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Schéma d'analyse de réseau de 65 sites à partir de la fin de l'âge du Bronze moyen (principalement de 1700 à 1400 avant J.-C.). L' épaisseur du lien est proportionnelle à la valeur du coefficient de Pearson

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Eneolithic copper jewellery from grave 7 of the Lublin-Volhynian culture at site 2 in Książnice, Świętokrzyskie Province, Poland. Typological and physical metallurgy characteristic

Abstract: This article presents a typological and physical metallurgy analysis of copper artifacts found in child grave (no 7) at the Lublin-Volhynian culture cemetery in Książnice (Lesser Poland). The burial, dating to approx. 4050–3940 BC, contains a rich set of copper jewellery: a massive earring, small earring, bracelet - made of copper wire, and two beads made of a rolled piece of metal sheet. As part of metallographic analysis of metal finds from grave 7, site 2 in Książnice, quantitative and qualitative analyses were conducted, regarding chemistry and microstructure of all the five artifacts. In the artifacts tested, there were identified the elements significant from the perspective of raw material origin and smelting technology: arsenic, antimony, silver, tin, zinc, lead, bismuth, cobalt, nickel and iron. The highest total content of impurities was noted for the bracelet. Against the background of other elements, the arsenic content stands out here and it is 2.1%, and lead 0.26%. For the remaining artifacts, the arsenic content was 0÷0,24%, and lead 0÷0,039%. Antimony (0.098%) and zinc (0.15%) was only recorded for the one of the bead. Also, the highest content of silver (0.05%) was established in this case. In the remaining ornaments, the silver content was below 0.02%. Based on the X-ray fluorescent spectroscopy results, chemical profiles were established for the individual, and they were ascribed to raw material groups according to R. Krause: 1) pure copper, 2) arsenic copper and 3) antimony copper (Krause 2003: 90–91, Abb. 40–41). The presented inventory of copper artifacts from grave 7, having many analogies in the Carpathian Basin and the areas to the north and east of the Carpathians, confirms the thesis about wide, trans-Carpathian contacts of the group which was using the necropolis in Książnice at the turn of 5th and 4th millennium BC.

Keywords: copper jewellery, metallurgy analysis, graves, Lublin-Volhynian culture, Lesser Poland, archaeometallurgy, X-ray fluorescence (XRF)

1. Introduction

This article presents a typological and physical metallurgy analysis of copper artifacts found in grave 7 at the Lublin-Volhynian culture cemetery in Książnice, Świętokrzyskie Province.

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Grave 7, explored in August 2008, belonged to a child (girl) at the age of *infans* II (9–10 years old), deposited in a contracted position, on the left side, with the cranium to the south (Wilk 2015, fig. 5). The burial pit was orientated on the NE-SW axis. To the south and to the west, it has been partially destroyed by an underground trench which constitutes part of a water supply network.

The body was equipped with a rich set of copper jewellery (Table I). Under the skull, there was a massive earring made of wire (Fig. 1: A; Wilk 2015, figs 8: A, B; 9: C). At the height of her chest, there was a bead made of a rolled piece of metal sheet (Fig. 1: C; Wilk 2015, figs 8: D; 9: E). Another such bead was discovered during the search through the fill of the water supply trench (Fig. 1: D; Wilk 2015, fig. 9: D). Additionally, on the left humerus, some greenish discolouration was observed – possibly, a trace left by a bracelet (Wilk 2015, fig. 8: A), which was discovered – together with a small circular earring (Fig. 1: B, E; Wilk 2015, fig. 9: A, B)– at the height of the ceiling of the burial pit, in a mole hill, about 30 cm to the east of the pit (Wilk 2015, fig. 4: B). The location of these artifacts – close to the edge of the grave, at the level where the top of the cranium is outlined – indicates that they could have been elements of the burial inventory.

2. Comparative analysis of the artifacts

The earrings belong to the most frequently encountered pieces of jewellery in the Lublin-Volhynian culture. We know 21 such artifacts from 14 graves (Zakościelna 2010, 146, table 38; Wilk 2014, 232). They occur individually or in pairs, almost exclusively in female graves, and they can consist of one or multiple coils. One-coil earrings can be divided into two size categories: small ones (up to 50 mm in diameter) and big ones (51–85 mm in diameter).

The earrings from grave 7 represent both of the above types. The closest analogy for the Ks/w/4/08 specimen (Fig. 1: E) are the artifacts from grave 390 found at site Grodzisko II in Złota (Sałacińska, Zakościelna 2007, fig. 12:4,5), as well as one of the pair of earrings from grave 1 from site 4 in Gródek on the Bug river (Gąssowski 1954, 84).In the Tiszapolgár culture, a similar earring was found in grave 2 at site Deszk B (Bognár-Kutzián1972, fig. XXXIII:9). While, an artifact of a very similar shape, described as a ring, was found on the phalanges of a child's hand in grave 9 at site Tiszapolgár-Basatanya (Bognár-Kutzián 1963, pl. XIII:3). In the Cucuteni culture, a similar artifact, described as "an open ring", occurred at site Târpeşti (Mareş 2012, pl. 42: 2527). While, in the hoard in the village of Brad, two, slightly smaller, specimens were discovered. They were described as elements of a necklace (Ursachi 2012, fig. 33:1).

Analogies for the Ks/w/18/08 specimen (Fig. 1: A) were found in graves 2 and 8 at site 2 in Książnice. In grave 2, a massive earring was discovered. It was 72 mm in diameter and it was made of a wire 2 to 4 mm thick, and it weighed 13.1 g (Wilk 2004, fig. 11:2). While, the earring from grave 8, with the diameter of 81 mm and made of the wire 1.7–2.9 mm thick, weighed 8.6 g (Wilk 2014, fig. 11:G). The above described artifacts from the necropolis in Książnice comprise an assembly of the biggest and most massive earrings in the entire Eneolithic in Central Europe. In the Lublin-Volhynian culture, no other earrings can be classified within the same metric category (51–85 mm in diameter). The biggest are the remaining two ornaments in the shape of a single coil of a flat-convex sheet of metal, measuring approximately 40–44 mm and 49–50 mm (Zakościelna 2010, pl. LXXIX:3,4) from grave 2 in Żuków, and two earrings from a single coil of copper wire, measuring 45–46 and 47 mm, from a grave at site 7 in Garbatówka Kolonia (Polańska 1999, 10, fig. 3:10,12). However, a good context for these finds is lacking, as it was a chance discovery in the grave in which no skeleton had been preserved. Owing to their metric similarity to the ornaments found below the chest of the body buried in grave 8 in Książnice (Wilk 2014, table I, figs 6; 10:F,G), their interpretation as earrings is not so unequivocal.

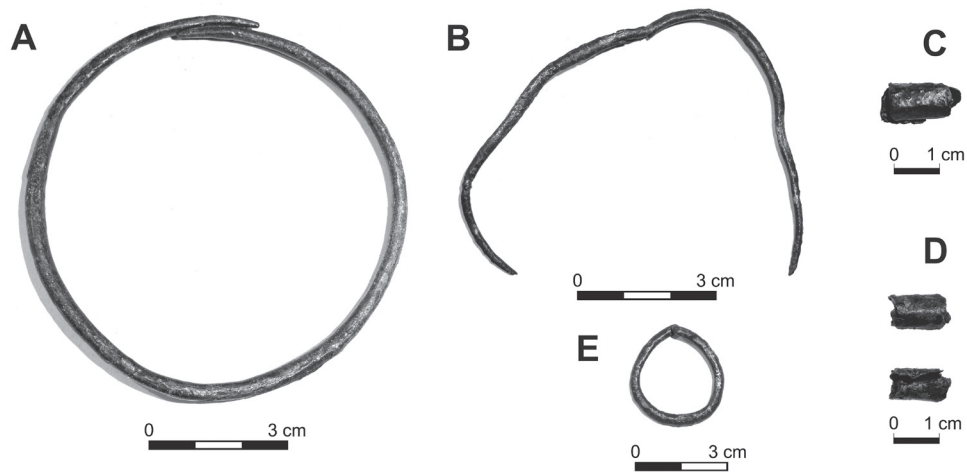

Fig. 1. Copper jewellery from the Lublin-Volhynian grave 7 at site 2 in Książnice (photo by S. Wilk)

The single-coil copper wire bracelet, Ks/w/3/08 (Fig. 1: B), has analogies among the finds of the Lublin-Volhynian culture from grave 101 in Grodzisko II in Złota (Sałacińska, Zakościelna 2007, fig. 21:17/XIX) and in grave 1 from site 3 in Stefankowice Kolonia (Kokowski, Koman 1985, pl. 332:2). In Wyciąże-Złotniki group, two copper wire bracelets, one of which consisted of one and a half coils, and the other one made as a single coil of wire with its ends overlapping each other, were found in grave I at site 7, 58, 65 in Kraków Nowa Huta-Cło (Kaczanowska, Tunia 2009, fig. 87:2,3).

We interpret the find as a bracelet rather than as a straightened earring, because on the left humerus of the skeleton from grave 7 we can observe some greenish discolouration, suggesting the presence of a bracelet. Also, there are analogies of the same shape found *in situ*, for example in grave 501 at the cemetery of Durankulak (Todorova 2002, pl. 79:6). Similar bracelet was discovered in feature 461 on the Balaton Lasinja culture settlement at Site 1 in Kaposvár in southwest of Hungary (Somogyi 2002, 342, 351, abb. 3:1).

More broadly, the occurrence of earrings and bracelets made of copper wire in the Eneolithic of Central Europe is discussed in the article about grave 8 from Książnice (Wilk 2014, 221–227, 232–234, see the relevant literature there).

Beads made of copper sheets are widespread in the Eneolithic societies of the Carpathian Basin and the territories located north and east of the Carpathians. They are divided into tubular beads (cylindrical), made of rolled sheets of copper, spirally coiled beads made of narrow strips of copper (the so-called *salta leone*, and by some authors also classified as tubular ones (Mareş 2012, 455), and ring-shaped beads resembling thin slices, made of a slightly thicker material.

To the oldest finds of tubular beads belong those found on late Neolithic sites on the Great Hungarian Plain, including those from the Polgár-Csőszhalom tell. They were found there in the layers dated to about 4700–4450 BC BC (Siklósi *et al*. 2015, 88, fig. 4; pl. 1). A slightly different variant of beads of copper sheets (they are made of thicker sheets, and they are a less regular in shape) were found on Lengyel culture cemeteries in southern Transdanubia, including Mőrágy Tűzkődomb (Zalai-Gaál 1996, fig. 6).In graves 12, 13, 24 and 39 at the cemetery of the Tiszapolg*ár* culture in Tiszapolgár-Basatanya, single cylindrical beads of copper sheets

Table I. Characteristic of the copper jewellery from grave 7 at site 2 in Książnice

Ordinal number	Inventory number	Depth in centimeters/ leveling in meters above sea level	Location in the grave	Description of the subject	Dimensions in millimeters (length, width, diameter, thickness)	Weight in grams	Number of the figure
1	Ks/w/3/08	35 199.91	At the height of the ceiling of the burial pit, in a mole hill, about 30 cm to the east of the pit	Single-coil copper wire bracelet	75×61 Ø 3 Ø 2	4,79	Fig. 1: B
2	Ks/w/4/08	35 199.91	At the height of the ceiling of the burial pit, in a mole hill, about 30 cm to the east of the pit	Small circular earring	22×20 Ø 2 Ø 1,5	1,75	Fig. 1: E
3	Ks/w/7/08	45–55 199.95	At chest height	Bead made of a rolled piece of metal sheet (in three pieces)	12 Ø 8×7? thickness of the sheet 1 mm	1,03	Fig. 1: C
4	Ks/w/18/08	45–55 199.84	Under the skull	A massive wire earring	87×86 Ø 4 Ø 2	21,15	Fig. 1: A
5	Ks/w/21/08	55–60	In the water supply trench	A bead made of a rolled piece of metal sheet	12 Ø 7×6 thickness of the sheet 1 mm	0,41	Fig. 1: D

were found; while, in grave 28, two more specimens of such beads were found (Bognár-Kutzián 1963, pls XX: 3; XXII: 2; XXXII: 1; XLVII: 5; XIII:6,7). Moreover, cylindrical beads of copper sheets formed part of two necklaces from Decea Mureşului (Mareş 2002, pl. 60:9, 11).

377 beads made of coiled copper sheets were found in the hoard from Karbuna in Moldova, dated to the A2 period of the Trypolye culture (Sergeev 1963). While, nine barrel-shaped beads made of copper sheets were found in the hoard from Horodnica (Sulimirski 1961, pl. 1), which contained, among other finds, a unique copper diadem decorated with repoussé indentations, whose only analogy is the bracelet from grave 2 in Książnice (Wilk 2004, fig. 11:4,5).

On the territories occupied by the Cucuteni culture, tubular beads were found – among other sites – at Traian and Târpeşti (Mareş 2012, pl. 43), as well as in the hoard from the site of Brad (Ursachi 2012, figs 28: 2; 35:4). It is interesting that they almost hardly ever occur in inventories of the cultures of Hamangia and Varna, which are very rich in other copper ornaments (Pernicka *et al*. 1997).

The specimens from grave 7 on site 2 in Książnice differ from other similar artifacts by their elongated shape and relatively large sizes (12 mm in length, and 6–8 mm in diameter). Finds, whose shape resembles that of the beads found in grave 7 (Fig. 1: C, D) are known from features 205 and 288 at the site of Třebestovice 1 (Čtverák, Rulf 1989, fig. 6, 7) and from grave 27 in Jordanów (Seger 1906, pl. VIII:5), which belongs to the Jordanów Śląski culture, as well as from graves LIV, LXX and LXXI from Osłonki (Grygiel 2008, figs 814; 833; 835), representing the Brześć-Kujawski culture. A slightly longer bead of copper sheet was found in feature 11 on site 6 in Kopydłowo (Marciniak *et al*. 2015, 40, fig. 17). In the Wyciąże-Złotniki group, "a small tubular copper bead", 9 mm in length, was found in grave I at site 7, 58, 65 in Kraków Nowa Huta-Cło (Kaczanowska 2009, 84; Kaczanowska, Tunia 2009, 267, fig. 87:4).

However, the overwhelming majority of beads made of copper sheets from the territories situated north of the Carpathians are spirally coiled, or much shorter than the discussed beads. Most often, such beads formed elements of rich necklaces (chokers) made of copper plates, and sometimes they occurred as elements of belts. In the Lublin-Volhynian culture, spirally coiled copper beads occurred only in the grave at site 8 in Mikulin (personal communication, courtesy of Anna Zakościelna). On cemeteries of the Jordanów-Śląski culture, in Jordanów and Domasław, there were numerous tubular and spirally coiled (*salta leone*) beads (Seger 1906, pl. VII:4, fig. 23; Mozgała, Murzyński 2012, 423, fig. 4:2; Gediga *et al*. 2012, figs 3: 6; 6:7). Similarly, in graves of the Brześć-Kujawski culture, numerous spirally coiled, small tubular and ring-shaped (resembling thin slices) beads were found, which once constituted elements of chokers (Jażdżewski 1938; Grygiel 2008).

In western Lesser Poland, a single bead made of spirally coiled, narrow copper plate was found in a child's grave (feature 40) at site 24 in Proszowice (Przybyła 2009).

3. The results of metallographic analyses

3.1. Methodology

As part of metallographic analysis of metal finds from grave 7, site 2 in Książnice, quantitative and qualitative analyses were conducted, regarding chemistry and microstructure of all the five artifacts. Because of unique value of the jewellery group from Książnice, the decision was made to resign from preparing proper metallographic samples, and only non-destructive tests were conducted directly on the objects. The surfaces were prepared for the analysis by partial removal of conservation coatings, with the exception of beads (Ks/w/7/08 and Ks/w/21/08), whose condition did not allow taking this step. Macroscopic observations were performed using a NIKON SMZ 745Z stereoscopic microscope with a Nikon Digital Sight DsFi1 microscopic camera and a Nis-Elements BR picture analysis system. Chemical composition tests were conducted using X-ray fluorescence spectrometry (XRF) with an energy dispersive X-ray fluorescence spectrometer SPECTRO Midex.

The microstructure observations were performed with a scanning electron microscope (SEM) Hitachi S- 3400N, equipped with Energy-Dispersive X-ray Spectrometer (EDS) by ThermoNoran, allowing for phase analysis in microareas. Also, microhardness tests were performed using Vickers method.

The tests aimed at describing metallographic and material characteristics of the copper jewellery from grave 7 at site 2 in Książnice. The macro-and microobservations of this material resulted in determining the material structure and allowed for qualitative description of the processes the material was subjected to during the manufacturing stages.

The scanning microscopy observations were conducted to describe the structure and chemical composition of individual artifacts. This method also allowed for microstructure evaluation with respect to metallic inclusions, defects and discontinuities as well as non-metallic impurities of the samples. The observations were performed on unetched samples.

Among the tests carried out, an important role was played by spectroscopy. The X-ray fluorescence spectroscopy method made it possible to prepare the qualitative and quantitative characteristics of chemical composition of the objects. In order to analyze varied surfaces of the samples, the excitation radiation was reduced by using the available apertures. The internal camera facilitated the choice of measurement points and photographic documentation of the research, with the measurement points being marked. In the case of archaeological material, also

the observation of objects with respect to their condition including identification of corrosion products is important. This characteristics makes it possible to choose the best conservation methods and it efficiently protects the objects against further destruction.

3.2. The research results

In chemical profiles of the tested artifacts, the highest copper concentration was noted for the objects marked as the earring, code number Ks/w/4/08 (99.8%), the bead Ks/w/21/08 (99.6%), the earring Ks/w/18/08 (99.5%) and the bead Ks/w/7/08 (98.8%). The lowest copper content (97.5%) was found in the bracelet Ks/w/3/08.

In the artifacts tested, there were also identified the elements significant from the perspective of raw material origin and smelting technology. Arsenic, antimony, silver, tin, zinc, lead, bismuth, cobalt, nickel and iron belong to this group. Looking from the smelting perspective, they belong to the impurities which remained from the ore composition and they are important markers to identify the origin characteristics of the raw material. The highest total content of impurities was noted for the bracelet Ks/w/3/08. Against the background of other elements, the arsenic content stands out here and it is 2.1%, and lead 0.26%. For the remaining artifacts, the arsenic content was 0÷0,24%, and lead 0÷0,039%. Antimony (0.098%) and zinc (0.15%) was only recorded for the bead Ks/w/7/08. Also, the highest content of silver (0.05%) was established in this case. In the remaining ornaments, the silver content was below 0.02%.

The tests did not show any mercury content (Hg<0.0010%), but a raised level of cobalt was established (0.50 – 0.73% Co), which points to the fact that maybe the artifacts were made from remelted copper (Pernicka *et al*. 1997; Adamczak *et al*. 2015). This is also confirmed by the oxygen content in copper, assessed on the bases of macroscopic observations and microareas analysis (Rzadkosz 2013; Garbacz-Klempka *et al*. 2016a).

The collation of the chemical composition results of the artifacts from grave 7, expressed in weight percentage, is presented in Table II. In Table III there are quantitative results of the bracelets tests, belonging to the Wyciąże-Złotniki group, graves 2 and 4, from site 5 in Kraków Nowa Huta-Wyciąże, and the grave I, at sites 7, 58 and 65 in Kraków Nowa Huta-Cło. The tests were performed using the same X-ray fluorescence spectroscopy method, as in the case of Książnice (Garbacz-Klempka *et al*. 2016a); also there are qualitative results of the two bracelets tests, from the grave 101 of the Lublin-Volhynian culture from the site Grodzisko II in Złota, conducted by T. Dziekoński with the help of emission spectroscopy (Dziekoński 1962). The impurities distribution in specific artifacts is presented graphically in charts (Figs 2; 3)

The results of chemical composition with the characteristic elements marked are also shown as X-ray fluorescence charts (Fig. 4: A–F). The last chart (Fig. 4: F) lists the results of all the five artifacts, prepared to show the similarities and differences of the chosen elements concentration, arsenic especially. The difference in content of a given element in the alloy is shown here as the difference in impulse intensity where it is identified on the chart. The spectra for the successive artifacts are differentiated by colour.

The metal artifacts from site 2 at Książnice were subjected to macroscopic tests, which showed varied surface, resulting from prehistorical technology or corrosion processes taking place in favourable conditions where they were deposited (Figs 5; 6).

The chosen artifacts (two earrings and a bracelet) were tested by light microscopy and scanning microscopy. The microstructure and corrosion-related impurities were observed on the unetched surfaces, which made the microstructure observation more difficult. The areas observed

are presented in photographs, in succession for Ks/w/3/08 (Fig. 7: A, B), Ks/w/4/08 (Fig. 7: C, D), and Ks/w/18/08 (Fig. 7: E, F).

The earing (Ks/w/4/08), observed at the magnification of 500 and 1500x, shows small but numerous areas taken up by copper oxides (Garbacz-Klempka *et al*. 2016b) Moreover, in the microstructure, outlines of grain crystallites of pure copper are visible (Fig. 7: D). Similar characteristics is shown by the Ks/w/3/08 bracelet microstructure (Fig. 7: A, B), while the Ks/w/18/08 earring (Fig. 7: E, F) showed numerous and small structure discontinuities observed at the 500 and 700× magnifications. The impurities are located at the grain boundaries. Arsenic, present in the earring at the level of 0.24%, got solved in copper, creatingαsolid solution (Garbacz-Klempka *et al*. 2015). The remaining impurities, like lead and oxygen, are visible as darker elements against the background of homogenous structure (Fig. 7: F).

The content identification of the individual microstructure phases was performed on the basis of X-ray fluorescence analysis in microareas. The observed inhomogeneity results from corrosive activity of the material, which results in, among others, the creation of copper(I) oxide [Cu_2O] and copper(II) oxide [CuO]. The presence of chloride salts accompanied by a limited amount of oxygen, influences the creation of copper chlorides (II) [$CuCl_2$] (Garbacz-Klempka *et al*. 2016b).

Based on the X-ray fluorescent spectroscopy results, chemical profiles were established for the individual, and they were ascribed to raw material groups according to R. Krause (Krause 2003: 90–91, fig. 40–41). The data is presented in Table IV. Chemical analysis results of the beads marked as Ks/w/21/08 and Ks/w/7/08, because of their high degree of destruction, could be encumbered by an error. It would be required to verify the results by repeating the tests after revealing the metallic core. Comparing them with the remaining analysis results, should be treated qualitatively.

The classification results of the copper ornaments from grave 7 at site 2 in Książnice, conducted within the raw material groups, point to their clear diversification, because the objects discussed can be ascribed to three copper classes: 1) pure copper, 2) arsenic copper and 3) antimony copper.

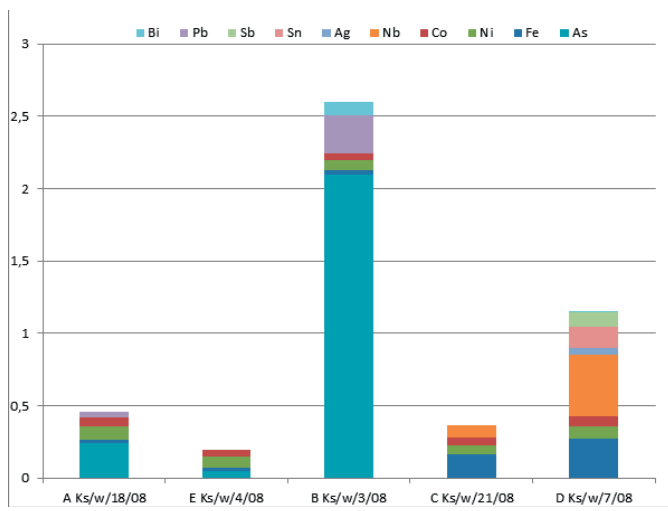

Fig. 2. Impurities distribution in specific artifacts (wt%)

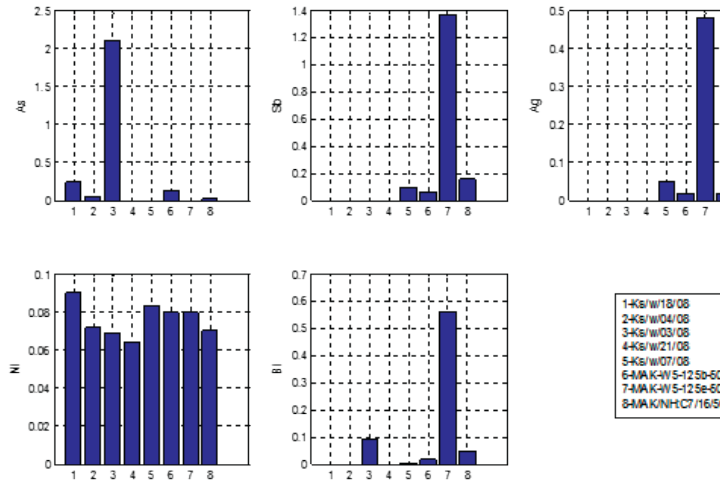

Fig. 3. Differences in the content of selected chemical elements of artifacts from Książnice, Kraków Nowa Huta-Wyciąże and Kraków Nowa Huta-Cło

Similar observations are valid for the artifacts from the Wyciąże-Złotniki group, at site 5 from Kraków Nowa Huta-Wyciąże (MAK_W5-125b-50; MAK_W5-125e-50). The only object that was analysed from grave I of the Wyciąże-Złotniki group, at site 7, 58, 65 in Kraków Nowa Huta-Cło (MAK/NH:C7/16/50) fits the chemical profile of the antimony copper group. Very low accuracy of the chemical analysis of the artifacts from grave 101 at the site Grodzisko II in Złota (0.0X or 0.X) conducted by T. Dziekoński at the beginning of the 1960's (Dziekoński 1962), makes it impossible to assign these artifacts precisely to the proper raw material groups.

The observed differences may suggest that the community of the Lengyel-Polgár group from Lesser Poland (Książnice, Kraków Nowa Huta-Wyciąże, Kraków Nowa Huta-Cło), imported the raw material or the ready artifacts from different sources. This tendency corresponds to the diversification of the copper objects which were discovered at the sites of Brześć-Kujawski culture in Brześć Kujawski and Osłonki (Grygiel 2008). R. Grygiel holds the opinion that copper and ready artifacts arrived there from the South part of Central Europe (Grygiel 2008, 1877). This is in line with the general direction of this trend, which could be identified for the historical objects from Książnice, Kraków Nowa Huta-Wyciąże and Kraków Nowa Huta-Cło (Krause 2003, 12).

The basis for the chemical characteristics presented here was the content of antimony, arsenic, nickel and silver. An important fact is that for antimony and arsenic in the metallurgical process

Table II. Chemical composition of the copper jewellery from grave 7 at site 2 in Książnice with XRF method (wt%)

Sample	Fe	Co	Ni	Cu	As	Nb	Ag	Sn	Sb	Pb	Bi	∑
Ks/w/18/08	< 0.025	0.060	0.090	99.5	0.24	< 0.020	< 0.020	< 0.051	< 0.051	0.039	< 0.0010	100
Ks/w/4/08	< 0.025	0.050	0.072	99.8	0.047	< 0.020	< 0.020	< 0.051	< 0.051	< 0.020	< 0.0010	100
Ks/w/3/08	< 0.025	0.053	0.069	97.5	2.1	< 0.020	< 0.020	< 0.051	< 0.051	0.26	0.092	100
Ks/w/21/08	0.16	0.052	0.064	99.6	< 0.00051	0.087	< 0.020	< 0.051	< 0.051	< 0.020	< 0.0010	100
Ks/w/7/08	0.27	0.073	0.083	98.8	< 0.00051	0.42	0.050	0.15	0.098	< 0.020	0.0051	100

there are the same conditions preserved for evaporation and absorption into slag, therefore their mutual relationship in the ore deposits and ready-made product stays at the same level.

The copper ornaments that were researched contain some impurities and porosity. This results from technology imperfection, which – because of problems connected with removing the redundant elements – caused their arrest in the solution. In the course of the research, against the homogenous copper background, numerous small imperfections were revealed, in the form of irregular precipitates or their clusters. These precipitates are mainly localized at the grain boundaries. Also, some natural admixtures were identified, present in the ores and products. In the bracelet Ks/w/3/08 silver precipitates were identified, which occur in copper. The remaining impurities are located in the solution and at the grain boundaries (Garbacz-Klempka *et al*. 2016b).

Table III. Chemical composition of the copper jewellery from: Wyciąże-Złotniki group cemetery at site 5 in Kraków Nowa Huta-Wyciąże, site 7, 58, 65 in Kraków Nowa Huta-Cło (Garbacz-Klempka *et al*. 2016a, tables 1–3) and cemetery of the Lublin-Volhynian culture at site Grodzisko II in Złota (Dziekoński 1962, 103, table II.1) (wt%)

Sample	Fe	Co	Ni	Cu	As	Nb	Ag	Sn	Sb	Pb	Bi	∑
NH:W5/125b/50	0.07	0.05	0.080	99.6	0.13	< 0.020	0.020	< 0.051	0.070	< 0.020	0.020	100
NH:W5/125e/50	0.04	0.06	0.080	97.4	< 0.00051	< 0.020	0.48	< 0.051	1.4	< 0.020	0.56	100
NH:C7/16/50	0.09	0.04	0.070	99.5	0.030	< 0.020	0.020	< 0.051	0.16	< 0.020	0.050	100
Złota 13/59/10	0.X	traces	0.0X	X	0.0X	–	0.X	–	0.X	traces	0.X	–
Złota 13/59/11	0.X	traces	0.0X	X	0.0X	–	0.X	–	0.X	traces	0.X	–

Table IV. Classification of the artifacts from the grave 7 at site 2 in Książnice and similar items from graves at site 5 in Kraków Nowa Huta-Wyciąże, from grave II at site 7, 58, 65 in Kraków Nowa Huta-Cło (Garbacz-Klempka *et al*. 2016a, tables 1–3), and grave 101 at site Grodzisko II in Złota (Dziekoński 1962, 103, table II.1), within groups of raw materials by R. Krause (Krause 2003, 90–91, figs 40–41)

Sample	As		Sb		Ag		Ni		Copper class
Ks/w/18/08	0.24	±0.02	< 0.051	N/A	< 0.020	N/A	0.090	±0.003	Arsenical copper with Ni and Bi
Ks/w/4/08	0.047	±0.04	< 0.051	N/A	< 0.020	N/A	0.072	±0.002	Pure copper with slight traces of As and Ni
Ks/w/3/08	2.1	±0.4	< 0.051	N/A	< 0.020	N/A	0.069	±0.004	Arsenical copper with Ni and Bi
Ks/w/21/08	< 0.00051	N/A	< 0.051	N/A	< 0.020	N/A	0.064	±0.001	Pure copper with slight traces of As and Ni
Ks/w/7/08	< 0.00051	N/A	0.098	N/A	0.050	N/A	0.083	N/A	Antimonical copper
MAK/W5-125b-50	0.13	±0.03	0.070	±0.001	0.020	±0.006	0.080	±0.03	Arsenic copper with Ni and Bi
MAK/W5-125e-50	< 0.00051	N/A	1.4	±0.3	0.48	±0.05	0.080	±0.005	Antimonical copper
MAK/NH:C7/16/50	0.030	±0.01	0.16	±0.07	0.020	±0.0	0.070	±0.01	Antimonical copper
Złota 13/59/10	0.0X	–	0.X	–	0.X	–	0.0X	–	Not applicable due to a low precision of the measurements
Złota 13/59/11	0.0X	–	0.X	–	0.X	–	0.0X	–	Not applicable due to a low precision of the measurements

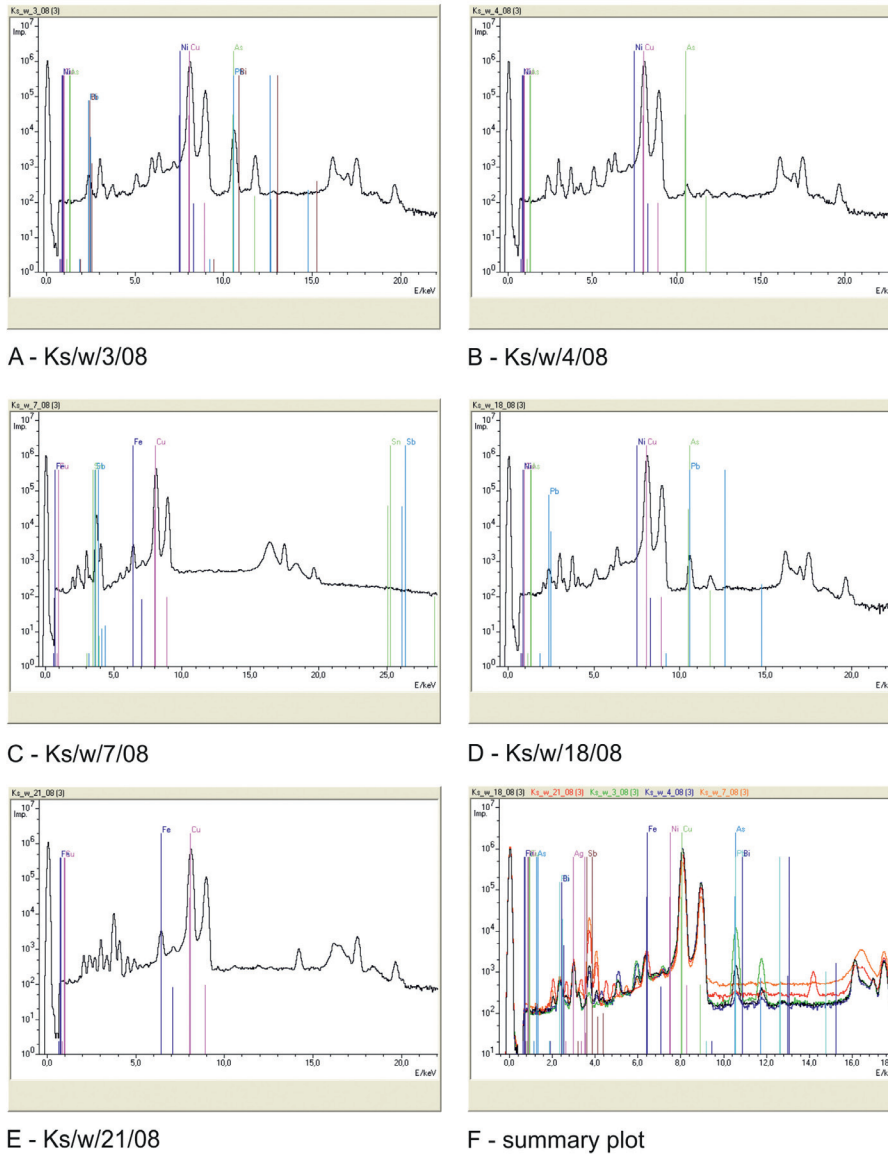

Fig. 4. A – XRF spectra for Ks/w/3/08, determined for copper, arsenic, lead, nickel, and bismuth; B – XRF spectra for Ks/w/4/08, determined for copper, arsenic, and nickel; C – XRF spectra for Ks/w/7/08, determined for copper, tin, antimony, and iron; D – XRF spectra for Ks/w/18/08, determined for copper, arsenic and lead, nickel; E – XRF spectra for Ks/w/21/08, determined for copper and iron; F – summary plot

From the perspective of impurities content, four of the artifacts tested showed significant similarity, but one of them, the bracelet Ks/w/3/08 (Fig. 4:A) significantly differs in respect to the arsenic content (2.1%) and lead (0.26%). There is no antimony in the artifacts under investigation, with the exception of the bead Ks/w/7/08, containing 0.09%Sb.

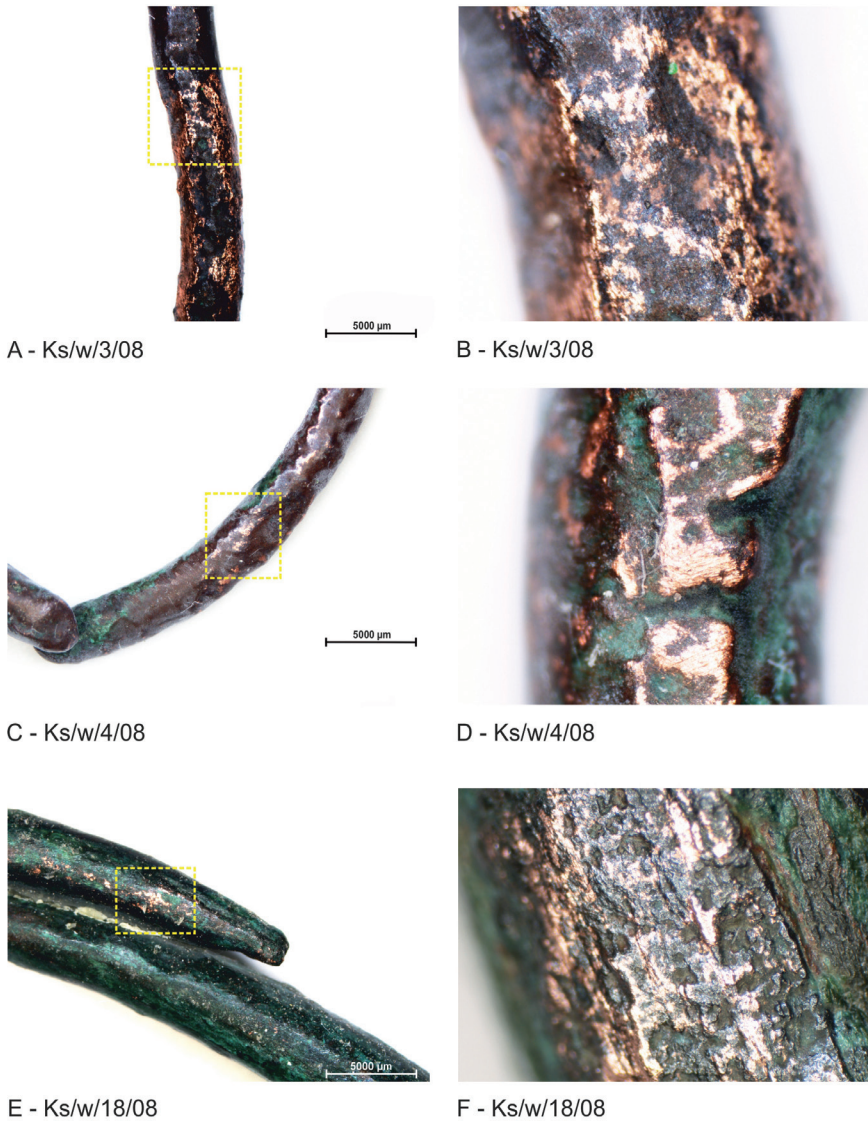

Fig. 5. Macroscopic pictures of the copper artifacts from grave 7 at site 2 in Książnice, A – bracelets Ks/w/3/08 (10×), B – bracelets Ks/w/3/08 (50×), C – earring Ks/w/4/08 (10×), D – earring Ks/w/4/08 (50×), E – earring Ks/w/18/08 (10×), F – earring Ks/w/18/08 (50×) (photo by A. Garbacz-Klempka)

The chemical characteristics of the earrings and beads from grave 7 in Książnice is similar to the bracelet NH:W5/125b/5, from the site 5 in Kraków Nowa Huta-Wyciąże, however, it clearly differs from the other bracelet (NH:W5/125e/5) in the antimony content (1.37%), silver (0.48%) and bismuth (0.56%).

The bracelets from the grave 101 from the site Grodzisko II in Złota, from T. Dziekoński research, had a determined content of antimony, arsenic, silver and nickel (Dziekoński 1962:

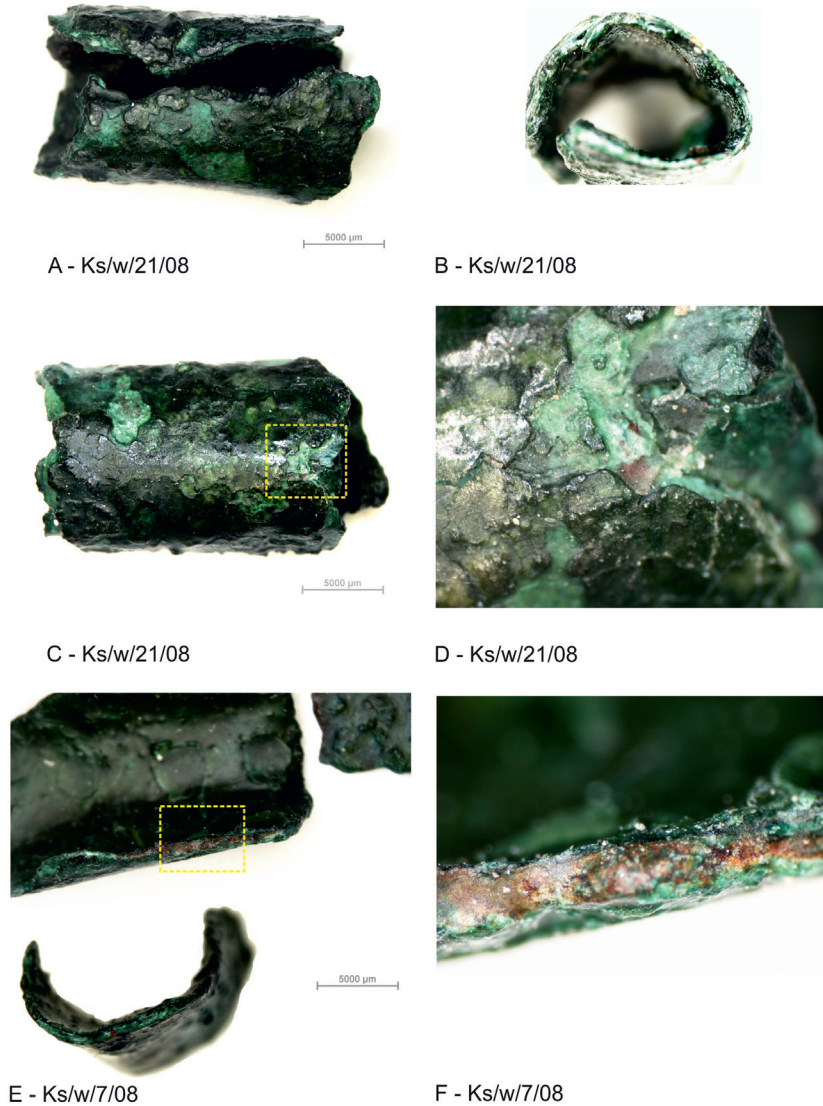

Fig. 6. Macroscopic pictures of the copper artifacts from grave 7 at site 2 in Książnice. A, B, C – bead Ks/w/21/08 (10×), D – bead Ks/w/21/08 (50×), E – fragment of bead Ks/w/7/08 (10×), F – fragment of bead Ks/w/7/08 (50×) (photo by A. Garbacz-Klempka)

103, table II.1). Low accuracy of the research results from Złota does not allow for comparing them with newer analyses of metallographic analyses.

It seems that the ornaments from grave 7 in Książnice were made by hammering from cast. An indirect proof in this case is a significant content of copper oxide [Cu_2O], identified in the microscopic tests and in chemical analysis in microareas.

The microhardness tests of the chosen artifacts using the $Vickers_{0,02}$ method showed the values within the 98÷101 $mHV_{0,02}$ range.

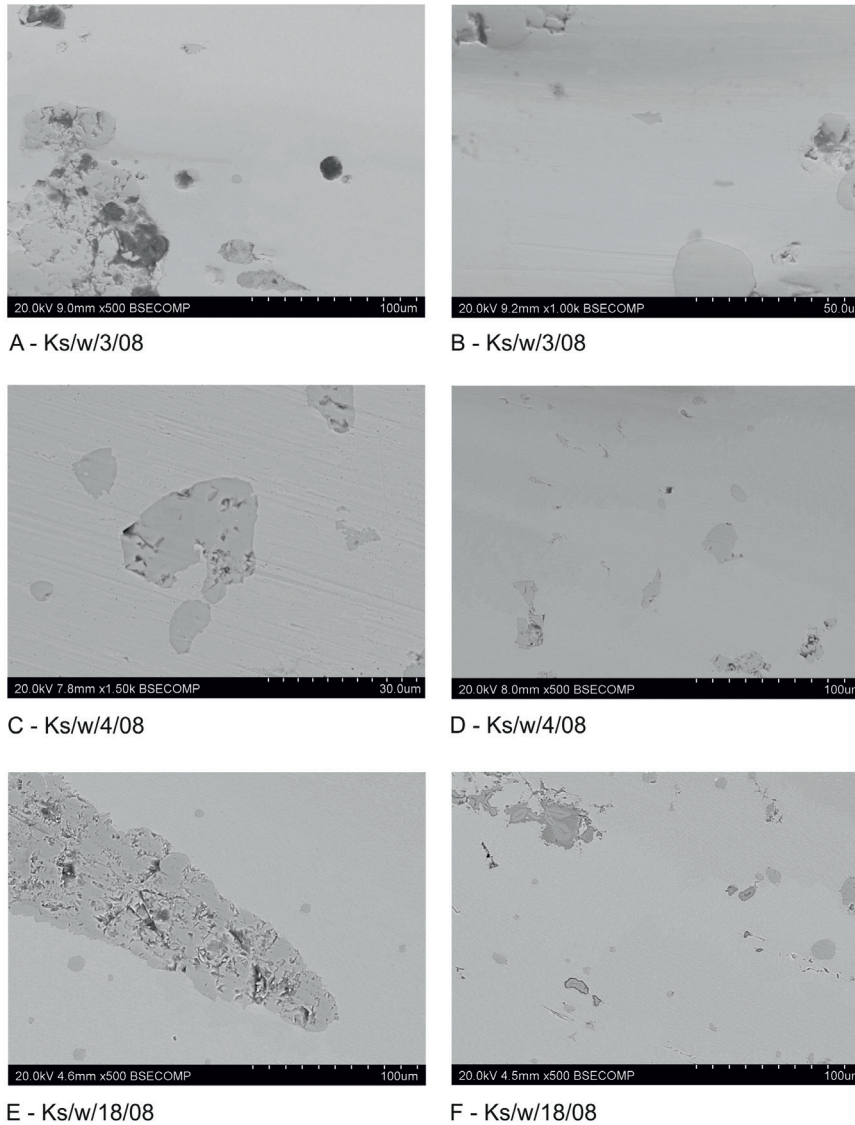

Fig. 7. BSE pictures of microstructure of the copper artifacts from grave 7 at site 2 in Książnice. A – bracelet Ks/w/3/08 (500×), B – bracelet Ks/w/3/08 (1000×), C – earring Ks/w/4/08 (1500×), D – earring Ks/w/4/08 (500×), E – earring Ks/w/18/08 (500×), F – earring Ks/w/18/08 (500×) (photo by M. Perek-Nowak)

In the microscopic tests also a number of extensive changes were noticed in the structure of the sample, which were caused by corrosive conditions connected with long deposition in soil. In the internal pores of the material, oxide and chlorine compounds were present. The localization of these corrosion products was the effect of precipitates segregation at the boundaries of matrix phases. Structure changes are visible at the grain boundaries that points to the intercrystalline corrosion character.

4. Conclusion

Based on the data from the location of the copper artifacts and the traces left by some of them (greenish discolouring) on the skeleton, the authors propose a reconstruction of how the jewellery described in the article could have been worn by the girl buried in grave 7 in Książnice (Fig. 8). At first glance, attention is drawn to the earrings sewn onto a textile or leather band worn on the head. The bigger one, found under the skull, was worn at the height of the left temple. The smaller one, found near the burial pit – at the height of the top of the skull – was worn at the height of the right temple. The bracelet was worn on the left arm, a little above the elbow. The entire jewellery set is complemented with two copper beads strung on a leather thong or a string, hanging on the chest.

The presented inventory of copper artifacts from grave 7 confirms the thesis about wide, trans-Carpathian contacts of the group which was using the necropolis in Książnice at the beginning of the 4th millennium BC.

Fig. 8. Reconstruction of the way of wearing copper jewellery discovered in grave 7 at site 2 in Książnice (drawn by K. Kielijańska)

Among the 17 burials found so far at the cemetery, as many as 7 are equipped with 23 copper artifacts altogether (bracelets made of wire and copper sheets, wire earrings, wire necklaces, spectacle-shaped pendants, an earring, an axe, a hatchet, a chisel and an awl). It is the biggest collection of such artifacts in Lesser Poland, and one of the biggest in all Poland (Wilk 2014; 2015).

The planned further research on the assembly of copper specimens from Książnice will allow us to determine its chemical characteristics, as well as its typological links with related assemblages from Polish and other Central European territories.

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Eneolityczna biżuteria miedziana z grobu nr 7 kultury lubelsko-wołyńskiej na stanowisku 2 w Książnicach, woj. świętokrzystkie. Charakterystyka typologiczna i metalurgiczna

Niniejszy artykuł prezentuje typologiczną i metaloznawczą analizę zabytków miedzianych znalezionych w grobie dziecięcym (nr 7) na cmentarzysku kultury lubelsko-wołyńskiej w Książnicach (Małopolska). Pochówek, datowany na przełom V i IV tysiąclecia BC (4050–3940 BC), zawierał bogaty zestaw biżuterii miedzianej, na który składały się: duża, masywna zausznica, mała zausznica i bransoleta – wykonane z drutu, oraz dwa paciorki ze zwiniętej blachy miedzianej. W ramach badań metaloznawczych, przeprowadzono ilościowe i jakościowe, analizy chemiczne i mikrostrukturalne wszystkich pięciu zabytków. W badanych zabytkach zidentyfikowano pierwiastki, istotne z punktu widzenia pochodzenia surowca i technologii wytopu. Należą do nich: arsen, antymon, srebro, cyna, cynk, ołów, bizmut, kobalt, nikiel i żelazo. Sumarycznie największą zawartość zanieczyszczeń zarejestrowano dla bransolety. Na tle innych pierwiastków wyróżnia się tu arsen, który wynosi 2,1% i ołów 0,26%. Dla pozostałych zabytków stężenie arsenu wynosiło 0÷0,24%, a ołowiu 0÷0,039%. Antymon (0,098%) i cynę (0,15%) zarejestrowano jedynie dla jednego z paciorków. W tym przypadku wykazano również najwyższą zawartość srebra (0,05%). W pozostałych ozdobach stężenie srebra wynosiło poniżej 0,02%. Na podstawie wyników analizy spektroskopii fluorescencji rentgenowskiej dokonano ustalenia profili chemicznych analizowanych zabytków oraz zaklasyfikowano je do grup surowcowych wg R. Krause: (1) miedzi czystej, (2) miedzi arsenowej oraz (3) miedzi antymonowej (Krause 2003: 90 – 91, ryc. 40 – 41). Zaprezentowany inwentarz zabytków miedzianych z grobu 7, mający liczne analogie w Kotlinie Karpackiej i na terenach położonych na północ i wschód od łuku Karpat, potwierdza tezę o szerokich transkarpackich kontaktach grupy użytkującej nekropolę w Książnicach na przełomie V i IV tysiąclecia BC.

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