Acta Musei Napocensis, 45-46/I, 2008-2009 (2011), p. 39-51

THE ANALYSES OF THE COPPER-BASED FINDS FROM THE LBA METALLURGICAL SITE AT PALATCA

ALESSANDRA GIUMLIA-MAIR

Riassunto: I risultati delle analisi condotte sugli importanti reperti provenienti da Palatca, ora nel Museo di Cluj, sono esposti e discussi nel presente articolo. I reperti sono un grande frammento di lingotto che ricorda una versione ridotta dei lingotti oxhide, un'incudine (o meglio uno strumento metallurgico con varie funzioni) e un lingotto del tipo piano-convesso. Tutti sono stati analizzati per mezzo di spettrometria di assorbimento atomico, prelevando i campioni con un trapano da gioielliere. "L'incudine" è risultata essere fatta di un rame con alte percentuali di piombo (circa 18% Pb). Il lingotto di tipo piano-convesso contiene invece varie impurità, in particolare notevoli tenori di ferro e di arsenico. Il reperto più interessante è il lingotto simile ai lingotti oxhide provenienti da Cipro, ma di misura inferiore. Le analisi hanno mostrato che si tratta di un metallo di composizione completamente diversa da quella dei lingotti oxhide che sono tutti di rame molto puro (98-99% Cu). L'esemplare di Palatca contiene invece varie impurità, in particolare oltre 3% di arsenico, e la sua composizione è dunque simile a quella di pani a piccone e pendenti a ruota della tarda età del bronzo, ma anche a quella dei pendenti di S. Lucia di Tolmino/ Most na Soči e da Vače in Slovenia e da Paularo in Italia nord orientale, datati alla piena Età del Ferro. Come recenti studi hanno dimostrato, sembra che questo tipo di materiale di colore argenteo avesse in questo periodo un particolare significato, perché era impiegato solo per la produzione di questo genere di ornamenti, portati solamente da donne di alto rango e con una particolare posizione sociale all'interno della comunità. È possibile che anche in Transilvania circolassero lingotti di questo materiale, riconoscibile solo attraverso analisi chimico-fisiche, e il lingotto di Palatca è il primo indizio a nostra disposizione.

Parole chiave: Palatca; lingotti; rame; pendenti a ruota; pani a piccone; arsenico.

Introduction

This paper presents and discusses the AAS analysis results of the important copper based finds from Palatca, the richest and the metallurgically most significant site of Late Bronze Age Transylvania, in the County of Cluj. Here a large fragment of what looked like a smallish version of an oxhide ingot, an anvil (or, more in general, a metallurgical tool with different functions), fragments of casting moulds, working remains and fragments of hand mills have been excavated from a workshop with several areas, apparently dedicated to different activities, such as drilling and melting down copper ingots, casting of objects, grinding and retouching[1].

[1] Rotea 2002-2003 (2004), p. 7.

The only other site, dated to roughly this period, in which certain metallurgical remains have been found, is the Wietenberg settlement at Derşida[2], where some casting moulds have been recovered.

The composition of the metal and the implications for the reconstruction of the local metallurgy will be discussed in the next pages.

Method of analysis

The samples were taken in the National History Museum of Transylvania Cluj-Napoca, with a jeweller drill and bits of 1 mm. Approximately 10-12 mg of clean metal were collected for each analysis. The surface material was discarded to avoid the contamination of the sample with elements coming from the burial environment, and only clean metal turnings were collected. In this way also problems of internal segregation are avoided.

The drillings were examined under the microscope and any visible remains of corrosion were removed from the clean metal turnings.

The samples were weighed, dissolved in aqua regia and diluted by following the common procedure for the preparation of AAS solutions, according to the method described by Hughes[3]. The analysis was carried out by atomic absorption spectrometry (AAS). Tin, bismuth and gold were sought, but were not identified.

The results have a precision of approx. ± 1-2% for Cu, ± 5% for elements present at a level greater than 1%, but deteriorating to ± 50% at the respective detection limits.

Discussion of results

Three objects have been analysed by AAS for this project: an ingot with a flattened side, a plano-convex ingot (or bun-ingot) and a large metal fragment which looks like a part of a small oxhide ingot.

The analysis of the "ingot" - a heavy piece of metal which had been most probably employed as an anvil as it has two flattened areas - gave the following values for the 12 elements determined by AAS:

Cu 80.94%; Fe 0.91%; As 0.02%; Sb -; Pb 18.15%; Sn -; Bi -; Mn 0.02%; Ni 0.01 %; Ag 0.02%; Au - %; S 0.03%.

The most striking characteristic of this object is the very high lead content, while, with the exception of iron, only very low trace elements have been determined. This might possibly indicate that the lead had been deliberately added to the copper or at least that an especially lead rich copper had been selected for this use.

The rather flat bun ingot has the following composition, with a slightly higher iron content, a noticeably higher arsenic content, and a very low lead percentage: Cu 97.66%; Fe 1.26%; As 0.49%; Sb 0.09%; Pb 0.09%; Sn -; Bi -; Mn 0.06%; Ni 0.01%; Ag 0.01%; Au -; S 0.34%.

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[2] Chidioşan 1980, p. 60; Rotea 2002-2003 (2004), p. 7.

[3] Hughes et alii 1976, p. 19-37.

The most interesting among these finds is the large fragment of ingot with a shape that very closely reminds of the shape of oxhide ingots.

Oxhide ingots are dated to the Late Bronze Age and are widely distributed and quite common, in particular in the Mediterranean area.

These large copper ingots can weigh between 25 and 35 kg and are characterized by their elongated rectangular shape with four "handles" at the corners. A large number of oxhide ingots and of fragments of ingots from different sites, especially those in Mediterranean countries, have been analysed for different projects and the analyses have shown that the material was invariably a copper with a purity of 98-99%[4]. Lead isotope analyses seem to indicate that all oxhide ingots analysed up to now are made of Cypriot copper.

The ingot from Palatca is relatively small, compared with the oxhide ingots known from other contexts; however its shape suggested the possibility that a rather smallish ingot from Cyprus had been imported to Transylvania, possibly along the river Danube.

However, when the ingot was sampled, this hypothesis immediately looked less convincing, because the metal was particularly soft and the metal turnings collected for analysis showed a silvery colour. This fact indicated that the metal was some sort of alloy, instead of the very pure copper which would be expected if the piece was an oxhide ingot.

The following values were determined for the elements sought by AAS: Cu 92.99%; Fe 3.07%; As 3.39%; Sb 0.88%; Pb 0.64%; Mn 0.31%; Ni 0.01%; Ag 0.01%; S 1.44%.

Tin, bismuth, cobalt and gold were also sought, but not detected.

As a comparison, the fragments of oxhide ingots found in the hoard under a wall on the acropolis of the island Lipari, in the North of Sicily[5], had a very high average purity of over 98%, with only very weak traces of iron and arsenic.

Also the analyses carried out in the past on oxhide ingots from Sardinia, Cyprus and from other sites all over the Mediterranean showed very similar results[6], therefore it is quite clear that the ingot from Palatca, with its very high trace elements, is made of a totally different copper which, as we will see in the following paragraphs, has striking characteristics and interesting peculiarities.

A similar composition, with a high arsenic content, is known from the pick ingots (Pl. I/1), dated to the Late Bronze Age, which have been studied by N. Trampuž-Orel[7]. She identified this material as an intermetallic phase formed during the smelting process of polymetallic ores as an intermediate layer between copper and slag and tentatively suggested that the origin of these ores might be the mines of polymetallic ores found in the so-called Grauwackenzone in the Eastern Alps, where important prehistoric mines were located, such as the Mitterberg mine or the ones in the Schladming and Liezen areas[8].

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[4] Giumlia-Mair 2009, p. 168-172; Lo Schiavo et alii 2009, passim.
[5] Giumlia-Mair 2009, p. 171-172.
[6] Lo Schiavo et alii 2009, digital archive on CD.
[7] Trampuž-Orel 2001, p. 143-171; Paulin et alii 2003, p. 205-218.
[8] Goldenberg et alii 2004, p. 39-54; Huijsmans et alii 2004, p. 55-64.

However, the ores from this area are also characterized by high impurities of antimony, nickel and cobalt. Some relatively high antimony is present in the ingot from Palatca, but no cobalt and nickel could be detected.

This does not necessarily exclude that the copper might have been extracted from the Grauwacken mines, however deposits with high arsenic percentages are also known from other areas and this metal composition cannot be taken as indication of the provenance of the copper.

It is however very important to point out that the properties of the metal change drastically when in the copper are present several percentage of arsenic and antimony.

Arsenical copper had been used in earlier times, at the beginning of copper metallurgy in Europe, already in the second half of the fifth millennium BC. Very early finds which testify the use of this material have been found for example on the Mariahilfbergl in Brixlegg (Austria)[9], or in Chalcolithic settlements in Spain, dated to the third Millennium BC[10], but this kind of metal alloy was used mainly in the Early Bronze Age and was diffused all over Europe.

Copper which contains a noticeable amount of arsenic hardens faster when wrought, but its more striking property is the beautiful silvery grey colour which develops on the surface of objects cast out of this metal. The silvery colour is due to the phenomenon of inverse segregation. This means that on the surface of the cast pieces of copper containing arsenic (but also antimony) there is the formation of the copper-arsenic alloy which has the lowest possible melting point. This alloy is copper containing 21% of arsenic, it develops inside the metal in the cooling phase and, being liquid, it is pushed through interdendritic filaments (or feeders) to the surface of the castings, where it solidifies and forms the typical silvery layer (Pl. I/2). This phenomenon is commonly called "arsenic sweat".

Laboratory experiments showed[11] that the phenomenon of inverse segregation (or arsenic sweat) can occur in copper alloys already with 1-2% of arsenic in the alloy. The maximum limit of solid solubility of arsenic in copper is 7.5% As. The microstructure of the eutectic shows a solid solution phase α and a compound γ, containing 29.65 As (Cu_3As).

The compound γ is still malleable and can be worked. Copper alloys containing antimony also form a segregation layer on the surface and behave like copper-arsenic alloys. Therefore the presence of both arsenic and antimony greatly enhances the segregation phenomenon and produces a more compact silvery layer. It has to be noted that also inverse segregation of tin in copper exists. This is the so-called "tin sweat", but this compound is extremely fragile and it breaks easily when it is wrought or, in general, when worked by hammering[12].

From all this it is quite clear that the metal of the ingot from Palatca had a very noticeable silvery colour and good working properties.

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[9] Höppner et alii 2005, p. 293-315.
[10] Craddock 1995, p. 134-135.
[11] Budd et alii 1991, p. 132-142; Giumlia-Mair 2000, p. 300-301.
[12] Northover 1989, p. 111-118.

With the introduction of copper-tin alloys in the Middle Bronze Age, copper-arsenic alloys were forgotten, as bronze alloys have better working properties and do not produce poisonous fumes like arsenical copper, however, in some special cases, these alloys were employed again for the production of special objects with a particular social and most probably religious significance.

As several studies carried out on different materials have shown[13] in the Late Bronze Age and in the Iron Age, a special class of decorative objects - which were apparently prerogative of women who had special powers and exceptional functions in the society of the time - were still made of arsenical copper or at least of copper rich in arsenic, antimony, nickel and cobalt, i.e. of the metal employed for the pick ingots. The objects are the well known wheel pendants (Pl. II/3-4) and, in the Iron Age, some anthropomorphic pendants which seem to be in clear connection with the very ancient cult of a moon goddess, connected with water, life and death, fertility and abundance[14].

Several finds of wheel pendants are known in the archaeological literature. The best known and thoroughly studied group is that from Kanalski Vrh in Slovenia[15], but important hoards are also those from Villethierry in France[16], from Grünwald[17] and Gammertingen[18] both in Southern Germany, from Thunau am Kamp in Austria[19], and from Velem-Szentviden in Hungary[20].

Among the objects of the hoard from Chiusa di Pesio (Cuneo) in the Italian region of Piedmont there were around 50 wheel-pendants, however these seem to be made of a bronze alloy which was superficially treated, to achieve a light, silvery colour. However the analyses carried out by SEM/EDS and PIXE determined in some of the pieces similar concentrations of As (0.4-2.2%), Sb (up to 0.8%) and Ni (0.2-0.4%). No data are given for Co, but also relatively high Ag concentrations (0.4-1.3) were identified[21].

In Italy there are several examples, e.g. from the region Friuli[22], from the famous S. Francesco hoard in Bologna with 2 examples[23], from the famous site of Verucchio, also in Emilia Romagna, from Capriano-Renate in Lombardy, from Fontanella di Casalromano near the river Po, from Coste del Marano in Lazio with 5 pieces etc. These amulets are also diffused in Central Europe, for example from Lengyeltóti III,

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[13] Giumlia-Mair 2000, p. 300-301; Heath et alii 2000, p. 53-70; Trampuž-Orel, Heath 2001, p. 143-171; Paulin et alii 2003, p. 205-218; Giumlia-Mair 2005a, p. 363; Giumlia-Mair 2008, p. 110-117; Giumlia-Mair 2009b, p. 149-163.

[14] Giumlia-Mair 2008, p. 110-117; Giumlia-Mair 2009b, p. 149-163.

[15] Žbona-Trkman, Bavdek 1995-1996, p. 31-71; Heath et alii 2000, p. 53-70; Trampuž-Orel, Heath 2001, p. 143-171; Paulin et alii 2003, p. 205-218; Giumlia-Mair 2008, p. 110-117; Giumlia-Mair 2009b, p. 149-163.

[16] Mordant et alii 1976, p. 169, fig. 144-154.

[17] Wels-Weyrauch 1991, p. 54.

[18] Wels-Weyrauch 1978, p. 67-75.

[19] Lochner 1998-1999, p. 181-186, figs. 2, 4.

[20] Bándi, Fekete 1977-1978, p. 101-133.

[21] Angelini et alii 2007, p. 210.

[22] Giumlia-Mair 2005a, p. 359-367.

[23] Antonacci Sanpaolo 1992, p. 159-206.

Gyermely, Csákberény, Sághegy, Hódmezővásárhely and Magyarkeresztes in Hungary, from Smolenice-Molpír in Slovakia, and from Sierre VS, Oberriet SG, Montlingerberg SG, Estavayer-le-Lac VD and Auvernier NE in Switzerland[24].

Two casting moulds for wheel pendants have been found in Switzerland at Auvernier NE and at Grandson VD (Les Corcelettes)[25] and a further example is known from Freghera-Cermenate near Como[26].

Up to now only other three objects made of arsenic rich alloys, dated to the Iron Age, have been scientifically identified. These are the anthropomorphic pendants found in the graves of socially important women in the famous necropolis of S. Lucia di Tolmino/Most na Soči (Pl. III/5) in Slovenia, (the object is now in the Civici Musei di Arte e Storia, Trieste, Italy), in the necropolis of Paularo (Pl. III/6), in the region Friuli Venezia Giulia, Italy (now in the Museum of Zuglio, Udine, Italy), and in the necropolis of Vače Pl. III/7), Slovenia (this piece is now in the Naturhistorisches Museum in Vienna, Austria).

The graves are dated to the late 6th-early 5th century BC and in all cases they were by far the richest burials in the three cemeteries.

The shape, the size and the ornaments of the three pendants are astonishingly similar so that they seem to come from the same mould.

The anthropomorphic pendants were all produced by casting, only slightly cold worked and carefully polished. They seem to represent a female deity on a boat, decorated on both sides with animal heads. The animals were interpreted as aquatic birds and in some cases as horses. More anthropomorphic pendants of smaller size were originally hanging from the stylised boat.

Other small anthropomorphic pendants of different types, belonging to the same large composite ornament, some kind of pectoral, were found in the same graves.

The first pendant analysed by XRF was that from the necropolis of S. Lucia di Tolmino/Most na Soči and the results showed that, surprisingly, the alloy was copper containing 8% Sn, 4.5% of As, 5% Pb, 1.5% Ag and around 1% Fe.

At a later point also the pendants from Paularo and Vače were analysed. The results were similar to that of the first pendant, with high As, some Ag and 7-9% of Sn. The small anthropomorphic pendants and the triangular pendants belonging to the same sets are made of the same alloy, with only slight differences, however the fibula which supports the pendants was made of common leaded bronze[27].

It is important to underline that in previous researches around 150 copper-based finds from the necropolis of S. Lucia[28] and 130 from the necropolis of Paularo[29] had been analysed in the frame of different research projects and that none of the objects was made of a similar metal. Obviously this distinctive material was employed for special objects only and had a special significance.

[24] Giumlia-Mair 2008, p. 110-117.
[25] Wyss 1989, p. 91-99, fig. 3.
[26] Frigerio 1981, p. 81-147.
[27] Giumlia-Mair 2008, p. 110-117; Giumlia-Mair 2009b, p. 165-211.
[28] Giumlia-Mair 1998a, p. 665-672; Giumlia-Mair 1998b, p. 94-122 and the table of results.
[29] Giumlia-Mair 2003, p. 62-64.

Conclusions

Many more object made of "white metal" dated to the Bronze Age and the Iron Age are mentioned in the archaeological literature, in various regions of Central Europe however not many analyses of these materials exist. Most probably copper containing some arsenic and antimony was considered a precious material and circulated in a vast area.

Not many people could distinguish it from silver.

In Roman times this alloy was employed by a few specialists only, who carefully kept secret the procedure and the ingredients as a workshop recipe "to make silver"[30].

In the Middle Ages the phenomenon of colour change was known by the alchemists who called the process of producing arsenical copper *dealbatio aeris* (the whitening of copper). Several important Medieval texts, such as for example the *Mappae Clavicula,* a collection of alchemistic recipes dated to the early Middle Ages[31] or the treatise *De Mineralibus* (On Minerals)[32] of Albertus Magnus, one of the most important scholars of this time (1193-1280), theologian, philosopher and alchemist, mention this material as one of the most important recipes of alchemy.

The ingot from Palatca is for the moment the only identified ingot of this shape and characterised by this composition. The pick ingots which, as discussed above, have very similar characteristics, are found in a wide area, around Slovenia and the Alps, but are also found in graves in the Villanova territory[33]. This indicates that they were considered an especially appreciated metal and were traded to different regions.

It is possible that in Transylvania there was a similar trade of silvery coloured ingots and that the example from Palatca is the first indication of a more widespread phenomenon.

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30 Giumlia-Mair 2001, p. 218-221.

31 Smith, Hawthorne 1974.

32 Goldschmidt 1983.

33 Chiavari et alii 2007, p. 233.

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Alessandra Giumlia-Mair
AGM Archeoanalisi
Via E. Toti 8, Merano (BZ), Italy
giumlia@yahoo.it

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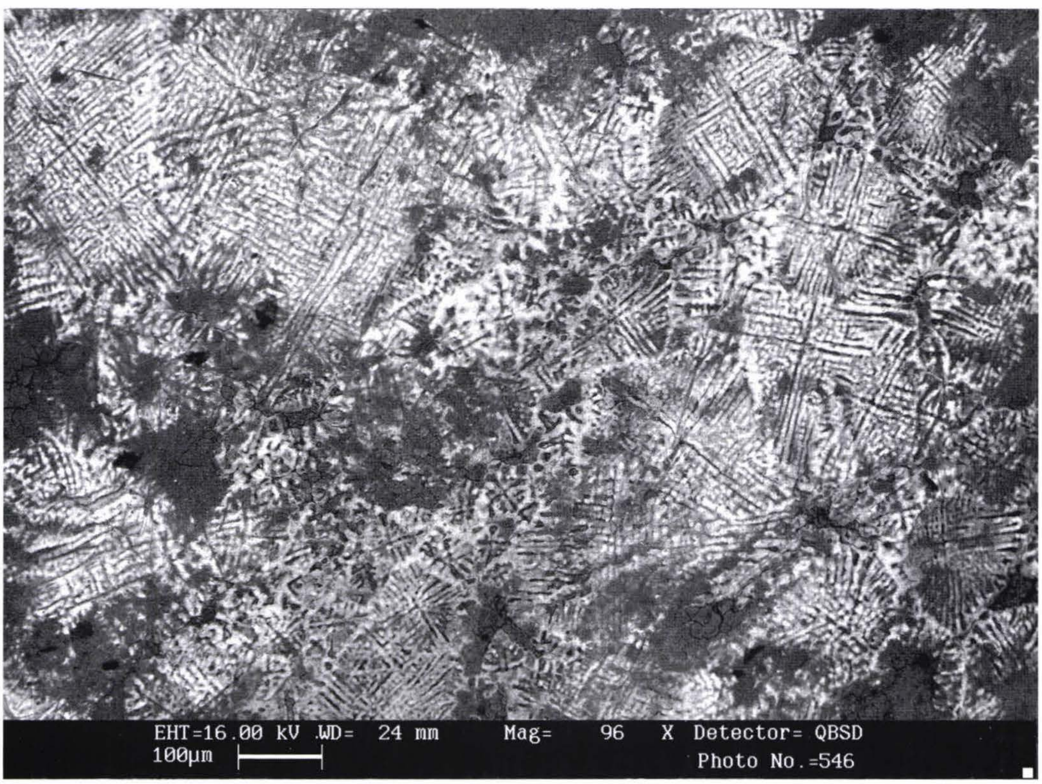
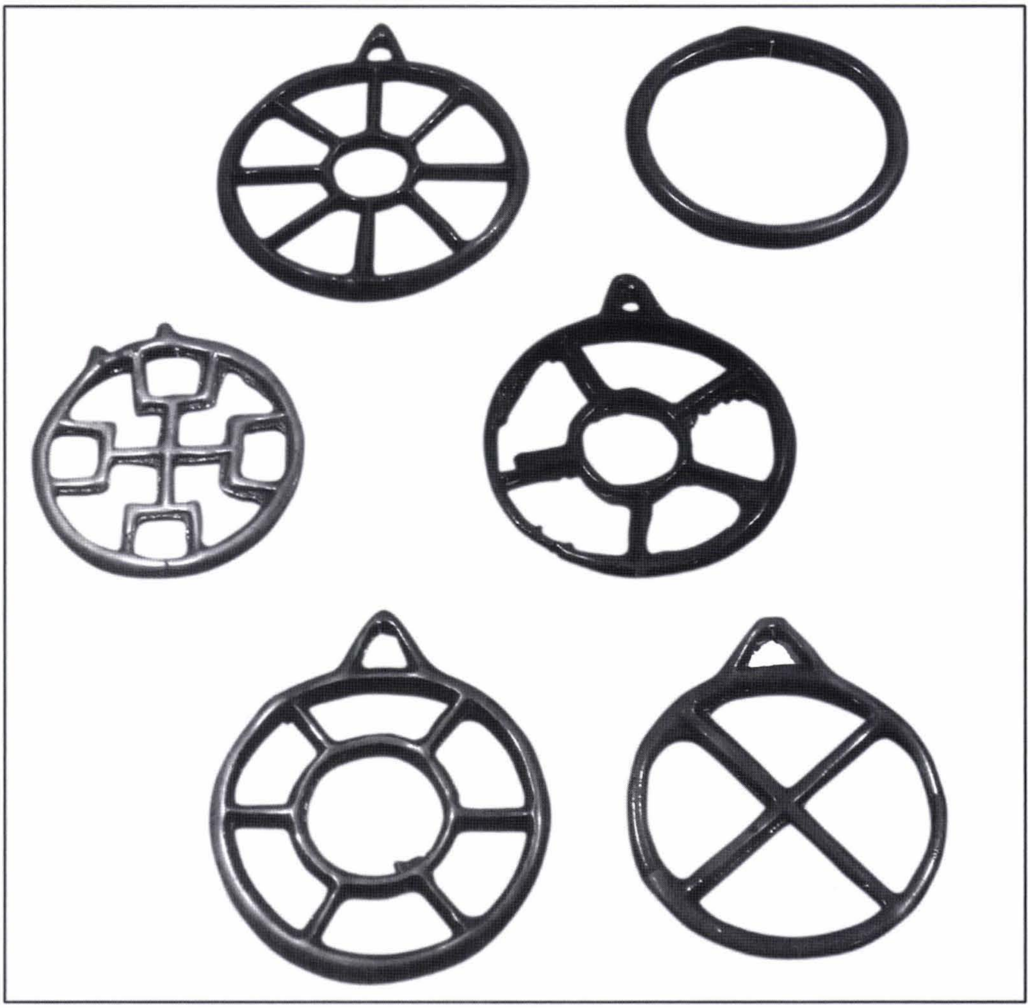


2

Pl. I. 1. Examples of pick ingots from the Eastern Alps; **2.** The SEM micrograph shows the typical silvery formations on the surface of an arsenic-rich object (photos A. Giumlia-Mair).



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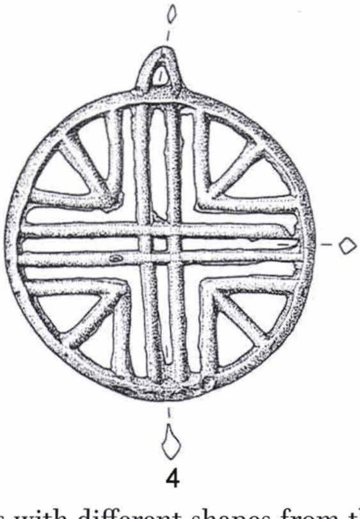

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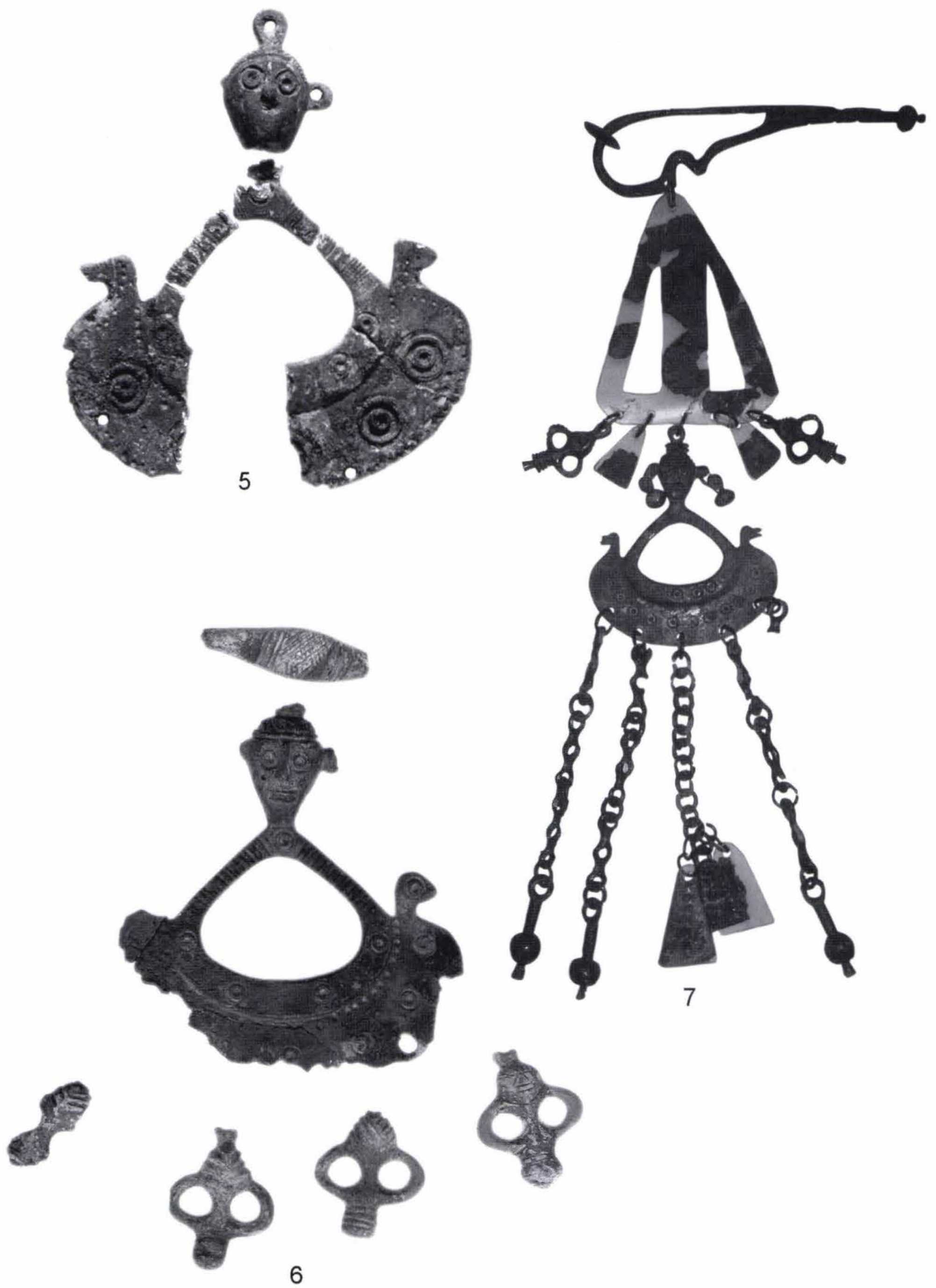
Pl. II. 3. Selection of pendants with different shapes from the Slovenian site of Kanalski Vrh (photo A. Giumlia-Mair); **4.** One of the wheel pendants found at Thunau am Kamp in Austria (drawing after Lochner 1998-1999, p. 183, fig. 2).



Pl. III. 5. Anthropomorphic pendant, made of an arsenic-rich alloy, found in the necropolis of S. Lucia-Most na Soči in Slovenia, now in the Civici Musei di Arte e Storia in Trieste, Italy; **6.** Anthropomorphic pendant, made of an arsenic-rich alloy, found in the necropolis of Paularo (Udine, Italy), now in the Museum of Zuglio, Udine; **7.** Anthropomorphic pendant, made of an arsenic-rich alloy, found in the necropolis of Vače, Slovenia, now in the Naturhistorisches Museum in Vienna, Austria (photos A. Giumlia-Mair).