

Copper sulphosalts in early metallurgy (2600–1900 BC) – chemical-mineralogical investigation of artefacts from southern Poland

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We describe a methodology of investigation of both Cu metal matrix and its mineral inclusions that aims at increasing the effectiveness of identifying the type of ore used in metal production. We point to sulphosalt ores as the main source of metal for the Final Neolithic/Early Bronze Age copper artefacts from southern Poland. The inclusions, rich in Ag, As, Sb and Sn, document the type of ore, regardless of the metallurgical process leading to depletion of As and Sb. The copper metal should contain neither Sb nor As, hence both of these elements, if originally present in ore, can be preserved only in inclusions. The concentrations of Ag, Sb, As and Sn in the artefacts investigated, the presence of inclusions, and their chemical composition, are the key indicators for the determination of the mineralogical composition of the original ores. Given the high concentrations of Sb, As and Ag in the Cu metal and mineralogy of the inclusions, the ore must have contained varying proportions of Ag-bearing tetrahedrite $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$ and tennantite $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$. Mineralogical compositions of the copper ores indicate the deposits in Slovakia (Špania Dolina) as the source of metal for the artefacts investigated. The results of Pb and Cu isotopic analyses carried out for this study support those conclusions.

Key words: copper metallurgy, SEM-EPMA, Pb isotopes, Cu isotopes, Final Neolithic/Early Bronze Age, Mierzanowicka culture.

INTRODUCTION

“Thread and wire” metallurgy, in which we should also count the Bronze Age part of the artefacts investigated, is a very widely spread copper-based industry in the Eneolithic and Early Bronze Age in Europe. The *Löckenringe* (willow-leaf shaped pendants), its main representatives, are considered to originate stylistically from the Near East (Zaharia, 1959: fig. 1:3, 12:6); the oldest pendants of that kind were found in Ur and are dated back to the Early Dynastic period III (2600–2400 BC; Śliwa, 1997: 273). The ornament style spread quickly from Mesopotamia to Anatolia (Troy II/III – ~2300 BC, Śliwa, 1997: 41) and the Balkans (Moldova Veche – Cotofeni IIIc; Roman, 1976: fig. 8; tab. 8: 19c, d). Two or three centuries later it appeared in Central Europe (southeastern Poland, southwestern Slovakia) and the Caucasus (Georgia, Dagestan). The golden age of the

Löckenringe production falls within the Early Bronze Age Carpathian epi-Corded Ware circle (Mierzanowicka culture) which, with reference to metallurgy, was solely based on the “thread and wire” technology. As a research subject it has been so far neglected in archaeometallurgical studies, while the contemporaneous Únětice culture (western Poland, eastern Germany and Czech Republic) and its metallurgical tradition has received much attention. It is therefore timely to shed some light into technological and provenance aspects of the “thread and wire” metallurgy. The earlier, Final Neolithic metal finds of the Corded Ware culture, which constituted the core part of cultural tradition, continued into the Bronze Age, have been chosen for comparison in terms of their chemical and mineralogical composition and technology.

Our study shows how detailed microprobe chemical analyses of both matrix and inclusions of a copper object can be combined in order to acquire more detailed metallographic characteristics of artefacts and how this affects inferences regarding the sources of ores and location of the areas exploited. These results were then compared with the lead and copper isotope analyses obtained.

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METHODOLOGICAL BACKGROUND

That chemical analysis can be the basis of provenance studies of metal dates back to the nineteenth century (Pernicka, 1999). Its development was stimulated by the introduction of spectrographic methods that allowed minor and trace element concentrations to be accurately determined. Initially, provenance studies were focused on connecting minor ore deposits to the circulation of metal in Central Europe (Witter, 1938; Otto and Witter, 1952; Neuninger et al., 1957). However, in this research was placed on the importance of the Eastern Alps as an early source of copper, while some attention was also given to potential supply from other ore deposits, such as those in central Germany, the Slovakian mountains and the Balkans. By the 1960s, chemical analysis was being used to identify early metal types in other parts of Europe. The largest of these studies was the Stuttgart programme, which provided analyses of some 20'000 prehistoric metal objects from across Europe (Junghans et al., 1960, 1968, 1971, 1974). These results were used to identify the circulation of distinct metal groups, which could potentially be traced back to their geological source. With some exceptions (e.g., Coghlan and Case, 1957; Coghlan et al., 1963) this type of source provenancing was not a success. This was mainly because of complex changes that occurred during the conversion of ore to metal by smelting and by subsequent thermal processes such as casting. The research also exposed a limited understanding of relevant sources of copper ores and their geochemistry, which restricted any direct comparison with the analysis of the finished metalwork (cf. Pernicka, 1999).

The perceived failure of the Stuttgart programme in terms of source provenance studies of prehistoric metalwork cast a shadow over this area of research for many years. There were important successes in later research, such as the analysis of Copper Age metalwork in the Balkans and its relationship to ore sources (Pernicka et al., 1993, 1997) but mostly it showed how difficult it is to establish direct links with particular ore sources.

Regarding copper mining in prehistoric Europe, three major types of copper mining can be distinguished (O'Brien, 2012). This division is based on both the types of ore sources exploited and the technology applied. The earliest mining of copper ore involved the extraction of secondary minerals from surface zones of oxidation, such as malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$ and azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. These minerals are rich in copper and easy to smelt using a primitive hearth or crucible technology. They were first used in the Chalcolithic, when the deposits were locally exploited continuously throughout the Bronze Age. The use of these ores declined significantly by the later second millennium BC, suggesting widespread exhaustion of accessible deposits.

The second mining tradition involved the use of fahlore (Fahlerz), namely copper sulphosalts of the tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ – tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ solid solution. These are rich in copper (~50%), and like the oxidized ores could be smelted using a low temperature, non-slagging technology. Fahlore (Fahlerz) mining is particularly associated with the spread of Beaker culture metallurgy in Western Europe in the third millennium BC (O'Brien, 2012) but, according to evidence from the Inn Valley in Austria, it commenced already in the Neolithic (Höppner et al., 2005). The use of fahlore declined significantly with the adoption of tin bronze around 2000 BC, but was developed further in central Europe during the Late Bronze Age.

The final copper mining tradition in Europe focused on the extraction of primary sulphide ore (cf. Bachmann, 2003: 28), particularly copper-iron sulphides such as bornite Cu_5FeS_4 and chalcopyrite CuFeS_2 . Their earliest exploitation is not well dated, possibly beginning in the late Chalcolithic/Early Bronze

Age, e.g. the Mitterberg complex in Austria (Stöllner, 2003). While copper-iron sulphides, such as chalcopyrite, can be reduced using a primitive process, the efficient recovery of metal required an advanced furnace technology that was only developed at a later stage in the Bronze Age (Craddock, 1999). Hence these mining traditions often overlapped in different parts of Europe. This would have occurred where separate mines with different ore types were worked at the same time using different technologies, and even in the same mine operation where different ore types were encountered. There is a general chronological trend from the mining of native copper and oxidized ores, to the extraction of fahlores, to the extraction of copper-iron sulphides. This does not have to reflect the depth zonation within ore bodies, but rather the development of new technologies and mining strategies that allowed different types of ore deposit to be mined. Such could have been the case of the fahlores due to the ease of extraction and perceived quality of the resulting metal.

The first attempts to identify ore types used in prehistory were made in 1950s by Otto and Witter (1952), who identified prehistoric copper with high concentrations of arsenic, antimony and silver and concluded that the ores used for the production of this copper contained an appreciable fraction of fahlores. In the 1960s, based on investigation of minor and trace elements found in copper artefacts, it was indicated that silver, arsenic, bismuth, iron, antimony and lead were the most diagnostic metallic impurities for discrimination of ore type (Friedman et al., 1966). Two decades later this approach was refined (Rapp, 1988) involving analysis for sulphur (Rapp, 1989: 107). The significance of inclusions in the Cu metal had already been noted in the studies by Rehren (1991) and Rehren and Northover (1990). Based on analyses of copper ingots from Cyprus, they emphasized the selenium and tellurium inclusions and discussed the influence of ore composition and smelting technology on the contents of these elements in the Cu metal.

However, it has been shown from laboratory experimentation (Pollard and Bray, 2014) that if a copper ore contains nickel, arsenic and antimony, then all the antimony (Sb) in the charge is transferred to the metal at all temperatures between 700 and 1100°C. By contrast, the nickel (Ni) will not appear in the smelted metal at all unless the temperature is above 950°C, while only low percentages of the original arsenic (As) content will be transferred at temperatures below 950°C. Thus, if the "impurity pattern" of interest consisted of the presence or absence of Sb, As and Ni (all important elements in early copper-based metallurgy) then the impurity pattern of the metal smelted of the same charge changes dramatically if the furnace temperature goes above 950–1000°C. Using the standard model of provenance, such an observation would be taken as indicating a switch in ore source. This counsels caution if considering only one possible explanation of such a change.

In addition to the chemical composition of an object, another key attribute that can be measured is the isotopic composition. The advantage of looking at the isotopic composition of an element, rather than at abundances of minor and trace elements, is that in heavy element like lead this does not change on the way from the ore to the artefact. Regardless of the processes involved in the treatment of ore or metal, the isotopic composition remains constant. Lead isotope ratios of single artefacts can be compared with those of an ore deposit. If they are different, it can be concluded that the artefact does not derive from that specific ore source. Conversely, it is not possible to regard the provenance of an artefact as proven even if it shares the same isotopic signature as an ore deposit. The reason for this is that although the variations of lead isotope ratios

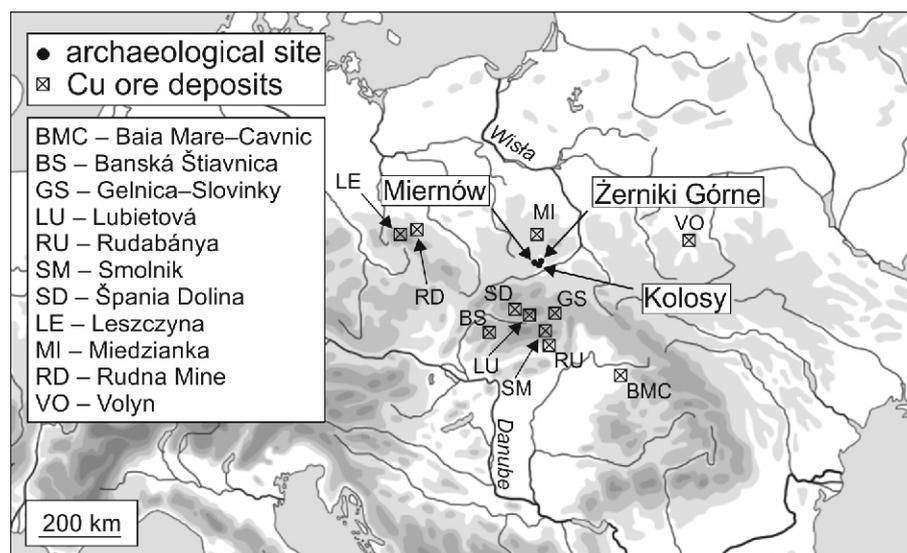


Fig. 1. Location of the archaeological sites (Miernów, Żerniki Górne, Kolosy) and Cu ore deposits in the Carpathians and adjacent areas

in ore deposits are much smaller than that of trace element concentrations, there exists the possibility that another deposit has the same isotope ratio. The isotopic composition of lead was identified as a source of information concerning ancient copper in 1982 (Gale and Stos-Gale, 1982) and since then isotopic analyses of lead have been widely used for determining the origin of Bronze Age metals.

Advances in our understanding of copper isotopes and their variance with respect to copper ore mineral composition (cf. Powell et al., 2017) provides a new approach to investigating ancient mining practices through analysis of copper artefacts, the final product of the metallurgical process. Copper isotopic analysis provides no direct insights into the specific location from which copper ore was extracted (provenance). Rather, it identifies the nature of the mineral that comprised the ore, and aspects of the climate in which copper ores weathered. It has been demonstrated that neither ancient nor modern techniques for processing of copper ores fractionate copper, and so the copper isotope composition of metallic artefacts corresponds to that of the ores from which they were made.

Copper isotope ratios differ between primary (hypogene) sulphidic, secondary (supergene) sulphidic and oxidized ore sources. Traditional lead isotope signatures of ancient metals are specific to deposits, while copper isotope signatures are specific to the ore minerals used for metal production in ancient times (Jansen et al., 2018).

The first attempts to use copper isotopes in archaeometallurgy were conducted in the mid-1990s (Gale et al., 1999; Woodhead et al., 1999). Through the analysis of material from copper smelting and fire refining experiments, fractionation of Cu isotopes during metallurgical operations was not detected. The first systematic investigations were carried out on Roman coins, ingots and bronzes which were compared to deposits from the Iberian Peninsula, Siegerland and Lahn-Dill (Germany; Klein et al., 2002, 2004, 2007, 2009). These studies discerned deposits with overlapping Pb isotope signatures by using Cu isotopes, and the analysis of coins allowed the detection of shifts in using those deposits through time. For any copper deposit, the copper isotope values in all three reservoirs are controlled by the starting composition of the non-weathered ore, the degree of weathering, and the mineral species being

weathered. This degree of variability among numerous ore deposits would likely result in the overlap of copper isotope composition between populations of artefacts. Therefore, shifts in the mean copper isotope values and associated standard deviations would best reflect changes in ore use.

MATERIAL AND METHODS

METAL SAMPLE AND ARCHAEOLOGICAL BACKGROUND

The metal samples for this research were selected based on three general criteria: (a) material: copper objects in order to exclude distortions inevitable in analyzing copper-tin alloys, (b) technology: one “technological” group (the so-called thread and wire metallurgy), (c) well-defined archaeological context.

All twelve metal artefacts analysed come from graves dated to the third millennium BC from Lesser Poland (Małopolska) (Fig. 1 and Table 1). These graves were discovered during excavations of burial mounds performed in the 1960s and 1970s by A. Kempisty at sites in Kolosy, Miernów (both Kazimierza Wielka county) and Żerniki Górne (Busko Zdrój county; Kempisty, 1978; Włodarczak, 1998; Kempisty and Włodarczak, 2000). Beneath the burial mounds and in their surroundings many Final Neolithic and Early Bronze Age graves were discovered.

The metal objects found in graves can be assigned to two chronological horizons:

- ~2600–2400 BC – Corded Ware culture graves – Kolosy, grave 4 (K-1); Żerniki Górne, graves 78 (Z-1, Z-2) and 138 (Z-5);
- ~2100–1900 BC – older and classical phase of the Mierzanowice culture (Miernów, tumulus II, graves 6 and 8 (M1a-f); Żerniki Górne, grave 121 (Z-3, Z-4).

Metal objects chosen for analyses (Fig. 2) represent typical forms common for grave furnishings from Lesser Poland (Małopolska). The predominant category of both of the chronological horizons is ornament, in most cases earrings. They started to appear in the catacomb graves of the Corded Ware culture ~2500 BC. The most commonly form used was a spiral-shaped earring with one end tapped and the other sharpened

Table 1

Inventory of the artefacts analysed

No.	Sample	Site	Grave	Type of artefact	Archaeological culture
1	K-1	KOLOSZY	4	awl	Corded Ware
2	M-1a	MIERNÓW II	6	fragment of ring	Mierzanowice
3	M-1b	MIERNÓW II	6	fragment of ring	Mierzanowice
4	M-1c	MIERNÓW II	6	fragment of earring	Mierzanowice
5	M-1d	MIERNÓW II	8	fragment of ring	Mierzanowice
6	M-1e	MIERNÓW II	6	earring	Mierzanowice
7	M-1f	MIERNÓW II	8	Tube	Mierzanowice
8	Z-1	ŻERNIKI GÓRNE	78	earring	Corded Ware
9	Z-2	ŻERNIKI GÓRNE	78	earring	Corded Ware
10	Z-3	ŻERNIKI GÓRNE	121	earring	Mierzanowice
11	Z-4	ŻERNIKI GÓRNE	121	earring	Mierzanowice
12	Z-5	ŻERNIKI GÓRNE	138	knife/head of pin	Corded Ware



Fig. 2. The artefacts analysed (photo by M. Osiadacz)

(e.g., earrings from grave 78 in Żerniki Górne). Later, in the Early Bronze Age assemblages, willow leaf-shaped earrings dominate, like the ones from grave 6 from Miernów (M1a–e) and grave 121 from Żerniki Górne – Z-3 and Z-4 (Kadrow, 2000). Their shapes are considered as a typological development of the Final Neolithic ornaments (Kempisty, 1982). The metal series includes also two tools found in the catacomb graves of the Corded Ware culture: an awl from Kolosy (K-1) and a small “knife” from Żerniki Górne – Z-5 (grave 138). The first one represents the only tool group that appears repeatedly in the Final Neolithic burials. Awls of that kind occur in male graves and are interpreted as tools used in flint manufacturing. The number of the Final Neolithic burials furnished with metal artefacts in the Małopolska Uplands is relatively large in comparison to those of other regional groups of the Corded Ware culture. The tradition of furnishing the dead with golden or copper objects continued into the Early Bronze Age. It seems as though, in this region over ~1000 years, the aesthetic preferences regarding metal items as well as the technological process and ore mining remained unchanged. Given the lack of rich local copper ore deposits, the main issues here concern not only the provenance and organization of import of copper to the territory of southern Poland but also its local technological treatment.

METHODS

Small pieces of copper artefacts, of a few cubic millimetres, were cut and mounted in one block 2.54 cm in diameter (Fig. 3), using 2020 Araldite resin (Huntsman LLC). This was lapped and polished using diamond abrasive materials. During the lapping a metallic bond diamond (40 µm) Tissediam disk (Presi-Métallographie) was used in order to expose relevant sections of the artefacts mounted in the block. The process was carefully controlled under a stereoscopic microscope. During the polishing, diamond gels with diamond grains of 9 µm, 3 µm and 1 µm were used, with polishing times of 40, 15, and 3 minutes, respectively. Polishing materials with 0.25 µm diamond grains were avoided in order to avoid the possible incorporation of fine-grained diamond into the soft copper material.

Chemical and mineralogical analyses of the copper artefacts were carried out using electron microscopes and a CAMECA SX100 electron microprobe at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances at the Faculty of Geology, University of Warsaw. The microprobe was equipped with 4 wavelength dispersion spectrometers (WDS), worked at accelerating voltage of 15 keV, with the beam current and beam diameter respectively of 20 nA and 2 µm. The counting time at the peak maximum was 20 seconds and 10 seconds at background, measured at both sides of the peak.

The calibration of Cu (K α , LIF) was done using pure KGHM 99.99 wt.% electrolytically refined copper, that was finally polished together with the samples analysed for the investigations. The mean detection limit for Cu was 0.07 wt.%. The other elements were calibrated using natural and synthetic standards supplied by CAMECA and SPI Ltd. Standards, analytical lines, diffracting crystals, and mean detection limits expressed in wt.% for these were as follows: InAs – As (L α , TAP, 0.08); InSb – Sb (L α , PET, 0.04); Ag₂Te – Ag (L α , PET, 0.05); cassiterite – Sn (L α , PET, 0.03); NiO – Ni (K α , LIF, 0.04); CoO – Co (K α , LIF, 0.02); Bi₂Te₃ – Bi (M α , PET, 0.02), sphalerite – Zn (K α , LIF, 0.07), PbS – Pb (M α , PET, 0.08); Fe₂O₃ – Fe (K α , LIF, 0.03); CuFeS₂ – S (K α , PET, 0.02), and Bi₂Se₃ – Se (L α , TAP, 0.03). Au, Te and In were also analysed but their amounts were below detection limits in all artefacts examined. The raw microprobe counts were reduced with the PAP routine (Pouchou and Pichoir, 1985).

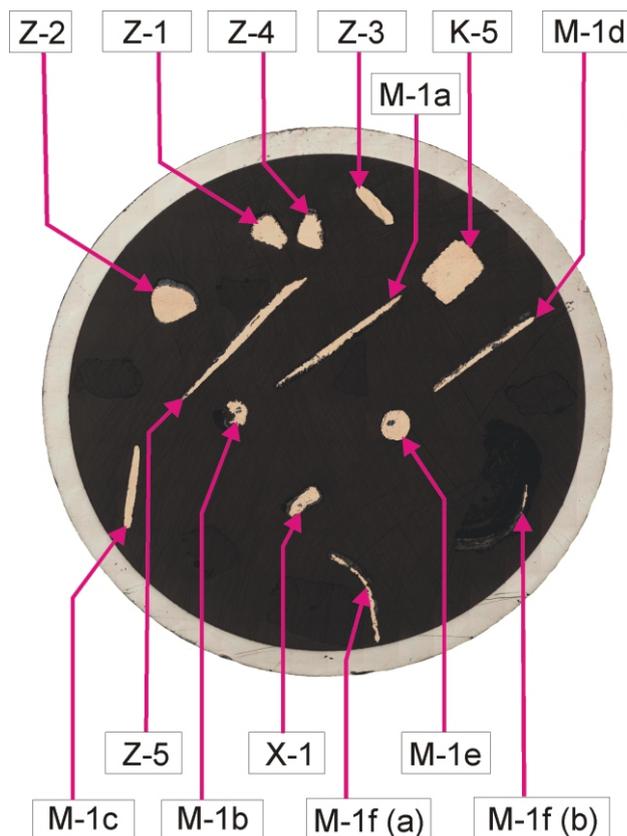


Fig. 3. The araldite block with mounted samples of copper artefacts

All samples were cut perpendicular to the long axis of the objects; the aluminum ring is 2.54 cm in outer diameter

Electron microprobe compositions at 323 points within the matrix of 12 objects were obtained (Table 1). The number of analytical points in the samples analysed range from 20 to 30, being higher in inhomogeneous samples and samples containing numerous inclusions. The selection of the elements analysed was based both on already published results of chemical analyses of archaeological artefacts (Junghans et al., 1960, 1968, 1974) and mineralogical compositions of the Carpathian copper deposits that contain enhanced concentrations of As, Sb, Pb, Zn, Ag, Au, Ni, Co, Se and Te (Chovan et al., 1994; Szakáll, 2001; Ľudá and Ozdín, 2012). In the discussion section below only the concentrations of the elements that significantly exceeded the calculated detection limits were taken into account.

The inclusions study was performed using an ultra-high-resolution analytical FE-SEM Hitachi SU-70 fitted with a Schottky field emission source, which ensures both a sufficiently high probe current and high resolution for the analytical techniques. During SEM observations, chemical analysis of the samples (matrix and inclusions) were performed at an acceleration voltage of 15–20 keV with an energy dispersive spectrometer (EDS) equipped with a Thermo Scientific™ UltraDry EDS Detector. The microscope is also fitted with a YAG back-scattered electron detector (YAG-BSE) which allows observation of samples in compositional contrast. In all samples, the chemical composition of each type of inclusion was defined by at least three measurements depending on the size of the inclusion. The accuracy of the instrument is (in most cases) 0.1 wt.% and the detection limit is also ~0.1 wt.%. However, these parameters change since heavier elements in a heavy matrix are ana-

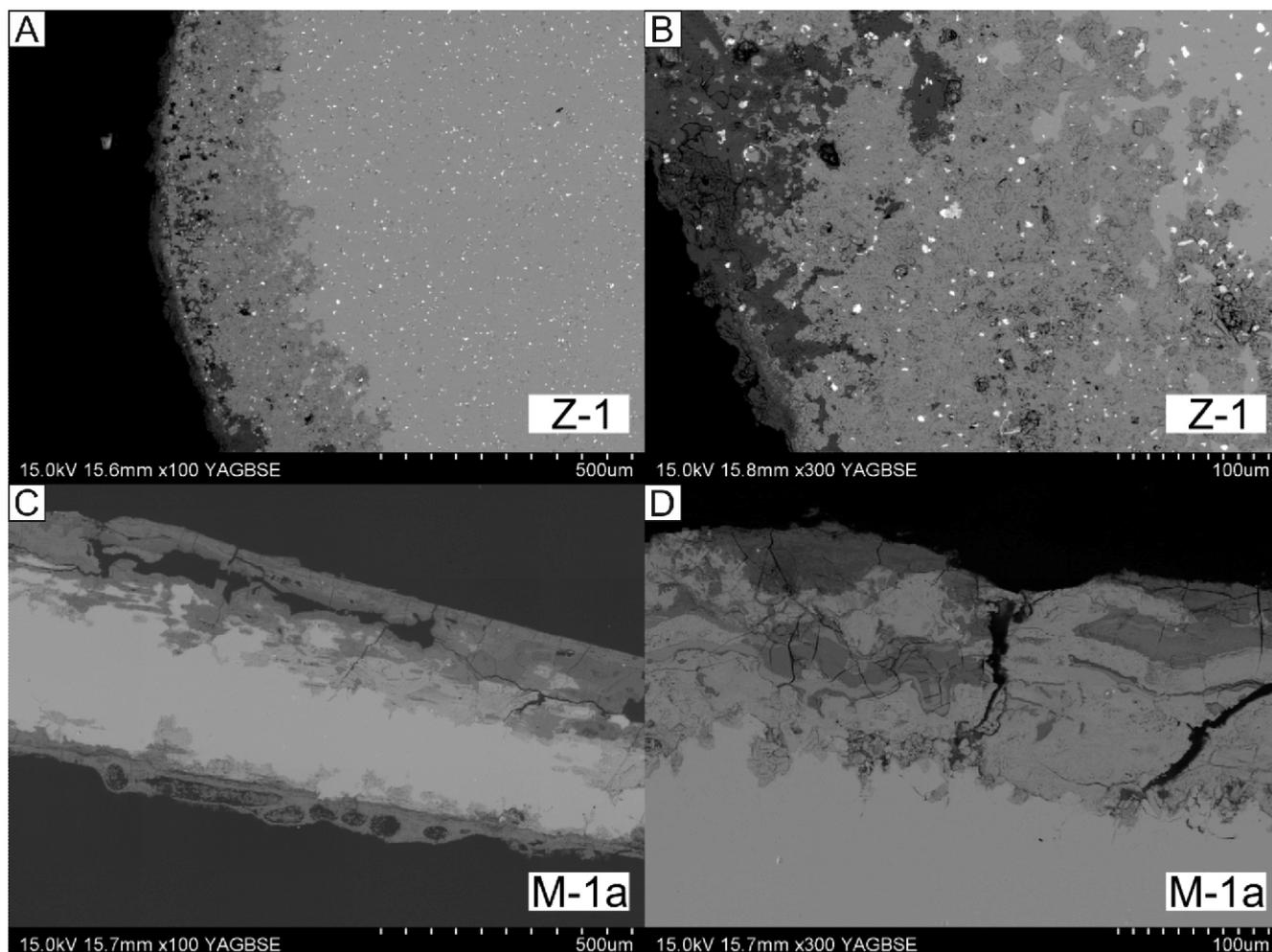


Fig. 4. SEM images of cross-sections of the samples analysed with corrosion layers: Z-1 (A, B), M-1a (C, D)

See text for further explanations

lysed with higher precision than lighter ones; this might be the case of the present study since the copper matrix analysed comprises from different elements in variable amounts. Therefore, the chemical composition of the inclusions is considered half-quantitative.

The analyses of Cu and Pb isotopes of the artefacts and copper ore samples from Poland, Ukraine and the Carpathian Basin was performed in Sweden, at ALS Scandinavia AB. The copper ore samples were prepared using the ALS Scandinavia standard procedure, i.e. after grinding they were subjected to microwave-assisted digestion in a concentrated $\text{HNO}_3 + \text{HCl}$ mixture. The analyses were carried out by MC-ICP-MS (NEPTUNE, Thermo Scientific). Delta values for Cu were calculated against a NIST SRM 976 standard. Standard deviation values (SD) were calculated based on two independent consecutive measurements of isotope ratios. The amount of Cu, Pb and other trace elements in the samples analyzed were checked using ICP-MS before the analysis.

RESULTS

The fragments of artefacts studied are characterized by the presence of corrosion layers developed at the surface of objects, while the inner parts of the samples (copper matrix) comprise dispersed inclusions of different shape and spatial distribution (Figs. 4 and 5). The SEM observations and chemical investigations dealt with each of these two entities distinguished with major emphasis on the latter.

However, due to their importance in terms of provenance studies, detailed analyses of selected inclusions was also performed. The weathered rims, usually green, 0.25 to 3 mm thick (Fig. 4A, B), consist of malachite and cuprite¹. There are also numerous small inclusions of native silver (Ag) within the outer rims (bright objects marked by arrows in the BSE images, see Fig. 4A, B and 5B), especially in Ag-bearing artefacts.

The surface of the artefacts was partially degraded due to exposure to a corrosive environment when buried in the

¹ According to the International Mineralogical Association (IMA) official guidelines, the phases described in this paper are not minerals (for details see www.ima-mineralogy.org). However, for the sake of clarity and relevance to other published papers, we assign them names of mineral species but only due to their similarity in terms of chemical composition.

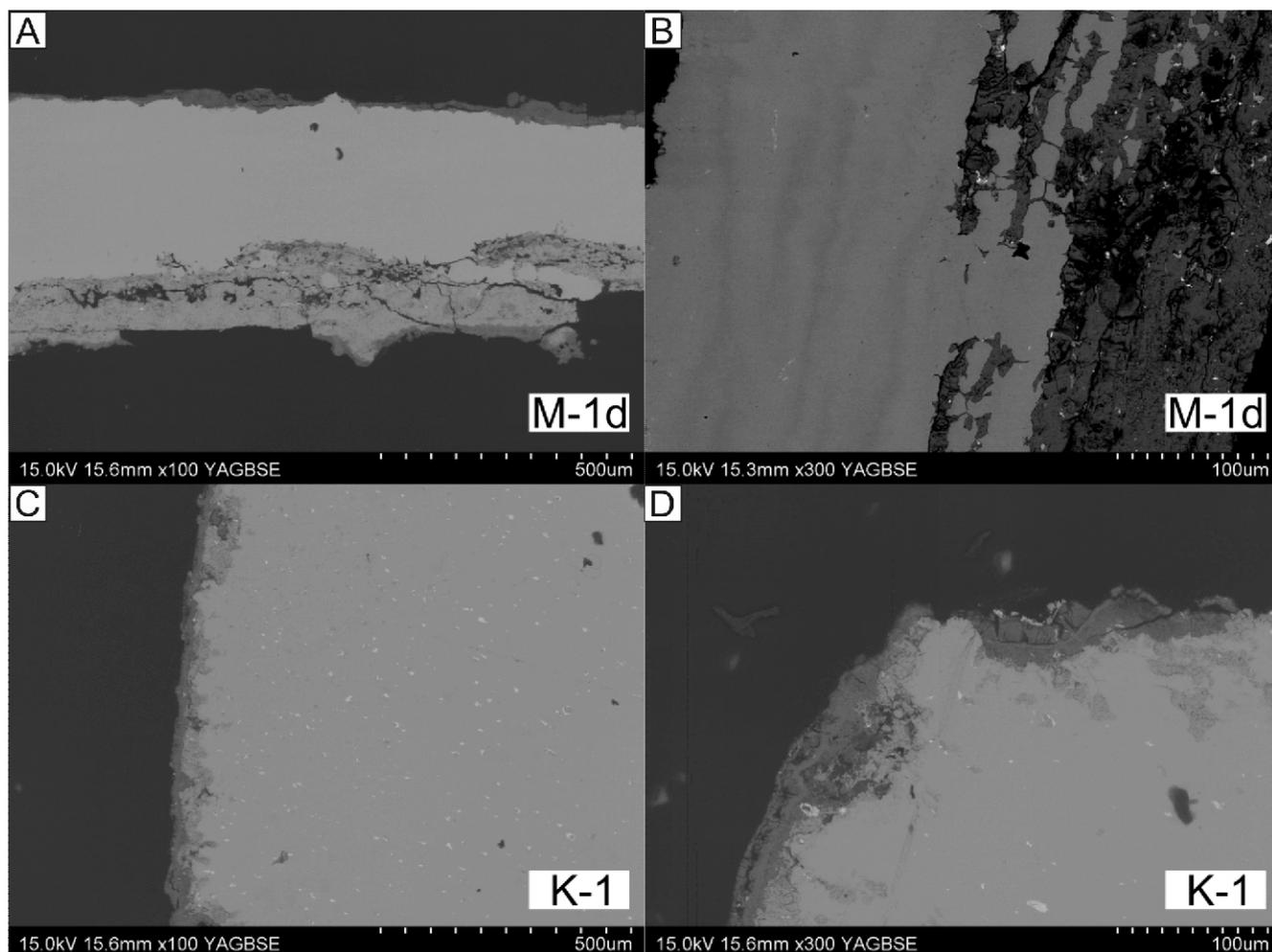


Fig. 5. SEM images of the cross-section of the samples analysed with corrosion layers: M-1d (A, B), K-1 (C, D)

ground. The samples with circular (Z-1) and square (K-1) cross-sections have homogeneous corrosion layers over the whole surface. The layers are composed mainly of malachite, cuprite and rare brochantite. The thickness of the corrosion layer of the earring (Z-1) and the awl (K-1) was ~330 µm and 100 µm, respectively. However, in the case of the planar artefacts (M-1a and M-1d), corrosion layers of different thickness were observed on the opposite surfaces.

CHEMICAL FEATURES OF METAL MATRIX

The study of the Early Bronze Age artefacts documents a complex chemical composition of the Cu metal (matrix) that is additionally controlled by the occurrence of numerous Cu-O, Pb-Sb-O, Pb-As-O, Sn-Co-Ni-Se inclusions (Figs. 6 and 7). The concentration of Cu, measured by electron microprobe (EPMA) of the volume of a few cubic micrometres, ranges from 94.41 up to 99 wt.%. The other most common elements determined are As, Sb, Ag, Ni and Sn (Appendix 1*) The As and Ag concentrations are elevated in most of the samples. The highest concentrations of As and Ag reach up to 2.12 and 1.41 wt.%, respectively. In two samples, Z-1 and M-1d, Sb is

also present as a major admixture. In sample Z-1 the Sb concentrations vary from 0.51 to 0.71 wt.%, while in sample M-1d they range from 0.68 to 3.04 wt.%.

Sample M-1d is unique in the set analysed not only in its high concentrations of Sb, Ag, but also of Ni (0.77–1.77 wt.%), As (0.13–0.53 wt.%) and Sn (0.01–0.36 wt.%). The high concentrations of these metals in the Cu matrix also correspond to enhanced concentration of Co (up to 0.13 wt.%) and numerous inclusions of Sn-Co-Ni-Se-rich phases, probably originating in melting of the ore. Higher concentrations of Sn (up to 0.12 wt.%) were determined also in some parts of the Z-4 sample (Appendix 1).

Beside As, Sb, Ag, Ni and Sn, the presence of Pb, Bi, Zn, Cd and Au was ascertained. Their contents do not exceed 0.34 wt.% (taking into account their respective detection limits). In many samples the following pattern was observed: the occurrence of numerous As-, Sb-, Pb-, and Bi-rich inclusions correlated inversely with the contents of these elements in the Cu matrix, e.g. low contents of Pb and Sb in sample K-1 was compensated for by numerous Pb-Sb-O inclusions (cf. Figs. 6, 7 and Appendix 1).

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1473

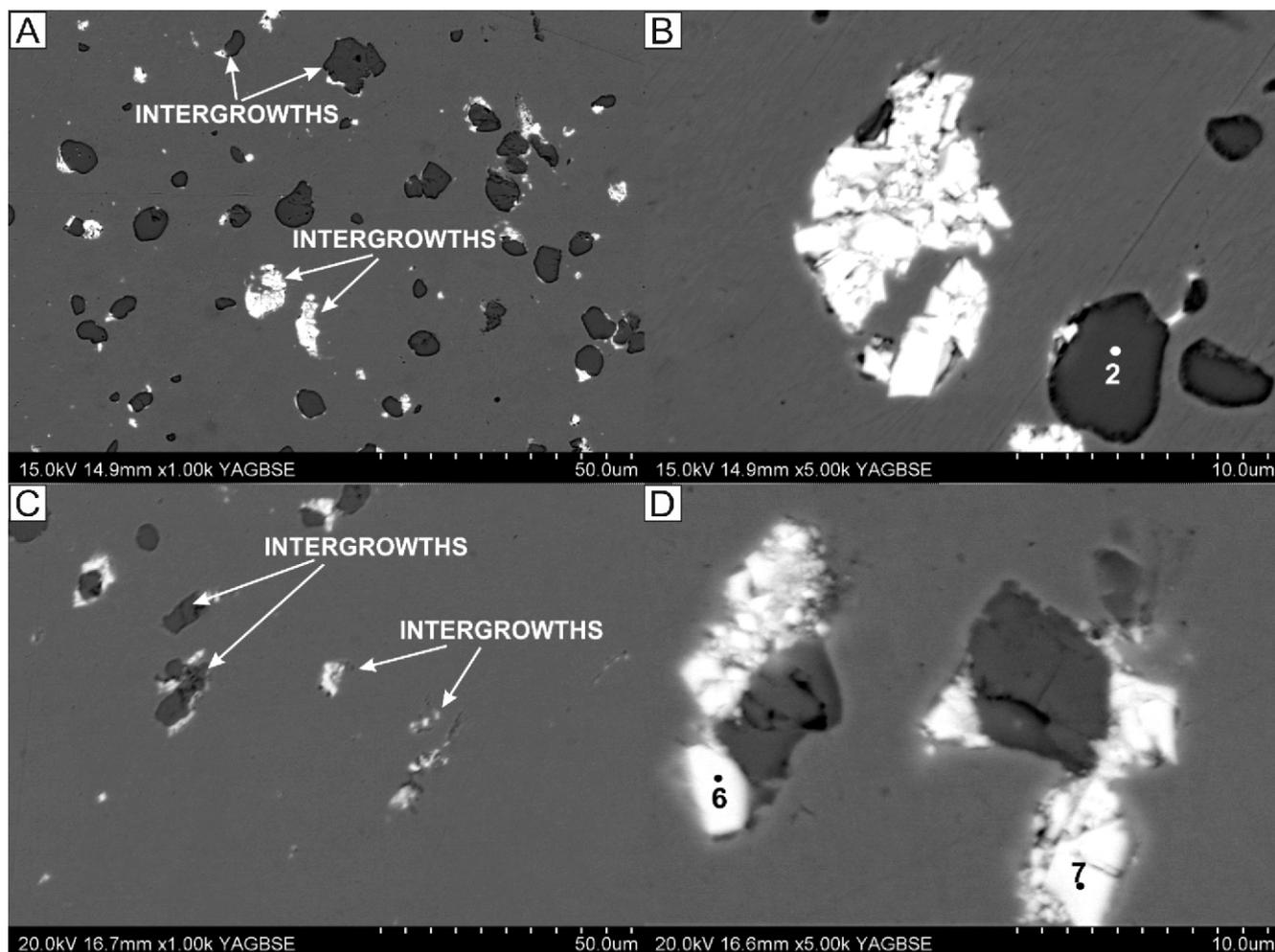


Fig 6. SEM images of the inclusions observed on the cross-sections of the earring Z-1 (A, B) and the awl K-1 (C, D)

White inclusions are composed mainly of Pb, Sb and As, dark ones are composed of Cu-O and were probably formed as a result of the removal of inclusions during the sample preparation process; numbered dots in B and D denote spots where chemical analyses were performed (see Table 2 for results); see text for further explanations

In the samples studied copper does not demonstrate significant variation in its chemical composition (with constant brightness in the BSE images), except for some samples (Fig. 5B) where parallel zoning of chemical composition was observed. These textural patterns probably reflect later metallurgical treatment of the material.

CHARACTERISTICS OF THE MINERAL INCLUSIONS

The SEM observation of the samples taken from the earring and the awl revealed the presence of bright inclusions in the matrix of the copper artefacts (Figs. 5A and 6D). In order to characterize in detail their morphology and chemical composition, SEM observation at magnifications between 500 and 5000x (Figs. 6 and 7) as well as standardless chemical analysis (EDS) were performed. Table 2 shows selected examples of chemical compositions of all major types of inclusion and samples in which they were observed. However, in each sample the chemical composition of the same type of the inclusion is slightly different due to the presence of additional minor elements. The full set of analyses of the inclusions (including major and minor elements) is provided in Appendix 2. The chemical

analyses given in Table 2 were carried out at chosen points (Fig. 6B, D).

Samples Z-1 and Z-2 have the highest number of inclusions (Fig. 6A, B). Sample K-1 (Fig. 6C, D) also shows a high concentration of inclusions. By contrast, in samples Z-3, Z-4, M-1a and M-1d, concentrations of inclusions are very low. In sample Z-5 only individual inclusions were observed.

The inclusions studied have similar morphology (Fig. 6). Most of them are round or oval in shape, some with irregular with uneven or, rarely, flat boundaries. The inclusions' length (or diameter) usually does not exceed 15–20 μm . Within these objects there are rectangular or rhomboid plates and laths (bright in BSE image, Fig. 6B). These phases are up to a few μm long; in some aggregates ~ 1 μm long grains occur together with those ~ 3 –4 μm long. Independently of their size, the arrangement of these small objects within the aggregates is random (Figs. 6A and 7A). In sample M-1f there were some local aggregations of inclusions (Fig. 7A, B).

The EDS analyses show that in all samples the inclusions are composed of Cu, O and most commonly of Pb and Sb. Moreover, depending on the sample, the inclusions comprise other elements such as Bi and As. In the BSE images the

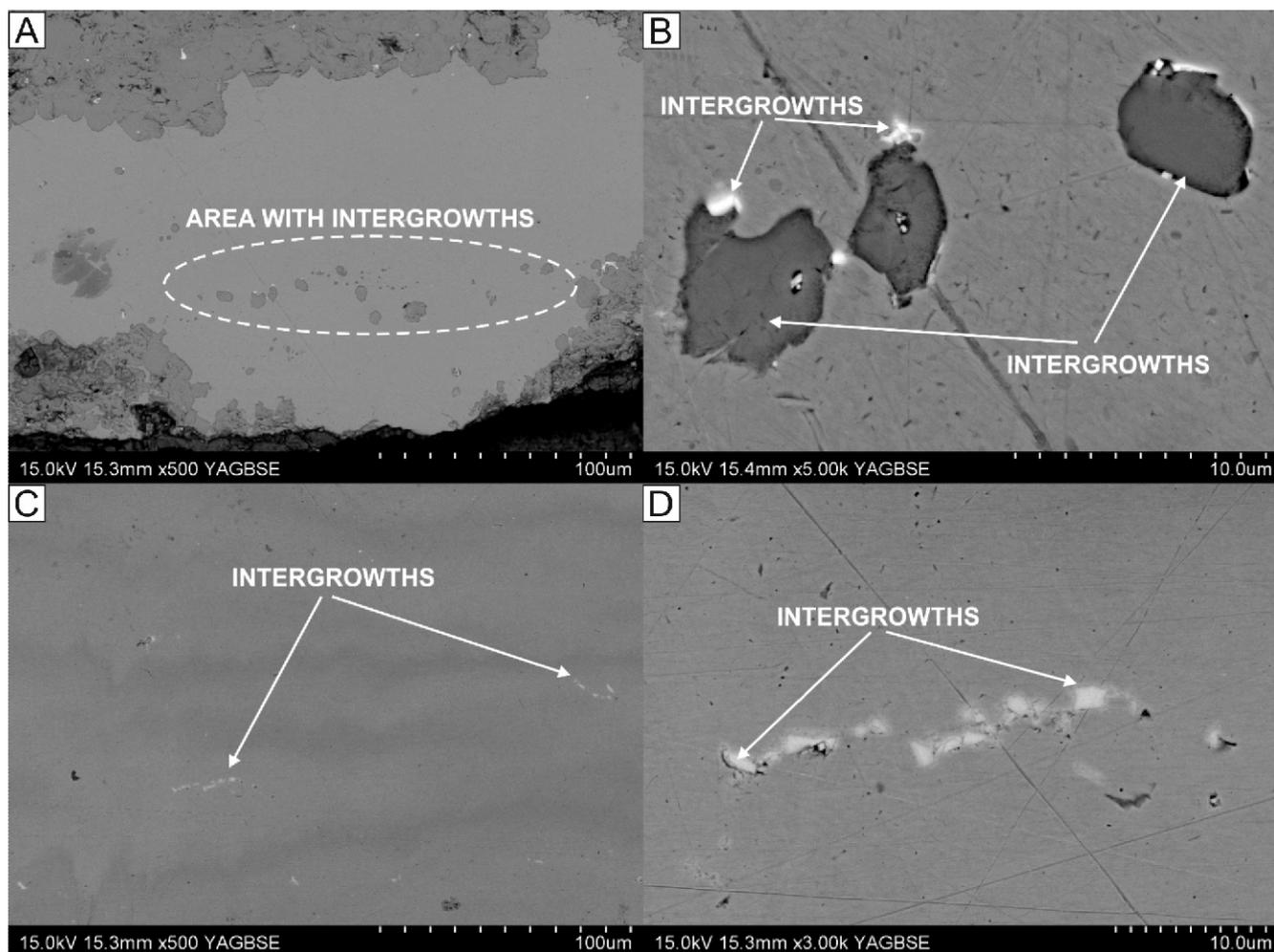


Fig 7. SEM images of the inclusions observed in the tube M-1f (A, B) and the ring M-1d (C, D)

White inclusions are composed mainly of Pb, Sb and As, dark ones are composed of Cu-O

Table 2

Selected chemical analyses (semi-quantitative, standardless EDS mode) of inclusions in the Final Neolithic/ Early Bronze Age artefacts

Type of inclusion	Cu-S-Se	Cu-O	Pb-Sb-Cu-O	Cu-As-O	Cu-Sb-O	Sb-P-Cu-O	Sb-Pb-Cu-As-O	Pb-Cu-As-O	Pb-Cu-Bi
Samples with the inclusion type present	Z-5, Z-3	All samples	K-1, Z-2, M-1a	Z-3	Z-4, M-1d	K-1	K-1, M-1b, M-1f	M-1a, M-1c, M-1e,	Z-1, Z-2
Analysis number/sample	1/Z-5	2/M-1b	3/Z-2	4/Z-3	5/Z-4	6/K-1	7/K-1	8/M-1a	9/Z-1
As	0.0	0.0	0.0	39.1	0.0	0.0	4.4	17.3	0.0
Si	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
S	8.3	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0
Sb	0.0	0.0	35.3	0.0	9.0	40.1	41.0	1.4	0.0
Pb	0.0	0.0	35.9	0.0	0.0	30.8	26.7	46.1	67.9
Sn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu	84.4	89.5	13.7	48.5	84.0	14.2	11.6	28.5	7.1
O	0	10.5	15.1	12.2	6.7	14.9	16.3	6.7	2.6
Se	7.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bi	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.3
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

All concentrations in wt.%; for full data set see [Appendix 2](#)

Pb-Sb-Cu(±As, Bi)-rich inclusions are bright, whereas the dark areas observed in SEM are composed solely of Cu and O (Figs. 6 and 7). The Cu-O inclusions in sample M-1b were composed of 89.5 wt.% Cu and 10.5 wt.% O₂ which is equivalent to 68.2 at.% Cu and 31.8 at.% O₂. Thus, such concentration of elements suggests that the composition corresponds to that of cuprite. Moreover, this conclusion was supported by additional Raman spectroscopy. This type of inclusion occurs in every sample. In sample M-1f only cuprite (Cu-O type) inclusions with remnants of the Pb-As-rich phase at the edges were observed (Fig. 7B). Rarely, sulphur is present and copper sulphide inclusions enriched in Se appear (Table 2).

ISOTOPE ANALYSIS

Copper and lead isotope ratios have been determined for 21 ore samples from copper ores from the Carpathian Basin, the Miedzianka region (Świętokrzyskie Mountains), Lower Silesia (Lubin and Sieroszowice regions, and the Leszczyzny syncline) and Ukraine (Volyn). These samples represent various kinds of primary copper deposit, both hydrothermal and sediment-hosted. The detailed mineralogical descriptions of the samples investigated and their locations are given in Appendix 3 and Figure 1. The samples come from waste heaps, for it was not possible to access the mine workings of the old, closed mines. The artefacts subjected to isotopic analyses represent different stylistic groups. Major and trace elements compositions were determined for both ore and artefact samples and the results are shown in Appendices 4A and B. The results of Cu and Pb isotope ratios analyses are given in Appendices 4C and D.

The study of the isotopes ⁶³Cu/⁶⁵Cu for copper ores revealed a large variation of ⁶⁵Cu values, from –1.086 to 2.108 ‰. Pb isotope ratios in the ore samples investigated also fall within a large range of variation (see Appendix 4C). The ores investigated in our study represent the ore mineral sources available from the largest deposits in the Carpathian Basin. The best known in ancient times was Špania Dolina-Piesky. The Cu isotope composition of the ore samples from that deposit significantly vary by ⁶⁵Cu = –0.146 to 1.308. Cu and Pb isotope ra-

tios in the copper artefacts investigated fall within a significantly smaller range of variation (Appendix 4D). ⁶⁵Cu values vary from –0.065 to 0.439 ‰. ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁴Pb ratios vary from 2.4650 to 2.4760, from 0.8346 to 0.8412 and from 18.511 to 18.754, respectively.

DISCUSSION

CHEMICAL COMPOSITION – INCLUSIONS

Copper oxide inclusions. The presence of copper oxide in the inclusions can be related either to the ore composition or to the reaction which occurs during the smelting process (cf. Hauptmann, 2007: 243). As for the ore composition, when oxide ores are used, it is possible that the ore material is not entirely melted. Thus, oxide inclusions can be the residues of the original oxide ores. On the other hand, melted copper absorbs oxygen from the atmosphere and forms oxides. Since the chemical analyses show that copper oxides are composed only of oxygen and copper while no other chemical elements were detected, it is most likely that these inclusions were formed during the metallurgical process (oxidation of the melted copper in crucibles).

The real technological challenge seems to have been keeping both the conditions of temperature and atmosphere in an ideal balance during the smelting process. This might be the reason for the high copper oxide contents. Those inclusions substantiate the high smelting temperatures as well as the incomplete reduction of the ore (Hauptmann, 2007: 227). However, in both cases the occurrence of copper oxide inclusions indicates the imperfections of the technological process as regards obtaining copper products (cf. Scott, 1991: 90). The highest number of copper oxides were observed in samples Z-1, Z-2 and K-1 which are the oldest objects analysed (~2600–2400 BC, the Corded Ware culture). Also, in these samples, other types of inclusions containing chemical elements such as Pb, Sb, Bi, As (Tables 2 and 3) were observed. Thus, it can be concluded that the smelting process was less developed and oxidation of the melted copper was more pro-

Table 3

Chemical characteristics of the four types of Cu metal distinguished within the artefacts studied and the assumed mineralogical composition of copper ores used for their production (see text for further explanations)

Metal type	Samples	Chemical characteristics of the copper metal	Inclusions	Inferred Cu ore
A	Z-1	rich in As (up to 1.67 wt.%), Sb (up to 0.71 wt.%) and Ag (up to 0.43 wt.%)	Pb-Cu-Sb-As-O Pb-Cu-Bi Cu-O	ores with predominance of tetrahedrite over tennantite, or with varying proportions of both minerals
	M-1f		Pb-Sb-As-O Cu-O	
B	M-1a, M-1b, M-1c, M-1e	high contents of As (range from 0.25 to 2.12 wt.%), Ag generally low (<0.08 wt.%), sometimes reach up to 0.43 wt.%, Sb constantly below 0.08 wt.%	Pb-Cu-As-O, Cu-O	ores with predominance of tennantite, and/or possible As-rich weathered ores (pseudomalachite)
	Z-3, Z-4		Cu-As-O, Cu-Sb-O	
	Z-5		Cu-S-Se	
C	M-1d	rich in Ag (from 0.35 to 1.41 wt.%), Sb (from 0.68 to 3.04), and Ni (from 0.77 to 1.77 wt.%), Sn-rich (up to 0.36 wt.%)	Cu-Sb-O	stannine- or other Sn mineral-rich ores, containing also Ni and Co sulphides and arsenides, Sb sulphides and sulphosalts
D	K-1, Z-2	Ag-rich (0.23–0.58 wt.%), varying Sb content (up to 0.75 wt.%), depleted in As (<0.06 wt.%)	Pb-Cu-Sb-O, Cu-O	tetrahedrite and galenite are the most abundant ore minerals

nounced. The presence of copper oxide in the copper objects formed due to oxidation of melted copper is also described in the literature (e.g., Hauptmann et al., 2002). Interestingly, in sample Z5 which is assigned to the same chronological horizon, almost no inclusions were observed. This sample shows a high content of As in the matrix, shown by the WDS analyses. This suggests that this object could have been obtained from As-rich copper ores. The hydrothermal ores with predominance of tennantite, and/or possible As-enriched weathered ores containing copper arsenates (e.g., olivenite, tyrolite, conichalcite) are the most likely ore sources here (Table 3). The weathered copper ore types may also contain significant amounts of native copper and copper oxides such as cuprite. However, the lack of copper oxides in this sample could be explained also by a different method of casting of the copper metal or, more likely, by the fact that this object was shaped by the hammering of a previously rendered copper ingot. According to Rehder (1994), with the presence of cuprite in copper a number of minor and trace elements are oxidized, meaning that during crucible smelting a refining effect might occur due to the tendency of copper to oxidize. This is in accordance with Merkel's (1990) observations that a noticeable change in the trace element pattern only occurs with a deliberate input of air into the copper bath.

Interesting results were also obtained during investigation of the younger objects (2100–1900 BC, the Mierzanowice culture). For example, samples M-1e and M-1f are characterized only by the presence of copper oxide inclusions. In the rest of the samples analysed copper oxides occur together with other types of inclusion containing Pb, Sb and As. Thus, it can be concluded that the objects M-1e and M-1f were produced using oxide ores or remelted material (recycling). The younger objects are characterized by smaller amounts of copper oxide inclusions by comparison with the older ones. That implies that the smelting process was then more advanced, resulting in products of higher quality.

Pb-As-Sb inclusions. Another type of inclusions observed in the samples was composed of chemical elements such as Pb, As and Sb. The highest amount of these inclusions, as in case of copper oxides, was observed in samples Z-1 and Z-2, as well as in sample K-1. However, the chemical analyses revealed that inclusions present in the earrings (Z-1, Z-2) differ from those in the awl (K-1). In the case of sample Z-1, the major elements of inclusions are Pb, As, O and S (low amounts), while the inclusions of samples Z-2 and K-1 are composed mostly of Pb and Sb. On the other hand, the inclusions in samples Z-1 and Z-2 have additional amounts of Bi. Thus, these results suggest that the samples analyzed could have been produced with different copper ores.

The size and irregular shape of the Pb, Sb and As inclusions suggest that they were formed by crystallization from the melted phase and their chemical compositions correspond to the composition of the ore. Thus, the type of the ore can be defined based on the chemical composition of these inclusions. They were composed of rectangular or rhomboid plates and laths. The microstructure of the matrix with large and brittle inclusions is not advantageous since it decreases the mechanical properties.

Determination of the oxidation states of the chemical elements, stoichiometric ratios of the inclusions and crystallization/formation of the inclusions would have been necessary for description of the smelting technology. However such detailed analyses go far beyond the scope of the analyses presented.

CHEMICAL COMPOSITION – MATRIX

Taking into account solely the concentration of the most common minor elements in an artifact's matrix, five types of Cu

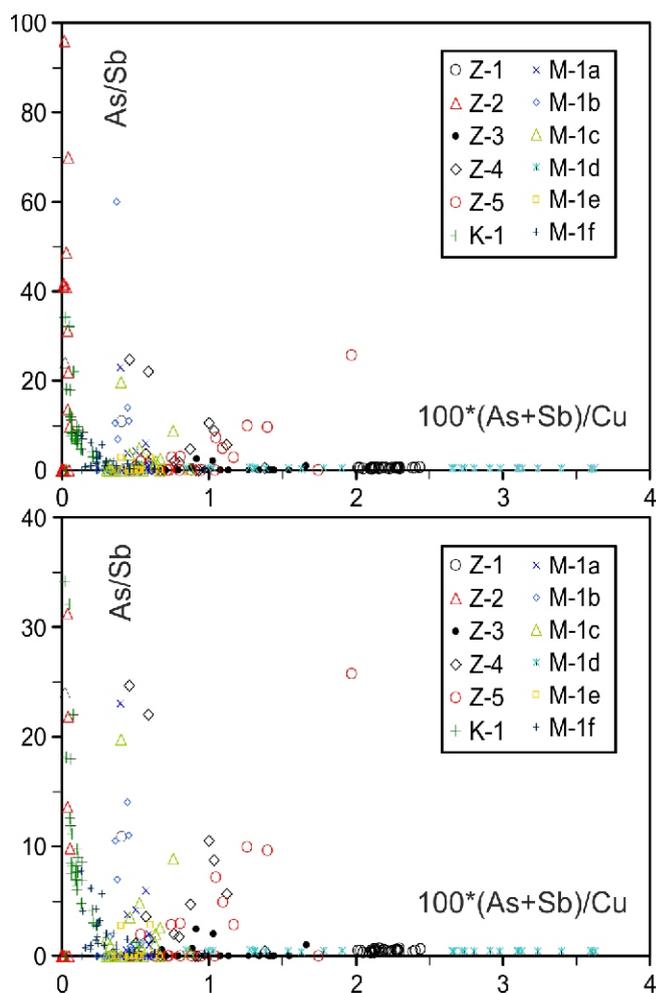


Fig. 8. Ag/Sb versus $100*(As+Sb)/Cu$ showing chemical varieties of the copper artefacts examined from southern Poland; the lower diagram shows the enhanced lower part of the upper diagram where the samples with Ag/Sb ratios <40 plot

metal can be distinguished: (1) Ag-rich (samples Z-2 and K-1), (2) As-rich (samples Z-3, Z-4, M-1a, M-1b, M-1c, M-1e), (3) As- and Ag-rich (sample Z-5), (4) As-, Sb-, Ag-rich (samples Z-1 and M-1f), (5) Ni-, Sb-, Ag-, As- and Sn-rich (sample M-1d).

Strong differences in chemical composition of the copper metal in the samples analysed are reflected by the Ag/Sb and $100*(As+Sb)/Cu$ ratios, particularly in the samples in which all these elements were successfully measured (values above detection limits) and vary from 0.24 up to 100 and from 0.03 up to 3.6, respectively (Fig. 8). However, if the division of Cu metal into chemical groups is to reflect the mineralogical composition of ore, it should include both chemical composition of Cu metal (matrix) and the phases that occur in the inclusions embedded in the matrix. To this end the data sets for the matrix and inclusions have been combined and four types of metal were distinguished (see Table 3). This division is based on two features: (1) chemical composition of matrix and (2) chemical composition of inclusions. All types (A, B, C, D) show compatibility of both features. Since the inclusions and matrix are composed of the same chemical elements, it can be concluded that the inclusions probably crystallized or precipitated from the matrix during technological processes. Thus, they do not directly originate from the ores.

Type A. The samples Z-1 and M-1f are characterized by high concentrations of As (0.07–1.67 wt.%) moderate concentrations of Ag (0.04–0.43 wt.%) and numerous inclusions containing Pb and Sb. The concentration of Sb in the copper metal varies; in sample Z-1 (numerous Pb-Cu-Sb-As-O inclusions) the measured concentration of Sb is high and ranges from 0.51 to 0.70 wt.%, while in sample M-1f it is <0.1wt.%. Enhanced concentration of Ag and Sb strongly suggest the presence of tetrahedrite, while As signals the occurrence of tennantite in the ore. The composition of metal matrix clearly indicates the presence of tetrahedrite in the ore, in this case a very common and widespread Ag-bearing sulphosalt (Ramdohr, 1975). Only sample Z-1 is different here in its low Ag content (<0.03 wt.%). Thus, the metal of type A was probably smelted from tennantite-dominant Cu ore, or from ores with varying proportions of both minerals. The most likely sources of such a type of ore are As-Sb-rich sulphosalts from Špania Dolina and/or Lubietová (Fig. 1).

The inclusions in the samples of this group differ in chemical composition, mainly regarding the presence of major to trace elements (Pb, As, Sb) as well as in their sizes and concentrations. However, these differences are more likely to be connected with the technology of production than with the type of ore (cf. Bachmann, 2003: 28). The parameters of the metallurgical process (timing, temperature, cooling and heating rates) influence the formation of new phases (inclusions) in the matrix. Thus, a change in any of these parameters can cause either a high concentration or the absence of inclusions (cf. Hauptmann, 2007: 178).

Type B. The copper matrix in samples M-1a, M-1b, M-1c, M-1e, Z-3, Z-4 and Z-5 are enriched in As (0.25–2.12 wt.%) and depleted in Sb (<0.08 wt.%). The concentration of Ag is generally low (<0.08 wt.%) but locally (in samples Z-4 and Z-5) reach up to 0.43 wt.%. This metal type is characterized by the occurrence of numerous inclusions usually containing Pb and As. Only in sample M-1f are the inclusions rich in Pb and Sb. Metal of type B presumably comes either from tennantite-dominant ores, which are usually not enriched in Ag (Ramdohr, 1975), or from ores comprising simple Cu-sulphides (chalcocite group), malachite, azurite, and/or copper arsenate minerals mined from the weathering zone of the primary hydrothermal ores (e.g., a blanket-type deposit). The most likely sources of Cu ore in this case are Špania Dolina, Rudabánya and Lubietová.

Type C. This type is defined by a single sample, M-1d. While the rest of the samples show low contents of Sn (up to 0.03 wt.%), this sample is characterized by a high concentration of this element (0.37 wt.%) together with Ni (up to 1.69 wt.%), Bi (up to 0.25 wt.%), and Co (up to 0.11 wt.%). The concentrations of Sb and As are very high and range from 0.68 to 3.04 wt.% and from 0.13 to 0.53 wt.%, respectively. The sample contains also many inclusions rich in Sn, Co, Ni and Se. This small admixture of Sn documented as ore component requires further explanation. Sn-bearing phases were not recognized either in hydrothermal siderite barite-tetrahedrite veins of Slovenske Rudohorie or in ores from the weathering zones that consist mainly of malachite or copper arsenates. However, small admixtures of Sn-bearing phases were recognized in many high temperature ore associations related to calc-alkaline volcanic rocks in Banská Štiavnica, Slovakia (Kodera et al., 2005; Lexa et al., 1999; Neubauer et al., 2005; Ďuda and Ozdin, 2012) and Baia Mare-Cavnic (northern Romania). The other sulphide deposits from Slovakia, e.g. Slovinky, Smolnik and Zlatá Baňa also contain small amounts of Sn-bearing phases (probably stannine, Szakáll et al., 2002).

Type D. This type is defined by samples K-1, Z-1 and Z-2. It is similar to type A in terms of high concentrations of Ag (0.38–0.75 wt.%). The concentration of Sb varies, ranging from below EPMA detection limits to 0.49 wt.% in sample K-1. The As content is very low in all samples (up to 0.09 wt.%). Based on the high concentration of Ag and the presence of inclusions enriched in Pb and Sb, we can assume that the copper metal was smelted from ores containing significant amounts of tetrahedrite and galena. The metal of types A and D (Table 3) was extracted from Ag-rich ores consisting of tetrahedrite. Both types are characterized by an enhanced concentration of Ag in Cu metal and varying amounts of Sb-, As-rich inclusions as a result of control during high-temperature oxidation of sulphosalt ores. The presence of Ag seems to be distinctive here as it was not burnt off in smelting. To put it another way, if Ag is present in a copper ore it will occur in the copper metal (see also Rehren and Northover, 1990: 227). The most probable sources of such an ore type are tetrahedrite Cu ores from Špania Dolina, Gelnica-Slovinky (Slovakia) or Rudabánya (Hungary).

Cu AND Pb ISOTOPE COMPOSITIONS OF COPPER ORE SAMPLES AND ARTEFACTS

Study of the isotopes $^{63}\text{Cu}/^{65}\text{Cu}$ showed a large variation in ^{65}Cu values, from –1.086 to 2.108‰. That reflects the effective fractionation of Cu during the ore's weathering (Powell et al., 2017; Jansen, 2018). According to Powell (Powell et al., 2017), fractionation of Cu isotopes in Cu ore weathering zone can reach up to 3‰. Such a high level of fractionation of Cu isotopes can also be fostered by crystallization of secondary copper sulphides enhanced by microbial activity during weathering (Asael et al., 2012). Pb isotope ratios in the ore samples investigated also fall within a large range of variation (see Appendix 4C). The results obtained are in keeping with the data reported by Schreiner (2007; Figs. 9–11). Taking into account Pb isotope ratios one can assume that the samples K-1, Z-1 and Z-2 derive from copper produced from one deposit. Sample M1-b has a different isotopic signature, which suggests a different kind of ore within the same deposit or an entirely different copper deposit.

ARCHAEOLOGICAL RECORD

Archaeological data on mining activities attributed to the Final Neolithic and Early Bronze Age in the Carpathian region is scarce, so there is very little information to support all the considerations outlined above. According to research conducted in the vicinity of Špania Dolina in 1960s–1980s (Točík and Žebrák, 1989), intensive Cu ore processing must have taken place in Špania Dolina Revier already in the Middle Neolithic (or Middle Eneolithic in the Slovakian periodization, see also Farkaš and Gregor, 2012: 4). Some of the artefacts of the 150 stone picks collection from that site, based on the Lengyel culture stylistic analogies – incorrectly dated by Točík and Žebrák (1989: 72) to the mid-3rd Millennium BC – should be dated to the 4th/5th Millennium boundary interval and the early 4th Millennium BC (e.g., Pavúk and Bátor, 1995). The correction of this dating, however, leaves us with no trace of mining activities in Špania Dolina that could be connected with the mid-3rd Millennium BC – i.e. the older horizon of the artefacts analysed. All the same, there is no data on mining activities of that time regarding other Cu ore regions indicated above as possible sources for producing these artefacts. It is also impossible to

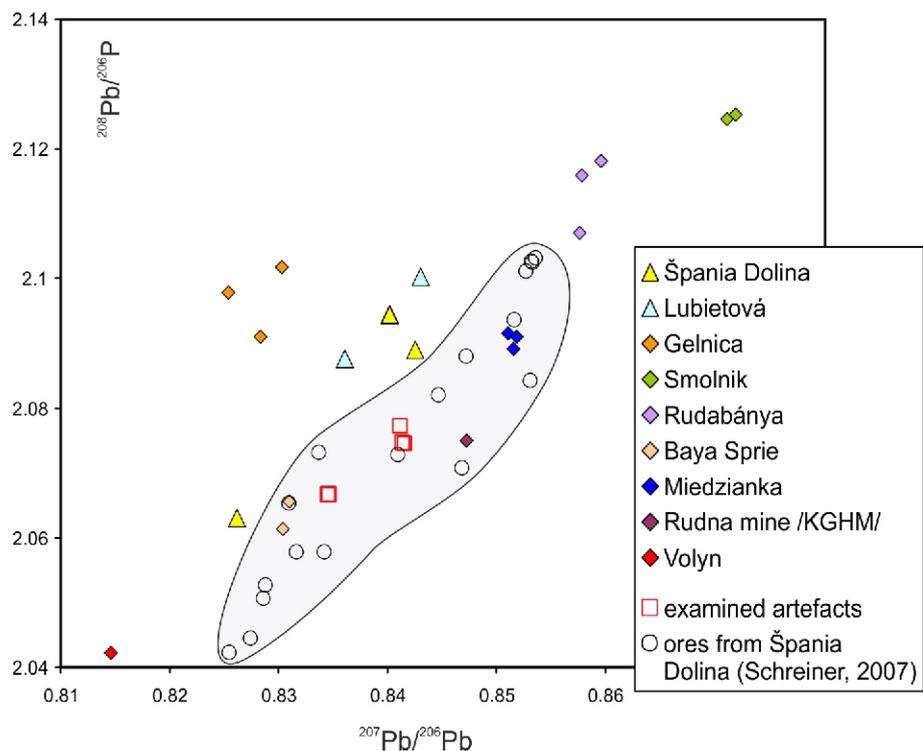


Fig. 9. $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ diagram showing isotopic data for the artefacts and ores examined

The area marked with a grey color shows the variability of the isotopic composition of the ores from the vicinity of Špania Dolina (data after Schreiner, 2007)

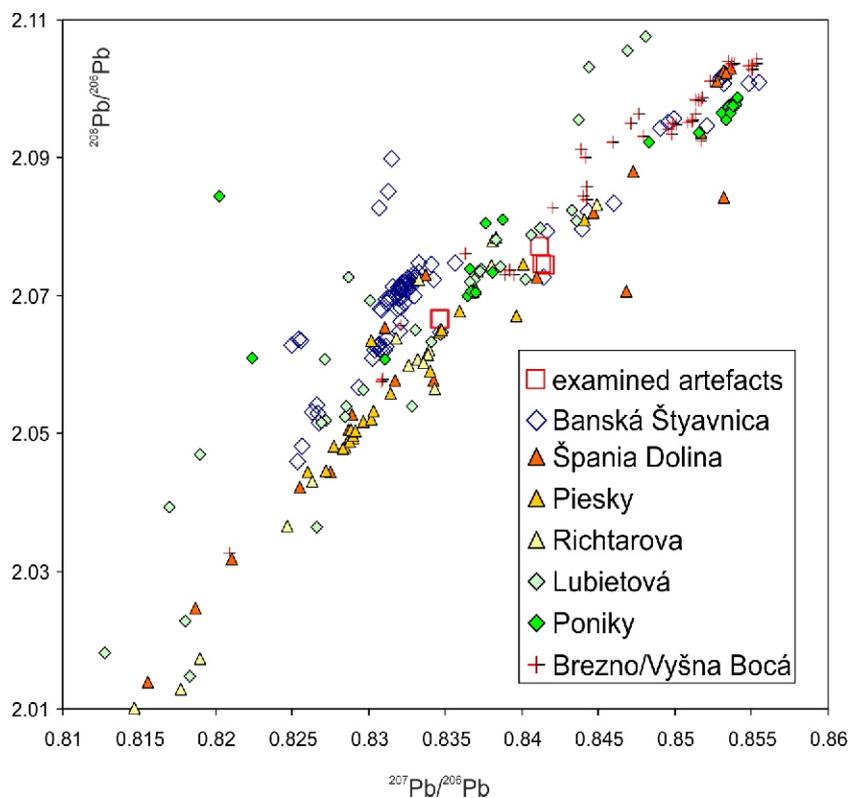


Fig. 10. Comparison of lead isotope ratios in the studied artefacts studied with the Pb isotopic ratios of ore from the Hron Valley (data after Schreiner, 2007)

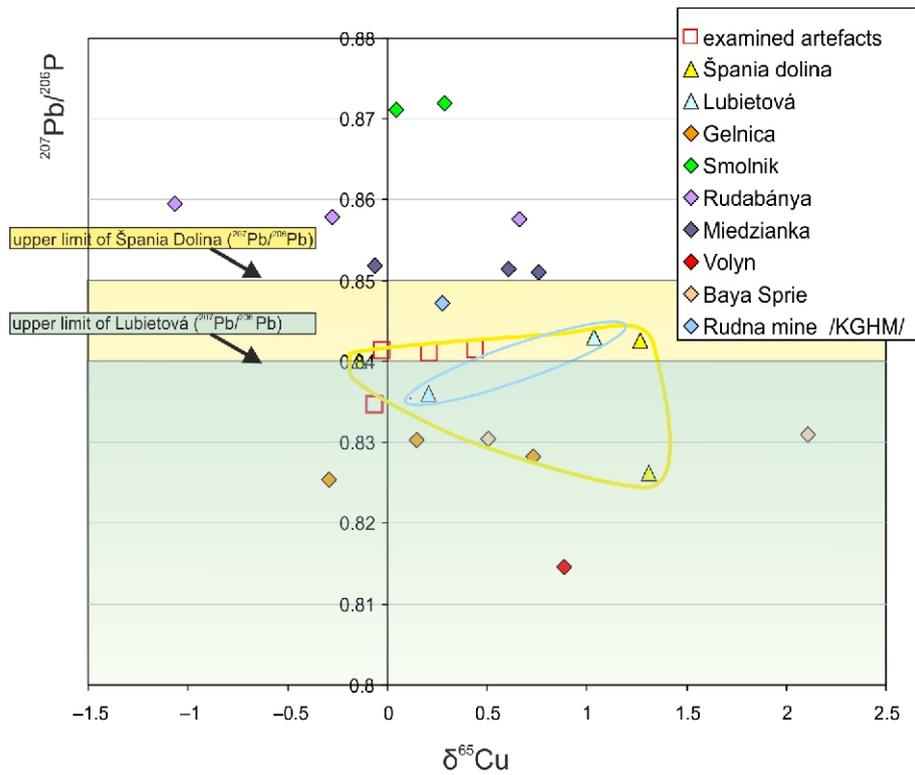


Fig. 11. $^{207}\text{Pb}/^{206}\text{Pb}$ versus ^{65}Cu diagram showing isotopic composition of the artefacts examined and the ore samples analysed

$^{207}\text{Pb}/^{206}\text{Pb}$ upper limit of ores from Špania Dolina and Lubietová on the basis of Schreiner (2007) isotopic dataset

ascertain if it was metal objects that were imported or some kind of raw material primarily processed in the mining area since we do not know any analogous metal finds from the northern Carpathian region that could be dated to that time. Moreover, it is difficult to trace extensive contacts between the Corded Ware culture societies from southern Poland and Slovakia. One possible explanation is that the metal objects were produced in the territory of Lesser Poland (Małopolska) using Cu material originating in the south. This would be corroborated by the characteristic “tendency” being assigned in the literature to the “Corded Ware” societies, which was to import the particular material for producing some kinds of objects, despite local availability of material that could have been used instead (e.g., selected raw materials for battle-axes or flint tools).

Interpretation of the Early Bronze Age finds, i.e. most of the objects analysed in this article, seems to be less complicated. According to Točík and Žebrák (1989: 75) the Špania Dolina Revier was also used during the Bronze Age. Numerous copper finds in graves both in Slovakia (the Nitra group in western Slovakia and the Košťany group in eastern Slovakia) and southern Poland (the Mierzanowice culture) are classified within the same stylistic trend called “the willow-leaf style” (e.g., Kadrow, 2000). We can presume, therefore, that during the first centuries of the second millennium BC copper products were distributed using exchange networks connecting the Mierzanowice culture and the Nitra group and reached the Małopolska Uplands as imports.

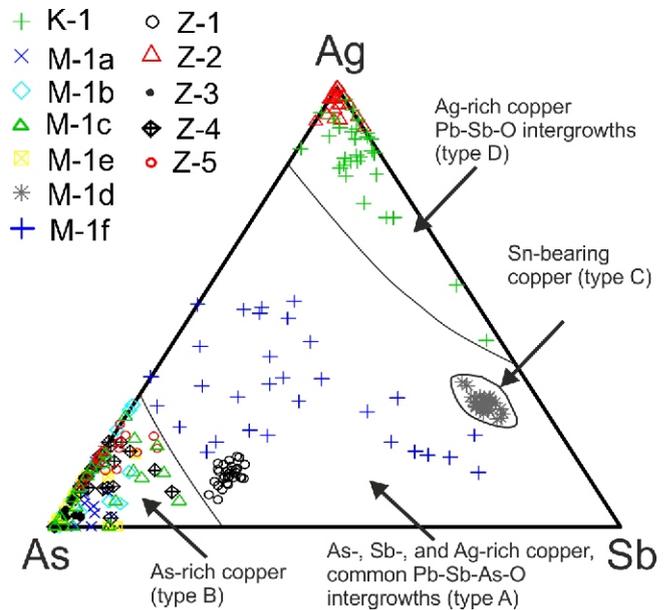


Fig. 12. Variation of chemical composition in As-Ag-Sb diagram of the types of metal distinguished – the Final Neolithic and Early Bronze Age copper artefacts from southern Poland

Finally, one more issue should be addressed, i.e. the difference in the smelt quality that can be observed on the diagram (Fig. 12). The older, “Corded Ware” Cu objects (samples K-1, Z-1, Z-2, Z-5) seem to be different products than the younger ones. Their chemical composition is more homogeneous. Due to the small number of samples analyzed we have to leave this question open.

CONCLUSIONS

We demonstrate how analyzing both matrix and inclusions enhances opportunities to indicate the nature of copper raw material, especially in terms of the type of Cu ore and how it corresponds with the results of Pb and Cu isotopic analyses.

The concentration of Ag, Sb, As and Sn in the Final Neolithic/Early Bronze Age copper artefacts, the presence of inclusions and their chemical composition are the key indicators allowing determination of the mineralogical composition of the processed ores. Our study points at sulphosalt ores as the main source of metal for the artefacts investigated.

As- and Sb-rich inclusions document types of ore, since the metallurgical process leads to depletion of these very elements. A flawless cast Cu metal should contain neither Sb nor As, and their presence in ore can be traced only in inclusions. Both of the elements are removed during the metallurgical process, thus neglecting the analysis of As- and Sb-rich inclusions makes the proper interpretation of mineralogical composition of ore impossible. Other metal elements such as Ag, Co, Ni and Sn do not burn off during ore processing and always remain in Cu metal, hence the presence of Ag, Co, Ni and Sn in inclusions indicates which elements of the original ore remained in the “alloy”.

The varying amounts of As-Sb-O and Cu-O inclusions reflects unstable furnace conditions, that did not lead to complete oxidation of As and Sb and the removal of both elements from the final copper metal. This indicates, therefore, the quality and technological progress of the smelting process; the less developed and primitive the process was, the greater amount of inclusions occurs in the copper metal produced. Alternatively, the abundance and chemical composition of inclusions may depend on which part of the smelting product the metal (solid solution) was acquired from (i.e. the upper, middle or lower part of it).

Given the high contents of Sb, As and Ag in the Cu metal and the mineralogy of the inclusions, the processed ores must have contained tetrahedrite $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$ and tennantite $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$ with varying proportions of both minerals (Cu metal of types A, B and D). The analyses of one of the artefacts (Cu metal of type C, see Table 3) imply deposits with a small admixture of Sn minerals (e.g., stannine $\text{Cu}_2\text{FeSnS}_4$). Copper ore deposits characterized by domination of Cu-Sb-As sulphosalts are located in the Inner Carpathians, i.e. in Slovakia, Hungary and Romania (Chovan et al., 1994; Neubauer et al., 2005). Although it is now impossible to point out more precisely which of those deposits could have been used as a source of metal for the Final Neolithic artefacts under investigation, it is very likely that the copper material to produce the Early Bronze Age objects came from complex sulphide-sulphosalts and weathered Cu ores from Špania Dolina.

More precise localization of copper ore deposits used for production of the investigated artefacts from Małopolska (Lesser Poland) is possible based on the analyses of Pb and Cu isotopes. Heavy isotopes of those elements do not fractionate during the metallurgical process (Gale et al., 1999;

Mathur et al., 2009), moreover some of them can be used for monitoring the processes of weathering Cu ores (Powell et al., 2017; Jansen et al., 2018). All 21 ore samples (Appendix 4A) have been taken from Cu deposits located in the vicinity of the sites where the four artefacts investigated were found (Fig. 1). The study of ^{65}Cu values reports only a varied state of oxidation of ores used in the metallurgical process while Pb isotopes ratios allow distinction of two groups of artefacts produced from ores of different isotopic signatures. The first group includes samples Z-1, Z-2 and K-1, the second group comprises sample M1-b.

The results of isotope analyses of the artefacts and the ores as well as the results of comparable research performed by Schreiner (2007) have been used to collate comprehensive information on the provenance of the artefacts in question.

Pb isotope ratios in the ore samples (e.g., $^{208}\text{Pb}/^{207}\text{Pb}$) fall within a large range of variation from 2.4373 to 2.5069. Despite the small number of samples analyzed per Cu deposit, representing ores of diverse Cu mineralogy, one can observe a significant variation of Pb isotope ratios, that probably reflects the multistadial genesis of some of the deposits (e.g., Špania Dolina with Pb isotope ratios varying from 2.4793 to 2.4971, or Rudabánya from 2.4569 to 2.4665). The comparison of Pb isotopic analyses for the artefacts and for the ore deposits does not conclusively demonstrate the copper ore provenance. But, consideration of a large data set consisting of analyses of Cu ores from Špania Dolina (Schreiner, 2007) shows that the isotopic signatures of the artefacts investigated from Małopolska fall within the variety range confirmed for Cu ores from this area. Based on the results of isotopic study, the artefacts investigated might have been produced using copper originating from the Lubietová–Poniky and Bereznovo–Vysna Boca areas.

Porphyry copper deposits from Banská Štjávnica can be unequivocally excluded as a source of copper for the artefacts in question, as well as the Miedzianka area (the Świętokrzyskie Mountains) – the nearest deposit, and native copper deposits in Volyn, discovered by Małkowski (1929, 1931, 1951).

Combining the two isotopic systems, Pb and Cu (Fig. 9) allows indication of the source copper ores with greater precision. Hence, the most probable source of copper ore for the artefacts investigated is the deposit from Špania Dolina (samples Z-1, Z-2, K-1) and/or Lubietová (sample M1-b). The results of isotopic analyses show that the batch consisted of primary hydrothermal ores rich in As and Sb copper sulphides with different contents of the oxidized Cu ores, that contained probably large quantities of malachite, azurite and copper oxides.

We already know, that coppers with a range of As or/and Sb content are a feature of early metallurgy (e.g., Northover, 1989: 111). We also know that the introduction of sulphidic ores probably marks a technological shift in copper processing (Powell et al., 2017). Although considerable archaeometallurgical research has been devoted to early copper-based objects, the vast majority of them are large, cast items. Hardly any attention has been paid to the products of “thread and wire metallurgy”, let alone analyses more complex than standard chemical “whole-metal” determinations (e.g., Kempisty, 1978). There is still a great deal of work to be done to characterize the metal production of the Final Neolithic/Early Bronze Age post-Corded Ware cultures in Central Europe. This is a gap to be bridged in the inferential process regarding the beginnings of Bronze Age metallurgy in that region.

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