Wiadomości Numizmatyczne, R. LXVI, 2022, z. 210
Polish Numismatic News X (2022)
DOI 10.24425/wn.2022.141936

EWELINA MIŚTA-JAKUBOWSKA

MICROANALYSIS OF EARLY MEDIEVAL ARCHAEOLOGICAL OBJECTS MADE OF SILVER ALLOY

ABSTRACT: Modern archaeological research uses physico-chemical methods to answer questions beyond the scope of the conventional historian's workshop. This applies to research on the borderline of fields, including material research into the elemental and isotopic composition of artefacts. The results of such analyses make it possible to address issues relating to the distribution of raw materials and the technology of artefact production. The paper discusses the SEM-EDS and LA-ICP-QMS micro-analysis methodology, addressing the limitations that result from the specification of techniques and the state of preservation of archaeological artefacts due to corrosion processes and conservation treatment. We present the preliminary results of technological research and provenance study of early medieval objects made of silver alloys, considered by typological group, i.e. coins, cake, and jewellery. Two hundred objects were analysed, revealing clear evidence for the use of remelted dirhams as the main source of raw material. The results of the research allowed for a material description of the phenomenon of the existence of cores in cross denarii, distinguishing two types of cores: based on copper and brass. In the case of jewellery, the research provided evidence for technological distinction, indicating the use of copper-based solders, as well as tin- and lead-based dolders, which have analogies in goldsmithing material from the Czech Republic. Recipes based on the marked composition are described in ancient sources. Silver cakes, on the other hand, can be divided into three extraction groups related to the degree of purification of the raw material. The preliminary results indicate that these objects were made of Asian dirhams and native lead, perhaps as an additive in the cupellation process.

ABSTRAKT: We współczesnych badaniach zabytków archeologicznych metody fizykochemiczne wykorzystywane są w celu udzielenia odpowiedzi na pytania wykraczające poza obszar zainteresowań konwencjonalnego warsztatu historyka. Dotyczy to badań na pograniczu dziedzin, w tym badań materiałowych pozwalających na określenie składu pierwiastkowego i izotopowego zabytków. Wyniki takich analiz pozwalają na przybliżenie zagadnień dotyczących dystrybucji surowców oraz technologii wykonania zabytków. W pracy przedstawiono propozycję metodyki mikro-analizy SEM-EDS i LA-ICP-QMS uwzględniając jej ograniczenia wynikające ze specyfikacji technik, jak i stanu zachowania zabytków będącego efektem procesów korozyjnych i złej konserwacji. Przedstawiono wstępne wyniki badań technologicznych i proweniencji wczesnośredniowiecznych zabytków wykonanych ze stopów srebra uwzględniając podział na grupy typologiczne to jest monety, placki srebrne i ozdoby. W sumie analizie poddano 200 obiektów wskazując jako główne źródło surowca przetop z dirhamów. Wyniki badań pozwoliły na materiałowy opis zjawiska istnienia rdzeni w denarach krzyżowych wyróżniając dwa rodzaje rdzeni: na bazie miedzi i mosiądzu. W przypadku ozdób umożliwiły ich rozróżnienie technologiczne wskazując na użycie lutowania opartego o związki miedzi ale też cyny i ołowiu, co ma swoje analogie w materiale złotniczym z terenu Czech. Receptury bazujące na oznaczonym składzie są opisane w źródłach antycznych. Placki srebrne natomiast można podzielić na trzy grupy ekstrakcyjne związane ze stopniem oczyszczenia kruszcu. Wstępne wyniki wskazują, iż obiekty te zostały wykonane z kruszczu azjatyckiego przy udziale ołowiu rodzimego, być może jako dodatku w procesie kupelacji.

KEYWORDS: Early Medieval silver, micro-analysis, provenance and technological study, archaeometallurgy

SŁOWA KLUCZOWE: wczesnośredniowieczne srebro, mikroanaliza, badania proweniencji złożowej i technologicznej, archeometalurgia

1. Introduction

The early Middle Ages was a period of state formation across continental Europe. In Poland, this process is associated with the Piasts, a Slavonic dynasty that created a new Polish state. Owing to a shortage of written sources describing the activities of the Piasts, archeology is the primary source of research material for this period. Other than ceramics, much of our evidence for this period takes the form of silver coins, bars, and ornaments, which are represented in hundreds of hoards. The custom of hoards came to Piast Poland from Scandinavia in the middle of the 10th century, where the tradition of depositing precious metal objects was already old in the Viking Age (beginning of the 8th to 12th centuries), and where the number of discovered hoards is very high: more than 800 hoards are known from the small island of Gotland alone. Eastern Europe belonged to the same "hoarding zone", where numerous hoards of silver, and sometimes gold, are associated with the Swedish colonization from the middle of the 8th century onwards. Early medieval hoards are also known from the West Slavic territories of Poland and Połabie, but are otherwise rare. These hoards have mainly been of interest to numismatists, but have sometimes also interested archaeologists as collections of jewllery, most often divided into larger or smaller pieces. These collections of jewellery have been ordered using typological methods,[1] and have also very occasionally been subjected to physicochemical tests,[2] which have generally been too simplistic for their results to offer significant insights

---

[1] Jakimowicz 1933; Kóčka-Krenz 1993.

[2] E.g. Zoll-Adamikowa, Dekówna, Nosek 1999; Duczko 1985; Koziorowska 2000.

into the period of study. However, analysis of the chemical composition of hoarded objects, including elemental and isotopic analysis, allows us to not only study the origins of their raw material, but also to define their technological basis, distinguishing the activities of workshops, including goldsmiths. Comparing specific objects and their chemical compositions helps to create a comprehensive historical perspective. The results of material research into archaeological objects allows us to reconstruct the processes that the artifact was subject to, both technological and secondary – depositional. By selecting appropriate reference materials, including geological and technological groups, they enable the analysis of the origin of the raw material and thus, thanks to the knowledge of the historical use of the deposit or technology, the relative dating of objects. Due to the heterogeneity of the raw material, which result from the processes that the artifact was subject to, it is important in archaeometallurgic research to maintain appropriate measurement statistics. This allows for a more detailed analysis of raw material variability, which result from material changes in the artifact. Study of cultural and art objects requires non-destructive procedures. Surface tests are often used, the results of which are the product of technological and post-deposit processes to which the object was subjected. Despite this, the results obtained in this way sometimes are useful in techological study of producing the artifact.[3] In study of the origin of the raw geological material isotope analyzes are used,[4] where tests are carried out on samples taken from the object, or where the object surface is analyzed using micro-sampling (in the laser ablation process).[5] When testing the elemental composition of the surface, as a supplement to the research of geological provenance, the data obtained should be related to reference samples consisting of alloy samples aged in laboratory-controlled conditions (or simulated by programs), on which destructive tests can be performed. However, such reference materials are still lacking. In view of this situation, it seems optimal to examine of artifacts in cross-section, in order to capture the chemical composition and structure changes of the objects resulting from their technological production. Unfortunately, due to the destructive nature of the process, this is not always possible. For this reason, technological and raw material inference based on the results of non-destructive analyzes for archaeological objects characterized by a high degree of material heterogeneity is difficult, and is useful as a preliminary diagnosis only in cases where it is possible to analyze a large group of artifacts and maintain the appropriate measurement statistics per object. Despite the many variables that should be taken into

---

[3] E.g. Scrivano *et al.* 2013; Scrivano *et al.* 2017a; Scrivano *et al.* 2017b; Ontalba Salamanca *et al.* 1998; Šmit *et al.* 2000; Demortier *et al.* 1999; Ashkenazi *et al.* 2017; Miśta-Jakubowska *et al.* 2019; Miśta-Jakubowska *et al.* 2019a; Miśta-Jakubowska *et al.* 2019b; Miśta-Jakubowska *et al.* 2019c.

[4] E.g. Chamberlain, Gale 1980; Gale 1979; Baker, Stos, Waight 2006; Balcaen, Moens, Vanhaecke 2010; Pernicka 2014; Stos-Gale, Gale 2009.

[5] Miśta-Jakubowska *et al.* 2019a.

account when analyzing the results of physicochemical studies, these specialized analyzes are an inseparable element of archaeological research.

The aim of this research was to examine the raw material and technological provenance of a large series of silver artifacts from selected Polish hoards, and to attempt to characterise the differences between them that result from a specific craft workshop.[6]

2. Methodology

2.1. Studied objects

The paper presents the selected results of research into the micro-scale elemental composition of a large group of early medieval artifacts made of silver alloy from selected Polish hoards. The selected objects were tested using lead isotope ratio analysis (LIA) and related to ores using published data. The results were analyzed on the basis of typological group: coins, silver cakes, and jewellery. The examined collection included:

1. coins of various types and varieties, including three coins from a private collection – 109 in total. Varieties and numbers of the studied coins from museum collections: Palatine Sieciech's denarii (1095–1100 A.D.) – 20 objects (Słuszków hoard), Otto and Adelaide's denarii (10th/11th c.) – 24 objects (Słuszków hoard), dirhams (mid-10th c.) – 10 objects (from aš-Šāš, Ma'din and Andaraba mints) (Zalesie and Obra Nowa hoards), cross denarii of different varieties of CNP (48 objects) (Słuszków hoard). Three cross denarii came from private collections, and it was therefore possible to conduct invasive tests on them. Cross-section cuts were made on two of them. This allowed for the study of the variability in elemental composition across their entire volume (no LIA tests were performed for them).
2. jewellery and jewellery fragments – 58 pieces in total; from Kalisz-Rajsków (17 pieces) and Słuszków (5 pieces) hoards, Obra Nowa (28 pieces), Stojkowo (8 pieces).
3. "raw" silver objects, silver cakes – 19 objects (from Kalisz-Dobrzec and Jastrzębniki hoards).

2.2. Laboratory tests

Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS) was used to determine the elemental composition of the objects. This used the standard-less method for semi-quantitative analysis,[7] where at least 3 measurements were made

---

[6] Miśta-Jakubowska *et al.* 2019a; Miśta-Jakubowska *et al.* 2019c; Miśta-Jakubowska *et al.* 2020; Miśta-Jakubowska 2020.

[7] Trincavelli, Limandri, Bonetto 2014.

for one object, differentiating its surface into technological areas and maintaining the given measurement statistics/area.[8] Inductively Coupled Plasma Mass Spectrometry with Laser Ablation (LA-ICP-QMS) was used for LIA.[9] The series of numerical data obtained from the measurements of elemental and LIA was subjected to multivariate statistical analysis using the following models: kernel density estimation (KDE),[10] and principal components analysis (PCA).[11]

3. Results and Discussion

3.1. Introduction

Modern archeology uses physiochemical techniques. Due to their non-destructive nature, techniques using X-rays (mainly XRF, EDS) are very popular in material testing. They make it possible to obtain information on the elemental composition of the tested surface layer only.[12] If a museum object made of silver alloy (after conservation) is analyzed in its entirety, without destructive preparation, the inference about the technology or origin of the object may be subject to significant error. The analyzed surface is changed in relation to the original alloy by corrosion and conservation processes.[13] For example, preservation with edetic acid (EDTA) solution (disodium edetate) leaches most of the alloying elements into the EDTA chelating solution.[14] However, it may happen that the state of preservation of objects (their surface) after conservation allows for preliminary semi-quantitative differentiation of the elemental composition in the *a priori* typological groups and within the micro areas of the object (using the SEM-EDS technique) that have a different method of manufacture (as shown below). The characteristics obtained in this way are, however, relative and helpful in archaeometallurgical research, but do not carry full geological ore deposit information through the elemental composition. When the isotopic data of geological deposits that contribute to the raw material are similar or even the same, research into deposit origin based on LIA analyzes also seems to be burdened with significant inference error (see Fig. 7: a, some of European ores). Another drawback of the LIA technique is that objects dating to the Middle Ages are the product of numerous remeltings and foreign technological additions based on lead alloys and copper (also in a form with the

---

[8] Miśta-Jakubowska 2020.

[9] Miśta-Jakubowska *et al.* 2019a; Miśta-Jakubowska *et al.* 2019c; Miśta-Jakubowska *et al.* 2020.

[10] Baxter 2003; Baxter 2016; Żabiński *et al.* 2020.

[11] Baxter 2003; Baxter 2018; Żabiński *et al.* 2020.

[12] Gójska *et al.* 2019.

[13] See the phenomenon of silver enrichments: e.g. Linke, Schreiner 2000.

[14] E.g. Costa 2001; Żołędziowski, Miśta-Jakubowska, Czech-Błońska 2021.

addition of lead).[15] The addition of copper in a silver alloy above 2.6% is considered to be an intentional improvement of the properties of the alloy.[16] In addition, jewellery made with the filigree and granulation techniques are soldered with copper compounds[17] as well as lead.[18] A proposal for the development of LIA results, taking into account isotopic heterogeneities as a technological effect (also with the addition of foreign lead), has been previously presented in four papers.[19] Unfortunately, this method is still underdeveloped; due to the use of insufficient measurement statistics that could, through the use of the KDE model,[20] eliminate spreads in numerical results that result from mass interference occurring in mass spectrometry undertaken with a low-resolution quadrupole analyser. Nevertheless, the preliminary results of LIA research using the QMS technique reveal isotopic heterogeneities of silver found in the Polish hoards dated to 10th–11th centuries (see Fig. 7:b). Despite the fact that the methodology of LIA determination is already well-established in the literature on the subject,[21] in the light of the results obtained for some of the tested objects, it still seems to be methodologically inexhaustible and lacking in a so-called "a golden mean for everything". Selected results of the analyzes are presented below.

3.2. Coins

The studied groups of coins, despite having undergone conservation processes, differ in their elemental composition (surface analysis). This is shown in the diagrams in Figs 1:a, b, where Fig. 1:b also contains data obtained for the surface of the cross denarius from the private collection prior to conservation (mechanically cleaned of loose dirt, rinsed in water and acetone).

In the case of museum coins, the surface data does not indicate the initial composition of the mint alloy. This composition is altered by conservation process, which effectively cause silver enrichments (see in Fig. 5:c).[22] Assuming that the nature of the conservation process was similar for all coins, an initial attempt can be made to differentiate objects in typological groups. The results of the analysis of the surface composition of coins presented graphically in Fig. 1 show that:

---

[15] Miśta-Jakubowska *et al.* 2020.

[16] Askhenazi *et al.* 2017.

[17] Miśta-Jakubowska *et al.* 2019a.

[18] Miśta-Jakubowska *et al.* 2021; Figs 12a, 13a.

[19] Miśta-Jakubowska *et al.* 2019a; Miśta-Jakubowska *et al.* 2019c; Miśta-Jakubowska *et al.* 2020; Miśta-Jakubowska 2020.

[20] E.g. Baxter 2003.

[21] E.g. Merkel 2016.

[22] E.g. Beck *et al.* 2004.

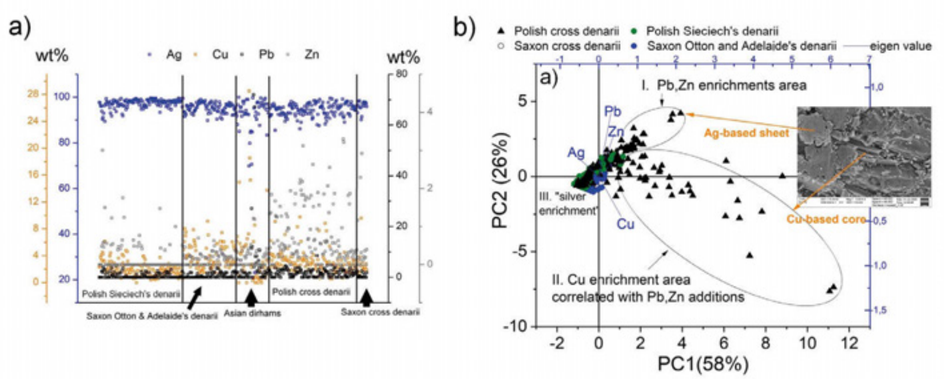

Fig. 1. Coins. Elemental composition results (presented in wt% normalized to 100) for silver (Ag), copper (Cu), lead (Pb) and zinc (Zn) obtained by SEM-EDS technique for surface of the objects: a – 2d diagram for museum coins; b – PCA (correlation) diagram for museum coins include results obtained for cross denarius from private collection (SEM image of the coin's surface presents on the right side of the diagram b). Raw numerical data obtained from EDS analysis are available in Author

1. Otto and Adelaide's denarii contain more copper in the alloy than the Sieciech's coins;
2. Asian dirhams are characterized by a significant degree of heterogeneity in the composition on the micro scale (see Fig. 1:a). This is due to the poor degree of mixing of the initial alloy material, hence local precipitation in the form of copper (Cu) and lead (Pb) enrichment (see Fig. 2:a). Fig. 2 shows the surface morphology of the dirham (Fig. 2:a) in association with the surface morphology of the cross denarius (Fig. 2:b, c);

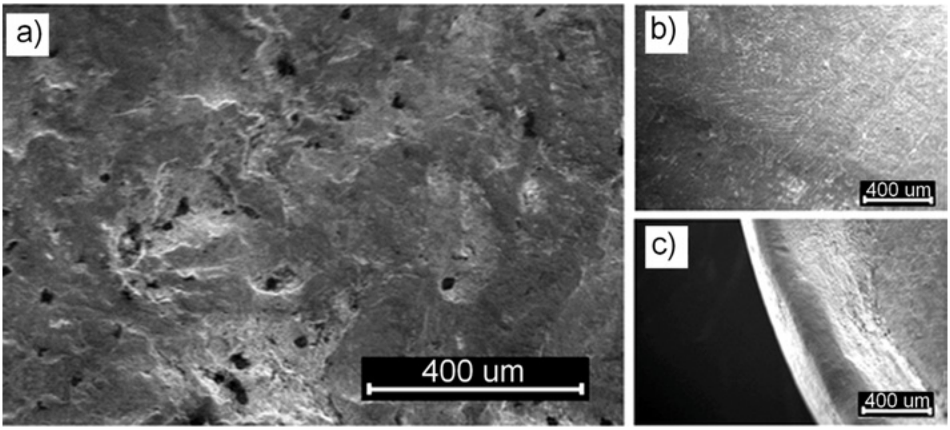

Fig. 2. SEM-SE images of the coins surface obtained for: a – dirham; b – midle part of the cross denarius; c – the rolled up edge of the cross denarius. Bad degree of raw material mixing in dirhams is shown in relation to cross denarii

3. The surface of Palatine Sieciech's coins is characterized by silver enrichment, which in seems to be related to the phenomenon of silver enrichment caused by conservation – the examined series of coins was very "shiny". Nevertheless, a slight local zinc enrichment (up to 2 wt.%) is also noted here, but only for one coin from the series analyzed. The research on the Sieciech's coin series published by Kędzierski[23] indicates a significant share of zinc (av. 11.7 wt%) and copper (av. 40.8 wt%) in the monetary alloy (the composition of the alloy is marked below the silver enrichments layer as a result of microdestructive tests).
4. Cross denarius of younger CNP varieties[24] show enrichment in copper, zinc and slightly lead on the surface. This is due to the existence of copper alloy coin cores (pure copper: see Fig. 7 and copper-zinc alloy see Fig. 5). The results indicating a similar technological characteristic were obtained by Kędzierski[25] in the case of the CNP 858 and 813 varieties, and may therefore indicate some technological similarities between Sieciech's coins and the cross denarii.

SEM analyzes of the surface of cross denarii allowed for the registration of micro-corrosion loss sizes up to 400 microns presented in Fig. 3.

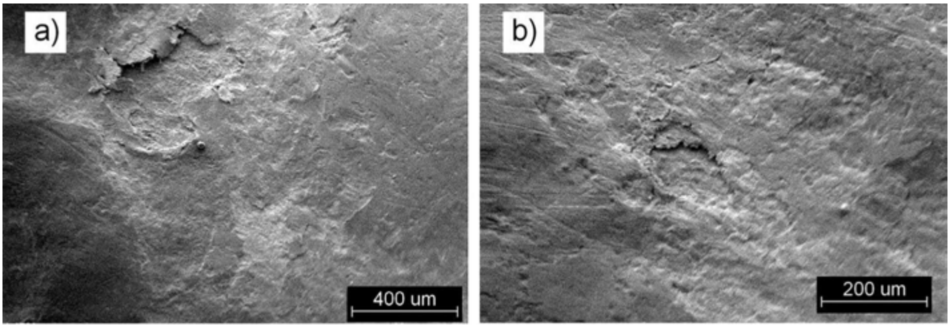

Fig. 3. Examples of SEM-SE images of cross denarii surface with visible coin's core in the corrosion loss: a – larger with diameter 400 microns and b – smaller – over 200 microns. The surface changes are not detectable by naked eyes

As shown in Fig. 4 below, a copper alloy core is noticeable inside the corrosion loss cavities. An exemplary cross-section of a core coin shows the optical image in Fig. 5 (image obtained from a private collection coin).

---

[23] Kędzierski 1998.

[24] Gumowski 1939.

[25] Kędzierski 1998.

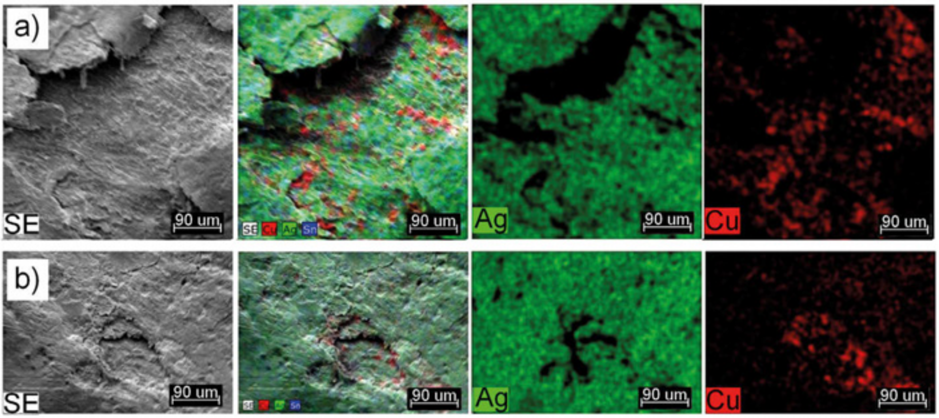

Fig. 4. SEM-EDS elements distribution maps.
The core in cross denarii visible in a corrosion loss cavity

On the basis of SEM imaging in the studied series of cross denarii from the museum, the cores were selected as follows (due to the small size of the corrosion loss cavities, they could not be noticed during the analysis):

1. for the CNP 858 variant – 20 coins were analyzed, of which four turned out to be core: 20/4 (20%),
2. for the CNP 860 variant – 8/2 (25%),
3. for the CNP 813 variant – 10/5 (50%),
4. for the CNP 851–860/848 variant – 7/0, no core,
5. for Saxon cross denarii – 4/0, no core.

The phenomenon of the existence of cores in cross denarii is known and so far interpreted as a kind of forgery.[26] However, the scale of this phenomenon and its technological context are still unrecognized. The results of destructive analyzes of cross denarii from private collections reveal the technological diversity of these forgeries.[27] Figs 5–7 present the preliminary results of research on technologically different core crosses.

Fig. 5 shows the results of a microscopic analysis of a cross-section of a cross denarius (see Fig. 5:a) showing some kind of material anomaly indicating the existence of a specific thin brass-based core.

The above microscopic image shows a thick (approximately 20 microns) layer of silver enrichments (see Figs 5:b, c), suggesting that the coin has undergone a conservation process. The inside of the coin, the potential core, is in the shape of a teardrop (see Figs 5:A–C). The core composition is in average value (in wt%): silver (Ag) – 47.8, copper (Cu) – 42.7, lead (Pb) – 1.8, zinc (Zn) – 7.7, with the silver enriched outer layer: in average value (in wt%): Ag – 90.5, Cu – 3.1, Pb – 2.5, Zn – 3.9.

---

[26] Bogucki 2008.

[27] Bogucki 2008.

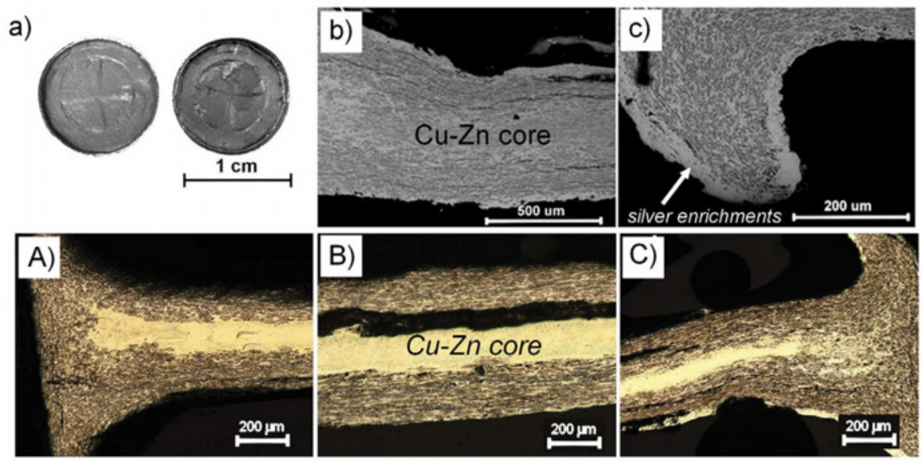

Fig. 5. Results of microscope analysis of cross-section of the cross denarius from private collection: a – photo of the coin; b – SEM-BSE image of middle part; c – SEM-BSE image of rolled up edge; A-C – LOM image of whole cross-section

The arrangement of the layers in the central part of the coin shown in Figs 5:B, b is puzzling. It looks as if the coin was made using the plating technique, in which a thin silver sheet, about 200 microns thick, was placed on the core and vaulted in the thermal process with the inside of the coin.

Fig. 6 shows the results of a cross-section test of a cross denarius without a core (Fig. 6:a). In this case, the composition of the silver enrichment layer, i.e. the surface (see Figs 6: b, c) is in average value (in wt%): Ag – 96.6, Cu – 2.2, Pb – 1.2, Zn <0.1.

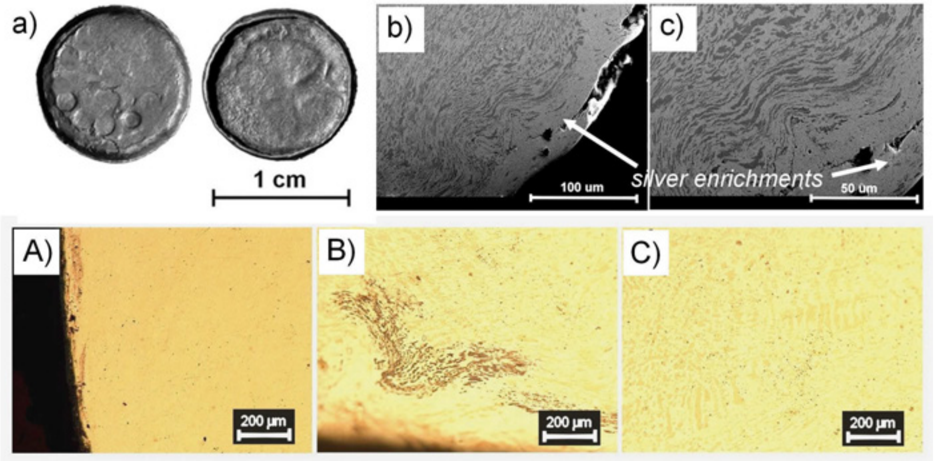

Fig. 6. Results of microscope analysis of cross-section of the cross denarius from private collection: a – photo of the coin; b and c – SEM-BSE images of rolled up edge; A–C – LOM images of cross-section

The composition in the center of the coin corresponds to the mint alloy and is in average value (in wt%): Ag – 62.4, Cu – 35.3, Pb – 2.4, Zn <0.1.

What differentiates the above coins from the private collection is the increased addition of zinc in the silver alloy in the case of the core coin. This regularity is also shown in Fig. 1 for a museum cross denarius.

The zinc content in the silver alloy probably comes from the use of silver-bearing deposits rich in sphalerite (ZnS) for monetary production.[28] Such deposits are found in the Czech Republic (Příbram, Kutná Hora) and in the Olkusz region. The Rammelsberg deposits also contain sphalerite but much less. Therefore, it is difficult to distinguish the deposit origin on the basis of zinc content alone. It would seem helpful to identify the origin based on LIA. Attempts have been made and published[29] and indicate the use of mainly Asian silver remelted from dirhams (see Fig. 7:a). The LIA data presented in Fig. 7:a show that there are no significant differences in provenance of the raw material in the studied varieties of coins. All coins with folded edges are minted using Asian raw material. Why, then, the increased content of zinc or lead in them in relation to dirhams? Perhaps the answer to this question lies within the coins, beyond the reach of surface analyzes. This topic is, therefore, still open, and needs to be pursued, as there is no comprehensive answer for where the raw material used in cross denarii came from. We know that the silver is largely Asian, but the source of potential raw material for the cores is still unknown.

Furthermore, in LIA study of medieval objects, it is necessary to consider the potential remelting factor, i.e. the presence in the alloy of foreign lead added furing the cupellation process, or the addition of lead-rich copper.[30] The sampling process for LIA seems to be capable of averaging these technological heterogeneities. This, in turn, can lead to incorrect deposit matching.

Fig. 7:b shows the lead isotope ratio scatter obtained for a series of silver cakes (from Kalisz-Dobrzec hoard), that could be a semi-finished monetary product, in comparision to the spread for one cake (obtained by KDE modelling). The spread of the results obtained for one cake indicates its isotopic heterogeneity resulting from the use of different silver.

As previously shown,[31] silver cakes as a group have slightly different lead isotope ratio signatures to coins.

However, some silver cakes and Polish coins discussed in this paper may have been augmented with Asian silver from dirham melting (in total 36 coins). Some of the silver cake results are situated in the Silesia and Kraków Upland deposits area (3 objects) and other European ores (Fig. 7).

---

[28] Chabrzyk, Młodecka 2013.

[29] Miśta-Jakubowska *et al.* 2019c.

[30] Miśta-Jakubowska *et al.* 2020.

[31] Miśta-Jakubowska 2020; Miśta-Jakubowska *et al.* 2019c.

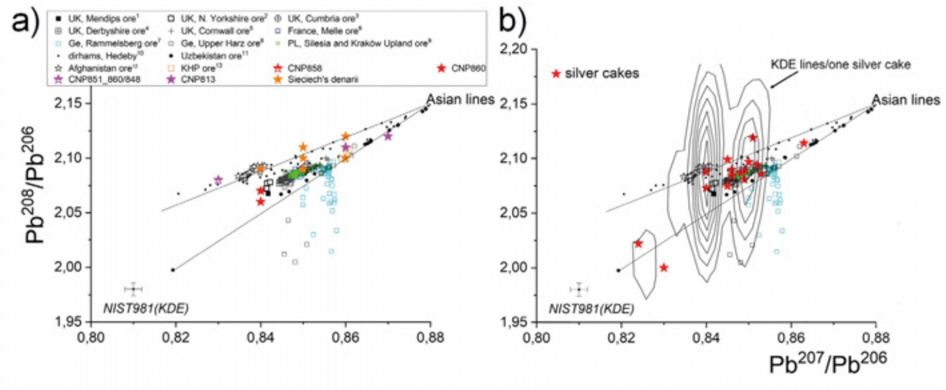

Fig. 7. Lead isotope data (LI) presented as a 2D diagram of the $Pb^{208}/^{206}$ and $Pb^{207}/^{206}$ in relation to deposits from Poland, Czech Republic, Germany, Great Britain, France, Afghanistan, Uzbekistan and dirhams as reference material for Asian deposits from the settlement in Hedeby:[32] a) for cross denarii and Palatine Sieciech's denarii; b) silver cakes from Kalisz presenting results spread obtained for one of them (recalculated by KDE model) in comparision with ore data from a)

In view of the above, the origin of silver used in early medieval production, and not only in the period of the 10th–12th centuries, remains an open topic requiring the continued study of a larger series of test objects. The problem of poorly-separated deposits using just two lead isotope ratios cannot be avoided here (see Fig. 7). Perhaps this will be explained by specialized analyzes using other equipment for isotope measurements,[33] which is expensive and requires sampling. However, sampling seems to lead to the averaging of the result, and the loss of information concerning possible re-melts. In general, the usefulness of lead isotope analyzes for provenance study, in cases where silver was used in remelting and as an addition to the starting alloy, seems complicated. Another method is trace analysis, which allows for the determination of elements that may be a tracer of a given deposit (but in the case of coins after conservation process, this analysis also requires sampling). However, trace analysis also seems to be imperfect, even if a sample is taken. This is due to the fact that there are no references to deposits (or the data are not completed), and the objects could undergo compositional transformations during heat treatment in relation to these deposits.

A different technological view on the problem of cross denarii was provided by the results of the surface analysis of another coin from the private collection presented in Fig. 8. The previously described private (see Figs 5, 6) and museum cross denarii had already been subjected to conservation processes, so their surface composition was depleted. The coin shown in Fig. 8:c consists of a pure copper core

---

[32] Rohl 1996; Téreygeol, Hoelzl, Horn 2005; Zartman, Pawlowska, Rubinowski 1979; Church, Vaughn 1992; Lehmann 2011; Hatz *et al*. 1991; Merkel 2016; Ettler *et al*. 2015.

[33] High-resolution mass spectrometry according to Pernicka 2020: research being in progress.

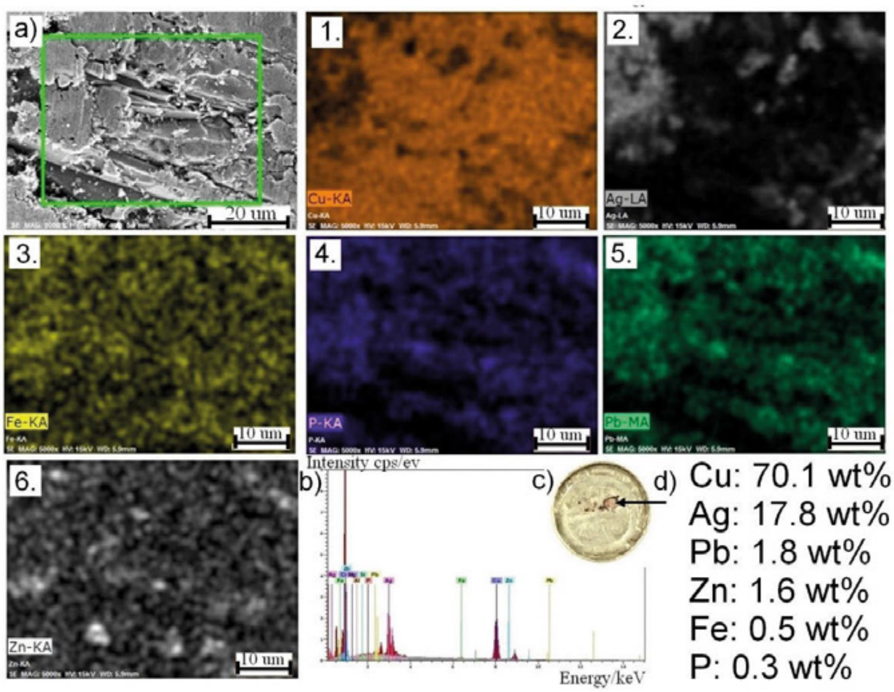

Fig. 8. SEM-EDS results of cross denarius (private collection) surface before conservation process: a – SEM-SE image of analysed microares with visible core; 1–6 – elements distribution maps in area a; b – EDS spectra obtained form area a; c – studied coin; d – semi-qualitative results

(Figs 8:1, 2, b, d) while the silver alloy of the cladding contains iron (Fe) (Figs 8:3, b, d), phosphorus (P) (Figs 8:1, 2, b, d), lead (Pb) (Figs 8:5, b, d), and zinc (Zn) (Figs 8: 6, b, d) additives. The content of lead, zinc, iron and phosphorus in silver may be related to the process of purifying litharge (PbO-X) with iron compounds.[34] The most desirable initial monetary silver is silver with a purity of 97–98%, and as you can see, cross denarii are a highly contaminated product (Fig. 8:d).

Comparing the results obtained for coins from the private collection, a hypothesis arises concerning the connection between the local production of coins and the existence of specific types of core and silver cladding compositions. The current results of LIA (calculated by use of LDA model) obtained for the cross denarii, the coins of Palatine Sieciech, and the Saxon denarii do not differentiate their deposit origin, reflecting a significant addition of Asian raw material in their production (see Fig. 7:a).[35]

---

[34] Karbowniczek, Suliga 2005; Karbowniczek *et. al.* 2006, pp. 36–40.

[35] Miśta-Jakubowska *et al.* 2019c.

In the case of cross denarii, an important aspect of their minting technology and is the increased content of zinc and lead in their alloy[36], as well as accompanying elements such as iron and phosphorus that may be related to silver and lead metallurgy, more specifically the metallurgical process consisting of:

1. purification of galenic litharge by reduction with iron compounds;[37]
2. use of iron-rich deposits, which are sometimes found in sphalerite related with silver-bearing ores. Silver deposits containing significant amounts of iron (approximately 2%) are found in the Czech Republic[38] but also in Poland (Olkusz area: these are poor in silver). The ores mined at Rammelsberg (Otto and Adelaide's denarii have less zinc, see Fig. 1) have a small amount of iron.

This again introduces ambiguities to the inference about origin of the cross denarii. However, considering that the preferred monetary alloy should be pure (97–98% Ag), the degree of contamination of the cross denarii alloy indicates rather the use of raw material (not re-melted), and, looking at the scale of minting of these coins, it would rather suggest the use of local raw material (i.e. Olkusz; while the use of Asian deposits may be typical for some of the cross denarii, this is only a hypothesis). Perhaps there is a moment of raw material transformation, when Asian raw material ran out and local raw materials began to be used for coinage? However, this has not yet been captured. Relevant to this issue are the analytical from the so-called "Hoard of the Steelworker" found on the metallurgical settlement in Dąbrowa Górnicza-Łosień.[39] These results indicate the use of local ores in the production of objects from the hoard: the lack of bismuth eliminates the Harz deposits, while the lack of selenium eliminates the Czech deposits. In the collection of the analyzed coins, which mainly date to the beginning of the 12th century, only the 11th-century cross denarius has a significant content of copper, zinc and lead.[40] Silver cakes from this hoard are characterized by a significant amount of lead, with traces of copper and zinc. Similar results were obtained for the silver cakes from the Kalisz-Dobrzec hoard (see Fig. 9 below). In this study,[41] the composition characteristics were used to develop a hypothesis about their non-local origin, possibly from copper-containing polymetallic deposits like those found in Silesia. However, LIA of some silver cakes from Kalisz-Dobrzec reveal the addition of ore from the Olkusz region.[42] Perhaps the silver purification process in the 12th century was so advanced that it allowed the removal of impurities to a large extent (Figs 9, 10).

---

[36] Chabrzyk, Młodecka 2013; Bogucki 2008.

[37] Karbowniczek, Suliga 2005; Karbowniczek *et. al.* 2006, pp. 36–40; Rozmus, Suliga 2012.

[38] Lead, iron and phosphorus: Štefan, Zavřel, Taibl 2020.

[39] Garbacz-Klempka *et al.* 2013.

[40] Garbacz-Klempka *et al.* 2013; Fig. 21.

[41] Garbacz-Klempka *et al.* 2013.

[42] Miśta-Jakubowska *et al.* 2019c; see Fig. 7: c.

On the other hand, in the 11th century, when cross denarii functioned, the process of obtaining silver was not perfected. And perhaps it was dictated by the need for "fast" and "economical" (using copper alloys as the coin core) monetary production, also using the local raw material (Fig. 7:b) obtained from Pb-Zn-rich ores, and the purification of this silver using iron compounds (see Fig. 7:c). The content of low-melting zinc and lead in the silver alloy could improve plasticity and lower the melting point of the silver cladding, thus accelerating the minting process. Due to their chemical characteristics,[43] Palatine Sieciech's denarii could be minted in a technology similar to that of cross denarius, using poorly refined silver, possibly with inclusion of cleaning waste (litharge) as an addition to the initial mint alloy. The above-mentioned hypotheses can direct not only the future direction of archaeometallurgy research on the cross denarii, but also for early medieval silver in general. The function of lead in early medieval metallurgy seems to be important. To bring the issue closer, it is necessary to examine a large series of artifacts, preferably before their conservation process. Only the newly discovered hoards and artifacts offer such opportunities, including the Słuszków II hoard, consisting mainly of ca. 6,500 cross denarii and silver cakes.[44]

3.3. Silver cakes

The results of the microanalysis of the surface of silver cakes from the Kalisz-Dobrzec hoard are consistent with the results obtained from the Dąbrowa Górnicza-Łosień settlement.[45] These are objects with a very low copper and zinc content. They are characterized by an increased lead content in micro-areas (up to 6wt% on the cross-section and up to 70 wt% on the surface). Depending on the lead content and its surface adhesion, the 19 tested objects from Kalisz-Dobrzec can be divided into:

1. silver cakes with micro-precipitation of lead (up to 70.2 wt% / 5 objects) in the form of oxide "cloud" structures called Ist group (see Fig. 9:a);
2. silver cakes with no micro-precipitates of lead, but with an increased content above 4 wt% (up to 14.8 wt%) in surface, called IInd group /6 objects (see Fig. 9:b);
3. silver cakes without micro-precipitations, with a lead content on the surface below 3.9 wt% / 8 objects, called IIIrd group (see Fig. 9:b).

---

[43] Kędzierski 1998.

[44] *Odnaleziono kolejną część skarbu ze Słuszkowa. Tysiące średniowiecznym monet i złote pierścienie w polu kukurydzy*: www.national-geographic.pl/artykul/odnaleziono-kolejna-czesc-skarbu-ze-sluszkowa-tysiace-sredniowiecznym-monet-i-zlote-pierscienie-w-polu-kukurydzy, access 29.07.2021.

[45] Garbacz-Klempka *et al.* 2013.

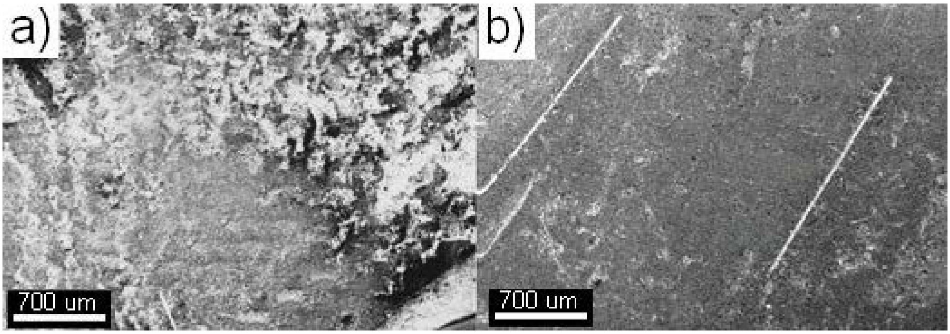

Fig. 9. Examples of SEM-SE images of silver cakes (Kalisz-Dobrzec hoard): a – Ist group with cloudy-shape lead oxide micro-precipitations; b – IInd and IIIrd groups characterized by lack of micro-precipitations of lead oxide

Fig. 10 shows the selected results of X-ray microanalysis (SEM-EDS) obtained from a series of objects.

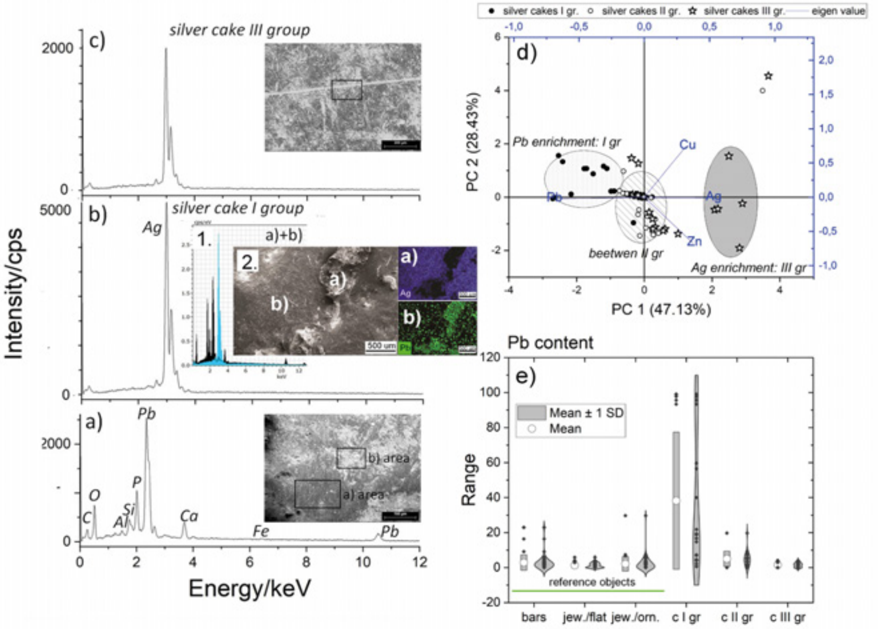

Fig. 10. Results of SEM-EDS study of micro-regions of silver cakes from Kalisz-Dobrzec hoard. EDS spectra obtained for surface of the Ist group: a – area with lead micro-precipitation visible in SEM images; b – silver enriched microregion. The studied areas are marked in SEM image (b2) and in SEM from diagram a; b1 – comparisons of EDS spectra of different Ist group microregins; d – PCA (correlation) diagram of silver (Ag), copper (Cu), zinc (Zn) and lead (Pb) content in separated silver cakes groups; e – lead content presented as a range of variation and mean value in silver cake groups in comparision to reference silver objects (bars, jewelleries – with surface ornament/orn. and without ornament/flat from Stojkowo hoard)

Lead precipitation on the surface (see Figs 10:a, b) indicates that the silver cakes are a product of silver refining[46], as can be seen in Fig. 7 mainly from Asian dirhams (mayby by use of lead from Olkusz areas). The silver purification process took place in a vessel called a "cupel", hence the addition of calcium, alkali, iron (from clay) and phosphorus (from iron clay substance or from bone meal – a substance that absorbs the removed impurities in the form of oxide) in the areas of lead precipitations (the objects were not well surface cleaned after cupellation process), see Fig. 10:a. First group contains uncleaned microregions (Fig. 10:a) and silver-enriched microregions (Fig. 10:a). The remaining groups are characterized by a significant degree of cleaning of the surface from litharge compounds (Fig. 10:c). The division into three groups presented above (Fig. 3) seems to suggest that we are dealing with three groups with a different degree of surface cleaning after the cupellation process, ranging from the product with the highest degree of purification (IIIrd group) to the product with the lowest degree (Ist group). The division by the degree of purification is well presented in the PCA diagram (see Fig. 10:d), where IInd group appears compositionally between the extreme groups with the minimum (Ist) and the maximum degree of purification (IIIrd). Fig. 10:e shows a summary of the lead content results (as a range of variability and as an average value) obtained from the silver cakes groups in relation to other silver items. The diagram shows that the Ist group stands out significantly in the presented set of artifacts.

3.4. Silver jewellery

Jewellery made using filigree and granulation are a separate analytical problem. During microanalysis, three technological areas related to the soldering process were distinguished: the base surface (the first area) is the base on which the ornament (i.e. granulate, filigree is the second area) was attached by soldering (the third area – the soldering area). Recipes for making chemical solder are described in historical sources, including the early 12th century receipts of Theophilus Presbyter, the early 3rd century Leyden Papyrus X and the 1st century natural philosopher Pliny the Elder.[47] The analytical results reveal the use of these recipes both in jewellery typologically assigned to the Slavic horizon and in those characteristic of the Kievan Rus.[48]

Fig. 11 shows the results of compositional analysis obtained for the series of analyzed jewellery. As can be seen, the area of soldering with granulation and filigree (Figs 12:b, c, e) is characterized by a significant degree of oxidation and copper enrichment. This is consistent with the solder recipes shown in the histori-

---

[46] E.g. Agricola 1950; Tylecote 1992; Merkel 2016; L'Héritier *et al.* 2015; Hawthorne, Smith 1979.

[47] Pliny 1929; Duczko 1985; Hawthorne, Smith 1979; Stawicki 1987.

[48] Miśta-Jakubowska *et al.* 2021.

cal sources, based mainly on copper compounds, also in the oxidized form. Scandinavian jewellery with flat ornament/stamps (see Fig. 12:d) fall between the areas typical of solder and base. This is due to the addition of lead and zinc in their alloy, as shown in the PCA (correlation) diagram in Fig. 12.

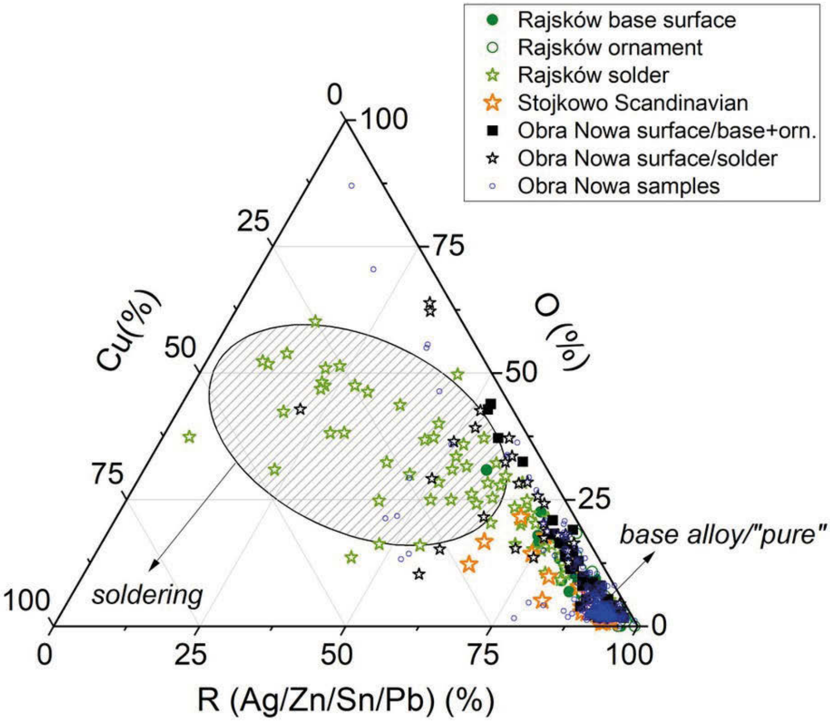

Fig. 11. Jewellery. EDS results presented as a ternary diagram of copper (Cu), oxygen (O) and other elements R (silver: Ag, zinc: Zn, tin: Sn, lead: Pb) content in jewellery from the Kalisz-Rajsków, Stojkowo and Obra Nowa hoards. In the case of objects made with granulation and filigree, the division into technological areas is taken into account (base surface, ornament, solder), Scandinavian objects are flat or stamped (flat ornament). The samples (elements that had fallen off spontaneously) from jewellery from Obra Nowa were also examined (base alloy/"pure") (see Fig. 12: f)

Fig. 12 shows the results of the principal component analysis (correlation PCA), i.e. the content of lead, zinc, silver, copper, tin with oxygen degree obtained for the series of jewellery and their fragments with differential surface morphology.

In the diagram of Fig. 12:a, two areas relating to the soldering process are distinguished, i.e. the oxidation area enriched in copper and tin and the area enriched

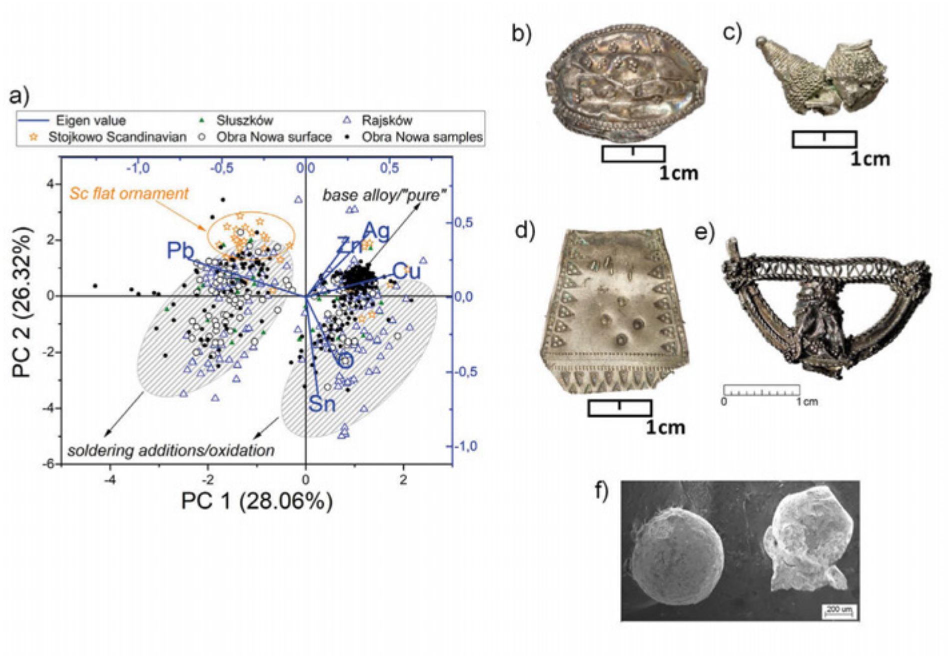

Fig. 12. Jewellery: a – EDS results presented as a PCA (correlation) diagram of silver (Ag), copper (Cu), zinc (Zn), lead (Pb), tin (Sn), oxide (O) obtained form different type of jewellery and their samples from Obra Nowa hoard. Examples of studies artifacts: b – bead from Słuszków hoard (West Slavic type); c – fragment of the earring from Kalisz-Rajsków hoard (West Slavic type); d – fragment of Scandinavian jewelries from Stojkowo hoard; e – fragment of the earring from Obra Nowa hoard (West Slavic type); f – SEM-SE image of the samples fallen off spontaneously form objects form Obra Nowa

in lead. For the samples from Obra Nowa, these two types of soldering were recorded and shown below in Fig. 13.

The first type of soldering identified is lead-based (Fig. 13:a). The additions of phosphorus, calcium, alkali and possibly strontium indicate the use of a recipe variant: "Carefully clean the lead with tar and bitumen, unless you take tin; mix cadmium and litharge in equal parts with lead. Stir until it solidifies. It can be use as natural asem".[49] Carbonized and temperature-modified remains of tar and bitum from the soldering process are recognized in EDS spectrum as carbon (C).[50] However, in order to discover where this coal-based substance comes from, other analytical tools are needed.[51] A similar characteristic of soldering was noted by the Czechs, but they interpret it differently as deposit additives.[52]

---

[49] Leyden Papyrus X, Recipe 11: Stawicki 1987; Demortier *et al.* 1999.

[50] Hoffman, Davidson 1965, p. 46.

[51] Miśta-Jakubowska *et al.* 2021.

[52] Kolářová, Děd, Ottenwelter 2014.

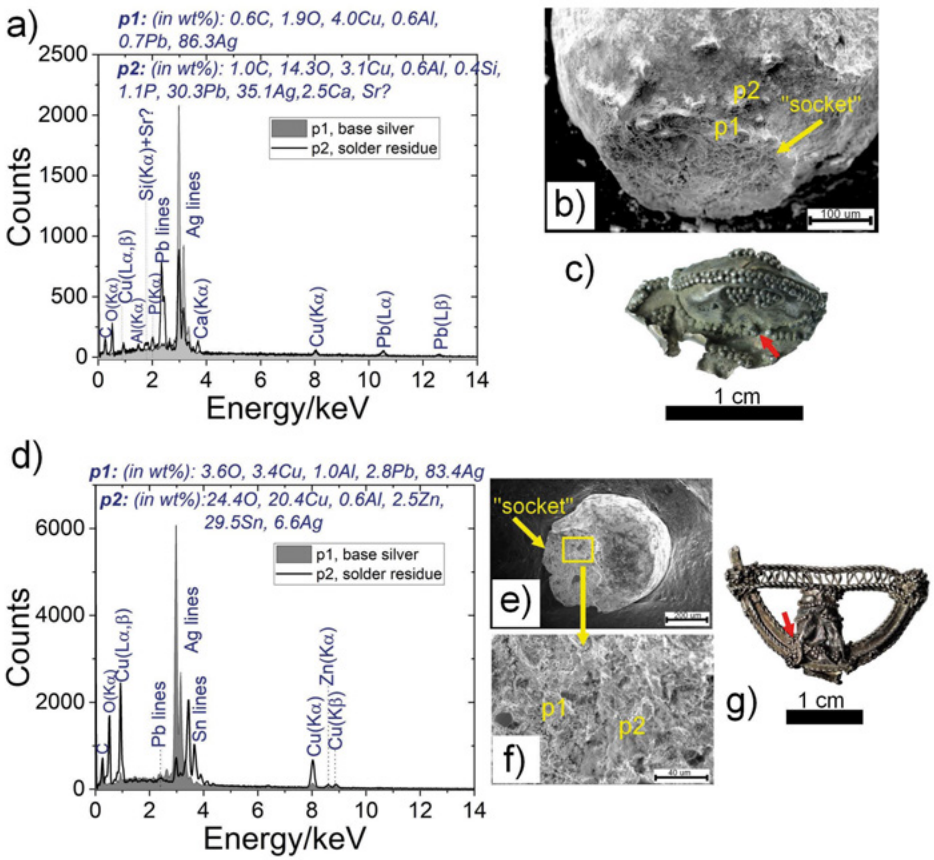

Fig. 13. Jewellery. SEM-EDS results (a, d) obtained for samples (granules presented in b, e respectively obtained from fragments of jewellery (c, g); b, e, f – micro-areas of EDS sampling of the “socked” area of the granules

The second type of soldering is based on tin and copper (Fig. 13:b), although lead additives are here possibly due to the spill of the solder onto the surface of the jewellery.[53] Several similar recipes are described in sources.[54]

4. CONCLUSIONS

This study has identified the problems and benefits of using microanalysis in the study of archaeological material, specifically technologically different silver alloys. Elemental composition tests with the use of non-destructive techniques

---

[53] Duczko 1985; Miśta-Jakubowska *et al.* 2019a.

[54] Including Recipes 8, 18 from Leyden Papyrus X; Stawicki 1987.

(EDS, XRF) allow only for the preliminary identification of the material (unless it has been significantly changed by conservation), and is primarily technological rather than geological. The comprehensive description of the technological workshop for heterogeneous artifacts is possible primarily by sampling at different technological locations. In the case of artifacts made of alloys with different visual characteristics, it seems intuitive; for objects made of silver alloys, however, such important details may be omitted during the macroanalysis.

The study of the geological provenance of archaeological objects seems to be still a complicated matter, despite the availability of measurement tools of various specifications. The results of lead isotope analyzes are unambiguous when dealing with historically recognized artifacts for which the knowledge of the deposits used in a given period is almost certain. In the case of artifacts from the 10th–12th centuries (and even earlier and later) from Poland and other territory, where at that time territorial and commercial mobility is significant and historical data – including information on the exploited deposits – may be incomplete, provenance study is difficult. Moreover, the melting and technological factors related to the processing of silver, copper and lead ores should be taken into account in such studies.

Nevertheless, the presented results of studies on a series of early medieval silver items indicate the existence of a relationship between the metallurgy and goldsmiths of that time and the Czech region,[55] while goldsmithing additionally linked to workshops at Kievan Rus.[56] The functional contribution of Polish metallurgical centers also seems to be significant, and here the settlement in Dąbrowa Górnicza-Łosień should also be considered as a supplier of both silver and lead (separately) from the 10th century, when the phenomenon of depositing hoards still functions, with numerous cross denarii and jewellery. The research results so far are only an introduction to a broader study of archaeological material relating to the functioning of early medieval silver, lead and also tin (associated with the presence of objects made of lead) metallurgy in Poland.

ACKNOWLEDGEMENTS

This work was carried out with financial support from the National Science Centre in Cracow, Poland (grants no. UMO-2013/09/B/HS3/03289 and 2016/23/N/HS3/03160). I would like to thank Aldona Garbacz-Klempka for taking microscopic photos.

---

[55] Štefan, Zavřel, Taibl 2020; Miśta-Jakubowska *et al.* 2019a; Kolářová, Děd, Ottenwelter 2014.

[56] Miśta-Jakubowska *et al.* 2021.

Bibliography

Agricola G.
1950 *De Re Metallica*, translated from the 1st Latin ed. of 1556 by H.C. Hoover and L.H. Hoover, New York.

Ashkenazi *et al.*
2017 D. Ashkenazi, H. Gitler, A. Stern, O. Tal, *Metallurgical investigation on fourth century BCE silver jewellery of two hoards from Samaria*, Scientific Reports 7, pp. 1–14.

Baker J., Stos S., Waight T.
2006 *Lead isotope analysis of archaeological metals by multiple-collector inductively coupled plasma mass spectrometry*, Archaeometry 48, pp. 45–56.

Balcaen L., Moens L., Vanhaecke F.
2010 *Determination of isotope ratios of metals (and metalloids) by means of inductively coupled plasma-mass spectrometry for provenancing purposes – a review*, Spectrochimica Acta Part B: Atomic Spectroscopy 65, pp. 769–786.

Baxter M.
2016 *Multivariate Analysis of Archaeometric Data: An Introduction.* https://www.academia.edu/24456912/Multivariate_Analysis_of_Archaeometric_Data_An_Introduction.

Baxter M.J.
2003 *Statistics in archaeology*, London.

Beck *et al.*
2004 L. Beck, S. Bosonnet, S. Réveillon, D. Eliot, F. Pilon, *Silver surface enrichment of silver-copper alloys: a limitation for the analysis of ancient silver coins by surface techniques*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 226, pp. 153–162.

Bogucki M.
2008 *Forged coins in early medieval Poland*, Wiadomości Numizmatyczne LIII/2 (186), pp. 209–236.

Chabrzyk P., Młodecka H.
2013 *Obecność cynku w monetach pochodzących z wczesnośredniowiecznych skarbów z Polskiej Środkowej*, [in:] *Argenti fossores et alii. Znaczenie gospodarcze wschodnich części Górnego Śląska i zachodnich krańców Małopolski w późnej fazie wczesnego średniowiecza (X–XII wiek)*, ed. P. Boroń, Wrocław, pp. 243–256.

Chamberlain V., Gale N.H.
1980 *The isotopic composition of lead in Greek coins and in galena from Greece and Turkey*, [in:] *Proceedings of the 16th International Symposium on Archaeometry and Archaeological Prospection, Edinburgh 1976*, eds E.A. Slater, J.O. Tate, Edinburgh, pp. 139–155.

Church S.E., Vaughn R.B.
1992 *Lead-isotopic characteristics of the Cracow-Silesia Zn-Pb ores, southern Poland*, U.S. Department of Interior U.S. Geological Survey, Open-File Report 92–393, https://pubs.usgs.gov/of/1992/0393/report.pdf.

CNP – see Gumowski 1939

Costa V.
2001 *The deterioration of silver alloys and some aspects of their conservation,* Studies in Conservation 46 (Supplement-1), pp. 18–34; http://dx.doi.org/10.1179/sic.2001.46.Supplement-1.18.

Demortier *et al.*
1999 G. Demortier, F. Fernandez-Gomez, M.A. Ontalba Salamanca, P. Coquay, *PIXE in an external microbeam arrangement for the study of finely decorated tartesic gold jewellery items*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 158, pp. 275–280.

Duczko W.
1985 *Birka V. The filigree and granulation work of the Viking Period. An analysis of the material from Björkö*, Uppsala.

Ettler *et al.*
2015 V. Ettler, Z. Johan, J. Zavřel, M.S. Wallisová, M. Mihajlevič, O. Šebek, *Slag remains from the Na Slupi site (Prague, Czech Republic): evidence for early medieval non-ferrous metal smelting*, Journal of Archaeological Science 53, pp. 72–83.

Gale N.H.
1979 *Lead isotopes and Archaic Greek silver coins*, Archaeophysica 10, pp. 194–208.

Garbacz-Klempka *et al.*
2013 A. Garbacz-Klempka, A. Łukaszczyk, D. Rozmus, J. Tokaj*, "Skarb hutnika" w* świetle *badań metaloznawczych*, [in:] *Argenti fossores et alii. Znaczenie gospodarcze wschodnich części Górnego Śląska i zachodnich krańców Małopolski w późnej fazie wczesnego średniowiecza (X–XII wiek)*, ed. P. Boroń, Wrocław, p. 203–224.

Gójska *et al.*
2019 A. Gójska, E. Miśta-Jakubowska, D. Banaś, A. Kubala-Kukuś, I. Stabrawa, *Archaeological applications of spectroscopic measurements. Compatibility of analytical methods in comparative measurements of historical Polish coins*, Measurement 135, pp. 869–874, doi: 10.1016/j.measurement.2018.11.089.

Gumowski M.
1939 *Corpus Nummorum Poloniae, zeszyt 1*, *Monety X i XI wieku*, Kraków.

Hatz *et al.*
1991 G. Hatz, V. Hatz, U. Zwicker, N. Gale, Z. Gale, *Otto-Adelheid-Pfennige. Untersuchungen zu Münzen des 10./11. Jahrhunderts*, Stockholm (=Commentationes de Nummis Saeculorum IX–XII. In Suecia Repertis. Nova Series 7).

Hawthorne J.G., Smith C.S.
1979 *On Divers Arts. The Treatise of Theophilus*, New York.

Hoffman H., Davidson P.F.
1965 *Greek Gold: Jewelry from the Age of the Alexander*, Brooklyn.

Ilisch *et al.*
2003 L. Ilisch, S. Lorenz, W.B. Stern, H. Steuer, *Dirham und Rappenpfennig. Mittelalterliche Münzprägung in Bergbauregionen*, Zeitschrift für Archäologie des Mittelalters 17, Bonn.

Jakimowicz R.
1933 *O pochodzeniu ozdób srebrnych odnajdywanych w polskich skarbach wczesnośredniowiecznych*, Wiadomości Archeologiczne 12, pp. 103–136.

Karbowniczek M., Suliga I.
2005 *Próba rekonstrukcji wczesnośredniowiecznej technologii redukcji rud ołowiu na podstawie wykopalisk archeologicznych w Dąbrowie Górniczej-Łośniu*, Śląskie Sprawozdania Archeologiczne 47, pp. 135–143.

Karbowniczek *et al.*
2006 M. Karbowniczek, I. Suliga, R. Bodnar, D. Rozmus, B. Szmoniewski, *An Attempt of Reproduction of the Medieval Technology of Lead Metallurgy*, [in:] *Wczesnośredniowieczna ceramika szkliwiona z Dąbrowy Górniczej-Łośnia. „Skarb hutnika”*, eds D. Rozmus, B. Szmoniewski, Kraków, pp. 36–40.

Kędzierski A.
1998 *Polskie denary krzyżowe w skarbie ze Słuszkowa*, Wiadomości Numizmatyczne XLII/1–2 (163–164), pp. 21–48.

Kolářová K., Děd J., Ottenwelter E.
2014 *Metallographic examination of silver jewellery from "Lumbe's Garden" cemetery*, [in:] *Castrum Pragense. Pohřebiště v Lumbeho zahradě na Pražském hradě*, vol. 2, *Studie*, pp. 289–310.

Kóčka-Krenz H.
1993 *Biżuteria północno-zachodnio-słowiańska we wczesnym średniowieczu*, Poznań.

Koziorowska L.
2002 *Materiały złotnicze w świetle wyników analiz składu chemicznego srebrnych przedmiotów antycznych i wczesnośredniowiecznych* Archeologia Polski XLVII, pp. 101–204.

Lehmann R.
2011 *Archäometallurgie von mittelalterlichen deutschen Silberbarren und Münzen*, unpublished PhD thesis, Leibniz University Hannover.

L'Héritier *et al.*
2015 M. L'Héritier, S. Baron, L. Cassayre, F. Téreygeol, *Bismuth behaviour during ancient processes of silver – lead production*, Journal of Archaeological Science 57, pp. 56–68.

Linke R., Schreiner M.
2000 *Energy Dispersive X-Ray fluorescence Analysis and X-Ray Microanalysis of Medieval Silver Coins. An Analytical Approach for Non-Destructive Investigation of Corroded Metallic Artifacts*, Mikrochimica Acta 133, pp. 165–170.

Merkel S.W.
2016 *Silver and the Silver Economy at Hedeby*, Bochum.

Miśta-Jakubowska E.
2020 *Mikroanaliza wczesnośredniowiecznych zabytków zawierających stopy srebra*, unpublished PhD thesis, National Centre for Nuclear Research, Poland.

Miśta-Jakubowska *et al.*
2019 E. Miśta-Jakubowska, I. Fijał-Kirejczyk, R. Diduszko, A.M. Gójska, P. Kalbarczyk, J.J. Milczarek, K. Trela, G. Żabiński, *A silvered shield grip from the Roman Period: a technological study of its silver coating*, Archaeological and Anthropological Sciences 11/7, pp. 3343–3355, doi: 10.1007/s12520-018-0761-0.
2019a E. Miśta-Jakubowska, R. Czech Błońska, W. Duczko, A.M. Gójska, P. Kalbarczyk, G. Żabiński, K. Trela, *Archaeometric studies on early medieval silver jewellery from Central and Eastern Europe*, Archaeological and Anthropological Sciences 11/12, pp. 6705–6723, doi: 10.1007/s12520-019-00935-z.
2019b E. Miśta-Jakubowska, R. Diduszko, A.M. Gójska, B. Kontny, A. Łozinko, D. Oleszak, G. Żabiński, *Material description of the unique relief fibula from Poland*, Archaeological and Anthropological Sciences 11/1, pp. 973–983, doi: 10.1007/s12520-017-0576-4.
2019c E.A. Miśta-Jakubowska, R. Czech Błońska, W. Duczko, A.M. Gójska, P. Kalbarczyk, A. Turos, G. Żabiński, M. Widawski, *Origin and Production of Silver in Early Medieval Poland*, Archaeologia Polona 57, pp. 241–255, doi: 3858/APa57.2019.017.
2020 E. Miśta-Jakubowska, R. Czech Błońska, W. Duczko, A.M. Gójska, P. Kalbarczyk, G. Żabiński, K. Trela, *Correction to: Archaeometric studies on early medieval jewellery from central and Eastern Europe*, Archaeological and Anthropological Sciences 12, p. 108, doi: https://doi.org/10.1007/s12520-020-01071- 9.
2021 E. Miśta-Jakubowska, R. Czech Błońska, W. Duczko, A. Gójska, G. Żabiński, P. Ciepielewski, R. Diduszko, A. Kosińska, A. Brojanowska, *Research on chemical soldering in early medieval jewellery: the case of lunula-type Viking Age ornaments*, Archaeometry 64/3, pp. 698–713.

Ontalba Salamanca *et al.*
1998 M.A. Ontalba Salamanca, G. Demortier, F. Fernandez Gomez, P. Coquay, J.-L. Ruvalcaba-Sil, M.A. Respaldiza, *PIXE and SEM studies of Tartesic gold artefacts*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 136–138, pp. 851–857.

Pernicka E.
2014 *Provenance Determination of Archeological Metal Objects*, [in:] *Archaeometallurgy in Global Perspective*, eds B.W. Roberts, C.P. Thornton, New York. pp. 239–267, doi: 10.1007/978-1-4614-9017-3_11.
2020 *Lead isotope ratios and the provenance of medieval silver. A comment on "Archaeometric studies on early medieval silver jewellery from Central and Eastern Europe" by Ewelina Miśta-Jakubowska, Renata Czech Błońska, Władysław Duczko, Aneta M. Gójska, Paweł*

Kalbarczyk, Grzegorz Żabiński, Krystian Trela. Archaeol. Anthropol. Sci. 11 (12), 6705–6723, Archaeological and Anthropological Sciences 12, p. 165.

Pliny E.
1929 *Metals: mostly gold, silver and mercury*, [in:] Pliny the Elder, *The Natural History*, Book 33, chap. 25, 29.

Rohl B.M.
1996 *Lead Isotope Data from the Isotrace Laboratory, Oxford: Archaeometry Data Base 2, Galena from Britain and Ireland*, Archaeometry 38 (1), pp. 165–180.

Rozmus D.
2014 *Wczesnośredniowieczne zagłębie hutnictwa srebra i ołowiu na obszarach obecnego pogranicza Górnego Śląska i Małopolski (druga połowa XI–XII/XIII wiek)*, Kraków.

Rozmus D., Suliga I.
2012 *Piece i paleniska o przeznaczeniu hutniczym do wytopu ołowiu ze stanowiska nr 5 w Sosnowcu-Zagórzu – wstępne wyniki badań prowadzonych w latach 2009–2010*, Śląskie Prace Prahistoryczne 7, pp. 250–286.

Scrivano *et al.*
2013 S. Scrivano, B. Gómez-Tubío, I. Ortega-Feliu, F.J. Ager, A.I. Moreno-Suárez, M.A. Respaldiza, M.L. de la Bandera, A. Marmolejo, *Identification of soldering and welding processes in ancient gold jewelry by micro-XRF spectroscopy*, X-ray Spectrometry 42, pp. 251–255.
2017a S. Scrivano, B. Gómez-Tubío, I. Ortega-Feliu, F.J. Ager, A. Paul A., M.A. Respaldiza, *Compositional and microstructural study of joining methods in archaeological gold objects*, X-ray Spectrometry 46, pp. 123–130.
2017b S. Scrivano, I. Ortega-Feliu, B. Gómez-Tubío, F.J. Ager, M.L. de la Bandera, M.A. Respaldiza, M.A. Ontalba-Salamanca, *Non-destructive micro-analytical system for the study of the manufacturing processes of a group of gold jewels from "El Carambolo" treasure*, Radiation Physics and Chemistry 130, pp. 133–141.

Stawicki S.
1987 *Papirusy Tebańskie: antyczne źródło wiedzy o technikach artystycznych*, Warszawa.

Stos-Gale A.Z., Gale H.N.
2009 *Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID)*, Archaeological and Anthropological Sciences 1, pp. 195–213.

Suliga *et al.*
2013 I. Suliga, T. Karwan, M. Karbowniczek, D. Rozmus, *Wczesnośredniowieczna technologia strącania ołowiu żelazem na stanowiskach w Dąbrowie Górniczej-Łosieniu i Sosnowcu-Zagórzu. Badania materiałoznawcze*, [in:] *Argenti fossores et alii. Znaczenie gospodarcze wschodnich części Górnego Śląska i zachodnich krańców Małopolski w późnej fazie wczesnego średniowiecza (X–XII wiek)*, ed. P. Boroń, Wrocław, pp. 151–174.

Šmit *et al.*
2000 Ž. Šmit, M. Budnar, P. Pelicon, B. Zorko, T. Knific, J. Istenič, N. Trampuž-Orel, G. Demortier, *Analyses of gold artifacts from Slovenia*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 161–163, pp. 753–757.

Štefan I., Zavřel J., Taibl P.
2020 *Středověké sídliště u Suchomast na Berounsku: k proměnám sídelní struktury a práci s neželeznými kovy ve venkovském prostředí / A medieval settlement near Suchomasty in the Beroun district, Central Bohemia: on the transformation of settlement structures and non-ferrous metallurgy in the rural environment*, Archaeologické Rozhledy LXXII, pp. 102–145, https://www.arup.cas.cz/publikace-prodej/publikace-on-line/archeologicke-rozhledy/ar2020-4/.

Téreygeol F., Hoelzl S., Horn P.
2005 *Journee archaeologique de Melle - Le monnayage de Melle au haut Moyen Age: état de la recherche*, Bulletin de liaison et d'information. Association des Archéologues de Poitou-Charentes 34, pp. 49–56.

Trincavelli J., Limandri S., Bonetto R.
2014 *Standardless quantification methods in electron probe microanalysis*, Spectrochimica Acta Part B: Atomic Spectroscopy 101, pp. 76–85, doi.org/10.1016/j.sab.2014.07.016.

Tylecote R.F.
1992 *A History of Metallurgy*, London.

Zartman R.E., Pawlowska J., Rubinowski Z.
1979 *Lead isotopic composition of ore deposits from the Silesia-Cracow mining district: in Research on the genesis of zinc-lead deposits of upper Silesia, Poland*, Prace Instytutu Geologicznego 95, Warszawa, pp. 133–151.

Zoll-Adamikowa H., Dekówna M., Nosek E.M.
1999 *The Early Medieval Hoard from Zawada Lanckorońska (Upper Vistula River)*, Warszawa.

Żabiński *et al.*
2020 G. Żabiński, J. Gramacki, A. Gramacki, E. Miśta-Jakubowska, T. Birch, A. Disser, *Multi-classifier majority voting analyses in provenance studies on iron artefacts*, Journal of Archaeological Science 113, 105055, doi: 10.1016/j.jas.2019.105055.

Żołędziowski K., Miśta-Jakubowska E., Czech-Błońska R.
2021 *Sokoły, złoto i alchemiczne manuskrypty, czyli rzecz o pożytkach płynących ze współpracy archeologa, konserwatora i chemika,* [in:] *Zachowanie i konserwacja zbiorów muzealnych / Preservation and Conservation of Museum Collections*, ed. K. Wisłocki, Poznań, pp. 67–85.

MIKROANALIZA WCZESNOŚREDNIOWIECZNYCH ZABYTKÓW ARCHEOLOGICZNYCH WYKONANYCH ZE STOPU SREBRA

(Streszczenie)

Aby udzielić odpowiedzi na pytania spoza obszaru zainteresowania konwencjonalnego warsztatu historyka, nowoczesne badania archeologiczne korzystają z metod fizykochemicznych. Dotyczy to m.in. badań archeometalurgicznych, czyli badań materiałowych zabytków archeologicznych wykonanych ze stopów metali opartych na określaniu m.in. ich składu pierwiastkowego i izotopowego. Wyniki takich analiz z reguły umożliwiają badanie proweniencji geologicznej oraz przybliżanie techniki wykonania zabytku w oparciu o interpretację wyników analiz metalurgicznych rozpatrywanych w odniesieniu do danych historycznych i geochemicznych. Praca przedstawia propozycję metodologii i wstępne wyniki prac badawczych nad srebrem wczesnośredniowiecznym pochodzącym ze skarbów z terenu Polski. W projekcie przeanalizowano około 200 obiektów z ośmiu skarbów, przy czym w niniejszej pracy, w celu pokazania metody opracowania danych, przedstawiono wybrane wyniki. Mikroinwazyjna technika spektrometrii mas w plazmie indukcyjnie sprzężonej z ablacją laserową (LA-ICP-QMS) została użyta do oznaczenia stosunków izotopowych ołowiu w zabytkach. Uzyskane dane uwzględniające niejednorodność obiektów opracowano przy użyciu modelowania statystycznego (KDE: jądrowy estymator gęstości) próbując zmniejszyć dla zastosowanej statystyki pomiarowej 40 punktów/obiekt w ten sposób błąd oznaczeń wynikający ze specyfikacji techniki. Wyniki porównano z danymi złożowymi przeprowadzając analizę proweniencyjną. Badania proweniencji pokazały, iż dominującym żródłem kruszczu jest zastosowanie przetopu azjatyckich dirhamów. Niemniej ze względu na ograniczenia techniki LA-ICP-QMS badania te muszą zostać zweryfikowane z użyciem techniki o lepszej rozdzielczości masowej wymagającej pobierania próbek (badania obecnie są prowadzone we współpracy z laboratorium geochemicznym w USA). Wstępne wyniki badań izotopowych dla poszczególnych grup technologicznych zabytków, tj. monet, ozdób i srebra surowego wsparto analizą zmienności składu pierwiastkowego w mikroobszarach wykonaną przy użyciu elektronowej mikroskopii skaningowej z mikroanalizą rentgenowską (SEM-EDS). Wyniki badań pozwoliły na opis materiałowy zjawiska istnienia rdzeni w monetach typu denary krzyżowe wyróżniając w nich dwie odmiany rdzenia tj. na bazie miedzi i mosiądzu z innym układem geometrycznym. Denary krzyżowe ze względu na ich masowe bicie w zestawieniu z istnieniem w nich rdzeni i znacznym udziałem w ich produkcji srebra źle oczyszczonego, wydają się być produktem szybkiego pozyskiwania srebra ze złóż galenowo-sfalerytowych, choć analizy izotopowe wskazują na pochodzenie srebra z przetopu dirhamów. Wobec tego pochodzenie kruszczu użytego w ich produkcji wydaje się nadal niejasne, być może sprawa wymaga wstępnego różnicowania monet w zależności od ich technologii wykonania i wymaga prowadzenia badań na większą skalę na licznej grupie badawczej. Grupa analizowanych placków srebnych pokazuje zróżnicowanie ich na stopnie oczyszczania przy użyciu obcego ołowiu. Przy czym dominującym nośnikiem kruszczu są tutaj również dirhamy natomiast pochodzenie ołowiu kupelacyjnego można wiaząć z użyciem złoż z terenu Wyżyny Śląskiej i Krakowa.

Adres autorki/The author’s address:
dr Ewelina Miśta-Jakubowska
National Centre for Nuclear Research
Andrzeja Sołtana 7, PL 05–400 Otwock, Poland
Ewelina.Mista@ncbj.gov.pl
ORCID: 0000-0002-0053-8711