the objects is gold, or gold and silver. Their composition – based on the available data – is partly or wholly identical to that of the technically outstanding items. Consequently, there is no or little difference in the quality of their material. This consistency rules out the option of forgery, implied by the obscure context of the objects (Craddock 2009, 370.). The direct use of the gold of great fineness available in the form of *solidi* must have been disadvantageous from a practical aspect. Pure, unalloyed gold is too soft, and has little tensile strength. Although it can be shaped well, it is less resistant to be damaged, and the surface of finished objects gets easily worn. Thus, the purity of gold may indicate not only the status of the customers, but the professional knowledge of the makers as well. Ideally, the craftsman adjusted the raw material to the character of the object: prepared and alloyed the gold according to need. In the majority of the discussed items, this step – by negligence or through necessity – was omitted from the workflow.

Discussion

These artefacts raise many intriguing questions. The low technical standards, the contrast between the high-quality raw materials and the poor workmanship, the similarities between high standard masterpieces and these items combining poor technical quality with high valued materials: how could we explain the low technical standards? What does it imply? Who were the owners? Same of the high-quality counterparts or others?

All of the poorly-made items – whether unique artefacts or objects rich in identical traits – have high-quality analogues among the pieces of fine metalwork. Due to their rare occurrence they are typically overlooked. The lower level of workmanship observed is not related to the traditions of the region or to the typical characteristics of the individual artefacts. It

may be explained by the practices special for the particular production sites or makers. Necessity driven unique conditions as well as intentional individual decisions played decisive roles in the development of the special practices of individual workshops. The organisational frames of workshops, the available equipment and set of tools limited the technical possibilities of goldsmiths working there. Similarly, the knowledge and skills of the goldsmiths were restricting them to certain techniques at a certain level, setting thereby the steps of manufacturing workflow, as well as the quality of the execution. On the other hand, the individual styles of goldsmiths also had decisive impact on the workshops. The artistic intention – practically the taste and creativity of goldsmiths – could have influenced the practice of workshops by setting the conservative or innovative steps of production (Horváth 2018, 356-357.). The finds discussed here represent particular cases, where the identified imperfect technical solutions were consequences of different constraints.

The differences versus good-quality analogues are much more obvious today due to the methods of archaeometry than it was for the naked eye at the time of wearing. The similarities, however, could be perceived in the past, just like today. This was certainly the intention of customers or makers. The latter ones might have consciously used other objects as models and had their own ideas how to reproduce them. However, the result was below the standard of the original items due to the lack of a profound knowledge of them or certain professional skills. The design suggests that the customers did not have (regular) contact with workshops and goldsmiths making high-quality products. That is why they had their objects manufactured by less skilled craftsmen.

All of the listed items must be regarded as products of workshops of local significance following high-standard contemporary models, in other words, they may be labelled as imitations. If the imitation was the intention of the maker, he was most probably focusing on the quality of the object; if it was driven by the customer, the mediated status and prestige could have been an additional motivation. Unfortunately, we do not have any evidence about the identity of the customers/owners, except for the Bátorfő find assemblage, which certainly represented a prominent member of the ruling circles. In the absence of an archaeological context, we can only set hypotheses within the frames of the given economic and social conditions.

On the one hand, we can start with the assumption that the owner did not belong to the elite, but wanted to appear as he was – hence, he imitated not only the object, but also the related content, i.e. status and prestige. From the examples discussed above, the three small buckles can be connected to this interpretation the most. Their incongruously varied parts suggest that their wearers were not the primary recipients of

obtained gold (presumably the golden tribute) but acquired the valuable raw materials and other components in alternative ways. The processing – i.e. their reuse – was also unusual. It cannot be explained by a general shortage of raw materials. The abundant gold supply attested by written sources and archaeological evidence, as well as the average quality of 5th-century finds rule out this explanation.

On the other hand, we must also consider the possibility that the goldsmiths' items owned by the members of the elite did not represent equally high standards. The status and wealth of the customers did not necessarily go hand in hand with the demand for high-quality fine metalwork. Despite their high status, they might have had to settle for the products of less experienced goldsmiths and their potentially available raw materials, for example, due to craftsmen working at a high standard becoming temporarily inaccessible. A similar scenario could explain the production of the solid gold bracelet terminating in animal heads of the Kárász's collection. The weight of the object and its gold material imply a wealthy customer, belonging probably to the elite. The clumsy design of the animal heads, the simplified production technique, the lack of post-casting treatment as well as garnet inlays, however, indicate the poor skills of the maker and his limited access to resources.

The sheet mounts of the Bátaszék *spatha*, might lead to the same conclusion except the difference in their use/function. The thin sheets prepared for a ritual deposit were primarily of symbolic significance and were not intended for permanent use. That is why they were originally made during a simplified and shortened workflow, and it also provides a reasonable explanation for the direct use of the metallic raw material without alloying (corresponding to the fineness as *solidi*). However, it does not explain the poor workmanship below standards: the careless execution of the chosen techniques and the mismatched character of the garnets, some of which showed the signs of secondary use. The context of the finds and their gold material – considered to be the highest standard in this period – leave no doubt that they were indicators of status: their owner certainly belonged to the ruling circles. Therefore, although they were produced as imitations, the meaning conveyed by them is authentic.

Concerning the earrings from Miskolc and Békéscsaba, we do not have enough information to decide between the options mentioned above or to derive another one. In their case, material analysis may again provide further, valuable insights. However, the production of the Kárász's bracelet and the Bátaszék mounts raises another intriguing question: how important was the technical execution of the objects in the period under discussion? Was there a generally accepted quality, a required standard of appearance in the case of status indicators? The case of the bracelet gives the impression that the large amount of gold alone was

sufficient for representation. Furthermore, the garnet inlaid sheet mounts of the *spatha* make it clear that – despite the technical deterioration – the sacrifice was considered to be complete and the ritual took place.

Considering the question further, in addition to the examples above, mention must be made about a pair of brooches decorated with spiral ornaments belonging to the hoard from Szilágysomlyó (today: Șimleu Silvaniei, Romania) (Fettich 1932, 30-32.) (**Fig. 13a**). Although the hoard clearly comprises the most outstanding finds of the era, these brooches show some kind of imperfection in their details. The gold-plated silver brooches are decorated with filigree ornaments and gemstone inlays, the quality and technical execution of which are not uniform. While the cellwork reflects careful design and perfect implementation, the bezel settings were made carelessly. The inlays equally comprise beautifully cut garnets, as well as secondarily used pieces and replacements in glass. The strip-twisted and beaded wires were manufactured evenly and accurately, but they were used imprecisely and negligently (**Fig. 13b**). The general picture is therefore rather controversial. This unusual phenomenon rules out the possibility of imitation, in contrast with the items above. The lack of consistency may have been caused by co-operation within the workshop (i.e. the division of work between craftsmen). On the basis of the differences observed, the pair of brooches must have been manufactured by two craftsmen, at least: one of them was responsible for the preparation of small ornaments and the other for their arrangement and fixing (Horváth 2018, 365-366.).

Artefacts that are different from the average are always exciting, valuable parts of find assemblages, as through the analysis of these, we may arrive at fundamental questions, or gain fresh insights about the whole period. This holds true here as well, even though the number of finds discussed in our paper is relatively small. Summarising our work, we can conclude that the polychrome gold artefacts from the 4th- and 5th-century Carpathian Basin do not represent uniformly high standards. As the twelve items presented above attest, the high-quality raw materials do not necessarily go together with high-standard workmanship. We have discussed some of the potential background aspects, and addressed topics such as the differences between the influence of the customer or the craftsman, and the distinction between conscious imitation or the force of circumstances as possible explanations.

It is important to note that although the discussed technological differences were visible at the time of wearing, they must have been less disturbing than one would interpret today. Based on these concrete examples, lower technical standards had presumably no major consequences for the judgment of their wearers. It rather depended on the outstanding quality of the processed gold – that is its value in absolute terms. As the saying goes, dress does not make a man

great, to which we may add that in the Hunnic period it was not even the perfect technical execution of jewellery that made a man look great, but the quality and quantity of gold used for it.

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PRELIMINARY ARCHAOMETRIC STUDIES AND RESULTS OF FAKE DENARS FROM FRIESACH FOUND IN THE INHERITANCE OF A COMMUNITY IN THE ÁRPÁD-ERA DEALING WITH MONEY EXCHANGE*

EGY PÉNZVÁLTÁSSAL FOGLALKOZÓ ÁRPÁD-KORI KÖZÖSSÉG HAGYATÉKÁBAN (OROSHÁZA, BÓNUM, FALUHELY) FELLELT HAMIS FRIESACHI DENÁROK ELŐZETES ARCHAOMETRIAI VIZSGÁLATÁNAK EREDMÉNYEI

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Abstract

One has to know the geographical environment determining the possibilities of people living in a particular geographical region, in order to attain knowledge on their everyday life. Orosháza is a very important city in this point of view and it had an outstanding road-network. In the surrounding of this city a large number of metal artefacts was discovered in a Muslim settlement next to Orosháza dating back to the 12-13th century. The majority of these artefacts are coins, including few dozens of denars coming from Friesach. According to archaeological assumptions most of them are counterfeit. These fake coins are very exciting for us because they refer to the period and the place of the money exchange and may shed light to methods and variegation of forgery in that time. Due to this we aimed to accomplish archaeometric studies on these coins. The first method was non-destructive chemical analysis with handheld and portable X-ray fluorescence spectroscopy (pXRF). The chemical composition of 25 coins was determined and the first results show that most of the coins are bronzes (tin-copper alloy) with 1-4 wt% lead content, yet, there was one coin with significantly high lead content (14 wt%). In three coins high level of silver content was measured (86 - 97 wt%) but according to the concentration of some trace metals (Cu, Bi, Pb, Au), which can indicate different provenance of the silver material, these three coins differ from each other. Among these 25 pieces of coins, mercury was detected on the surface of 14 indicating amalgam silvering which could be a method of counterfeiting. Besides pXRF which is fundamentally a surface analytical technique, further examinations are planned to get more precise and suitable information.

Kivonat

Ahhoz, hogy egyes földrajzi régiókban élő emberi közösségek életét megismerhessük, meg kell ismernünk magát a földrajzi környezetet, ami nagyban meghatározza a benne élők lehetőségeit. Orosháza tekintetében, annak kiváló úthálózatát kell elsősorban kiemelni, valamint azt, hogy a város környékén igen nagy számban kerültek elő fémleletek egy 12-13. századi, muszlim kereskedők lakta telepről. Az itt talált fémleletek többsége pénzérme, melyek között megtalálható pár tucat friesachi dénár is, amik többségükön korabeli hamisítványok a régészeti feltételezések szerint. Ezek a hamis érmék a legizgalmasabbak, melyek a korszakolás mellett kijelölik a pénzváltás helyét is számunkra, és rávilágítanak a korabeli pénzhamisítás sokszínűségére is. Hogy közelebb jussunk ehhez a kérdéskörhöz, archeometriai vizsgálatokat terveztünk a pénzérméken, amely során elvégeztük az érmék roncsolásmentes kémiai elemzését kézi hordozható röntgenfluoreszcens spektrométerrel (pXRF). Meghatároztuk a 25 darab pénzérme kémiai összetételét, amely azt mutatta, hogy a legtöbb érme anyaga bronz (ón-réz ötvözet) 1-4 tömeg % ólomtartalommal. Ezek közül volt egy pénzérme jellemzően magas (14 tömeg %) ólomtartalommal. Három érme esetében mutattunk ki kiemelkedően magas ezüsttartalmat (86 – 97 tömeg %), valamint eltérő nyomelem összetételt (Cu, Bi, Pb, Au), ami az ezüst alapanyag eltérő provenienciájára, így a három ezüst érme különböző eredetére utalhat. A 25 darab vizsgált pénzérméből 14 esetben mutattunk ki higanyt

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a felületeken, ami a tűzi ezüstözésre utal, amely technika a pénzhamisítás egyik lehetséges módszere. A pXRF technika mellett, ami alapvetően felületanalitikai módszer, egyéb mérési módszereket is tervezünk a még pontosabb és megbízhatóbb információk szerzése céljából.

KEYWORDS: FRIESACH DENARS, FORGERY, SILVERING, pXRF, MULTIVARIATE DATA ANALYSIS

KULCSSZAVAK: FRIESACHI DÉNÁROK, HAMISÍTÁS, EZÜSTÖZÉS, pXRF, TÖBBVÁLTOZÓS ADATELEMZÉS

Introduction, archaeological background

Orosháza played an important role in merchantry among Hungarian cities in the 12-13th century owing to its excellent road-network (Langó & Rózsa 2012; Rózsa & Tugya 2012; Rózsa 2017). At the bend of the ancient Maros river an earth fort was formed in the Late Bronze Age and in the 20th century there was an army base at the border which was located at the ancient salt trading route explaining the presence of Muslim money-changers at that time (Rózsa & Tóth 2018). The heritage of this community is well-known for archaeologists from excavations and intensive metal detecting works in the area. During this activity several weights made of lead and parts of balances and many coins from Friesach, called Friesach denars, were found and this latter has special information for us due to their importance in dating. The most exciting denars artefacts are the counterfeits or fake Friesach denars showing us location of the money exchange and various methods of contemporary forgery. In the first half of the 12th century the Salzburgian archbishop founded a mint in Friesach, a city located in Carinthia, from the name of denars is originated. There are other coins which were produced in other mints of the archbishop, dukes and lords from Carinthia and South Austria are called Friesach denars as well. Therefore this kind of denars was produced mainly in the area of Austria and Slovenia (Baumgartner 1949). By the end of the 12th century the Hungarian denar became weaker comparing denars from Köln, Friesach and Regensburg due to inflation (Hóman 1916) and owing to rising of the economy and prosperity of trading connections outlandish currency played more significant role in the cash flow of the Kingdom of Hungary resulting the dominance of Friesach-type money at the turn of 12-13th century. This kind of denars form the biggest part of treasure-trove and coin artefacts from the first half of the 13th century in Hungary (Tóth 2007). Among these coins there are no any faked ones at all excepting denars found in village of Bónum located next to Orosháza and these fake denars were strained off presumably by the Muslim money-changers working in this village (Rózsa 2018). By studying and examining these denars we may get more complete knowledge about counterfeit and money circulation of the Árpád-era and the history of Bónum village as well.

Materials and methods

Handheld, portable X-ray fluorescence analysis (pXRF)

The non-destructive chemical analysis of the coins was performed using a Thermo Scientific Niton X13t GOLDD+ instrument with 50 kV X-ray tube with silver target (Ag anode) and geometrically optimized large area drift detector which is able to detect the elements from Mg to U. This spectrometer has company-preset calibrations for given matrices and in our case “General Metals” and “Precious Metals” were used. For all analysis two energy filters for radiation were applied including ‘Main’, and ‘High’ filter. The third one (‘Light’ filter) was not used in order to get complete and real composition of the studied alloys eliminating non-relevant elements (Si, Al, Ti) coming from surface contaminations (soil or dust layer). Measuring time was 60 sec in all cases using 30-30 sec for each filter. Measuring spot size (irradiation area on the object surface) was 8 mm in diameter. Before measuring the surface of the coins was cleaned to remove contaminations (dust, soil, etc.) to measure real material of the artefacts. Standardless fundamental parameters method with Compton-normalization is used by the pXRF for quantitative analysis and results were also checked by evaluating the corresponding spectra with NDT software (Niton Data Transfer, version 8.0.0). Mathematical and statistical data processing was done with Excel and Statistica 12 software.

Results and discussion

The chemical composition of the coins (**Fig. 1a, Fig. 1b**) is reported in **Table 1**. The concentration values are given with taking into account the average uncertainty of pXRF method (5-10 %). Most of the analysed coins were made of bronze with varying Cu-Sn ratio, according to the pXRF results. In case of two coins the Sn content is higher than the Cu content. In all cases a slight concentration level of Zn was measured (0.15 – 2.5 wt%) except two coins with very high copper content (97 wt%) close to pure copper. Every coin has a few percent Pb (0.1 – 7.0 wt%) content, except one coin where this value is 14 wt%. Among the 25 analysed coins there are three with significantly high Ag content (86 – 98 wt%) so these can be considered as silver coins or silver denars (23, 24, 25).

Table 1.: Results of the pXRF measurements of the coins expressed in wt%. In the column of Hg, the ++ indicates the presence of mercury. The exact value of mercury concentration is not indicated because quantitative evaluation of this element is not included in the calibration package of the pXRF.

1. táblázat: A pénzérme kémiai összetétele tömeg %-ban kifejezve a pXRF mérések alapján. A Hg oszlopban lévő ++ jelek mutatják a higany jelenlétét az adott érme felületén. A számszerinti higanykoncentráció nincs feltüntetve, mert a Hg elem mennyiségi értékelése nincs benne a spektrométer gyárilag beépített kalibrációjában.

Sample number	Cu	Sn	Zn	Sb	Pb	Bi	Ag	Au	Hg
1	93.5	3.96	0.15	0.12	0.92	0.08	0.42	0.14	++
2	87.2	7.10	0.66	1.37	1.89	0.02	< 0.02	< 0.002	
3	97.3	1.91	< 0.02	0.21	0.07	< 0.01	< 0.02	< 0.002	
4	85.4	9.61	0.30	0.03	3.49	0.07	0.36	0.24	++
5	44.0	44.1	2.49	0.05	6.90	0.04	< 0.02	< 0.002	
6	35.4	60.3	0.30	0.11	0.98	< 0.01	< 0.02	0.04	++
7	67.2	26.4	0.29	< 0.05	2.73	0.08	0.33	< 0.002	
8	54.2	38.5	0.83	0.05	3.88	0.15	0.76	0.32	++
9	91.8	3.87	0.12	0.05	2.66	0.23	0.45	0.03	
10	90.5	4.55	0.17	0.08	2.77	0.26	0.39	< 0.002	++
11	95.0	1.56	0.15	0.11	1.37	0.04	0.38	0.16	++
12	81.3	14.3	1.03	0.38	2.27	0.08	< 0.02	< 0.002	
13	52.5	32.2	0.17	< 0.05	13.6	0.07	0.53	< 0.002	++
14	65.7	25.5	0.55	< 0.05	4.53	0.11	0.77	0.25	++
15	86.1	10.3	0.27	0.03	2.41	0.06	0.26	0.22	++
16	78.0	19.9	0.39	0.39	0.67	0.01	< 0.02	< 0.002	
17	17.9	75.3	0.24	0.06	4.04	0.10	< 0.02	< 0.002	++
18	94.1	2.86	0.12	0.35	1.19	0.02	0.32	0.06	++
19	65.1	30.8	0.52	1.08	0.51	< 0.01	0.22	< 0.002	++
20	70.4	26.0	0.25	< 0.05	1.64	0.04	0.27	0.27	++
21	81.7	14.2	0.30	0.85	0.45	< 0.01	< 0.02	< 0.002	
22	96.7	0.94	< 0.02	0.10	0.31	< 0.01	0.36	0.10	++
23	12.7	< 0.3	< 0.02	0.24	1.30	0.27	85.8	< 0.002	
24	1.46	< 0.3	< 0.02	< 0.05	0.19	0.46	97.6	0.05	
25	3.17	< 0.3	< 0.02	< 0.05	0.56	0.03	96.3	< 0.002	



Fig. 1a-b: Photo of the front and back side of studied coins
1a-b ábra: A vizsgált pénzérmék elő- és hátlapjainak fotói

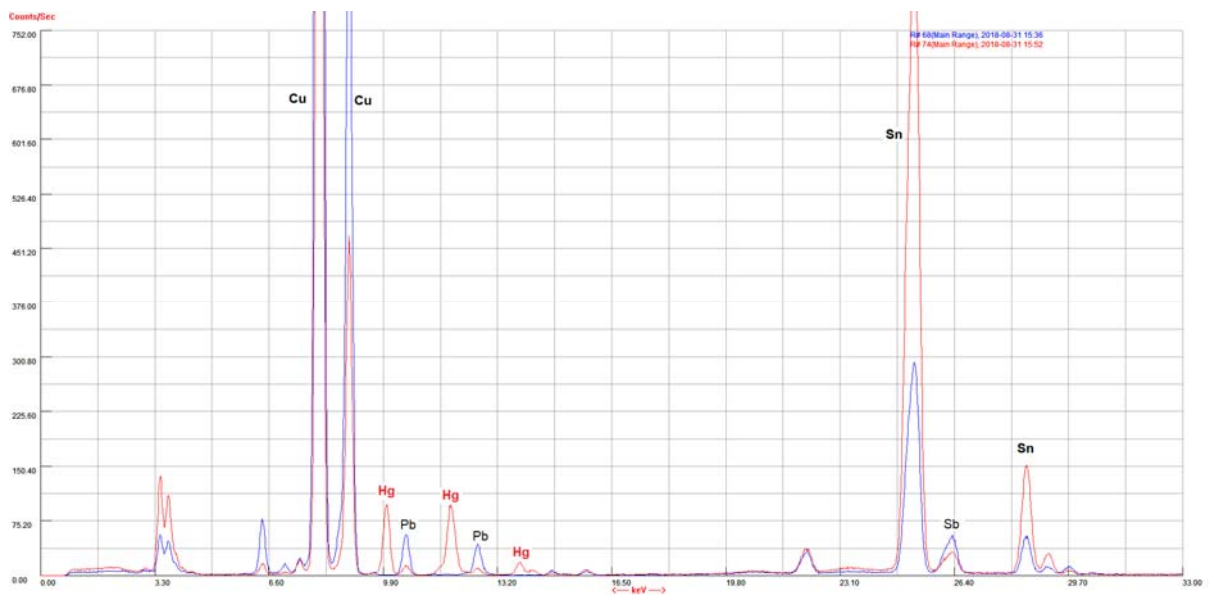


Fig. 2.: A detailed and magnified XRF spectra of an amalgam silvered (red spectrum) and a non-silvered (blue spectrum) coin surface.

2. ábra: Egy tűzi ezüstözött és egy nem ezüstözött pénzérméről felvett XRF spektrum nagyított részlete.

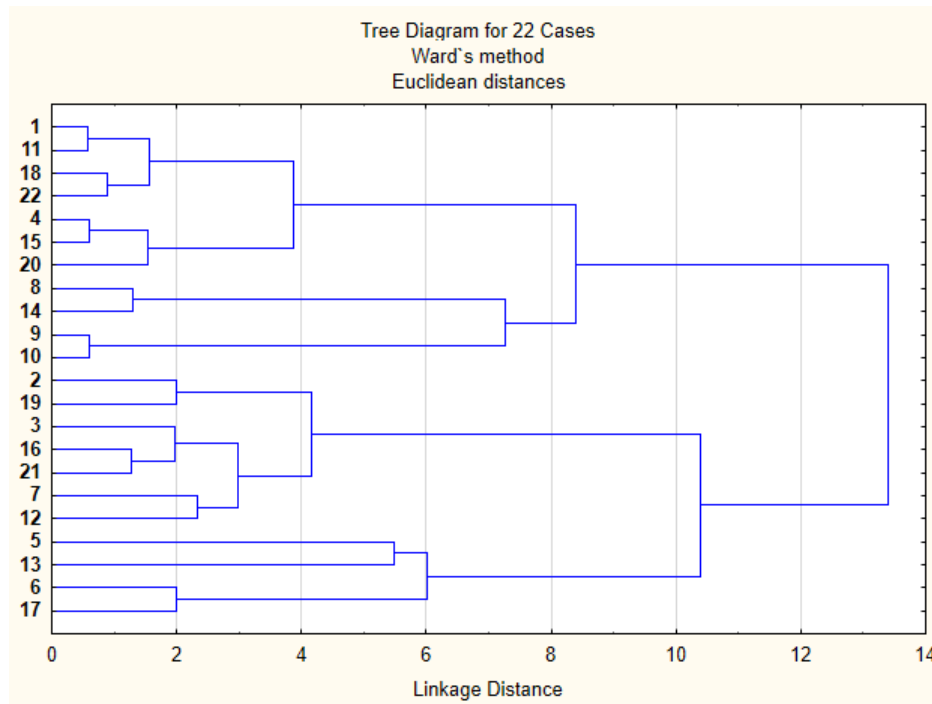


Fig. 3.: Diagram of the cluster analysis (dendrogram) of 22 coins based on their chemical composition measured with pXRF.

3. ábra: A 22 pénzérme pXRF módszerrel mért kémiai összetétele alapján ábrázolt dendrogram (klaszterelemzés).

This result is in good accordance with an earlier study about coins from the time of Tatar Invasion (Nagy 2013). In the case of 14 coins Hg content can be detected according to the XRF spectra as it can be seen in Fig. 2. Exact values of Hg concentrations are missing at the moment due to the limits of the factory settings of the XRF device. The presence of mercury on the coin surfaces may indicate a method of forgery where the silvering process of the bronze coin was done with amalgam silvering, producing a coin that looks like a real silver one. The three silver denars do not contain mercury.

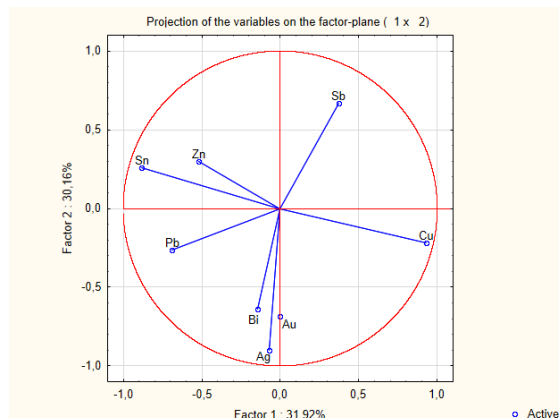


Fig. 4.: Diagram of the principal component analysis of 22 coins based on their chemical composition measured with pXRF.

4. ábra: A 22 pénzérme pXRF módszerrel mért kémiai összetétele alapján számolt főkomponens elemzés ábrája

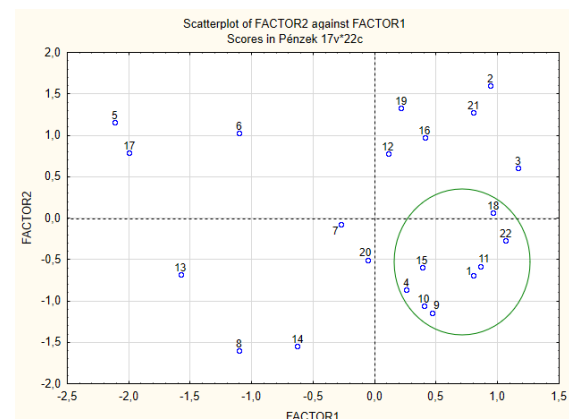


Fig. 5.: Diagram of the factor analysis (dendrogram) of 22 coins based on their chemical composition measured with pXRF. 8 coins (number 11, 18, 22, 1, 15, 4, 9 and 10) belong to a well-defined group (green circle) indicating the same workshop of producing them.

5. ábra: A 22 pénzérme pXRF módszerrel mért kémiai összetétele alapján számolt faktorelemzés ábrája. 8 pénzérme (mintaszám szerint: 11, 18, 22, 1, 15, 4, 9 és 10) egy jól meghatározott csoportot alkot (zöld körben jelölve), ami arra utal, hogy ezek azonos műhelyben készülhettek.

We conducted multivariate data analysis on the pXRF results in order to find tendencies, groups and connections between the analysed denars based on their chemical composition. The three silver coins are not included in this statistical evaluation, because they form a very differing group separated from the other 22 pieces of coins due to their very high silver content.

Results of cluster, principal component and factor analysis of the 22 pieces of denars can be seen in **Fig. 3., 4. and 5.** In **Fig. 4.** (PCA) the chemical elements measured with pXRF can be seen and the directions in this new coordinate system of Factor 1 and 2. With comparison of PCA and FA figure we can clearly see which elements cause separation of the samples into groups during statistical evaluations. Similarly cluster analysis (CA) also gives useful information about similarity and groups of the analyzed samples but this method itself without PCA or FA is not reliable enough. In our case there is an important group of eight pieces of coins (1, 11, 18, 22, 4, 15, 10, 9) according to the FA analysis (**Fig. 5.**, in the green circle) and four of them form a subgroup (1, 11, 18, 22) which can be also seen in the CA figure (**Fig. 3.**) having relatively high Cu content (> 93 wt%) and coins number 11, 18 and 22 belong to the same type of blank according to archaeological studies.

Conclusions

Most of the analysed (25 pieces) denars are made of bronze with various Cu/Sn ratio. More than half of the coins have mercury content which may indicate amalgam silvering method of forgery. During the first macroscopic examination it could be stated that there is a close connection between three coins (11, 18, 22) historically and it was supported by this preliminary pXRF measurements. This group of 3 denars was completed by further 5 pieces of coins with help of multivariate data analysis methods. These denars are supposed to have been produced in the same workshop and they imitate three types of real denars which were minted between 1170-1200, 1181-1202 and 1200-1246 suggesting that the workshop, where the counterfeits were produced, operated in the first or second decade of the 13th century (Koch 1994). The relatively large number of coins originating from the same place may indicate an adjacent counterfeiter workshop.

These preliminary results and work will be continued and it is planned to accomplish other type of examinations and methods such as SEM-EDX, ICP-AES, ICP-MS to make more precise measurements and get more information and it is also planned to increase the number of analysed coins extending our dataset to do further statistical evaluations.

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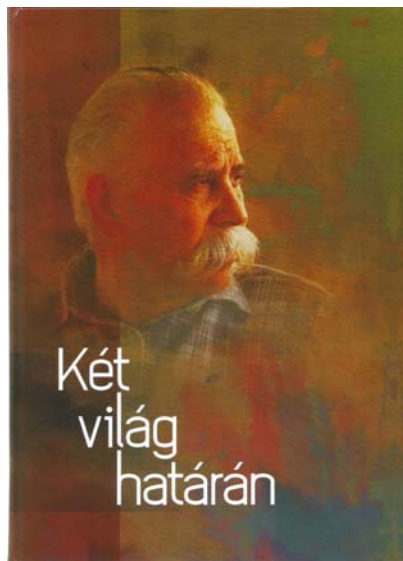
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KÖZLEMÉNYEK

*



Két világ határán. Természet- és társadalomtudományi tanulmányok a 70 éves Költő László tiszteletére. Szerkesztők: Varga Máté, Szentpéteri József. A kaposvári Rippl-Rónai Múzeum Közleményei 6, Kaposvár, 2018. 389 p.

Természetesen szubjektív a véleményem, arról a színes, kemény táblás borítójú remek munkáról, amely Költő Lászlót ünnepli élete jeles napján. A borítóportrét Kohári Gabriella fotózta és Balla Krisztián tervezte. A tárgyszerű, de mégis baráti hangvételű „Előszó”-t Ábrahám Levente, az ünnepeletnek múzeumi vezetői székében utódja jegyzi. A vegyészt és régészt, a két tudomány és világ határán tevékenykedő embert joggal emeli piedesztálra a könyv címe. A köszöntőt, „Egy igaz ember” címmel Padányi József, a Nemzeti Közszerkeleti Egyetem rektorhelyettese, vezérőrnagy írta. Ő az utóbbi években Zrínyi-Újvárnál Költő kutatótársa. Jól fogta és fogalmazta meg Költő László emberi-kutatói nagyságát: „Egyszerű, érthető, világos és mégis zseniális.”

E helyütt engedtessek meg nekem némi „személyeskedés”. Ha jól emlékszem Lacival a MTA VEAB (Veszprémi Akadémiai Bizottság) Iparrégészeti Munkabizottsága egyik – az 1980-as évek második felében tartott – ülésén, Veszprémben ismerkedtem meg. Órák alatt jutottunk el az avar kori szíjvégek vizsgálatától a késő bronzkori bronztárgyak elemzésének szükségességéig. Ez azután évtizedekig volt meghatározója kapcsolatunknak, barátságunknak. Meghívtam és 1994-től rendszeresen tömbösített órákat tartott a szombathelyi Tanárképző Főiskola régésztechnikus képzésén. Természetesen „A régésztechnikus kézikönyve I.”-be (1998, 2002) Ő írta az „Archeometria” alfejezetet. Jártam Nála,

amikor a Régészeti osztályt irányította, vagy amikor tanítványaim a vörsi ásatáson dolgoztak. 2000-ből közös cikket is jegyzünk az egyik, a velemi bronzkincséről. Itt került elő az az öntőforma is, amelyről ebben a kötetben írtam.2013-ban Vele együtt örültem, amikor akkori lakóhelyemen, Kőszegen vehette át a Schönvisner Isván-émlékérmét.

A Függelékben, a kötet végén (pp. 353–356.) olvashatjuk disszertációjának értékelését professzora, László Gyula tollából. De itt (pp. 357–371.) találjuk 1975 és 2018 közötti szakirodalmi munkásságának bibliográfiáját, amit a szerkesztők, Varga Máté és Szentpéteri József állítottak össze. Ezt a „Hetven év emlékei fényképeken” követi (pp. 373–387.), egyúttal zárja a tisztelgő könyvet.

Lacit 32 szerző 21 tanulmánnyal köszönti. A szerzők között értelemszerűen a természettudományokat képviselő- többek között – antropológusok, metallurgusok és vegyészek mellett régészeket találunk. „Érkezésük” felől nézve lefedik az egész országot Vas megyétől Szolnokon át Szabolcs megyéig. Ez világosan leírja Költő László emberi és szakmai kapcsolati hálózatát. Az avar (7) és a honfoglalás kort (3) tárgyaló tanulmányok képezik a kötet gerincét. Ez azonos az Őt évtizedeken át leginkább érdeklő történeti időszakokkal. Az ünnepelet elsődleges munkaterületét, azaz Somogy megyét 6 tanulmány (M. Aradi Csilla, Buzár Ágota, Bernert Zsolt, Gömöri János, Molnár István, Nagy László, Négyesi Lajos, Padányi József, Rózsás Márton) reprezentálja, ami nem kíván magyarázatot. A vaskohászat és a vasfeldolgozás 4 tanulmány (Gallina Zsolt és Török Béla, Gömöri János, Madaras László, Rózsás Márton) tárgya, ami nem meglepő, hiszen a somogyfajsi kohótelep feltáróját és a bemutatóhely megvalósítóját ünnepli a kötet.

Kérem a Tisztelt Olvasókat és a Szerzőket, nézzék el nekem, hogy az írárok közül a számomra a legkülönösebb élményt nyújtókat emelem csak ki.

Fórizs István, Rózsa Zoltán, Mester Edit, Szabó Máté és Tóth Mária tanulmánya (pp. 51–60.) egy Orosháza határában található Árpád-kori – a tatárjárással megszűnt – muszlim település 2 db üvegtöredékének problémakörét járja körül. Ez valóban problémakör, hiszen a korai iszlám és a velencei üvegek kémiai összetétele szinte teljesen azonos. Ráadásul mindkét „gyártó” féltékenyen őrizte a titkot. Ugyanakkor az iszlám területén bizonyosan több műhely tevékenykedett. Mindezek megnehezítik a két töredék eredetének megállapítását. Ezt a szerzők a nemzetközi szakirodalomban megjelent adatok széleskörű összehasonlításával tudták elvégezni.

Összegzésükben megállapítják, hogy elsősorban a nyomelemek vezethetnek el a gyártó műhelyhez. Végezetül egy szíriai eredetű nyers üvegből dolgozó velencei fabrika mellett teszik le a voksukat.

Gallina Zsolt és Török Béla (pp. 61–75.) az avar kori vasművesség munkafolyamatainak és mesterségeinek tömör összefoglalását adja a legújabb, jól dokumentált nagy kohótelepek (Kaposvár, Zamárdi) alapján. A részletes és remek, látványos mellékletekkel ellátott logikus feldolgozást olvasva bennem azonban az alábbi két, megválaszolatlan kérdéskör merült fel: 1. egy kohótelepen egyszerre valóban csak 2-3 kohó és csapat dolgozott? (p. 64.) És egy évben vajon hány olvasztást végeztek? Azaz ezek összességében hány kg nyers vasbucát eredményezhettek? 2. Ha a vasfeldolgozás központilag (p. 72.) a kovácsmunka pedig falusi (p. 72.) szinten szervezett, akkor ebből hogyan lesz (nek) szervezett módon felfegyverzett több ezer főt számláló hadsereg(ek)? ... a munkaeszközök gyártása esetében el tudom képzelni a falusi szintű szervezést. Én úgy látom, hogy a több mint 6 évtizedes múltra visszatekintő intenzív és céltudatos régészeti-történeti vasas kutatás ellenére még jónéhány probléma vár megválaszolásra.

Járó Márta több évtizedes archeometriai tevékenységének és írott forrásokat feldolgozó kutatásainak itt olvasható summázata (pp. 139–155.) lenyűgöző. A „magyar” illetve „török” arany- és ezüsthonalak meglétéről értekezik a 17. századi magyar hímzések kapcsán. A fémfonalaknak a korabeli forrásokban előforduló négy alaptípusától (2. ábra) indulva csak néhány magvas, de világosan kifejtett végeredményére utalnék. Az egy oldalon aranyozott ezüsthonal az ezredfordulón tűnt fel Európában, amit azután a 14–16. század közepéig szinte „egyeduralkodóként” használtak (p. 144.). A 14. századtól Közép-Ázsiában már ismert és a 16. században török területen is elterjedt, két oldalon aranyozott ezüst hímzőfonalak „népszerűsége” kiemelkedő. 27 tárgyból vett 34 minta ebbe a csoportba tartozik (p. 145.). Az 1600-as évek hímzéseihez importból származó fémfonalakat alkalmaztak, amelyeket elsősorban Bécsben és Konstantinápolyban szereztek be (pp. 147–148.). Véleménye szerint a „török” jelzős arany- és ezüsthonal nagy valószínűséggel a selyem bélfonalra szakaszosan font ezüst- illetve két oldalon aranyozott ezüstszalag lehetett (p. 150.). A lajstromokban szereplő „magyar” kifejezéssel a jobb minőségre aranyozott ezüsthonalakat írták le, függetlenül attól, hogy ezek honnan származtak. A hímződrótot skófiumnak nevezték, utalva ezzel vélt vagy valós keleti/török eredetére. Ilyenkor a szakaszosan font, két oldalon aranyozott ezüst- és ezüsthonalat, bélfonalra font drótot, vagy egyéb drótokból álló fémfonalat írtak le (p. 151.).

Madaras László az Alföld közepe táján élő avar kori ötvösök és kovácsok emlékanyagát vizsgálta (pp. 171–185.). Ennek során újraközölte Kisújszállás–Nagykert téglagyári agyagbányászás során feldúlt ötvössírjának anyagát. Közben megjegyzi (p. 173.): „Minden kétséget kizáróan a halott mellékletei közé tartoztak a neolitikus kőeszközök. ... A mester munkavégzéséhez gyakorlati közük aligha lehetett. ... Minden további találgatás az igazolhatatlan feltételezések világába vezetne bennünket, ezért még csak tippelni sem szándékozunk ebben a kérdésben.” Ugyanígy, minden értelmezés nélkül közölte a kérdéses kőtárgyakat Rác Zsófia 2014-ben, Mainzban kiadott *Die Goldschmiedegräber der Awarenzeit* című munkájában (pp. 161–164.). Nekem viszont lenne néhány megjegyzésem. Az eltemetett mellett, edényben talált kő véső-baltákat a neolitikumtól a késő bronzkorig igazolhatóan használták, ahogy a feje mellé helyezett nyéllyukas kőbaltát is (7–9. ábra). A halott nyakában talált neolitikus kögyöngyökön kívül – a sír nem azonosítható részéből – néhány darab olyan gömb és kocka alakú valamint ellipszis átmetszetű, csiszolt kő is származik, amelyeket a nemzetközi kutatás őskori súlyokként értelmez. Súlyadatokat azonban egyikük sem publikált. Bizonyos, hogy minden kőtárgy újkőkori? Nem elképzelhető, hogy a nyilván véletlenül talált kőtárgyak egy részét azután mégis csak tudatosan (mérésnél?) használta az ötvös? Ezért is tartom fontosnak e kőtárgyakat mielőbb alaposan megvizsgálni.

Szentpéteri Józsefnek az avar kori Kárpát-medence tárgyairól ismert, oroszán-motívumot tárgyaló nagyívű tanulmánya legalább három tudományos „világ” határán mozog (pp. 321–342.). Ezek a régészet, a mitológia és a művészettörténet. Térben Észak-Afrikától Euráziáig, időben pedig az ókori Egyiptomtól a Római Birodalmon át az egyiptomi kopt kereszténységig vizsgálódik. A tárgyakon, az elsőként általa alkalmazott színezési technika, mint virtuális dombormű segíti Őt a sokszor kaotikusnak tűnő motívumelemek láthatóvá tételében, ezáltal tanulmányozásukban.

Végezetül szeretném kijelenteni, hogy az Ünnepelet évfordulója kapcsán egy kiváló szakirodalmi gyűjteménnyel gazdagodott a magyar tudományosság több területe, így az archeometria is.

A kötet az alábbi honlapon érhető el:

<http://smmi.hu/publikaciok/2018/ketvilag/ketvilaghataran.html>

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