Archeometriai Műhely

2024.
XXI. évfolyam 3. szám

Archeometriai Műhely
elektronikus folyóirat

Kiadja a Magyar Nemzeti Múzeum

Felelős kiadó: Hammerstein Judit, általános főigazgató helyettes

Szerkesztő: Szilágyi Veronika

ISSN: HU ISSN 1786-271X
URN: urn:nbn:hu-4106

Tartalom / Contents

Archeometriai Műhely / Archaeometry Workshop No. 2024/3.

Archaeometry session at the 20th World Congress of the International Union of Prehistoric and Protohistoric Sciences (UISPP) – Interdisciplinarity in archaeology / Az International Union of Prehistoric and Protohistoric Sciences (UISPP) 20. világkongresszusának archeometriai szekciója – interdiszciplinaritás a régészetben

A kötet szerkesztői / eds.: Török Béla, Szilágyi Veronika

Cikkek / Articles

INTRODUCTION

ARCHAEOMETRY SESSION AT THE 20TH WORLD CONGRESS OF THE INTERNATIONAL UNION OF PREHISTORIC AND PROTOHISTORIC SCIENCES (UISPP) – INTERDISCIPLINARITY IN ARCHAEOLOGY

AZ INTERNATIONAL UNION OF PREHISTORIC AND PROTOHISTORIC SCIENCES (UISPP) 20. VILÁGKONGRESSZUSÁNAK ARCHEOMETRIAI SZEKCIÓJA – INTERDISZCIPLINARITÁS A RÉGÉSZETBEN •

The International Union of Prehistoric and Protohistoric Sciences (UISPP) brings together all disciplines that contribute to the study of Prehistory and Protohistory. The study of mechanisms of adaptation and behavioural dynamics of human societies is the core of the scientific interest of the UISPP. To achieve these goals, the UISPP organ-ises periodically a world congress on prehistoric and protohistoric sciences, to develop the progress of knowledge and to define common research objectives. For this purpose, the UISPP installs scientific commissions dedicated to specific research themes.

The 20th anniversary World Congress of the organisation was held in Timisoara from 5 to 9 September 2023, hosted by the West University of Timișoara (https://uispp2023.uvt.ro/). This major event was organised two years after the previous hybrid congress, which was postponed for a year due to the Covid pandemic, instead of the "usual" three years between congresses.

The slogan of the 20th World Congress was "Exploring the world's prehistory" and the general theme was "Interdisciplinarity in Archaeology".

The Commission “Archaeometry of Pre- and Protohistoric Inorganic Artefacts, Materials, and their Technologies” was founded in 2015 and has been one of the largest and most active commissions of the UISPP since its inception (https://uispp.net/en/commissions/archaeometry).

At the 2018 Paris congress and the 2021 Meknes (hybrid) congress, we held a full-day archaeometry session with a large number of presentations and a high level of professional interest, so naturally we have submitted a proposal for a dedicated archaeometry session for the 20th congress as well. Our session (Archaeometry of prehistoric and protohistoric stone, metal, ceramics, and glass) was held on 7 September at the West University in Timisoara.

• doi: 10.55023/issn.1786-271X.2024-018

The main goal of the session was to cover all aspects of analytical approaches applied to the study of archaeological finds of stone, metal, ceramics, and glass. Materials of all periods from Prehistory to medieval protohistoric cultures and civilizations were taken into consideration. Special cases on how general problems concerning the various materials can be solved by applying diverse analytical methodologies, case studies on ancient quarries, the production of stone artifacts from various contexts, research on mining, analyses of smelting remains, metal finds, metal workshop remains, ceramics of all kinds and periods, and research on glass production, colouring of glass/glaze and pigment were collected and presented. A further aim of this session was to share the latest results and experiences that can provide useful information, the comparison of several methods and technologies, and the possibilities of standar-dization of test and database protocols.

The programme of the session consisted of 17 papers, two of which were poster presentations, making it one of the largest sections of the 45 sessions of the World Congress. It was chaired by the president (the author of these lines) and the secretary of the Commission (Alessandra Giumlia-Mair). The presentations ranged from case studies to research on a general topic or papers on the experience of a specific archaeometric method of investigation. The speakers of ten presentations were members of our scientific UISPP commission for archaeometry. We have tried to provide the opportunity to publish papers as early as possible in the year following the session, at the same time, we have made every effort to ensure that the articles are published in a peer-reviewed journal of an appropriate level of archaeometric science. This is the first time that the articles of an organised scientific event of the UISPP commission for archeometry have been published in a special issue of Archaeometry Workshop. Unfortunately, for various reasons, only six presentations were finally received and reviewed. Nevertheless, these papers are good representatives of the full professional spectrum of the section, both in terms of types of materials and methods of analysis.

A team of researchers from the Department of Prehistory and Archaeology at the University of Granada, together with Ignacio Montero-Ruiz, present the results of metallographic and microhardness analyses of metal assemblages from several sites of the Bronze Age Argar culture (South-Eastern Iberia). Compositional analysis of more than 700 copper-based artefacts revealed a clear correlation between the use of tin bronze for decoration and the use of arsenic copper for functional objects.

The research of Mohammadamin Emami and colleagues will focus on the characterisation of the typical Shahdad (Iran, 3rd millennium BC) pottery styles, the metallurgical slags scattered in the area, and the remains associated with metallurgical activity such as copper ores, moulds, crucibles, furnaces, and metal residues. The study of the slags and ceramic fragments presented in this paper may provide new information on the preparation techniques, microchemistry, and possible uses of ceramics for metallurgical processes.

Carlo Bottaini and Dirk Brandherm present a recent research project aimed at investigating and identifying the primary ore sources used for copper production in Late Bronze Age Ireland, with a particular focus on the analytical methods used in the research.

Michał Krueger's paper presents observations based on the use of a handheld XRF spectrometer in ceramic research in recent years and attempts to highlight both the advantages and disadvantages of the instrument. To illustrate the possibilities, he draws on the results of two archaeological sites in Western Andalusia, the settlement and necropolis of Setefilla, which are located in close proximity to each other.

The joint complex project of archaeologists from the Institute of Archaeology of Eötvös Loránd University and researchers from the Archaeo-metallurgical Research Group of the University of Miskolc includes the metallographic analysis of samples selected from large amounts of iron raw material pieces at the Early Iron Age fortified settlement of Dédestapolcsány-Verebce-bérc in North-Eastern Hungary. One of the main questions of the research was which step of the ironworking process these raw materials belong to.

The Institute of Archaeology of the Russian Academy of Sciences carried out an intensive architectural and archaeological excavation of the Cathedral of St. George in Veliky Novgorod (Russia), collecting a large number of wall painting fragments. The study of these fresco fragments is reported in a joint paper by the Russian and Italian researchers involved in the project, with a special focus on the most common lapis lazuli pigment and its origin.

HU ISSN 1786-271X; urn: nbn: hu-4106

Fig. 1: Internal meeting of the Commission for Archaeometry. Participants from left to right: E. Ottenwelter (invited guest), M. Krueger, I. Montero-Ruiz, B. Török, A. Giumlia-Mair, M.P. Riccardi, G. Moiraghi (invited guest), A. Arena, A. Abdrabou, J. Hošek.

1. ábra: Az Archeometriai Bizottság zártkörű ülése. Résztvevők balról jobbra: E. Ottenwelter (meghívott vendég), M. Krueger, I. Montero-Ruiz, B. Török, A. Giumlia-Mair, M.P. Riccardi, G. Moiraghi ((meghívott vendég), A. Arena, A. Abdrabou, J. Hošek.

Fig. 2: UISPP Executive Committee meeting

2. ábra: AZ UISPP bizottsági ülése

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An internal meeting of the UISPP Archaeometry Commission was also held during the Congress on 8 September (**Fig. 1**). The meeting was attended in person by those commission members who were in Timisoara, and votes were also sent by those who were on the original programme of the section but could not attend. By unanimous vote, the 19-member commission was enlarged by two new members who had been speakers in the previous day's session. Thus, the Commission on Archaeometry closed the year 2023 with 21 members from 16 countries on four continents. Since the term of office of the board of each commission always runs until the current UISPP Congress, it was necessary to renew the leadership for the term until the next Congress. No nominations were received for any of the leadership positions other than the current individuals, so the question put to the vote was to re-elect the current board (President: Béla Török, Secretary: Alessandra Giumlia-Mair, Treasurer: Maria Pia Riccardi). The result of the vote was a unanimous 'yes'.

At the Executive Committee meeting (**Fig. 2**), held on the same day, composed of the board of the UISPP and the leaders of the scientific commissions, a vote was taken on the location of the 2026 World Congress. Of the two candidates, Poznań and Tübingen, the former received the most votes and the 21st UISPP World Congress will be held in Poland.

Béla TÖRÖK
President of the UISPP Commission
"Archaeometry of Pre- and Protohistoric Inorganic Artifacts, Materials and their Technologies"

HU ISSN 1786-271X; urn: nbn: hu-4106

WHAT ROLE DID REALLY TIN BRONZE PLAY IN THE ARGARIC SOCIETY?

MILYEN SZEREPET JÁTSZOTT AZ ÓNBRONZ AZ ARGAR TÁRSADALOMBAN?•

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Abstract

The transition from arsenic copper to tin-bronze in ancient metallurgy has long been attributed to the superior physical and mechanical properties of tin-bronze. However, recent archaeometallurgical studies have cast doubt on this theory, suggesting that the functional and productive advantages of tin-bronze over arsenical copper may not be as clear-cut as traditionally thought.

In this paper we present the results of metallographic and microhardness tests conducted on the metallic assemblages from several Bronze Age Argaric sites (Southeast Iberia). Compositional analyses of more than 700 copper-based objects revealed a distinct correlation between the use of tin-bronze for ornaments and arsenical copper for functional objects. This fact suggests that the choice of tin-bronze was influenced by factors beyond mere productivity. The results presented in this paper show that both arsenic copper and tin-bronze could exhibit similar mechanical properties. According to them, their microhardness levels depend on the final processes of their manufacture and the intensity of these processes, rather than on the alloy's composition. This challenges the notion that bronze was adopted solely for its functional efficiency. Therefore, alternative interpretations must be considered to explain the adoption of this new alloy.

Kivonat

Az ősi metallurgiában az arzéntartalmú rézről az ónbronzra való áttérést sokáig az ónbronz jobb fizikai és mechanikai tulajdonságainak tulajdonították. A legújabb archeometallurgiai tanulmányok azonban kétségbe vonják ezt az elméletet, és arra utalnak, hogy az ónbronz funkcionális és termelési előnyei az arzénes rézzel szemben talán nem olyan egyértelműek, mint ahogyan azt hagyományosan gondolták.

Ebben a tanulmányban a bronzkori Argar-kultúra (Délkelet-Ibéria) több lelőhelyéről származó fém leletegyütteseken végzett metallográfiai és mikrokeménységi vizsgálatok eredményeit mutatjuk be. Több mint 700 réz alapú tárgy összetételének elemzése egyértelmű összefüggést mutatott ki az ónbronz díszítésre és az arzéntartalmú réz használati tárgyakra történő felhasználása között. Ez a tény arra utal, hogy az ónbronz választását a puszta termelékenységen túlmutató tényezők is befolyásolták. Az ebben a tanulmányban bemutatott eredmények szerint mind az arzéntartalmú réz, mind az ónbronz hasonló mechanikai tulajdonságokkal rendelkezhet. Mikrokeménységük inkább készítésük végső folyamataitól és azok intenzitásától függ, mint az ötvözet összetételétől. Ez megkérdőjelezi azt az elképzelést, hogy a bronz kizárólag funkcionális hatékonysága miatt terjedt el és alternatív értelmezés szükséges az új ötvözet alkalmazására.

KEYWORDS: BRONZE, ARSENIC COPPER, ALLOY, MICROHARDNESS TEST, METALLOGRAPHY, IBERIAN PENINSULA, EARLY BRONZE AGE.

KULCSSZAVAK: BRONZ, ARZÉNES RÉZ, MIKROKEMÉNYSÉG MÉRÉS, METALLOGRÁFIA, IBÉRIAI-FÉLSZIGET, KORA BRONZKOR

• How to cite this paper: MURILLO-BARROSO, M.; MORENO ONORATO, A.; ARANDA JIMÉNEZ, G.; LACKINGER, A.; CONTRERAS CORTES, F.; MONTERO-RUIZ, I., (2024): What role did really tin bronze play in the Argaric society?, *Archeometriai Műhely* **XXI/3** 237–252.
doi: https://doi.org/10.55023/issn.1786-271X.2024-019

Fig. 1.: The Argaric territory in South-East Iberia

1. ábra: Az Argar-kultúra elterjedési területe Délkelet-Ibériában.

Introduction

Traditionally, societies have been classified by their technology and, therefore, the origin of metallurgy has usually represented a central aspect in historical explanation. From an evolutionary point of view, societies progress as technology is developed. Actually, the chronological division in 'Stone Age, Bronze Age or Iron Age' following Thomsen's scheme of the 'three ages' is not coincidental: this cultural framework underscores the significance attributed to metallurgy in historical interpretation and reflects the belief that technological development drives social change and cultural progress. Oversimplifying, technological advances let communities increase their resources and, hence, population grows, specialists are needed, and societies become more and more complex. However, while it is true that certain technological improvements can qualitatively modify some production processes and have a decisive impact in societies, it cannot be considered a general rule. In fact, this is the case of the first metallurgy in Iberia and the role played by tin-bronze in the Argaric communities.

The Argaric society

Before going into metallurgical questions in some detail, it may be worth presenting here some general information on the Argaric society, which corresponds to South-Eastern Iberia's Early Bronze Age (c. 2250–1550 cal BC) (**Fig. 1**). As a general rule, Argaric sites tended to be strategically located in mountains and hills with natural defensive features and a commanding view of the surrounding area. In addition, some of these sites have impressive stone fortifications.

Differences in settlements size, location and material culture suggest that there was a hierarchical settlement pattern, whereby different sites had specialized strategic, social and/or economic functions (Aranda et al. 2015).

Due to its peculiar nature, one of the most significant features of the Argaric societies is the location of burials within the settlement area, usually under the floors of the dwellings in four main types of containers: ceramic urns, cists, pit-graves and *covachas* (small artificial caves cut into the rock). Funerary ritual mainly consisted in individual, double or, more rarely, triple inhumations that were placed in a flexed position (**Fig. 2**). Argaric communities generally buried their dead with a series of objects that constituted the funerary offering. Grave goods are different in number, type and quality, ranging from none at all in some tombs, to important accumulations of wealth items in others. Ritual offerings can be cluttered in five main groups: pottery vessels; metal weapons such as swords and halberds; tools (axes, daggers/knives, awls); ornaments (made from copper/bronze, silver or gold) such as rings, bracelets, earrings, diadems and necklaces (usually made of stone beads); and faunal remains (usually limbs from cattle, sheep and goats) (**Fig. 3**).

Most scholars accept the image of a deeply stratified society, with evidence of ascribed status

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Fig. 2.: Argaric burial in a cist from the Cerro de la Encina (Monachil, Granada) site (Photo GEPRAN)

2. ábra: Argar sír a Cerro de la Encina-ban (Monachil, Granada) feltárt temetőből. (Fotó: GEPRAN)

due to differences in funerary wares and the first appearance of wealth children graves (for further discussion see Chapman 2008 and Aranda et al. 2015). Recent extensive excavations have provided a wealth of new data which constitutes the basis of current socio-political interpretations of the Argaric society – cf. Castro et al. 1999; Contreras Cortés 2000; Schubart et al., 2000; Aranda & Molina 2006; Aranda et al. 2012; Lull et al. 2021 –; however, the excavations of Louis and Henry Siret, Belgian mining engineers and archaeologists, mainly from the 1880s to the 1886s still provide important evidence for the Bronze Age burials in the region (Siret & Siret 1890).

Argaric metallurgy can be characterized by an important intensification of production. In contrast with the previous Copper Age societies, metal objects presented a 5-fold increase in quantity. Ornaments like bracelets, rings, earrings and diadems were the type of object primarily produced, especially from 1800 BC onwards, amounting for more than 50%, followed by tools (axes, daggers/knives, awls, etc.), and then specialized weaponry in the form of halberds and swords, which make their appearance for the first time in the Iberian Peninsula (Montero Ruiz 1993; 1994; Lull et al. 2017).

Fig. 3.: Argaric grave goods from burial 21 of the Cerro de la Encina (Monachil, Granada) site (Photo GEPRAN)

3. ábra: Argar sírmelléklet a Cerro de la Encina (Monachil, Granada) lelőhelyen feltárt 21-es számú sírból. (Fotó: GEPRAN)

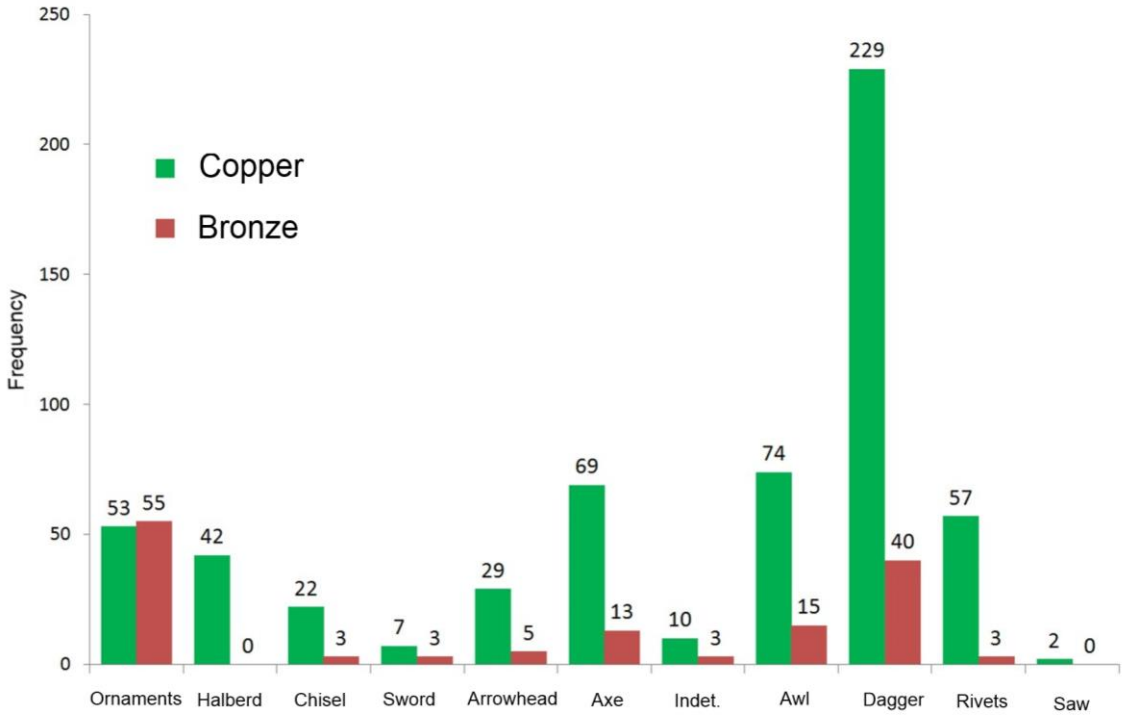

Fig. 4.: Frequency of copper and bronze in Bronze Argaric metals according to their typology (after Montero Ruiz et al. 2019, fig 1)

4. ábra: A réz és a bronz gyakorisága az Argar-kultúra réz alapú fémtárgyai esetében, tárgyfajták szerint (Montero Ruiz et al. 2019, 1. ábra után).

Copper was the primary metal used in Argaric communities from their inception, although gold and, particularly, silver eventually became significant for ornament production. The tin-bronze alloy was not in use when the Argaric society emerged and never became widespread (Montero Ruiz et al. 2019) (**Fig. 4**). Therefore, the adoption of this alloy does not appear to be the origin, or even a significant cause, of the changes that occurred at the beginning of the Early Bronze Age which shaped the Argaric society.

Why were bronze alloys introduced and what role did they play, then? As we will discuss here, one of the most intriguing debates related to bronze production is whether this alloy was chosen for specific tasks by replacing copper or arsenic copper due to its superior mechanical properties, or if it was used because of fashion, its colour, or any other social values.

The adoption of tin-bronze alloy has been the subject of different theories: some archaeologists state that tin-bronze substituted arsenic copper because of its better mechanical properties in terms of hardness and strength, which supposed an increase of productivity (Childe 1944; Kristiansen 1987). Other scholars suggest that tin-bronze is a deliberate alloy while arsenic copper is not, so the amount of tin is better controlled than the amount of arsenic, thus improving the final properties of objects (Tylecote 1976; Pernicka 1998). Even the "healthier" properties of tin technology in contrast with the toxicity of arsenic fumes have been also proposed as an explanation (Charles 1967).

Mechanical and physical properties of copper, arsenic copper and tin bronze

Here we will comment the mechanical and physical properties of copper, arsenic copper and tin bronze in order to understand why the Argaric society adopted this significant technological change.

The first physical property that becomes evident is that certain amounts of either arsenic or tin can reduce the melting point of copper (1083 ºC). It is assumed that under equilibrium conditions, the eutectic point of arsenic copper (i.e. the lowest melting point, 689 ºC) will be reached with an arsenic content of 21.5% (weight percent). However, in the range of Argaric alloys – As average of 2.4% for arsenic coppers and Sn average of 8.0% for tin-bronzes, considering bronze those containing >1% Sn (Montero Ruiz 1994: 244-245) – the decrease of the melting point is not significant and remains similar in both cases.

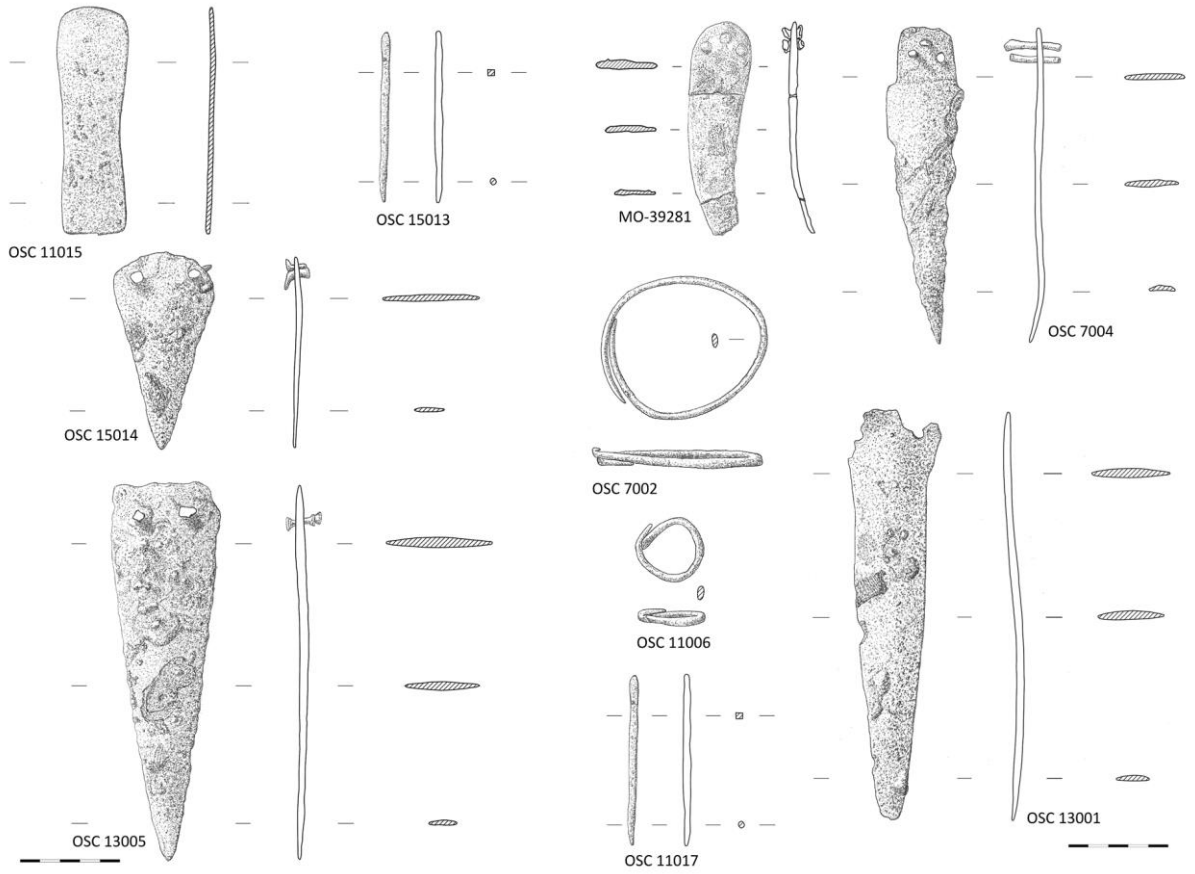

Fig. 5.: Some of the objects analyzed from Cerro de San Cristobal (OSC) and Cerro de la Encina (MO) (After Murillo-Barroso et al. 2015, Figures 4 and 5).

5. ábra: Néhány vizsgált tárgy a Cerro de San Cristobal (OSC) és a Cerro de la Encina (MO) lelőhelyről (Murillo-Barroso et al. 2015 után, 4. és 5. ábra).

According to phase diagrams, for the average value of 2.4% As the melting point will be reduced to c. 1050 ºC, and for the highest arsenic concentration value documented (12.7%, Rovira Llorens et al. 1997), the melting point will be reduced to c. 900 ºC. Those values are similar to the ones obtained with tin-bronze alloys: the average for tin concentration documented in Argaric bronzes is of 8.0% Sn (Montero Ruiz 1994: 244), which would decrease the melting point to c. 1020–1030 ºC, and the maximum amount of Sn measured is of 14.4% (Rovira Llorens et al. 1997), which would reduce the melting point to c. 970 ºC. Although these temperatures correspond to alloys under equilibrium conditions, and those are not usually reached in practice, – according to experimental studies, under practical conditions eutectic segregates can appear with a much lower amount of arsenic, around 2–3% (McKerrel & Tylecote 1972: 211; Lechtman 1996: 486; Mödlinger et al. 2018) –, it seems that in a first instance, both types of alloy reduce the melting point of copper in a similar way, so this might not be the main reason for the adoption of tin-bronze alloy.

Another significant characteristic is the increase in hardness that arsenic and tin provide due to their differences in atomic size compared to copper. In a solid solution alloy, the solute atoms are generally of a different size than the atoms of the metal in which they are dissolved, and the resulting distortion of the crystalline structure contributes to the final hardness of the alloy. The result of the addition of arsenic or tin to copper exemplifies this chemical principle. Arsenic atoms are larger than copper ones, but not as big as tin atoms, therefore tin is expected to increase hardness more than arsenic.

Experimental studies show that hardness and malleability of arsenic copper alloys begin to change with 0.5% or 1% As and 2% Sn (Lechtman 1996; Northover 1989). In all cases, some overlapping of both alloys' properties seems to be detected: Marechal (1958 cf. Lechtman 1996) and more recently Northover (1989) stated that the hardness achieved with an 8% arsenic concentration is very similar to the one achieved with 8% tin (over 250 HV). Scott (1991) points out that with 4% tin or arsenic, for a reduction of 50% of

thickness, arsenic copper remains harder than tin bronzes. On the other hand, Lechtman (1996) indicates that tin bronze with a 2% tin content after 75% reduction of thickness, is far harder than a 2% arsenic copper hardened up to the same point. However, Lechtman also concludes that there is a lot of overlap in the mechanical properties of both alloys in the documented concentration ranges.

As a matter of fact, the mechanical properties of arsenic copper and tin-bronzes are sometimes difficult to measure comparatively in experimental studies due to same-conditions concerns that must be considered; even with no thermo-mechanical processes applied to them, there are several features, like cooling rate, which relates to the grain size, or impurities in the metal, that can influence the final result (Sabatini et al. 2020)

As these results are from tests conducted on experimental alloys, metallographic and micro-hardness analyses on 54 archaeological samples (12 bronzes and 42 arsenic coppers) from several archaeological sites were carried out in order to compare and contrast the properties of both types of alloys in original artifacts (**Fig. 5**).

Methodology

Elemental composition was determined by Inductively Coupled Plasma-Mass Spectrometry with a Sector Field (ICP-SFMS) and Energy Dispersive -X Ray Fluorescence (ED-XRF). ICP-SFMS analyses were conducted by Dr. Michael Bode at the Archaeology and Materials Science laboratories of the *Deutsches Bergbau-Museum* (Bochum, Germany) using a spectrometer Thermo Scientific ELEMENT XR (for further method-logical questions about ICP-SMFS cf. Renzi et al. 2014). ED-XRF was conducted at the National Archaeological Museum (Madrid, Spain) using a portable spectrometer INNOV-X serie Alpha. Working conditions, using an X-Ray detector with silver anode, were of 35 kV and 20 μA. Patina and corrosion products were mechanically removed and analyses were conducted on an area of 25 mm^2 of the clean metallic surface (for calibration and further methodological questions about XRF analysis procedure see Rovira Llorens & Montero Ruiz, 2018). All the values of the elements used in the text refers to weight percent (wt%).

For metallographic examination, samples were embedded in epoxy resin, ground and polished to 0.25 μm grit size, following the conventional procedure (Scott, 1991). Samples were etched with an aqueous ferric chloride solution (120 ml H_2O: 30 ml HCl: 10 g $FeCl_3$) and were observed under an optical microscope Leica DMLM. Microhardness tests were carried out using a REMET HX1000 tester. Given results are the average of between 4 and 20 indentations, depending on the sample size. Both types of analyses were conducted at the laboratories of the Institute of History (CCHS-CSIC, Madrid, Spain). Methodological questions on metallographic preparation and microhardness analyses followed the recommendations of Scott (1991) and Rovira Llorens & Gómez Ramos (2003).

Table 1.: Working techniques, average Vickers microhardness and composition of Argaric copper-based artifacts. C=As Cast, A=Annealed, CW=Cold Working. Working techniques in brackets show low intensity; in bold + italics show high intensity. Composition is given in wt%. (nd=not detected, Tr=traces)

1. táblázat: Argar-kultúra réz alapú tárgyainak megmunkálási technikái, átlagos Vickers keménységei és összetételei. C=öntött, A=lágyított, CW=hidegalakított. A zárójelben lévő készítési technikák kis gyakoriságot, a félkövér+dőlt betűk a nagy gyakoriságot jelzik. Az összetételt tömeg%-ban adtuk meg. (nd= nem detektálható, Tr=nyomokban)

Site	ID	Type	Working Techniques	HV	As %	Sn %
Llano de la Gabiarra	PA2984B	Rivet	C		Nd	nd
Cerro de la Virgen	PA0927	Awl	C		1.97	nd
Peñalosa	BE-9533	Rivet	C + A	60	3.9	nd
Hoya de la Matanza	PA2967A	Dagger	C + A + CW		1.25	nd
Peñalosa	PA14034	Dagger Rivet	C + A + CW	205	10.9	0.01
Cerro San Cristobal	OSC 7004_R	Dagger Rivet	C + *CW*	170	Nd	nd
Peñalosa	BE-28882	Awl	C + CW	177	Nd	nd
Peñalosa	PA14032	Awl	C + CW	117	0.66	0.04
Hoya de la Matanza	PA2970	Dagger	C + CW		0.8	nd
Mina Alianza-Herrerías	AA1148B	Halberd Rivet	C + CW		0.94	0.07
Cerro San Cristobal	OSC 13006_60	Staple	C + CW	116	1	Tr
Las Angosturas	PA2433	Dagger	C + CW		1.32	0.02
Peñalosa	PA14048	Awl	C + CW	134	1.41	nd

Table 1., cont.

1. táblázat, folyt.

Site	ID	Type	Working Techniques	HV	As %	Sn %
Peñalosa	PA14053	Awl	C + CW	116	1.45	0.04
Peñalosa	PA14036	Awl	C + CW	153	1.7	nd
Cerro de la Virgen	PA0924	Chisel	C + CW		2.2	0.02
Peñalosa	PA14051	Dagger	C + CW	209	2.37	0.03
Cerro San Cristobal	OSC 11010_R	Rivet	C + CW	158	2.39	nd
Peñalosa	PA 20107	Dagger	C + CW	97	2.6	nd
Peñalosa	BE-10249	Awl	C + CW	173	2.7	nd
Peñalosa	PA13631	Bead	C + CW	135	2.75	nd
Cerro San Cristobal	OSC 15014_R	Dagger Rivet	C + CW	127	2.98	nd
Peñalosa	PA 14049_R	Dagger Rivet	C + CW	205	3.43	nd
Cerro San Cristobal	OSC 15014_H	Dagger	C + CW	151	3.51	nd
Cerro de Enmedio	PA2612L	Awl	C + CW + A		1.28	Tr
Peñalosa	PA14033	Dagger	C + CW + A	106	2.12	0.02
Cerro de la Encina	MO-39261	Bracelet	C + (CW + A)	62	2.52	nd
Peñalosa	PA14047	Dagger	C + CW + A	197	3.55	nd
Peñalosa	PA13632	Axe	C + CW + A + CW	132	0.31	nd
Hoya de la Matanza	PA2967B	Awl	C + CW + A + CW		0.9	nd
Cerro San Cristobal	OSC 13006_37	Nail	C + CW + (A + CW)	146	1.09	Tr
Cerro San Cristobal	OSC 13006_71	Nail	C + CW + (A + CW)	144	1.23	Tr
Cerro San Cristobal	OSC 13006_15	Nail	C + CW + (A + CW)	134	1.29	Tr
Peñalosa	PA14049	Dagger	C + CW + A + CW	145	2.3	0.03
Cerro de la Virgen	PA0922	Awl	C + (CW)		2.3	nd
Hoya de la Matanza	PA2968	Dagger	C + CW + A + CW		2.37	nd
Cerro San Cristobal	OSC 15013	Awl	C + CW + A + CW	200	4.08	nd
Cerro San Cristobal	OSC 13005_R	Dagger Rivet	C + CW + A + CW	142	4.3	nd
Cerro San Cristobal	OSC 13005_H	Dagger	C + CW + A + CW	186	5.05	nd
Cerro de la Encina	MO-39257	Awl	C + CW + A + CW	200	5.28	nd
Cerro San Cristobal	OSC 13001_H	Dagger	C + CW + A + CW	196	6.47	nd
Cerro de la Encina	MO-21292	Dagger	C + CW + A + CW	175	6.73	nd
Peñon de la Reina	PR-PUNZON	Awl	C		Nd	10.7
Cerro de la Encina	MO39264_H	Dagger	C + CW		2.3	4.38
Cerro de la Encina	MO39281_H	Dagger	C + CW		0.09	8.7
Cerro de la Encina	MO-39255	Bracelet	C + CW + A	90	0.13	4.1
Peñon de la Reina	PR-ARET-19	Ring	C + CW + A		nd	4.99
Cerro San Cristobal	OSC 7002	Bracelet	C + CW + A	108	0.42	5.58
Peñalosa	PA 20106	Sword	C + CW + A	149	1.3	9.92
Cerro de la Encina	MO-39260	Ring	C + CW + A		0.24	8.93
Cerro San Cristobal	OSC 11006	Ring	C + CW + A + CW	183	0.01	4.47
Cerro San Cristobal	OSC 11015	‘Scraper’	C + (CW + A + CW)	149	0.87	4.91
Cerro San Cristobal	OSC 11017	Awl	C + CW + A + CW	198	0.01	6.61
Peñalosa	PA14050	Dagger	C + CW + A + CW	184	0.4	9.4

Results and discussion

Table 1. summarizes the results of the analyses. Full data has been previously published in several papers (Rovira Llorens et al. 1997; Murillo-Barroso et al. 2015 or Moreno Onorato & Contreras Cortés, 2015). The average content of arsenic and tin in the assemblage studied (2.7% As, Std. 2.05, and 6.9% Sn, Std. 2.46) is consistent with previous analyses of Argaric metallurgy, featuring low tin bronzes and arsenic coppers with a 2.4% As average (Montero 1994: 245), but in our case also with some high As levels (the rivet with 10% As stands out but is included in the 2.7% As average value).

The arsenic in the metal has been related with the smelting of As-rich copper ores (Rovira Llorens & Montero Ruiz 2013) and it is assumed that its presence is not deliberate, unlike the case of tin bronzes, but the identification of arsenic-rich ores and its selective mining cannot be rejected (Hook et al. 1991; Moreno et al. 2003). This is suggested by the fact that tin is not detected in copper or arsenic copper items, while tin bronzes can contain significant arsenic levels, even higher than 1%.

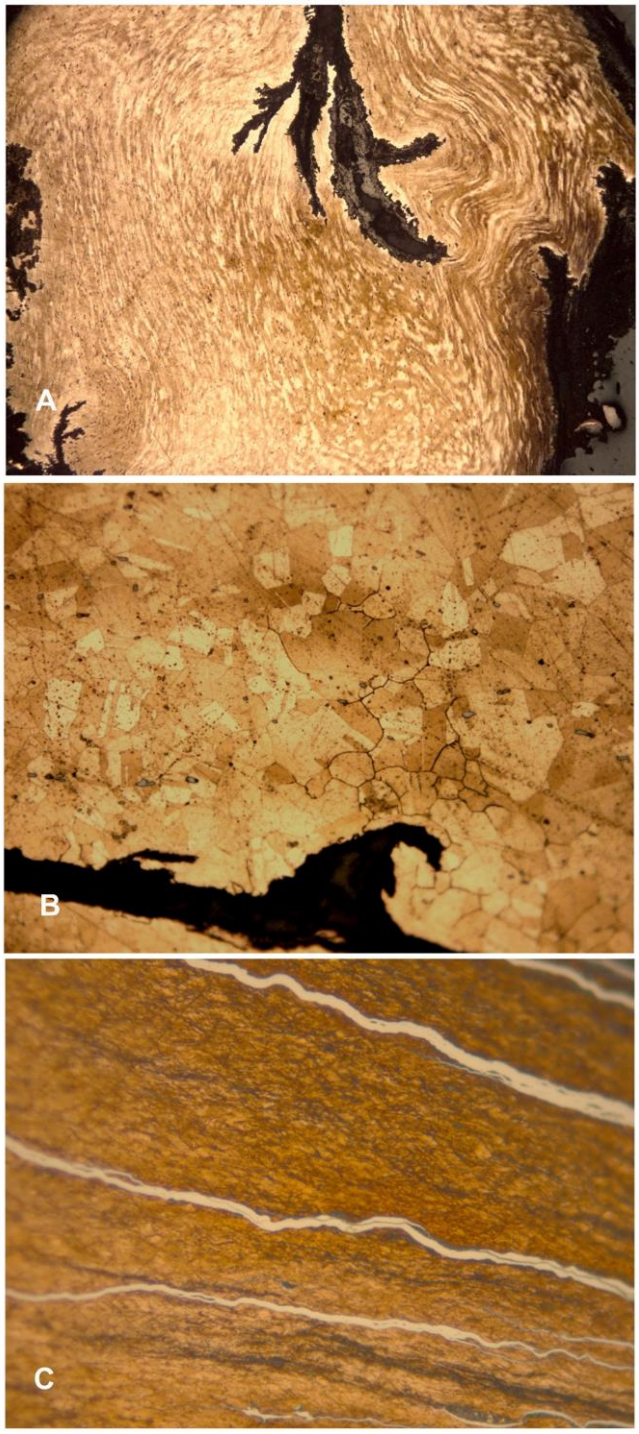

Fig. 6.:
Microstructures of the main *chaîne opératoires* documented in the Argaric assemblages. All samples have been etched with aferric chloride solution.
(A) Rivet OSC15014_R, Cast and Cold Worked. Note the deformation of the dendritic structure, especially on the right side of the rivet (100X).
(B) Bracelet OSC7002. Cast, Cold Worked and Annealed. Note that rectilinear grains have formed as a consequence of annealing. Bands inside the grains indicate that the bracelet was previously hammered (200X).
(C) Dagger OSC13001_H with 6.47% As. Cast, Cold Worked, Annealed and Cold Worked. The dagger was heavily hammered and the microstructure is completely deformed. Note that arsenic has been segregated in bright As-rich bands that can be easily identified (500X).

6. ábra:
Az Argar-kultúrabeli leleteken megfigyelt készítési folyamatok mikroszkópos felvételei. A mintákat vas-klorid oldattal maratták.
(A) Szeg OSC15014_R, öntött és hidegen alakított. Dendrites szerkezet deformációja, különösen a szeg jobb oldalán (100x).
(B) Karkötő OSC7002. Öntött, hidegen alakított, lágyított. Egyenes vonalú szemcsék alakultak ki a lágyítás következtében. A szemcsék belsejében látható sávok arra utalnak, hogy a karkötőt korábban kalapálták. (200X).
(C) Tőr OSC13001_H 6.47 % As-tartalommal. Öntött, hidegen alakított, lágyított és hidegen alakított. A tőrt erősen átkalapálták, így a mikroszerkezete teljesen deformálódott. Az arzén jól elkülöníthető, világos sávokban szegregálódott (500X).

Table 2.: Average hardness of each type of artifacts

2. táblázat: A különböző tárgytípusok átlagos keménységértékei.

Type	Number of samples	Mean HV	StD
Awls	9	163	34.6
Bracelets	3	87	23.3
Daggers	10	165	38.9
Rivets	11	146	40.5

Metal production follows different *chaîne opératoires*, and some objects only prepare the edges with cold working while others use longer actions combining annealing and cold working (**Fig. 6**). The chosen process is essential in the microhardness get in the final stage independently of the elemental composition of each object.

Microhardness averages range from 60 HV to 209 HV. Typologically, daggers and awls are the hardest objects, with an average of 164 HV and 163 HV respectively (**Table 2.**). However, we have to take into account that these are mean values, and daggers usually present a high standard deviation (20–30 Std) while awls have a low one (5–9 Std) due to the fact that daggers have hardened edges while awls have a more homogeneous hardness.

If the highest values for daggers are considered, there is no doubt that this is the group with the hardest HV values. **Fig. 7.** shows this selective working on dagger edges: Vickers values drop as soon as measurements are taken in the inner part of the dagger. Even light cold working can, under the right conditions, produce a significant increase of the hardness, as it is shown in the case of the object OSC11015 (**Fig. 5**). While its dendritic structure was identified at a low magnification (**Fig. 8/A**), the evidence for annealing and cold hammering could only be identified, in the edges, at a higher magnification (**Fig. 8/C**). Annealing and hammering might not be too intense, as the remnant dendritic structure suggests, however it was intense enough to get high hardness values (230 HV) in the edges (**Fig. 7**).

If we compare microhardness values for arsenic or tin alloys, we see that there is not direct correlation between hardness and composition, and that bronzes are not necessarily harder. Average Vickers micro-hardness measurements of both arsenic copper and tin-bronze objects have been graphically plotted in **Fig. 9**. This graph shows how artifacts with low arsenic content could be as hard as tin-bronzes or even harder, and how metals with a similar *chaîne opératoire* have a similar hardness, regardless of their bronze or arsenic composition.

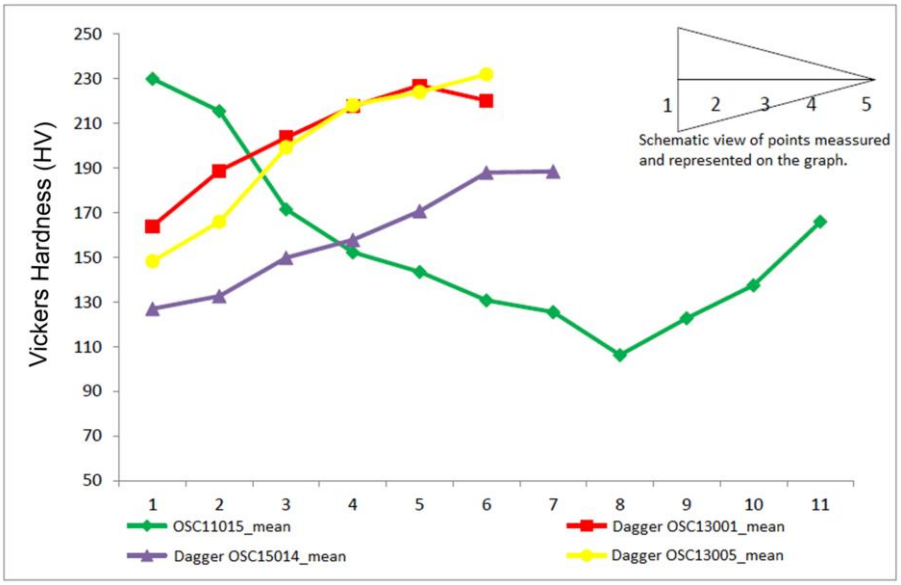

Fig. 7.: Microhardness values of longitudinal axes of some edged objects and the 'scraper' OSC 11015. Hardness has been measured in at least three points on the longitudinal axis, as shown in the schematic drawing.

7. ábra: Éllel ellátott tárgyak, valamint egy „kaparóvas" (OSC 11015) hosszanti tengelye mentén mért mikrokeménységi értékei. Legalább három ponton mértünk keménységet a hosszanti tengely mentén, ahogy ezt a sematikus rajzon is lehet látni.

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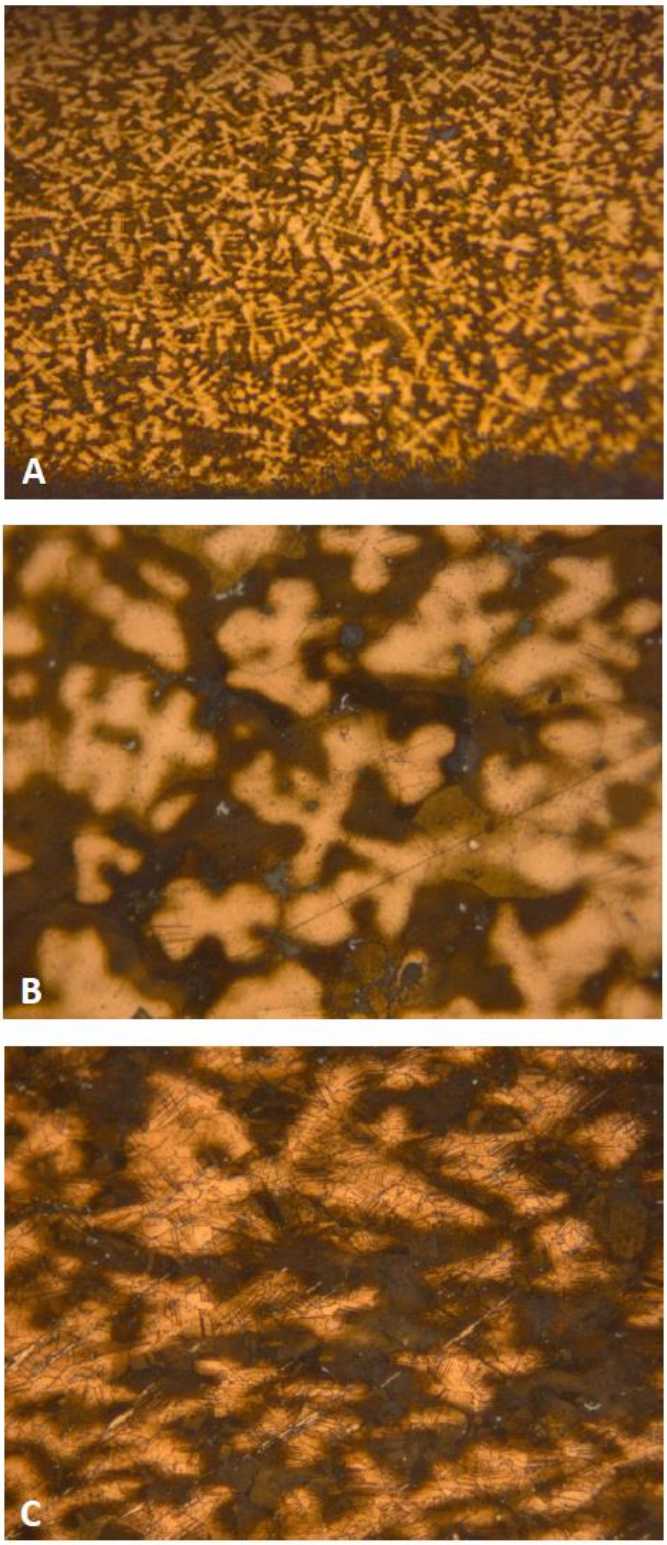

Fig. 8.:
Metallographic section of OSC11015. (A) General view (50X). Note the dendritic structure as a consequence of slow cooling. (B) Inner area (500X). Only the dendritic structure can be identified and no grains or slip bands can be recognized. (C) Edge area (500X). Twinned grains and slip bands can be now recognized in the remnant dendritic structure due to selective cold working.

8. ábra:
Az OSC11015 számú tárgy metallográfiai felvételei. (A) A minta általános szerkezete (50X). A dendrites szerkezet a lassú hűlés következménye. (B) A minta belső területe (500X). A dendrites szerkezet nem láthatók szemcsék és nyírási sávok. (C) Él felé eső terület (500X). A hidegmegmunkálás hatására megmaradt dendrites szerkezetben ikerszemcsék és nyírási sávok láthatók.

This is the case, for example, of two daggers, both cold worked, annealed and cold worked again: the arsenic copper one (5.05% As; OSC13005 in **Fig. 5.**) reaches an average hardness of 186 HV (with a maximum of 232 HV in the edge) while the bronze one (9.4% Sn; PA14050) has an average hardness of 184 HV (with a maximum of 239 HV in the edge). Something similar happens with three awls: the arsenic ones (OSC1503 and MO39257 with 4.08% and 5.28% As respectively) have an average hardness of 200 HV and the bronze one (OSC11017 in **Fig. 5.**, with 6.61% Sn) shows a similar value of 198 HV. Even some copper artifacts with low amounts of arsenic or tin (even <1%) display a hardness similar to that of bronzes. For example, one pure copper awl has a hardness of

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177 HV (BE28882), and one arsenic copper rivet with 2.3% arsenic and a final stage of hammering exhibits a hardness of 209 HV (PA14051), still harder than bronzes with more than 9% tin such as the dagger PA14050 (184 HV). Contrarily, artifacts with a final stage of annealing have a lower hardness: a bronze bracelet (MO39255, with 4.1% Sn) cold hammered and annealed features a hardness of 90 HV, and a rivet, equally hammered and annealed and with 3.9% As shows a hardness of 60 HV (BE9533), while objects with similar amounts of Sn or As but a final stage of hammering have higher microhardness values so far (for example the above mentioned awl with 4% As and 200 HV, OSC15013).

Hence, main differences in microhardness can be established on account of the final stage of the *chaîne opératoire* and its intensity: with one exception in each case, all objects with a final stage of annealing have a hardness below 110 HV, and all artifacts with a final stage of hammering (annealed or not) show a hardness over 115 HV. This is because cold working provides more hardness although at the price of causing the object to eventually become brittle. The process of annealing reduces brittleness while also decreasing hardness, which increases ductility and malleability. This is why, up to a point, annealing is necessary to continue hammering intensely, for example when significantly reducing thickness. Probably this is the reason that explains why almost all the bronzes studied in this article are annealed (either with annealing being the last stage in the *chaîne opératoire* or not). According to Lechtman, 13% tin bronzes become brittle at deformations of about 50% thickness reduction, and annealing is necessary to continue working them, but it is probable that bronzes with c. 7% Sn also require annealing to be extensively cold worked without any risk of cracking (Lechtman 1996).

Therefore, it is the final stage of the *chaîne opératoire*, more than the amount of arsenic or tin in the alloy composition, what seems to determine the final hardness of Argaric artifacts. In order to clarify if prehistoric metalworkers were aware of this fact, these differences in the *chaîne opératoire* have been related with the type of objects, classified in two main categories: body ornaments (mainly rings for different parts: finger, arm or ears) and 'functional' ones (including all objects, mainly tools and weapons, which potentially could have had other purposes than display, even if the possibility of some weapons being used for ostentation rather than for violence is not discarded, see for instance Aranda et al. 2009).

Only 7 body ornaments and 12 tin-bronzes of the assemblage studied were available for sampling, so even if some patterns can be initially deduced, one has to be cautious, as they could change when more analyses are developed. Bearing this in mind, a distinct trend on working techniques can be seemingly inferred: a majority of ornaments have a final stage of annealing (71.5%) while most of functional objects have a final stage of hammering (89.4%).

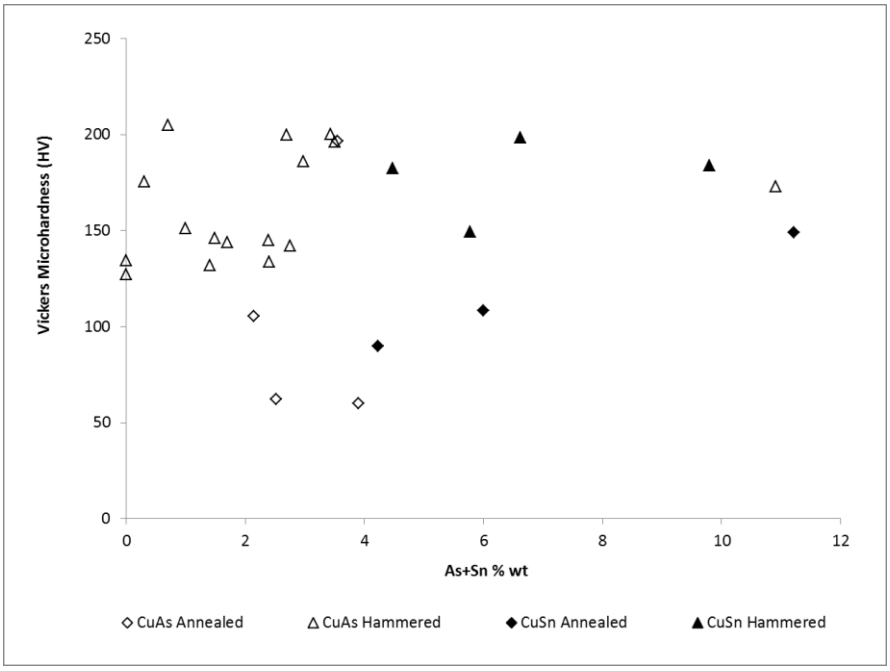

Fig. 9.: Microhardness values of arsenical copper and bronze artifacts. Note how some artifacts with low levels of arsenic are harder than some bronzes.

9. ábra: Az arzéntartalmú réz és bronz tárgyak keménységértékei. Néhány esetben a kis arzéntartalmú tárgyak keményebbek a bronztárgyaknál

This is not surprising, since, as we have seen, a final cold working stage will increase the hardness of metals, a desirable quality in functional items, while annealing will re-homogenize the alloy, increasing its ductility and malleability, a quality probably more desirable for the manufacture of mainly spiral ornaments that in any event do not need hardness as a fundamental mechanical property and that instead it is desirable to preserve the condition of their surface, which would be destroyed by hammering. Although more metallographic analyses are needed, this trend shows some awareness on working techniques and metals properties by Argaric metalworkers.

The fact that different type of artifacts featured different working techniques could be also related with their chemical composition, which is also consistent with the above results. Elemental analyses of c. 700 copper-based Argaric objects have been conducted since Siret´s first study (Montero Ruiz et al. 2019). The relationship between their variables shows a positive correlation between chemical composition and type of artifacts. There seems to be a trend by which most of the ornaments analysed (51%) are in fact bronzes, being tools and weapons mostly made of arsenic copper: 100% of the halberds, 85% of the daggers, 84% of the axes, 83% of the awls and 70% of the swords analysed (Montero Ruiz et al. 2019).

It is in a late phase of the Argaric period (c. 1800 cal BC) that tin bronze appears for the first time, being mainly used in ornament manufacture (Montero Ruiz et al. 2019): this is suggested by some grave goods where copper or arsenic copper tools can be found together with tin-bronze ornaments. This is the case of graves number 1034 from El Argar site (Antas, Almería), 164 and 237 from El Oficio (Cuevas de Almanzora, Almería) or grave number 6 from Cerro de San Cristóbal (Ogíjares, Granada). Other late graves contain tools made with both types of metals (arsenic copper and tin bronze). This is the case, for example, of the grave 21 at Cerro de la Encina (Monachil, Granada) (**Fig. 4.**), with two inhumations dated by AMS at the end of the Argaric period (Beta-230005, 1650–1460 cal BC 2σ and Beta-230006, 1730–1510 cal BC 2σ) (Aranda et al. 2008) what shows that arsenic copper was not substituted by tin-bronze in the Argaric period. We have no knowledge of graves where tools are made of tin-bronze and ornaments with copper or arsenic copper.

With all this, it becomes apparent that copper or arsenic copper was not completely substituted by tin-bronze. The innovation of tin-bronze occurred in a late period of the Argaric society and its adoption and generalization were a slow process, being more related to ornamental and aesthetic motivations than to productive ones. However, most of the metallic assemblages are recovered from the funerary record.

We can also see that some of the copper-tin alloys have also some amounts of arsenic, which could suggest that the same copper ores were used in the production of arsenic copper and tin-bronze objects, while arsenic is not detected in other tin-bronzes, suggesting the exploitation of different ores or some technological issues in the co-smelting of copper and cassiterite which might prevent arsenic to alloy with copper. The recent identification of tin bronzes with a likely provenance from areas outside the Argaric territory (Pedroches, Pyrennes or the Alps) and the identification of some unusual objects (decorated daggers) suggest that an exchange of manufactured metal objects underlies in this demand (Montero Ruiz et al. 2022). However, the option of the ap-pearance of bronze artifacts exclusively as imported objects does not explain the technological change and their adoption. Unfortunately, we do not have archaeological evidence (tin ores, slags or smelting debris) to support the local production of bronze, except the lead isotope analysis confirmation of the involvement of local copper resources in this production.

Conclusion

Although more analyses are needed, some social patterns and issues regarding technological change, such is the adoption of tin-bronze and the later abandonment of arsenic copper in Argaric societies, can be pointed out.

Physical and mechanical properties of both alloys have been discussed, evaluating the possible adoption of bronze due to its superior utilitarian properties. However, although tin bronze objects can be hardened more than arsenic copper ones, especially in alloys over 8% tin, most Argaric bronzes have a low tin content and present a significant overlap with the mechanical properties of arsenic coppers within the recorded compositional ranges for both alloys in the period studied. Under these conditions, it has been shown that the hardness of metal artifacts depends more on the final stage of the *chaîne opératoire* than on their content of arsenic or tin, and that arsenic coppers can be as hard as tin bronze objects or even harder. Moreover, tin bronze alloy was preferably used in the manufacture of body ornaments. All these characteristics of Argaric metallurgy imply that the potential improvements of mechanical and physical properties of this new alloy were not being exploited.

If tin bronze was not chosen because of its mechanical properties, other explanations should be considered. Colour, shining, reflectivity, symbolic and aesthetic values of metals have also been proposed in other cultural contexts and an

anthropological view of the use and consumption of metals, more based on sensory and symbolic aspects (Comendador Rey 2010) must be considered. This perspective also affects to the operational technical chain of metal, attending the sensory aspects of metallurgy (smell, sound, colour, etc.) as it has been proposed and related to skills (Kuijpers 2013, 2017).

Leaded high-tin bronzes reflectivity was highly valued in mirror fabrication in China or the Roman Empire (Scott 1991; Mei 2000; Wang 2002) and this quality was also considered when manufacturing bronze drums or bells in India, Southeast Asia or China (Rajpitak 1983; Srinivasan 1997; Srinivasan & Glover 1995; Murillo-Barroso et al. 2010). However, in all these cases, tin values were far higher than those found in the Argaric society.

Metallurgical studies in Latin America have also stressed properties other than "functional" or "utilitarian" in alloys used. The importance of color (especially silver and gold) in the cosmologies and political ideologies in Andean Societies was discussed by Lechtman (1993) with a gender approach; and in Western Mexico sonority and colour of metals seem to have played a role in the selection of the alloys for making bells and other 'status items' (Hosler 1995: 100). In pre-Columbian metal objects of Muisca (Bogotá), alloys of different proportions of copper and native gold have been documented in offering assemblages, although symbolism, rather than color, has been proposed to explain differences in compositions (Uribe Villegas & Martinón-Torres 2012). In Argaric societies, cosmological and gender approaches in the use of silver and gold have also been proposed (Perea 2011), in which silver or silvery objects would be preferably associated to women and gold or golden objects to men.

In recent years, the influence of arsenic and tin on the colour of copper alloys has been intensively studied and described (Fang & McDonnell 2011; Mödlinger et al. 2017; Radivojevic et al. 2018). In the case of copper-based alloys, it is known that high tin will provide a silvery resemblance to copper and the characteristic reddish color of copper is progressively lightened as more tin is added, but the yellowness of the alloy will only decrease with tin contents over 18% and hence the silvery resemblance is only accomplished in alloys between 18–33% Sn. Therefore, in the Argaric bronzes, with an average of 6.9% Sn in this study, colour will surely be modified, and even if the silvery colour was not obtained, the redness of copper would have been significantly lightened to a more golden appearance, so the addition of tin would have been conspicuous. The change of colour depending on the metal could explain the combination in the same grave of body ornaments made of arsenic copper, tin bronze and silver (Montero Ruiz et al. 2019: 22).

The scarcity of tin in the area compared with the easy acquisition of copper and arsenic copper (which occurs abundantly in Southeast Iberia) can be also considered a key issue. Adding a scarce raw material to copper would have increased its social value (Gilman 1981, De Marrais et al. 1996). In this sense, the adoption of tin-bronzes, together with the expansion of copper-based and silver ornaments, chronologically a contemporaneous phenomenon c. 1800 cal BC, can be linked with the ideological and social role played by metals in the visibility and materialization of social power and status of the Argaric elite. In the Argaric society, tin-bronzes would be part of these mechanisms which would have contributed to legitimate and reproduce asymmetrical social relations and political power. We could therefore consider bronzes as a way of wealth accumulation and ostentation.

More analytical studies must be carried out, but up to now all evidence seem to indicate that the adoption of bronze by the Argaric society could respond more to ideological mechanisms of ostentation and status consolidation than to mechanical improvement concerns or productive requirements, and therefore it should be considered more a consequence of social stratification processes than a cause of them.

Contribution of authors

Mercedes Murillo-Barroso Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Auxilio Moreno Onorato** Validation, Investigation, Writing – Original Draft, Writing – Review and Editing. **Gonzalo Aranda Jiménez** Investigation, Resources, Writing – Review and Editing, Funding acquisition. **Aaron Lackinger** Formal analysis, Investigation, Writing – Review and Editing, Visualization. **Francisco Contreras Cortés** Investigation, Resources, Writing – Review and Editing, Funding acquisition. **Ignacio Montero-Ruiz** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization.

Acknowledgements

This research has been supported by the R & D Project PID2022-137494NB-I00 (*Redes Sociales y de Intercambio en la Sociedad Argárica)* funded by MICIU/AEI/10.13039/501100011033 and by FEDER, UE and the Research Groups (HUM 065) GEA: *'Material Culture and Social Identity in Recent Prehistory of the Iberian Southeast' and* (HUM 274) GEPRAN: *Group for the Study of the Recent Prehistory of Andalusia*. We are very

grateful to Isidro Toro Moyano, director of the Archaeological Museum of Granada, for allowing us to take samples of Argaric metal artifacts, and to Marc Gener, CENIM-CSIC, Madrid, for his comments on the text and editing improvements. Thank you to the reviewers for the useful comments to improve the paper. All errors remain our own.

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TRACING THE PYRO-TECHNOLOGICAL EVIDENCE DURING THE 3rd MILLENNIUM BC IN "SHAHDAD" THROUGH ARCHAEOMETALLURGICAL REMAINS

SHAHDAD KR.E. 3. ÉVEZREDI PIROTECHNOLÓGIAI BIZONYÍTÉKAINAK NYOMON KÖVETÉSE AZ ARCHEOMETALLURGIAI MARADVÁNYOK ÁLTAL •

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Abstract

Shahdad is located on the western side of the great "Lut" desert in the south-central Iranian Plateau. Shahdad has been a major focus of archaeological research in the region due to extensive metallurgical activities, which were documented at the site and supposedly have the most abundant remains of copper metallurgy in south-eastern Iran during the Bronze Age (3rd millennium BC). Due to the archaeological studies of the vast peripheral area, the settlement was a permanently occupied city during the 3rd millennium BC. New excavations at Shahdad offer a unique opportunity to reconsider the pyro-technological remains which were probably related to metallurgical practices during this era. This research will focus on the characterization of typical Shahdad pottery styles and remains of metallurgical slags scattered across the area in association with amounts of other metallurgical remains such as copper ores, moulds, crucibles, furnaces and metallic residues. The typical characteristic style of pottery are their dense structure heavy with rough fabrication. The objects have been studied through optical microscopy, ICP-MS, and XRF to determine their chemistry, micro-chemistry, and mineralogy. The evident complexity of pottery production at Shahdad may eventually allow a better understanding of the timing of innovations and/or the adaptation of technological features observed in the overburden of Shahdad that as yet have not been scientifically documented. The scientific examination of slags and pottery sherds presented here recognizes new information regarding the microchemistry and production techniques of pottery and their possible potential application for metallurgical purposes.

Kivonat

Shahdad a nagy „Lut" sivatag nyugati oldalán, a Dél-Közép-iráni-fennsíkon található. Shahdad a régió régészeti kutatásainak egyik fókuszpontja a helyszínen dokumentált, kiterjedt kohászati tevékenységek miatt, amelyek feltételezhetően a bronzkor (Kr. e. 3. évezred) alatti rézkohászat leggazdagabb maradványait szolgáltatják Délkelet-Iránban. A kiterjedt peremterület régészeti vizsgálatai szerint a település a Kr. e. 3. évezredben állandóan lakott város volt. A Shahdadban végzett új ásatások egyedülálló lehetőséget kínálnak a – valószínűleg a korszak kohászati gyakorlatához kapcsolódó – pirotechnológiai maradványok újraértelmezésére. Ez a kutatás a jellegzetes shahdadi kerámiastílusok, a területen szétszórtan található kohászati salakok és a kohászati tevékenységhez kapcsolódó maradványok (pl. rézércek, öntőformák, tégelyek, kemencék és fémmaradványok) jellemzésére összpontosít. A kerámiák stílusára jellemző a tömör szerkezet és a durva kidolgozás. A tárgyakat optikai mikroszkópia, ICP-MS és XRF segítségével vizsgáltuk, hogy meghatározzuk kémiai, mikrokémiai és ásványtani jellemzőiket. A shahdadi kerámiakészítés nyilvánvaló összetettségének vizsgálatával jobban megérthetjük az újabb innovációk megjelenését és/vagy az új technológiai jellegzetességek alkalmazását, amit eddig még tudományosan nem dokumentáltak. A tanulmányban bemutatott salakok és kerámiatöredékek vizsgálata új információkkal szolgálhatnak a kerámiák készítéstechnikájáról, mikrokémiájáról, illetve azok lehetséges kohászati célú felhasználásáról.

• How to cite this paper: EMAMI, M., ELIKAY DEHNO, S., ESKANDARI, N. & PRITZEL, Ch., (2024): Tracing the pyro-technological evidence during the 3rd Millennium BC in "Shahdad" through archaeometallurgical remains, *Archeometriai Műhely* **XXI/3** 253–264.

doi: 10.55023/issn.1786-271X.2024-020

KEYWORDS: ARCHAEOMETALLURGY, COPPER, SLAG, POTTERY, MINERALOGY, SHAHDAD, IRAN

KULCSSZAVAK: ARCHEOMETALLURGIA, RÉZ, SALAK, KERÁMIA, ÁSVÁNYTAN, SHAHDAD, IRÁN

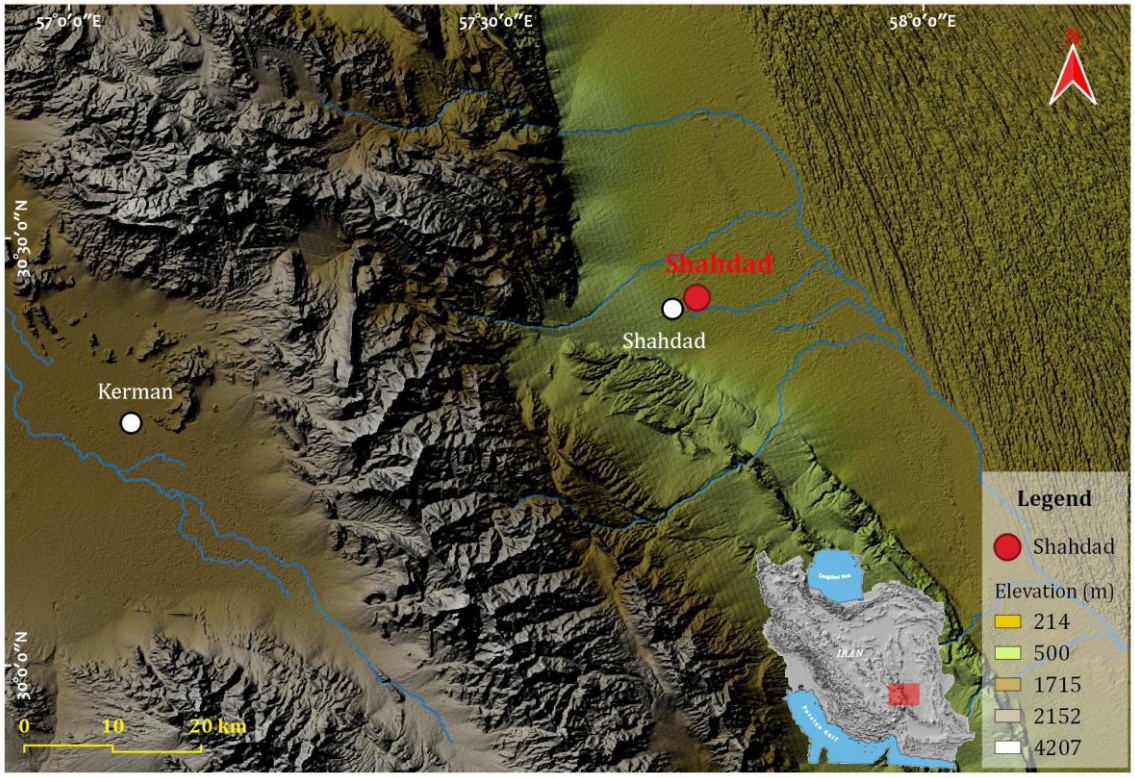

Fig. 1.: Geography and location of Shahdad in the Central Iranian Plateau
1. ábra: Shahdad földrajzi elhelyezkedése a Iráni-fennsík központi területén.

Introduction

One of the aspects of the early metallurgy and metal extraction in the Central Iranian Plateau compared to the neighbouring regions of the Indus Valley in the east to the Mesopotamia in the west is the abundance of metal finds. Although there are many ore deposits and metal-bearing geological formations in the central part of Iran, as is the case in the Kerman region, mainly Shahdad which has been outcroped with diverse metalogenic compositions. The Early Bronze Age civilizations and re-excavated sites in the highlands of Iran had direct access to the ores and mines (Helwing 2021). The importance of the Shahdad in the southern part of the Lut Desert in the manufacturing and trade of metal in central Iranian archaeology was reflected in textual archives of the ancient archaeological peripheries which were well described as Aratta Culture (Majidzadeh 1976) (**Fig. 1**). The ancient texts of Ebla in the second half of the 3rd millennium BC (Steinkeller, 2016) and the archives of Kanesh and Mari in the first half of the 2nd millennium BC, debated the dynamic role of lands east of Mesopotamia (e.g., Elamite cities, in particular Susa) (Weeks 2016) in the trade of metal ores and artefacts in western Asia via various transit and commercial hubs in West Asia such as Uruk. The Iranian sites offer a rich collection of metal artefacts and a long history of metal utilization in the south-central Iranian plateau (Larsen 1967; Joannes 1991). Results of lead-isotope analyses from Byblos and Tell Arqa at the eastern shore of the Mediterranean, however, have indicated that metal-bearing ores from the Iranian plateau had reached the southern Levant on the western border of Mesopotamia (Morr et al. 2013).

Shahdad as a centre of metal extraction in Iran is located in the highlands of Kerman and the southern part of the Lut Desert, and it provides a long and unique sequence of metallurgical remains and artefacts from the beginning of the fourth to the middle of the 3rd millennium BC (Eskandari 2017, 2021b). The context and later chronology of the material culture of Shahdad, and in particular the substantial finds from early excavations, are still unknown and that is also true for metallurgical remains. 24 years after the publication of Curtis and colleagues (2000), which was established based on many archaeological excavations, research, and publications in Iran and Mesopotamia, today we can reassess the chronology of previously dated objects as well as suggest dates for some of the

undated artefacts in south-central Iran (Curtis et al. 2000). This paper focuses on the study of metallurgical remains and artefacts collected from Shahdad. Pottery and slags have been selected covering the results from the late 3rd millennium BC to the middle of the 2nd millennium BC.

Due to the lack of an organised settlement sequence and also the lack of absolute C14 dating, it is hard to present an absolute chronology of Shahdad. The comparative analysis of the funerary goods from the cemetery of Shahdad reveals that the site dates to the middle 3rd millennium BC and lasts until the late 3rd millennium BC. This dating is based on the comparative studies on pottery, chlorite and marble vessels, bronze objects and seals of the site with the contemporaneous regions of south-eastern Iran and its neighbours such as Shahr-i Sokhta, Jiroft, Bampur, Tepe Yahya, Mundigak, Umm-al Nar, Susa and the sites of central Asia (Eskandari 2019, 2021a; Eskandari et al. 2021). Furthermore, the existence of a linear Elamite inscription in Shahdad (an old Iranian writing system related to the second half of the 3rd millennium BC) confirms this relative dating of the site.

Ever subsequently the emergence of remaining archaeomaterials such as pottery, slag, and crucibles, followed by smelted metal in the late 3rd Millennium BC in Shahdad, high-temperature industrial processes performed a fundamental role in any subsequent technical and economic development. Despite all these remains, systematic studies and recent insight into past societies are strongly required towards burials, and finalized artefacts, looking to the expertise and creativity that left multiple and often complex features of production behind.

Material and Methods

The ancient periphery of Shahdad is about 9 km^2 and is covered with metallurgical remains and pottery sherds. Ten pieces of slag and three ores in addition to the slags with five pottery sherds have been considered and studied in this paper. The styles of the pottery in Shahdad are the same and all of them are crashed sherds with coarse-grained additives and reddish color due to the exposed heating to the fabrication. In accordance with their form and typology, these sherds can be clarified as crucibles. Typical samples which belong to the same style are shown in **Figs. 2** and **3**. Concerning the chemical aspects and elemental composition related to eventual copper extractions, slag and ores have been assembled from the region and studied via XRF and ICP-MS. It should be mentioned that all the studied artefacts (pottery and slags) in this paper were certainly manufactured in the Shahdad area during the 3rd millennium BC.

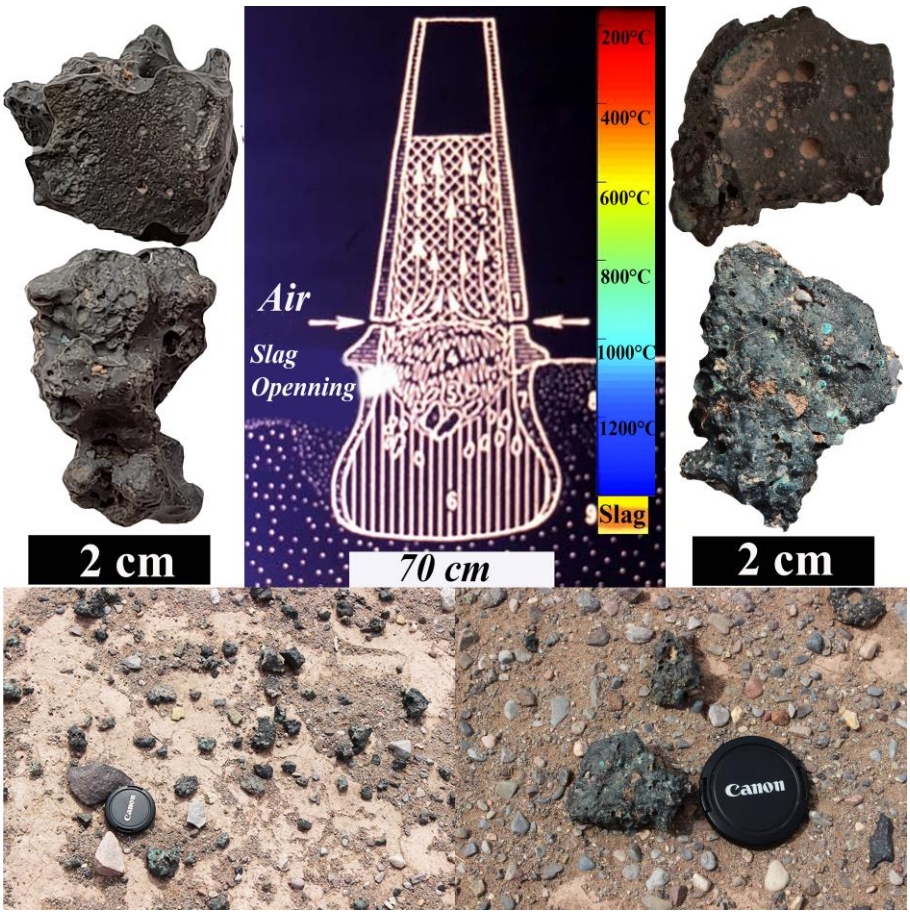

Fig. 2.: Some slag artefacts from the region and an illustration of the place of their production within the kiln.

2. ábra: A területen talált néhány salakmaradvány és a kemencén belüli képződésük helyét mutató modell.

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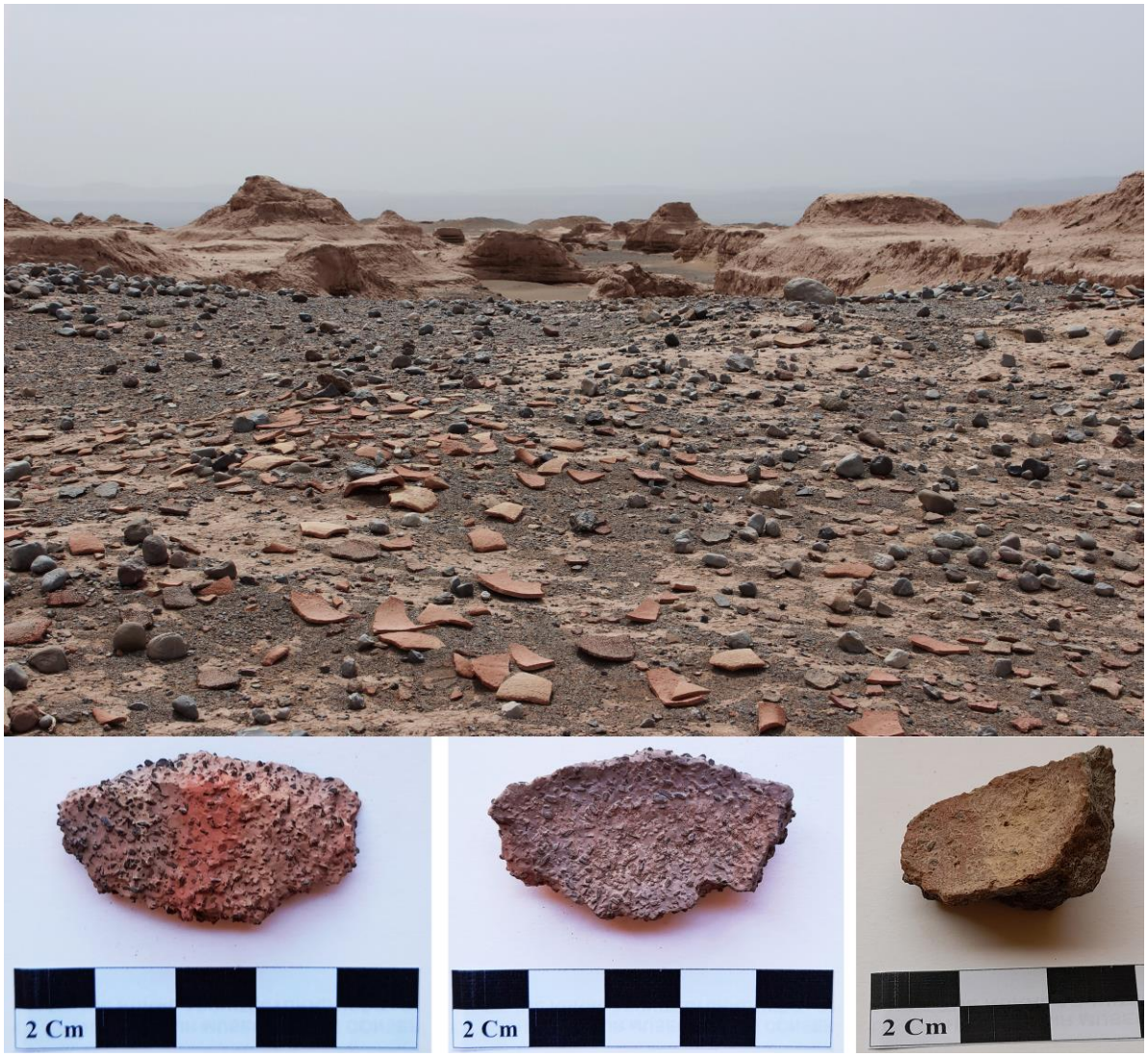

Fig. 3.: Pottery-type collection from Shahdad. All the sherds scattered on the surface belong to the same style

3. ábra: Shahdadi kerámiatípusok. A szétszórtan található töredékek mind egy típushoz tartoznak.

The materials have been studied via mineralogical-chemical methods. Microscopic investigations and observations to define textural properties of slag and pottery (petrography and petrology of the finds) have been completed with an Olympus microscope (model X51), at the Department of Chemistry and Structure of Novel Materials at the University Siegen, Germany. The bulk chemical composition of the slags and ores has been studied with an XRF spectrometer (ARL model 8420). UniQuant software has been utilized for qualitative and quantitative measurements. For measurement of the loss on ignition (LOI), the samples were exposed to heat at about 1050 °C for one hour. Trace element concentrations have been done by PerkinElmer's NexION 1000® ICP mass spectrometers at the Zaminrizkavan Co. Ltd., Tehran, Iran. The instrument is an ultimate high-throughput system for routine, multi-elemental, trace-level analyses that meet regulatory standards.

Results and Discussion

Chemical composition of the slags

Artefacts associated with copper-extraction activity have some added elements as the signature of the ore deposit to the charge. The chemical composition of the slags shows that they can be classified into three groups I, II, and III regarding SiO_2 constituents in the system SiO_2-CaO-Fe_2O_3 (**Table 1.** and **Fig. 4**). Group I can be described as high silica slag (30.7–53.1 w%) compositionally enriched with iron and calcium that led to the formation of olivine-type texture through green birefringence color of these minerals (fayalite slag) (**Fig. 4A**). The lower amount of MgO consents to the presence and building of the kirschsteinite (monticelite) type of olivine. Due to the rapid cooling rate olivines are crystallized in skeletal form and are very fine in texture (Hezarkhani &

Keesmann 1996). Group II is classified as pyroxene slags because it forms more iron-rich pyroxene with hedenbergite composition (more Ca-Fe rich) (**Fig. 4B**). Due to the higher portion of the metal to silica (Me:Si), which is responsible for pyroxene building within the matrix, the melting point of these groups is higher than the others. Group III, however, can be mentioned as the ore-bearing mother rocks with more silica-calcium rich composition, e.g., dolomite-bearing copper impregnations. The olivine, as well as pyroxene-type slags, have possibly smelted from Ca-rich melt (10.2–24.5 w%). MgO amounts in analysed slag vary from 2.0 to 6.5 w%, and these can be reflected in different color within the lath-crystals of olivine in different samples (Addis et al. 2016).

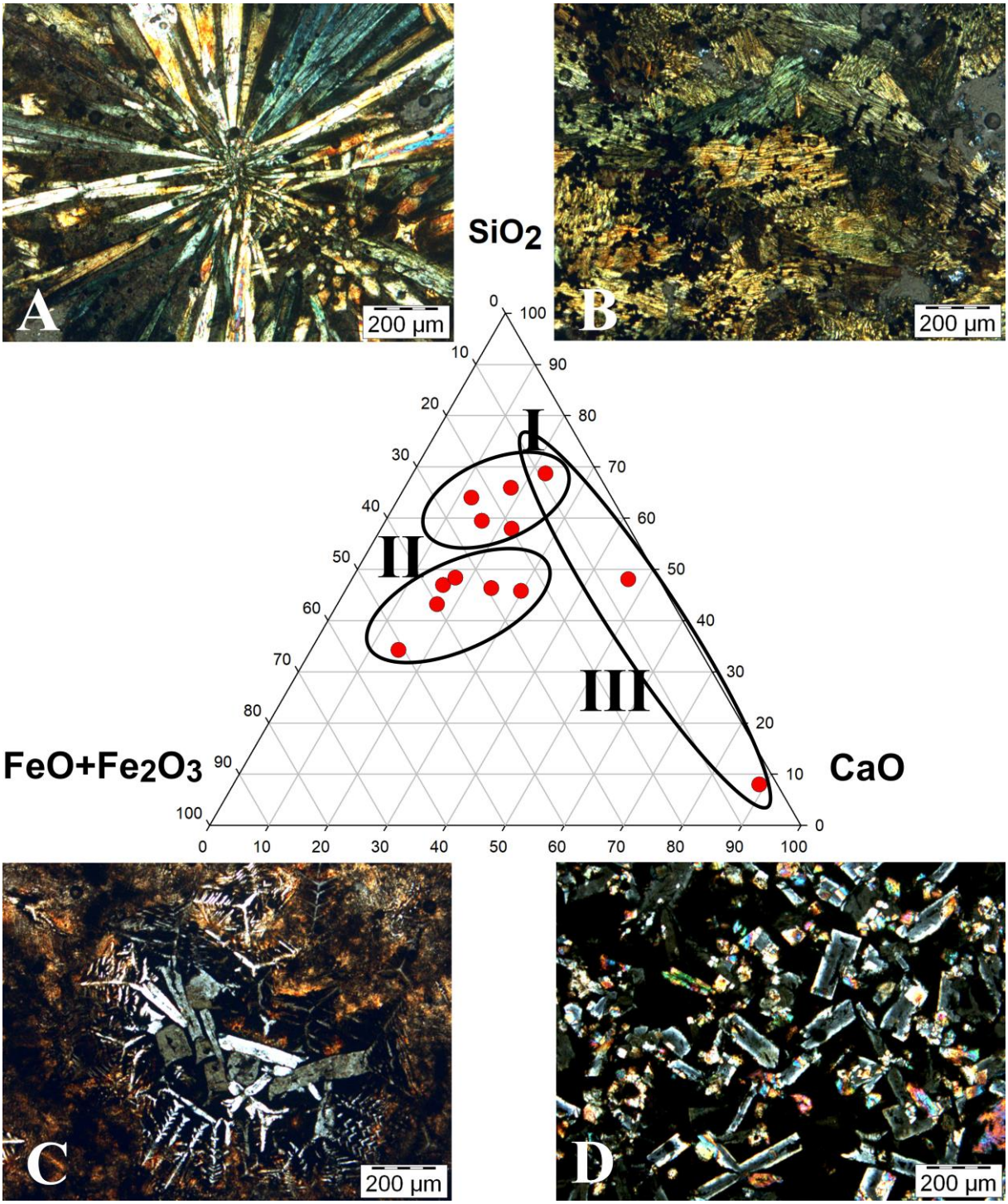

Fig. 4.: The chemical composition of the slags and their relationship to the silicate minerals within their texture
4. ábra: A salakok kémiai összetétele és a szerkezetükben lévő szilikátásványok.

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Table 1.: Bulk chemical composition of the slags and ores in w%. LOI is measured after heating the samples to 1050 °C for one hour. The sample order is stated based on the found numbers ascending and the types of them as slag and ore.

1. táblázat: A salakok és az ércek kémiai összetétele tömeg%-ban megadva. Az izzítási veszteséget (LOI) egy órán át tartó, 1050 °C-ra való hevítés után mértük. A minták sorrendjét a leltári számok alapján növekvő sorrendben, a típusokat pedig salakként és ércként adjuk meg.

Sample	058-1	067-0	070-4	063-2	055-1	059-14	050-14	057	061-1	058-0	061-0	059-2	059-13
Na_2O	1.5	0.84	0.72	0.56	0.76	1.2	0.58	0.64	0.74	0.97	1.3	0.58	0.26
MgO	4.8	2.9	2.3	2.0	2.0	3.0	2.9	2.6	6.4	2.9	3.9	4.5	2.7
Al_2O_3	9.7	7.8	5.5	6.3	7.3	8.1	6.3	9.2	5.6	9.6	12.9	7.0	2.1
SiO_2	37.6	40.6	40.1	30.7	53.1	54.1	39.9	43.4	35.3	45.0	47.4	31.5	7.3
P_2O_5	0.45	0.29	0.29	0.16	0.31	0.29	0.38	0.41	0.44	0.29	0.48	0.20	0.14
SO_3	0.044	0.27	0.58	-	1.1	0.61	0.25	1.4	0.56	1.3	1.6	0.061	0.83
Cl	0.020	0.53	0.64	0.11	0.72	0.51	0.30	1.0	0.55	0.79	0.031	0.012	0.015
K_2O	0.29	0.20	0.13	0.15	0.21	0.16	0.14	0.22	0.17	0.19	0.40	0.24	0.052
CaO	24.5	14.6	13.7	13.3	10.2	14.8	21.1	11.9	13.8	17.2	15.5	30.7	81.7
TiO_2	0.42	0.36	0.27	0.20	0.37	0.40	0.30	0.40	0.25	0.49	0.58	0.46	0.14
Cr_2O_3	0.034	0.095	0.063	0.024	0.024	-	-	-	-	-	-	-	-
MnO	0.045	0.067	0.036	0.063	0.049	0.066	0.098	0.046	0.032	0.13	0.036	0.014	0.23
Fe_2O_3	20.1	28.8	31.7	45.7	19.7	13.2	25.2	17.7	32.7	15.5	6.1	3.4	2.8
CuO	0.21	2.4	3.7	0.44	3.9	3.3	2.3	8.8	3.2	5.4	9.49	21.20	1.50

Table 2.: Trace element analysis of five slag samples by ICP-MS in ppm.

2. táblázat: Öt salakminta ICP-MS módszerrel mért nyomelem összetétele, ppm-ben megadva.

Sample	57	059-14	061-1	063-2	067-0
Ag	103	16	5	<5	8
Al	41408	39927	29257	30819	39209
As	1018	246	285	160	1091
Ba	979	289	370	497	631
Be	<5	<5	<5	<5	<5
Bi	<5	17	<5	<5	<5
Ca	70818	88011	88060	92130	92275
Cd	13	<5	<5	<5	5
Co	64	28	54	58	119
Cr	130	138	132	394	1405
Cu	129787	56066	51893	9363	37523
Fe	105326	75954	200741	273996	172175
Ga	12	9	20	29	18
K	11250	7877	9632	8691	10935
La	16	15	12	30	15
Li	39	31	27	22	38
Mg	12327	16798	35653	12722	15834

Sample	57	059-14	061-1	063-2	067-0
Mn	1233	1749	976	1693	1818
Mo	31	26	21	15	24
Na	7203	11864	7906	7777	8708
Ni	88	33	211	207	1492
P	1055	802	1070	321	814
Pb	43673	387	738	231	82
S	4524	3053	3830	1348	1814
Sb	3343	35	21	38	35
Sc	9	6	5	6	8
Se	21	12	11	11	9
Sr	1546	1925	1611	1045	1377
Ti	1980	1953	1429	1293	1963
V	72	57	49	64	60
Y	25	16	19	41	29
Zn	1273	46	148	174	170
Zr	114	134	96	100	112

HU ISSN 1786-271X; urn: nbn: hu-4106

Pyroxene slag from Shahdad has been demonstrated after Ca-rich melt and recrystallization in some reaction zones, e.g., around the furnace wall or within the furnace wall where oxygen fugacity is higher than the core of the melt. Thereafter black dots of iron oxide in different charges can be observed on the pyroxene laths (**Fig. 4B**). Consequently, the Fe-rich slag presents iron constituents in the form of spinel crystals with magnetite compositions (**Fig. 4C**). Melilithe is the by-product of copper slag smelting (Emami et al. 2016). The higher Ca- and Si-rich melt within the slag's texture is the best requirement for building melilite. Melilite cannot be observed within the olivine slag (fayalitic slag) because the Ca-Si composition and temperature are not sufficient for crystallizing the mineral. Within the pyroxene-type slag (Group II), however, they are mostly visible with a zone-effect color of bluish-white (**Fig. 4D**). Normally, Mg-rich melilites present a pinkish-orange color within the core of the crystal. Due to the lack of enough Mg within the melt, however, melilite does not represent an orange color in these samples, and it will be classified as Fe-rich akermanite crystals (**Fig. 4D**) (Hezarkhani & Keesmann 1996).

ICP-MS of ten slag and three ores are given in **Table 2**. According to the trace element composition, the studied slag samples seem to be similar to each other. The only contrast can be observed in sample 057 and the presence of lead within it, which is higher than the others. Except for all major elements such as Fe, Cu, Al, Ca, Na, K, and Mg, the other trace elements varied or remained stable within the fabrication of the slags that have been used within this periphery. The higher variation among Cu, Fe, As, Ag, Bi, and Pb can be related to the usage of porphyry-bearing ores (a Fahlerz) from ophiolitic regions, which are well known in southeastern Zagros Orogeny.

Mineralogical composition and texture of the slag

Following microscopic observation of the slag through the polished section, the texture of the slag will be classified by different sulfide, oxide, and metallic constituents. Indeed, the formation of the slag can be determined both through the smelting condition and the location of the formation within or outside the kiln. Slag compositions viewed with reflected light microscopy are described as copper-rich. Metallic copper can be determined as tiny, isolated droplets of different sizes within the glassy matrix (**Fig. 5A**). The color hue of metallic copper (reddish to white with higher reflection) has changed by the presence of the diverse amount of As, Fe, Bi, and S within the metal droplets (Bachmann 1982). The droplets made of metallic copper are formed via rapid cooling within the high-viscosity character of silica melts. Thereafter, droplets scatter and remain stable as rounded shapes within the cooled melt. In this stage of formation, copper droplets can be formed in association with metallic iron or iron oxide in the composition of magnetite (creamy bright color) and covellite (CuS) with reflected bluish-white color (**Fig. 5B**).

The sulfides can be characterized by higher or lower temperature reactions via smelting. Sulfide composition has formed, and it is seen in various stages within the slag texture as follows.

Crystallization products from sulfide-rich melt

In this case, the typical crystallization character will be observed through the droplets which have been surrounded by sulfide composition (Cu, S and Fe) in blue/grey color (**Fig. 5C**). Nevertheless, another complex crystallization can be allocated via different solubility factors of sulfides (in different sulfide compositions) in the form of iron-rich spinel (dendritic structure) around the sulfide phases within a fayalite rich matrix (prismatic structures in grey) (**Fig. 5D, E**). In smelting processes for primary copper production, the main composition through out of the smelting is the presence of typical fayalite slag with high FeO content, especially near the bottom. The formation of a solid magnetite structure obove fayalite is the reason for oxidation reaction under higher oxygen fugacity ($fO2$).

Decomposition and conversion of the primary sulfides

The primary sulfides from the ore deposit have a high tendency to form segregation due to their temperature and composition. In this case, the use of Fahlerz as primary sulfide can be modified by the observation of yellow pyrrhotine-chalcopyrite paragenesis within the slag texture. Ex-solution of sulfides can be seen mainly in form of bornite-digenite lamella within covelite as from the copper-rich sulfide phases (**Fig. 5F**).

Remains of primary sulfides

The relic and remains of primary ore have been detected in all slag in the form of the covellite composition. Covellite used as primary ore for copper extraction had orange inner-reflect, in comparison to chalcocite (Keesmann et al. 1991).

Crystallization products from silica melt

Crystallization from the melt has typically formed a diverse composition between the metallic droplets and sulfide composition within the glassy slag (**Fig. 5C**). These characters that some phases will be recrystallized from the contact area between silica melt and different sulfide-rich phases have been described in many German texts as "Zwickelfüllungen" (Keesman 1993).

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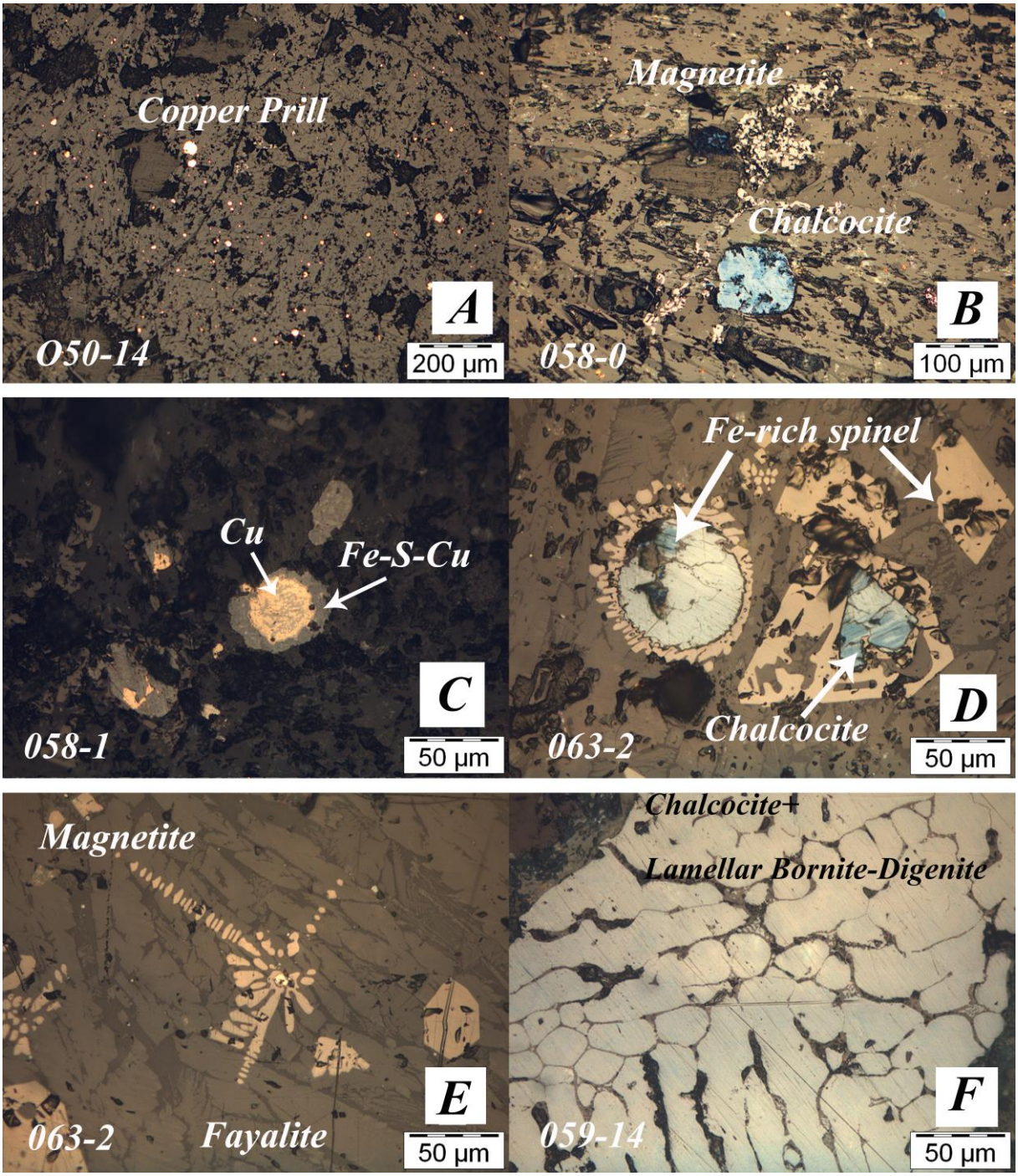

Fig. 5.: Microscopic investigation of the slag and their mineralogical constituents and textures.

5. ábra: A salakminták ásványi komponenseinek és szerkezetének mikroszkópos vizsgálata.

Reaction products (decomposition)

As mentioned above all the slags have to be classified as iron and copper-rich composition with chalcopyrite and chalcocite relics within the silica melts. However, metallic droplets are iron-poor and completely rich in Cu or Cu-S composition; this can be seen as an ex-solution effect on the iron-rich phases (**Fig. 5F**).

Petrography and texture of the pottery from Shahdad

Pottery from Shahdad has been studied petrologically and petrographically because they might have preserved some aspect of metallurgy within their fabric. The pottery sherds from Shahdad have typically been characterized as porous sherds. According to the additives applied within the potter, they are classified as coarse-grained sherds with different color in thickness with

coarse-grained black sand and flint as additives. The sherds were studied through different magnifications for better clarifying their textural and fabrication features (**Fig. 6**). Observation via loop shows the visible coarse-grained additives and cracks (**Fig. 6A**). Cracks appeared normally within the inner part of the fabric and might have been produced via temperature shock through shrinkage. Cracks are not visible in the surface area. Petrographically, the matrix contained crushed quartz of almost the same size concerning similar processing approaches through preparation and separation (**Fig. 6B**). Muscovite minerals appear orangish red because the temperature did not exceed 900°C (Emami 2020). The matrix has two colors because two different clayey raw materials were used (Anaya et al. 2024).

Internal reflection light microscopy in the dark-field shows the green light which may pass through the polished surface of a mineral and be reflected from below and specify the presence of copper-bearing phases within the matrix of the sherds (**Fig. 6C**). Many cracks are caused due to temperature shock via rapid cooling within the fabric. The observation through reflected light mode in the bright field shows exactly how many copper droplets are within the sherds (**Fig. 6D**). The droplets are surrounded with sulphide ores as the relics from silica melt as explained above. The sulphides are in the same composition and crystal stage as have been determined within the slag, and they show similar use in these objects. The pottery sherds thus have been used as technical pottery throughout copper extraction. The microtexture of the Shahdad pottery shows that they have been used for metal extraction and are the pieces from chimneys.

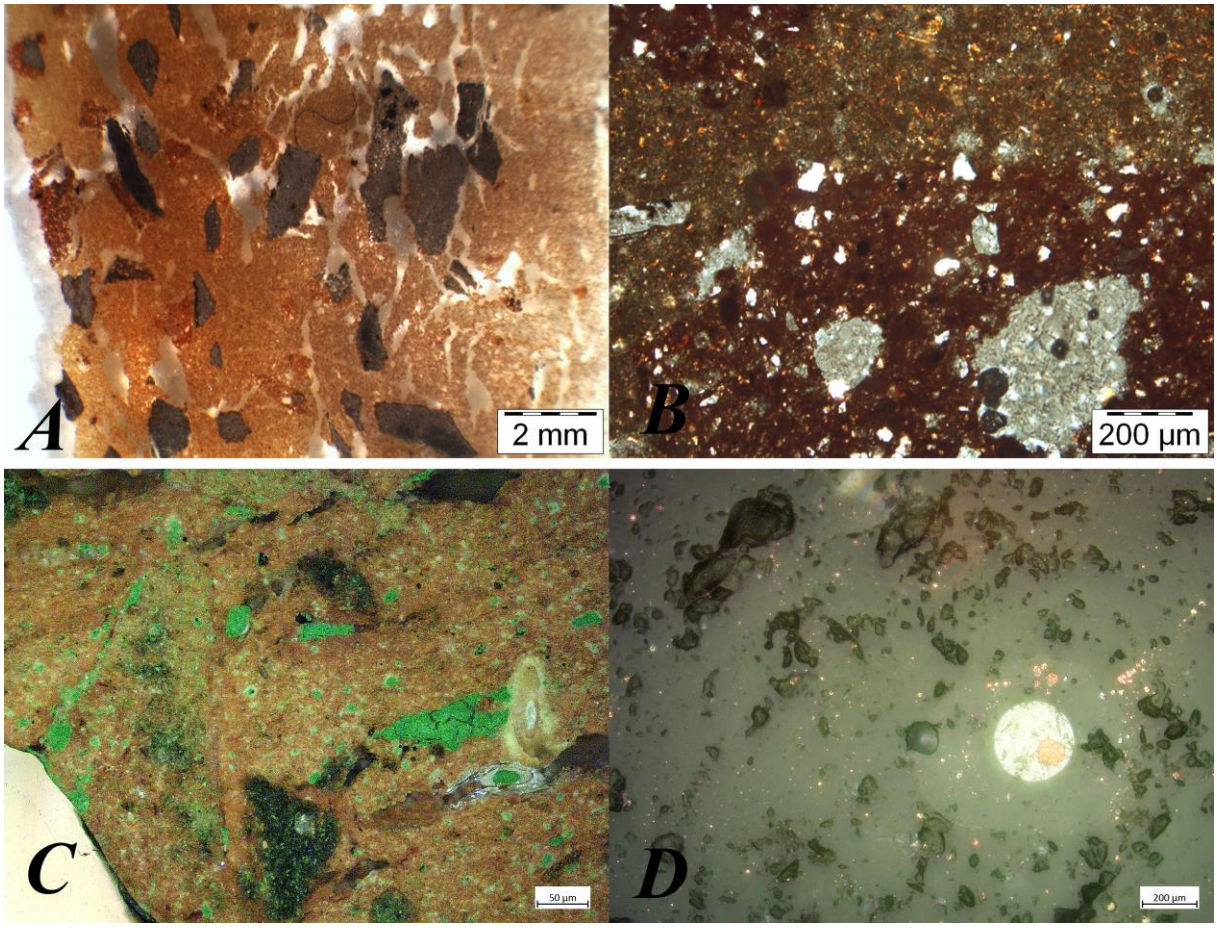

Fig. 6.: Microtexture of the Shahdad pottery types used for metal extraction through different types of observation: (a) viewed with a loop; (B) observation with a polarized microscope under cross-polarized light; (C) observation with a polarized microscope under reflected light and dark field; (D) microscopic view under reflected light mode.

6. ábra: Fém kinyerésére használt shahdadi kerámia (Sh.C_01) mikroszerkezetéről készült különböző felvételek: (A) nagyítóval készült felvétel; (B) polarizációs mikroszkóppal készült kép merőleges polarizátor állás esetén; (C) polarizációs mikroszkóppal készült visszaszórt felvétel sötét látóterű megvilágítás esetén; (D) mikroszkópos felvétel visszaszórt fénnyel.

Conclusion

Shahdad is one of the essential localities for the study of the early beginning and use of copper in the Central Iranian Plateau. Shahdad is located close to the Lut Desert in the Central Iranian Plateau. Archaeometallurgical researchers have been interested in Shahdad due to the widespread metallurgical activities (and remains of such activities) during the Early Bronze Age. Field surveys have already confirmed the early use of copper through metallurgical remains, e.g., slags and pottery. Archaeological studies have shown that the periphery of Shahdad to be a permanent city dating back to the 3rd millennium BC. Shahdad was prosperous due to the presence of important evidence of ancient metallurgical remains related to copper extraction. In accordance with the landscape of Shahdad, consisting of many fragments of metal tools, copper ores, moulds, crucibles, and additionally remains of furnaces, scientific research still can be enforced.

Pottery sherds and slags have been observed macroscopically and microscopically to find particular traces of metallurgy from the heyday of this region.

Investigations were supplied with a new synopsis by re-tracing the copper metallurgy. It is revealed that they mainly used copper sulphide (covellite) as Cu-bearing ores. Two different types of slag were identified regarding their color, texture, and fabrication. Pottery sherds were also associated with copper metallurgy based on copper carbonate and copper oxide enrichments often occurring inside their porosity. Microscopic observation of slag and sherds indicate that the used copper ores mostly consist of covelline-chalcocite bearing ores. The smelting strategy is implemented under the control of accessible technological factors such as the level and type of technology at that time in the Early Bronze Age, accessible raw materials (ores), and technological circumstances, e.g., vegetation for producing the heat and clayey soil for earthen based constructions. Moreover, the complexity of metallurgy in Shahdad established a precise knowledge of innovation and/or adaptation of technological features, which were transferred to other areas such as Jiroft and Tal-e Iblis in the south and southeast of Kerman province.

Contribution of authors

Mohammadamin Emami Conceptualization, Resources, Writing – Original Draft, Writing – Review and Editing, Formal Analysis, Investigations, Supervision. **Soraya Elikay Dehno** Methodology, Formal Analysis. **Nasir Eskandari** Data Curation. **Christian Pritzel** Methodology, Formal Analysis, Visualization.

Acknowledgements

The experimental work presented in this paper has been carried out in the framework of the research project, "Archäometrische Untersuchungen an Keramiken aus ARATTA Kultur, Jiroft (4th – 3rd B.C.) im Südzentraliran: Ein Einblick in die Verfahrenstechnik und Herkunft", with reference number AZ 53/V/22 financed by the Gerda Henkel Stiftung at the department of Chemistry & Structure of Novel Material, University of Siegen, Germany. The corresponding author deeply appreciates this support. The corresponding author is also sincerely thankful to the colleagues from the Department of Chemistry & Structure of Novel Material especially Prof. Manuela Killian director of the department, Dr. Torsten Kowald and Andrea Born for their collaboration and support during this research. The corresponding author is grateful for constructive comments from two anonymous reviewers; any remaining errors are our own.

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HU ISSN 1786-271X; urn: nbn: hu-4106

HU ISSN 1786-271X; urn: nbn: hu-4106

FROM BOOM TO BUST ON THE ATLANTIC FRINGE - COPPER SUPPLY NETWORKS IN THE IRISH LATER BRONZE AGE. AN INTRODUCTION TO A RECENTLY FUNDED RESEARCH PROJECT

A FELLENDÜLÉSTŐL A BUKÁSIG AZ ATLANTI PEREMVIDÉKEN – RÉZELLÁTÁSI HÁLÓZATOK A KÉSŐ BRONZKORI ÍRORSZÁGBAN. BEVEZETÉS EGY ÚJONNAN INDULÓ PROJEKTBE •

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Abstract

A recently funded project aims to investigate and identify the primary ore sources employed in the production of copper during the Later Bronze Age (1500–800 BC) in Ireland. We introduce the project and its objectives, with a focus on analytical methodologies.

Kivonat

Az újonnan indult kutatási projekt célja a réz előállításához használt elsődleges ércforrások vizsgálata és azonosítása a késő bronzkori Írországban (Kr. e. 1500–800). A cikkben bemutatjuk a projektet, annak célkitűzéseit, különös tekintettel a kutatás során alkalmazott vizsgálati módszerekre.

KEYWORDS: IRELAND, LATER BRONZE AGE, COPPER, METALWORK PRODUCTION, SOCIAL NETWORKS

KULCSSZAVAK: ÍRORSZÁG, KÉSŐ BRONZKOR, RÉZ, FÉMFELDOLGOZÁS, KÖZÖSSÉGI KAPCSOLATOK

Introduction

Throughout the European Bronze Age (c. 2500–800 BC), metallurgy played a crucial role as a catalyst for significant societal change. Despite regional variations, archaeological evidence suggests that the adoption of this new technology and the development and use of metal tools, ornaments and weapons had a profound impact on the economic dynamics, social hierarchies and political structures of the communities of the time (Pare 2000; Kienlin et al. 2009; Roberts et al. 2014; Earle et al. 2015). In particular, the rapid development and adoption of metallurgy across Europe led to an escalating and widespread demand for raw materials that were not always available locally, such as gold, copper, and later tin, but which were essential for metalwork production.

As shown by laboratory studies on Chalcolithic and Bronze Age copper-base metals from different European regions (e.g., Melheim et al. 2018; Canovaro et al. 2019; Holmqvist et al. 2019; Ling et al. 2019; Radivojević et al. 2019; Nørgaard et al. 2021; Aragón et al. 2022; Berger et al. 2022; Bottaini et al. 2022; Brandherm et al. 2022; Čivilytė et al. 2023; Artioli et al. 2024; Bruyère et al. 2024, just to mention a representative group of papers from recent years), the search for these new raw materials in areas beyond their direct control would have led Bronze Age communities to make new contacts in order to obtain them. This would have provided the basis for the establishment of new networks of exchange and a complex web of interactions, still to be fully explored, facilitating connections between societies that had previously been isolated from one another.

• How to cite this paper: BOTTAINI, C. & BRANDHERM, D. (2024): From Boom to Bust on the Atlantic Fringe - copper supply networks in the Irish Later Bronze Age. An introduction to a recently funded research project, *Archeometriai Műhely* **XXI/3** 265–274.
doi: https://doi.org/10.55023/issn.1786-271X.2024-021

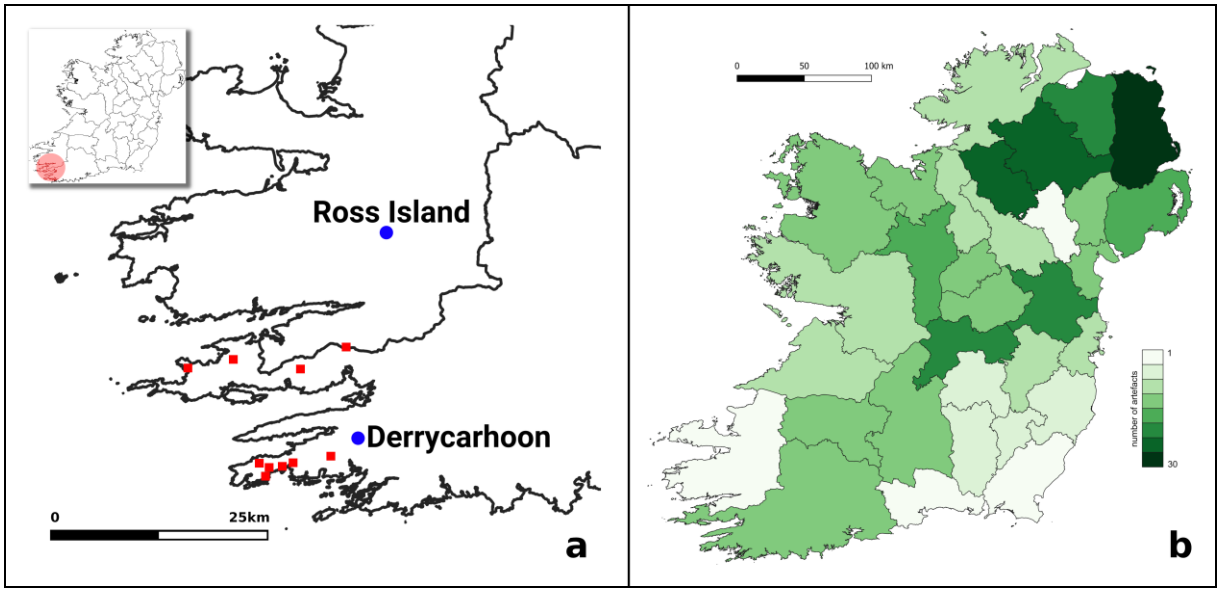

Fig. 1.: (a) Location of the copper mining sites cited in the text (based on O'Brien 2013, 192). Red squares refer to Mount Gabriel-type mines. (b) Geographical distribution of the artefacts to be analysed in the project by county.

1. ábra: (a) A szövegben említett rézbányászati helyek (O'Brien 2013, 192 alapján). A piros négyzetek a Mount Gabriel-típusú bányákat jelzik. (b) A vizsgálandó régészeti leletek földrajzi eloszlása megyék szerint.

In Ireland, for example, early metal artefacts appear around the middle of the 3rd millennium BC. This may be due to the mobility of specialised metalworkers or the limited migration of small, skilled groups from mainland Europe, possibly related to the expanding Beaker network, which fostered links across Atlantic Europe (Case 1966; O'Brien 2023a, 147).

Copper objects in circulation during this first phase included a limited range of artefacts, including copper and bronze flat axes, halberds and daggers (Harbison 1969a; 1969b). They were predominantly made from unalloyed copper, with arsenic in the 1–5% range, and other impurities, namely antimony and silver. The presence of this distinctive arsenic-antimony-silver trace-element pattern was found to be characteristic of ore from Ross Island, Co. Kerry (**Fig. 1A**). The use of this mine dates back to around 2400 BC, making it one of the oldest known copper mines in north-west Europe (O'Brien 1995, 43). Analytical data indicate that Ross Island was the sole source of copper for Ireland during the Beaker period, supplying not only the island but also much of Britain (Northover 1982, 51; Rohl & Needham 1998, 87; Northover et al. 2001, 40; Bray 2012, 72) and, eventually, Brittany (Gandois et al. 2019).

The introduction of tin alloys, generally accepted from 2200–2100 BC onwards (see O'Brien 2023b, 304 for further discussion), and the subsequent widespread adoption of tin bronze as the standard copper alloy during the Irish Bronze Age, brought about changes in the Irish mining industry, which materialised with the decline in the exploitation of arsenic-rich ores at Ross Island. While the existence of Irish tin mined during this period is not currently supported by archaeological findings (Budd et al. 1994; Warner et al. 2010), it is noteworthy that the abandonment of Ross Island is documented to have occurred around 1900–1800 BC (O'Brien 2011, 354). Interestingly, this period coincides with the beginning of the exploitation of new copper resources, characterised by shallow deposits of oxidised ores.

These new deposits proved to be less rich but more accessible to copper miners than the copper ore previously mined on Ross Island. The newly established mines were located on Mount Gabriel and other sites on the West Cork Peninsula (O'Brien 1994; 2003, 49; Briggs 2003). The supply of copper from Mount Gabriel-type mines continued until about 1400 BC (O'Brien 2013, 193), marking an era of increasing scale of metal production and a diverse range of products.

During the Later Bronze Age (i.e., the Middle Bronze Age, c. 1600/1500–1200 BC, and Late Bronze Age, c. 1200–800 BC), evidence for copper mining in Ireland becomes increasingly scarce. After the exhaustion of the Mount Gabriel-type mines, the only evidence of Irish mining activity is documented at Derrycahoon, which remains active until around 1100 BC (O'Brien 2019, 137; among others, see also O'Brien & Hogan 2012; Kearney & O'Brien 2021; O'Brien 2022). If by the end of the

Early Bronze Age Ireland was no longer self-sufficient in copper and had lost its role as the main supplier of this raw material to the rest of the Atlantic Archipelago, the abandonment of Derrycarhoon marks the definitive end of pre-historic mining on the island, which had begun more than a millennium earlier on Ross Island. Interestingly, as Irish copper mining experienced a significant decline, we witness a notable expansion in the scale and variety of metal artefacts produced on the island, which became particularly pro-nounced during the Late Bronze Age (Eogan 1964; Ó Faoláin 2004).

Within this context, a question that aligns with the central line of inquiry of the project 'From Boom to Bust on the Atlantic Fringe: Copper Supply Networks in the Irish Later Bronze Age' arises: Where did the copper used by Later Bronze Age Irish metalworkers come from?

In contrast to the well-documented nature of the origin of copper in the Beaker period/Early Bronze Age, the prove-nance of the raw material for Irish Later Bronze Age metalwork represents a signi-ficant gap in the available data. To date, only nine copper-base Middle and Late Bronze Age axes from Ireland have been analysed for both elemental composition and lead isotope ratios. Although statistically limited, the available data are sufficient to suggest that the end of mining activity in Ireland marked a significant shift in the supply of copper. Indeed, if Irish copper fuelled metalworking throughout the island until the mid-2nd millennium BC, none of the axes analysed appear to have been made from Derrycarhoon ore, and only one object has analytical characteristics consistent with the Mount Gabriel mines. Six objects are consistent with the geochemistry of the Great Orme (Wales), while three others have lead isotope compositions similar to those typically associated with copper ores from southern Spain. The available data, although based on an extremely limited number of objects, suggest a clear change in copper supply from the beginning of the Later Bronze Age at the latest, when Ireland went from being a net exporter to a net importer of copper, suggesting that copper arrived in Ireland via a rather complex long-distance network (O'Brien 2022: 168-173).

The project

Project aims

As outlined above, although the archaeological evidence from Derrycarhoon suggests that Irish mining continued into the Middle Bronze Age, it is undeniable that the archaeological record points to a gradual decline in local copper mining across Ireland in the second half of the 2nd millennium BC. The mines explored during the Beaker/Early Bronze Age phase appear to have been exhausted, while the Derrycarhoon exploitation phase does not extend beyond the beginning of the Late Bronze Age.

Based on these premises, the 'From Boom to Bust' project aims to identify the sources of copper that supplied Irish metalworkers with this raw material between the mid-2nd and early 1st millennium BC. At the same time, an extensive radiocarbon dating programme on organic materials directly associated with metal artefacts will be undertaken to provide a reliable chronological framework for examining the changing patterns of copper supply over the course of the Later Bronze Age.

Archaeometallurgical analyses

Tracing the origin of raw materials used in the production of artefacts is a key issue in archaeo-logical research, contributing to the understanding of exchange networks and interactions between past communities at different geographical scales. Provenancing methodologies are often based on the observation that finished objects retain certain chemical and isotopic characteristics of the raw materials used in their production. This principle is not limited to metal artefacts, but also applies to other materials such as lithic tools (Kuzmin et al. 2020; Pétrequin et al. 2017), pigments (Velliky et al. 2021), and glass (Henderson 2013).

In the field of archaeometallurgy, the most common and widely used analytical approach for identifying the copper mining centres involved in meeting the demand for metals is to determine the isotope ratios of trace-element lead present in a metal artefact and compare them with the isotope ratios of ores that could have served as the source of that metal. The reliability of the isotope approach is due to the fact that the isotopic signature of lead is preserved during the metallurgical processes, meaning that the isotopic ratios of lead in a particular ore are reflected in the metal produced from that ore (Hauptmann 2020, 488-491; Villa 2009; Ceuster et al. 2023).

In addition to lead isotope analysis, chemical analysis intended mainly for the identification of trace element patterns is considered as a valuable complementary tool in identifying sources of raw materials for metal artefacts. Indeed, different geological sources and mining regions often have characteristic trace element patterns, and its combination with lead isotope analysis can be critical where isotope fields overlap or where isotope analysis alone has limitations in distin-guishing potential sources (Pernicka 2014).

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Fig. 2.: Group of objects analysed within the project from the Archaeology & Palaeoecology teaching collection at the School of Natural and Built Environment, Queen's University Belfast. 1. Unknown; 2-5. "Ireland"; 6. Clogher (Co. Tyrone); 7. Portora (River Erne, Co. Fermanagh); 8. River Bann.

2. ábra: A projekt keretein belül megvizsgált tárgyak csoportja a Queen's University Belfast, School of Natural and Built Environment régészeti és paleoökológiai tangyűjteményéből. 1. Ismeretlen lelőhelyű tárgy; 2-5. „Írország"; 6. Clogher (Tyrone megye); 7. Portora (Erne folyó, Fermanagh megye); 8. Bann folyó.

However, this combined approach of isotopic and trace-element analysis is not without limitations of its own and can present challenges that sometimes prove insurmountable. From an analytical perspective, for example, the recycling and re-melting of scrap metal artefacts made from ores from different deposits can be a major limitation, as chemical and isotopic signatures can be obscured during the process, making it difficult to identify and differentiate the original sources (cf. Pernicka 1999; Bray et al. 2015; Pollard et al. 2018; Radivojević et al. 2019). In other cases, the chemical and isotopic signatures of different deposits may be very similar and overlapping, making it very difficult to distinguish them individually (cf. Stos-Gale & Gale 2009, 202; Vlad et al. 2011, 54; Ceuster et al. 2023, 19602).

Within the framework of our project, archaeometallurgical analyses will be carried out on a selected range of artefacts from across Ireland (**Fig. 1B**) and held in national and regional museums, including the National Museums of Northern Ireland, the British Museum, the Hunt

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Museum in Limerick and the Navan Centre & Fort in Armagh. These artefacts, comprising approximately 200 objects, mainly consist of palstaves, socketed axes, swords, and spearheads. The geographical spread of the sample aligns with the general distribution of Later Bronze Age metalwork deposits, which cluster towards the north and east of the island, away from the ore sources that fuelled Irish metalwork production particularly during the Early Bronze Age (**Fig. 2**). It is not envisaged to undertake additional analyses on Irish copper ores as part of this project, as the ore bodies known to have been mined during prehistory in the island are reasonably well characterised and their exploitation mostly predates the study period (Northover et al., 2001; O'Brien 2004; 2022).

Analyses will be conducted on metal shavings drilled from the bulk of the relevant artefacts, in order to avoid any possible distortion from surface corrosion layers. Samples will be then analysed through a multi-analytical protocol that combines Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) for lead isotope analyses, and Energy-Dispersive X-ray Fluorescence (ED-XRF) for major, minor and trace-element analyses. As an alternative to ED-XRF, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can occasionally be employed for trace element analysis.

The choice to use ED-XRF as the main technique for chemical analysis rather than IPC-MS, which has traditionally been the most widely used technique in archaeology for provenance studies of raw materials, has several reasons in the context of our project. Most importantly, comparative studies have shown that ED-XRF performed on drill samples of copper-base archaeological objects is competitive in terms of sensitivity with a number of other techniques, such as Neutron Activation Analysis (NAA), Atomic Adsorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and that it provides reliable results (Lutz & Pernicka 1996). The credibility and effectiveness of ED-XRF in carrying out trace element analyses is also supported by the fact that it is now part of the standard analytical methodology in a range of specialist archaeometallurgical laboratories, having been used routinely in a number of recent studies (Pernicka 2013; Nørgaard et al. 2019; 2021; Berger et al. 2022; 2023; Cornelis et al. 2023).

The case for ED-XRF as the primary technique for major, minor and trace element analysis over ICP-MS is further strengthened by the preservation of the relevant sample material during analysis. This is a clear advantage, especially when the amount of metal to be sampled needs to be minimised, as it allows MC-ICP-MS lead isotope analysis to be performed on the same drill shavings used for ED-XRF, significantly reducing the sample volume required to obtain reliable results. Finally, ED-XRF is known to be faster, allowing a greater number of objects to be analysed, and less expensive to run, reducing financial pressures on the project budget.

Radiocarbon dating

Archaeometallurgical analyses can help to determine the movement of the metal in space at a given point in time. To provide data with a diachronic dimension, taking into account temporal variation and historical context, our project will also undertake a programme of radiocarbon dating of organic materials directly associated with sampled metal objects. Through this broader approach, the project aims to understand how the spatial movement of metals has changed through time, and to capture shifts in metal supply patterns during the Later Bronze Age.

At present, the chronology of metalworking phases in the Irish Bronze Age is still largely dependent on typological comparisons with relevant British material, due to the limited availability of radiocarbon dates from the archaeological contexts of diagnostic Irish metalwork types (Brindley 2001; Becker 2011). New radiocarbon determinations of organic remains directly associated with metal objects will therefore have a dual impact. On the one hand, they will provide, for the first time, an independent and more reliable chronological framework than is currently available for Irish Middle and Late Bronze Age metalwork. Secondly, they will allow archaeometallurgical data to be interpreted within a robust chronological framework, and spatial changes in metal supply patterns revealed by elemental and lead isotope analyses to be placed within the same framework. This will be instrumental in relating both the metalworking stages and metal-supply patterns identified by this project to other economic and societal changes evident in the archaeological record of the period.

In a broader perspective, properly contextualised archaeometallurgical data become a crucial tool. Not only do they help to identify changes in the composition of the metal pool available at different metalworking stages and potential sources of supply, but they also help to assess how these changes relate to other transformations in the archaeological record. These changes include aspects such as population density, land use, settlement patterns and the emergence of powerful chiefdom-type polities that controlled key economic resources and trade. By undertaking this analysis, our project aims to facilitate the contextualisation of these developments within a broader insular and European framework.

HU ISSN 1786-271X; urn: nbn: hu-4106

Conclusions. Unravelling ancient networks through raw-material studies

Recent decades have seen a remarkable development in the archaeological study of the circulation and origin of raw materials during European prehistory, which has greatly improved our understanding of the use of resources in the past. This increased emphasis on material mobility has become an essential tool for reconstructing ancient trade networks and human interactions, improving our understanding of the socio-economic dynamics associated with exchanges and contacts between communities living in different regions.

However, the development of research in this area has not been uniform across Europe. The Irish Later Bronze Age is paradigmatic in this respect, highlighting a gap in our knowledge of the provenance of the copper used for domestic metalwork production. While the picture is sufficiently clear for the first millennium of copper processing (c. 2500–1500 BC), with Irish miners extracting sufficient copper to meet domestic demand and exporting surplus outside the island, the scenario becomes considerably blurred for the Later Bronze Age. From the mid-2nd millennium BC, the Irish mining industry appears to go bust, while copper-base metalwork manufacturing clearly booms. In the absence of local mining, where did the raw materials come from to meet the demand for domestic metalwork production? The data available so far, based on a dozen or so recently analysed objects, is inconclusive, although it suggests with some degree of certainty that the raw materials must have come from outside Ireland.

The data provided by our project aims to fill this gap in our knowledge, by shedding new light on the processes that governed the circulation of metal during the Later Bronze Age in Ireland. The close integration of state-of-the-art archaeometallurgical analysis and scientific dating methods will allow us to combine minor/trace element and lead isotopic 'fingerprints' of Irish Later Bronze Age metalwork with a radiocarbon-based chronological framework for reliably dating changes in the copper supply patterns inferred from the statistical analysis of these 'fingerprints'.

This, in turn, will allow us, for the first time, to assess the relationship between changes in copper supply patterns and other major transformations in the archaeological record of the Irish Later Bronze Age, and it will also permit us to trace new connections between Ireland, the wider Atlantic world and the rest of Europe, enabling us to re-assess the role of a geographically peripheral region such as Ireland within this/these network(s). The project will thus make a significant contribution to the ongoing international debate on the interconnection and interaction of Later Bronze Age communities across Europe and the Mediterranean.

Contribution of authors

Carlo Bottaini Conceptualization, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Dirk Brandherm** Conceptualization, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition.

Acknowledgements

The project is funded by the Portuguese FCT through the projects From Boom to Bust on the Atlantic Fringe – copper supply networks in the Irish Late Bronze Age and 'Laboratório HERCULES – Herança Cultural, Estudos e Salvaguarda'. Carlo Bottaini also acknowledges the UKRI's guarantee funding for his Marie Curie Individual Fellowship.
http://doi.org/10.54499/2022.04844.PTDC
https://doi.org/10.54499/UIDB/04449/2020
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HU ISSN 1786-271X; urn: nbn: hu-4106

HANDHELD XRF IN CERAMIC RESEARCH: A CASE STUDY FROM THE LOWER GUADALQUIVIR REGION

KÉZI XRF MÓDSZER A KERÁMIAKUTATÁSBAN: ESETTANULMÁNY AZ ALSÓ-GUADALQUIVIR RÉGIÓBÓL •

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Abstract

Handheld X-ray fluorescence spectrometer in the last 15 years become very popular and nowadays is a well-established device in archaeometry. This paper presents reflections based on the practice of using a spectrometer over the last years, trying to highlight both the advantages and disadvantages of this tool. To illustrate the potential of the device for research on more general than technical issues in archaeology, the results of spectroscopic analyses from two, closely located archaeological sites in western Andalusia, Setefilla necropolis and Setefilla settlement, is presented. Thanks to the potassium-titanium test it can be noticed that the results vary for each site, and the differences in elemental composition are interpreted as manifestations of the intentional use of different paste recipes for specific social practices.

Kivonat

A kézi röntgenfluoreszcens spektrométer az elmúlt 15 évben nagyon népszerűvé vált, és ma már jól bevált eszköz az archeometriában. Ez a tanulmány az elmúlt évek spektrométer-használati gyakorlatán alapuló észrevételeket mutat be, és megpróbálja kiemelni az eszköz előnyeit és hátrányait egyaránt. Annak illusztrálására, hogy a készülék milyen lehetőségeket rejt magában az inkább általánosabb, mint technikai kérdésekkel kapcsolatos régészeti kutatásokban, két, egymáshoz közel fekvő nyugat-andalúziai régészeti lelőhely, Setefilla nekropolisz és Setefilla település spektroszkópos vizsgálatának eredményeit mutatjuk be. A kálium-titán arány vizsgálatának köszönhetően megállapítható, hogy az eredmények az egyes lelőhelyeken eltérőek, és az elemösszetételben mutatkozó különbségeket a különböző kerámiapép receptek szándékos, meghatározott társadalmi gyakorlatokhoz igazodó használatának megnyilvánulásaként lehet értelmezni.

KEYWORDS: HANDHELD XRF, POTTERY STUDIES, POTASSIUM-TITANIUM TEST, ANDALUSIA, SETEFILLA

KULCSSZAVAK: KÉZI XRF, KERÁMIA TANULMÁNYOK, KÁLIUM-TITÁN ARÁNY, ANDALÚZIA, SETEFILLA

Initial remarks

The aim of this work is, on the one hand, to present the potential of a handheld X-ray fluorescence spectrometer for the study of archaeological ceramics, its advantages and disadvantages, and on the other hand, to demonstrate the usefulness of spectrometric results as a basis for formulating hypotheses in the field of social archaeology. The literature on the subject abounds with works presenting analysis results, but not all of them include data interpretations that are significant for understanding social phenomena.

Specialized analysis of archaeological artefacts has a remarkable tradition dating back to the 19th century. Researchers have long been interested in the material, from which the artefact was made, as well as its technology and chronology. Artefacts were sometimes sent to laboratories where chemical composition analyses were carried out. One of the earliest examples of interest in the chemical composition of artefacts is the work of Albin Węsierski, a researcher of the Ostrów Lednicki stronghold, who as early as 1870 collaborated with pharmaceutical laboratories by sending them medieval artefacts (Fogel 1991: 23).

• How to cite this paper: KRUEGER, M., (2024): Handheld XRF in ceramic research: a case study from the Lower Guadalquivir region, *Archeometriai Műhely* **XXI/3** 275–284.
doi: 10.55023/issn.1786-271X.2024-022

Another example is the research conducted by Hans Dragendorff, who in 1895 provided samples of terra sigillata pottery to a pharmaceutical laboratory at the University Dorpat (nowadays the University of Tartu) to determine their elemental composition (Helfert 2023, 409).

In the post-war period, chemical analyses of archaeological objects have been facilitated by the use of handheld spectrometers. Early models of portable spectrometers used for the analysis of artefacts appeared in the 1960s, with the University of Berkeley being the first academic centre where XRF was applied (Shackley 2011, 11). Interestingly, one of the first handheld spectrometers was developed in Krakow, Poland in the Experimental Department of the Nuclear Technology Office, officially named FAR-1 in 1968 (Manecki & Niewodniczański 1988, 647). It was also used for studying archaeological artefacts, especially coins. Ceramic materials began to be commonly examined using handheld spectrometers only in the current century.

It's interesting to consider the relationship between theoretical currents in archaeology and archaeological science. The appearance of the first XRF spectrometers coincided with the birth of a new theoretical perspective called New Archaeology or processual archaeology with its program aimed to understand past societies through the analysis of cultural processes and their environmental contexts (Johnson 2008, 20-25). Processual archaeologists believed that the introduction of technical research tools and precise measurements can turn the results into objective facts and allow for the formulation of laws of cultural dynamics (Marciniak & Rączkowski 2001, 9-11). Methods adopted from the natural sciences were thought to ensure objectivity of cognition (Marciniak & Rączkowski 2001, 9). In consequence, an increasing amount of archaeological data was studied using scientific techniques. For this reason, X-ray fluorescence spectrometers, like other technical equipment, have become valued tools in archaeology.

In the next decades, the development of compact spectrometers took place, finding applications in geology, environmental sciences, and of course, archaeology, especially in the 21st century. From the beginning of the 1980s, another theoretical perspective, postprocessualism, emerged. The postprocessualists had a critical attitude towards the program of processual archaeology. They were convinced that it is crucial to consider the broader cultural, social, and symbolic contexts (Johnson 2008, 107; Jones 2002, 74-75) of the raw data generated by technical devices, such as handheld XRF, in order to construct multifaceted interpretations of the past. What is more, the emphasis on individual human actions sidelined more detailed analytical activities (Marciniak & Rączkowski 2001, 11). Changes in the perception of archaeology and its goals have diminished interest in archaeological science. In consequence, visible separation of archaeology and archaeological science took place. The results of specialized analysis will be utilized in this study to demonstrate their usefulness for social archaeology.

It is worth adding that the analysis of Andalusian ceramic samples using handheld spectrometers from the transition period between the Bronze Age and Iron Age has a several-year tradition. It has been argued that ceramics from some archaeological sites have different chemical characteristics (Krueger & Brandherm 2019), and the elemental composition of various types of ceramics characteristic of this region and period has been determined (Krueger et al. 2020, Krueger 2022b, 2023).

Handheld XRF in the archaeologist's practice

After presenting the general development of portable spectrometers in the context of the history of archaeological thought, it is necessary to focus on to the strengths and weaknesses of this analytical tool. There is no doubt that handheld X-ray fluorescence (XRF) analysers have some limitations, such as lack of laboratory precision, a limited detection range, and elemental interference (Chubarov et al. 2024; Holmqvist 2017; Hunt & Speakman 2015; Shackley 2011). Handheld XRF analysers can provide qualitative information about the elemental composition of a sample, but the precision of their quantitative results can fluctuate based on the calibration of the specific instrument in use. This is clearly evident in the case of trace elements. Determining elements with a low atomic number using handheld XRF is possible but subject to a relatively high margin of error. This is influenced by several factors such as the low-energy radiation emission by light elements, their low concentration in ceramics, or spectral interferences (Hunt & Speakman 2015, 627-629). Additionally, the method of sample preparation can also affect the results (Chubarov et al. 2024, 264-266; Marino et al. 2022; Niedzielski et al. 2020, 1457).

The scope of analysis is limited to the surface of an investigated artefact. Pottery is not a homogeneous material, and in consequence, surface analysis outcomes may show fluctuations. What is more, the temper can affect the results (Mecking 2017, 202). The solution is to carry out multiple analyses in different points of a sherd and calculate the average. However, the results of investigations using a handheld spectrometer will not be as precise as those obtained through destructive laboratory analyses.

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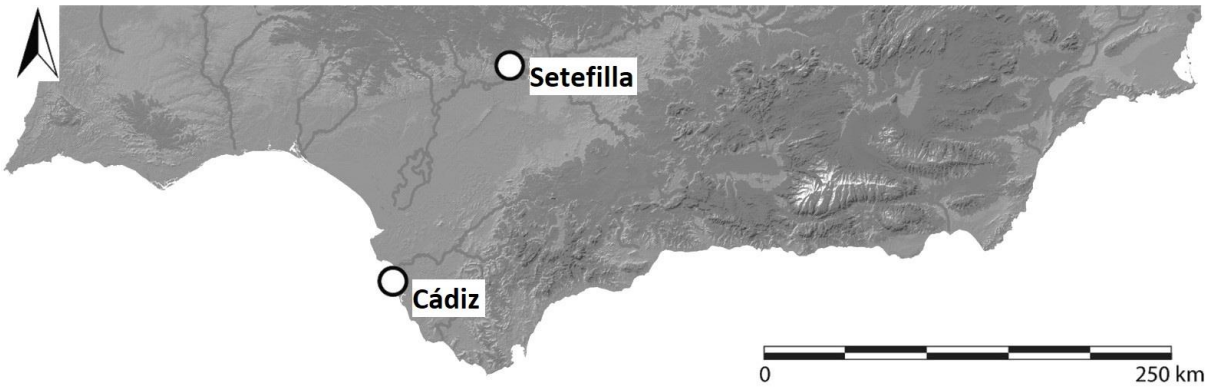

Fig. 1.: Location of Setefilla

1. ábra: Setefilla elhelyezkedése.

On the other hand, there are several arguments in favour of using handheld XRF. The spectrometer is relatively small and user-friendly, and it can be employed both in the laboratory and in the field (Shackley 2011). Besides pottery, it can also analyse other artefacts such as metals or obsidian. It enables determination of about twenty chemical elements depending on the device model and analytical mode. The analyses are quick and typically last from a few seconds to a few minutes. Its non-destructive character means that artefacts can be analysed in their natural state without special preparation. However, practice shows that, for example, grinding the sample can yield more precise results (Niedzielski et al. 2020).

Its greatest advantage, however, is that this device allows for obtaining important results to resolve archaeological problems. Rosemary Joyce, known primarily for her works in the field of social archaeology, posed a question about the value of conducting research using a handheld spectrometer (Joyce 2011). Her opinion was clearly positive and was based on the statement that technological issues are strictly linked to social relations. In the past, the choice of raw materials and technologies depended on factors such as tradition, beliefs or social organization. Using specific objects and techniques former communities could manifest their own identity or attachment to local traditions. From this perspective, results of XRF analysis may become of interest also to social archaeology (see also Krueger 2021, 448).

Setefilla case study

An exemplification of this viewpoint is the latest archaeometric research conducted on pottery samples from Setefilla necropolis and Setefilla settlement, archaeological sites located in south-western Spain.

These are sites of indigenous population situated approximately 150 km northeast of the main Phoenician colony on the Iberian Peninsula, Gadir (now Cádiz) (**Fig. 1**). Setefilla necropolis is one of the best-known sites in the Lower Guadalquivir region. It was excavated by J. Bonsor (Bonsor & Thouvenot 1928) in the 1920s and by M. E. Aubet (1975, 1978, 1980-81) in the 1970s. The archaeological materials from this site underwent numerous specialized analyses, mostly archaeometric (e.g., Brandherm 2022; Czarnetzki 2022; Krueger 2022a; Moreno 2022). The settlement, located less than 1 km to the north from the necropolis, is significantly less known. The most comprehensive work on it is the monograph edited by M. E. Aubet et al. (1983).

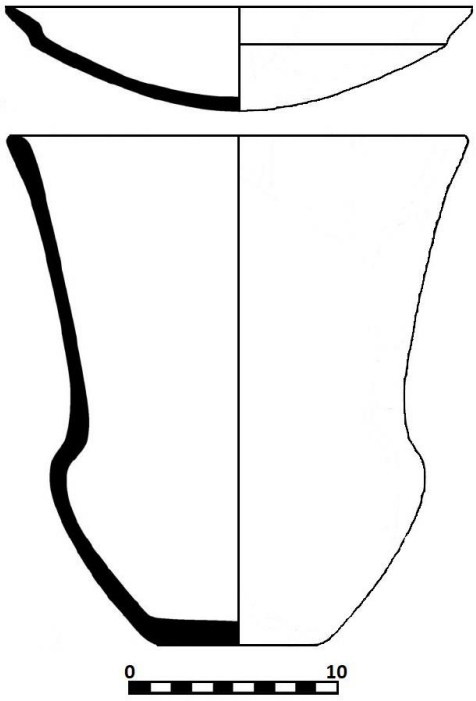

Fig. 2.: Example of a carinated bowl and *à chardon* vessel (digital drawing based on Aubet 1978, 192).

2. ábra: Példa egy karéjos tálra és egy à chardon edényre (digitális illusztráció Aubet 1978, 192 alapján).

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The use of the handheld XRF enabled the obtainment of interesting results about the pottery from these two sites. It became possible to identify different elemental composition of Late Bronze Age/Early Iron Age local, handmade vessels: carinated bowls and *à chardon* containers (**Fig. 2., Table 1.** and **2.**, initial results and standard deviation values see Krueger 2022a, 2022b, 2023). These types of vessels constitute emblematic ceramic forms of the Lower Guadalquivir region used in settlements and in cemeteries.

The bowls belong to an open type characterized by the presence of a shoulder separating the rim from the body and very often they have burnished surfaces of dark colours. This type of ceramic vessel is widespread in Andalusia in the Bronze Age and the Early Iron Age. Very characteristic for the Early Iron Age is the *à chardon* vessel, it has a globular body and a bell-shaped neck. Due to the vessel's function as either an urn or a storage container, its size is typically large (Moreno 2023).

Table 1.: List of the samples from Setefilla necropolis and Setefilla settlement (stratigraphic trench 3). The range of the radiocarbon dates is based on Brandherm 2022.

1. táblázat: A setefillai nekropoliszból és településről származó minták listája (3. rétegtani árok). A radiokarbon kormeghatározás tartományai Brandherm 2022 alapján jelölve.

Sample ID	Inventory number	Form	Chronology	Location	Archaeological context
1	St. A. 148-172	*à chardon*	Early Iron Age (754–412 cal BC)	necropolis	grave A8
5	St. A. 173	*à chardon*	Early Iron Age (808–543 cal BC)	necropolis	grave A10
10	St. A. 102	*à chardon*	Early Iron Age	necropolis	grave A3
11	St. A. 592	*à chardon*	Early Iron Age (749–391 cal BC)	necropolis	grave A31
13	St. A. 30-44	*à chardon*	Early Iron Age	necropolis	grave A1
14	St. A. 54	bowl	Early Iron Age	necropolis	grave A1
16	St. A. 121	bowl	Early Iron Age	necropolis	grave A6
17	St. A. 83-103	*à chardon*	Early Iron Age	necropolis	grave A2
26	St. A. 632	*à chardon*	Early Iron Age	necropolis	grave A34
28	St. A. 776	bowl	Early Iron Age	necropolis	grave A38
35	St. A. 893	*à chardon*	Early Iron Age (749–408 cal BC)	necropolis	grave A43
36	St. A. 868	bowl	Early Iron Age (749–408 cal BC)	necropolis	grave A43
53	S-79-3-XI-1637	bowl	Early Iron Age	settlement	stratum XI
58	S-79-3-XIII-2252	bowl	Final Bronze Age	settlement	stratum XIII
61	S-79-3-XIIA-1777	bowl	Final Bronze Age	settlement	stratum XIIA
62	S-79-3-XIIB-2152	bowl	Final Bronze Age	settlement	stratum XIIB
63	St. A. 499	*à chardon*	Early Iron Age	necropolis	grave A24
67	St. A. 534	bowl	Early Iron Age	necropolis	grave A25
68	St. A. 542	bowl	Early Iron Age	necropolis	grave A27
73	S-79-3-X-1601	*à chardon*	Early Iron Age	settlement	stratum X
74	S-79-3-X-1601	*à chardon*	Early Iron Age	settlement	stratum X
75	S-79-3-IX-1467	bowl	Early Iron Age	settlement	stratum IX
80	S-79-3-VIII-1266	bowl	Early Iron Age	settlement	stratum VIII
87	St. A. 1085	bowl	Early Iron Age	necropolis	A61
88	St. B. 61	*à chardon*	Early Iron Age	necropolis	grave B1
90	St. B. 70	*à chardon*	Early Iron Age (830–569 cal BC)	necropolis	grave B2
91	St. B. 100	bowl	Early Iron Age	necropolis	grave B6
112	St. A. 894	*à chardon*	Early Iron Age (749–408 cal BC)	necropolis	grave A43
114	St. A. 79-57	*à chardon*	Early Iron Age	necropolis	tumulus fill
120	St. B. 79-6	*à chardon*	Early Iron Age	necropolis	grave B31
172	St. A. 541	*à chardon*	Early Iron Age	necropolis	grave A27

Table. 2.: Elemental composition (in wt%) of samples taken from hand-made bowls and *à chardon* vessels.

2. táblázat: Kézzel készített tálból és à chardon edényből származó minták elemösszetétele (tömeg%-ban).

Sample	Mg	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ba
1	3.138	11.439	22.531	0.176	0.400	0.776	3.267	0.429	0.018	0.016	0.033	7.356	0.003	0.002	0.006	0.008	0.053
5	2.274	14.268	21.981	0.151	0.207	1.631	3.633	0.495	0.019	0.000	0.251	6.355	0.003	0.004	0.006	0.005	0.094
10	2.709	9.606	19.844	0.093	0.366	0.209	4.472	0.784	0.024	0.002	0.064	6.350	0.003	0.001	0.008	0.005	0.167
11	6.135	10.542	24.457	0.107	0.381	0.447	2.854	1.005	0.034	0.016	0.038	5.105	0.003	0.004	0.007	0.006	0.247
13	5.550	11.735	23.967	0.197	0.348	0.212	3.512	0.579	0.025	0.011	0.049	7.916	0.004	0.003	0.009	0.005	0.132
14	3.560	8.912	20.165	0.116	0.393	0.209	2.973	0.724	0.034	0.011	0.046	7.569	0.004	0.002	0.008	0.005	0.134
16	8.876	11.473	24.393	0.147	0.191	0.156	2.697	0.816	0.029	0.013	0.021	7.093	0.004	0.001	0.006	0.002	0.085
17	5.322	8.144	19.279	0.386	0.096	0.405	6.953	1.051	0.023	0.000	0.102	5.805	0.004	0.000	0.008	0.005	0.436
26	5.616	10.114	21.711	0.121	0.176	0.333	2.569	0.967	0.042	0.008	0.032	6.275	0.004	0.002	0.008	0.001	0.177
28	4.661	12.228	23.691	0.144	0.184	0.870	2.911	1.039	0.029	0.002	0.058	5.419	0.004	0.000	0.006	0.006	0.276
35	4.403	9.007	23.345	0.086	0.241	0.320	2.699	0.901	0.032	0.007	0.034	5.284	0.003	0.003	0.006	0.005	0.188
36	5.729	11.264	23.731	0.125	0.171	0.175	2.810	0.802	0.033	0.022	0.037	5.949	0.003	0.003	0.006	0.004	0.179
53	0.780	9.352	24.660	0.072	0.220	2.646	1.191	0.456	0.016	0.013	0.028	5.884	0.003	0.005	0.008	0.007	0.043
58	2.177	7.731	21.168	0.298	0.248	1.639	3.287	0.765	0.030	0.002	0.105	6.450	0.004	0.001	0.007	0.006	0.244
61	1.148	9.616	21.700	0.201	0.225	3.186	2.444	0.568	0.013	0.004	0.047	6.216	0.003	0.000	0.005	0.002	0.159
62	0.756	10.552	25.820	0.114	0.258	3.187	1.315	0.342	0.008	0.011	0.026	5.280	0.002	0.003	0.008	0.005	0.117
63	1.179	7.746	18.521	0.106	0.190	0.060	2.555	0.865	0.029	0.004	0.080	6.183	0.004	0.001	0.006	0.005	0.132
67	0.869	6.922	20.392	0.064	0.209	0.127	1.507	0.944	0.032	0.009	0.008	5.655	0.004	0.002	0.005	0.004	0.086
68	0.969	8.336	20.803	0.059	0.182	0.164	3.247	0.551	0.022	0.009	0.032	5.831	0.003	0.002	0.006	0.005	0.016
73	1.285	8.047	20.415	0.075	0.193	0.974	3.149	0.482	0.017	0.014	0.028	6.653	0.003	0.001	0.006	0.004	0.047
74	1.595	9.843	22.990	0.143	0.386	0.923	3.266	0.384	0.007	0.012	0.033	6.463	0.003	0.001	0.005	0.004	0.273
75	1.657	8.542	23.267	0.131	0.220	0.932	2.866	0.586	0.017	0.012	0.022	5.942	0.003	0.002	0.004	0.006	0.180
80	1.125	6.695	19.545	0.311	0.301	1.528	3.393	0.623	0.018	0.010	0.043	6.457	0.003	0.002	0.006	0.005	0.355
87	2.322	8.043	22.000	0.112	0.222	0.149	1.910	1.013	0.049	0.005	0.033	5.545	0.004	0.001	0.006	0.004	0.134
88	2.360	8.657	21.205	0.129	0.520	0.126	2.396	0.828	0.025	0.005	0.028	6.092	0.003	0.001	0.005	0.005	0.124
90	1.341	10.841	22.876	0.178	0.190	2.276	6.834	0.505	0.003	0.009	0.029	4.378	0.002	0.005	0.006	0.009	0.137
91	1.339	7.194	18.098	0.161	0.155	0.149	3.527	1.255	0.057	0.002	0.021	4.313	0.004	0.001	0.005	0.005	0.316
112	3.093	5.158	12.663	0.000	0.105	0.035	1.590	0.340	0.000	0.001	0.012	5.548	0.002	0.000	0.006	0.009	0.000
114	1.226	7.138	17.348	0.197	0.130	0.429	7.223	0.522	0.010	0.008	0.033	6.494	0.003	0.002	0.007	0.006	0.096
120	0.441	5.751	17.219	0.001	0.129	0.352	2.247	0.249	0.012	0.015	0.054	2.799	0.001	0.017	0.015	0.016	0.015
172	0.407	6.783	17.475	0.044	0.135	0.085	2.234	0.833	0.027	0.008	0.039	5.741	0.003	0.001	0.005	0.006	0.053

HU ISSN 1786-271X; urn: nbn: hu-4106

31 samples from two sites, the necropolis and the settlement of Setefilla, were analysed. 14 samples were taken from bowls and 17 were taken from *à chardon* vessels (see **Table 1**). The vast majority of the samples are dated to the Early Iron Age (840/820–500 BC), only three pieces are dated to the Final Bronze Age (1300/1200–840/820 BC). All samples dated to the Final Bronze Age are from the settlement.

The samples were measured three times in different points of a sample using the analytical mode provided by the spectrometer manufacturer: Major Mud Rock (15 kV, 25 µA). This is a commonly used factory calibration intended for the analysis of ceramics and soils. The acquisition time of each measurement was 15 seconds and vacuum pump was employed. The accuracy of the readings was verified by analysing a sample of contemporary pot with a known chemical composition. Then the average of the results was calculated. The initial analysis of the results revealed that the only element that significantly differentiates the samples is potassium. Therefore, the K-Ti test was applied. The test, which allows for grouping artefacts based on their chemical characteristics, holds significant value, first emphasized in the article on the origin of cuneiform tablets (Goren et al. 2011).

Thanks to this tool, it can be seen that the group from the settlement exhibits relatively similar characteristics: it is characterized by high levels of potassium and generally low titanium content, while the samples from the funerary context are characterized by a relatively high levels of titanium and low potassium content (**Fig. 3**). There are some exceptions like sample 5 and 90, but despite this, the tendency is clear.

In general, high potassium content in pottery is related to the presence of high quantities of feldspar used as a temper, this is characteristic of pottery from various archaeological cultures (Iordanidis et al. 2009, 297, Mecking et al. 2017, 200). Potassium-rich minerals are illite (Darab 1972), muscovite (Reichenbach & Rich 1969), vermiculite and biotite (Wilson 2004). It has been observed that in case of handmade Neolithic ceramics, high potassium contents are found predominantly in coarse pottery (Mecking et al. 2017, 201). It has been also suggested that, apart from its natural occurrence in rocks, potassium levels can be raised by adding wood ash (Mitrai & Davit 2001, 25).

In the case of vessels from Setefilla, no clear petrographic differences were detected between vessels from the settlement and those from the cemetery. The high potassium content is also characteristic of carinated bowls, which cannot be classified as “coarse pottery”. Probably these trends cannot be associated with changes in tempering material, as there are no visible differences between the pottery from the settlement and necropolis in petrographic terms: the vast majority of samples from the settlement and the Setefilla necropolis belong to the same group classified by V. Moreno Megías as Group I (Moreno 2022, 216-218). Therefore, the high potassium content may be associated with the addition of wood ash to the clay used to produce vessels used in the settlement.

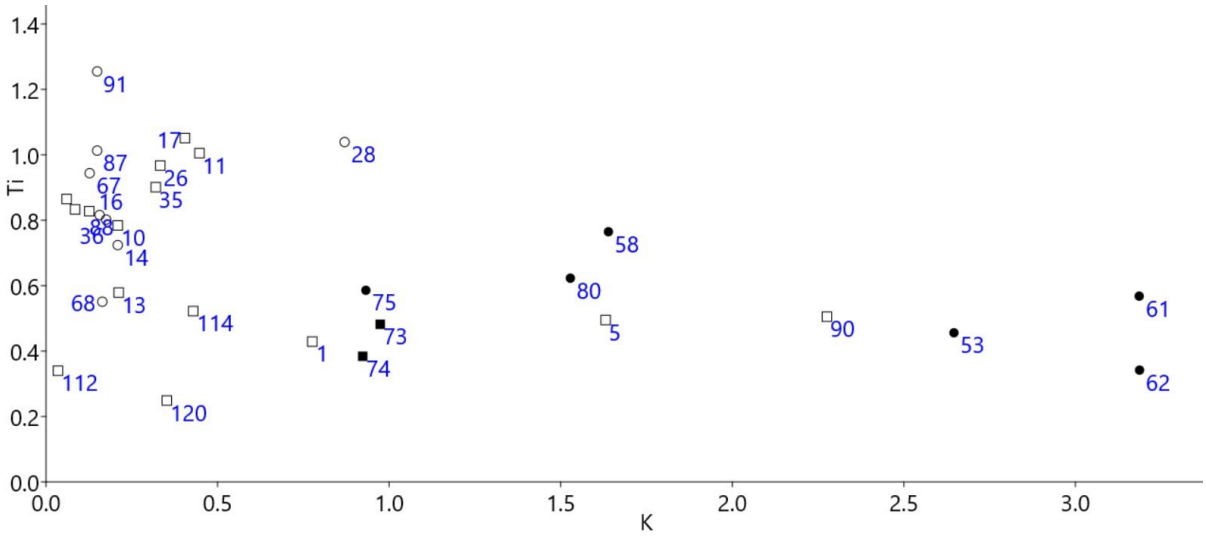

Fig. 3.: K-Ti test of the samples. Data plotted as wt%. Description of symbols: circle – bowl from the necropolis; black circle – bowl from the settlement; square – *à chardon* from the necropolis; black square – *à chardon* from the settlement.

3. ábra: A minták K-Ti aránya. Az adatok tömeg%-ban ábrázolva. Szimbólumok: kör - a nekropoliszból származó tál; fekete kör – a településről származó tál; négyzet – a nekropoliszból előkerült *à chardon* edény; fekete négyzet – a településről előkerült *à chardon* edény.

Another option is that that there was a gradual geological variation in the local clay deposits. These formations could have varied in potassium content. The high potassium concentration could also have been caused by weathering of biotite during which potassium is released and enters the soil (Wilson 2004, 251). The same applies to muscovite (Reichenbach & Rich 1969). Therefore, the clay itself, from which the vessels are made, can be a source of potassium. This could be the reason for the varying potassium content in vessels from two archaeological sites. It seems unlikely that differences in potassium content result from postdepositional processes; other studies (Stoner et al. 2014; Stoner & Shaulis 2021) have ruled out such a possibility.

What seems probable is that clay with slightly diverse chemical characteristics was sourced from other locations, or ceramic paste was prepared differently for vessels used for funerary purposes compared to those used in the settlement. The changes in potassium content suggest the use of special clays for different purposes: domestic and ritual. Differences in the chemical composition of the clay, although not visible macroscopically and microscopically, may reflect the need to produce pottery used as urns or as burial accompanying vessels. In this context, the presence of two samples (5 and 90) with a high potassium content in the necropolis is particularly interesting. Perhaps the vessels from which the samples originated were initially used as utilitarian containers in domestic environment, and at a certain point, it was decided to use them as funerary vessels. It should be emphasized that this applies to only two samples out of over thirty included in the study.

Ethnoarchaeological studies show that the selection and processing of clay are not random processes. Potters, when making specific choices, are guided by knowledge and experience, which include practical, social, ritual or symbolic factors (Gosselain & Livingstone Smith 2005, 41). The function of ceramic vessels may influence the choice of raw materials and production techniques: pottery used in ritual contexts may be produced using rare raw materials or more complex techniques to reflect their unique cultural significance.

It is worth mentioning O. Gosselain's research on the interaction between culture and technology in the context of ceramic studies in Africa. This author notes (Gosselain 1999, 218) that the use of sherds from vessels that belonged to deceased individuals to produce new ceramics may symbolize the continuity of life and connection with ancestors.

In the case of the ceramics from Setefilla, it is difficult to unequivocally interpret the detected differences in the elemental composition of sherds from the settlement and the necropolis, but issues related to cultural prohibitions and precepts seem to be a probable cause of the observed changes. This can be inferred because the examined vessels come from a settlement (profane sphere), and from a necropolis (sacred sphere). The preparation of vessels by the potter for different purposes was likely governed by distinct rules and practices.

Conclusions

Handheld X-ray Fluorescence (XRF) analysers despite their important limitations, offer several advantages; the most significant is the possibility to carry out a non-destructive elemental analysis of archaeological artefacts. The XRF results presented in this study complete the traditional image based on macroscopic attributes of the pottery: it is possible to verify that there were differences in the production of carinated bowls and *à chardon* vessels in two archaeological sites, one that is less than a kilometer away from the other. If we consider artefacts, including ceramics, as embodiments of norms and concepts, then the results of spectroscopic analysis can be interpreted as an exemplification of the belief in the close relationship between technological issues and social relations.

Contribution of the author

Michał Krueger Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition.

Acknowledgements

The author would like to thank the two reviewers of this text for their valuable comments. The research on the pottery from Setefilla was financed by the National Science Centre, Poland.

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HU ISSN 1786-271X; urn: nbn: hu-4106

HUGE AMOUNTS OF IRON RAW MATERIAL FROM THE EARLY IRON AGE SETTLEMENT OF DÉDESTAPOLCSÁNY-VEREBCE (N-HUNGARY) – A PRELIMINARY ARCHAEOMETALLURGICAL STUDY

KIEMELKEDŐEN NAGY MENNYISÉGŰ VAS NYERSANYAG DÉDESTAPOLCSÁNY-VEREBCE-BÉRC KORA VASKORI TELEPÜLÉSÉRŐL - BEVEZETŐ ARCHEOMETALLURGIAI TANULMÁNY •

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Abstract

The team of the Institute of Archaeological Sciences of the Eötvös Loránd University has been investigating the Early Iron Age hillfort at Dédestapolcsány-Verebce-bérc (Northeast Hungary) since 2020. The settlement was destroyed by siege in the late 7th century BC, as evidenced by hundreds of early Scythian bronze arrowheads and burnt buildings. Based on the recovered metal and pottery findings the settlement dated to the Early Iron Age in the Carpathian Basin (end of the 7th century – beginning of the 6th century BC).

The quantity of the Early and Middle Iron Age iron and bronze artefacts and pieces of iron raw material on the site is exceptionally high. More than 30 depots were unearthed which include pieces of iron raw material. In the whole territory, the number of these finds is more than 600. The average weight of the pieces was 1.54 kg. A few selected objects were sampled and subjected to archaeometric analysis (OM and SEM-EDS). The main aim of the examinations carried out by the experts of the Archaeometallurgical Research Group of the University of Miskolc (ARGUM) was the material characterisation of the samples to figure out what kind of processing has been applied and reveal how the iron raw materials can be connected in any way to the other iron objects found at the site.

Based on the results, it can be concluded that the iron pieces are compacted with a slightly heterogeneous structure. Each one is a part of a single bloom, not several pieces of different blooms assembled together. Numerous pores and cavities were observed in the microstructure of the samples. Their basic character is similar, although, they differ from each other, mainly in terms of carbon content and degree of forming. These pieces are not typical semi-finished products; they can be identified somewhere halfway between primary bloom and compacted bar.

Kivonat

Az Eötvös Loránd Tudományegyetem Régészeti Intézetének kutatói 2020 óta vizsgálják a Dédestapolcsány-Verebce-bércen (Északkelet-Magyarország) feltárt kora vaskori erődített települést. A települést a Kr. e. 7. század végén egy ostrom pusztította el, amit az itt előkerült több száz, bronzból öntött, korai szkíta nyílhegy és a leégett épületek maradványai bizonyítanak. A megtalált fém- és kerámia leletek alapján a település a Kárpát-medence korai vaskorára (Kr. e. 7. század vége – 6. század eleje) keltezhető.

A lelőhelyen előkerült vas- és bronz tárgyak, illetve nyersanyagtömbök mennyisége kiemelkedően magas. Több mint 30 olyan gödröt tártak fel, amelyben vas alapanyagok darabjai voltak. A teljes területen több mint 600 ilyen darab került elő. A vasdarabok átlagos súlya 1,54 kg. A leletek közül három kiválasztott darabon a Miskolci Egyetem Archeometallurgiai Kutatócsoportjának munkatársai archeometriai vizsgálatokat végeztek (OM és SEM-EDS). A vizsgálat fő célja a minták anyagszerkezeti sajátosságainak feltérképezése, feldolgozásuk lehetséges módszereinek feltárása. A kutatás során kérdés volt továbbá az is, hogy ezek az alapanyagok a

• How to cite this paper: TÖRÖK, B., BARKÓCZY, P. & V. SZABÓ, G., (2024): Huge amounts of iron raw material from the Early Iron Age settlement of Dédestapolcsány-Verebce (N-Hungary) – A preliminary archaeometallurgical study, *Archeometriai Műhely* **XXI/3** 285–294.
doi: 10.55023/issn.1786-271X.2024-023

vasfeldolgozási munkafolyamat melyik részéhez tartoznak és egyáltalán kapcsolatba hozhatóak-e a lelőhelyen előkerült többi vastárggyal.

Az eredményekből kiderült, hogy a vasdarabok tömörítettek és enyhén heterogén szövetszerkezetük van. Mindegyik önmagában egy darab kohósított buca része, nem több bucadarabot dolgoztak össze. A minták szövetszerkezetében számos pórus és üreg volt megfigyelhető. A vizsgált minták alapvető jellege hasonló, karbontartalmuk és alakítottságuk mértéke által mégis különböznek egymástól. A darabok nem tekinthetők tipikus félkész termékeknek, valahol a primer vasbuca és a tömörített tuskó között azonosíthatók.

KEYWORDS: IRON AGE; SCYTHIAN; RAW MATERIAL; ARCHAEOMETRY; METALLOGRAPHY

KULCSSZAVAK: VASKOR; SZKÍTA; NYERSANYAG; ARCHEOMETRIA, METALLOGRÁFIA

Introduction – archaeological background

The hillfort of Dédestapolcsány-Verebce is located on the north-western edge of the Bükk Mountains. This fortified settlement is divided into residential areas which covers ca. 150 hectares. The settlement was founded in the Early Iron Age, and it was destroyed by the siege in the late 7th century BC. An early Scythian military venture from the east, from the territory of the steppe horse nomads, besieged and occupied the flourishing center, as evidenced by hundreds of early Scythian bronze arrowheads, burnt buildings and melted bronze objects (V. Szabó 2023; V. Szabó & Bakos 2022, 337-343).

The last research work in this area started in 2020 and hundreds of iron, bronze and gold artefacts (jewellery, tools, daggers, sickles, etc.) and huge amounts of iron raw material were unearthed during the excavation. Interestingly, more than 30 depots, including pieces of iron objects (bloom or bar?), were found in this area. In the whole area, the number of these finds is more than 600 (V. Szabó et al. 2022; 2023). One of the most outstanding depots is the no. 2022/9. which contained altogether 96 pieces of such kind iron find (**Fig. 1**). The assemblage was discovered in the western parts of the examined territory in the summer of 2022. The average weight of the pieces was 1.54 kg, and the depot weight was ca. 145 kg in total. Based on the characteristic pottery found in the pit in question, the depot was dated to the Early Iron Age in the Carpathian Basin (end of the 7th century – beginning of the 6th century BC) (V. Szabó et al. 2022, 218).

Regarding the iron pieces some questions have arisen: what kind of semi-finished production are these pieces? Which manufacturing phase of the ironworking do they belong to?

Fig. 1.: Depot No. 2022/9 found at the hillfort of Dédestapolcsény-Verebce-bérc.

1. ábra: Dédestapolcsány-Verebce-bérc földvárának 2022/9. sz. depója.

The examined finds and the methods of analysis

Three iron finds (No. 1; 27; 46) were chosen for metallographic analysis. To examine the whole cross-section, 1 cm wide samples were taken from each object (**Fig. 2**). Considering the size of the artefacts, the sampling process was carried out by an industrial water jet cutter which ensured that the material did not heat up during the operation and avoided the changes in the microstructure of the samples. However, considering the technical possibilities of the microscopy, the samples were also cut into smaller pieces (**Fig. 2**), thus, none of them were longer than 6 cm so the samples were easily applicable for the examinations.

Before microscopic investigations, the samples were ground, polished, and etched with 2% Nital solution.

After that, the microstructure of the samples was examined with an optical microscope (Zeiss Stereo Axio Imager) equipped with a computer-controlled stage featuring mosaic imaging for the examination of the whole surface. Besides this, with the help of optical microscopy, it was possible to characterize the general phases and inclusions of the objects.

To identify the different phases in higher magnification and to perform elemental analysis, SEM-EDS measurements (Zeiss EVO MA10 scanning electron microscope equipped with EDAX energy dispersive spectroscopy) were taken. This method allows us the observe the phases, morphology, and structures in higher magnification. The examinations were carried out by the experts of the Archaeometallurgical Research Group of the University of Miskolc (ARGUM).

Although there is an abundant and growing literature on the early archaeometallurgy of iron, there are relatively fewer studies of primary iron blooms and the intermediate products of iron bars. In the comprehensive studies by Pleiner (2000; 2003) and Buchwald (2005), the basic characteristics of ancient iron blooms and bars are well-defined. However, there are few examples of detailed metallographic studies of iron blooms and even fewer studies in which the results of metallographic studies of primary blooms and the intermediate product made from them are discussed. Examples of the former include the study by Strobl and colleagues (2010) on the structure of medieval blooms with a diameter of 18–19 cm, and the latter is the article by Saage and colleagues (2017) on metallographic studies of iron blooms and bars found in 14th–17th century smithy sites. The medieval bloom from Styria was not forged and different microstructures of hypo-eutectoid and hyper-eutectoid materials were observed (Strobl et al. 2010). The metallographic analysis of iron blooms and bars from the smithy site of Käku (Estonia) has provided evidence for different steps in iron processing. Little or no marks of forging indicate that primary forging was done, and varying levels of quality could be detected among the iron bars (Saage et al. 2017). The study of Navasaitis and Selskienė (2007) should be mentioned for its unique topic. In this study, they report on the structural analysis of a small lump composed of separate cast iron trickles.

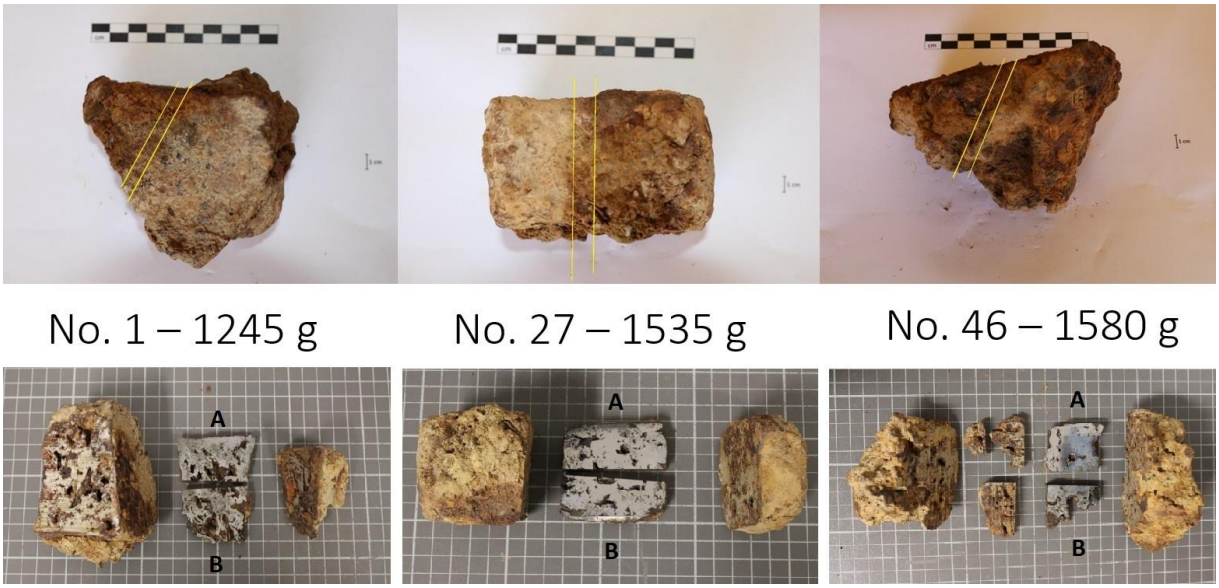

Fig. 2.: The iron objects examined. The yellow lines show the places where the samples were taken from.
2. ábra: A vizsgált vasleletek. A mintavételi helyeket sárga vonal jelzi.

Several metallographic studies have been carried out by our research group on samples of iron blooms, amongst which early medieval pieces weighing around 10 kg (Török et al. 2018) and iron blooms of extraordinary size from a Pannonian Late Roman fortress (Török & Barkóczy 2023) could be found. Regarding the Early Iron Age, metallographic analysis of an iron fragment from the tumulus of Regöly (Hungary) revealed a very specific microstructure, indicating that the supposed bloom fragment is not a direct product that came directly from the bloomery furnace; it could be a secondary (intermediate) product instead (Török et al. 2022).

Results and discussion

Sample No. 1/A and 1/B

Sample1/A shows a heterogeneous structure with a huge number of pores and cavities. The mosaic image in **Fig. 3.** is a good illustration of this diverse microstructure where areas with cementite, ferrite-pearlite and ferrite can also be distinguished. In a higher magnification, pearlite and secondary cementite can be identified beside the ferritic-pearlitic areas.

Because of this, the carbon content of the sample is relatively high (~ 0.7–0.8 wt%). Secondary cementite was also found in the microstructure of Sample No. 1/B. Areas with this structure were more common near the fragmented part of the sample (**Fig. 4**).

Inclusions were found in small quantities in the microstructure of Sample No. 1/A. They are located mostly near cavities and pores. These inclusions consist mainly of iron-oxide, but in a few instances, traces of Al-silicate grains were also observed which can originate from the lining of the bloomery furnace or forge.

In the case of Sample No. 1/B, extended inclusions with slaggy structures were detected in several places in the microstructure. SEM analysis revealed that such slag inclusions have heterogeneous structures. They typically originate from the smelting process. Wüstite dendrites (**Fig. 5A, 1**) and complex oxides of light elements (**Fig. 5A, 3**) were found between the fayalitic parts (**Fig. 5A, 2**), which are commonly present in the smelting slags and inclusions of ancient iron artefacts as well (Buchwald 2005, 96-104). Mn-, and P-contents indicate a smelting origin as well. Moreover, in some parts higher K-, and Na-contents were detected which may be derived from charcoal ash residues (**Fig. 5B, 4**). In certain areas, the metal formed islands with ferritic structures that are interspersed with thin pearlite bands. Between the ferrite grains, bridge-like slag-melt can be seen which is a kind of agglomerate (**Fig. 6**). This phenomenon does not mean metallic bounding, albeit the solid grains were coagulated together, and the formation of grain boundaries can already be observed in some places. In this process, the molten slag is a kind of accelerating passive medium (liquid phase sintering for rapid diffusion). It is a kind of conservation of a certain phase of the direct reduction process of the smelting.

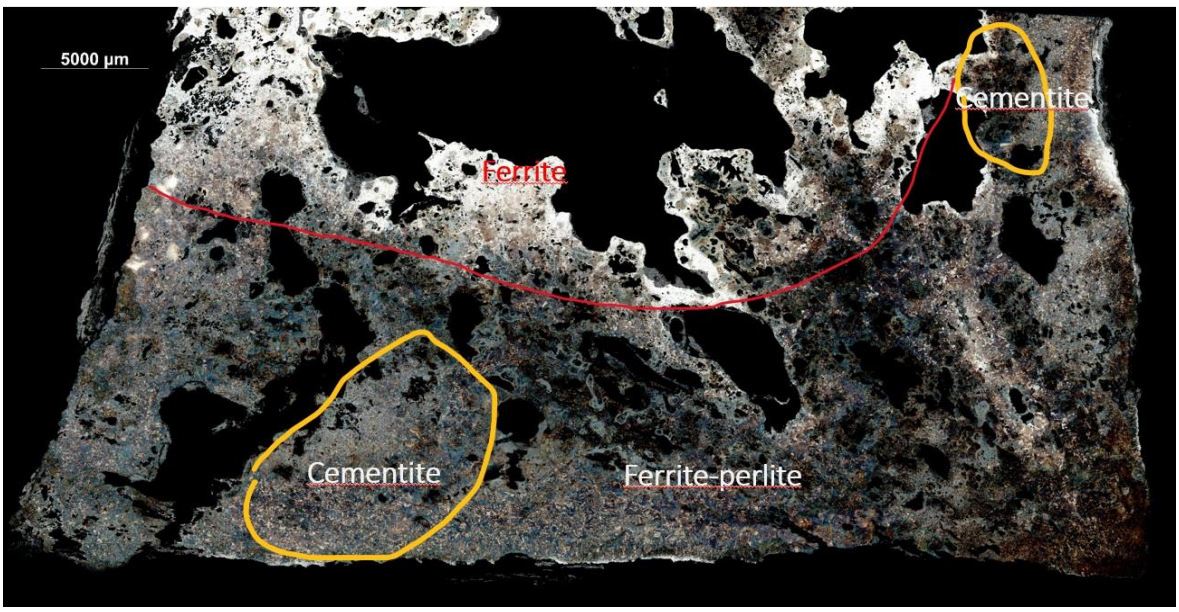

Fig. 3. SEM-BSE (back scattered electron) mosaic image of sample No. 1/A.

3. ábra: Az 1/A minta SEM-BSE (visszaszórt-elektron) mozaikfelvétele.

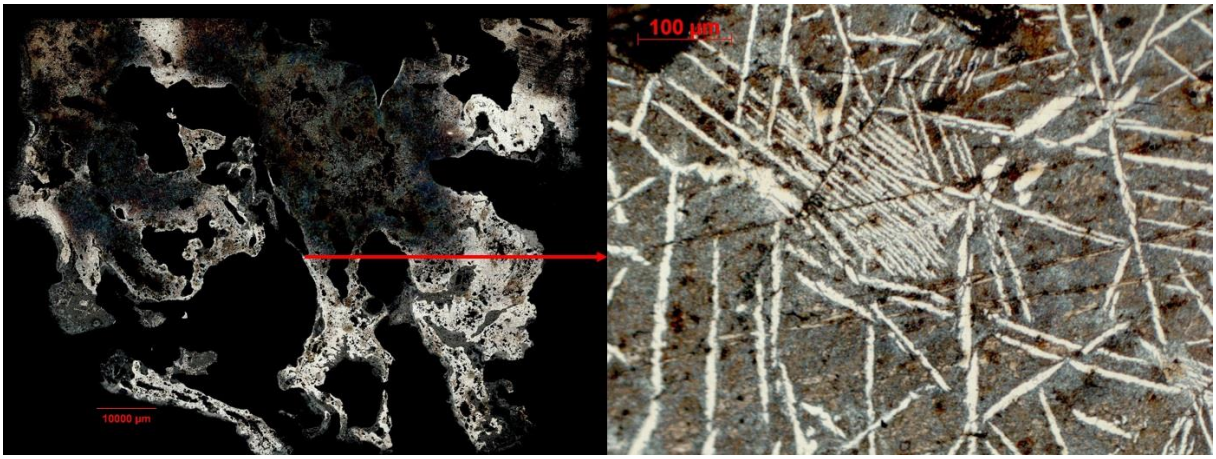

Fig. 4.: Secondary cementite (right) in the fragmented part of sample No. 1/B (left: SEM-BSE, left: OM image).

4. ábra: Szekunder cementit (jobbra) az 1/B minta töredékes részében (bal: SEM-BSE, jobb: optikai mikroszkópos felvétel).

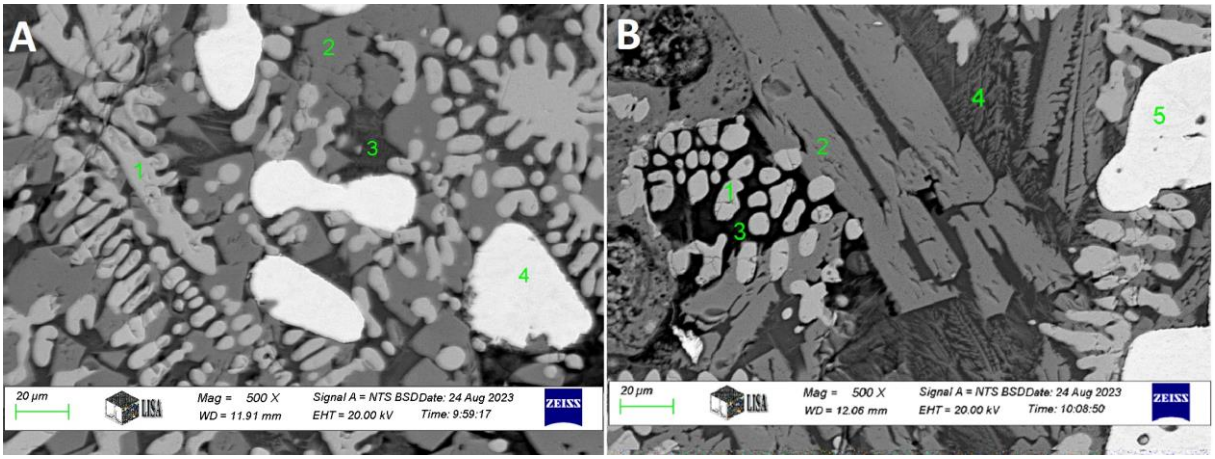

Fig. 5.: SEM-BSE images of inclusions in Sample 1/B.

Chemical compositions in wt%: A/1: O: 15.50; Al: 0.46, Fe: 84.04; A/2: O: 24.52,Al: 0.25, Si: 17.56,Ca: 2.05,Mn: 1.62, Fe: 54.00;A/3: O: 26.57, Na: 1.18, Mg: 0.25, Al: 7.70, Si: 21.05, P: 1.01, K: 4.78, Ca: 10.53, Ti: 0.38, Mn: 0.62, Fe: 25.94; A/4: Fe: 100; B/1: O: 15.45, Fe: 84.55; B/2: O: 23.18, Mg: 1.39, Si: 17.03, Ca: 2.61, Mn: 1.71, Fe: 54.08; B/3: O: 23.37, Mg: 0.22, Al: 10.59, Si: 11.92, P: 1.70, Ca: 4.11, Fe: 48.09; B/4: O: 25.49, Na: 1.05, Mg: 0.16, Al: 5.57, Si: 19.76, P: 0.80, K: 3.84, Ca: 11.53, Mn: 0.69, Fe: 31.12; B/5: Fe: 100.

5. ábra: Az 1/B minta zárványainak SEM-BSE felvételei.

Kémiai összetételek tömeg%-ban: A/1: O: 15,50; Al: 0,46, Fe: 84,04; A/2: O: 24,52, Al: 0,25, Si: 17,56, Ca: 2,05, Mn: 1,62, Fe: 54,00; A/3: O: 26,57, Na: 1,18, Mg: 0,25, Al: 7,70, Si: 21,05, P: 1,01, K: 4,78, Ca: 10,53, Ti: 0,38, Mn: 0,62, Fe: 25,94; A/4: Fe: 100; B/1: O: 15,45, Fe: 84,55; B/2: O: 23,18, Mg: 1,39, Si: 17,03, Ca: 2,61, Mn: 1,71, Fe: 54,08; B/3: O: 23,37, Mg: 0,22, Al: 10,59, Si: 11,92, P: 1,70, Ca: 4,11, Fe: 48,09; B/4: O: 25,49, Na: 1,05, Mg: 0,16, Al: 5,57, Si: 19,76, P: 0,80, K: 3,84, Ca: 11,53, Mn: 0,69, Fe: 31,12; B/5: Fe: 100.

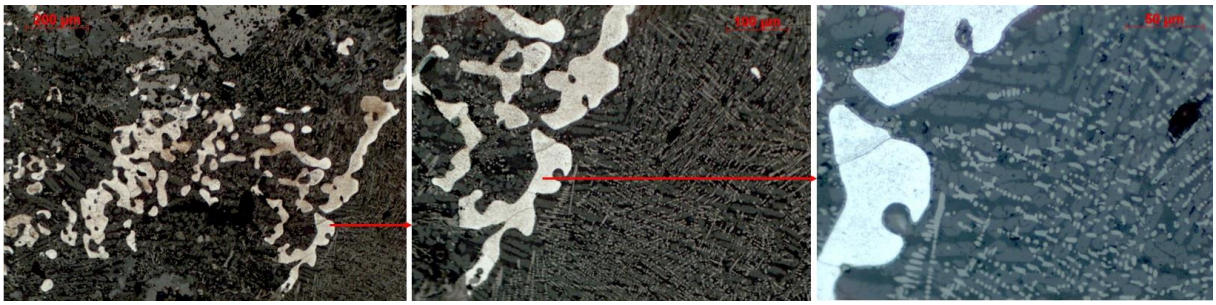

Fig. 6.: OM images of Sample 1/B

6. ábra: Az 1/B minta optikai mikroszkópos képe

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Sample No. 27/A and 27/B

The Sample No. 27 is different in character than the previous one. This piece of bloom (No. 27/a) is compacted, and its shape is smoother, and more brick-like whereas the shape of the Sample No. 1. is irregularly fragmented. Although larger pores and cavities were also found in this bloom (**Fig. 7**). The microstructure of the object is basically ferritic with ferrite-pearlitic areas. The carbon content in this case is significantly lower (~ 0.4–0.5 wt%) than in the first case. In the ferritic areas, line-like fractures or gaps were observed but these are not cracks. Along these gaps, inclusions were detected. However, the mentioned cavities were often filled with non-metallic material which is presumably a product of corrosion.

During the compression hammering of the iron, the parts of the heterogeneous carbon containing bloom with different microstructures were squeezed together, thus, a larger gap was formed between the parts (**Fig. 8**). A good example is the SEM image made by secondary electrons in the bottom left corner of **Fig. 8**, showing separated ferritic and ferritic-pearlitic areas at higher magnification.

Fig. 7.: OM mosaic image of Sample No. 27/A

7. ábra: A 27/A minta optikai mikroszkópos mozaikfelvétele

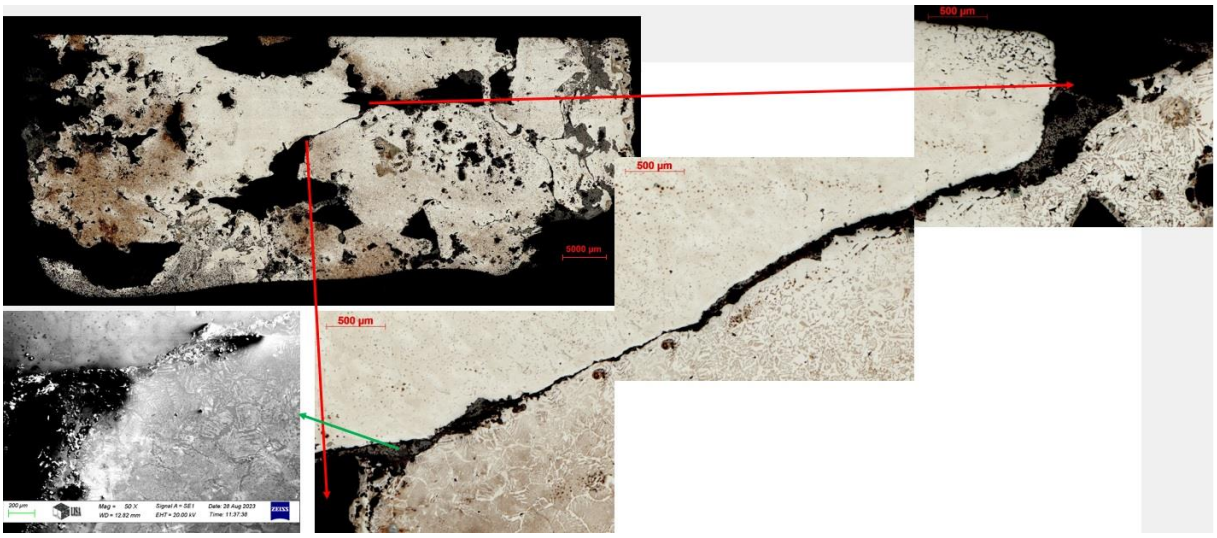

Fig. 8.: OM and SEM-SE (secondary electron) images of a gap in the Sample No. 27/B

8. ábra: OM- és SEM-SE (szekunder elektron) felvételek a 27/B minta egyik hézagjáról

HU ISSN 1786-271X; urn: nbn: hu-4106

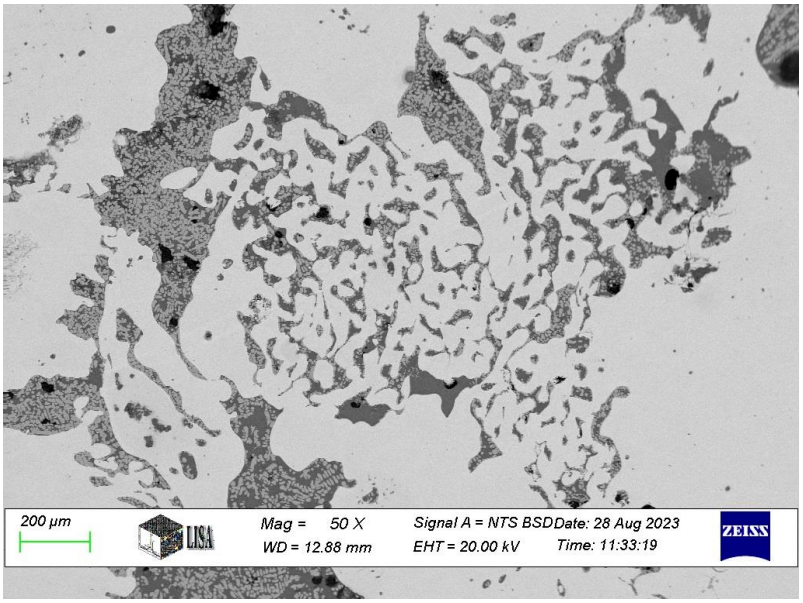

Fig. 9.:
SEM-BSE image of modified inclusions in sample No. 27/B

9. ábra:
A 27/B minta egyik módosult zárványának SEM-BSE felvétele

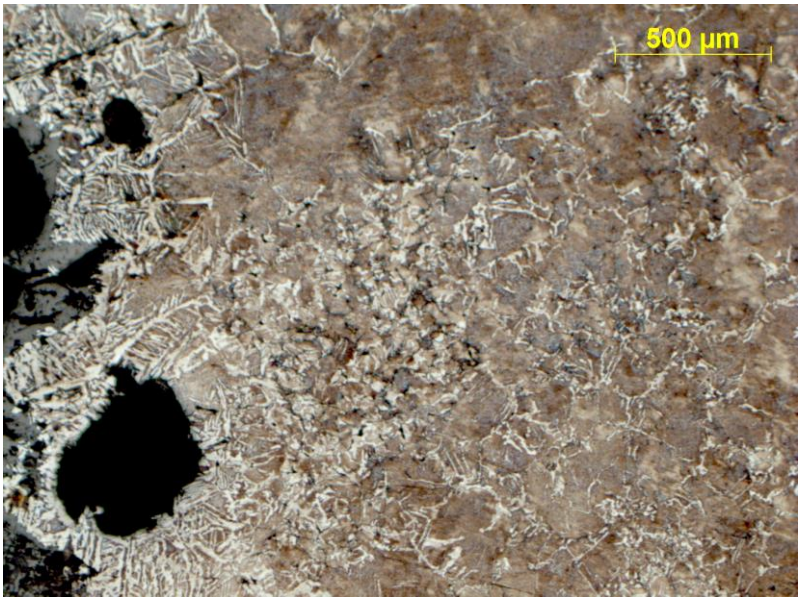

Fig. 10.:
OM image of sample No. 46/B

10. ábra:
A 46/B minta optikai mikroszkópos felvétele

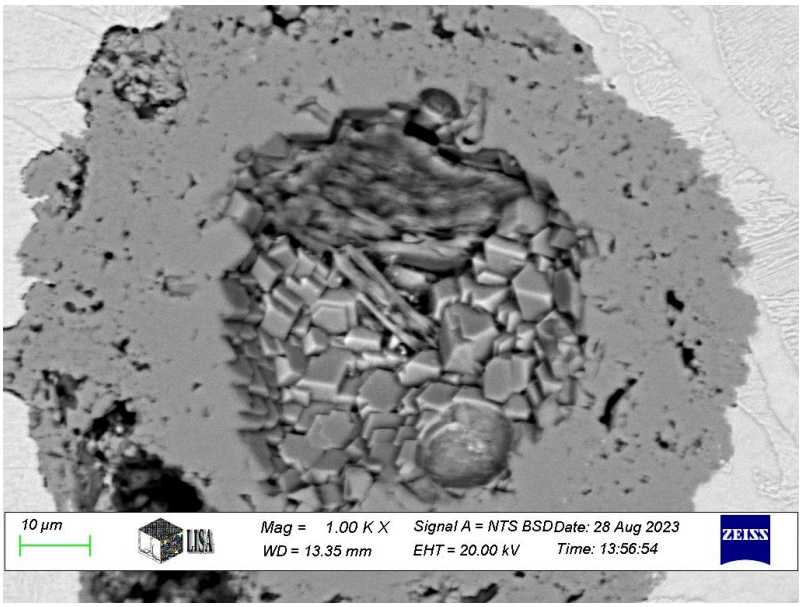

Fig. 11.:
SEM-BSE image of inclusion in sample No. 46/B

11. ábra:
A 46/B minta egyik zárványának SEM-BSE felvétele

HU ISSN 1786-271X; urn: nbn: hu-4106

These different parts may even have different mechanical behaviour during hammering, but it is still the same bloom. If several pieces of different blooms had been hammered together, there would also be such a gap in the areas with identical microstructure. However, this case generates an interesting perception. If we are examining a finished, heavily corroded iron artefact and due to this corrosion only two different layers can be distinguished, this does not necessarily mean the application of the folding technique during the forging process. It could also be caused by the heterogeneity and structure of the raw material, such as in this example. This piece of bloom was thoroughly compacted and formed into a bar, but despite this, a lot of large cavities and numerous inclusions remained in the material which is typical in the case of ferritic structure (Buchwald & Wievel 1998). The SEM-EDS analysis of inclusions revealed that besides the typical three-phase metallurgical inclusions locked into the metal, there are also slag inclusions of smelting origin, whose structure (**Fig. 9.**) has already been modified by corrosion products or by the scale produced during compaction hammering.

Sample No. 46/A and 46/B

The microstructure of the Sample No. 46/A and B is mostly ferritic-pearlitic. Just like in the case of Sample No. 27, small gaps at the slightly different microstructure can also be detected. This may be the result of the fact that the reduced metallic grains did not fully weld together during the smelting, nor did they do so during the hammering process (**Fig. 10**).

The shape of this bloom is also brick-like, it is well visible that the piece was compacted. In the microstructure of the sample, no inclusions specifically originating from smelting were found. The non-metallic details that appear in the cavities or are observed as inclusions are iron oxide or iron silicate in various forms and compositions, respectively, some of them are Fe-Al silicates (**Fig. 11**). The latter may have remained from the clay wall of the furnace, but most of them may be mainly corrosion products.

Conclusion

Three samples were taken from iron objects found at the Early Iron Age settlement at Dédestapolcsány-Verebce-bérc. The slices of the samples were cut into smaller pieces. The OM and SEM-EDS examinations revealed that the blooms are compacted and more or less purified from slag. The essential characteristic of the objects is the heterogeneous microstructure caused by the different carbon content. In the microstructure, numerous pores and large cavities were observed, which is usual in the cases of historical blooms and bars (Pleiner 2000; Buchwald 2005; Strobl et al. 2010; Saage et al. 2017). Based on the results, it can be stated that each object examined is a part of a single bloom, which means it does not consist of several pieces of different blooms assembled together. Although their basic characteristics are similar, they still differ from each other, mainly in terms of carbon content and the degree of compacting and forming.

The most compacted object is No. 27, its shape is more brick-like and has a smoother surface, than the others. The carbon content in this object is not very high, just like in the case of No. 46. However, the microstructure of No. 1 showed a broad variety of Fe-C phases. Besides ferrite and ferrite-pearlite, secondary cementite (close to the surface) was also found in the microstructure but only in the case of No. 1. Several gaps were observed in the microstructure of objects No. 27 and 46, which were surely formed during already the smelting process.

Besides reoxidation-caused iron-oxide inclusions, slag inclusions specifically formed during the smelting process were found in samples No. 1. and 27. At the same time, no classic smelting slag inclusions were found in sample No. 46. In some inclusions of sample No. 1, a small amount of phosphorus (1.1–1.7 wt%) was detected, but this element was found only in the slag inclusion not in the metal, so phosphorus did not play a role in the later forging process.

Returning to the questions posed at the beginning of this study, it can be assumed, that these iron pieces are albeit well compacted, yet not typical semi-finished products. They are neither a bloom nor a bar, being somewhere halfway between them. Their differences from one another reflect the different technical conditions of the smelting (i.e. time, temperature, charging, etc.) and maybe the different characteristics and the works of the bloomeries.

Another interesting question would be the connection between the objects examined and the other iron artefacts found in the territory. Samples were taken from four iron axes found in the hillfort of the site, which had been analysed by OM and SEM-EDS. In the cases of metallographic examinations of socketed axes, it was possible to identify such types of raw material that were represented by the samples of this study. However, a detailed study of the axes found in the Dédestapolcsány-Verebce-bérc is still underway and the results will be reported in another paper.

Contribution of authors

Béla Török Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing,

Visualization, Funding acquisition. **Péter Barkóczy** Validation, Investigation, Writing – Original Draft, Writing – Review and Editing. **Gábor V. Szabó** Investigation, Resources, Writing – Review and Editing, Funding acquisition.

Acknowledgment

We are grateful to Attila Árvay („KIS" Szerelő és Kereskedő Kft.) for the waterjet cutting and Zoltán Gyökér (Institute of Physical Metallurgy, Metal-forming and Nanotechnology at the University of Miskolc) for the cooperation in the SEM-EDS analyses.

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HU ISSN 1786-271X; urn: nbn: hu-4106

LAZURITE AT NOVGOROD: TECHNIQUES, MIXTURES, PROVENANCE

LAZURIT NOVGORODBAN: TECHNIKÁK, KEVERÉKEK, SZÁRMAZÁS •

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Abstract

An extensive collection of wall-painting fragments that in the 19th century was removed from the walls and buried under the floor of the Cathedral of St. George was collected during the 2013-2023 architectural and archaeological excavations on the area of the St. George's Monastery at Veliky Novgorod (Russia), conducted by the Institute of Archaeology of the Russian Academy of Sciences. Among the pigments there were different kinds of blue, but the most common was rather pure lapis lazuli (lazurite), identified with XRF, SEM-EDS and XRD. Lazurite was the most valuable and expensive ancient pigment, as it was extracted and imported from few deposits, the most important of which was that of Sar-e-Sang in the Afghanistan region of Badakhshan.

Lazurite contains a significant amount of sulphur; therefore, the $\delta^{34}S$ values of the blue pigment can be used to identify the lazurite deposit. The sulphur isotope analysis was carried out using the CF IRMS technique with FlashHT element analyzer. Lapis lazuli reference samples from Badakhshan (from +15.7 to 22.3‰), Tajikistan (+17.6‰), and the Baikal (+45.4‰) deposits were analyzed and compared with the sulphur isotope composition of the blue pigment employed at Novgorod. The $\delta^{34}S$ values of blue pigment from fresco fragments (from +21.1 to +23.5 ‰) are close to the Badakhshan lapis lazuli reference samples. Therefore, we can confirm that the origin of the blue pigment employed at Novgorod was the region of Badakhshan in Afghanistan.

Kivonat

Az Orosz Tudományos Akadémia Régészettudományi Intézetének munkatársai 2013 és 2023 között intenzív építészeti és régészeti feltárás végeztek a Velikij Novgorodban (Oroszország) található Szent György-katedrálisban, amely során olyan falkép töredékeket gyűjtöttek nagy számban, amelyeket a 19. században távolítottak el az épület faláról, majd a katedrális padlója alá temettek el. A pigmentek között többféle típusú kék színt találtak, de a leggyakoribb a meglehetősen tiszta lapis lazuli (lazurit) volt, amit XRF, SEM-EDS és XRD módszerekkel azonosítottak. A lazurit volt a legértékesebb és legdrágább korabeli pigment, mivel kevés lelőhelyről termelték ki és importálták. A források közül a legfontosabb az afganisztáni Badakhshan régióban található Sar-e-Sang lelőhely volt.

A lazurit jelentős mennyiségű ként tartalmaz, ezért a kék pigment $\delta^{34}S$ értékei felhasználhatók a lazurit lelőhelyének azonosítására. A kénizotóp vizsgálata FlashHT elemanalizátorral ellátott CF IRMS technikával történt. A Badakhshanból (+15,7 és 22,3‰ között), Tádzsikisztánból (+17,6‰) és a Bajkál-tó vidéki lelőhelyről (+45,4‰) származó lapis lazuli referenciamintákat elemeztük és összehasonlítottuk a Novgorodban alkalmazott kék pigment kénizotóp-összetételével. A freskótöredékekből származó kék pigment $\delta^{34}S$ értékei (+21,1 és +23,5‰ között) közel állnak a badakhshani lapis lazuli referenciamintákéhoz, ezért megerősíthetjük, hogy a Novgorodban használt kék pigment eredete az afganisztáni Badakhshan régió volt.

KEYWORDS: FRESCOES, NOVGOROD, ST. GEORGE'S CATHEDRAL, XRF, SEM-EDS, XRD, CF IRMS

KULCSSZAVAK: FRESKÓ, VELIKIJ NOVGOROD, SZT. GYÖRGY-KATEDRÁLIS, XRF, SEM-EDS, XRD, CF IRMS

• How to cite this paper: GIUMLIA-MAIR. A.R.G.; DUBININA, E.; VDOVICHENKO, M.V.; ZUBAVICHUS, E.; RICCARDI, M.P. & MUSA, M., (2024): Lazurite at Novgorod: Techniques, Mixtures, Provenance, *Archeometriai Műhely* **XXI/3** 295–306.
doi: 10.55023/issn.1786-271X.2024-024

Introduction

Some time ago three of the authors, together with Prof. Vladimir Sedov, published a paper presenting the first data from the analyses carried out on fragments from the Cathedral of St. George (Giumlia-Mair et al. 2022). A second paper, dealing with the preparation layers of the murals, was published one year later (Giumlia-Mair et al. 2023a). A further paper presenting the latest analyses of earlier and later pigments and on the differences in the plasters has been recently published in this journal as well (Giumlia-Mair et al. 2023b). The present paper focuses on lazurite pigments, and the aim is that of deepening the knowledge on the blue colour pigments, the mixtures, how they were applied and especially the provenance of the pigment. The analyses were carried out with different methods: XRF, SEM-EDS, Raman, and CF IRMS technique with FlashHT element analyzer. The most important analysis for this paper is the isotopic study of the sulphur present in the pigment that determined the provenance of the lazurite samples from the fragments of the wall-paintings.

The history of the monument

The Cathedral of St. George in the Yuriev Monastery in Novgorod is one of the oldest surviving architectural monuments in Russia. Several researchers addressed various aspects of the temple in the past (Karger 1946; Sarabyanov 1998; Sarabyanov 2002; Lifshits et al. 2004; Sarabyanov 2012; Sedov et al. 2014, 2015, 2016, 2019).

The beginning of construction by order of prince Vsevolod Mstislavich in 1119 is known from the Novgorod chronicle. The cathedral was consecrated in 1130, but there exists no written evidence on the wall-paintings that were certainly completed around 1130. The wall-paintings of the 12th century were renovated at the turn of the 17th–18th centuries and again later in the 18th century (Sedov 2021; Etinhof 2016). The paintings were first removed from the walls in the 1820s and were buried under the new iron floor. In 1825-1827 the cathedral was re-painted, however in 1898-1902 these murals were also removed. The wall-paintings now visible in the Cathedral were depicted in 1902.

The study of the pre-Mongolian wall-paintings was one of the main goals of the architectural and archaeological excavations in 2013-2023. These paintings are one of the earliest monumental ensembles of pre-Mongolian Russia, the time of the birth of Russian art. They have exceptional artistic quality, testifying to their creation by talented and experienced artists coming to Novgorod from Kiev or even Byzantium.

The excavations

Fragments of the 12th century paintings were first discovered during the 1930s research by M. K. Karger, who removed the cast-iron floor of the 19th century in the two western transepts and found a 25–30 cm thick filling of "fragments of plaster with fresco painting" (Karger 1946). The most significant fragments were published in 1946 in the journal "Soviet Archaeology", as first presentation of pre-Mongolian paintings to the scientific world. Later, there were single finds of fragments around the monastery, and in the 1990s, during the repair of the Oryol building; more were discovered in its vaults and in a trench along it (Etinhof 2016). In 2013, the team of the Institute of Archaeology of the Russian Academy of Sciences, led by V. V. Sedov, laid a pit in the central apse, and discovered 12th century fragments under the cast-iron floor of the 1820s. About 60 trays (0.47 x 0.65 m) were collected from one pit and transferred to the Novgorod Museum, but among them there were no exceptional specimens.

The 2014-2015 excavations in the interior of the Cathedral yielded instead amazing results with over one hundred thousand fragments gathered in the eastern half of the temple. Among them are more than one hundred fragments of faces and parts of faces and bodies (**Fig. 1.**). Historically important graffiti inscriptions were also recovered (Gippius & Sedov 2015). Between 2015 and 2021, more excavations were carried out around the cathedral. The collection was annually augmented by 30–50 trays. In 2022, a new layer with fragments was recorded in a pit to the east of the St. George's Cathedral and yielded 120 trays of fragments (measuring 0.26 x 0.41 m).

Fig. 1.: The photo shows a number of boxes filled with fragments and one of the boxes containing blue fragments

1. ábra: Faltöredékekkel teli tartódobozok, amelyek egyike kék színű töredékeket tartalmaz.

HU ISSN 1786-271X; urn: nbn: hu-4106

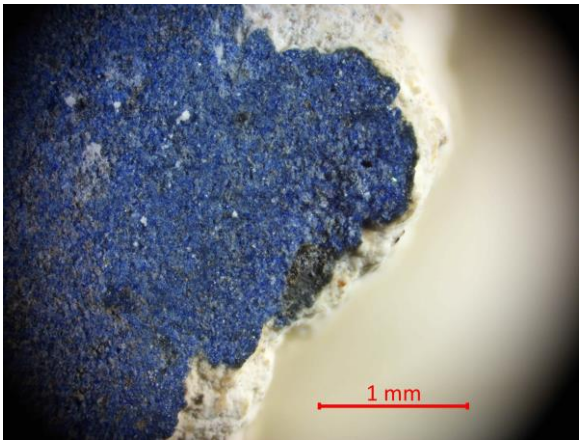

Fig. 2.: Optical microscopy shows the blackish substrate (called *reft*) under the lazurite pigment. Fragment No. 3481.

2. ábra: A lazurit pigment alatt látható fekete aláfestés (*reft*) optikai mikroszkópos felvétele. 3481-es minta.

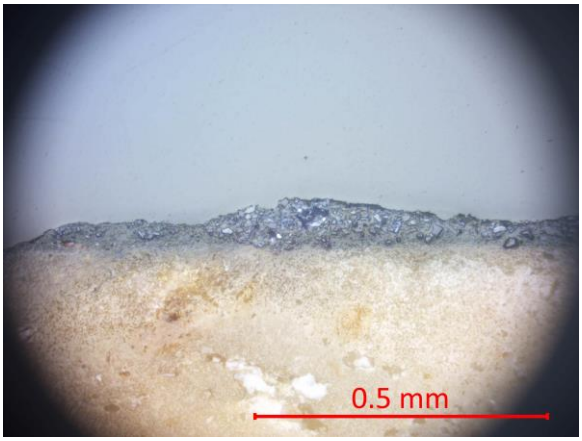

Fig. 3.: In the case of fragment No. 1469 the lazurite pigment had been applied directly on plaster, without any blue clay or *reft* substrate (optical microscopy, carried out with a Modular Microscope ADF W300 in reflected light, and micro photos taken with a microscope camera ADF STD 16).

3. ábra: Az 1469-es minta esetében a lazurit pigmentet közvetlenül a vakolatra vitték fel, kék agyag vagy *reft* aláfestés nélkül (ADF W300 moduláris mikroszkóppal visszavert fényben végzett optikai mikroszkópos vizsgálat, ADF STD 16 mikroszkópos kamerával készített mikrofotó)

In 2023, the excavation area was enlarged and about 400 trays of wall painting were recovered. More fragments might be under the pavement of the paths. We hope to extract the part under the lawn in the next archaeological seasons.

Lazurite pigments at Novgorod

The area of wall-paintings with lapis lazuli as calculated from the blue fragments recovered up to now (about 7% of all collected fragments) was at least around 70–80 m^2. The surface painted with the blue pigment would have covered around 180 m^2 and, in the entire temple, it would have been around 226 m^2. As an average layer is around 50 µm (0.05 mm) thick, the lazurite employed for the entire painted surface inside the church would be 9.2 liters of dry lazurite (without taking the binder into account). This indicates an unprecedented rich order, made by prince Vsevolod Mstislavich, for a monumental painting in the Cathedral. As discussed elsewhere (Giumlia-Mair et al. 2023b), the analyses showed that the blue pigment, applied for the 12th century paintings, consists of lazurite, i.e., ground lapis lazuli. Further studies showed that the lazurite was employed in different ways to achieve a variety of nuances.

In our 2023 publication (Giumlia-Mair et al. 2023b) we pointed out that, contrary to what was stated in a previous article reporting the opinion of a conservation expert based only on naked eye and microscopy observations (Etinhof 2022), most of the fragments painted with lazurite show a dark substrate, called *reft* in all Russian literature (**Fig. 2.**). Most of them also show a special preparation with a layer of blue clay under lazurite and reft (see Giumlia-Mair et al. 2022, 114, fig.10). It is generally thought that *reft* was a mixture of calcium carbonate white and powdered charcoal (Giumlia-Mair et al. 2023a, 2023b). Only in very few specimens, for example No. 1469 (**Fig. 3.**), the lazurite layer was directly applied on the white plaster, typical for the 12th century, with only very little straw, wood shavings or fine sand grains as aggregates (**Fig. 4.**). For this paper we analysed several blue-painted fragments dated to the 12th century. When a more intense blue was required, the painter added a dark layer (the one we call *reft*) under the lazurite fragment, however the SEM failed to recognize fragments of powdered charcoal in the blackish layer under the lazurite (see **Fig. 4.**). This means that, instead of charcoal, some soot (i.e. amorphous carbon) was mixed with the blue clay (or part of it), employed as a substrate for the lazurite. As discussed elsewhere, on one of the late samples a mixture of synthetic azurite, lead white, white barium sulphate and a small amount of lazurite were identified (Giumlia-Mair et al. 2022). Because of the technique employed in applying the pigment, the plaster rich in rough sand as additive, and the synthetic azurite and barium sulphate white, we date the mixture to the renovations that happened at the turn of the 17th–18th or later in the 19th century (see also Giumlia-Mair et al. 2022, 115, figs. 13-15).

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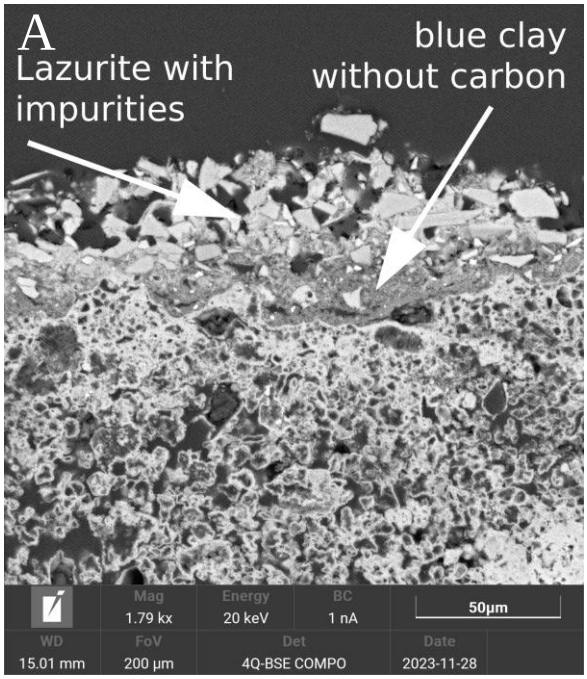
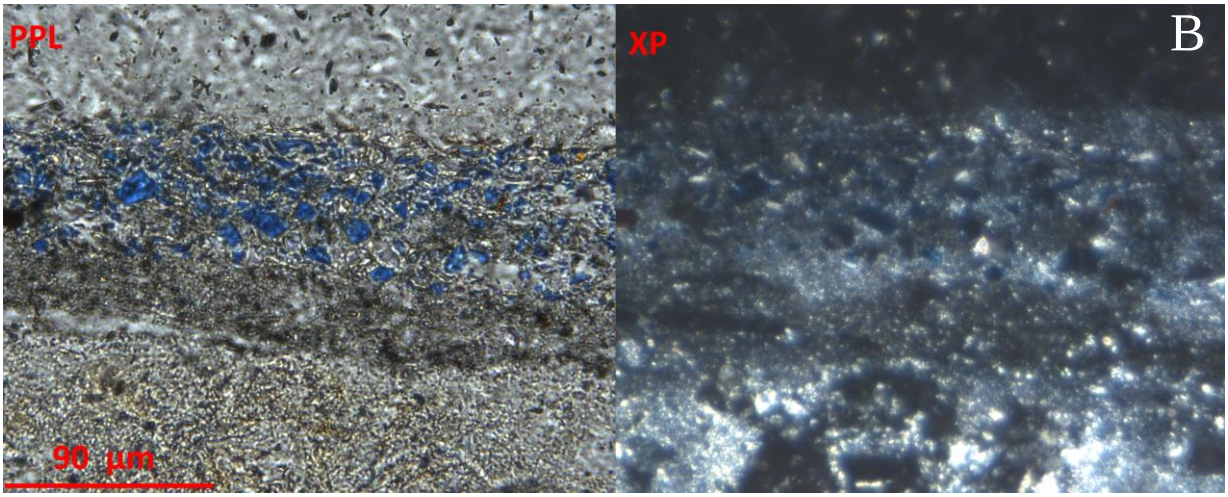


Fig. 4: Cross section of fragment No. 3481 (see also Fig. 2). (A) SEM-BSE micrograph showing the stratigraphy: the upper layer consists of natural lazurite containing phlogopites, sodalite, diopside and other minerals, applied on a thin layer of blue clay. The SEM examination did not show charcoal particles in the black lower layer, visible instead, for example, in sample No. 1502. The black colour is probably due to an admixture of the clay with soot (amorphous carbon). (B) Cross section with PPL and XP showing the lazurite pigment layer and the *reft* layer.

4. ábra: A 3481. sz. minta keresztmetszete (lásd még a 2. ábrát). (A) A rétegrendet mutató SEM-BSE felvétel. A felső réteg természetes lazuritból áll, amely flogopitot, szodalitot, diopszidot és más ásványokat tartalmaz, és vékony kék agyagrétegre van felhordva. A SEM-vizsgálat nem mutatott ki faszénszemcséket az alsó fekete rétegben, amelyek például az 1502. sz. mintában láthatóak. A fekete szín valószínűleg az agyag korommal (amorf szénnel) való keveredésének köszönhető. (B) A lazurit pigmentréteget és a *reft* réteget mutató optikai mikroszkópos (PPL és XP) felvételek.



Further, on a preparation dated to later phases, powdered charcoal mixed with a small amount of lazurite, was employed to achieve a deep bluish colour (**Fig. 5.**). Optical microscopy and SEM-EDS showed a thick substrate of red ochre with charcoal under the bluish layer.

One of the most important observations is that, even in the case of later specimens, the blue colour was always obtained by mixing at least some lazurite with other pigments or *reft*.

For the characterization of the phases micro-Raman spectroscopy has been also applied without sample preparation. We focused the laser source (532 nm) by the optical system (80x magnification) on the blue crystals and obtained the spectra of **Fig. 6A**.

The Raman bands at 257, 280, 546, 584, 804, 1091, 1120 and 1640 cm^{-1} are ascribable to the lazurite phase. On the other hand, when analysing the darker blue-greyish samples, we detected characteristic bands corresponding to G and D vibrational modes in graphite structure (**Fig. 6B)**.

The broad aspect of those bands must also be noted, as it suggests low crystallinity of the graphite or only hexagonal carbon-carbon bonds as per graphene disorder layers (Zaitsev 2010). Thus, the Raman data acquired on the samples' surface without preparation, confirmed the interpretation of the previous analyses.

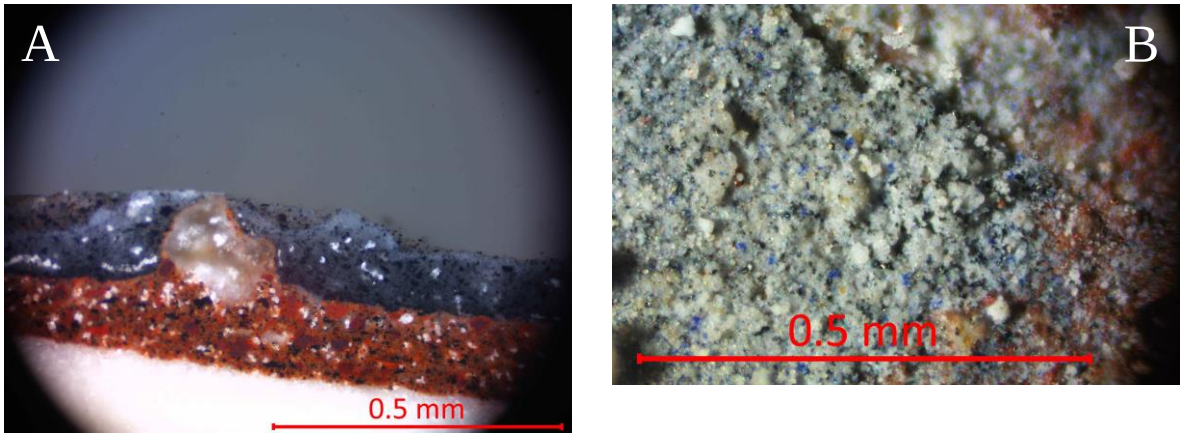


Fig. 5: Later dated fragment No. 1502. (A) Optical microscopy showing a layer of blue pigment consisting of a mixture of calcium carbonate, powdered charcoal and a small amount of lazurite applied on a red layer of red ochre mixed with powdered charcoal. A large quartz sand grain and small charcoal inclusions can be recognized in both pigments. (B) The higher magnification shows both the lazurite and the charcoal particles in calcium carbonate.

5. ábra: A későbbre datált 1502. sz. minta optikai mikroszkópos vizsgálata. (A) A kék pigmentréteget, amely kalcium-karbonát, faszénpor és kis mennyiségű lazurit keverékéből áll, vörös rétegre vittek fel, amely faszénporral kevert vörös okkerből készült. Egy nagyméretű kvarc homokszemcse és apró faszénzárványok felismerhetők mindkét rétegben. (B) A nagyobb nagyításon mind a lazurit, mind a faszénszemcsék jól megfigyelhetők a kalcium-karbonátban.

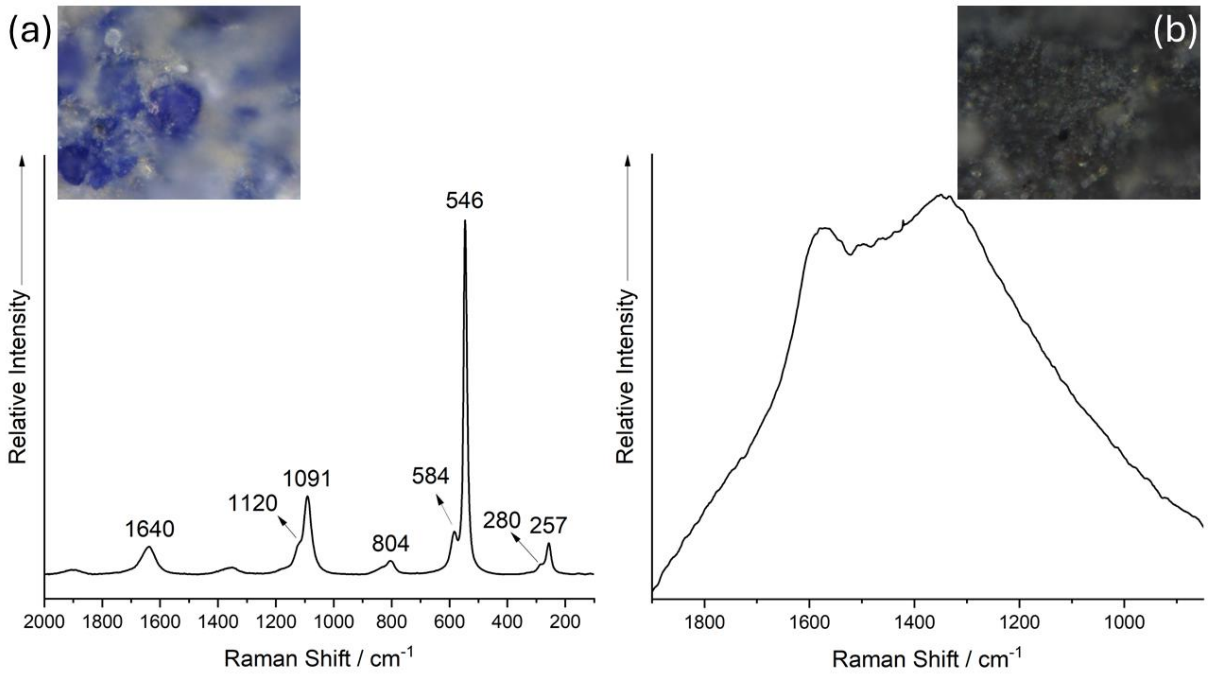


Fig. 6: Raman spectra acquired by focusing the source on the blue crystal (A) and on the darker grey ones (B), corresponding to lazurite and graphene, respectively. The 532 and the 633 nm Raman laser sources have been focused by 80x objective on the crystals shown in the micrograph images.

6. ábra: A kék kristályra (A) és a sötétebb szürke kristályokra (B) fókuszálva felvett Raman-spektrumok, amelyek lazuritnak, illetve grafénnek felelnek meg. Az 532 és a 633 nm-es Raman-lézerforrást 80x objektívvel fókuszáltuk a mikroszkópos képeken látható kristályokra.

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The provenance of the lazurite pigment

Lazurite had to be imported from far away and was expensive, indeed the most precious pigment in use in antiquity. Now lapis lazuli is also found in Siberia, near Lake Baikal. It is known that the exploitation of the Baikal deposit began no earlier than the 18th century, but, as there are other possibilities, such as for instance the deposits in Tajikistan, and the minerals from the various deposits differ from each other, it still seemed useful to investigate the place of origin of the blue pigment from the Cathedral. Numerous studies for the determination of the provenance of lazurite exist, so that only a few can be mentioned here (see for example Guidorzi et al. 2022; Lo Giudice et al. 2009; Schmidt et al. 2009; Re et al. 2011, 2013; Law 2014). Several methods have been used to determine the origin of the mineral: more traditional like Raman, X-ray diffraction, micro-XRF, but also particle-induced X-ray emission (PIXE), particle-induced gamma-ray emission (PIGE), prompt-gamma activation analysis (PGAA) and ionoluminescence (IL). To confirm the origin of our lapis lazuli, we needed samples from various deposits, which were kindly provided by the A. E. Fersman Mineralogical Museum. After consultations with the museum staff and geologists, it was decided to conduct an isotopic analysis on the sulphur from the lapis lazuli admixture for determining its provenance. This analysis is relatively innovative in the study of pigments (Law 2014) and was carried out by E. O. Dubinina, Laboratory of Isotope Geochemistry and Geochronology of the Institute of Geology of Ore Deposits of the Russian Academy of Sciences, co-author of this article, and a specialist in sulphur isotopes. Three samples of blue pigment from the Cathedral and five samples from modern lapis lazuli deposits, such as the Pamirs and Siberia were provided.

Sulphur isotope composition of natural lapis lazuli and pigment of the wall-paintings

Rationale for the approach

The main feature of lapis lazuli is the diverse content of different forms of sulphur in the mineral molecule - from reduced (S^{2-}) to completely oxidized, or as sulphate (SO_4^{2-}). Between these forms of sulphur, a significant thermodynamic isotope fractionation takes place. For example, at 400 °C the isotopic fractionation of sulphur $\Delta^{34}S$ ($\approx\delta^{34}S(SO_4^{2-})$- $\delta^{34}S(S^{2-})$) between its oxidized and reduced forms is 20.3‰, at 600 °C it is 11.3‰, and at 800 °C - about 6‰ (Sakai 1968). Consequently, the amount ratio of the sulphur reduced to oxidized in the mineral molecule will affect the total sulphur isotopic composition of lapis lazuli if it was formed under open system conditions. As a rule, the lapis lazuli formation is associated with high temperature metasomatism (Korzhinsky 1947, 1953; Blaise & Sesbron 1966; Efimov & Suderkin 1967; Davydchenko 1972), which is quite consistent with the conditions of an open system. In turn, the ratio of reduced and oxidized forms of sulphur in the mineral is determined, first of all, by the redox conditions of lapis lazuli formation, and this parameter can also be a diagnostic feature of a particular deposit.

Therefore, the isotopic composition of sulphur in lapis lazuli is a reliable parameter. On one hand, it reflects the isotopic composition of sulphur in mineral-forming solutions. On the other hand, it also shows the redox conditions and temperature of mineral deposition. In addition, the total sulphur content in lapis lazuli can also be a diagnostic feature, since it is determined by the sulphur content in the rock through which high temperature metasomatism occurs (Korzhinsky 1947, 1953; Khoreva 1955). Thus, when identifying lapis lazuli and blue pigments from archaeological samples, it makes sense to determine not only the $\delta^{34}S$ values in lapis lazuli, but also to estimate the total sulphur content in the same sample in order to use two diagnostic features instead of one. In the case of a pigment, this approach works only for samples consisting of almost pure lapis lazuli.

One of the methodological problems is the presence in lapis lazuli of thin invisible inclusions of pyrite, which are difficult to physically separate from the mineral. The methodological recommendations to remove pyrite before the sulphur isotope analysis of lapis lazuli (Law 2014) are certainly correct, but when analysing lapis lazuli to solve problems of its provenance the removal of pyrite is not necessary. Firstly, the amount of invisible pyrite is a feature of specific lapis lazuli deposits, and secondly, we would have to assume that during the manufacture of pigments in the 12th century, special and efficient operations were carried out to completely separate pyrite and lapis lazuli. It is just possible that the flotation method was used to purify the ground raw material, however this method does not eliminate microscopic inclusions of dispersed pyrite. Nevertheless, we have to keep in mind that, if in the laboratory the flotation purification of a sample is applied, it would be a subjective factor that is difficult to correlate both with natural variations in the parameters (content, isotopic composition) of sulphur in the sample, and with the variations in the archaeological materials.

According to Law (2014), the sulphur isotopic composition of pyrite impurities is close to the isotopic composition of lapis lazuli due to the high-temperature origin of this mineral. For Badakhshan lapis lazuli, the difference between the $\delta^{34}S$ values of lapis lazuli and pyrite is 4.6‰, and for lapis lazuli from Tajikistan it is 6.6‰ (Law 2014). With

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such a difference in the isotopic composition of sulphur, pyrite impurities can affect the results of isotopic analysis, which is currently carried out with an accuracy of ±0.3‰ (1σ), when the pyrite amount exceeds ≈2%. However, in this case the pyrite content in the sample is visible, and it renders possible to mechanically clean it.

These considerations elucidate the approach used in our work to identify the 12th century pigments from the Cathedral of St. George. At first, we analysed some samples of natural lapis lazuli from known deposits in Afghanistan, Tajikistan, and Russia, to obtain the diagnostic sulphur characteristics ($\delta^{34}S$ and C(S)) of lapis lazuli of different origins.

Analytical procedures

The sulphur isotope analysis was carried out by isotope mass spectrometry in a constant flow of helium (CF-IRMS) on a DELTA V+ mass spectrometer combined with a FlashHT1112 elemental analyzer (Thermo, Germany) in the Laboratory of Isotope Geochemistry and Geochronology of the IGEM RAS (Moscow). The calibration of the measured $\delta^{34}S$ values relative to the international standard VCDT was carried out by analysing IAEA reference materials (S-1, S-2 and S-3) that were analysed simultaneously with the studied samples.

The top layer of blue pigment was scraped off the surface of the fresco fragments using a diamond needle. The scraping depth was controlled under a binocular lens. The substance obtained was ground to a fine powder in an agate mortar. Samples of natural lapis lazuli were ground in the same way. The weight of both lapis lazuli and pigment samples was exactly the same (0.9 mg). The same portion (0.9 mg) of the V_2O_5 oxidizing agent (analytical grade) was added to each sample. The mixture of the sample and the oxidizing agent were placed in a tightly packaged tin container. The containers were placed, together with the standards put in similar containers, into the autosampler (AS-2000) for solids mounted on a FlashHT1112 peripheral device. The samples packed in tin containers were loaded by autosampler into a quartz reactor, filled layer by layer with tungsten oxide and electrolytic copper and heated to T = 1020 °C. The entire system was purged with high purity helium (grade 6.0) with the rate of 90 ml/min.

When the sample entered the reactor, a small portion of oxygen was supplied, resulting in instant high-temperature (1800 °C) combustion of the sample container. The released gas passed through the appropriate layers of the reactor in a helium flow, a special dehydrator, and entered a chromatographic column heated to 105 °C.

Table 1.: Isotopic composition ($\delta^{34}S$) and sulphur content (C(S)) in samples of natural lapis lazuli and blue pigment of the frescoes of the Cathedral of St. George (Novgorod).

1. táblázat: Természetes lapis lazuliból és a Szent György-katedrális (Novgorod) freskóinak kék pigmentjéből származó minták izotópösszetétele ($\delta^{34}S$) és kéntartalma (C(S)).

Sample No.	Sample description	C(S), µg/mg	$\delta^{34}S$ (VCDT), ‰
Natural lazurite samples			
FN-807	Baikal (Slyudyanka), Russia	32	45.3
FN-804_900	Baikal (Malaya Bystraya), Russia	32	45.4
FN-808	Badakhshan, Afghanistan	8	22.3
FN-805	Badakhshan, Afghanistan	20	15.7
FN-806	Lyajvar-Dara, Tajikistan	12	17.6
Blue pigment samples of the frescoes of the Cathedral of St. George			
Lasur_2021	Novgorod, Russia	11	22.6
Lasur_21B17		15	23.5
Lasur_21BI47		14	21.1

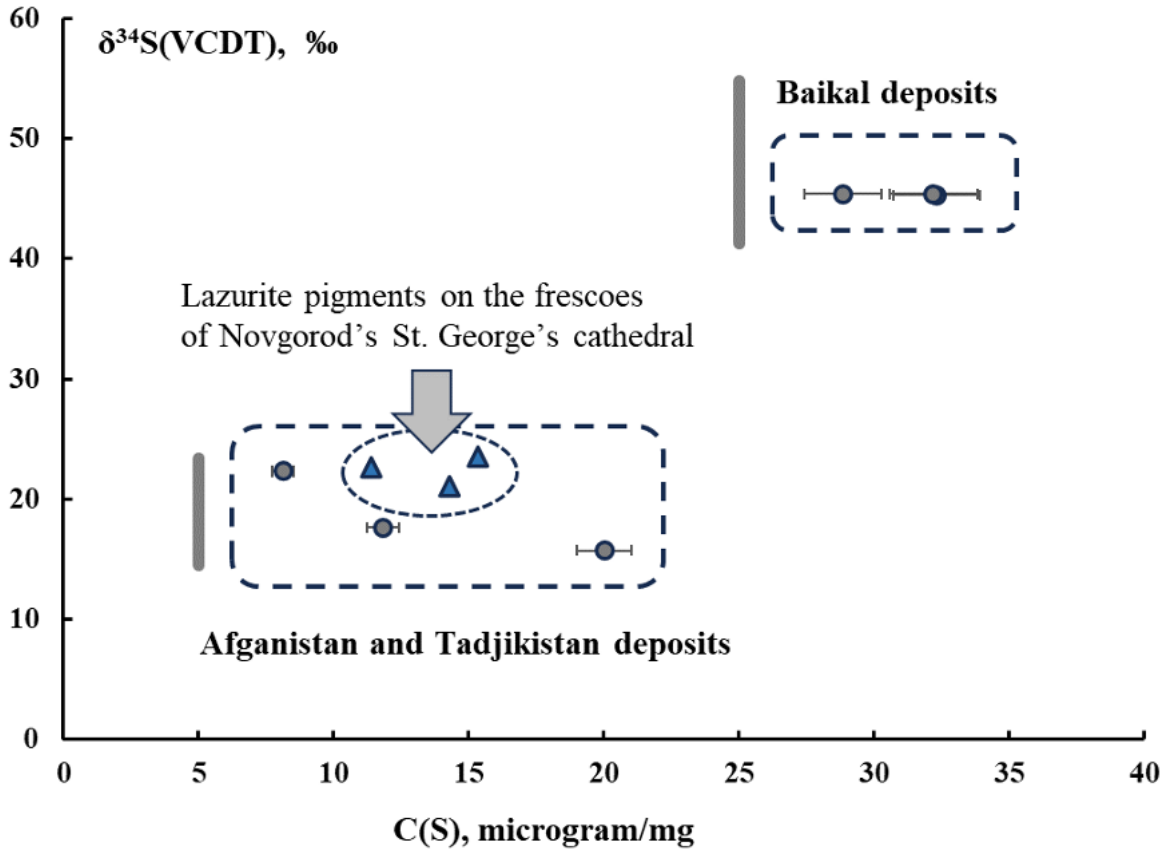

Fig. 7.: Diagnostic diagram C(S)-$\delta^{34}S$ for natural lapis lazuli. Data are applied for the pigment of the frescoes of the Cathedral of St. George (12th century, Novgorod), which fully correspond to the composition of lapis lazuli of Afghan and Tajik origin. Thick vertical lines are the interval of variations in the $\delta^{34}S$ value for lapis lazuli of the corresponding deposits according to Law (2014).

7. ábra: A természetes lapis lazuli C(S)-$\delta^{34}S$ diagnosztikai diagramja. Az adatokat a Szent György-katedrális (12. század, Novgorod) freskóinak pigmentjére alkalmazzuk, amely teljes mértékben megfelel az afgán és tádzsik eredetű lapis lazuli összetételének. A vastag függőleges vonalak a megfelelő lelőhelyek lapis lazulijának $\delta^{34}S$-értékében a Law (2014) szerinti eltérések intervallumát jelölik.

As a result of chromatographic purification, the sample, represented by a portion of SO^2 gas in a helium flow, was transferred through the ConFloIV gas commutator device to the inlet system of the DeltaV+ mass-spectrometer (Thermo, Germany). The accuracy of the $\delta^{34}S$ value determination obtained by the multiple analyses of IAEA standards, was ±0.3‰ (1σ). The sulphur concentration was determined by calibrating the chromatographic peak area with the accuracy ±5% (1σ). The results of the isotopic composition measurements ($\delta^{34}S$ in per mil, ‰) and sulphur content (C(S) in micrograms of sulphur in one mg of the sample are given in **Table 1.**

Analysis of natural lapis lazuli

As follows from **Table 1.**, lapis lazuli from the Baikal deposits contains the maximum amount of sulphur (32 μg/mg). Lapis lazuli from Afghanistan (Badakhshan) and Tajikistan (Lyajvar-Dara) are characterized by sulphur contents 2 to 4 times lower. The isotopic composition of sulphur also differs: the highest $\delta^{34}S$ values are characteristic of lapis lazuli from the Baikal deposits (≈ 45‰), and the lowest for deposits of Afghanistan and Tajikistan (15.7–17.6‰). Based on these data, it is possible to draw up a preliminary diagnostic diagram, which can later be supplemented by the results obtained both for lapis lazuli from other deposits and pigments from known archaeological objects (**Fig. 7.**). Unfortunately, the few published data do not contain information about the sulphur content of the sample and cannot be plotted on this chart. However, for comparison, we present the intervals of variations in $\delta^{34}S$ values from the review by Law (2014). Our preliminary data show that for lapis lazuli of Afghan and Tajik origin there is an inverse correlation between C(S) and $\delta^{34}S$ values, which can be explained by variations in the content of trace pyrite in the sample. This explains why the $\delta^{34}S$ value decreases with increasing sulphur content. For the Baikal samples, such

relationship between the C(S) and $\delta^{34}S$ values was not found. This may be due to the minor effect of dispersed pyrite impurities compared to the high sulphur background in lapis lazuli from Baikal deposits.

Analysis of pigments from the Cathedral of St. George (Novgorod)

The data obtained by analysing scrapings of fragments with blue pigment from the Cathedral of St. George in Novgorod are fully consistent with the composition of natural lapis lazuli of Afghan or, possibly, Tajik origin (**Fig. 8.**). However, the greatest agreement is observed between the samples from the Cathedral ($\delta^{34}S$ from 21.1 to 23.5‰) and the Afghan lapis lazuli sample FN 808. It is interesting that the sulphur content in this sample is minimal (C(S) = 8 μg/mg). Apparently, the lapis lazuli was carefully chosen for producing pigments with a minimal amount of pyrite impurities, as they worsen the properties of the pigment. Therefore, we can assume that when selecting raw materials for the blue pigment, lapis lazuli with few foreign inclusions, including pyrite, would be favoured. The sulphur content in the scrapings from the Novgorod samples is close to the sulphur content in samples of pure Afghan lapis lazuli. This indicates that the composition of the pigment is close to that of pure natural lapis lazuli.

Conclusions

The blue pigments employed in the 12th century in the mural paintings of the Cathedral of St. George at Novgorod consisted of lazurite, mainly applied in combination with *reft*, the mixture of calcium carbonate white and powdered charcoal or soot, and mainly with a substrate of blue clay. In very few cases the lazurite pigment was applied on the plaster, without any preparation underneath.

After XRF and SEM-EDS it was decided to determine the provenance of the lazurite in use at the St. George Cathedral by isotopic analysis of sulphur. The investigation was carried out by CF IRMS technique with FlashHT element analyzer at the Laboratory of Isotope Geochemistry and Geochronology of the Institute of Geology of Ore Deposits of the Russian Academy of Sciences, by E. O. Dubinina. The results of the analysis indicate that the lapis lazuli employed as a pigment at Novgorod came from the deposits in the region Badakhshan in Afghanistan.

Contribution of authors

Alessandra Giumlia-Mair Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Elena Dubinina** Formal analysis, Investigation. **Marina Vdovichenko** Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Evgenius Zubavichus** Formal analysis, Investigation. **Maria Pia Riccardi** Formal analysis, Investigation. **Maya Musa** Formal analysis, Investigation.

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HU ISSN 1786-271X; urn: nbn: hu-4106

KÖZLEMÉNYEK

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Konferencia beszámoló

6th International Conference on Archaeometallurgy in Europe (AiE) 2024. június 11-14. Falun, Svédország •

Immár hatodik alkalommal került megrendezésre a legnagyobb nemzetközi archeometallurgiai tudományos konferencia. A legutóbbi, miskolci rendezvény óta – a svédországi rendezők financiális okok miatti kérésére – ezúttal nem négy, hanem öt év telt el. A konferenciának Falun, egy Stockholmtól mintegy 200 km-re lévő, mintegy 100 ezer lakosú tradicionális réz- és nemesfém bányászváros adott otthont, amely a bányászati területeivel együtt felkerült az UNESCO világörökségi helyszíneinek listájára is. A rendezvény konkrét helyszíne a város egyik hotelje – ahol egyúttal a résztvevők is el voltak szállásolva – és múzeuma volt.

A négy szakmai napból az elsőn a regisztráción és köszöntőkön kívül Alessandra Giumlia-Mair és Richard Bindler plenáris előadása volt látható, illetve hallható. A következő három nap alatt négy párhuzamos helyszínen – három teremben a hotelben és egy teremben a Dalarna Múzeumban – mintegy 40 szekcióban, csaknem 130 szóbeli előadás, és két helyszínen összesen 50 poszter prezentáció volt a programban. A szekciókban jellemzően a különböző fémfajták, valamint a bányászat, a fémtechnológiák történeti és társadalmi vonatkozásai, illetve a kutatási fókuszok alapján csoportosították az előadásokat. Az archeometallurgia igen széles spektrumban képviselt interdiszciplináris jellege visszatükröződött az előadások sokszínűségében és többször is felvetődött, hogy a jövőben lehetőség szerint kevesebb párhuzamos helyszínen célszerűbb a különböző szekciókat megtartani.

A párhuzamos szekciókban a 15 perces előadások (5 perces hozzászólási lehetőséggel) a réz és rézalapú ötvözetek; a vas; illetve a nemesfém ötvözetek archeometallurgiájának, valamint a fémek és fémtechnológiák társadalmi hatásának fókuszában voltak csoportosítva. Az utolsó szakmai napon a korabeli bányák és történeti bányászati tevékenységek, illetve a legújabb, archeometallurgiához kapcsolódó archeometriai vizsgálatok és vizsgálati módszerek külön szekciókat kaptak. Az előadások és prezentációk nagyobbik fele esettanulmányról, illetve valamilyen időszaki, földrajzi vagy technológiai vezérfonalra felfűzött tanulmányról szólt, amelyekben rendszerint fontos szerepet kaptak az archeometriai vizsgálatok, de korszakokat, alapvető technológiát átfogó aspektusban is hallhattunk előadást.

Az AiE-konferenciák történetében először a programot, a tudnivalókat és az absztraktokat sem papír alapon, sem pendrive-on nem osztották ki a résztvevők között, hanem a honlapon (https://www.aie2024falun.com/), illetve letölthető applikáción keresztül volt minden technikai, ismeretterjesztő és szakmai anyag hozzáférhető. A svéd rendezők tervezik a prezentációkból készülő írások publikálását, de ennek részletei csak később tisztázódnak.

A magyar vonatkozású szóbeli előadások a következők voltak (elől az előadóval):

Béla Török, József Szentpéteri, Francesco Grazzi, Francesco Cantini, Antonella Scherillo: Scandinavian influences on 10th–11th century bronze finds from the Carpathian Basin

Béla Török, Anita Jenei, Antónia Horváth, Viktor Gál, Árpád Kovács: Remains of 10th–12th century iron metallurgy near Kazincbarcika (Northern Hungary) – Archaeometallurgical analysis of slag finds

Bernadett Bajnóczi, Zsuzsanna Siklósi, Stefano Nisi, Igor M. Villa, Viktória Mozgai, Zsuzsanna M. Virág: Spread of the products and technology of copper metallurgy in the Carpathian Basin from 5000 BCE to 3000 BCE

Eszter Horváth, Viktória Mozgai, Bernadett Bajnóczi: From unique to mass products – the ways of standardisation by the polychrome jewellery from the 5th–6th-century Carpathian Basin

Viktória Mozgai, Eszter Horváth, Zsolt Mráv, Mária Wolf, Anett Miháczi-Pálfi, Bernadett Bajnóczi: Niello through the ages – scientific analysis of niello-inlaid silver objects from Roman to Medieval times from the Carpathian Basin

Tena Karavidović, Ádám Thiele: The technology of massive split bloom production in the early Middle Ages – experimental approach

• doi: 10.55023/issn.1786-271X.2024-025

1. ábra: A köszöntő előadás közönsége.

Fig. 1.: The audience of the welcome speech.

2. ábra: Kirándulás Dalarnában.

Fig. 2.: Excursion in Dalarna.

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A konferencián bemutatott magyar poszter prezentációk:

Béla Török, Boglárka Tóth, Péter Barkóczy, Árpád Kovács, Péter Langó: Swords of Székesfehérvár – Technological analysis of two double edged swords from the 10th century Carpathian Basin

Zsolt Gallina, Gyöngyi Gulyás, Béla Török: One of Europe's largest excavated Early Medieval iron making areas from the Carpathian Basin – Latest results of the research of Avar bloomery centres

Béla Török, Emese Polónyi: The knowledge and application of gilding techniques in the Kingdom of Hungary during the Árpádian Era (11–13th century AD)

Viktória Mozgai, Valéria Kulcsár, Martin Borsódi, Eszter Horváth, Bernadett Bajnóczi: Reflecting the past – Material study of high-tin bronze mirrors from the migration period Carpathian Basin

Eszter Horváth, Viktória Mozgai, Bernadett Bajnóczi, Béla Miklós Szőke: Scientific study of early medieval "gombiky" from Mosaburg / Zalavár (Hungary), the seat of the easternmost county of the Carolingian Empire

Bár a felsorolt 11 prezentáció alapvetően két tudományos közösséghez köthető, amelyek egyes kutatókon keresztül egyébként egymással is folyamatos kapcsolatban vannak, ez a szám igen szép képviseletet jelent hazánk számára az ezen a speciális szakterületen vezető nemzetközi rendezvényen. Személyes jelenléttel a mintegy 150 fős konferencián (**1. ábra**) Magyarországot öt fő képviselte, köztük az Archeometriai Műhely szerkesztőbizottságának két tagja.

A tudományos szakmai részen kívül a konferencia programja természetesen ismeretterjesztő és szakmai jellegű kirándulásokat és bemutatókat is tartalmazott. Az első este a fogadó rendezvény az ipari műemlékké alakított, helyi Falu rézbányában volt, ahol a bánya külszíni fejtése mellett az egykori tárnákba is le lehetett menni. A városban már a 13. századtól bányásztak rézércet, és a bánya a 17. századi virágkora, illetve városi kiváltságai után még több mint 300 évig működött, majd 1992-ben zárt be. A buszos kirándulás a környező Dalarna térség jellegzetes faházas-farmos településeit és korábbi érckitermelő helyeit járta be (**2. ábra**), illetve egy plusz napon hosszabb kirándulásra is be lehetett fizetni.

A konferencia programja díszvacsorát is tartalmazott, a záróceremónián pedig az AiE elnöke bejelentette, hogy a hetedik konferenciát 2027-ben a spanyolországi Granadában tartják majd meg. A dátum nem véletlen, a 2019-es miskolci konferencia óta eltelt öt év apropójából, illetve az archeometallurgiai kutatások intenzív nemzetközi fejlődésére hivatkozva e sorok írója, mint az AiE Standing Committee tagja javasolta, hogy ezentúl a korábbi négyéves ciklus helyett innentől háromévente rendezzék meg az Archaeometallurgy in Europe konferenciákat.

Dr. Török Béla

az AiE Standing Committee tagja

HU ISSN 1786-271X; urn: nbn: hu-4106

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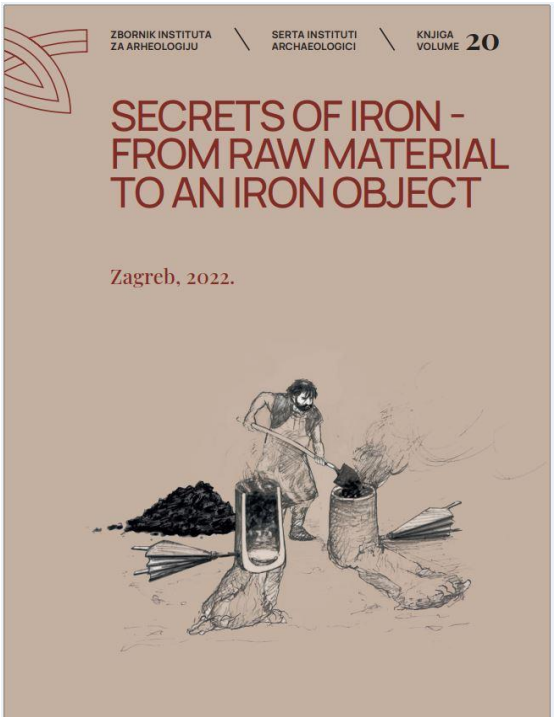
Könyvismertetés



Review: Secrets of Iron – From Raw Material to an Iron Object. Proceedings of the 7th International Conference of Medieval Archaeology of the Institute of Archaeology Zagreb, 10th – 11th September 2020.

Editors: Tajana Sekelj Ivančan; Tena Karavidović; Tatjana Tkalčec; Siniša Krznar; Juraj Belaj

Publisher: Institute of Archaeology, Zagreb, Croatia, 2022. 220 p.

ISBN 978-953-60-64-66-3 •

The book contains 16 studies from the presentations of the international scientific conference entitled *"Secrets of Iron – From Raw Material to an Iron Object"* which was organised by the Institute of Archaeology in cooperation with the Archaeological Museum in Zagreb in 2020. The topics of the conference and the book were mainly related to the medieval archaeology but at the same time, they covered multiple historical periods from the early Iron Age up to the Modern Age.

The majority of the papers focus geographically on East-Central Europe and a wide range of aspects is represented: in terms of the contemporary professions, mining, iron metallurgy, including metal production and processing.

Hungarian experts participated in the conference and in the reviewing process of the book. The opening presentation of the conference was held by János Gömöri (Hungarian Academy of Sciences, VEAB Group on Industrial Heritage). Furthermore, he also assisted in the reviewing process of the book. Béla Török (Archaeometallurgical Research Group of the University of Miskolc) participated in the reviewing work of the book.

The series of the studies start with two methodological research. *Sandra Rončević* presents an interesting overview about the advanced instrumental analytical methods used during the chemical profiling of archaeological samples alongside with the advantages and disadvantages of the different analytical methods. The author points out the importance of the selection of an appropriate method for compositional analysis with several crucial questions: like the costs of the investigations, whether the analytical methods are invasive or not or how much sample is required for the chosen analytical methods? Beside this, the importance of the multi-method approach (the combination of different analytical methods) in analysing the artefacts from early iron-production was highlighted in this paper and also very well represented in the second study written by *Ivan Nemet* and *Tena Karavidović*. The examined early-iron production remains were unearthed at Okuje site (Turopolje region, Croatia) and were analysed by using a combination of plasma spectrometric methods with X-ray fluorescence (XRF) and electron microscopy (SEM-EDS). The whole process was supplemented by principal component analysis and hierarchical cluster analysis. The study proved that this method, along with an extended elemental signature, is useful for identifying sub-groups within visually similar slags.

The following studies cover the topics of non-invasive methods of sites with remnants of iron production activities, geological studies of ore sources, excavations of different iron smelting sites, technological studies and technological transfer.

The paper, written by *Branko Mušič* and his co-workers, presents geochemical examinations of an iron-smelting area in the complex of Cvinger, Southeast Slovenia. The aim of this article is to examine the possibility of effective use of geophysical prospecting for the discovery of iron-smelting centres in the examined territory. The next study, written by *Branko Mušič, Barbara Horn* and *Tajana Sekelj Ivančan,* is also interesting since they present the results of magnetic prospection of the late antique and early medieval iron production sites in the Podravina Region, Northeast Croatia. The authors identified the former bloomery iron production site on the basis of their magnetic properties.

• doi: 10.55023/issn.1786-271X.2024-026

The next study was written by *Tomislav Brenko* and his colleagues. Their paper provides new data on soil characteristics and new evidence for possible bog iron ore formation of the area in Podravina Region (Northeast Croatia). The position of the possible bog iron ore formations was indicated by a previous archaeological excavation. *Vladimir I. Zavyalov* and *Nataliya N. Terekhova's* paper deals with the ore sources of the Ryazan Principality (Russia). The authors highlighted in their study that the discovered ore occurrences were located near to the major medieval craft centres. Presumably, these ore layers were easily accessible to the former miners. However, the authors successfully determined the characteristics of the ore used by the medieval ironmakers of Ryazan. The next study written by *Ladislav Lazić* and *Aleksandar Durman* presents the mining and metallurgy in the Mount Trgovi and Northwestern Bosnia. The main objective of the research was to show the importance of iron production and trade in the examined territory, which led to the emergence of settlements and the constructions of roads. The paper also gives a short description of the technology of iron production. *Tena Karavidović* and *Ivan Drnić* in their study present the analysis of findings related to iron production from two Iron Age Sites (Gornje Pokupje and Sisak-Pogorelac, Croatia). The objectives of the research were to understand the activities carried out at the sites and to determine the potential of local iron production at that time in the Pokuplje region (central Croatia). This paper contributes new data to the study of iron metallurgy within the region paving the way for more intensive future research. The article by *Aleksandra Bugar* presents the results of the archaeological excavations at the Okuje Site which is located in Turopolje, south of Zagreb. The author points out the traces of metallurgical activity. According to the author, this area is probably at the edge of a workshop complex where metallurgical waste was disposed. The study also contains a short summary of the chemical analysis of the waste.

Ivan Valent's article aims to present a preliminary interpretation of the slag from the Study Archaeological Collection of the Koprivnica Town Museum and the newly conducted excavation in the River Drava Basin. Besides this, the author discusses the type and the intensity of metallurgical activities within the Iron Age and Antiquity.

The next study written by *Brigitte Cech* deals with the production of iron in Hüttenberg (Carinthia, Austria). Ferrum Noricum was known for its high-quality steel in the ancient times, and the researchers assume that Hüttenberg was the centre of production of this famous steel. The author presents in her paper the steps of the excavation which was carried out in Schemlach/Eisner. This was a highly important industrial site (from the 1st century BC until the 4th century AD) and at the same time clear evidence of a settlement was also found. In the following paper, the results of an interdisciplinary research were presented by *Ana Konestra* and her co-authors. The research was carried out at Podšilo bay in Lopar on the island of Rab (northeastern Adriatic) where the remains of iron smelting has been detected in a Roman rural site. Another interesting paper can be read about metallurgical site of Pržanj, near Ljubljana. The interdisciplinary study was written by *Daša Pavlovič* and *Jaka Burja.* They present the results of mineralogical and chemical analysis of 22 iron slag, ore and furnace lining samples from the examined territory. The following article by *Silviu Oța* discusses the iron processing at Caransebeș (Romania) in the Early Modern Age. The use of the discovered workshop started from the 14th century and operated until the integration of the territory into the Habsburg Empire. However, the article focuses only on the 16th and 17th century. Based on the results of the excavation, the author assumes that the common use iron objects like nails, spikes, horseshoes were produced here.

A very unique study is written by Damir Doračić and his colleagues which shows the technological analysis and conservation process of an early medieval double-edged sword accidentally discovered at the quarry at Bojna-Brekinjova Kosa in Sisak-Moslavina (Croatia). After the restoration and conservation of the weapon, metallographical examinations were carried out in order to reconstruct the manufacturing techniques and trace the potential source of iron used for the sword. The authors established that the blade was pattern-welded and constructed from nine pieces.

The last paper, written by *Gašper Oitzl* discusses a significant progress in ironworking technologies in Slovenian territory between the 14th and 16th centuries. In this process, foreign ironworking masters, presumably originated from Italy, played an important role in the implantation of new technologies.

The studies presented in this book are interdisciplinary and show the readers various approaches and sub-topics with different methodology of the discussed subjects, for instance, archaeological excavations of preserved furnaces and workshops or discussions on long-term iron production and knowledge transfer. The value of the interdisciplinarity is very clearly represented not only in the individual papers but in the whole volume as well. The authors of the book present new findings and because of this, it can be useful to the professionals concerned, not only in the country of the publication, but also internationally. The book's target readers are scholars and researchers dealing with archaeology, history of ironmaking and processing, but it is also recommended for students and PhD students concerned in this topic.

HU ISSN 1786-271X; urn: nbn: hu-4106 © by the author(s)

Overall, the subject of the book is specialized but the different approaches of the various topics mean that it would be of interest to humanities and technical-scientific specialists who are not directly worked with this field.

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HU ISSN 1786-271X; urn: nbn: hu-4106