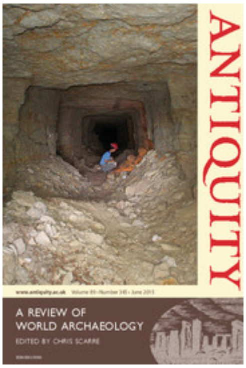

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Tainted ores and the rise of tin bronzes in Eurasia, *c.* 6500 years ago

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The earliest tin bronze artefacts in Eurasia are generally believed to have appeared in the Near East in the early third millennium BC. Here we present tin bronze artefacts that occur far from the Near East, and in a significantly earlier period. Excavations at Pločnik, a Vinča culture site in Serbia, recovered a piece of tin bronze foil from an occupation layer dated to the mid fifth millennium BC. The discovery prompted a reassessment of 14 insufficiently contextualised early tin bronze artefacts from the Balkans. They too were found to derive from the smelting of copper-tin ores. These tin bronzes extend the record of bronze making by c. *1500 years, and challenge the conventional narrative of Eurasian metallurgical development.*

Keywords: Eurasia, Serbia, Bulgaria, Pločnik, Belovode, fifth millennium BC, Vinča culture, copper, tin, bronze, metallurgy, compositional analysis

Supplementary material is provided online at http://antiquity.ac.uk/projgall/radivojevic338/

Introduction

From their earliest appearance in the third millennium BC to their widespread adoption during the second millennium BC, tin bronzes had a significant impact on Bronze Age societies in Eurasia, including major changes in the economic, political and social lives of

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consumer communities (e.g. Harding 2000; Anthony 2007; Kuz'mina 2008). Bronze is an alloy of copper and other metals with copper as the major component. Tin is the most common alloying agent but other bronzes may incorporate arsenic, aluminium, silicon or phosphorus (Caron *et al.* 2004). To avoid ambiguity it has become common practice in archaeology to call the alloy of copper with tin 'tin bronze' and the alloy of copper with arsenic 'arsenical copper'.

Extensive scholarship has been devoted to the 'tin question' in pursuit of the sources of tin, the evidence for its production and the trade routes by which it travelled across the Old World (Muhly 1973; Pigott 1999; Yener 2000; Giumlia-Mair & Lo Schiavo 2003). The earliest known tin bronze artefacts, mostly pins or flat axes, have been discovered in Mesopotamia and Anatolia, and date to the early third millennium BC (Stech & Pigott 1986; Weeks 1999; Begemann *et al.* 2003; Helwing 2009). These objects contain up to 10 weight per cent (wt%) tin, and this is commonly thought to be due to the intentional addition of tin ore (cassiterite, SnO_2) to copper ores (co-smelting) or copper metal (cementation) (e.g. Cleziou & Berthoud 1982). These areas of early tin bronze consumption, however, lack significant tin sources. A quest for *the* tin source in Anatolia prompted extensive research on archaeological, geological and textual evidence, and likely origins were announced and subsequently dismissed in heated academic debates (Muhly 1993; Yener *et al.* 1993). More recently, multiple cassiterite sources exploited during the Bronze Age have been identified in modern Iran, Afghanistan, Uzbekistan and Tajikistan (Weisgerber & Cierny 2002; Nezafati *et al.* 2006, 2011; Pigott 2011; Stöllner *et al.* 2011).

Alongside the important issue of the sources is the question of how the early production of tin bronze fits into the traditional narrative of the evolution of Eurasian metallurgy. This narrative seeks to follow a relatively simple, unilinear model of the inception and development of metallurgy from a single region. It begins with copper minerals and the first working of native copper in the Neolithic, which led to small-scale copper smelting from oxidic ores in the Chalcolithic. By the end of this period and well into the Bronze Age, mixing of ores was practiced to produce arsenical copper, followed by the large-scale smelting of sulphidic copper ores. By the Middle to Late Bronze Age, pure copper was alloyed with tin metal to mass-produce tin bronze. Iron production eventually emerged by the end of the Late Bronze Age (e.g. Wertime 1964). While this narrative is sufficient for interpreting broader consumption patterns that did indeed evolve in this order, a higher-resolution regional perspective on metallurgical production and innovation modulates this established sequence considerably, as, for instance, in the Middle East (Thornton 2009), or in the Americas, where the evolutionary trajectory of metallurgy is entirely independent of its development in the Old World (Lechtman 1980; Ehrhardt 2009). Multiple origins must therefore be envisaged.

The hypothesis of a single origin for Eurasian metallurgy (most recently Roberts *et al.* 2009) has been challenged by the discovery of copper smelting evidence some 7000 years old at a location outside the Near East: Belovode, a Vinča culture settlement in eastern Serbia (Radivojević *et al.* 2010). Here, smelting of metal continued for several centuries alongside substantial malachite bead production, exploiting multiple local copper sources. Compositional analyses indicate a clear distinction between the malachite deposits exploited for bead making and those for copper smelting. Pure green malachite was favoured for bead making, while black-and-green ores, a copper and manganese mineral paragenesis, were used for copper metal extraction. Such consistent selection indicates a good understanding of the technological properties of various raw materials. The manganese content in copper minerals, indicated by the black-and-green colour composite, had a decisive role in selecting the best copper source for making metal. The pure green bead minerals were, on the other hand, sought for the strong symbolism of their colour (cf. Bar-Yosef Mayer & Porat 2008). The colour dichotomy of the black-and-green ores used for smelting and of pure green minerals processed for bead making makes the former appear as stained or 'tainted' ores, which is how they are termed in our research.

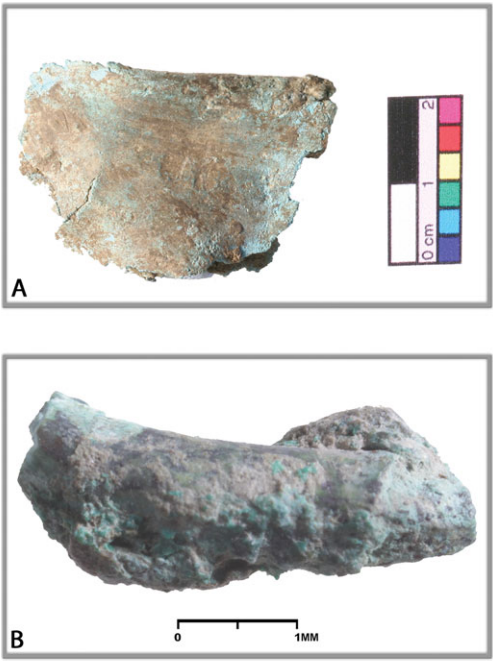


Figure 1. Fifth millennium BC tin bronze artefacts from Vinča culture sites in Serbia: (A) tin bronze foil from Pločnik, securely dated to c. *4650 BC; (B) tin bronze ring from Gomolava, tentatively dated to the mid fifth millennium BC.*

Here we present analyses of a tin bronze foil, from the Vinča culture site of Pločnik in southern Serbia, that may have been used for wrapping a ceramic vessel (Figure 1A). The site of Pločnik has been solely occupied by the Vinča culture, and no later cultural intrusions have, thus far, been documented (e.g. Šljivar *et al.* 2012). The tin bronze foil was excavated from an undisturbed context, on the floor of a dwelling structure next to a copper workshop (Šljivar & Kuzmanović-Cvetković 2009; Šljivar *et al.* 2012: 33). It lay approximately 1m from a fireplace, and was found among several late Vinča culture pottery vessels (Figure 2). This securely contextualised find comes from a single undisturbed occupation horizon that has been dated to *c.* 4650 BC (Borić 2009: 214). According to the field evidence, the date is a *terminus ante quem* for the Pločnik foil. The tin bronze foil from the site of Pločnik is therefore the earliest known tin bronze artefact anywhere.

Early tin bronzes in the Balkans: background

The Pločnik foil is not the only find of early tin bronze artefacts in the Balkans. Fourteen other early tin bronze artefacts were discovered during the last century, but these were either poorly dated or insufficiently contextualised beyond their broad 'Chalcolithic' assignation (Chernykh 1978; Ottaway 1979; Tasić 1982; Pernicka *et al.* 1993). A piece of copper-tin slag deposited in one of the burials in the late fifth millennium BC cemetery of Zengővárkony in Hungary (Glumac & Todd 1991) represents further evidence of tin use in this period; however, its context has been questioned (Pernicka *et al.* 1997). The Pločnik foil thus is the only securely dated artefact among the entire Balkan early tin bronze assemblage.

Twelve of the previously analysed Chalcolithic finds originate from Bulgarian sites (Ruse, Karanovo, Gradeshnica, Smjadovo, Zaminec and Bereketska Mogila), and two from Serbian

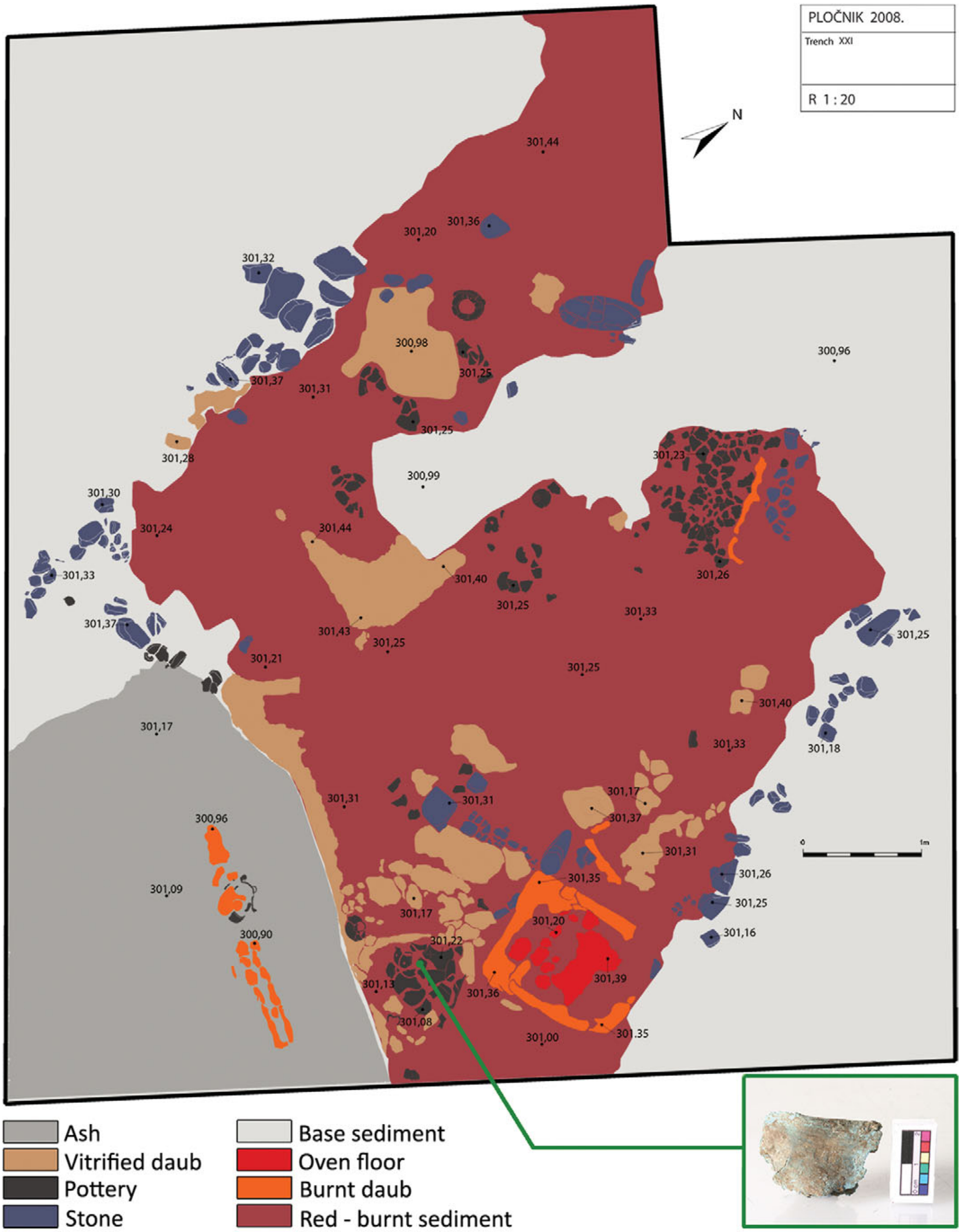


Figure 2. The context of the tin bronze foil from Pločnik. The rectangular outline of the dwelling structure is indicated by the red burnt sediment; the foil was discovered in its south-eastern corner, among a dozen pottery sherds, and close to the oven.

sites (Gomolava and Lazareva Cave) (Figure 3). They consist of awls, rings, needles, borers and a rod and have tin concentrations from 1–10wt%, followed consistently by significant levels of lead, arsenic, nickel, cobalt, iron and gold (Table 1). Although the exact concentrations of these elements vary widely from sample to sample, they appear qualitatively similar, which suggests an origin from similar types of ores. They are typologically similar to contemporary copper finds, and some of them directly match counterparts in pure copper from the fifth millennium BC Balkans. All of the objects were discovered in multilayered sites within disturbed Chalcolithic occupations, except a ring from Ruse (ASM 10882) that is reported to come from a child's burial belonging to an undisturbed Chalcolithic horizon. The cultural and chronological attribution of these tin bronzes was tentatively assumed to be Chalcolithic on the basis of their distinctive composition, different from later bronzes, and their limited quantity (Chernykh 1978: 81). Furthermore, no other tin bronze artefacts are known in the Balkans before the third and second millennia BC (Chernykh 1978; Schickler 1981; Pernicka *et al.* 1997; Pare 2000), making it very unlikely that these early finds are intrusions from later layers.

Results

Two artefacts were newly analysed for this study: the foil from Pločnik (no. 63) and the Gomolava ring (no. 212) (Figure 1B), previously studied by Ottaway (1979); our methodology is reported in the online supplementary material.

The Pločnik sample has on average 11.7wt% tin (Table 1), together with lead, nickel, and iron at levels of between one tenth and half of one per cent each. The Gomolava ring has only 8.5wt% tin, but significantly higher levels of lead, arsenic, antimony and nickel, all between a quarter of one per cent and one per cent. Sulphur and selenium concentrations are relatively high in both samples.

The high level of metallic iron in the Pločnik foil demonstrates that this is freshly smelted metal, not re-melted during alloying (Craddock & Meeks 1987), while the presence of significant levels of antimony and arsenic in Gomolava 212 is typical of copper smelted from *fahlerz* ores (or fahlores). Both objects have a completely homogenised structure (Figure 4), which for tin bronzes above 8wt% tin requires annealing temperatures in the range of 500–800°C (Scott 1991). The foil is fully recrystallised, with grain sizes of *c.* 0.2mm (Figure 5). A single annealing twin in the microstructure is probably a result of cold working and prolonged annealing, which left the foil soft enough to be wrapped around a (presumably) ceramic vessel.

The Gomolava ring has an incompletely recrystallised structure with much smaller grain size (*c.* 0.025mm) indicating several cycles of working and annealing (Figure 6). This is consistent with a high degree of cold reduction, estimated at between 60 and 80 per cent (Rostoker & Dvorak 1990) on the basis of elongated sulphur-rich inclusions. The incompletely recrystallised structure may indicate that the last annealing process before final working was not carried through to completion, leaving the metal in a work-hardened state, suitable for use as jewellery.

In summary, the samples consist of chemically complex copper metal rich in tin and a range of minor and trace elements. They were made using different working sequences, carefully

Table 1. Compositional data for early tin bronze artefacts from the Balkans, given in wt%. Data for artefacts other than Pločnik (63) and Gomolava (212) taken from Chernykh (1978: 112, 339–52) and Pernicka *et al.* (1993: 10, tab. 3; 1997: 121–26, tab. A1). Compositional patterns distinguished three separate groups, based on the potential ores used for their production: predominant stannite; fahlore with stannite (high-tin fahlore); and fahlore with some stannite (low-tin fahlore). The bottom row represents an average of 40 contemporary copper metal artefacts from the Early (EC) and Middle Chalcolithic (MC), based on data from Pernicka *et al.* (1993: 190, tab. 3; 1997: 147–48, tab. A1), demonstrating that the trace element signature of the bronzes is unlikely to originate from the copper.

Site of origin	Sample label	Object	Cu wt%	Sn wt%	As wt%	Fe wt%	Co wt%	Ni wt%	Ag wt%	Sb wt%	Au wt%	Pb wt%
Smjadovo	HDM 2720	borer	90.5	8.6	0.34	0.44	0.01	0.02	0.016	0.020	0.002	0.05
Karanovo	ASM 12043	ring	92.5	7.0	0.20	0.05	0.02	0.15	0.004	0.005	0.001	0.02
Bereketska Mogila	ASM 12103	needle	92.9	6.0	0.35	0.70	0.012	0.02	0.002	0.010	0.003	0.005
Bereketska Mogila	ASM 12105	awl	89.6	10.0	0.01	0.30	0.04	0.06	0.002	nd	0.003	0.004
Karanovo	ASM 12051	needle	92.1	7.0	0.07	0.20	0.01	0.50	0.0003	nd	0.003	0.15
Lazareva pećina	HDM 1330	borer	98.0	7.1	0.02	0.06	0.0003	0.004	0.007	0.013	0.004	0.006
Pločnik	Pločnik 63	sheet	87.4	11.7	0.03	0.12	0.07	0.16	nd	nd	0.016	0.40
First group (stannite)	**Average**		**91.8**	**8.2**	**0.15**	**0.27**	**0.02**	**0.13**	**0.005**	**0.01**	**0.004**	**0.09**
Gomolava	Gomolava 212	ring	89.4	8.5	0.35	0.005	0.025	0.25	0.08	0.45	0.002	0.82
Ruse	ASM 10853	awl	89.2	6.0	0.60	0.20	0.015	0.20	0.04	0.20	0.001	3.5
Ruse	HDM 2046 (ASM 10875)	borer	86.0	7.3	0.35	0.31	0.016	0.28	0.03	0.30	0.003	0.05
Ruse	ASM 10863	borer	88.4	10.0	0.40	0.07	0.02	0.40	0.03	0.50	0.030	0.18
Ruse	ASM 10882	ring	92.1	7.0	0.50	0.07	0.04	0.10	0.03	0.06	0.003	0.05
Second group (high-tin fahlore)	**Average**		**89.0**	**7.8**	**0.44**	**0.13**	**0.023**	**0.25**	**0.04**	**0.30**	**0.008**	**0.92**
Bereketska Mogila	ASM 12138	rod	96.8	1.0	0.06	0.02	nd	0.008	0.02	0.07	0.0029	2.0
Gradeshnica	ASM 10686	awl	94.3	4.5	0.35	0.01	0.003	0.04	0.05	0.50	0.0030	0.2
Zaminec	HDM 2733	borer	95.9	3.1	0.26	0.04	0.002	0.06	0.108	0.33	0.0014	0.14
Third group (low-tin fahlore)	**Average**		**95.8**	**2.9**	**0.22**	**0.02**	**0.003**	**0.036**	**0.06**	**0.30**	**0.002**	**0.78**
Typical EC/MC (n = 40)			***100***	***0.005***	***0.04***	***0.04***	***0.001***	***0.01***	***0.04***	***0.01***	***0.001***	***0.013***

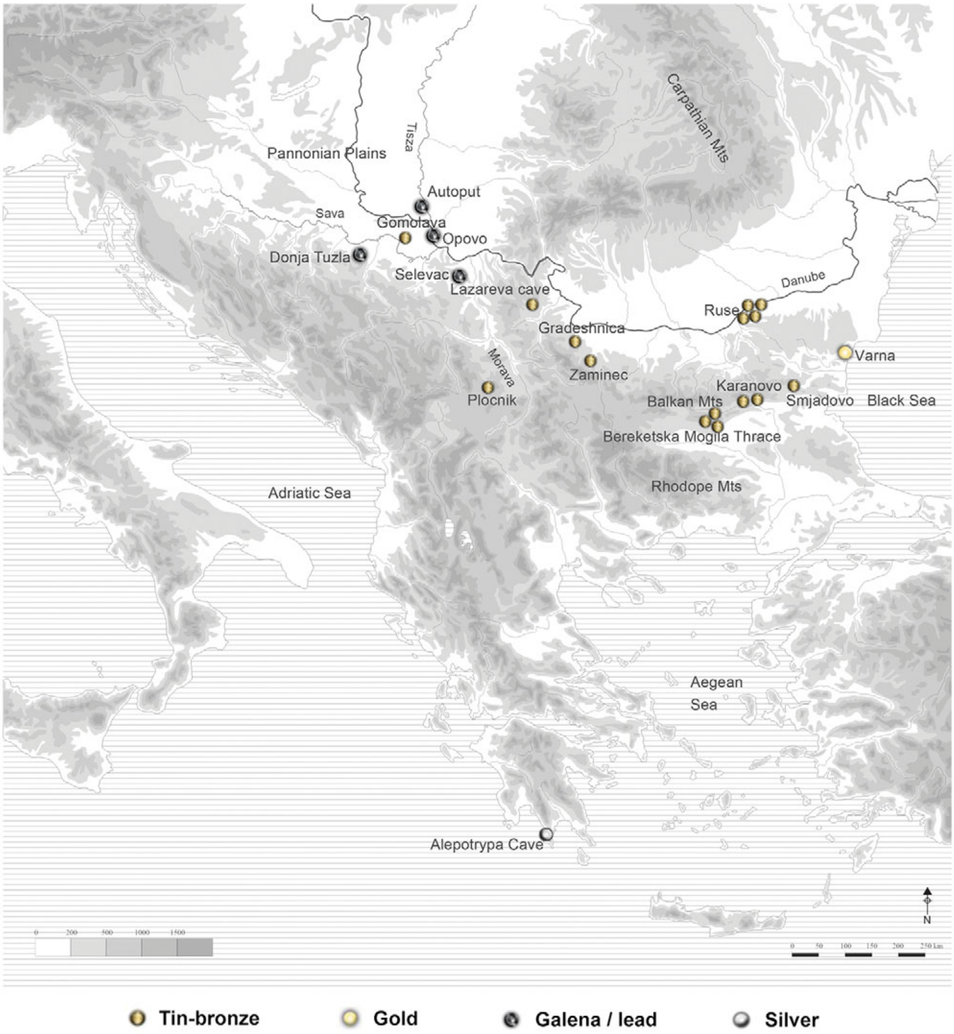
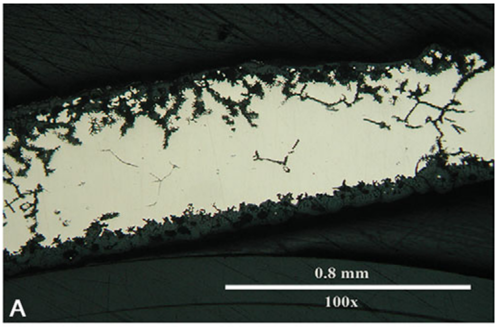


Figure 3. The fifth millennium BC 'polymetallic' map of the Balkans, showing locations of sites mentioned here. Symbols indicate the type of metal in artefacts discovered at these sites. Base map courtesy of M. Milinković, Faculty of Philosophy, Belgrade; adapted by Lj. Radivojević.

adjusted to the different properties required by the two objects, and with considerably higher annealing temperatures than those used for pure copper. This demonstrates that the metal smiths understood clearly the specific properties and requirements of tin bronze, as opposed to the more commonly used copper.

Tin bronzes in the Balkans: comparative analysis

The Pločnik and Gomolava objects are similar in composition to 13 previously analysed early tin bronzes from Bulgaria and Serbia. Compared to contemporary Early and Middle Chalcolithic (EC/MC) Bulgarian copper artefacts, levels of iron, cobalt, nickel and arsenic



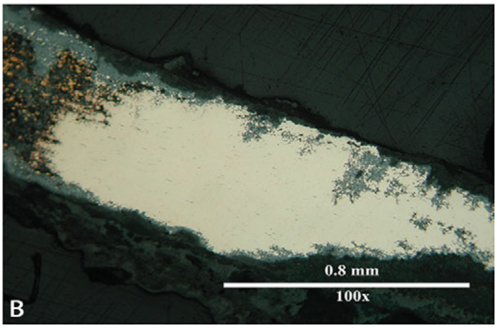


Figure 4. Photomicrographs of unetched sections of Vinča culture tin bronzes: (A) the Pločnik foil; (B) the Gomolava ring. Both samples show a homogenised structure with grey sulphur-rich inclusions.

are on average about one order of magnitude higher, and those of antimony and lead up to two orders of magnitude higher (Table 1). Such a trace element pattern is not found in later tin bronzes, and is unlikely to originate from the addition of tin metal or cassiterite to ordinary copper; most cassiterite deposits and the tin smelted from them are very low in these base metals. Instead, the trace element pattern indicates the use of other, more complex ores for the production of these objects.

The analyses fall into three groups (Table 1). Traditionally, copper with significant impurities of arsenic, antimony, silver and nickel is thought to originate from fahlore smelting (Otto & Witter 1952; Merkl 2010). Fahlore copper, however, does not normally contain more than a few tens of ppm tin. Instead, the tin in these early bronzes is thought to originate from stannite, Cu_2FeSnS_4, a copper-tin mineral structurally similar to chalcopyrite, and visually a dark metallic-grey like fahlore. The three compositional groups presumably originate from a copper ore containing varying amounts of fahlore and stannite, probably mixed with other metal-rich minerals. The association of primary copper deposits, such as chalcopyrite, with both stannite and fahlore is not uncommon in sulphidic ore bodies in tin-rich provinces (Ramdohr 1980: 549–62; see also online supplementary material), and tin deposits are widespread throughout the Balkans (Glumac & Todd 1991). Ore batches used as a charge in the smelting process, retrieved from such ore deposits, would inevitably vary in their relative proportions of chalcopyrite, stannite and fahlore, resulting in the variable composition of the alloys seen here. The high sulphur content in both of the samples that were studied microscopically further indicates the sulphidic nature of the primary ore source, even if the smelted charge may have been dominated by secondary minerals formed from these sulphides. Thus, the three groups are tentatively labelled stannite bronze, high-tin fahlore bronze and low-tin fahlore bronze, indicating the possible ore types that could have underpinned their production.

The next horizon of bronzes in Serbia, dated to the third millennium BC, is characterised by significant arsenic (As) content (on average *c*. 1wt%, and reaching up to 4wt%), alongside traces of tin (Sn) (<400 ppm at most, with one exception of *c*. 2wt%) (Pernicka *et al.* 1993: 12, tab. 3). In Bulgaria, the fourth millennium BC sites yielded only arsenical copper, with significant arsenic content (average *c*. 1wt%, and reaching up to 8.4wt%), and almost no tin (<0.1wt% at most, with one exception of *c*. 2.3wt%). Third millennium BC metal

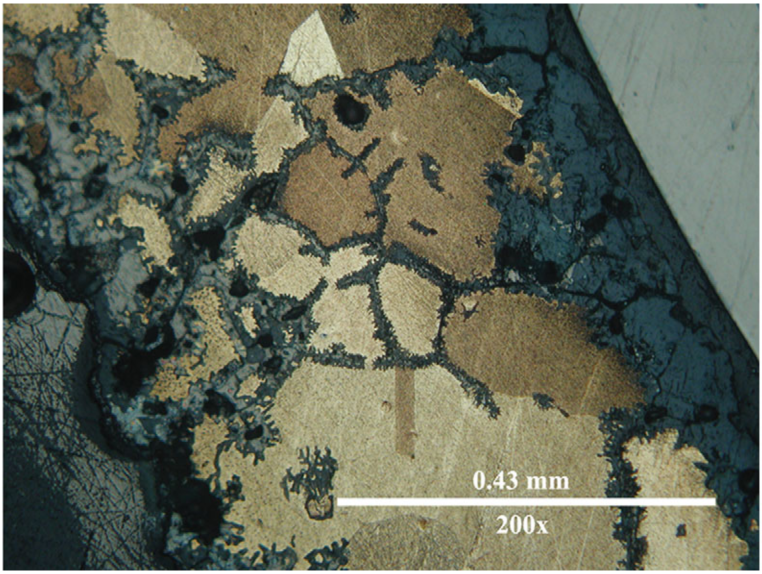


Figure 5. Photomicrograph of the etched section of the Pločnik foil (sample no. 63), showing fully recrystallised grain structure and a single annealing twin (visible in lower centre of image), consistent with light working of the artefact.

production in Bulgaria was mainly concentrated around pure copper and arsenical copper, save for a few artefacts containing variable tin (between 0.8wt% and 15wt%), alongside considerable arsenic levels (>1wt%) in some examples (Chernykh 1978: 368–69). Tin bronzes enter more regular circulation during the second millennium BC in Bulgaria (Late Bronze Age), with average concentrations of tin and arsenic at *c.* 5wt% and *c.* 0.3wt% respectively (Pernicka *et al.* 1997: 155–56, tab. A1). These LBA tin bronzes from Bulgaria come from different sites to those considered here, except for the awl from Gradeshnica, where three other tin bronze artefacts dated to the second millennium BC have also been found. The composition of these three LBA tin bronzes (all of which are stray finds) differs from the Gradeshnica awl (ASM 10686): one is more likely to be brass than tin bronze, the second shows the composition of a cassiterite bronze, while the third has half as much arsenic, and almost an order of magnitude more iron and nickel levels than the tin bronze awl in Table 1 (Pernicka *et al.* 1993: 156). Hence these LBA objects differ significantly from the tin bronze awl under consideration here.

In summary, the unique compositional pattern of the 15 tin bronzes (Table 1) differs significantly from that of later metal artefacts in Serbia and Bulgaria. It is therefore reasonable to assume a temporal as well as geographical and technological connection among the 15 early complex tin bronzes that supports their attribution to the fifth millennium BC.

Noteworthy is a group of 25 tin bronze artefacts (tools and decorative items), which is compositionally similar to the 15 tin bronze artefacts we discuss here (Govedarica *et al.* 1995: 275–77, tab. 1, clusters 1, 2, 7, 9 and 11). These were discovered in several sites in Croatia (Dalmatia) and Bosnia and Herzegovina, and dated to the Early Bronze Age (early second millennium BC in this part of the Balkans), thus showing no temporal or spatial connection to the Chalcolithic tin bronzes. They are, however, very likely indicating a

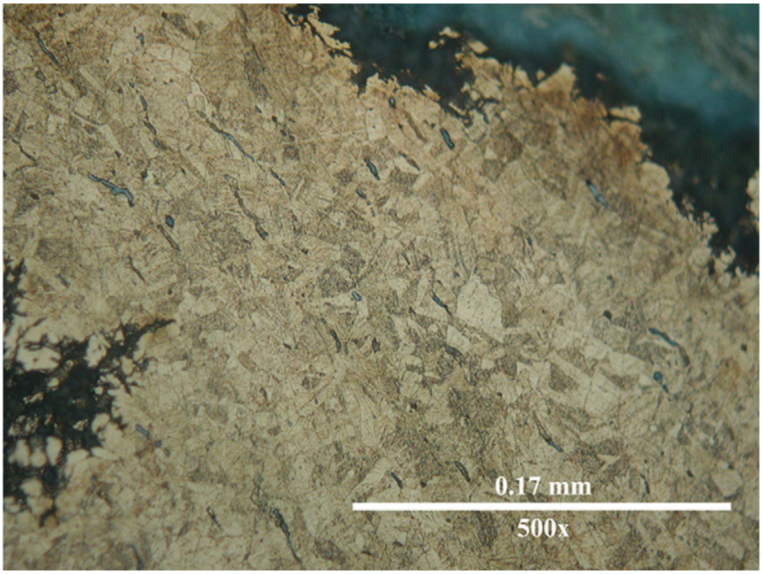


Figure 6. Photomicrograph of the etched section of the Gomolava ring (sample no. 212), with significantly reduced grain structure, deformation marks and elongated inclusions, together suggesting several cycles of annealing.

regional source of such a complex copper-tin-bearing ore that was used for their making, and possibly exploited even earlier, in the fifth millennium BC, for producing earlier examples of complex tin bronzes.

Discussion

The Vinča culture tin bronzes from Pločnik and Gomolava were carefully made artefacts smelted from complex ores, and worked with a combination of techniques well suited for the desired function. Their shape implies that they were used for decorative purposes; visual appearance played a significant role in their use. The foil from Pločnik was left in a soft annealed state so that it could be wrapped around a ceramic vessel, while the ring from Gomolava was left in the work-hardened state. The annealing temperatures used were much higher than those required for annealing the pure copper that was the dominant metal of the time, and indicates an understanding of the particular properties and requirements of these tin bronzes.

The early tin bronzes share strong qualitative and quantitative similarities in their minor and trace element patterns, implying their origin from broadly similar complex tin-bearing copper ores. They form three compositional groups: stannite bronze, high-tin fahlore bronze and low-tin fahlore bronze. All three groups of artefacts probably had primary and secondary copper minerals present in the smelting charge, as well as other accessory base metal minerals. The large variability in detail yet similarity in principle of the compositions indicate that the groups possibly originated from a single deposit with variable stannite and fahlore contents in different ore batches, or from a few geologically very similar ore deposits. Further research, including lead isotope and trace element analyses, will be necessary to address this issue of provenance.

The smelting of stannite for early tin bronze artefacts has already been hypothesised by Charles (1978) and Wertime (1978). Stannite is present in the Bronze Age mines of Mushiston in Tajikistan (Weisgerber & Cierny 2002), Deh Hosein in Iran (Nezafati *et al.* 2006), the Bolkardağ mining district in Turkey (Yener & Özbal 1987), as well as in Iberia (Rovira & Montero 2003). It has a metallic grey lustre, similar to fahlore with which it is easily confused, with an olive-green tint, particularly when it is partly weathered and intergrown with secondary copper minerals. The overall appearance then is one of tainted, black-and-green ores.

The selection of a self-fluxing ore comprising green copper minerals intergrown with black manganese minerals (as opposed to the pure green minerals used for malachite beads), may have been a key feature of Vinča copper smelting at the turn of the fifth millennium BC (Radivojević *et al.* 2010). Visual appearance was also decisive in recognising copper minerals rich in stannite and/or fahlore. Weisgerber and Cierny (2002: 184) remark on the macroscopic appearance of the tin-copper paragenesis in Mushiston, Tajikistan: '. . .Mushistonite [$(Cu,Zn,Fe)Sn(OH)_6$]. . .is trapped in a white quartz. . .(as) the [hydrated] tin ore. . .(and) stains it as black spots. . . in fine grained yellow-greenish masses'. The black-and-green lustre of complex copper-tin ores could have been recognised as a desirable feature for tin bronze making well into the third millennium BC.

Significant tin mineralisations exist in western Serbia at Mount Cer and Bukulja, and at several localities in eastern Serbia, Bosnia, Croatia, Hungary and Romania; these are part of the extensive copper-sulphide-rich deposits within the Tethyan-Eurasian metallogenic belt (Glumac & Todd 1991; Janković 1997). The proximity of Pločnik and Gomolava to these deposits is remarkable, whereas no similar deposits have been reported in Bulgaria, where most of the tin bronzes have been found.

The characteristic composition of the tin bronze foil from Pločnik supports the fifth millennium BC date assumed for the other early tin bronzes that share this composition. That assumption is further strengthened by the absence of compositionally similar objects from later layers, and by the hiatus of more than a millennium before cassiterite tin bronzes appear in the Balkans. This makes it unlikely that these objects are intrusions from later levels. It also suggests that the particular deposit(s) yielding these ores were either exhausted or, more likely, were not the active cultural and technological choice of the Balkan Early Bronze Age cultural groups. The disappearance of the complex tin bronzes coincides with the collapse of large cultural complexes in north-eastern Bulgaria and Thrace in the late fifth millennium BC (Todorova 1995; Weninger *et al.* 2009). This suggests that these tin bronzes were 'cultural alloys', their production dictated by culturally embedded desires and preferences (Hamilton 1991), and not opportunistically or haphazardly made.

What were the advantages of tin bronzes? The presence of major impurities such as tin, arsenic and antimony improved their material properties: they melted at lower temperatures than pure copper objects and were easier to cast (Northover 1989; Lechtman 1996). These impurities also gave the artefacts a bright yellow colour. Colour has been recognised as crucial in the use of tin bronzes as an alternative to gold in central Asia (Kaniuth 2007), and for the early appearance of brasses (copper-zinc alloys also yellow in colour) from the early third millennium BC (Thornton 2007).

Colour is particularly interesting in light of the world's earliest gold objects, dated to the mid fifth millennium BC and deposited in the cemetery of Varna in Bulgaria to display social prestige (Renfrew 1986; Higham *et al.* 2007). Similar artefacts have been discovered in several mid to late fifth millennium BC settlements in Bulgaria (Makkay 1991). The colour and social significance of gold can be related to the emergence of the early tin bronzes, and the opportunities the latter might have offered as an imitation of gold. Tin bronze production in the Balkans during the fifth millennium BC may not only be intimately connected to copper, but to gold as well. To the visual similarity of gold and tin bronze we may add the relatively limited production of both metals, which stands in stark contrast to the massive production of contemporary copper metal implements (*c*. 4.7 tonnes extant) (Chernykh 1978). Access to gold and tin bronzes may have been reserved only for highly ranked individuals, as indicated by the Varna cemetery; it could also explain why so few yellow metal artefacts were in circulation at the time.

The polymetallic (r)evolution of the fifth millennium BC

Our study provides archaeological and analytical evidence for the independent emergence of tin bronze production, from complex copper-tin ores, some 1500 years before the first tin bronze alloys of south-western Asia. They also preceded by almost half a millennium the earliest use of natural alloys of arsenical copper (Roberts *et al.* 2009). Thus the fifth millennium tin bronzes fundamentally challenge the established sequence of the evolution of metallurgy in western Eurasia.

The selection of ores for these natural alloys was probably facilitated by their black-and-green colouration, similar to the black-and-green manganese-rich copper minerals already exploited in the initial stages of copper metallurgy in the Balkans. Tin bronze production was thus initiated by smelting ores that macroscopically resembled those already used for copper extraction.

The application of specific working techniques implies that the Vinča smiths were aware of the particular material properties of this new metal. Moreover, the colour of the final products could have been a key feature in their demand, particularly since it developed in parallel with the rise of gold production in the area. Hence the fifth millennium tin bronzes from the Balkans might have been produced to imitate gold.

Copper, tin bronzes and gold are not the only metals used in the Balkans at this period. There is evidence of mid fifth millennium BC use of both lead and galena from the Vinča culture sites of Selevac, Opovo, Autoput and Donja Tuzla (Glumac & Todd 1987). In the wider Balkan region the use of silver is attested by the hoard of more than 100 silver artefacts from the Alepotrypa Cave in Greece, and dated to the mid fifth–early fourth millennia BC (Muhly 2002). The near-contemporary use of tin bronze, gold, lead/galena and, most likely, silver in addition to the dominant copper in the Balkans during the mid to late fifth millennium BC defies the conventional narrative of a slow unilinear evolution of metallurgy. Quite the reverse, the early trajectory of metallurgy in the Balkans emerges almost from the very beginning as *polymetallic* in nature.

This 'polymetallism' has hitherto been considered exceptional, supported only by the evidence for smelting polymetallic (copper) ores from the late fifth millennium BC Bulgarian sites of Dolnoslav and Chatalka (Ryndina *et al.* 1999). The 15 tin bronze artefacts presented here demonstrate that the use of complex copper-tin bearing ores was more common than has been supposed. The polymetallic character of early Balkan metallurgy does not appear to be driven by the need for functional metals, but by demand for desirable visual properties in the final products. Thus, the co-occurrence of three, or possibly four, different metals next to copper with distinctive material properties requiring specific working techniques follows one common principle: their visual appearance. The visual appeal of new metals has been suggested before as the driving force behind their introduction (Lechtman 1977; Smith 1981; Hosler 1994; Kaniuth 2007; Thornton 2007); this research takes the argument further back in time to the very early stages of metallurgy in Eurasia.

Balkan polymetallism may have evolved from the aesthetic preferences of the consumer elite at the time. The black-and-green ores that gave rise to the tin bronzes were not the only ones being experimented with in this period. Exploitation of the material properties of other metals such as silver or gold indicates that metalworkers were actively pursuing various technological solutions. Their emergence marks both a polytechnological and polymetallic horizon. Interestingly, these polytechnologies were not utilised for the active alloying of two metal components; that only appears half a millennium later with arsenical copper and *c*. 1500 years later in the case of tin bronzes. The absence of alloyed metals in these early stages of Eurasian metallurgy has been traditionally ascribed to a lack of technological skills, but the evidence presented here challenges that conventional narrative by showcasing the significant level of metal craftsmanship in the fifth millennium BC. The reluctance to produce alloyed metals may well have been rooted in cultural as well as technological choices, for instance in the demand for a specific colour rather than advantageous material properties.

The production of complex tin bronzes in the Balkans declined towards the end of the fifth millennium BC. Significantly, this coincided with the collapse of the gold-using cultures in Bulgaria. Explanation could be sought in population dynamics, which were a powerful mechanism for both the generation and decline of innovations in prehistoric societies (Henrich 2004; Powell *et al.* 2009). Tin bronzes only re-appeared some 1500 years later, based on cassiterite tin. This alloy was widely adopted across central and south-western Asia but in a different cultural climate, when its production, consumption and trade acted as one of the driving forces behind the intensification of the economic, social and political lives of Bronze Age communities across Eurasia.

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