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A GLIMPSE INTO RAW MATERIAL MANAGEMENT IN THE EARLY IRON AGE: BRONZE INGOTS FROM A PRODUCTION SETTLEMENT IN WICINA (WESTERN POLAND) IN ARCHAEOMETALLURGICAL RESEARCH

Assessing the level of metallurgical and foundry technology in prehistoric times requires the examination of raw material finds, including elongated ingots, which served as semi-finished products ready for further processing. It is rare to find such raw material directly at production settlements, but Wicina in western Poland is an exception. During the Hallstatt period (800-450 BC), this area, situated along the middle Oder River, benefited from its favorable location in the heart of the Central European Urnfield cultures and developed networks for raw material exchange and bronze foundry production. Numerous remnants of casting activities, such as clay casting molds, casting systems, and raw materials, have been discovered at the Wicina settlement. This article aims to provide an archaeometallurgical interpretation of raw material management and utilization by prehistoric communities during the Early Iron Age. To achieve this, a collection of 31 ingots from the defensive settlement in Wicina, along with two contemporary deposits from Bieszków and Kumiałtowice, both found within a 20 km radius of the stronghold, were studied. Investigations were conducted using a range of methods, including optical microscopy(OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence spectroscopy (ED-XRF), powder X-ray diffraction (PXRD), AAS and ICP-OES spectrometer. The significance of ingots is examined in the context of increasing social complexity and the rising popularity of bronze products, which necessitated diversified production and a demand for raw materials with different properties and, consequently, different chemical compositions.

Keywords: Archaeometallurgy; Copper Alloys; Casting; Ingots; Early Iron Age; Wicina; ED-XRF; SEM-EDS

1. Introduction

Research on ancient metallurgical and foundry knowledge, as well as plastic working, encompasses various fields, including the analysis of ores, raw material acquisition methods, study of metallurgical semi-products and slags, examination of tools, crucibles, molds, and analysis of final products [1-6]. Within this context, understanding the origin and distribution of raw materials holds particular importance [7-10]. Recycling of raw materials, including scrap and damaged products, is also a notable aspect [11]. The contribution of trace elements from ores and their behavior during the melting process are also significant factors to consider [12-14]. To ensure high-quality castings with desirable functional and aesthetic properties, it was essential to use good-quality raw materials with appropriate alloying element compositions and employ well-executed melting and pouring processes, requiring specialized knowledge and experience. The preparation of molds and well-designed gating systems played a crucial role in ensuring proper filling of the mold cavity and feeding of the casting during alloy crystallization [15-16]. This sequential process encompasses multiple steps, with each element influencing the final product's quality. Understanding casting technologies in Bronze and Early Iron Age communities involves a multiparameter analysis based on preserved remains and modern research methods, including computer simulation processes [17-19]. In this study, metal material analysis was conducted on the raw materials, which is a necessary but not the sole prerequisite for a foundry workshop. In Europe, raw materials for casting processes were obtained from mining, smelting, and processing centers that emerged at the end of the Neolithic period. However, the existence of such centers in Polish territory has not yet been proven. Over time, standardization of metal products and intensive foundry production developed. Bronze scrap also became a significant source of raw material, with tin being imported as an alloying element in the form of bars and scraps from finished ornaments [20]. Raw material acquisition

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occurred through exchange contacts involving finished products, semi-finished products, and raw materials. While bars and rods were primary forms of transporting finished bronze raw materials over long distances, their discoveries, particularly in the Late Bronze Age and Early Iron Age, are rare. Noteworthy examples include exceptional copper and tin ingots from a probable Bronze Age shipwreck off the coast of Salcombe in southwest England [21-22], as well as significant finds of tin and copper ingots from the Uluburun shipwreck in the Mediterranean [23]. Tin ingots from the Late Bronze Age in Crete are also of significance [24]. Furthermore, copper ingots discovered at an underwater site on the coast of western Languedoc provide evidence of societal mobility in the early Iron Age and the distribution of raw materials in the Mediterranean region [25]. Findings from Bohemia indicate that copper in the Late Bronze Age originated from various sources, transported in the form of concave or concave-convex ingots, and then refined and alloyed in local workshops [26].

In the Early Bronze Age, the function of ingots was fulfilled by certain types of simple necklaces known as Ösenringe, which are looped rings with open ends. Central Europe areas have yielded a considerable number of mass deposits (hoards) containing hundreds of such rings [10,27-28]. It has been suggested that sickles may have played a similar role in the Late Bronze Age [29], but the primary form of raw material circulation during that time, as well as in the Early Iron Age, would have been straight bar-shaped ingots [30-32]. The importance of ingots should be understood in the context of increasing population numbers, social complexity and the resulting demand for bronze products, which necessitated the diversification of production and the subsequent need for raw materials with different chemical compositions. It is also possible that specific metal products were used to regulate social relations within a group and to signify and demonstrate local identity [33].

In the archaeological record of Poland, raw material for foundry production in the form of ingots, typically already in the form of a ready-to-use alloy, has been found mostly in hoards, and less frequently in settlements or graves. Deposits consisting of bronze scrap, unsuccessful or defective products intended for smelting, known as "foundrymen's hoards," are also known.

One noteworthy example of raw material hoards is the deposit from Słupsk, Pomerania, which consists of so-called rod ingots. This hoard comprises 143 ingots with a total weight of approximately 23 kg and an average length of approximately 47 cm (completely preserved pieces). The deposit also includes 4 socketed axes and a fragment of a band ornament. The examined rods from this hoard can be distinguished as copper rods and bronze rods with a small admixture of alloying elements, as well as a numerous group of bronze rods with a high content of an alloying element, primarily lead, with a small amount of tin [33]. Another similar discovery of raw material, which was unfortunately lost during World War II, was made in Swarzewo, Pomerania. It consisted of 151 rods with an average length of 40 cm and a total weight of approximately 27 kg [34]. Single finds of D-shaped cross-sectional bronze ingots are also known, for example, from the Chełmno Land [35] and from Dargoleza in Pomerania [36], the latter being part of a mass find similar to those described earlier.

Bronze rods of this type were likely semi-finished products intended for further processing, such as remelting, reshaping, forging, or wire drawing. Sometimes, these ingots were entirely forged into massive ornaments like ankle rings, as demonstrated by the study of such ornaments from the Early Iron Age cemetery in Świbie, Upper Silesia [37]. Another example from the same period is a massive rod from an uncoiled or stretched ankle ring, resembling a raw bronze bar that measures 57.5 cm in length and weighs 1.32 kg, found in a hoard at Gorzyce in Little Poland [38]. Of particular significance is in this context the discovery of numerous pieces of raw material directly in a production site, a defensive settlement at Wicina.

The fortified settlement in Wicina, located in the Lubuskie Voivodeship of western Poland, and its surrounding area are crucial for understanding the historical and economic dynamics of the communities during the Iron Age (Fig. 1:1). This includes the level of metalworking techniques and the interactions between groups, which can be inferred from the distribution and processing of raw materials. During the Hallstatt period (800-450 BC), the region benefited from its strategic position in the middle Oder River area, being at the heart of the Urnfield cultures in Central Europe. It developed extensive networks of exchange contacts that originated in the Late Bronze Age. However, the prosperity of the region in the Late Hallstatt period, specifically in the 6th century BC, was abruptly disrupted by the invasion of nomadic peoples with a Scythian cultural model [39,40].

This paper aims to provide a comparative material science characterization of the raw materials used in the casting of copper alloys in the Early Iron Age defensive settlement of Wicina and its surrounding areas. To achieve this, the metallurgical studies were conducted on ingot finds from the settlement at Wicina and two contemporary deposits (hoards) from Bieszków and Kumiałtowice. These hoards were found within a 20 km radius of the settlement and are currently located in the Żary district. The analyzed artifacts are preserved in the Archaeological Museum of the Middle Oder in Świdnica, near Zielona Góra (Muzeum Archeologiczne Środkowego Nadodrza). The fortified settlement in Wicina, which is shown in Fig. 1:2-3, was dated dendrochronologically to have been inhabited between 737 and approximately 560 BC (after 571 BC) [41,42]. Extensive remains of foundry activity, including fragments of disposable clay casting molds, metal waste from the casting process, and raw material fragments, have been discovered through excavations conducted by A. Kołodziejski during the 20th century. Metal objects from Kołodziejski's excavations and archeological materials from recent survey seasons (2008-2012) have been published up to date [43-44]. Previous reports also mention the existence of a "production part of the settlement" identified through concentrations of dug-in features (pits) and layers showing signs of intensive and prolonged fire use [39,45]. Furthermore, based on the data published so far, it is possible to identify extensive clusters of metal finds related to foundry work in the courtyard of the stronghold (Fig. 1:3).

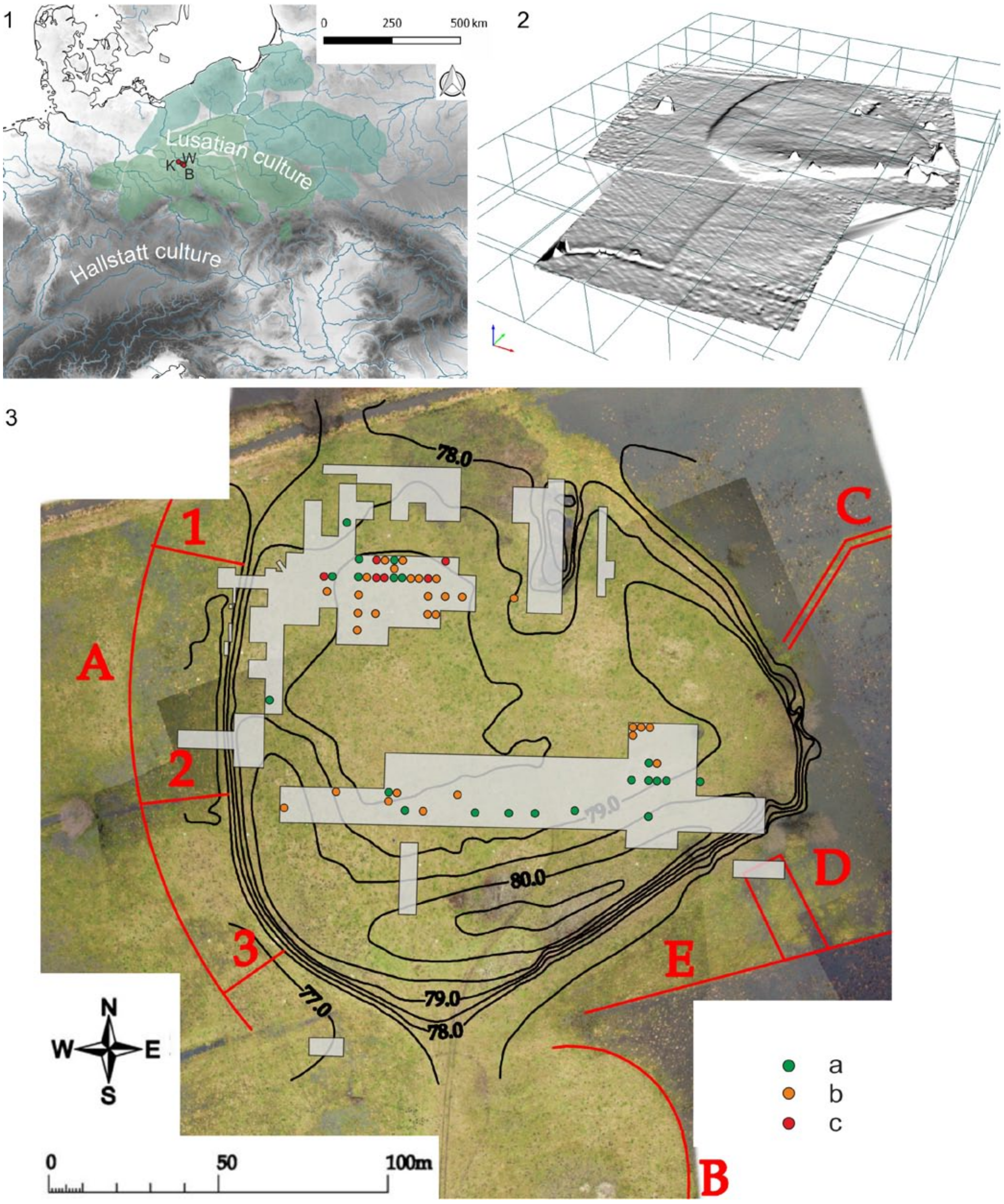


Fig. 1. 1: Locations of the analyzed ingot sites (W – Wicina, B – Bieszków, K – Kumiałtowice) in relation to the Lusatian culture and its peripheral groups during the onset of the Early Iron Age (approximately 800 BC). 2: Digital Elevation Model of the fortified settlement in Wicina, based on M. Bugaj [46]. 3: An orthophotomap from aerial photograph of the Wicina site with an altimetric layer. For the explanation of symbols A1-3, B, C, D, refer to [46]. The pale grey polygons represent exploration trenches conducted between 1966 and 1998, while the colored circles indicate metal finds associated with bronze foundry activity (a – ingots, b – casting waste, c – fragments of clay molds with remnants of cast items). Spatial data sourced from [43,45,46]

2. Materials and methods

Three series of copper alloy ingots, which were homogeneous in terms of shape (elongated bars), were selected for comparison in terms of raw material characteristics from three different sites. A total of twenty-four artifacts, representing almost all objects of this type from various stratigraphic contexts, were chosen from Wicina. In general, the collection is believed to date back to the beginning of the Iron Age (Hallstatt period: Ha C1b–C2 and D1–2), aligning with the settlement's functioning timeframe. However, it is possible (based on stratigraphic data as well) that most of the analyzed fragments are associated with the younger and most recent phase of the settlement, just before the episode of invasion and the downfall of the defensive site. The majority of the artifacts come from layers II and III, which are linked to the final phase of the stronghold (mid-6th century BC), while only two rod fragments originate from the lower (older) layer IV [45].

The assemblage of raw material selected from Wicina for this study includes a fully preserved ingot measuring 24 cm in length, along with 23 ingot fragments ranging from 1.8 to 6.3 cm in length (Figs. 2:5; 3; TABLE 1). No raw material lumps were examined, nor were any other forms of casting waste.

The hoard from Bieszków, Jasień Commune discovered approximately 4 km from the Wicina stronghold, consisted of over 300 bronze and iron items, including ornaments, tools, cast-

Fig. 2. Selected complete ingots. 1-4: Bronze cast-and-forged ingots from the Bieszków hoard (Bi_12_238, Bi_12_239, Bi_12_240, Bi_12_241). 5: Bronze cast ingot from Wicina (Wi_91_630). 6: Bronze cast ingot from the Kumiałtowice hoard (Ku_16_93)

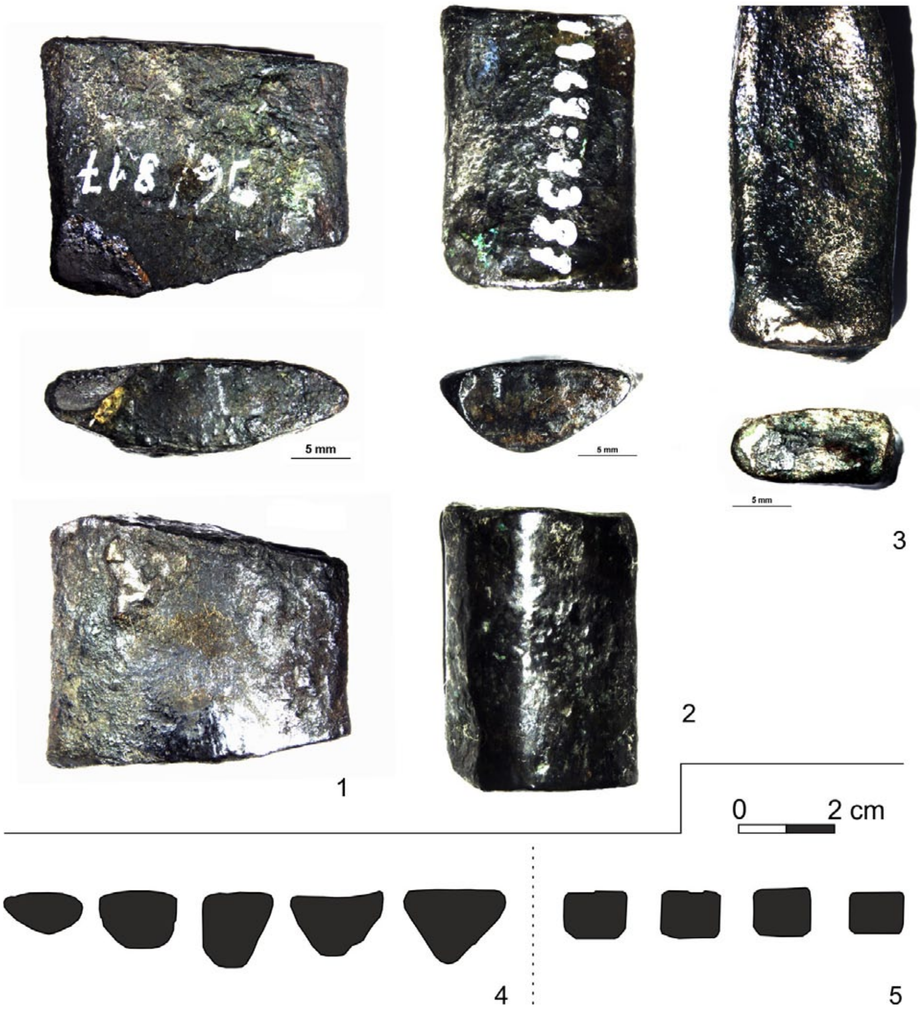


Fig. 3. 1-3: Selected fragments of cast ingots from Wicina (1: Wi_97_817, 2: Wi_69_2387, 3: Wi_69_2378). 4: Cross-sections of cast ingots from Wicina. 5: Cross-sections of cast-and-forged bronze ingots from the Bieszków hoard

ing molds, ingots, horse harness elements, armament, and sheet metal vessels, with some elements being scrap [47]. The hoard dates back to the Ha D1 period (around the turn of the 7th and 6th centuries BC). Most of the items have counterparts among the metal finds from the stronghold, while some (such as the chain harness) are evidently imports. It is probable that this deposit is associated with an individual or group of individuals with connections to metallurgy [47, pp. 507-508]. The numerous items related to foundry work may indicate a link between this find and the nearby settlement of Wicina, which was undoubtedly a local center of metallurgical production. All five raw material bars from this deposit were selected for this study [47, pp. 506, 574 nos. 239-243, photo 18]. They have elongated bar shapes with semi-oval or rectangular cross-sections (Figs. 2:1-4; 4). Three of them are completely preserved, ranging in length from 22.9 to 27.6 cm, while two have been shortened to lengths of 24 cm and 11.5 cm.

The hoard from Kumiałtowice, Brody Commune discovered approximately 22 km from the Wicina stronghold, comprised 94 bronze objects, 1 iron object, and 1 fragment of pottery [48]. The assemblage included ornaments, horse harnesses, and items related to metalwork, such as ingots and a bronze sheet (Fig. 2:6).

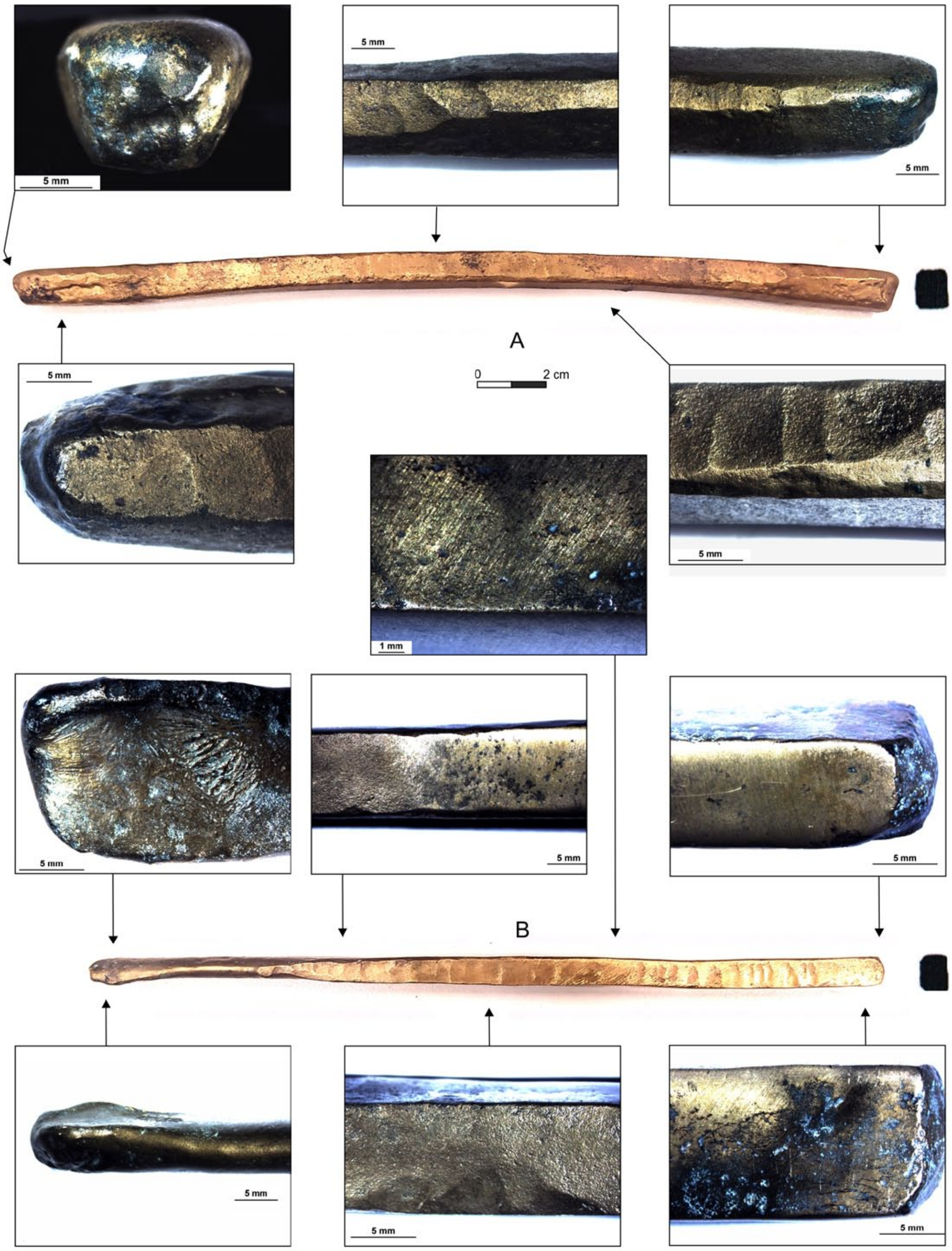


Fig. 4. Optical microscopy (OM) images of the cast-and-forged ingots from the Bieszków hoard (A: Bi_12_240, B: Bi_12_241). Different degrees of plastic processing are evident: in the case of Bi_12_240, forging of the top surface and edges; in the case of Bi_12_241, forging, modeling to rectangular section, and grinding of all planes, but limited to about two-thirds of the bar length

The hoard exhibits greater consistency in terms of the origin and function of the objects compared to the Bieszków hoard, which also contained non-local elements. It is also dated to the Ha D1 period (the turn of the 7th/6th century BC). Two raw material bars, similar in shape to those described above and measuring 17 cm and 16.8 cm in length, were selected for this study.

The objective of the present research was to determine the chemical composition and manufacturing techniques of the ingots used in foundry production from Wicina, Bieszków, and Kumiałtowice. Non-destructive methods were employed for the analysis. The observation of surface and microstructure, focusing on fabrication techniques, was conducted using optical microscopy (OM) with a NIKON SMZ 745T stereoscopic microscope equipped with a digital camera and NIS-Elements image analysis system, as well as scanning electron microscopy (SEM) with a high-resolution Tescan Mira microscope featuring a FEG Schottky electron emission source. The ingots' topography and microstructure were examined using solid-state detectors at a beam energy of 20 keV. Imaging was performed using the High Vacuum mode and Wide Field, Depth, and Resolution systems. The studies were conducted in secondary electron (SE) and backscattered electron (BSE and BSE COMPO) contrast, enabling differentiation of components based on material contrasts. The macro-area chemical composition analysis was carried out using an energy-dispersive X-ray fluorescence spectrometer (ED-XRF), specifically a Spectro Midex equipped with a Mo anode X-ray tube and Si SDD semiconductor detector. The micro-area analysis was conducted using energy-dispersive X-ray spectroscopy (SEM-EDS) with an SDD Ultim Max EDS detector from Oxford Instruments. The testing surface was prepared by mechanically removing corrosion products.

Supplementary studies were conducted to provide a comprehensive understanding of the mineral/phase and chemical composition of the ingot labeled as Wi_97_817. To determine the constituents of the ingot, structural X-ray diffraction (powder X-ray diffraction or PXRD) was employed using a Rigaku SmartLab diffractometer (Rigaku, Tokyo, Japan). This technique enabled the identification of the mineral and phase composition, relying on a microsample extracted from the ingot. Furthermore, the use of SEM-EDS microscopy was pivotal in precisely characterizing the intricate and variable phase-mineral composition of the material. The FEI QUANTA FEG 200 scanning microscope, equipped with a micro-area analyzer, was utilized for this purpose. The complexity of the material's phase-mineral composition necessitated the supportive application of SEM-EDS microscopy, again utilizing the FEI QUANTA FEG 200 scanning microscope with a micro-area analyzer.

For the analysis of the ingot's chemical composition, two methods were employed: Flame Atomic Absorption Spectrometry (FAAS) using the Thermo SCIENTIFIC iCE3000 series AAS spectrometer, and Inductively Coupled Plasma Excitation Optical Emission Spectrometry (ICP-OES) using the Optima 7300DV model from Perkin Elmer. These comprehensive studies took place within the laboratories of the AGH University, Faculty of Foundry Engineering and the Faculty of Geology, Geophysics, and Environmental Protection. Specifically, the investigations were carried out within the Laboratory of Phase, Structural, Textural, and Geochemical Analyses at the Faculty of Geology, Geophysics and Environmental Protection, the Environmental Analysis Laboratory of the Department of Environmental Protection, and the Accredited Hydrogeochemical Laboratory of the Department of Hydrogeology and Engineering Geology.

3. Research results and discussion

Manufacturing technique

The manufacturing techniques employed in the production of the ingots were identified and classified into two groups (Fig. 3:4-5). The first group consisted of longitudinal, D-shaped ingots that were cast in one-piece, open molds. These ingots exhibited a rough bottom surface, reflecting the mold cavity (Fig. 5), and a top surface showing signs of free solidification. The ends of the rods were semi-circular. Most of the ingots from Wicina and Kumiałtowice belonged to this group. However, two atypical specimens were identified in the Wicina collection. One was an oval cross-section ingot, marked Wi_90_189, cast in a closed, single use clay mold, as its both surfaces: top and bottom had the same features lacking a visible dividing plane. The other, marked Wi_11_3, was cast in a mold with a rectangular cross-section, showing visible casting defects on both top and bottom surfaces, indicating a high level of alloy outgassing.

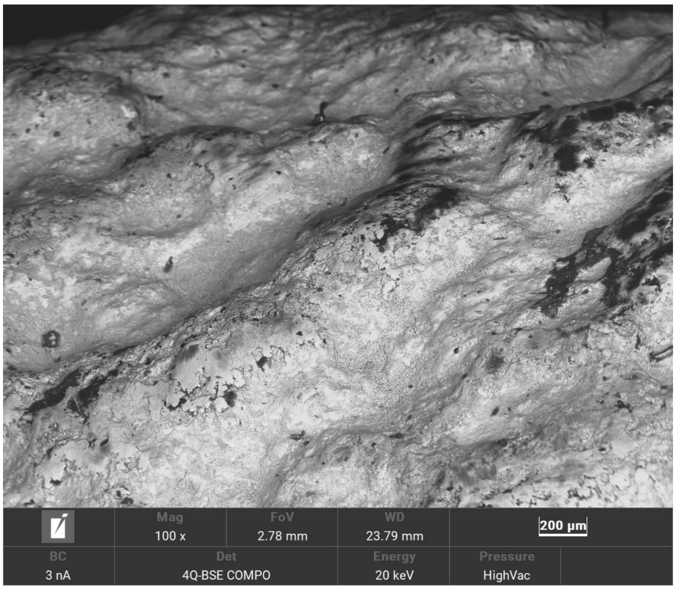


Fig. 5. Uneven bottom surface of ingot Wi_90_257 reflecting the structure of the mold cavity with high roughness

Stone and clay one-piece molds for casting elongated ingots have been found in various regions, including Halle (Saale) in Saxony-Anhalt and Gogolin in Upper Silesia, dating back to the Late Bronze Age (1300-800 BC) [31-32]. It is likely that such simple and reproducible shapes of raw material were also mass-produced using sand and metal molds.

The second group of ingots included bars from Bieszków, which stood out from the others in terms of their shape and surface elaboration. These bars had a square or rectangular cross-section (Fig. 4) and exhibited visible forging marks on almost their entire surfaces. The forging process involved shaping the ingots into a regular cross-section in defined segments. The cleaned and worked surface of these ingots indicated high-quality material with good plastic properties and no surface defects resulting from alloy outgassing. This suggests a higher standard of raw material quality, which was likely deliberately intended to be demonstrated with this technique. Similar worked ingots, although fragmentary, were also found in Wicina (Fig. 3:3). In addition to shaping them into a rectangular cross-section, the lateral surfaces of the Bieszków and Wicina ingots were processed through grinding and polishing, as revealed by microscopic photographs (Fig. 4:B; 6).

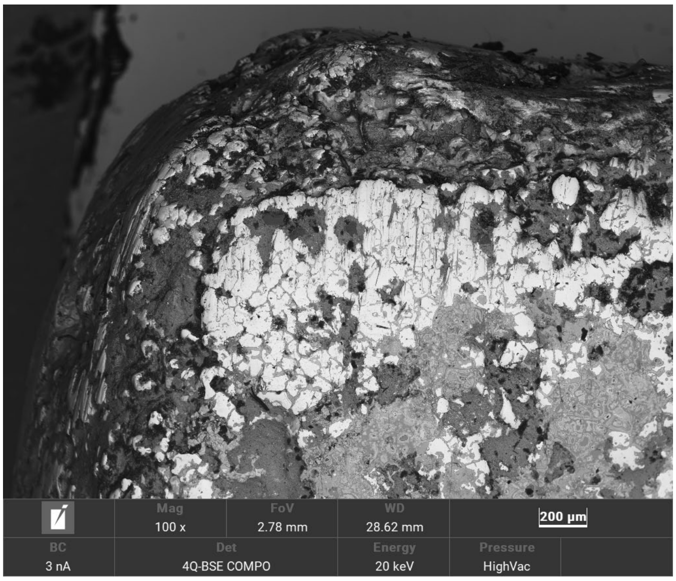


Fig. 6. The top surface of ingot Wi_69_2378 with visible traces of surface grinding

Chemical composition and microstructure analysis

A further distinction was made based on the chemical composition of the ingots. The classification was determined by the increased iron content, which is undesirable in bronze as it deteriorates the quality of the alloy. This differentiation helps identify the finished alloys from ingots that function more as master alloys, which are used to introduce alloying additives into the metal bath.

The first group consists of raw materials that are ready-to-use alloys, with a composition that ensures good mechanical and casting properties. The chemical compositions of these alloys are summarized in TABLES 1 and 2, which include cast ingots from Wicina and Kumiałtowice, as well as cast and forged ingots from Wicina and Bieszków. The majority of ingots in this group exhibit a high tin content.

In TABLE 1, the chemical composition of nine bronze ingots is presented. They are predominantly characterized by elevated levels of tin, with a maximum value of 17.6% (an average content of 12.5% Sn for the group). Bronze objects show Sn contents (wt. %): low (up to 9), medium (9-13) and high, above 13. The longest fully preserved ingot from Wicina (Wi_91_630; Fig. 2:5), has the highest tin content, while the lowest Sn content, 7.6%, is found in an ingot with a different, oval cross-section, which stands out in the collection due to being cast in a closed mold (Wi_90_189). The different chemical composition and manufacturing technique of this ingot may indicate a different origin. The ingot cast into a rectangular mold (Wi_11_3) falls within the group in terms of chemical composition, with average values of elemental contribution.

One ingot with a D-shaped cross-section (Wi_97_512) is devoid of tin, but it exhibits higher proportions of lead (8.7% Pb), antimony (5.5% Sb), arsenic (2.5% As), and silver (1.3% Ag). These concentrations significantly differ from the others in the group for the indicated elements, and their median or middle values are 0.37% Pb, 0.13% Sb, 0.14% As, and 0.06% Ag (TABLE 1).

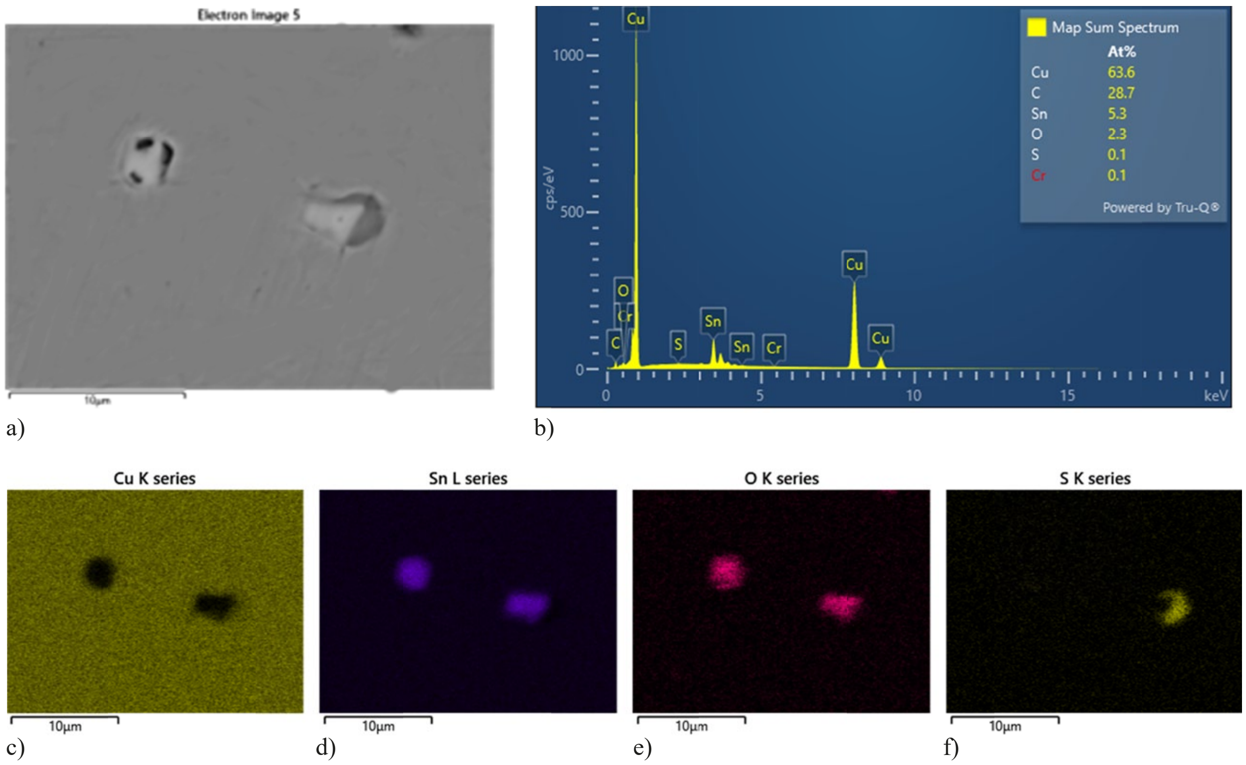
TABLE 1

Chemical composition of cast bronze ingots from Wicina and Kumiałtowice by ED-XRF (wt%)

Dimension	**Concentration (wt%)**											
Element	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Au**	**Pb**	**Bi**
Wi_11_3	0.17	0.07	0.24	86.81	0.13	0.26	0.07	11.62	0.14	<0.020	0.41	0.07
Wi_90_257	0.10	0.09	0.12	88.35	0.12	0.29	0.08	10.32	0.08	<0.020	0.37	0.07
Wi_90_189	0.13	0.07	0.49	87.39	0.71	0.76	0.32	7.62	1.06	<0.020	1.41	0.04
Wi_96_654	0.31	0.06	0.11	85.52	0.14	0.01	0.01	13.71	<0.05	<0.020	0.10	0.03
Wi_91_630	0.15	0.08	0.22	80.89	0.13	0.22	0.06	17.55	0.11	<0.020	0.54	0.04
Wi_96_654	0.31	0.06	0.11	85.52	0.14	0.01	0.01	13.71	<0.05	<0.020	0.10	0.03
Wi_97_512	<0.025	0.06	0.51	81.20	0.11	2.50	1.25	<0.051	5.53	<0.020	8.74	0.09
Ku_16_92	0.05	0.08	0.20	86.71	0.20	0.29	0.03	12.08	0.13	<0.020	0.22	0.03
Ku_16_93	0.48	0.06	0.09	85.27	0.15	0.26	0.04	13.31	0.05	<0.020	0.27	0.02
Min	0.05	0.06	0.09	80.89	0.11	0.01	0.01	7.62	0.05	0.00	0.10	0.02
Max	0.48	0.09	0.51	88.35	0.71	2.50	1.25	17.55	5.53	0.00	8.74	0.09
Mean	0.21	0.07	0.23	85.30	0.20	0.51	0.21	12.49	1.01	0.00	1.35	0.05
Median	0.16	0.07	0.20	85.52	0.14	0.26	0.06	12.70	0.13	0.00	0.37	0.04

Microstructural tests were conducted on the Wi_96_654 ingot (Fig. 7). The study revealed, against the background of the Cu-α solid solution, precipitates of fine Cu_2S sulphides, remnants of the copper smelting process from the ores (Fig. 7:f), and SnO_2 tin oxides, likely traces of the introduction of tin alloying additives, partially in the form of cassiterite (Fig. 7:d-e).

TABLE 2 provides a summary of the chemical composition for the twelve cast and forged bronze ingots. This group exhibited an average lower proportion of tin compared to the previous group, with an average of 10.7%. The ingots in this group contained a small amount of lead, averaging 0.4% (maximum 0.9% Pb). The highest tin proportion (12.1%) was found in ingots Wi_91_592 and Wi_12_238. On the other hand, ingot Wi_11_104 had the lowest tin content (2.2% Sn) but showed elevated concentrations of antimony (1.5% Sb), arsenic (0.5% As), silver (0.7%), and lead (0.8% Pb). With a lower tin proportion and fewer impurities, it can be concluded that the reshaped ingots had slightly better properties for plastic processing.



a) b)

c) d) e) f)

Fig. 7. a) SEM image of cast bronze ingot Wi_96_654. b) EDS analysis of the chemical composition in the image area. c) Maps of the distribution of copper (c), tin (d), oxygen (e), and sulphur (f)

TABLE 2

Chemical composition of cast-and-forged bronze ingots from Wicina and Bieszków by ED-XRF (wt%)

Dimension	**Concentration (wt%)**											
Element	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Au**	**Pb**	**Bi**
Wi_69_2370	0.11	0.11	0.11	88.94	0.15	0.12	0.01	10.27	0.01	<0.020	0.15	0.02
Wi_69_2378	<0.025	0.05	0.13	89.65	0.12	0.17	0.04	9.66	0.09	<0.020	0.08	0.01
Wi_90_183	0.20	0.07	0.22	86.23	0.1	0.41	0.07	11.58	0.18	<0.020	0.88	0.07
Wi_90_268	0.22	0.09	0.24	86.47	0.17	0.32	0.07	11.56	0.17	<0.020	0.64	0.08
Wi_11_104	0.03	0.08	0.56	93.47	0.15	0.54	0.73	2.15	1.45	<0.020	0.76	0.08
Wi_91_592	0.13	0.07	0.20	85.9	0.14	0.36	0.13	12.1	0.35	<0.020	0.58	0.03
Wi_92_170	0.18	0.08	0.18	88.79	0.13	0.28	0.05	9.59	0.13	<0.020	0.55	0.03
Bi_12_238	0.16	0.09	0.10	86.98	0.16	0.26	0.01	12.05	0.02	<0.020	0.13	0.04
Bi_12_239	<0.025	0.07	0.10	87.75	0.15	0.21	0.01	11.66	<0.051	<0.020	0.02	0.03
Bi_12_240	<0.025	0.07	0.11	87.43	0.15	0.23	0.01	11.9	0.03	<0.020	0.04	0.03
Bi_12_241	0.22	0.10	0.14	87.23	0.14	0.2	0.04	11.63	0.05	<0.020	0.22	0.03
Bi_12_242	0.38	0.08	0.14	87.62	0.13	0.2	0.04	10.92	0.06	<0.020	0.39	0.03
Min	0.03	0.05	0.10	85.90	0.10	0.12	0.01	2.15	0.01	0.00	0.02	0.01
Max	0.38	0.11	0.56	93.47	0.17	0.54	0.73	12.10	1.45	0.00	0.88	0.08
Mean	0.18	0.08	0.19	88.04	0.14	0.28	0.10	10.42	0.23	0.00	0.37	0.04
Median	0.18	0.08	0.14	87.53	0.15	0.25	0.04	11.57	0.09	0.00	0.31	0.03

Microstructural tests were conducted on ingot Wi_69_2378 (Fig. 8), revealing the presence of small copper sulphide precipitates (approximately 1 µm in size) as remnants from the copper smelting process (Fig. 8:f). Additionally, small spherical lead inclusions were visible against the copper-tin solid solution (Fig. 8:e).

TABLE 3 lists ingots characterized as semi-finished products or master alloys. These ingots had significantly increased iron content and contained other elements from the ores, making them suitable as alloy additives or for further processing. They were in the form of D-shaped ingots and differed significantly in composition, weight, microstructure, and properties from the investigated bronze ingots.

The tested material had a relatively low copper content ranging from 18.4% to 75.2%, with negligible tin content. In contrast, the investigated bronze ingots (TABLES 1-2) had copper content ranging from 80.9% to 93.5% and tin content ranging from 2.2% to 17.6%. In the discussed group (TABLE 3),

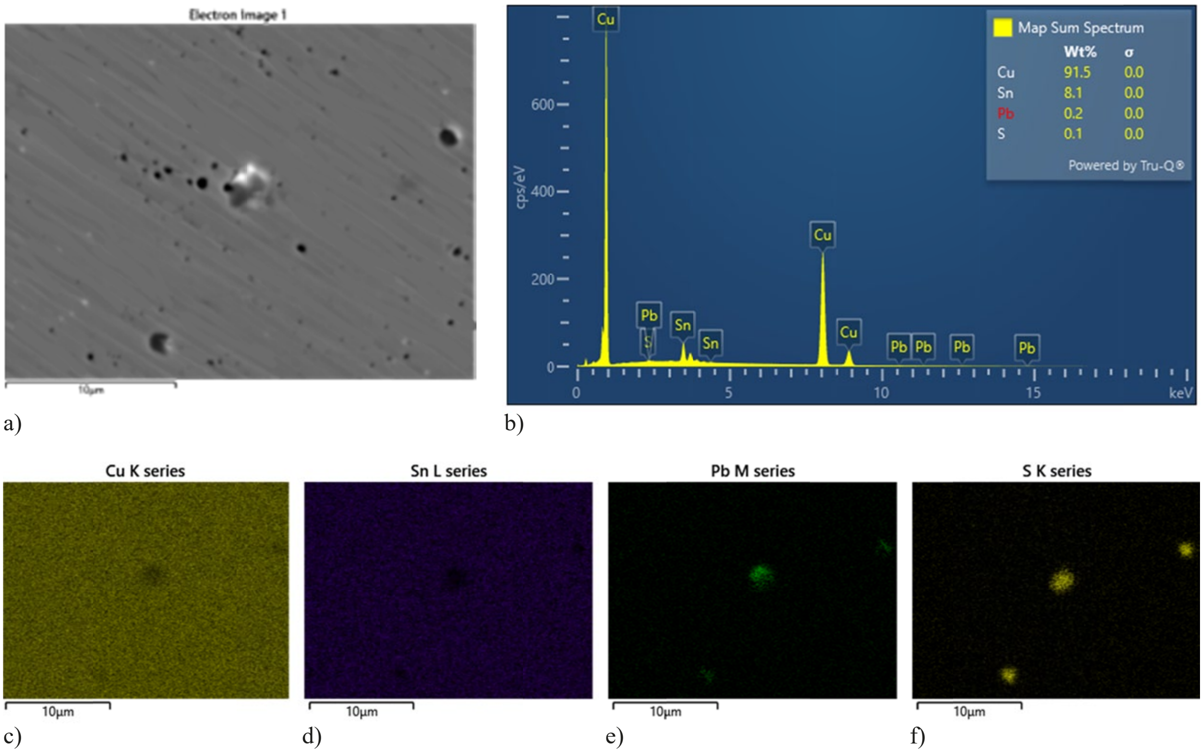


Fig. 8. a) SEM image of cast-and-forged bronze ingot Wi_69_2378. b) EDS analysis of the chemical composition in the image area. c) Maps of the distribution of copper (c), tin (d), lead (e), and sulphur (f)

TABLE 3

Chemical composition of impure cast ingots (master alloys) from Wicina by ED-XRF (wt%)

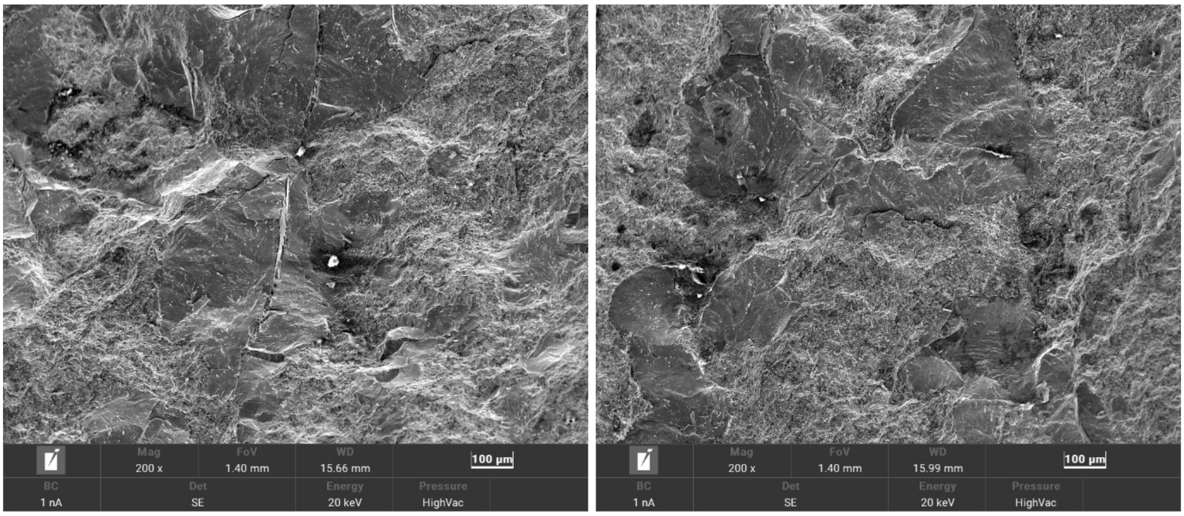
Dimension	**Concentration (wt.%)**											
Element	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Au**	**Pb**	**Bi**
Wi_34_09	5.12	3.28	5.14	24.03	0.08	11.07	2.58	<0.051	47.50	<0.020	0.20	0.08
Wi_68_3390	6.16	7.61	22.52	23.03	0.03	16.36	0.22	0.15	9.17	<0.002	0.17	0.01
Wi_69_2364	26.81	6.31	15.63	18.36	0.08	14.53	0.16	0.08	4.90	0.03	0.45	0.02
Wi_69_2387	11.83	7.54	17.66	27.47	0.04	23.52	0.23	0.11	7.54	<0.020	0.08	0.02
Wi_69_2418-a	7.67	4.62	10.78	20.00	0.04	16.34	1.16	<0.051	38.68	<0.020	0.11	0.04
Wi_69_2418-b	10.95	2.81	5.81	58.42	0.10	7.62	0.23	0.13	8.39	<0.020	5.42	0.07
Wi_11_101	10.11	5.80	17.23	29.22	0.06	14.06	0.22	0.07	9.77	<0.020	0.05	0.01
Wi_95_1348	13.48	3.40	5.60	55.22	0.10	13.83	0.60	0.39	3.85	<0.020	0.14	0.07
Wi_95_1398	3.32	1.15	2.52	46.63	0.09	7.46	1.41	0.95	35.63	<0.020	0.66	0.11
Wi_96_749	12.25	0.77	1.07	42.38	0.09	13.87	1.65	0.29	12.20	<0.020	0.25	0.04
Wi_97_514	5.40	0.29	0.81	75.17	0.11	3.09	0.77	0.12	4.38	<0.020	<0.02	0.01
Wi_97_817	45.43	5.26	10.26	21.53	0.06	7.35	0.33	0.07	8.96	<0.020	0.20	0.03
Min	3.32	0.29	0.81	18.36	0.03	3.09	0.16	0.07	3.85	0.03	0.05	0.01
Max	45.43	7.61	22.52	75.17	0.11	23.52	2.58	0.95	47.50	0.03	5.42	0.11
Mean	13.21	4.07	9.59	36.79	0.07	12.43	0.80	0.24	15.91	0.03	0.70	0.04
Median	10.53	4.01	8.03	28.34	0.08	13.85	0.47	0.13	9.06	0.03	0.20	0.03

it is worth noting the significantly elevated levels of iron (ranging from 3.3% to 45.4%), antimony (3.9% to 47.5%), arsenic (3.1% to 23.5%), nickel (0.8% to 22.5%), cobalt (0.3% to 7.6%), and silver (0.2% to 2.6%). The ingot with the highest iron content, along with elevated levels of antimony, arsenic, nickel, and cobalt (Wi_97_817), was subjected to microstructural sub-analysis (Figs. 9-12).

A brittle fracture was observed on the surface of this ingot (Fig. 9), contrasting with the plastic fracture observed in the bronze ingots. The microstructure revealed dendrites of copper sulphides (Cu_2S) against the structure of iron oxide (FeO) and intermetallic phases of Sb-As-Ni-Co (Figs. 10-11). The distribution of antimony, arsenic, nickel, and cobalt in the interdendritic spaces is shown in Fig. 12.

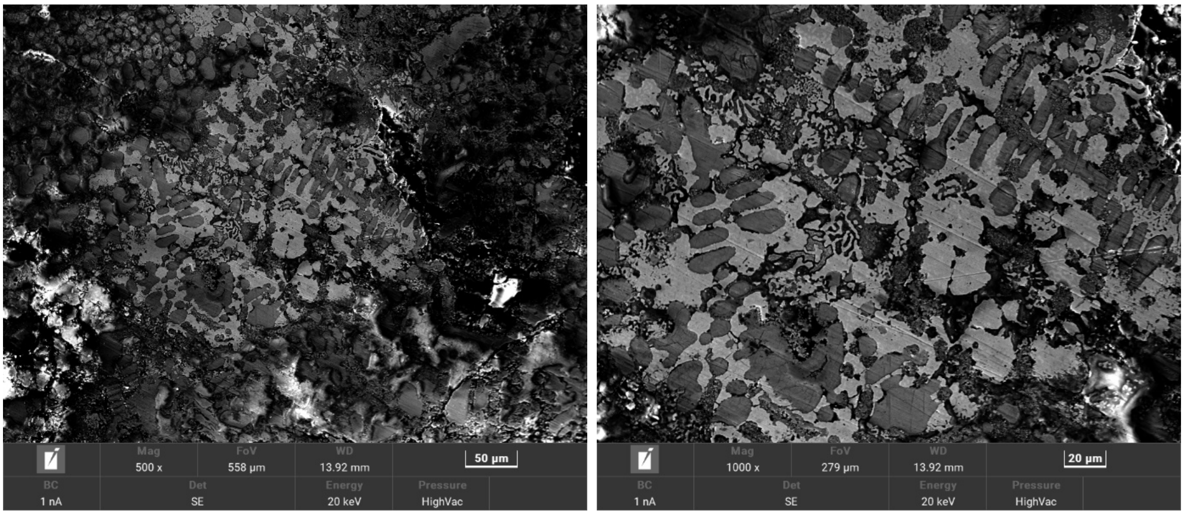
The presence of high iron content, as well as antimony, arsenic, nickel, and cobalt, suggests the origin of the material from tennantite-tetrahedrite ($Cu_{12}As_4S_{13}$-$Cu_{12}Sb$) fahlore ores and chalcopyrite ($CuFeS_2$)/pyrite (FeS_2) ores. These ores may have been intentionally mixed to utilize a raw material with inferior properties, combined with a raw material with fewer impurities to improve casting properties and enable plastic processing [49].

Chemically, the X-ray studies conducted on the Wi_97_817 ingot revealed the prominent phases within the sample, aligning with ore minerals such as sulphides, arsenides, and copper sulphosalts. These copper sulphosalts exhibit isomorphic substitutions of both As and Fe. The investigation also identified the presence of simple oxides of Sb and Fe, alongside more complex oxides involving Fe in conjunction with Co, Ni, and Sb (Fig. 13). Spectrograms acquired during scanning microscopy observations further confirmed the existence of diverse metallic and non-metallic mineral phases within the material. This is also evident in the SEM images, which highlight the sites of analysis (Fig. 14). In summary, it is pertinent to note that across all areas of the examined ingot particles, there is a presence of Cu, Fe, S, and O, albeit in varying proportions. The EDS analyses



a) b)

Fig. 9. SE image of ingot Wi_97_817 fracture (a, b), 200×



a) b)

Fig. 10. SE image of ingot Wi_97_817 microstructure, 500× (a), and 1500× (b)

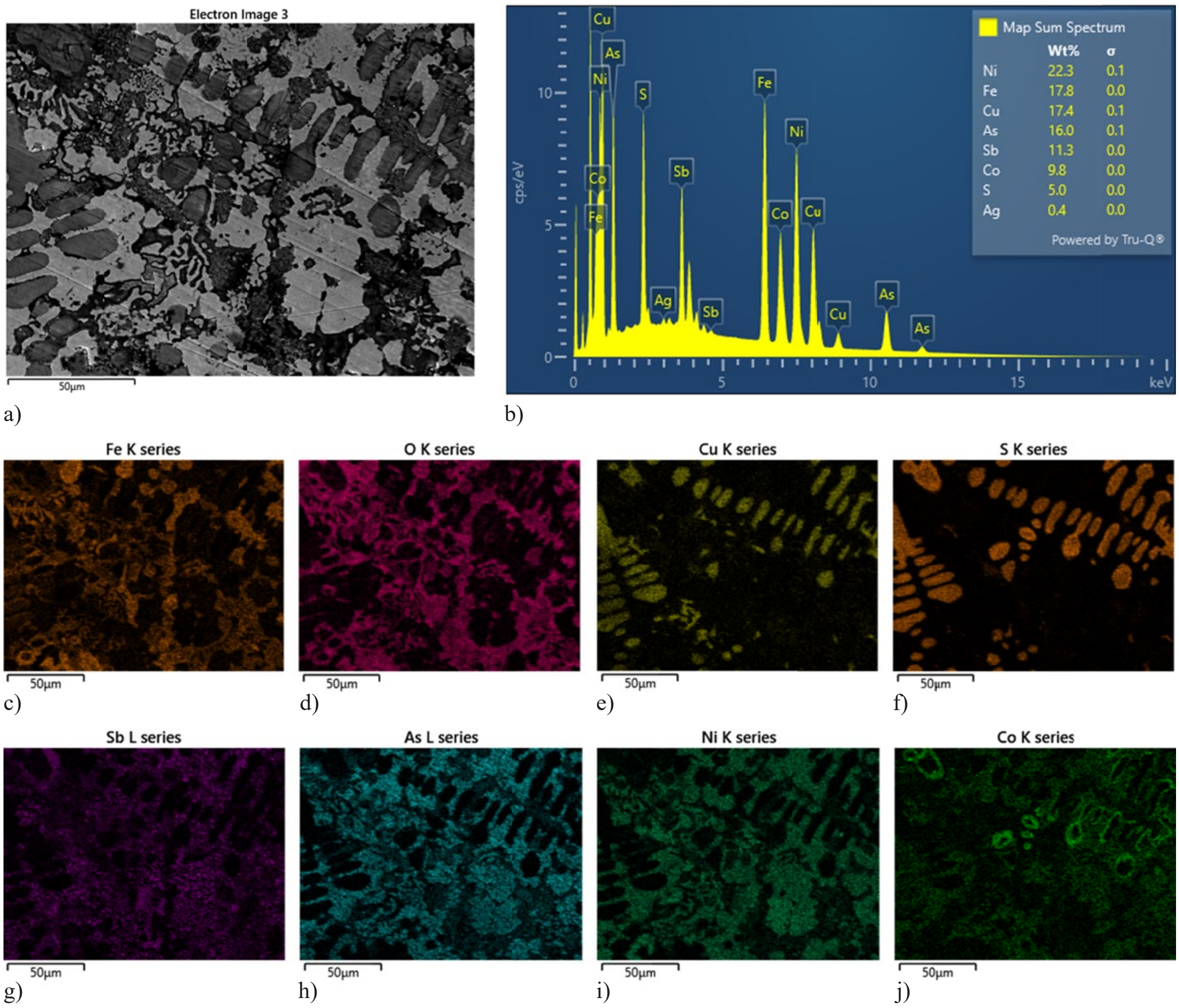


Fig. 11. a) SEM image of cast-and-forged bronze ingot Wi_97_817. b) EDS analysis of the chemical composition in the image area. c) Maps showing the distribution of iron (c), oxygen (d), copper (e), sulphur (f), antimony (g), arsenic (h), nickel (i), and cobalt (j)

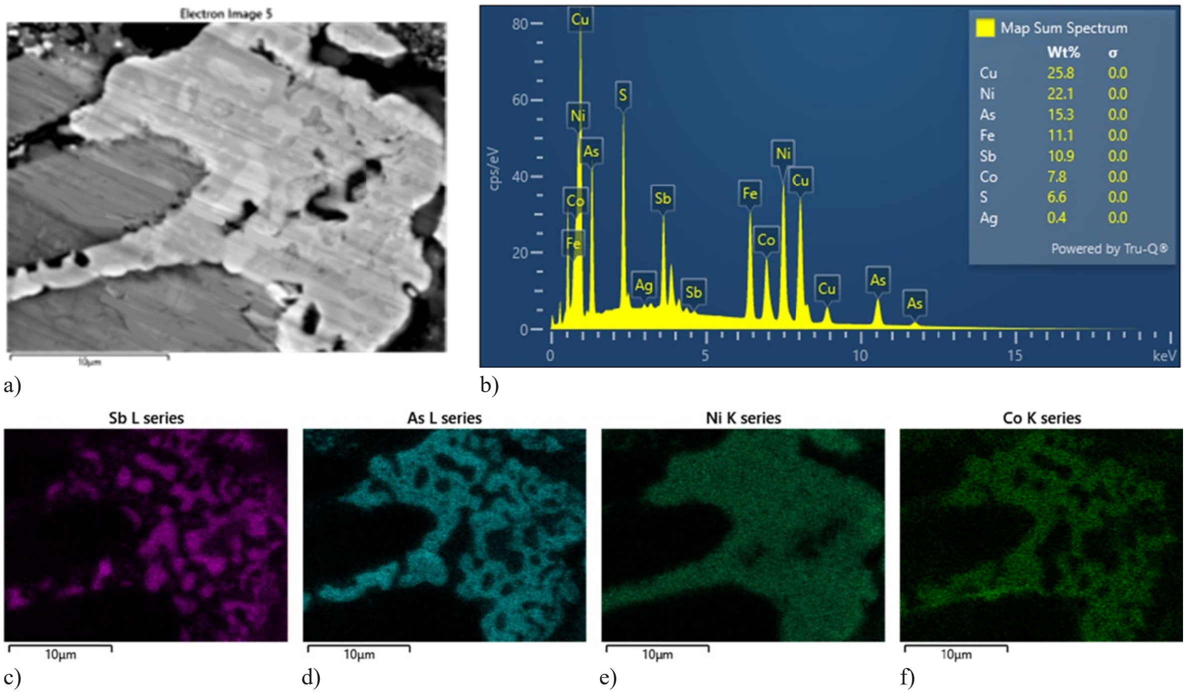


Fig. 12. a) SEM image of cast-and-forged bronze ingot Wi_97_817. b) EDS analysis of the chemical composition in the image area. c-f) Maps showing the distribution of antimony (c), arsenic (d). nickel (e), and cobalt (f)

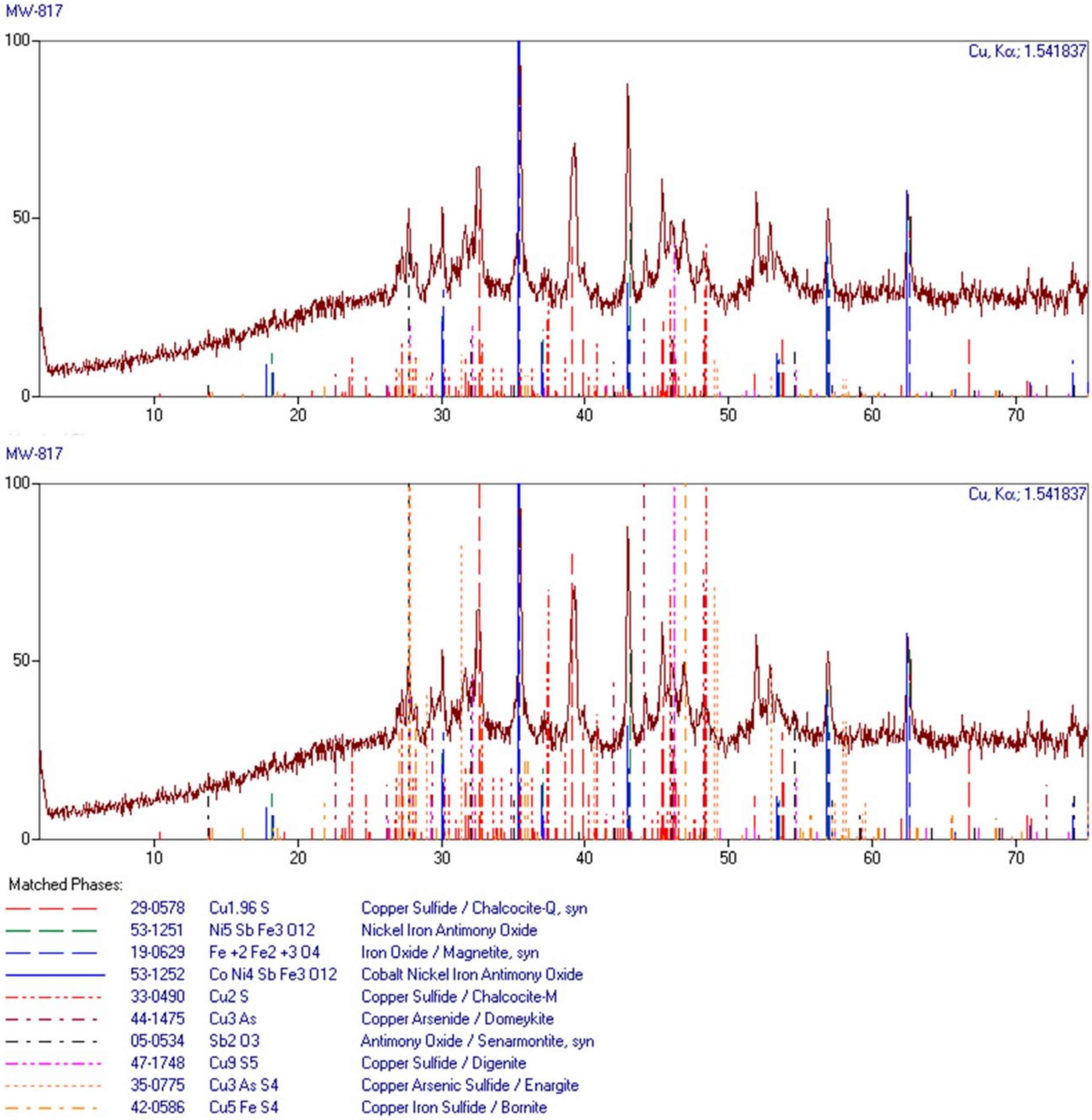


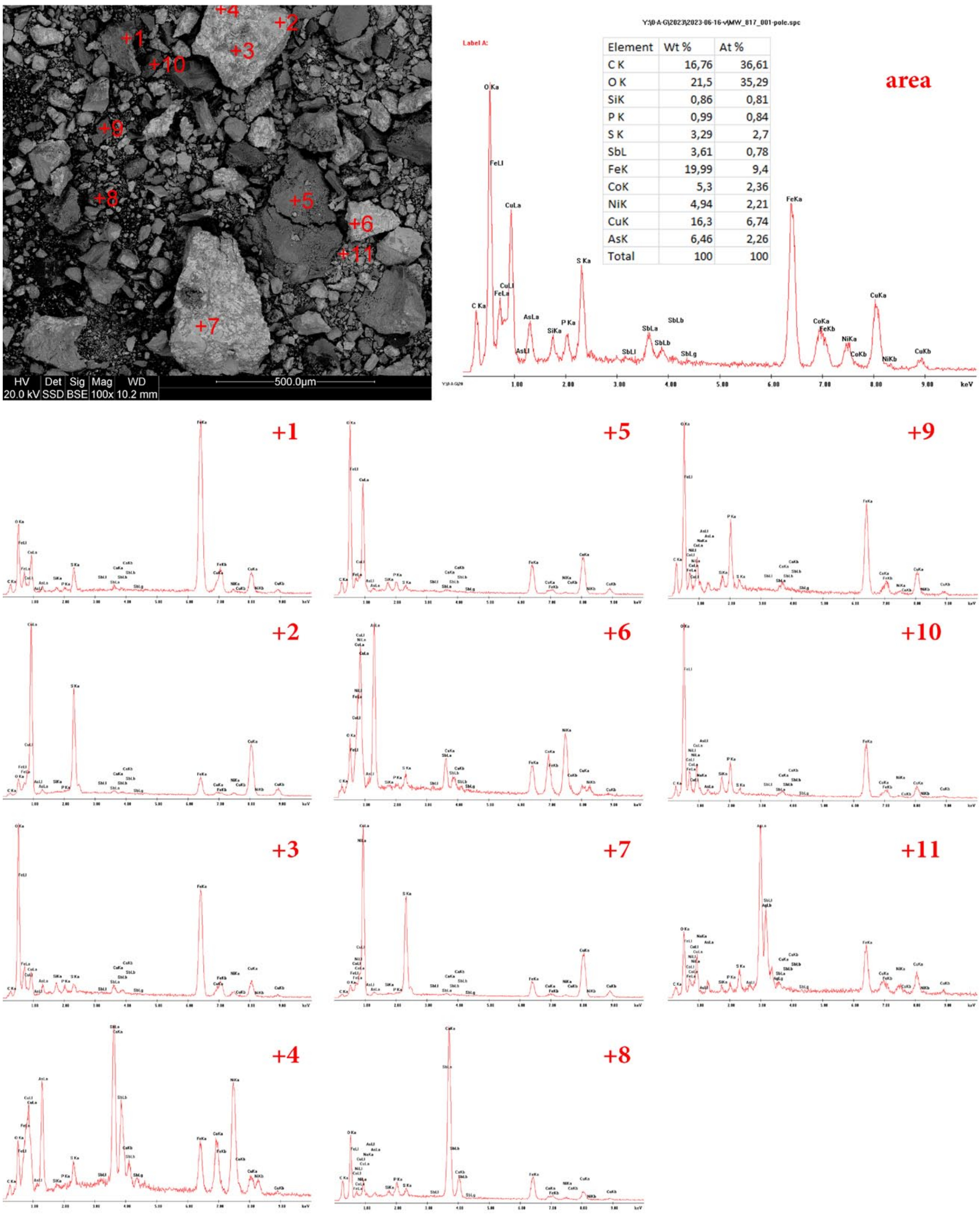
Fig. 13. X-ray diffraction data from powdered samples of the Wi_97_817 ingot, with the particle size on the order of 0.1 mm

corroborated the presence of S and O through the identification of sulphides and oxides in the X-ray structural studies. This points toward the possibility of dealing with an intermediate product, potentially a partially roasted Cu-As-Sb-S ore. Notably, the specific presence of Ni, whose concentration can play an indicative role in determining the ore's origin, particularly as potential Ni-fahlores, is significant.

According to FAAS analyses, the sample exhibited the following highest concentrations (wt.%): Cu – 25.74, Fe – 13.68, Ni – 9.65, Zn – 0.02, Pb – 0.02, Mn – 0.009. For the remaining elements, including trace elements, the ICP-OES method was utilized. The sample revealed the following concentrations (wt.%) for various metals and metalloids: As – 8.06, Co – 7.61, Sb – 0.13, Cd – 0.12, Sn – 0.01, Ag – 0.008, Cr – 0.007, Ba – 0.001, V – 0.001. The sulphur concentration in the ingot was determined to be 8.98 wt.%. Analytical outcomes for the mentioned ingots, as well as others ascertainable via ICP-OES, are graphically depicted (Fig. 15), with reference to the copper content. It is important to note that the tests were conducted on a limited sample fraction, hence the results should be interpreted as indicative. Nonetheless, it's evident that the ingot represents a semi-finished product intended for further processing and refinement.

4. Conclusion

The examination of bronze ingots from the production settlement in Wicina has provided valuable insights into the level of metallurgical and foundry technology in 1st millennium BC.



Element	Wt %	At %
C K	16,76	36,61
O K	21,5	35,29
SiK	0,86	0,81
P K	0,99	0,84
S K	3,29	2,7
SbL	3,61	0,78
FeK	19,99	9,4
CoK	5,3	2,36
NiK	4,94	2,21
CuK	16,3	6,74
AsK	6,46	2,26
Total	100	100

Fig. 14. SEM microstructure analysis, along with EDS spectra and semi-quantitative analysis conducted on the powdered zone of the Wi_97_817 ingot

The ingot finds indicate the local production of bronze products using the investigated raw material. The analyzed bronze ingots exhibited variation in chemical composition and manufacturing technique. Our results are in line with previously published XRF examinations of several ingots [50]. The composition of the ingots reflects intentional alloying with additives like tin and lead, as well as the presence of natural impurities such as iron, antimony, arsenic, nickel, and cobalt. These elements may offer clues about the origin of the copper ores, which can be further explored through lead isotope ratio studies.

Of particular interest is the coexistence of two different forms of bronze ingots in the analyzed series: cast ingots and

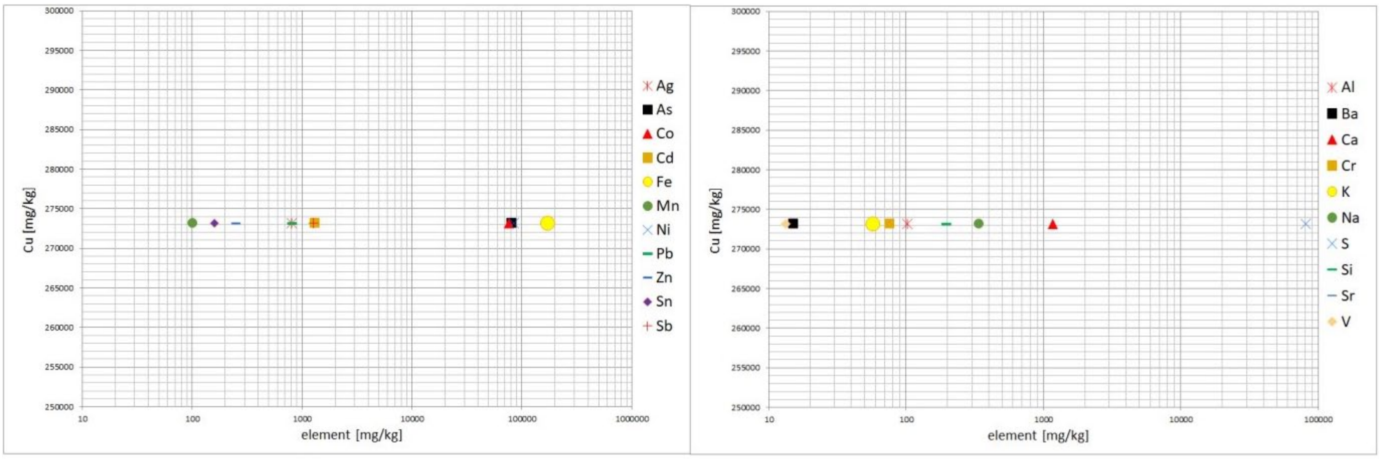


Fig. 15. The relationship between the concentrations (mg/kg) of metals, metalloids, and related elements, as well as their correlation to the Cu concentration in the Wi_97_817 ingot

forged ingots/bars. Cast ingots were likely produced using open molds, possibly made of clay or stone, and were characterized by a rough D-shaped cross-section and a surface showing free solidification (Fig. 3:4).

One ingot indicates the use of a closed, single use mold and the possibility of casting ingots using the lost-wax technique.

Additionally, there are indications of some ingots being forged after casting (Figs. 3:5; 4:A-B), as seen in the alteration of surface and structure. This process aimed to highlight the quality of the ingots resulting from their alloy properties. The clean and polished surface of the forged ingots indicates a higher standard of raw material quality, presenting finished semi-products with good plastic properties and free of surface defects.

The chemical composition analysis further supports the distinction between cast and forged ingots. The forged ingots generally exhibited lower levels of impurities compared to the just cast ingots. This suggests that the elaboration of ingots through forging were aimed at demonstrating their higher-quality raw material. This is consistent with the findings from the Bieszków hoard, where the majority of the ingots were additionally forged, suggesting that their enhanced quality was likely a factor in their selection for deposition. In contrast, in the larger series of ingot fragments from the Wicina production settlement, forged ingots were exceptions (e.g., Fig. 3:3). The deliberate selection of higher-quality ingots for deposition in the hoard provides insights into the significance of hoarding practices in the Wicina region [cf. 51].

The analysis of the copper alloy ingots from the Wicina production center during the Early Iron Age (750-550 BC) has provided insights into the management of raw materials in the area. The ingots predominantly consisted of Cu-Sn type bronzes with varying levels of impurities. The average values of impurities in the cast ingots were approximately 1% Sb, 0.5% As, and 0.2% Fe. Lead occasionally appeared as an alloying addition in Cu-Pb type alloys or as an additional component in Cu-Sn-Pb type alloys.

The cast-and-forged ingots, which were reshaped through forging, had a Cu-Sn binary alloy composition with slightly lower levels of impurities, averaging around 0.2% Sb and 0.3% As. The average tin content in these ingots was also slightly lower at 10.4% Sn. This indicates that the reshaped ingots had slightly better properties for plastic processing, suggesting their intended use for such purposes.

Both the cast ingots and cast-and-forged ingots exhibited small inclusions of copper sulphides in their microstructure, indicating traces of copper smelting from sulphide ores. Tin oxides, residues of tin ores, were identified in the cast ingots.

The most distinctive group of ingots was the third group, which had significantly higher levels of iron. Microstructural studies revealed the presence of copper sulphides and high concentrations of elements such as antimony, arsenic, nickel, and cobalt. This composition of the ingots suggests that they were not suitable for direct casting but rather served as mortar-like additives to enrich copper or copper-tin alloys with these elements. The chemical composition of such ingots suggests a raw material derived from a mixture of fahlore-type ores and chalcopyrite.

Summarizing the results of the chemical studies and based on the identified mineral composition, it can be concluded that we are dealing with an intermediate product formed from an alloy of a mixture of raw materials corresponding to fahlore-type copper and chalcopyrite copper. Research by Pernicka, Lutz, and Stöllner [52] has shown that by analyzing the content of elements such as Sb, As, Ni, Co, Ag, Se, and Bi, it is possible to geochemically distinguish the deposit from which the raw material originates. Logarithmic diagrams indicate a strong correlation between As and Ni, with significant concentrations of 8.063 wt.% As and 8.454 wt.% Ni. This concentration pattern is characteristic of copper ore occurrences from the Mitterberg region in the eastern Alps [52]. Additionally, concentrations of Ag and Sb oscillate around 0.1 wt.%, specifically, 0.0807 wt.% for Ag and 0.1268 wt.% for Sb in the ingot sample. The geochemical association of As and Sb is also similar to that observed in this region, with a notably higher concentration of As compared to Sb, exceeding 60 times in our case. Of particular interest are the significant concentrations of cobalt, with a value of 7.617 wt.%, found in the tested ingot sample. From a raw material perspective, this might indicate a deposit area within the Buchberg vein, known to be enriched in cobalt [52]. PXRD studies indicate the presence of both chalcozite and bornite copper sulphides in the sample. These sulfides may contain up to 80 wt.% Cu for chalcozite and up to 60 wt.% Cu for bornite. Additionally, minerals from the tennantite-tetrahedrite group, collectively referred to as fahlore, are also present. Their composition varies, with ranges of 0-20 wt.% As, 0-29 wt.% Sb, and 51.56 wt.% Cu for tennantite, and 45.76 wt.% Cu for tetrahedrite. These minerals contain significant amounts of dopants including Ag, Fe, Co, Ni, Pb, Zn, Hg, Ge, Sn, V, Bi, Se, and Te [53,54]. In the sample, the listed admixtures were present in decreasing concentrations (mg/kg) as follows: Fe – 170884, Ni – 84541, Co – 76172, Pb – 818, Ag – 807, and Sn – 160. The elevated Fe content is attributed to its presence in bornite, the Cu ore mineral, and also in magnetite. The presence of iron oxides suggests that the intermediate product is of lesser quality. In fact, during bronze alloy casting processes, efforts are made to eliminate conditions leading to spinel precipitation and the presence of components like magnetite, a component of post-copper slags, which can complicate smelting processes.

Based on the analysis of the bronze ingots containing copper sulphides, it can be inferred that the copper ores used in their production were rich in copper sulphides rather than copper-iron sulphides. This observation helps exclude the possibility of chalcopyrite ore being used in the production of this type of raw material. The presence of unreacted cassiterite in the alloy indicates that these ingots may have come directly from the ores as virgin, non-recycled raw material. The low-porosity structure of the ingots suggests refining treatments and casting under reducing conditions.

Utilizing the outcomes of indirect assessments, derived from the chemical composition of the extruded ingot's sample, an endeavor was undertaken to scrutinize the resultant contents, with a specific focus on As, Sb, and Ag. The relative concentrations of these elements, in conjunction with other trace elements, might potentially facilitate the identification of the source of the raw material employed in the casting of the ingot. This kind of procedure was used, among others, by Mödlinger and Trebsche in their archaeometallurgical study of a Late Bronze Age hoard from Mahrersdorf in Lower Austria [55] or by Lutz, Krutter and Pernicka in their project "Prehistoric copper production in the Eastern and Central Alps: Technical, social and economic dynamics in time and space", addressing aspects of the Fahlore deposits and technological processes as part of a broader 'chaîne opératoire', subsuming the state of research on prehistoric, Bronze Age and Early Iron Age copper exploitation in the Alps [56].

Overall, this study provides insights into the diverse manufacturing techniques used in the primary centers of bronze ingot production during the Early Iron Age. The techniques range from simple one-piece mold casting to more intricate shaping, forging, and surface refinement processes. It is likely that some of these latter manipulations were carried out at the destination or production sites. The observed variations in manufacturing techniques shed light on the different approaches to raw material procurement and the production of bronze objects during this period.

The analysis of the copper alloy ingots from the Wicina foundry center revealed a complex pattern of raw material management. The ingots, primarily in the form of cast ingots with Cu-Sn binary alloys and minor alloying additions, were used for ongoing casting production. Additionally, so-called master alloy ingots with high iron, antimony, arsenic content were used as a source of alloy additives. Cast Cu-Sn ingots with lower impurity contents were rarer but were likely forged, ground, and polished to emphasize their suitability for further plastic processing. This high-quality raw material was highly valued and chosen for hoarding, as evidenced by its over-representation in the Bieszków hoard.

In conclusion, the study of bronze ingots from Wicina and its surrounding area has shed light on the metallurgical and foundry techniques employed in the Hallstatt period. The variation in ingot composition and manufacturing techniques suggests a sophisticated understanding of alloying and metalworking processes. The deliberate elaboration of higher-quality ingots through forging indicate a desire to showcase the quality of the products. These findings contribute to our understanding of ancient metallurgy and the cultural significance of bronze production and hoarding practices in the Wicina region.

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Conflict of Interest

The authors declare no conflicts of interest.

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