archaeometry

Archaeometry **57**, 4 (2015) 653–676 doi: 10.1111/arcm.12104

THE COMPOSITION AND MICROSTRUCTURAL VARIATION OF THE BRONZE AGE METAL ORNAMENTS FROM LOWER SILESIA (SOUTH-WEST POLAND): CHEMICAL ANALYTICAL AND ARCHAEOLOGICAL ASPECTS*

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Metal ornaments from Únětice *(Mierczyce, Tomice, Jordanów and Opatowice) and* Urnfield *culture (Szprotawa, Żarek and Wrocław Żerniki) sites in south-west Poland are made of bronze of varying composition, with the exception of the early Bronze Age Przecławice site, where the copper items are found in graves from stages III/IV. The combined XRF and electron microprobe study of 37 ornaments (mostly pins) shows that those excavated from* Únětice *culture graves usually consist of cored dendrites, plus a Sb-rich phase in some. The copper objects from Przecławice correspond in composition to the East Alpine Copper or to the Ösenring copper and were produced from fahlore. Those from the* Urnfield *culture sites consist of homogeneous bronze. The* Únětice *culture ornaments were produced with little control of the effect of varying bronze composition on its microstructure. The results of XRF analyses of heterogeneous metal artefacts vary depending on the proportion of phases in the analysed site, and should be combined with micrometre-scale analytical data and microstructural information yielded by electron microprobe methods. The same refers to deeply weathered or corroded objects made of homogeneous metal, which contain irregularly dispersed decomposition products.*

KEYWORDS: ÚNĚTICE CULTURE, *URNFIELD* CULTURE, BRONZE AGE, SOUTH-WEST POLAND, BRONZE, COPPER, MICROSTRUCTURE, CHEMICAL COMPOSITION

INTRODUCTION

Knowledge about the chemical composition and internal microstructure of prehistoric metal artefacts is essential in their characterization. The chemical composition (major and trace elements) as well as the lead isotopic ratios are commonly studied in bronze and copper artefacts in order to gain knowledge about the ore provenance and the applied technology (e.g., Pernicka 1999 and references therein). Methods that allow chemical analyses without destruction of the studied item are obviously preferred during archaeological studies. However, in order to get information on the microstructure of the metal, it is usually necessary to prepare a section of the metal and this requires the cutting of small fragments of the artefacts.

We studied Bronze Age metallic ornaments from south-west Poland by means of XRF and electron microprobe methods. The first of these requires minimal action on the studied artefact (it is necessary to clean the analysed spot), whereas the other requires the preparation of metal

*Received 21 September 2013; accepted 5 February 2014
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sections. XRF analysis by machine, as applied by us, yields the composition of a spot the size of which is slightly less than 1 mm^2, whereas the electron microprobe method is able to analyse a 1 µm spot and to show the microstructure of the analysed site on the scale of few micrometres. Our intention was (1) to compare the results yielded by the two methods, which operate at different scales, and (2) to obtain microstructural and compositional data on the possibly broad spectrum of artefacts coming from the area of Lower Silesia in south-west Poland. We have studied the artefacts of the *Únětice* culture, found at five sites in south-west Poland, and those from the younger *Urnfield* culture (three sites). A significant part of the study was devoted to ornaments coming from the Przecławice cemetery in south-west Poland, 30 km south of Wrocław (Fig. 1). The cemetery is located in a region of very dense early Bronze Age settlements; however, the site is unique because the graves come from all stages of the *Únětice* culture. The other studied sites are Mierczyce, Tomice, Jordanów and Opatowice (the *Únětice* culture) plus

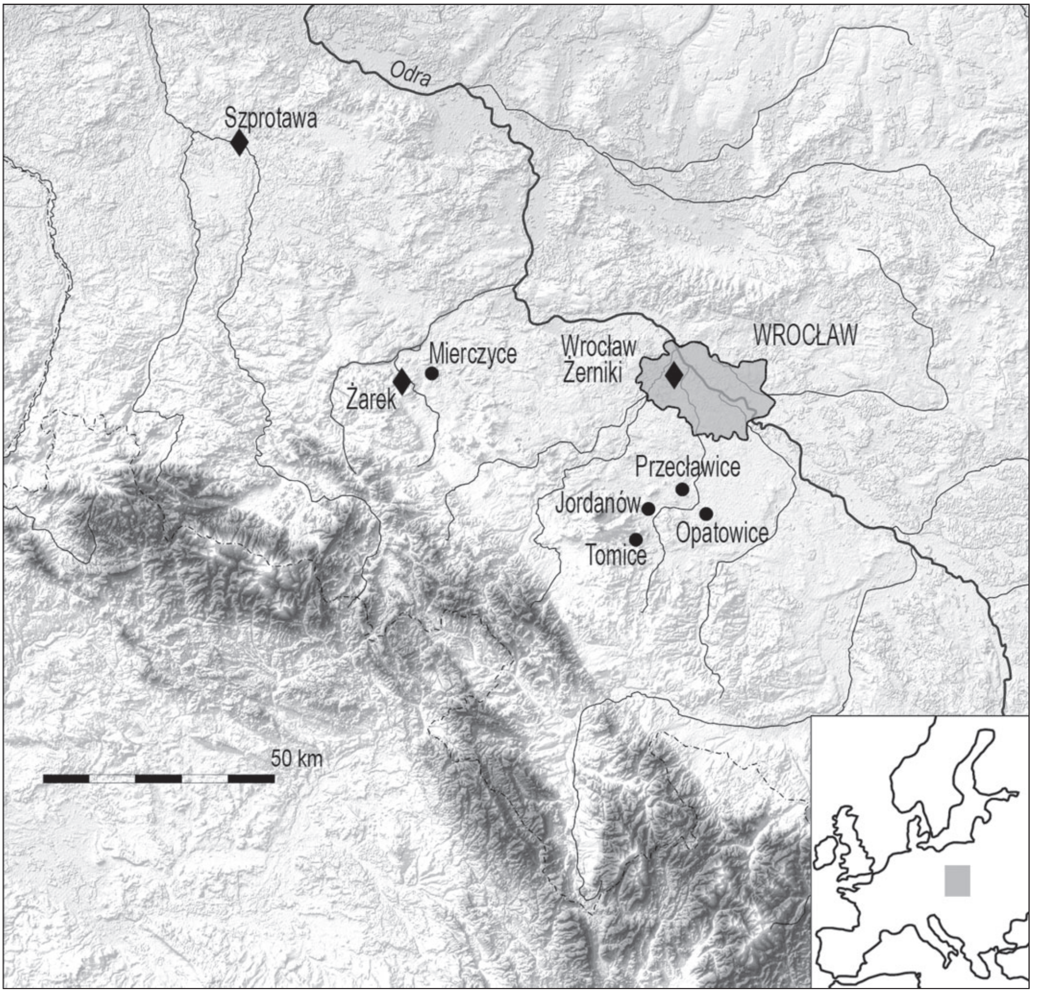

Figure 1 *The studied Bronze Age sites in south-west Poland.*

Żarek, Wrocław Żerniki and Szprotawa (the *Urnfield* culture). Our study shows that the XRF analyses are representative only for artefacts made of homogeneous metal. If the bronze or copper is heterogeneous and consists of two or more phases, the combination of both XRF and the electron microprobe method is necessary to get reasonable results.

ANALYTICAL METHODS

Small (1–2 mm) fragments of the studied artefacts were cut off, mounted in resin (Araldite) rings and polished. The polished surfaces were examined using a reflected light petrographic microscope and studied by the electron microprobe method and by X-ray fluorescence. The choice of analytical points for the electron microprobe analyses was done in the BSE (backscattered electron) image, which provided detailed microstructural and compositional information on the studied phases. We used both polished sections and cleaned spots on the artefacts for the XRF analyses.

To study the compositional variation in bronze and copper artefacts, we analysed for Cu, Sn, Sb, As, Ni, Fe and Pb. We also included Al, Si, Zn and S in the electron microprobe analytical protocol and Ag in the XRF one. This was to verify samples for contamination during polishing (Al) or to analyse the weathering phases and/or sulphide droplets using the same machine set-up. One set of electron microprobe analyses revealed the Al content (up to 0.6 wt%) in the analysed metals that had been polished using Al powder; the use of diamond powder eliminated that effect.

The CAMECA SX100 electron microprobe in the laboratory of the Department of Lithospheric Research at the University of Vienna, Austria was used to analyse the major element composition of phases. We used typical conditions for microprobe analyses, with pure metals as standards, except for Pb, Sb and As (standards, respectively, PbO, InSb and GaAs). Counting times of between 20 and 40 s (peak) were used, except for As, for which the peak counting time was 80 s. This assured the following detection limits (approximate values in ppm): Al, Si, 330; S, 380; Sb, 2200; Fe, 360; Ni, 530; Cu, 2000; Zn, 830; As, 900; Sn, 1400; Pb, 1450. The Zn, Fe, Pb and S occur in concentrations <0.09 wt% in the studied artefacts, except for the higher contents of S in sulphide droplets.

The 'bulk' metal composition was determined by XRF (using a Spectro Midex X-ray fluorescence spectrometer with energy dispersion), equipped with a molybdenum X-ray lamp, with an excitation energy of 44.6 kV, and a Si Drift Detector (SDD) with 150 eV resolution. For calibration, Certified Reference Material BCR 691 of the Institute for Reference Materials and Measurements was used. The analysed spot size was ~0.7 mm. The detection limits were as follows: Sn, Sb, 500 ppm; Pb, 200 ppm; Fe, 250 ppm; Ni, 150 ppm; Cu, Zn, 100 ppm; As, 50 ppm.

CULTURES AND SITES

The *Únětice* culture, with its characteristic pottery and metalwork, existed across large parts of Central Europe (e.g., Machnik 1977; Zich 1996; Bartelheim 1998). Its relative chronological division is based on P. Reinecke's system (covering early Bronze Age stages A1 and A2) and is composed of several internal stages, with the most developed one called 'the classical stage'. The earlier stages (between two and four, depending on areas studied) are dated to 2350–1950 BC, while the classical one is dated to 1950–1700 BC. In some areas, a post-classical stage was also identified and dated to 1700–1600 BC (e.g., Vandkilde 1996, 140–2).

The most common *Únětice* site types are small cemeteries, containing only a few graves in the older stages and larger cemeteries in the classical stage. Inhumation graves with bodies placed in the foetal position were a prevalent form of disposal; however, cremation graves (in both pit and urn versions) occur at the same cemeteries (Kadrow 2001, 121–3). All artefacts analysed in this study come from inhumation cemeteries.

Cemeteries of cremated burials deposited as urnfields are a pan-European phenomenon starting about 1350–1300 BC; however, cremation graves had been common in many parts of Bronze Age Europe before that date (for more on a cremation rite and the origins of the urnfields, see Mierzwiński 2012). In Poland, urnfields are considered as an essential component of the so-called 'Lusatian culture' that lasted up to about 500 BC; however, this term has been subject to criticism (e.g., Gediga 1984). The analysed artefacts come from graves of varying chronology. The sites of Żarek and Szprotawa are older, while Wrocław Żerniki represents the late stages. The sites and sample contexts are briefly presented in what follows.

Most of the sites are located on the alluvial plane of Lower Silesia, which is filled with fluvioglacial deposits, overlying Neogene sands and clays with brown coal layers. Isolated sand/gravel hills occur in the southern part of the plane, close to the border with the Fore-Sudetic Block, in which the Variscan crystalline basement is uplifted and covered by thin (tens of metres) younger deposits. The sites of Jordanów and Tomice are situated in the Ślęża Massif, in the Fore-Sudetic Block. The Ślęża Massif is the uplifted block of crystalline basement, consisting partly of granites and partly of ophiolitic sequences (gabbros, serpentinites and metabasalts). Jordanów and Tomice are located on serpentinites, and the former is known for the occurrence of nephrite.

Únětice *sites*

Przecławice The site of Przecławice is located 0.9 km south of a contemporary village of the same name, about 30 km south of Wrocław in Poland (Fig. 1). The cemetery, which lies on a north-western slope of a well-defined hill (Fig. 2), was discovered in 1975, when four skeletons were found in course of gravel exploitation in an elongated ~200 m long pit. Excavations were initiated in the same year by Irena Lasak from the Institute of Archaeology, University of Wrocław, Poland, to protect the site from further destruction. A total area of 2050 m^2, containing 51 graves, was explored in the course of a four-season campaign (Lasak 1988). Although the cemetery is located in a region of very dense early Bronze Age settlement, the site is unique due to its wide chronology and broad spectrum of finds. The excavations provided a *jar* grave and well-preserved coffin burials. The properties of the graves and the artefacts—mostly pottery and several metal items—allow the site to be dated to the early Bronze Age, thus representing five stages of the *Únětice* culture. Two ^{14}C dates obtained from two graves at Przecławice (1675 ± 75 and 1545 ± 45 BC) represent the youngest stage of the site use (Lasak 1988). To distinguish between graves of different ages, we follow the chronology defined by Lasak (1988), which was based on the studies of Moucha (1963) and Tichelka (1960). These authors defined the relative chronology based on material remains attributed to the *Únětice* culture. However, many graves contained grave goods of mixed chronological indicators, hence situating them in the transitional periods.

All the sampled artefacts come from variously preserved and furnished skeleton graves dated to various stages of the site use (for details, see Table 1 and Fig. 3). Sampling was not possible from the stage V (the so-called 'classical' stage) items. The individuals were buried in a coffin (grave 12) or lain/wrapped in matting made of organic materials (graves 17, 18 and 33). According to

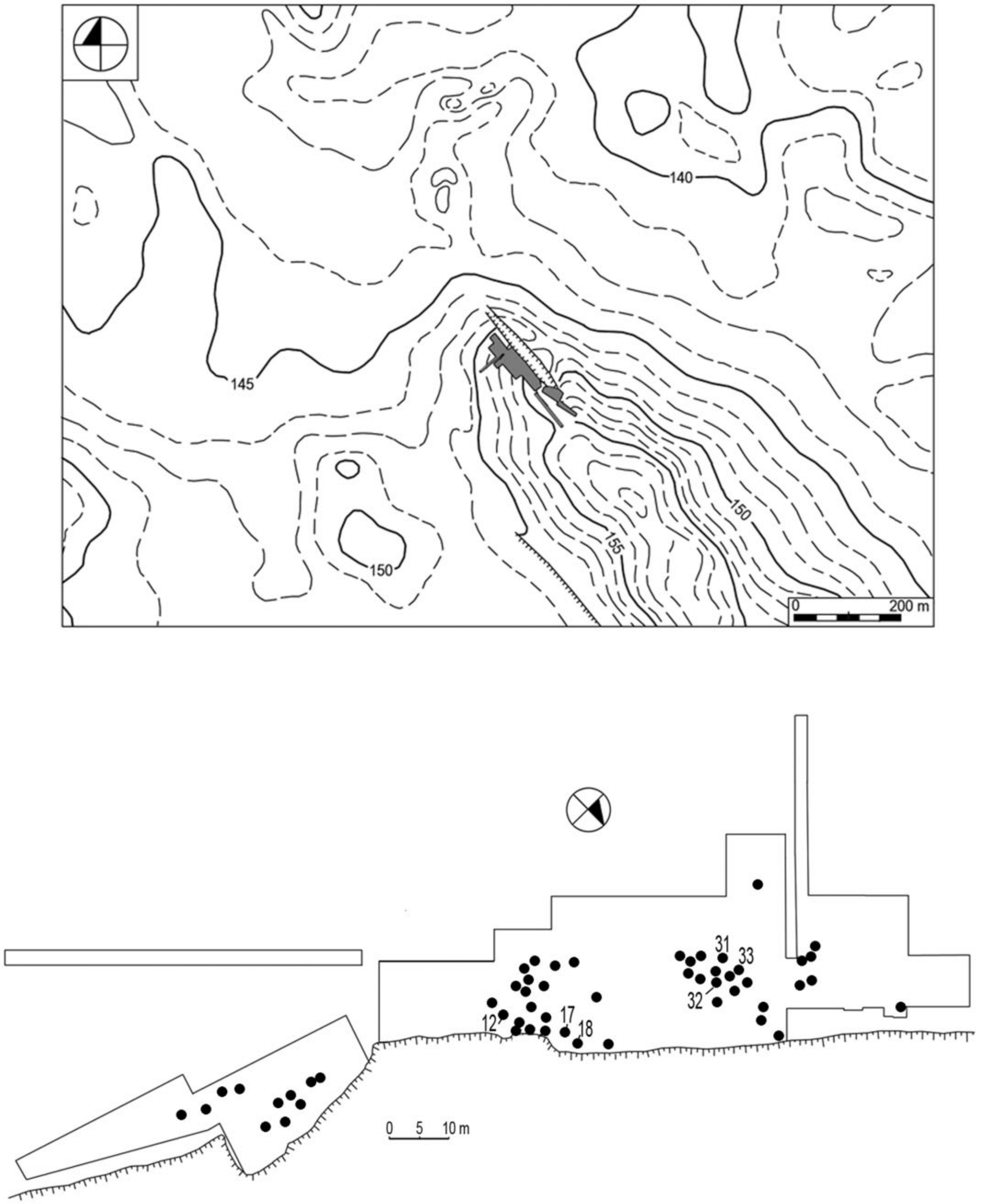

Figure 2 *The morphological situation of the Przecławice site and details of the excavated area. The numbers refer to the graves described in Table 1 (modified from Lasak 1988).*

early Bronze Age tradition, the bodies were arranged in the foetal position along the north–south axis and this rule most probably also applies to the poorly preserved graves (17 and 18).

Since the sample preparation for analyses is destructive, we decided to sample only poorly preserved—that is, already broken—small items (rings and beads) usually located near the skulls

Table 1 *An archaeological overview of the studied artefacts from the Przecławice site*

Sample no.	*Grave no.*	*Sampled artefact*	*Context*	*Relative chronology*	*Grave goods (including sampled ones)*	*Anthropological data*
PZ4	12	Willow leaf shape ring, 2.5 cm in diameter	Northern part of a coffin, between two vessels	UC II/III	Three vessels, metal ring	Two *Infantes I* (aged 1–2 and 5–6), aligned north–south
PZ3, PZ11	17	Two tubular beads, 1.2 and 1.3 cm long, 0.6 cm in diameter	South-eastern part of layer of dark brown soil—probably remains of a coffin or organic lining of the grave pit	UC I	Two vessels, lump of ochre, four metal beads, two stone beads	*Infans I* (6 months)
PZ2, PZ2a	18	Two fragments of two incomplete rings of various sizes	Southern part of layer of dark brown soil—probably remains of a coffin or organic lining of the grave pit, by the skull	UC	Two fragments of metal rings, piece of worked antler, one vessel	*Infans I* (6 months)
PZ5, PZ6	31	Two small rings, ~1.5 cm in diameter	At the skull	UC III/IV	Five small and poorly preserved metal rings, two large metal rings (one incomplete), one metal pin, four vessels (one containing cattle scapula and two ribs)	Female *Maturus* (aged 40–45)
PZ1, PZ7, PZ8, PZ9	32	One large and three small rings (diameters: 1.2, 1.5, 3 cm)	At and beneath the skull	UC III/IV	Three vessels, one large and three small metal rings	Female *Iuvenis* (aged ~20)
PZ10, PZ12	33	Open ring, 1.3 cm in diameter; ring, 1.8 cm in diameter	At the skull, in the layer of dark brown soil—probably remains of a coffin or organic lining of the grave pit	UC III/IV	Four vessels, two bone pins, one metal pin, four poorly preserved metal rings, four vessels	*Iuvenis* (aged 20–22)

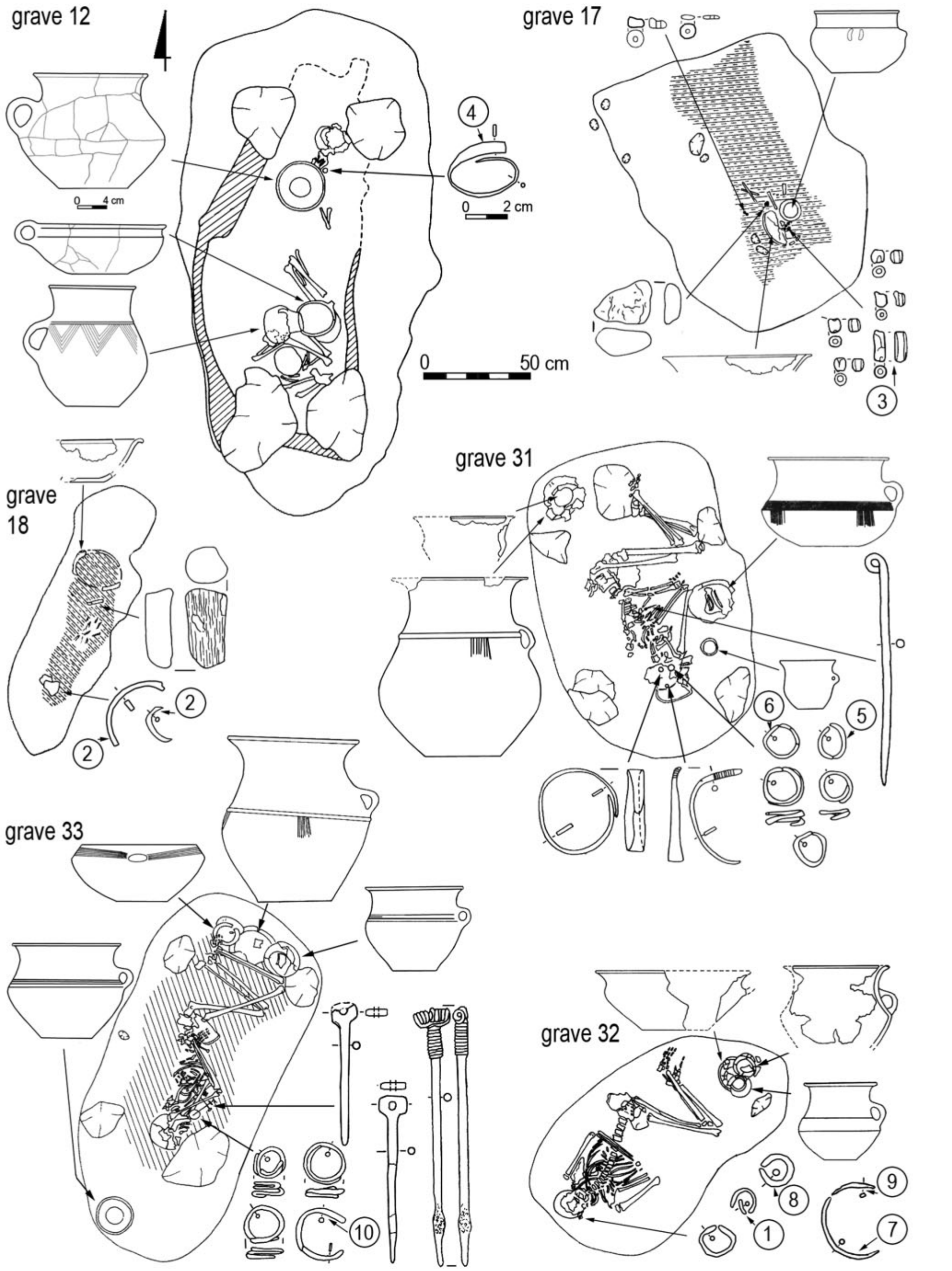

Figure 3 *The archaeological contexts of artefacts from the Przecławice site. The scale bars refer to a grave, pottery and non-pottery artefacts and are common for all graves in the picture (modified from Lasak 1988). The numbers in circles refer those of studied artefacts (cf., Table 1).*

of the buried individuals (Table 1 and Fig. 3). Owing to their location in the graves, they are believed to be parts of simple head decorations.

Jordanów Little is known about this large site, composed of both Neolithic and Bronze Age graves: the results of excavations carried out in the 1930s have never been fully published, and a substantial part of the archaeological evidence was lost during the Second World War. Brief notes mentioned inhumation graves, ceramics and bronze rings (Sarnowska 1969, 267). Some artefacts and bones survived and recently one ^{14}C date was obtained (3505 ± 35 BP; laboratory code Poz-43472, Marta Mozgała pers. comm.). Although it is not from the grave from which the sampled artefact comes, it confirms the late *Únětice* chronology of the site (1926–1741 BC cal).

Tomice This site, which lies on a small hill 550 m north-west of the contemporary village of Tomice, was excavated during two campaigns in 1967–8. In the course of the excavation, Neolithic, Bronze Age and early medieval pits and graves were unearthed. The early Bronze Age cemetery, dated to the classical stage of the *Únětice* culture, consisted of 36 inhumations and three cremation graves and covered an area of 1200 m^2. The complete results, including the archaeological and anthropological data, were published in 1973 (Romanow *et al*. 1973). All the sampled artefacts—three pins, ring and a fragment of a bracelet—come from five inhumation graves (Fig. 4).

Opatowice Human bones and pottery have been unearthed on the Gallow Hill near the village of Opatowice since the late 19th century and professional archaeological excavations in 1895 revealed two complete inhumation graves. Documentation stored in the Wrocław Museum shows that the site comprised about 20 graves. The report on the site has never been published and the documentation was mostly lost during the Second World War. The analysed artefact comes from one of the graves, but any precise context remains unknown.

Mierczyce The cemetery was discovered by chance and excavated in 1967. In total, 18 inhumation graves were unearthed in a small area (Kaletyn 1975). The bone materials are gone but the artefacts represent typical inventories of the classical stage of the *Únětice* culture. For this study, five artefacts from three graves were sampled (Fig. 5).

Urnfield *sites*

Wrocław Żerniki The site at Wrocław Żerniki was discovered by chance in 1925 but excavated in 2009 in advance of constructing the Wrocław motorway bypass. In total, 59 cremation graves were unearthed in the investigated area (Baron *et al*. 2010). A general chronology of the cemetery based on artefact studies covers late stages of the Bronze Age and early Iron Age (1100–700/600 BC). No absolute dating was possible due to poor preservation of the cremated bones and low collagen content. One artefact from this site, from an urn in grave 18, was analysed and dated to 900–700 BC.

Żarek This site was investigated in the 1970s as a rescue excavation and the results have never been fully published; thus the total number of excavated graves is unknown and part of the materials are lost. Both a settlement and a cemetery were discovered and their chronology covers both various stages of the Bronze Age and early Iron Age (~1300–700 BC). The sampled items

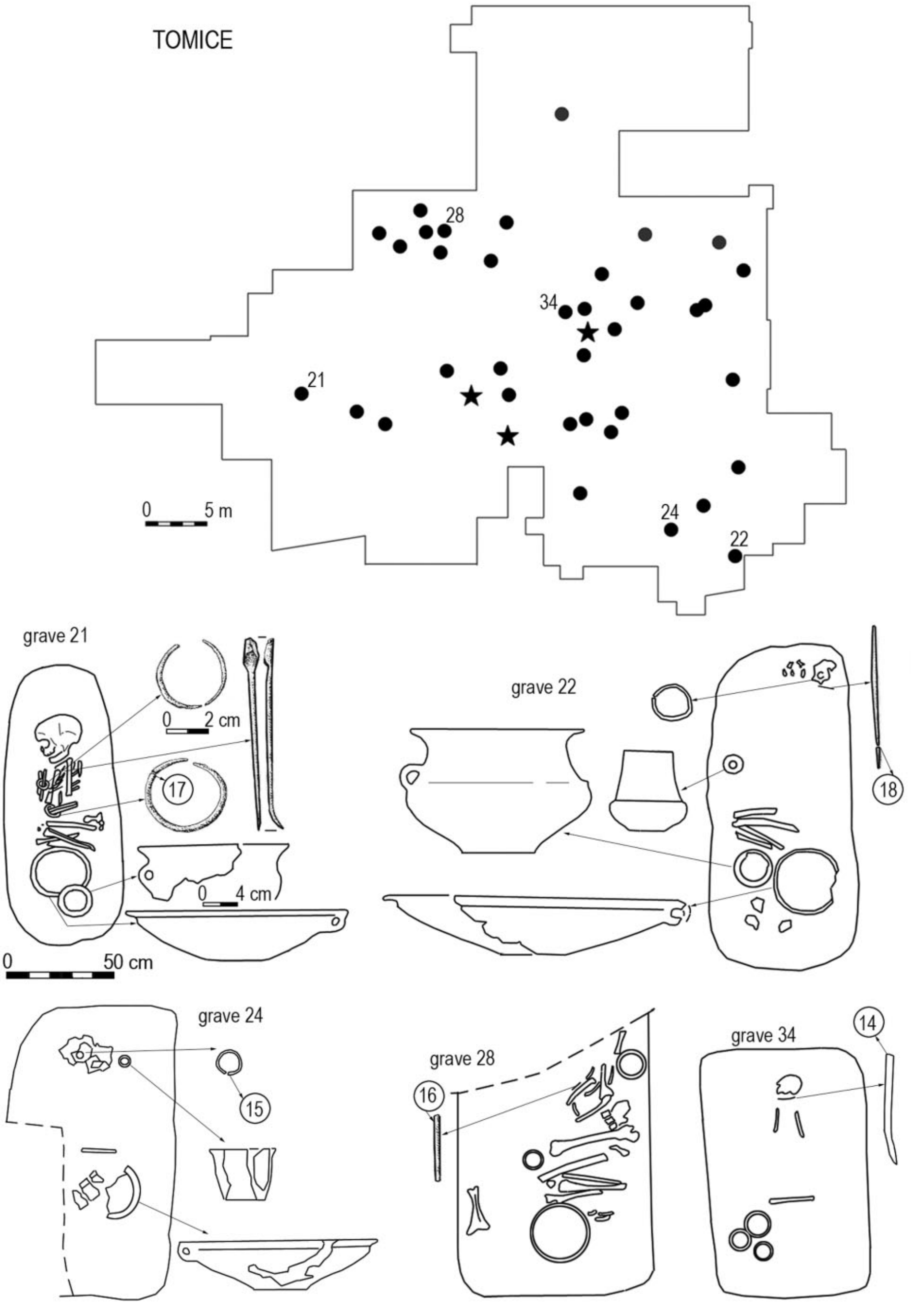

Figure 4 *The archaeological contexts of artefacts from the Tomice site. The numbers in circles refer to those of studied artefacts (cf., Table 2).*

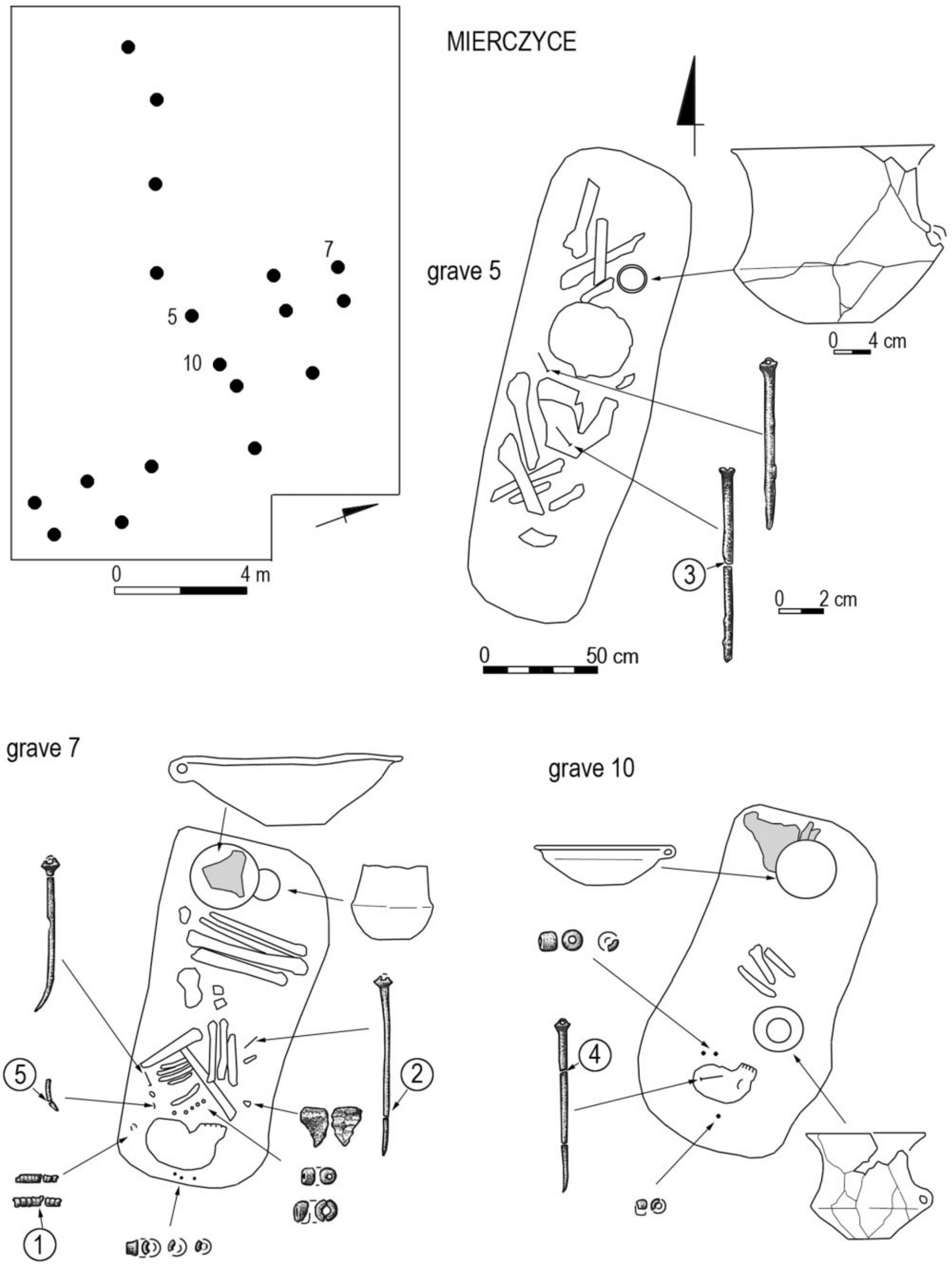

Figure 5 *The archaeological contexts of artefacts from the Mierczyce site. The numbers in circles refer to those of studied artefacts (cf., Table 2).*

come from three cremation graves excavated in 1977 and dated to early stages of the *Urnfield* culture (1300–1100 BC).

Szprotawa Five urn graves were excavated in during a rescue survey in 2012. Several stray finds of fragmented vessels and cremated bones accompanied the graves. Two of the graves were furnished with four metal items, one in grave 2 and three in grave 4 (Fig. 6). The bones from these graves gave two similar ^{14}C dates; that is, 2970 ± 35 BP for grave 2 and 2935 ± 30 BP for grave 4 (Table 2). These results correspond with the traditional, artefact-based chronology covering early stages of the *Urnfield* culture which, in this area, is dated to 1300–1100 BC (Lasak 2001, 30–3; Kaczmarek 2002, 290–1).

THE MICROSTRUCTURE AND COMPOSITION OF THE ARTEFACTS

Most of the studied artefacts are pins made of bronze. Besides copper and tin, some of them contain significant antimony, arsenic and nickel (see Tables 3–5 below). The silver content is <1 wt%, in many cases <0.1 wt%. The description presented in the following is based on the electron microprobe analyses. The XRF analyses are not used in the description but are included in Figures 8–12 below.

Únětice *culture, stages I and II/III*

The oldest ornaments (*Únětice* culture, stages I and II/III) available for this study come from the Przecławice site. Five small beads come from grave 17 in Przecławice, dated to stage I. They are covered by carapace of weathering products (Fig. 7 (a)) and consist of dendritic aggregates (cored dendrites) of composition B containing ~10–15 wt% of Sn (Table 3) embedded in a ~20–25 wt% Sn host A (Table 3, samples PZ3 and PZ11). The host is one of the most tin-rich compositions found in all of the analysed artefacts of the *Únětice* culture (cf., Figs 8–11). In the first analysed bead, alloy A contains significant amounts of As and Sb, whereas alloy B is impoverished in those elements (Table 3 and Fig. 8). The metal forming the second analysed bead is very pure and contains practically no other elements except for Cu and Sn (Table 3, sample PZ11).

The artefact coming from the Przecławice grave 12, dated to *Únětice* stage II/III, is homogeneous metal with small voids (Fig. 7 (b)), containing ~10 wt% of Sn. The metal is pure and contains no significant amounts of Sb, As or other elements (Table 3, sample PZ4).

Únětice *culture, stages III/IV*

The artefacts coming from the graves in the Przecławice site dated to *Únětice* stage III/IV consist of copper (>95 wt% Cu) and contain no tin (Table 3, samples PZ1, PZ2, PZ4, PZ5, PZ7, PZ8, PZ9, PZ10 and PZ12). They differ in their Sb, As and Ni contents (Fig. 5). In most of them the metal is homogeneous: some of the ornaments contain scarce, micrometre-size droplets of apparently immiscible Sb or Sn. Because of their small size, only qualitative analyses of these droplets by the EDS method were possible. Only one of the studied items exhibits a well-defined parallel arrangement of voids and intergrowths, suggestive of forging (Fig. 7 (c)). That one, plus another of stage III/IV, contain fine grains of copper sulphide (Cu_2S; Table 3, sample PZ2). The following compositional types can be defined in those artefacts:

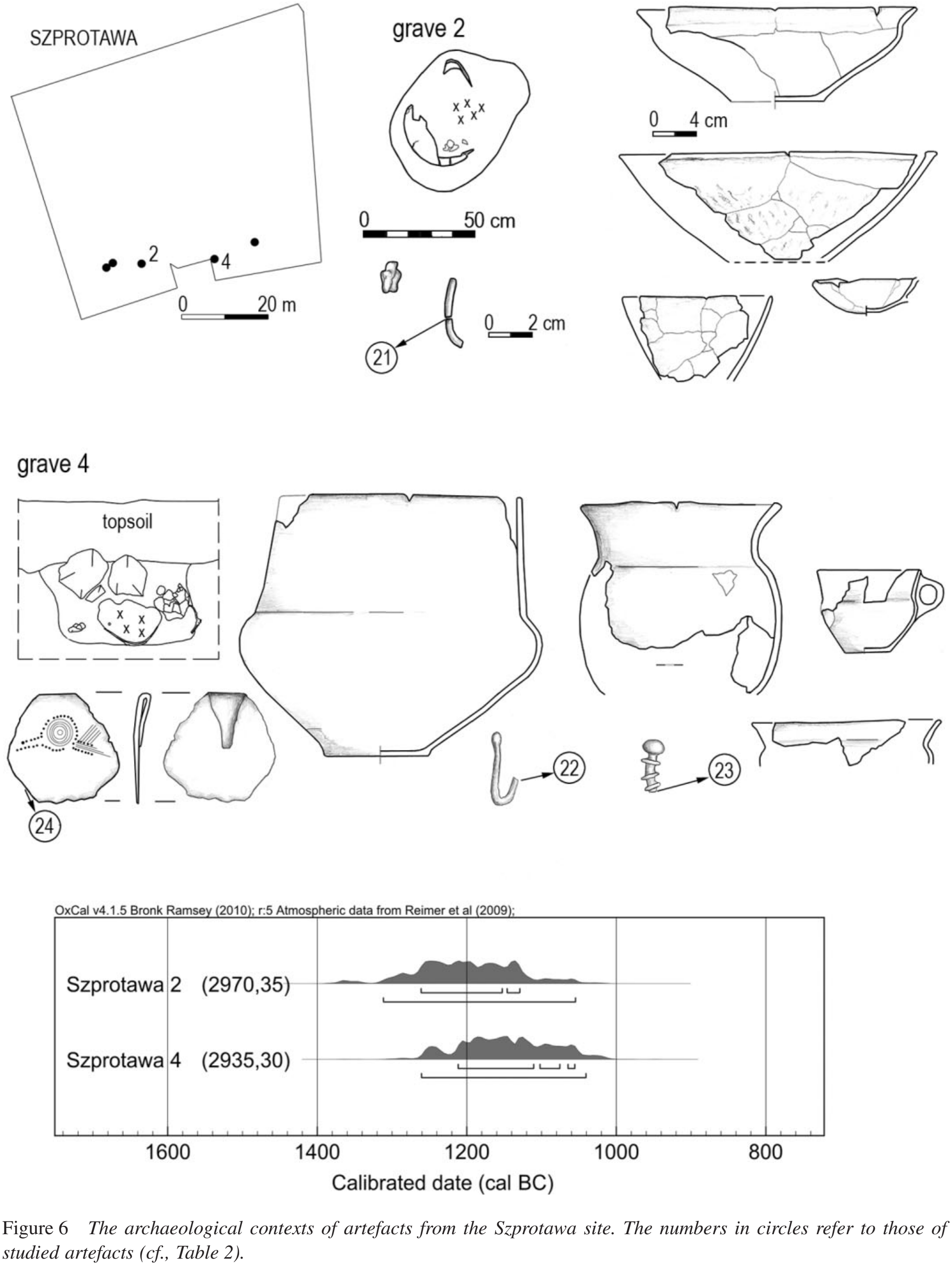

Figure 6 *The archaeological contexts of artefacts from the Szprotawa site. The numbers in circles refer to those of studied artefacts (cf., Table 2).*

Table 2 *An archaeological overview of the studied artefacts from Lower Silesia*

Sample no.	*Grave no.*	*Sampled artefact*	*Context*	*Relative chronology*	*Absolute chronology*	*Grave goods (including sampled ones)*	*Anthropological data*
Mierczyce site							
3	5	Pin	Skeleton grave	Classical stage of the *Únětice* culture	1950–1700 BC	Two ceramic vessels, two metal pins	Male, *adultus*
1	7	Ring				Two ceramic vessels, six amber beads, metal rings, two metal pins, one flint arrowhead	*Maturus/senilis*
2	7	Pin					
5	7	Pin					
4	10	Pin				Two ceramic vessels, three amber beads, metal pin	*Infans I* (7 years)
Tomice site							
14	34	Pin	Skeleton grave	Classical stage of the *Únětice* culture	1950–1700 BC	Three ceramic vessels, metal pin	*Infans I*
15	31	Ring				Two ceramic vessels, metal pin, two hand stones	*Adultus/maturus*
16	28	Pin				Three ceramic vessels, metal pin, cow scapula	*Adultus*
17	21	Bracelet				Two ceramic vessels, metal pin, two metal bracelets	*Infans II*
18	22	Pin				Three ceramic vessels, metal pin, metal ring	Female, *maturus*
Jordanów site							
19	163	Pin		*Únětice* culture	2350–7600 BC	No data available	No data available
Opatowice site							
20		Pin		Classical stage of the *Únětice* culture	1950–1700 BC	No data available	No data available
Żarek site							
8	2	Pin	Cremation grave	Early stage of the *Urnfield* culture	1300–1100 BC	Three ceramic vessels, three pieces of metal pin	No data available
6	13	Pin?				Two ceramic vessels, metal item (pin?)	
7	36	Pin?				No data available	
21	2	Pin	Cremation grave	Early stage of the *Urnfield* culture	2970 ± 35 BP (Poz-51497) 1312–1055 BC	Four ceramic vessels, three pieces of metal pin	*Adultus*?
Szprotawa site							
22	4	Pin			2935 ± 30 BP (Poz-51500) 1261–1041 BC	Four ceramic vessels, turned pin, piece of a pendant, head of a pin	*Adultus*?
23	4	Pin					
24	4	Piece of a pendant					
Wrocław Żerniki site							
1Z	18	Pin	Cremation grave	Late stage of the *Urnfield* culture	*c*.900–800 BC	Eight ceramic vessels	Male, *adultus*

Table 3 *Representative electron microprobe analyses of the studied Przecławice artefacts (wt%)*

Sample	*Description*	*Cu*	*Sn*	*Sb*	*As*	*Ni*	*Pb*	*S*	*Total*
PZ3	Grave 17, bead A, dendrite composition A	77.22	20.45	1.24	1.47	0.01	0	0.04	100.43
PZ3	Grave 17, bead A, dendrite composition B	87.59	12.05	0.20	0.64	0	0	0.01	100.49
PZ11	Grave 17, bead B, dendrite composition A	75.37	25.29	0.05	0	0	0	0	100.71
PZ11	Grave 17, bead B, dendrite composition B	85.86	14.86	0.04	0	0	0	0.01	100.77
PZ4	Grave 12, ring	90.86	9.47	0	0	0.05	0	0.02	100.40
PZ5	Grave 31, ring	95.85	0	0.52	2.75	0.45	0	0	99.57
PZ1	Grave 32, ring A	98.51	0.05	0.32	0.53	0	0.08	0.02	99.51
PZ7	Grave 32, ring B	96.16	0.68	1.22	0.36	1.13	0.09	0.01	99.65
PZ8	Grave 32, ring C	97.37	0	1.19	1.11	0	0	0.02	99.69
PZ9	Grave 32, ring D	95.85	0.63	0.98	0.68	1.56	0	0.01	99.71
PZ10	Grave 33, ring A	96.60	0.04	0.82	0.25	1.20	0.02	0	98.93
PZ12	Grave 33, ring B	91.71	0.13	2.17	1.24	4.40	0	0.01	99.66
PZ2	Grave 18, ring	87.15	10.02	1.37	0.28	1.62	0.05	0.03	100.52
PZ2	Grave 18, ring, droplet of Cu_2S	78.83	0.04	0	0	0.02	0.17	20.39	99.45

(1) (Sb + Ni)-enriched—ring 'B' from grave 33;
(2) As-enriched, Ni-poor—the ring from grave 31;
(3) As-bearing, Ni-free—ring 'C' from grave 32;
(4) mixed 1, containing small amounts of As, Sb and Ni—rings 'B' and 'D' from grave 32 and ring 'A' from grave 33; and
(5) mixed 2, containing small amounts of As and Sb, but no Ni—rings 'A' and 'C' from grave 32.

Únětice *culture, classical stage*

The studied set of ornaments comprises those from Tomice (three pins, one ring and one bracelet), Mierczyce (four pins and one ring) and two pins from Jordanów and Opatowice. They consist mainly of copper and all except one contain significant amounts of tin (cf., Figs 10 and 11).

The studied set of ornaments from Tomice contains two pins (graves 28 and 32) made of metal consisting of cored dendrites and Sn-rich eutectoid (Fig. 7 (d)). The end compositions of the cored dendrites contain approximately 11 and 6 wt% of tin, whereas the eutectoid contains 24 wt%; the Sn-richer compositions are also richer in Sb and As (Table 4, sample 16, and Fig. 10). They contain small amounts of Ni (~0.10–0.20 wt%). Two ornaments—the ring from grave 31 and the pin from grave 22—are made of homogeneous metal containing ~96 wt% of Cu and only 1 wt% of Sn, with small amounts of Sb and As (<1 wt% each) and traces of Ni (~0.10 wt%, Table 4, analysis samples 15 and 18). The bracelet from grave 21 is made of homogeneous metal containing ~93 wt% of Cu and 5 wt% of Sn plus some Sb and As (<1 wt% of each; Table 4, sample 17, and Fig. 10). The homogeneous metals contain sparse, small droplets of Ag-, (Ag + Bi)- or Sn-rich alloys.

The pins from Mierczyce exhibit a dendritic microstructure formed of the Sn-enriched (Sn ~ 9–11 wt%) and Sn-impoverished (Sn ~ 6 wt%; Table 4, samples 4 and 2) compositions,

Table 4 *Representative electron microprobe analyses of the studied artefacts from classical-stage* Únětice *culture sites and* Urnfield *culture sites (wt%)*

Sample	*Description*	*Cu*	*Sn*	*Sb*	*As*	*Ni*	*Pb*	*S*	*Total*
16	Tomice, grave 31, pin, eutectoid	71.38	24.66	2.55	0.65	0.20	0.01	0	99.45
16	Tomice, grave 31, pin, Sn-rich dendrite composition	88.76	10.13	0.62	0.52	0.12	0	0	100.15
16	Tomice, grave 31, pin, Sn-poor dendrite composition	93.63	5.72	0.11	0.15	0.14	0	0	99.75
15	Tomice, grave 31, ring	96.81	0.95	0.66	0.55	0.13	0.04	0	99.14
18	Tomice, grave 22, pin	96.79	1.19	0.78	0.67	0.11	0	0.01	99.55
17	Tomice, grave 21, bracelet	93.05	5.01	0.72	0.81	0.05	0	0	99.64
4	Mierczyce, grave 10, pin, Sn-rich dendrite composition	86.35	11.41	1.10	0.57	0.03	0.03	0.01	99.50
4	Mierczyce, grave 10, pin, Sn-poor dendrite composition	92.94	6.49	0.51	0.38	0.06	0.05	0.02	100.45
2	Mierczyce, grave 7, pin, Sn-rich dendrite composition	88.48	9.62	0.79	0.65	0.04	0	0.01	99.59
2	Mierczyce, grave 7, pin, Sn-rich dendrite composition	93.29	6.06	0.59	0.68	0	0.03	0.01	100.66
3	Mierczyce, grave 5, pin, eutectoid	69.46	24.55	6.06	0.26	0.16	0	0	100.49
5	Mierczyce, grave 7, pin, eutectoid	65.47	16.90	13.83	2.33	0.07	0	0	98.60
1	Mierczyce, grave 7, homogeneous ring	90.74	9.90	0.02	0	0.04	0	0.01	100.71
19	Jordanów, pin	88.88	10.62	0	0	0.25	0.01	0	99.76
20	Opatowice, pin, eutectoid	74.52	21.91	2.04	0.75	0.06	0	0	99.28
20	Opatowice, pin, Sn-rich dendrite composition	86.99	11.05	0.80	0.51	0.04	0	0	99.39
20	Opatowice, pin, Sn-poor dendrite composition	91.89	6.72	0.34	0.30	0.05	0.05	0.01	99.36

Table 5 *Representative electron microprobe analyses of the studied* Urnfield *culture artefacts (wt%)*

Sample	*Description*	*Cu*	*Sn*	*Sb*	*As*	*Ni*	*Pb*	*S*	*Total*
21	Szprotawa, grave 2, pin	91.15	5.82	0.76	0.30	0.95	0.11	0	99.09
22	Szprotawa, grave 4, pin 22	90.57	8.08	0.12	0.25	0.58	0.03	0	99.63
23	Szprotawa, grave 4, pin 23	91.31	6.90	0.10	0.37	0.53	0.04	0.01	99.26
24	Szprotawa, grave 4, pendant fragment	92.53	6.58	0.11	0.02	0.11	0	0	99.35
7	Żarek, grave 36, pin?	96.35	3.18	0	0.15	0.37	0.03	0	100.08
8	Żarek, grave 2, pin	93.71	4.95	0	0.29	0.41	0	0	99.36
6	Żarek, grave 13, pin?	87.94	12.61	0.09	0	0.05	0	0	100.69
6	Żarek, grave 13, pin?, inclusion of Cu–Sn	66.10	33.32	0.03	0	0.37	0.03	0	99.85
1Z	Żerniki, grave 18, pin	93.94	3.61	1.03	0.29	0.42	0.12	0.01	99.42

containing small amounts of Sb and As, and no Ni (Fig. 10). The Sn-enriched composition is also richer in Sb and As (cf., Table 4 and Fig. 10). The metal of the pins contains common small (typically a few micrometres) angular to rounded droplets of Cu–Sn–Sb–As eutectoid (Table 4, analyses 5 and 6) and those of pure Ag, or Bi–Ag, alloy. The ring is made of strongly weathered homogeneous bronze metal containing ~10 wt% of Sn and practically no Sb, As or Ni (Fig. 7 (e) and Table 4, sample 1).

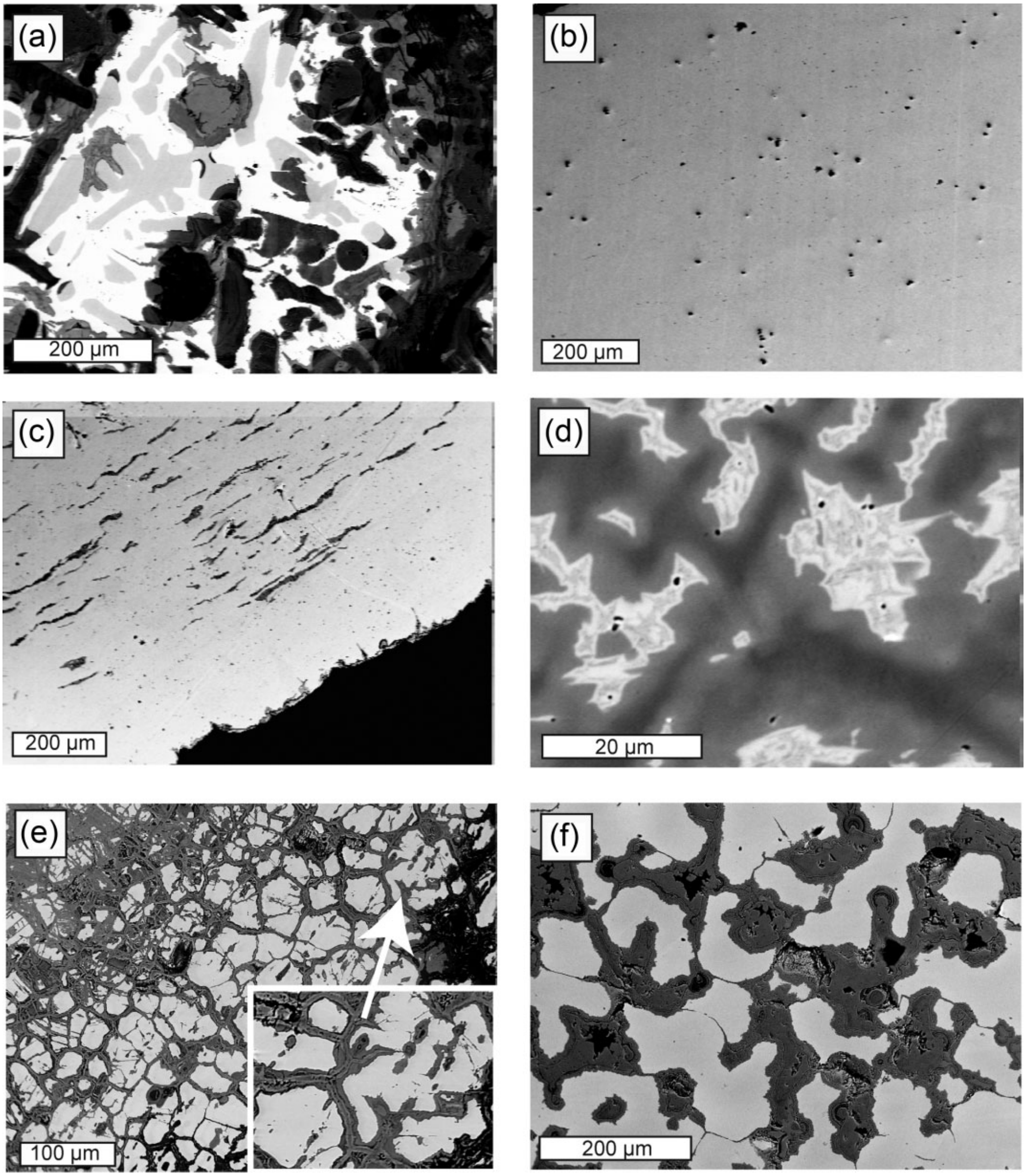

Figure 7 *Representative microstructures of the studied ornaments (BSE images). (a) Przecławice: the heavily weathered bead 'B' from grave 17 (*Únětice *stage I). The weathering products (grey, dark grey) surround the metallic core of the bead, which consists of dendrites (sample PZ11 in Table 1). (b) Przecławice: the homogeneous microstructure of the ring from grave 12 (*Únětice *stage II/III). This kind of microstructure occurs in all* Únětice *stage III/IV samples (sample PZ4 in Table 1). (c) Przecławice: the directional microstructure of the ring from grave 32 (*Únětice *stage III/IV), suggesting forging. The elongated black lamellae are voids (sample PZ8 in Table 1). (d) Tomice: an enlarged view of cored dendrites with Sn–Sb rich eutectoid (sample 16 in Table 2). (e) Mierczyce: the deeply weathered, homogeneous bronze ring. The inset shows an enlarged part of the ring, with fine intergrowths of weathering products in the bronze (sample 1 in Table 2). (f) Szprotawa: the weathered pin made of homogeneous bronze (sample 23 in Table 2).*

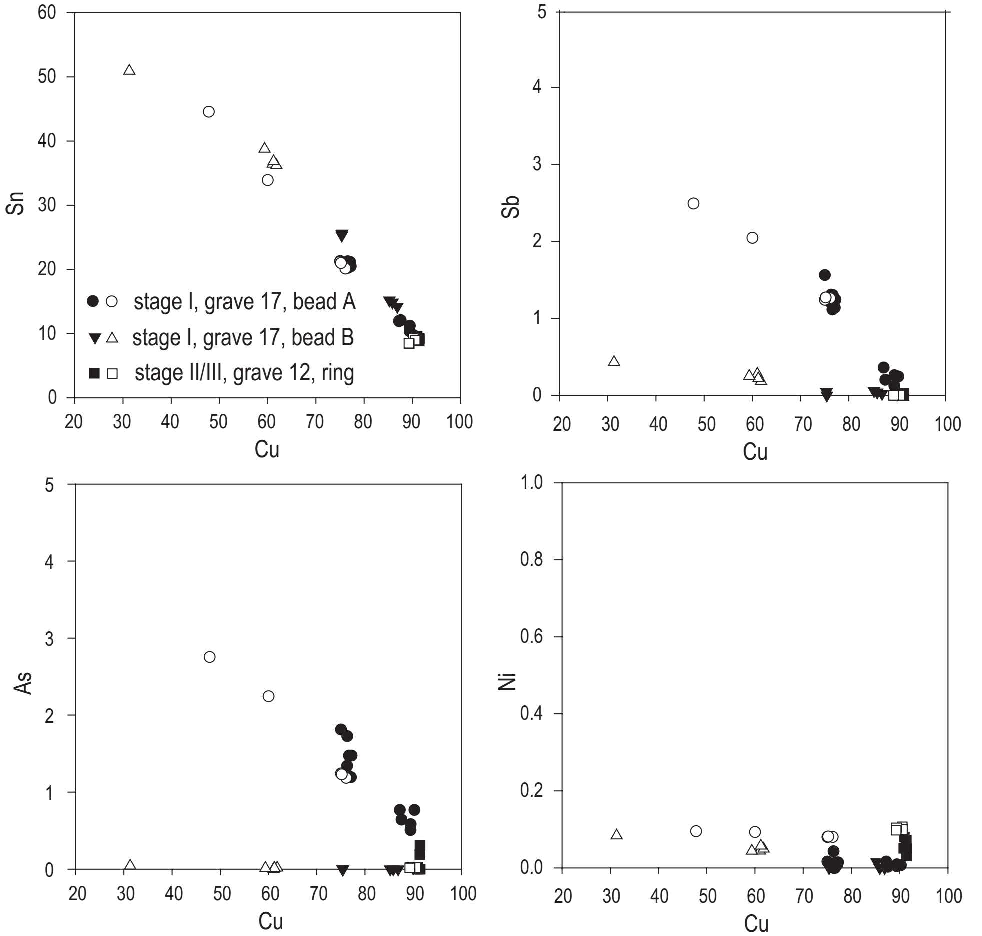

Figure 8 *Cu versus Sn, Sb, As and Ni variation diagrams (in wt%) for the artefacts from Przecławice, stages I and II/III. The solid symbols are for electron microprobe analyses, and the open ones are for XRF analyses.*

The composition of the metal forming the dendritic microstructure changes gradually, showing that these are cored dendrites. The changing composition results in a spread of the analytical results: those analyses that yield maximal values for each phase are supposedly the end-members of the cored dendrites.

The pin from Jordanów is made of homogeneous metal containing ~90 wt% of Cu, 10 wt% of Sn, no Sb or As and some (~0.3 wt%) Ni (Table 4, sample 19). The pin from Opatowice is made of dendritic-microstructure metal with characteristics similar to those of the dendritic metal of the pins from graves 28 and 32 at Tomice (Table 4, analyses 15–17).

Urnfield *culture, early stages*

The studied artefacts are made of homogeneous metal, exhibiting granular microstructure upon weathering (Fig. 7 (f)). The ornaments from Szprotawa (three pins and one fragment of pendant) contain ~6–8 wt% of Sn and 91–92 wt% of Cu plus small (<1 wt% each) amounts of Sb, As, Ni

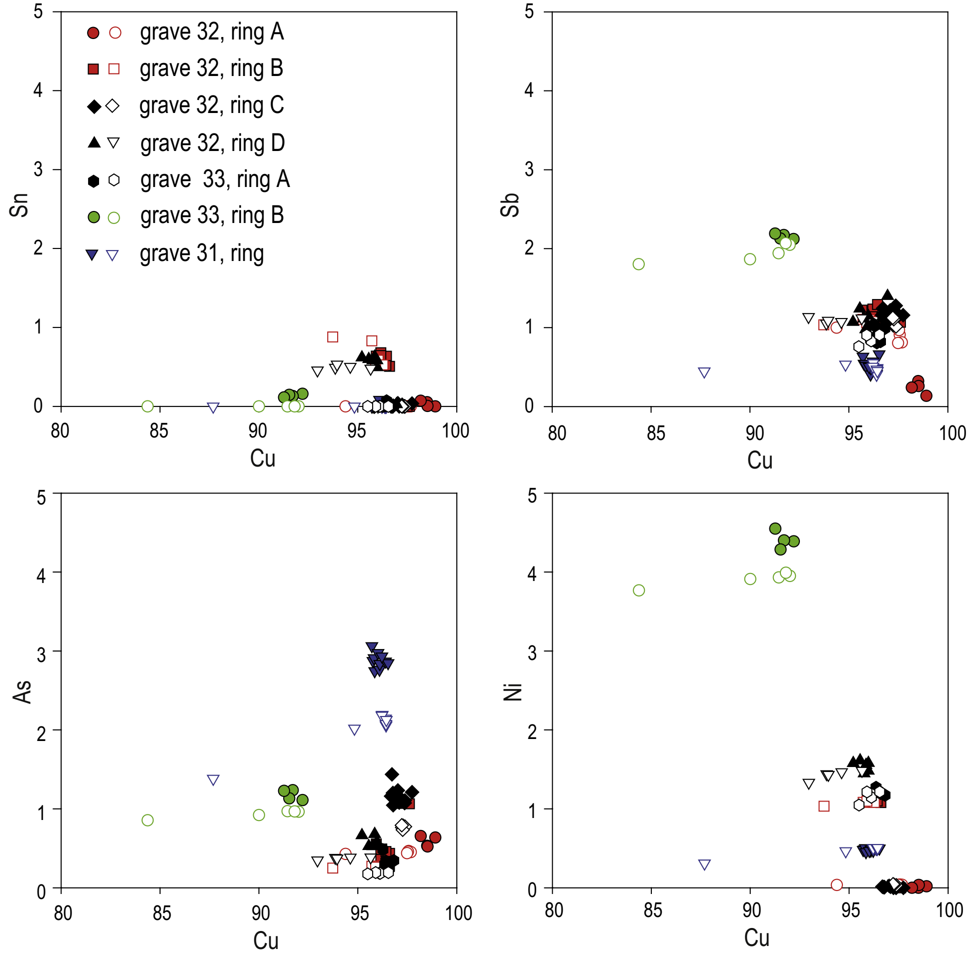

Figure 9 *Cu versus Sn, Sb, As and Ni variation diagrams (in wt%) for the artefacts from Przecławice, stage III/IV. The solid symbols are for electron microprobe analyses, and the open ones are for XRF analyses.*

and (the pin from grave 2) Ag (Fig. 12 and Table 5, samples 21–24). Two pins from Żarek contain 3–5 wt% of Sn and 93–96 wt% of Cu, some Ni (~0.4 wt%) and practically no other elements (Fig. 12 and Table 5, samples 7 and 8). The third one is much richer in Sn (~12 wt%) and contains 88 wt% of Cu and practically no other elements (Fig. 12 and Table 5, sample 6). It contains small (a few micrometres) inclusions of Sn-rich alloy (Table 5). The pin from Żerniki comes from the late stage of the *Urnfield* culture. It contains ~4 wt% of Sn and 94 wt% of Cu, significant Sb (~1 wt%) and some As, Ni and Pb (Fig. 12 and Table 5, sample 1Z).

DISCUSSION

The effect of the analytical method

The standard analytical approach to the composition of prehistoric metal artefacts comprises the analyses of elements the content of which in individual phases forming the metal exceeds

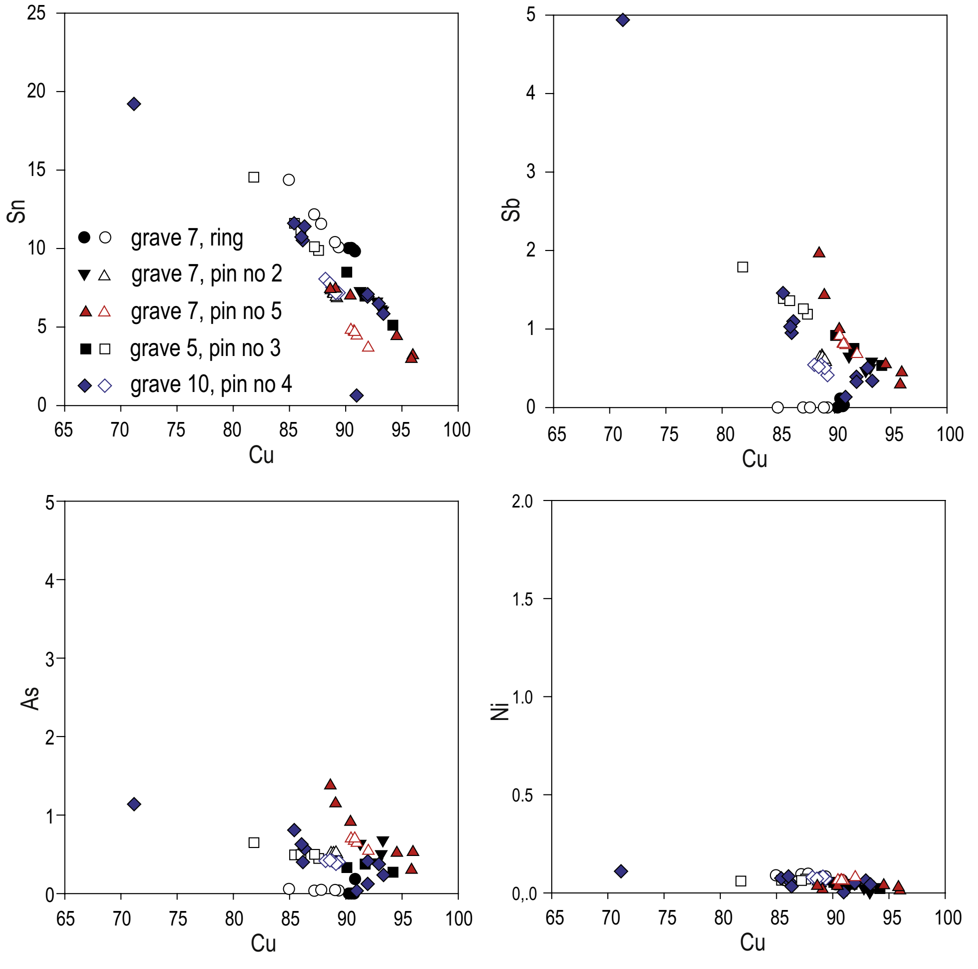

Figure 10 *Cu versus Sn, Sb, As and Ni variation diagrams (in wt%) for the artefacts from Mierczyce, stage III/IV. The solid symbols are for electron microprobe analyses, and the open ones for the XRF analyses.*

~0.1 wt%. It is relatively easy to analyse them by both XRF and the electron microprobe method, or (semi-quantitatively) using EDS systems connected to a electron scanning microscope, and they typically comprise Cu, Sn, S, Pb, As, Sb, Ag, Ni, Co and Fe (e.g., Kienlin 2008). The contents of these elements are shaped by the nature of the ore (oxide versus sulphide) and the content and relative proportions of the metals in it and can help to assess the ore provenance (Pernicka 1999). The lead isotopes are also commonly used to indicate the possible ore source (Gale and Stos-Gale 1982; see also, e.g., Ling *et al*. 2014). Other elements are rarely analysed; for example, besides the listed elements and lead isotopes, Cooper *et al*. (2008) also analysed Cr, Se, Cd and Au, which have been used to show the potential provenance of artefacts produced from native copper in the northern part of North America.

The XRF method applied by us is expected to yield reasonable results for homogeneous metals, where the size of the analysed spot is of little importance (cf., for example, the XRF and

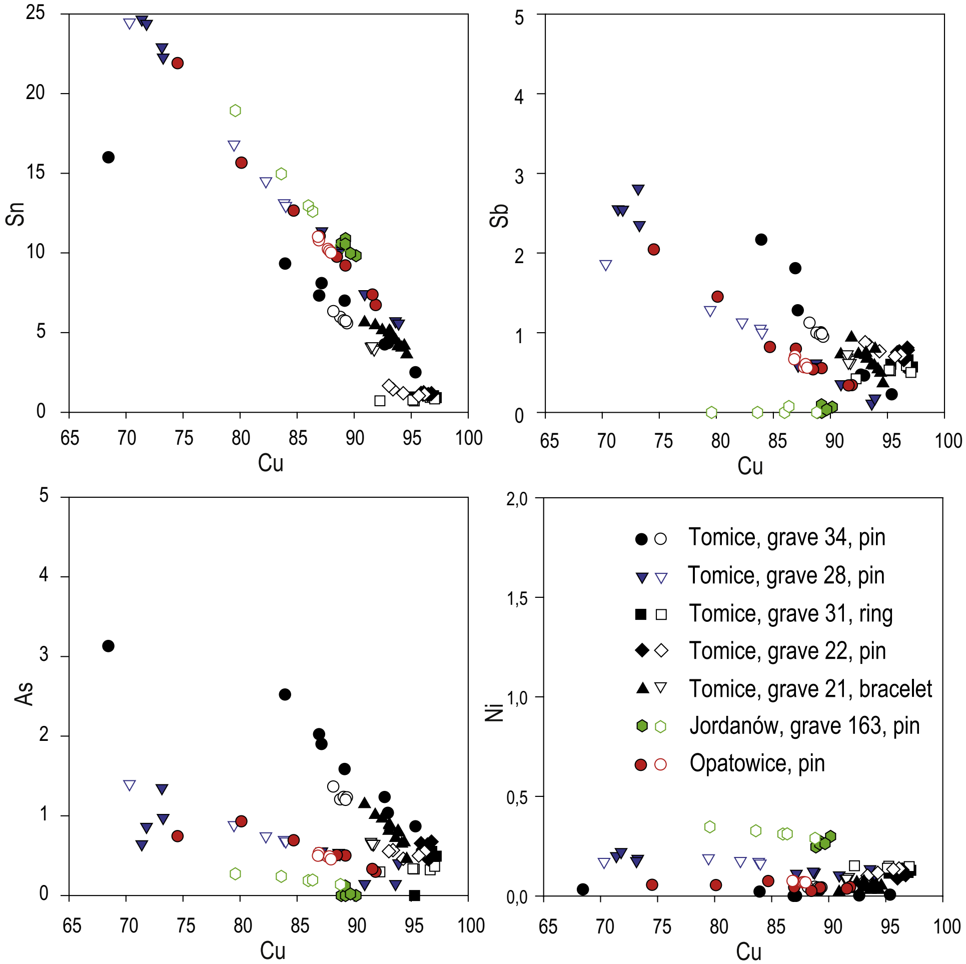

Figure 11 *Cu versus Sn, Sb, As and Ni variation diagrams (in wt%) for the artefacts from Tomice, Jordanów and Opatowice, stage III/IV. The solid symbols are for electron microprobe analyses, and the empty ones are for XRF analyses.*

microprobe data for homogeneous items from Tomice, Fig. 11: the ring from grave 31, the pin from grave 22 and the bracelet from grave 21). However, the ring from grave 7 at Mierczyce exhibits a significant spread of XRF data relative to the microprobe results (cf., Fig. 10), despite being made of homogeneous metal. The ring is, however, strongly weathered (cf., Fig. 7 (e)) and in our opinion the XRF analyses are affected by small intergrowths of decomposition products. This example shows that the XRF method alone may yield spurious results even if the analysed artefacts are composed of homogeneous metal.

The XRF analyses of polyphase metal show 'average' compositions, whereas those made using the electron microprobe yield information on the composition of single phases. Commonly, the XRF analyses show an element content that is intermediate between the extremes defined by the electron microprobe—compare, for example, the pins from Mierczyce, which are all dendritic (Fig. 10), or the dendritic pins from graves 28 and 34 in Tomice (Fig. 11). This effect is disturbed

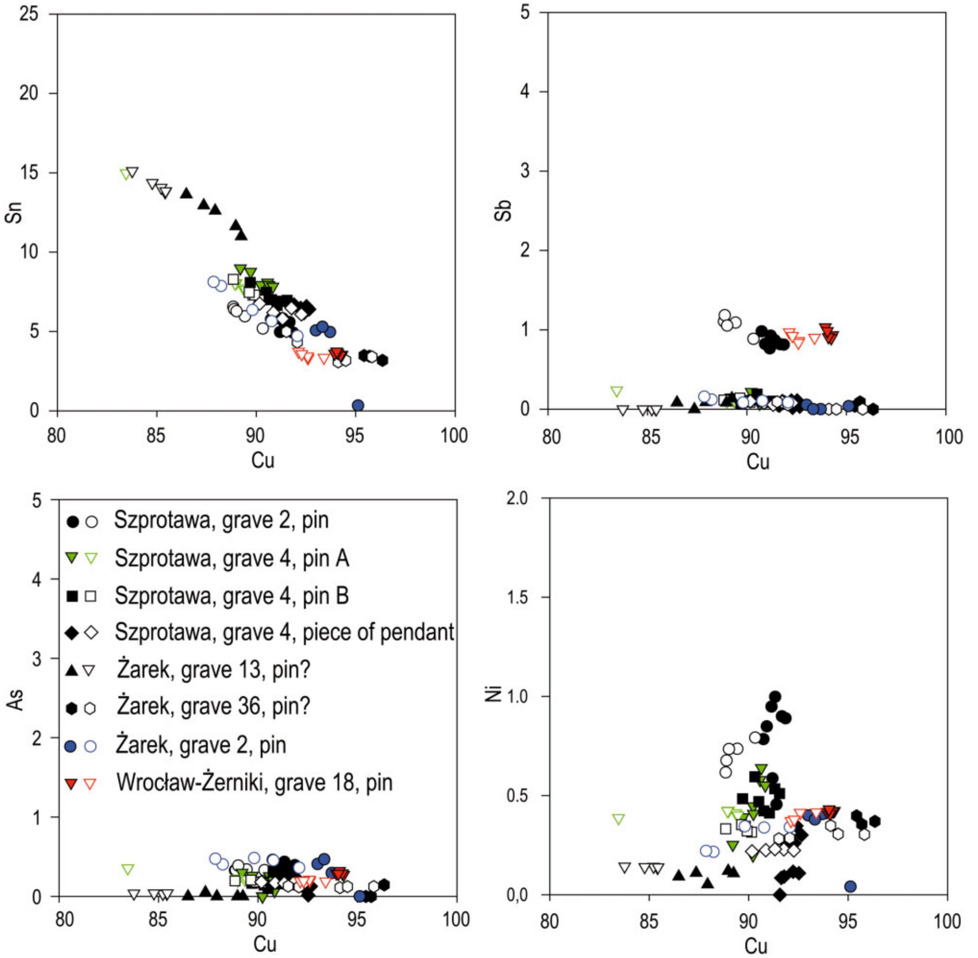

Figure 12 *Cu versus Sn, Sb, As and Ni variation diagrams (in wt%) for the artefacts from* Urnfield *sites, stage III/IV. The solid symbols are for electron microprobe analyses, and the empty ones are for XRF analyses.*

when the metal is deeply weathered and contains decomposition products, such as in the case of the beads from grave 17 in Przecławice (cf., Fig. 8).

The chemical variation of ornaments

The *Únětice* culture stage I and II/III ornaments from Przecławice are made of bronze and thus contain significant amounts of tin, whereas the artefacts from stage III/IV graves were produced from copper devoid of tin. The *Únětice* culture classical stage ornaments from neighbouring sites (Mierczyce, Tomice and Opatowice) are made of bronzes, except for the pin from grave 22 in Tomice, which is compositionally similar to the stage III/IV copper ornaments from Przecławice. Thus, the oldest *Únětice* culture ornaments in the studied set were made of bronze, stage III/IV is marked by the copper ornaments from Przecławice, and the younger ‘classical’ stage of the *Únětice* culture is characterized by bronze metal ornaments. Bronze is also used for the *Urnfield* culture products from Szprotawa, Żarek and Wrocław-Żerniki. The *Únětice* culture bronzes are typically dendritic and consist of cored dendrites plus Sn–Sb-rich eutectoid; they contain significant amounts of Sb and As and little Ni. The *Urnfield* culture bronzes are homogeneous, and contain little Sb and As and significant amounts of Ni (cf., Figs 8 and 10–12). This reveals the technological improvements, leading to the production of homogeneous metal. The flat distribution of points in the Cu/Sb and Cu/As diagrams that show the composition of the *Urnfield* culture ornaments suggests that the metal was multiply recycled or deliberately oxidized during smelting, which lowered the Sb and As contents, which are volatile in the form of oxides during smelting.

The As and Sb contents suggest that the studied ornaments of the *Únětice* culture have been produced from fahlore, which is a mixture of the metal sulphides with the prevailing tetrahedrite (ideally $(Cu,Fe)_{12}Sb_4S_{13}$) – tennanite (ideally $(Cu,Fe)_{12}As_4S_{13}$; for details of possible chemical composition variation, see Krismer *et al*. 2011) solid solution. The major element composition of the copper Przecławice ornaments makes them similar to the *East Alpine Copper*, produced from fahlore with Ni [Przecławice compositional types (1), (2) and (4)] or to *Ösenring* copper, produced from fahlore without Ni [compositional types (3) and (5)] (Krause 2003). The occurrences of tin in Europe are much less numerous than those of copper. The area of Lower Silesia is located between the Erzgebirge tin deposits to the west and the Slovakian (West Carpathians) deposits to the east. The Erzgebirge deposits are closer but, instead, the Slovakian deposits are considered to be the source of the tin used in the Bronze Age in Central Europe (Krause 2003 and references therein).

Archaeological comments

Silesia is considered to be the area that, compared to other parts of Poland, has provided the greatest amount of archaeological evidence on early copper and bronze metallurgy. Although evidence of local production is rather scarce, the distribution of local types of certain artefacts indirectly indicates its beginnings in the late stages of the *Únětice* culture (e.g., Gediga 1982, 110). *Urnfield* period sites have produced abundant data on stable and advanced local metalworking, with hundreds of casting moulds, semi-finished and completed products and workshop remains (Gediga 1982, 111–28).

The early Bronze Age ornaments have rarely been the subject of detailed material studies, which have focused rather more on later, massive artefacts such as axes or necklaces. Small simple beads and rings made of wire or sheet are the most common type of early Bronze Age metal products in south-western Poland prior to the classical (V) stage of the *Únětice* culture, when pins become more frequent (Butent-Stefaniak 1997, 234; Kadrow 2001, 92). The compositions of ornaments varies broadly and shows no well-defined time-composition trend (Sarnowska 1975, 97–9), as opposed to the composition of axes from several early Bronze Age Polish sites, which shows gradual change from older low-Sn alloys to the younger, Sn-richer ones (Sarnowska 1975, 101; Rassmann 2004). However, a simple axe-based model of evolving metal composition is commonly, although not generally, accepted (Kienlin 2010, 168, 171–2 and references therein). The Przecławice ornaments do not fit this model (early stages, Cu–Sn alloys; later stages, Cu alloys). This may be due to completely different properties sought by early metalworkers and, in consequence, different working strategies. In the case of tools, the hardness (obtained both by control of temperature and cold working; e.g., Kienlin 2007, 8) was the most desired property, while for ornaments it could have been of little interest, and colour or ductility were of greater importance (Kienlin 2010, 171). Unlike at Przecławice, the bronze ornaments dated to the classical stage of the *Únětice* culture from the other sites represent an advanced level of metalworking skills and probably the same strategies both in ornament and tool production. Data obtained from the ornaments dated to the *Urnfield* period prove that this model had been continued from the late early Bronze Age onwards.

CONCLUSIONS

Our data show that the best choice for the characterization of metal artefacts is the combination of methods yielding averaged chemical compositions with methods enabling micrometre-scale imaging of the metal microstructure, plus chemical analyses. These methods allow reasonable characterization of metal items that consist of dendrites or are polyphase, as well as of those that are weathered or corroded and contain micrometre-scale decomposition products dispersed in the host. We used XRF analyses plus electron microprobe BSE imaging and spot analyses, but other choices of analytical equipment can provide similar information (e.g., a scanning electron microscope equipped with an EDS module can be used instead of the electron microprobe).

The ornaments coming from *Únětice* culture sites in Lower Silesia are made of bronzes of varying Cu/Sn ratios. The chemical variation of their composition and their typically dendritic metal microstructure suggests rather poor control of the smelting and solidification process. The exception is the Przecławice site. The metal composition evolution in Przecławice ornaments (from bronze of the older *Únětice* culture to copper of the young stage) is the opposite of that accepted on the basis of axe composition studies, probably due to different working strategies used to produce tools/weapons and ornaments. The much younger ornaments of the *Urnfield* culture sites are made of homogeneous bronze, and show better smelting/reworking control and supposedly multiple recycling.

ACKNOWLEDGEMENTS

This study is a part of the project of the Polish National Centre for Science, NCN 2011/01/B/ST10/04440. The authors thank Irena Lasak from the Institute of Archaeology, University of Wroclaw, and also the Archaeological Museum in Wrocław, the Regional Museum in Jawor and the Copper Museum in Legnica, for providing an opportunity to sample the artefacts presented in the paper. The authors are grateful to Dr Marta Mozgała, of the Institute of Archaeology, University of Wrocław, for providing a recent ^{14}C date for the Jordanów site.

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