# WHY ARE THERE TIN BRONZES IN THE 5TH MILLENNIUM BC BALKANS?

**Miljana Radivojević**
UCL Institute of Archaeology, London
**Julka Kuzmanović-Cvetković**
Museum of Toplica, Prokuplje

**Thilo Rehren**
UCL Qatar, a partner of Hamad bin Khalifa University, Doha
**Marija Jovanović**
Museum of Vojvodina, Novi Sad

***Abstract:*** *The appearance of the earliest tin bronze artefacts is traditionally linked to the copper-tin alloying practice in the 3rd millennium BC Near Eastern Bronze Age settlements. Advocates of this model argue that tin for alloying may have come from deposits located in central Asia or southwest Iran; however, finding evidence for tin bronze production remains a challenge for archaeologists. Here we present a piece of tin bronze foil discovered in the Vinča culture site of Pločnik in Serbia, and securely dated to c. 4650 BC, which makes it the earliest known tin bronze artefact anywhere in the world. Compositional analysis links it to smelting a complex copper-tin ore, such as chalcopyrite intergrown with stannite and / or fahlerz, while metallographic analysis indicate its intentional production and understanding of material properties of the newly acquired metal. These results initiated a reassessment of the fourteen previously discovered and analysed artefacts of similar compositional pattern as the Pločnik foil. The rise of tin bronze metallurgy in the Balkans is also discussed in the light of the concurrent appearance of other colourful metal objects in this region.*

***Key words:*** *tin bronze, Vinča culture, Pločnik, Balkans, Chalcolithic*

***Apstrakt:*** *Pojava najranijih artefakata od kalajne broze tradicionalno je povezivana sa praksom legiranja bakra i kalaja u bronzanodobnim naseljima na Bliskom Istoku tokom III milenijuma pre nove ere. Zagovornici ovog modela tvrde da je kalaj za legiranje možda došao iz ležišta koja se nalaze u centralnoj Aziji ili jugozapadnom Iranu; ipak, dokazi o proizvodnji kalajne bronze ostaju izazov za arheologe. Ovde je predstavljen komad lima od kalajne bronze otkriven na Pločniku, lokalitetu vinčanske kulture u Srbiji, sigurno datovan u 4650. godinu p.n.e., što ga čini najranijim poznatim artefaktom od kalajne bronze u svetu. Analiza sastava povezuje ga sa topljenjem kompleksne bakarno-kalajne rude kao što su halkopirit u paragenezi sa stanitom i / ili tetraedritom, dok metalografska analiza ukazuje na njenu namernu proizvodnju i poznavanje materijalnih karakteristika novostvorenog metala. Ovi rezultati pokrenuli su preispitivanje 14 ranije otkrivenih i analiziranih artefakata slicne kompozicije kao i pločnički lim. Uspon metalurgije kalajne bronze na Balkanu je takođe razmotren u svetlu istovremenih pojava drugih raznobojnih metalnih predmeta u ovom regionu.*

***Ključne reči:*** *kalajna bronza, vinčanska kultura, Pločnik, Balkan, halkolit*

## Introduction

The emergence of the 3rd millennium BC tin bronze metallurgy has been recognised as the defining industry of the Bronze Age societies in Eurasia, and influencing major changes in political and social lives of consumer communities (e.g. Harding 2000; Anthony 2007; Kuz'mina 2008). The earliest documented tin bronze artefacts, mostly pins or flat axes from sites such as Troy in Turkey, Abraq in the United Arab Emirates or Susa in Iran, and dating to the early 3rd millennium BC (Stech, Pigott 1986; Weeks 1999; Begemann et al. 2003; Helwing 2009), contained up to 10 % tin, which was understood to derive from intentional alloying of tin metal or tin ore, cassiterite (SnO2, tin oxide) to either copper ore or copper metal (e.g. Cleziou and Berthoud, 1982). However, neither the production evidence for tin metal nor the geological tin source that was providing the Near Eastern communities with the alloying agent for copper have been identified thus far. The pursuit for the tin ore source in particular resulted in heated academic debates (Muhly 1993; Yener et al. 1993), and only recent data have shown that there were possibly multiple cassiterite source, located in modern Iran, Afghanistan, Uzbekistan and Tajikistan, that were exploited during the Bronze Age (Weisgerber, Cierny 2002; Nezafati et al. 2006; 2011; Stöllner et al, 2011; Pigott 2011).

Yet another important question is how the early production of tin bronze fits into the traditional narrative of the evolution of Eurasian metallurgy, which follows a relatively simple, unilinear model of development of metallurgy from a single region. It goes back to the use of copper minerals and native copper that were initially being worked in the Neolithic, which eventually led to the smelting of copper from oxidic ores in the Chalcolithic. Towards the end of this period mixing of ores was practiced to produce arsenical copper, and the large-scale smelting of sulphidic copper ores started. The Middle and Late Bronze Age are marked by the inception of alloying tin metal with copper to mass-produce tin bronze, while iron metallurgy comes into fashion by the end of the Late Bronze Age (e.g. Wertime 1964).

On a broader scale, this narrative proves sufficient in interpreting general consumption patterns; however, a higher-resolution regional perspective on metallurgical production defies the established order of sequence as for instance in the Middle East (Thornton 2009; 2014), or in the Americas, where the evolutionary trajectory of metallurgy is entirely independent from the one outlined above (Lechtman 1980; Ehrhardt 2009).

In the Balkans, the area of our interest in this paper, the most recent discovery of c. 7000 years old copper smelting evidence in the Vinča culture site of Belovode revived the possibility of independent, multiple inventions of metallurgy outside the 'core area' of the Near East (Radivojević et al. 2010). Compositional analysis of various archaeometallurgical materials from this site revealed that 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, where 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 (Bar-Yosef Mayer, Porat 2008).

This paper presents analytical data for a tin bronze foil from the Vinča culture site of Pločnik in south Serbia, which was possibly wrapped around a ceramic vessel (fig. 1). This foil was discovered in an undisturbed context of a dwelling structure within this site, surrounded by several Vinča culture pottery vessels, c. 1 m away from a fireplace (Šljivar et al. 2012, 33; Radivojević et al. 2013, 1033, fig. 2). This securely contextualised find comes from a single and undisturbed occupation horizon in the site of Pločnik, dated to c. 4650 BC (Borić 2009, 214). The tin bronze foil from Pločnik is therefore the earliest known tin bronze artefact, anywhere (Radivojević et al. 2013, 1032).


**Fig. 1** A tin bronze foil from the Vinča culture site of Pločnik, securely dated to c. 4650 BC (Radivojević et al. 2013, 1032, Fig. 1A)
**Sl. 1** Lim od kalajne bronze sa vinčanskog lokaliteta Pločnik, sigurno datovan u 4650. p.n.e. (Radivojević et al. 2013, 1032, Fig. 1A)

## Materials and Methods

The analytical work was carried out at the Wolfson Archaeological Science Laboratories, UCL Institute of Archaeology, and the metallographic examination at the Department of Materials, Oxford University. Samples were cut to size, mounted in epoxy resin discs, ground using abrasive disks (1200 and 2400 grit) and polished using diamond pastes (1 µm and ¼ µm). They were examined by reflected light microscopy (OM) prior to electron microprobe (EPMA) investigation. Metallographic examination was carried out using reflected light microscopy after etching with two different etchants, ammonia hydrogen peroxide and alcoholic ferric chloride, with the kind help of Dr Peter Northover, Department of Materials, University of Oxford, UK.

## Early Tin Bronzes in the Balkans: Background

The foil from Pločnik is not the first find of tin bronze in the Balkans of such early age. During the last century, fourteen other tin bronze artefacts were discovered, but they were either insufficiently contextualised or poorly dated, and were therefore only tentatively ascribed to the Chalcolithic period (Chernykh 1978; Ottaway 1979; Tasić 1982; Pernicka et al. 1993). In addition, a piece of copper-tin slag was uncovered from a late 5th millennium BC female burial in the cemetery of Zengővárkony in Hungary (Glumac and Todd 1991). However, its context has been questioned by Pernicka et al. (1997). The Pločnik foil thus is the only securely dated artefact among the entire Balkan early tin bronze assemblage, justifying a review of the earlier finds.

The Bulgarian sites of Ruse, Karanovo, Gradeshnitsa, Smjadovo, Zaminec, and Bereketska Mogila yielded 12 samples in total, while only two come from the Serbian sites of Lazareva cave and Gomolava (fig. 3); all samples were analysed previously both by Chernykh (1978) or Pernicka et al. (1993; 1997). This assemblage contains awls, rings, needles, borers and a rod, with tin concentrations between 1-10 wt%, and consistently with significant levels of lead, arsenic, nickel, cobalt, iron and gold (fig. 6). Although the exact concentrations of these elements vary widely from sample to sample, they appear qualitatively similar, which suggests their origins from similar types of ores. Some of them match typologically counterparts in pure copper from the 5th millennium BC Balkans (Chernykh 1978, 81). All objects originate from disturbed Chalcolithic occupation within multi-layered sites mentioned above, barring a ring from Ruse (ASM 10882), which is thought to come from a child's burial belonging to the undisturbed Chalcolithic horizon in this site.

The cultural and chronological provenience of these tin bronzes was assumed to be Chalcolithic based on their distinctive composition and the limited quantity of such metal finds. Tin bronze is widely adopted in the Balkans only from the 3rd and 2nd millennium BC onwards (Chernykh 1978; Schickler 1981; Pernicka et al. 1997; Pare 2000). Furthermore, the later tin bronzes from the studied areas (modern Croatia, Bosnia, Serbia and Bulgaria) have very different trace element compositions (Govedarica et al. 1995), making it unlikely for these finds to be intrusive.


**Fig. 2** A tin bronze ring from the Vinča culture site of Gomolava, tentatively dated to the mid-5th millennium BC (Radivojević et al. 2013, 1032, Fig. 1B)
**Sl. 2** Prsten od kalajne bronze sa vinčanskog lokaliteta Gomolava, uslovno datovan u sredinu V milenijuma p.n.e (Radivojević et al. 2013, 1032, Fig. 1B)

### Compositional analysis

Two artefacts were newly analysed for this study: the foil from Pločnik (No. 63) and the Gomolava ring (No. 212) (fig. 2), previously studied by Ottaway (1979). The Pločnik sample showed an average 11.7 wt% Sn (fig. 6), together with lead, nickel, and iron at levels of between one tenth and half of one percent each. The Gomolava ring has only 8.5 wt% Sn, but significantly higher levels of lead, arsenic, antimony and nickel, all present between a quarter of one percent and one percent. Sulphur and selenium concentrations are relatively high in both samples. The presence of metallic iron in Plocnik 63 foil demonstrates that this foil was made from freshly smelted metal, and not re-melted during alloying (Craddock, Meeks 1987). On the other hand, the presence of significant levels of Sb and As in the Gomolava 212 ring indicates that this artefact was possibly made by inclusion of fahlerz ores in the smelt (Radivojević et al. 2013, 1037).

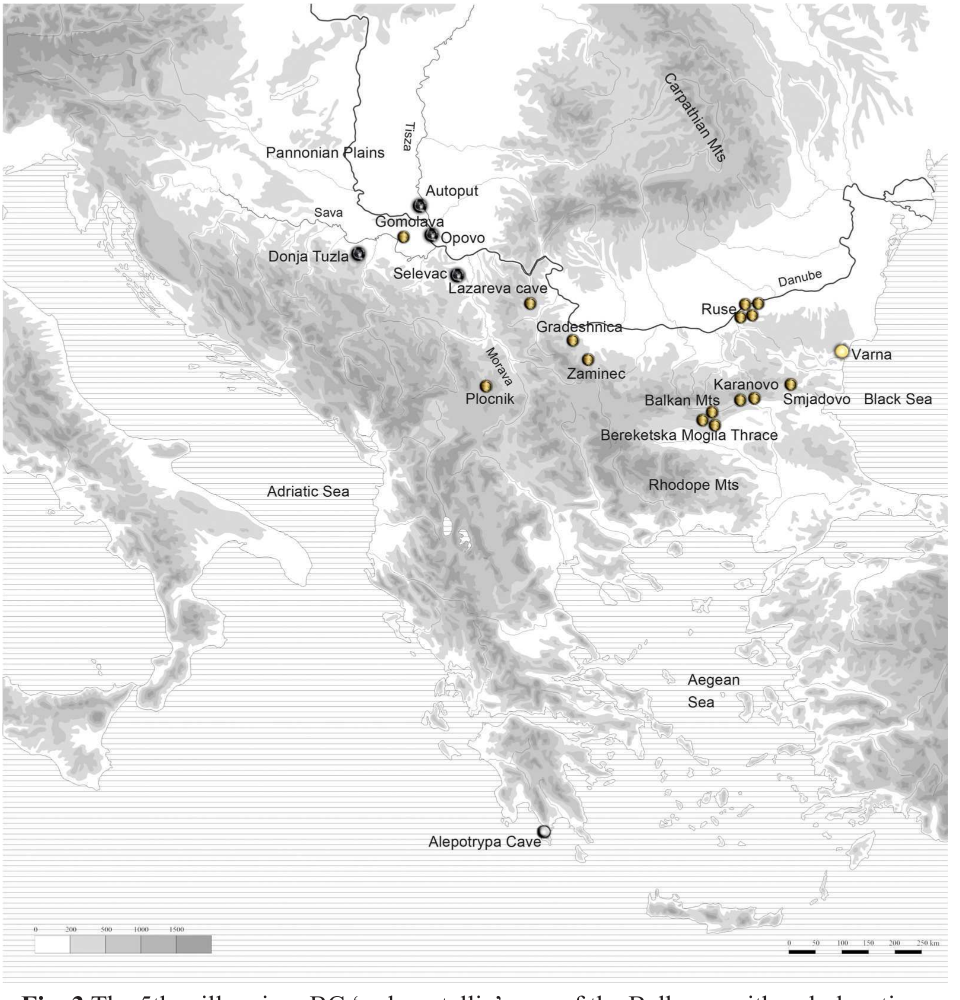



**Fig. 3** The 5th millennium BC 'polymetallic' map of the Balkans, with only locations of sites mentioned here. Symbols attached to sites correspond with the type of metal (artefact) discovered at these locations: (tin bronzes); (gold); (galena/lead) and (silver). The base map is courtesy of Prof. M. Milinković, Faculty of Philosophy, Belgrade, adapted by Lj. Radivojević (Radivojević et al. 2013, 1036, Fig. 3)

**Sl. 3** "Polimetalična" mapa Balkana u V milenijumu p.n.e., sa lokalitetima koji se pominju u tekstu. Simboli koji označavaju lokalitete odgovaraju vrsti metala (artefakata) otkrivenih na tim nalazištima: (kalajna bronza); (zlato); (galenit/olovo) i (srebro). Osnova karte dobijena je ljubaznošću prof. M. Milinkovića sa Filozofskog fakulteta u Beogradu, prilagođena od strane Lj. Radivojević (Radivojević et al. 2013, 1036, Fig. 3)

Both objects were worked at temperatures of 500–800 °C (Scott 1991). The Pločnik foil (63) appears fully recrystallised, with a single annealing twin presumably resulting from cold work and prolonged annealing, which left this object soft enough to be wrapped (possibly) around a ceramic (or possibly wooden) vessel (fig. 1; 4). The microstructure of the Gomolava ring (fig. 5) indicates several cycles of working and annealing, and reduction to between 60% and 80% of the thickness of initial working sheet or a bar (Rostoker, Dvorak 1990). The incompletely recrystallised structure may suggest that the last annealing process prior to final working was not carried through to completion, leaving the metal in a work-hardened state, suitable for regular use as jewellery.

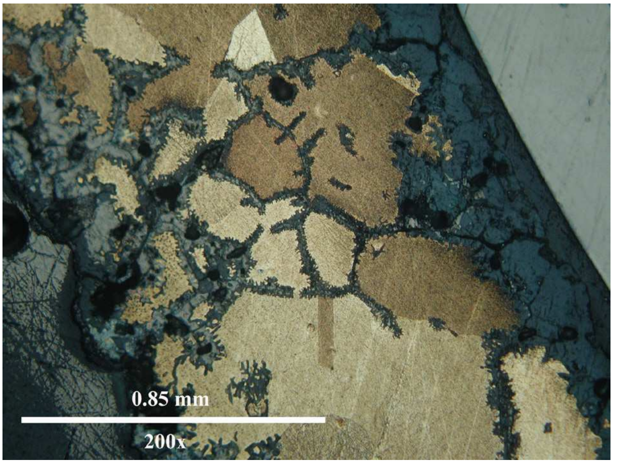



**Fig. 4** Photomicrograph of the etched section of Pločnik foil (sample No. 63), showing fully recrystallised grain structure and a single annealing twin, which indicates light working of the artefact (Radivojević et al. 2013, 1038, Fig. 5)
**Sl. 4** Mikroskopska fotografija preseka, nakon nagrizanja kiselinom, lima iz Pločnika (uzorak br. 63), na kome se vidi potpuno rekristalizovana zrnasta struktura i jedan prekaljeni blizanac koji ukazuje na lagano iskivanje ovog artefakta (Radivojević et al. 2013, 1038, Fig. 5)

In summary, the samples consist of chemically complex copper metal rich in tin and a range of minor and trace elements not commonly found in later tin bronzes. These objects were made using working sequences that were well adjusted to the different functions required from working of these two objects, and using considerably higher annealing temperatures than those used for working pure copper. The technological analysis therefore demonstrates that the metal smiths at the time had already a clear understanding of the specific properties of tin bronze making and working.

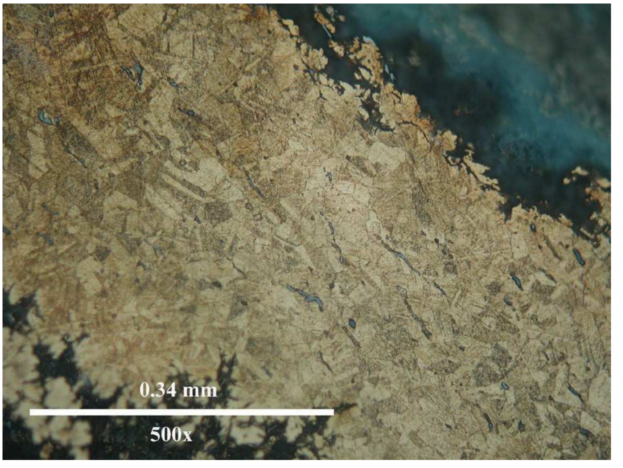



**Fig. 5** Photomicrograph of the etched section of Gomolava ring (sample No. 212), with significantly reduced grain structure, deformation marks and elongated sulphur-rich inclusions, all of which suggests several cycles of annealing (Radivojević et al. 2013, 1039, Fig. 6)

**Sl. 5** Mikroskopska fotografija preseka, nakon nagrizanja kiselinom, prstena sa Gomolave (uzorak br. 212), na kome se vidi znatno redukovana zrnasta struktura, znaci deformacije i izdužene inkluzije bogate sumporom, što sve ukazuje na nekoliko ciklusa kaljenja i iskivanja (Radivojević et al. 2013, 1039, Fig. 6)

## Comparison of early tin bronze objects from the Balkans

The Pločnik and Gomolava objects are similar in composition to thirteen previously analysed early tin bronzes from Bulgaria and Serbia, with which they therefore form a broad compositional group. To test whether these tin bronzes were the result of adding tin metal or cassiterite to copper metal, we studied the trace element pattern of the early bronzes in comparison to those of contemporary Early and Middle Chalcolithic (EC/MC) Bulgarian copper artefacts. Levels of Fe, Co, Ni and As are on average about one order of magnitude higher, and those of Sb and Pb up to two orders of magnitude higher in the early bronzes (fig. 6). Such a trace element pattern is not only not found in contemporary copper artefacts, but also not found in later tin bronzes that occur in the succeeding cultural horizons of the studied sites, and beyond. It is therefore very unlikely that this trace element pattern originates from the addition of tin metal or cassiterite to ordinary copper, or that the bronze finds are intrusive from later layers. Instead, the trace element pattern indicates the use of other, more complex ores for the production of these objects, restricted to the Chalcolithic period.

| 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 | 0.02 | 0.002 | 0.05 |
| Karanovo | ASM 12043 | ring | 92.5 | 7 | 0.20 | 0.05 | 0.02 | 0.15 | 0.004 | 0.005 | 0.001 | 0.02 |
| Bereketska Mogila | ASM 12103 | needle | 92.9 | 6 | 0.35 | 0.7 | 0.012 | 0.02 | 0.002 | 0.01 | 0.003 | 0.005 |
| Bereketska Mogila | ASM 12105 | awl | 89.6 | 10 | 0.01 | 0.3 | 0.04 | 0.06 | 0.002 | nd | 0.003 | 0.004 |
| Karanovo | ASM 12051 | needle | 92.1 | 7 | 0.07 | 0.2 | 0.01 | 0.5 | 0.0003 | nd | 0.003 | 0.15 |
| Lazareva pećina | HDM 1330 | borer | 98 | 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 |
| 1st 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 | 0.60 | 0.2 | 0.015 | 0.2 | 0.04 | 0.2 | 0.001 | 3.5 |
| Ruse | HDM 2046 (ASM 10875) | borer | 86 | 7.3 | 0.35 | 0.31 | 0.016 | 0.28 | 0.03 | 0.3 | 0.003 | 0.05 |
| Ruse | ASM 10863 | borer | 88.4 | 10 | 0.40 | 0.07 | 0.02 | 0.4 | 0.03 | 0.5 | 0.03 | 0.18 |
| Ruse | ASM 10882 | ring | 92.1 | 7 | 0.50 | 0.07 | 0.04 | 0.1 | 0.03 | 0.06 | 0.003 | 0.05 |
| 2nd group (high-tin fahlore) | Average | | **89** | **7.8** | **0.44** | **0.13** | **0.023** | **0.25** | **0.04** | **0.3** | **0.008** | **0.92** |
| | | | | | | | | | | | | |
| Bereketska Mogila | ASM 12138 | rod | 96.8 | 1 | 0.06 | 0.02 | nd | 0.008 | 0.02 | 0.07 | 0.0029 | 2 |
| Gradeshnica | ASM 10686 | awl | 94.3 | 4.5 | 0.35 | 0.01 | 0.003 | 0.04 | 0.05 | 0.5 | 0.003 | 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 |
| 3rd group (low-tin fahlore) | average | | **95.7** | **2.9** | **0.22** | **0.02** | **0.003** | **0.036** | **0.059** | **0.3** | **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*** |

**Fig. 6** Compositional data for the early tin bronze artefacts from the Balkans, given in wt% (Radivojević et al. 2013, 1035, Table 1). Data for artefacts other than Pločnik (63) and Gomolava (212) taken from Chernykh (1978: 112, 339–352) and Pernicka et al. (1993: 10, Tab. 3; 1997: 121–126, Tab. A1). The bottom line 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: 147–148, Tab. A1), demonstrating that the trace element signature of the bronzes is unlikely to originate from the copper

**Sl. 6** Podaci o sastavu za najstarije artefakte od kalajne bronze sa Balkana, predstavljeni u % u odnosu na težinu (wt%) (Radivojević et al. 2013, 1035, Table 1). Podaci koji se ne odnose na Pločnik (63) i Gomolavu (212) preuzeti iz Chernykh 1978: 112, 339–352 i Pernicka et al. 1993: 190, Tab. 3; 1997: 147–148, Tab. A1. Donji red predstavlja srednju vrednost za 40 istovremenih bakarnih artefakata iz ranog (EC) i srednjeg halkolita (MC), zasnovan na podacima iz Pernicka et al. 1993: 190, Tab. 3; 1997: 147–148, Tab. A1, pokazujući da prateći elementi u u bronzi verovatno ne potiču iz bakra

Within the 15 early tin bronzes we have recognised three distinctive groups of artefacts, based on their composition (fig. 6). They are labelled tentatively as stannite bronze, high-tin fahlore bronze and low-tin fahlore bronze, indicating the possible ore types that could have underpinned their production. It is assumed that the three compositional groups originate from smelting a copper ore containing varying amounts of fahlore and stannite, probably mixed with further metal-rich minerals. The archaeometallurgical literature knows a copper type known as fahlore copper (Otto, Witter 1952; Ottaway 1982; Schmitt-Strecker, Begemann 2005; Hoppner et al. 2005; Merkl 2010), characterised by elevated levels of arsenic, antimony and silver and often accompanied by increased levels of cobalt and nickel as well. Fahlore copper does not, however, normally contain more than a few tens of ppm tin. Instead, the tin in these early bronzes is thought to originate from stannite, Cu2FeSnS4, a copper-tin mineral structurally similar to chalcopyrite, and visually as dark metallic grey as fahlore. The association of primary copper ores such as chalcopyrite with both stannite and fahlore is not uncommon in sulphidic ore bodies in tin-rich provinces (Ramdohr 1980, 549-562). Significant tin mineralisations exist in western Serbia, at Mt. Cer and Bukulja, as well as in several localities in eastern Serbia, Bosnia, Croatia, Hungary and Romania; these are part of the massive copper sulphide-rich deposits within the Tethyan-Eurasian metallogenic belt (Janković 1997).

Thus, we argue that the early tin bronzes were produced by smelting complex ores based on chalcopyrite, stannite, fahlore and other accessory minerals in various proportions; the early date of these samples would suggest that the smelted ore was rich in secondary minerals, while the presence of sulphur and selenium in the metal may indicate that a significant part of the ore was still made up by primary minerals. The relative proportion of the various minerals would have differed in each batch of metal smelted. This is in our view the reason for the variable tin content and the fact that the metal smelted from such mixed ores does not remotely reach the theoretical content of 30% Sn of pure stannite. The idea for this is not new. Already a generation ago, Wertime (1978, 2) suggested that the role of stannite in the emergence of tin bronzes has been underestimated, and pointed out that the smelting of stannite would have yielded a natural bronze. Charles (1978, 28) supported this assumption stating that "...It [stannite] may have been the first primary source of tin to be alloyed with copper". However, here we argue for the first time based on analyses of excavated artefacts that this scenario did indeed happen, at the very beginning of metallurgy.

Tin bronzes enter more regular circulation from the 2nd millennium BC in Bulgaria (Late Bronze Age), with average concentrations of Sn and As present at c. 5wt % and c. 0.3 wt% respectively (Pernicka et al. 1997, 155-156, Table A1). These LBA tin bronzes from Bulgaria come from different sites than the ones we considered here, except for the Gradeshnica find (awl), which was discovered at the same site as three other tin bronze artefacts dated to the 2nd millennium BC. The composition of these three LBA tin bronzes (all of which are stray finds) differs from the Gradeshnica object (ASM 10686): one is more likely to be brass than tin bronze, the other one shows the composition of a cassiterite bronze, while the third has two times less As, and almost an order of magnitude more Fe and Ni levels than the tin bronze awl from Gradeshnica in figure 6 (Pernicka et al. 1993, 156). Taking all into account, these LBA objects differ significantly from the tin bronze awl under consideration here. Therefore, the unique compositional pattern of the 15 early tin bronzes taken into account here (fig. 6) differs from the artefacts appearing in the later cultural horizons. The converse of this argument is that there is a temporal, geographical and technological connection linking the fifteen early complex tin bronzes from the 5th millennium BC to each other.

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: 275-277, 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 third 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 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-adjusted for the desired function. Their shape implies that the more functional material advantage of tin bronzes over pure copper artefacts was not exploited; it was the visual appearance of them as decorative objects that played a significant role in their use. Even though, the use of specific heat treatment cycles including annealing temperatures higher than those required for working the pure copper dominant at the time indicates the material understanding that metal smiths developed for these tin bronzes. This in turn indicates an awareness of the specific properties of these metals, and therefore most probably intentionality of their production based on the smelting of ore 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 is required to pinpoint the possible sources of ores used for the making of these 5th millennium BC bronzes.

The smelting of stannite as a major tin-bearing copper ore for later tin bronze production has recently been suggested based on its occurrence 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). None of these Bronze Age mines, however, appear to be associated with fahlore as well as stannite. Worth noting is the metallic (grey) lustre of stannite, 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, giving it the overall appearance of tainted, black and green ores.

The selection of self-fluxing ore comprising green copper minerals intergrown with black manganese minerals, as opposed to pure green minerals used for malachite bead making, has recently been suggested as a key feature of the copper smelting carried out by the Vinča culture smiths at the turn of the 5th millennium BC (Radivojević et al. 2010). We suggest that this appearance was also decisive for collecting copper minerals rich in stannite and / or fahlore. Weisgerber and Cierny's (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'. Therefore, 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 3rd millennium BC.

The presence of major impurities, such as tin, arsenic and antimony improved the material properties of the metal: it melted at lower temperatures than pure copper and was easier to cast (Northover 1989; Lechtman 1996). Also, these impurities gave the artefacts a bright yellow colour when present at sufficient levels. The latter is recognised as crucial for the use of tin bronzes as an alternative to gold in Central Asia (Kaniuth 2007), and also for the early appearance of brasses (copper-zinc alloys) from the early 3rd millennium BC (Thornton 2007).

This is particularly interesting in light of the world's earliest securely dated gold objects, dated to the mid-5th millennium BC and deposited in the cemetery of Varna I in Bulgaria to display social prestige (Renfrew, 1986; Higham et al., 2007). There are earlier uses of gold ornaments (although not as directly dated) in the Varna II cemetery (Todorova and Vajsov, 2001: 54) as well as in the cemetery of Durankulak (Avramova, 2002: 193, 202, Tab. 24; Dimitrov, 2002: 147). The Durankulak finds are, for instance, dated to the Hamangia IV phase, which dates between c. 4650/4600 – 4550/4500 BC (Bojadžiev, 2002: 67) and therefore contemporary with the currently earliest dated tin bronze from the site of Pločnik.

We relate here the colour and social significance of gold to the emergence of the early tin bronzes, and the opportunities the latter might have offered as an imitation of gold. We argue that the tin bronze production in the Balkans during the 5th millennium BC is not only intimately related to the production of copper, but to that of gold as well. The visual similarity of gold and tin bronze artefacts is further underlined by the relatively limited scale of production of both metals, which stands in stark contrast to the massive production of contemporary copper metal implements, amounting to c. 4.7 t of extant objects (Chernykh, 1978). The limited production of gold and tin bronzes may suggest that access to them was reserved only for high-ranked individuals, as indicated by the Varna cemetery example; this could be one of the explanations why are there so few yellow metal artefacts in circulation at the time.

The characteristic compositional pattern of the securely dated tin bronze from the site of Pločnik supports the assumed Chalcolithic date (5th millennium BC) for the previously discovered tin bronzes in Bulgaria and Serbia. This assumption is further strengthened by the absence of compositionally similar objects from later layers and a gap of more than a millennium before cassiterite tin bronzes appear in the Balkans. In terms of their making, we anticipate that the particular deposit(s) yielding these ores were either exhausted, or, more likely, were no longer the active cultural and technological choice of the Balkan Early Bronze Age cultural groups.

## The 5th Millennium BC Polymetallism

Our study provides archaeological and analytical evidence for the independent emergence of tin bronze production by smelting complex copper-tin bearing ores as natural alloys, preceding the tin bronze alloys from southwest Asia by c. 1500 years. They also precede by almost half a millennium the earliest known natural alloys made of arsenical copper (Roberts et al. 2009). The 5th millennium BC tin bronzes, therefore, fundamentally challenge the established sequence of the evolution of metallurgy in western Eurasia.

The ores selected for making these natural alloys were resembling the black-and-green manganese-rich copper minerals already exploited in the initial stages of copper metallurgy in the Balkans, which may have facilitated the initial selection of tin-bearing ores. Therefore, the tin bronze production started as closely related to technological choices applied in selecting ores for copper metal extraction, but resulted in the emergence of a differently-coloured metal. Thus, the colour-coding appears to be crucial also for the end of the chaîne opératoire of early tin bronze production: these artefacts were probably made due to the demand for the golden hue of tin bronze, possibly even to imitate gold.

Copper, tin bronzes and gold are not the only metals used in the 5th millennium BC Balkans. There is evidence of mid 5th millennium BC use of both lead and galena from the Vinča culture sites of Selevac, Opovo, Autoput and Donja Tuzla (Glumac and Todd 1987). Also, in the wider Balkan region there is a record of using silver, attested by more than one hundred silver artefacts discovered in a hoard from the Alepotrypa Cave in Greece, and roughly dated to the mid 5th - early 4th millennium BC (Muhly 2002). Hence, the almost 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 5th millennium BC defies the conventional narrative of a unilinear and slow evolution of metallurgy. Quite to the contrary, the early evolutionary trajectory of metallurgy in the Balkans emerges almost from the very beginning as rather polymetallic in nature (Radivojević et al. 2013).

The 'polymetallism' of the 5th millennium BC Balkans has hitherto only been considered as an exception, with modest evidence for smelting polymetallic (copper) ores in the late 5th millennium BC Bulgarian sites of Dolnoslav and Chatalka (Ryndina et al. 1999). The fifteen tin bronze artefacts now significantly extend our knowledge of the use of tin bronze at this early stage of Eurasian metallurgy. The polymetallic character of the early Balkan metallurgy does not seem to be driven by the need for functional metals, but by demand for desirable visual properties of the final products. Thus, the co-occurrence of three or possibly four different metals next to copper is underlined by one common principle: their pronounced 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 to the very early evolution of metallurgy in Eurasia.

The 5th millennium BC Balkan polymetallism possibly evolved from aesthetic preferences of the consumer elite at the time. This means that the metal smiths at the time were employing different ores and techniques in order to produce and work different metals, which makes the 5th millennium BC in the Balkans polytechnological as much as polymetallic. The decline of the (natural) tin bronzes corresponds with the collapse of large cultural complexes in northeast Bulgaria and Thrace in the late 5th millennium BC (Todorova 1995; Weninger et al. 2009). This could suggest that these tin bronzes were 'cultural alloys', with their production potentially dictated by culturally-embedded desires and preferences (Hamilton 1991). The same applies to the gold-using cultures in Bulgaria; however, not gold itself, as it continues to be used in the Carpathians throughout the 4th millennium BC.

Potential explanations for the decline of tin bronze production could be sought in the population dynamics at the time, which are known as a powerful mechanism for both generation and decline of innovations in prehistoric societies (Shennan 2000; Henrich 2004; Powell et al. 2009). In discussing the early appearance of tin bronzes, we would like to stress that the 5th millennium BC examples are seen here as aesthetic alloys, since their mechanical advantage was not exploited in this early period. We therefore argue that these aesthetic alloys are by definition prestigious and hence limited in production. Accordingly, their impact on society is more likely to express social status on the consumer end of their production.

In contrast, the tin bronzes that occur only c. 1500 years later, are based mostly on cassiterite tin and followed by the widespread adoption of this alloy in a different cultural climate. As such, they are considered as both aesthetic and functional, and reflect different organisation of their production and use. Metal objects of this distinctive alloy appear widely adopted during the 2nd millennium BC from Atlantic to Pacific, via Central Asia, mapping out the path of what is later known as part of the Silk Road. The production, consumption and trade along its predecessor, which we for the purpose call the 'Bronze Road', acted as one of the driving forces behind the intensification of the economic, social and political lives of the Bronze Age communities across Eurasia.

In conclusion, the earliest appearance of tin bronzes as alloys of different quality and visual appearance does not correlate with the rise of the Bronze Age societies in Eurasia. Only at the dawn of the 2nd millennium BC does tin bronze emerge as one of the main accelerators of trade and exchange among the Bronze Age communities and thus their progress, but also as the commodity that was traveling along already established communication routes. The earlier aesthetic tin bronzes of the 5th millennium BC foreshadow this with their wide spread along the riverine network of the Danube and its tributaries.

***Acknowledgements***

*This paper is an adjusted version of the publication by Radivojević, M., Rehren, Th., Kuzmanović-Cvetković, J., Jovanović, M., & Northover, J. P. (2013). Tainted ores and the rise of tin bronze metallurgy, c. 6500 years ago. Antiquity, 87(338), 1030-1045. Antiquity Journal has kindly granted us permission to publish this research here as well.*

*This paper was substantially improved by comments from S.J. Shennan, B.W. Roberts, C.P. Thornton, V.C. Pigott and three anonymous reviewers of the related manuscript published in Antiquity. The authors are grateful to E. Chernykh and E. Pernicka for fruitful discussions on the results of this research. This study is part of MR's PhD project, funded by EPSRC jointly with the Freeport McMoRan Copper and Gold Foundation through the Institute for Archaeo-Metallurgical Studies (IAMS) in London. MR is also an active member of the Serbian Ministry of Science project No. 177012, hosted by the Serbian Academy of Arts and Sciences.*

## References

**Anthony, D. W. 2007.** *The Horse, the Wheel, and Language: How Bronze-Age Riders from the Eurasian Steppes Shaped the Modern World*, Princeton, N.J., Princeton University Press.

**Avramova, M. 2002.** Der Schmuck aus den Gräbern von Durankulak. *In*: Todorova, H. (ed.) *Durankulak, Band II - Die prähistorischen Gräberfelder von Durankulak, Teil 1*. Berlin-Sofia: Publishing House Anubis Ltd. Sofia, pp. 191-206.

**Bar-Yosef Mayer, D. E. & Porat, N. 2008.** Green stone beads at the dawn of agriculture, *Proceedings of the National Academy of Sciences* 105: 8548–8551.

**Begemann, F., Schmitt-Strecker, S. & Pernicka, E. 2003.** On the composition and provenance of metal finds from Beşiktepe (Troia), in: A. Wagner, E. Pernicka, H-P. Uerpmann (eds.) *Troia and the Troad: Scientific Approaches*, Berlin, Heidelberg, Springer-Verlag: 173–201.

**Bojadžiev, J. 2002.** Die absolute Datierung der neo- und äneolithischen Gräberfelder von Durankulak. *In*: Todorova, H. (ed.) *Durankulak, Band II - Die prähistorischen Gräberfelder von Durankulak, Teil 1*. Berlin-Sofia: Publishing House Anubis Ltd. Sofia, pp. 67-70.

**Borić, D. 2009.** Absolute dating of metallurgical innovations in the Vinča culture of the Balkans, in: T. L. Kienlin, B. W. Roberts (eds.) *Metals and Societies. Studies in honour of Barbara S. Ottaway*, Bonn, Verlag Dr. Rudolf Habelt GmbH: 191–245.

**Charles, J. A. 1978.** The development of the usage of tin and tin-bronze: some problems, in: A. D. Franklin, J. S. Olin, T. A. Wertime (eds.) *The Search for Ancient Tin: a seminar organized by Theodore A. Wertime and held at the Smithsonian Institu-*

*tion and the National Bureau of Standards, Washington, D.C., March 14-15, 1977*, Washington, D.C., Smithsonian Institution Press: 25–32.
**Chernykh, E. N. 1978.** *Gornoe Delo i Metallurgiya v Dreivneishei Bolgarii*, Sofia, Bulgarska akademia na naukite.
**Cleziou, S., Berthoud, T. 1982.** Early tin in the Near East: A reassessment in the light of new evidence from Afghanistan, *Expedition* 25: 14–19.
**Craddock, P. T., Meeks, N. D. 1987.** Iron in ancient copper, *Archaeometry* 29: 187–204.
**Dimitrov, K. 2002.** Die Metallfunde aus den Gräberfeldern von Durankulak. *In*: Todorova, H. (ed.) *Durankulak, Band II - Die prähistorischen Gräberfelder von Durankulak, Teil 1*. Berlin-Sofia: Publishing House Anubis Ltd. Sofia, pp. 127-158.
**Ehrhardt, K. 2009.** Copper working technologies, contexts of use, and social complexity in the Eastern Woodlands of Native North America, *Journal of World Prehistory* 22: 213–235.
**Glumac, P., Todd, J. 1987.** New evidence for the use of lead in prehistoric southeast Europe, *Archeomaterials* 2: 123–145.
**Glumac, P. D., Todd, J. A. 1991**. Early metallurgy in southeast Europe: the evidence for production, in: P. D. Glumac (ed.) *Recent Trends in Archaeometallurgical Research*, MASCA Research Papers in Science and Archaeology, Philadelphia, University of Pennsylvania: 9–19.
**Govedarica, B., Pernicka, E., Rittershofer, K.-F. 1995.** Neue Metallanalysen aus dem Westbalkangebiet, in: B. Jovanović (ed.) *Ancient Mining and Metallurgy in Southeast Europe: International Symposium Donji Milanovac, May 10–25, 1990*, Belgrade, Archaeological Institute; Bor, Museum of Mining and Metallrugy: 265–279.
**Hamilton, E. 1991.** Metallurgical analyses and the Bronze Age of Bohemia: or, are cultural alloys real? *Archeomaterials* 5: 75–89.
**Harding, A. F. 2000.** *European Societies in the Bronze Age*, Cambridge, Cambridge University Press.
**Helwing, B. 2009.** Rethinking the Tin Mountains: patterns of usage and circulation of tin in Greater Iran from the 4th to the 1st millennium BC. *TÜBA- AR (Türkiye Bilimer Akademisi Arkeoloji Dergisi)* 12: 209–221.
**Henrich, J. 2004.** Demography and cultural evolution: how adaptive cultural processes can produce maladaptive losses, the Tasmanian case, *American Antiquity* 69: 197–214.
**Higham, T., Chapman, J., Gaydarksa, B., Slavchev, V., Honch, N., Yordanov, Y., Dimitrova, B. 2007.** New perspectives on the Varna cemetery (Bulgaria) - AMS dates and social implications, *Antiquity* 81: 640-654.
**Hoppner, B., Bartelheim, M., Huijsmans, M., Krauss, R., Martinek, K. P., Pernicka, E., Schwab, R. 2005.** Prehistoric copper production in the Inn Valley (Austria), and the earliest copper in central Europe, *Archaeometry* 47: 293–315.
**Hosler, D. 1994.** *The Sounds and Colors of Power: The Sacred Metallurgical Technology of Ancient West Mexico*, Cambridge, MA, The MIT Press.
**Janković, S. 1997.** The Carpatho-Balkanides and adjacent area: a sector of the Tethyan Eurasian metallogenic belt, *Mineralium Deposita* 32: 426–433.
**Kaniuth, K. 2007.** The metallurgy of the Late Bronze Age Sapalli culture (southern

Uzbekistan) and its implications for the 'tin question', *Iranica Antiqua* 42: 23–40.
**Kuz'mina, E. E. 2008.** *The Prehistory of the Silk Road*, Philadelphia, University of Pennsylvania Press.
**Lechtman, H. 1977.** Style in technology – some early thoughts, in: H. Lechtman, R. S. Merrill (eds.) *Material Culture: Styles, Organization and Dynamics in Technology*, St. Paul, West Publishing: 3–20.
**Lechtman, H. 1980.** The Central Andes: metallurgy without iron, in: T. A. Wertime, J. D. Muhly (eds.) *The Coming of the Age of Iron*, New Haven, London, Yale University Press: 267–334.
**Lechtman, H. 1996.** Arsenic bronze: Dirty copper or chosen alloy? A view from the Americas, *Journal of Field Archaeology* 23: 477–514.
**Makkay, J. 1991.** The most ancient gold and silver in central and south-east Europe, in: J. –P. Mohen, C. Éluère (eds.) *Découverte du Métal*, Paris, Picard: 119–128.
**Merkl, M. B. 2010.** Bell Beaker metallurgy and the emergence of fahlore-copper use in central Europe, *Interdisciplinaria Archaeologica* 1: 19–27.
**Muhly, J. D. 1993.** Early Bronze Age tin and the Taurus, *American Journal of Archaeology* 97: 239–253.
**Muhly, J. D. 2002.** Early metallurgy in Greece and Cyprus, in: Ü. Yalçın (ed.) *Anatolian Metal II, Der Anschnitt,* Beiheft 15, Bochum, Deutsches Bergbau-Museum: 77–82.
**Nezafati, N., Pernicka, E., Momenzadeh, M. 2006.** Ancient tin: old question and a new answer, *Antiquity* 80: 308.
**Nezafati, N., Pernicka, E., Momenzadeh, M. 2011.** Early tin-copper ore from Iran, a possible clue for the enigma of Bronze Age tin, in: Ü. Yalçın (ed.) *Anatolian Metal V, Der Anschnitt,* Beiheft 24. Bochum, Deutsches Bergbau-Museum: 211–230.
**Northover, J. P. 1989.** Properties and use of arsenic-copper alloys. In: A. Hauptmann, E. Pernicka, G. A. Wagner (eds.) *Old World Archaeometallurgy, Der Anschnitt*, Beiheft 7, Bochum, Deutsches Bergbau-Museum: 111–118.
**Ottaway, B. S. 1979**. Analysis of the earliest metal finds from Gomolava, *Рад војвођанских музеја* 25: 53–59.
**Ottaway, B. S. 1982**. *Earliest Copper Artifacts of the Northalpine Region: Their Analysis and Evaluation*, Bern, University of Bern.
**Otto, H., Witter, W. 1952**. *Handbuch der ältesten Vorgeschichtlichen Metallurgie in Mitteleuropa*, Leipzig, J. A. Barth.
**Pare, C. 2000.** Bronze and the Bronze Age, in: C. Pare (ed.) *Metals Make the World Go Round*, Oxford, Oxbow Books: 1–38.
**Pernicka, E., Begemann, F., Schmitt-Strecker, S. 1993.** Eneolithic and Early Bronze Age copper artefacts from the Balkans and their relation to Serbian copper ores, *Prähistorische Zeitschrift* 68: 1–54.
**Pernicka, E., Begemann, F., Schmitt-Strecker, S., Todorova, H., Kuleff, I. 1997.** Prehistoric copper in Bulgaria. Its composition and provenance, *Eurasia Antiqua* 3: 41–180.
**Pigott, V. C. 2011.** Sources of tin and the tin trade in southwest Asia: recent re-

search and its relevance to current understanding, in: P. P. Betancourt, S. C. Ferrence (eds.) *Metallurgy: Understanding How, Learning Why. Studies in Honor of James D. Muhly*, Philadelphia, Pennsylvania, INSTAP Academic Press: 273–291.

**Powell, A., Shennan, S., Thomas, M. G. 2009**. Late pleistocene demography and the appearance of modern human behavior, *Science* 324: 1298–1301.

**Radivojević, M., Rehren, Th., Kuzmanović-Cvetković, J., Jovanović, M., Northover, J. P. 2013.** Tainted ores and the rise of tin bronze metallurgy, c. 6500 years ago. *Antiquity* 87: 1030–1045.

**Radivojević, M., Rehren, Th., Pernicka, E., Šljivar, D., Brauns, M., Borić, D. 2010**. On the origins of extractive metallurgy: new evidence from Europe, *Journal of Archaeological Science* 37: 2775–2787.

**Ramdohr, P. 1980.** *The ore minerals and their intergrowths*, Oxford, Pergamon Press.

**Renfrew, C. 1986.** Varna and the emergence of wealth in prehistoric Europe, in: A. Appadurai (ed.) *The Social Life of Things: Commodities in Cultural Perspective*, Cambridge, Cambridge University Press: 141–168.

**Roberts, B. W., Thornton, C. P., Pigott, V. C. 2009.** Development of metallurgy in Eurasia, *Antiquity* 83: 1012–1022.

**Rostoker, W., Dvorak, J. R. 1990**. *Interpretation of Metallographic Structures*, San Diego, London, Academic Press Inc.

**Rovira, S., Montero, I. 2003.** Natural tin-bronze alloy in Iberian Peninsula Metallurgy: potentiality and reality, in: A. Giumlia-Mair, F. LoSchiavo (eds.) *The Problem of Early Tin. Actes of the 14th UISPP Congress, University of Liège, Belgium, 2-8 September 2001*, Oxford, Archaeopress: 15–22.

**Ryndina, N., Indenbaum, G., Kolosova, V. 1999**. Copper production from polymetallic sulphide ores in the northeastern Balkan Eneolithic culture, *Journal of Archaeological Science* 26: 1059–1068.

**Schickler, H. 1981.** Neolithische Zinnbronzen. In: H. Lorenz (ed.) *Studien zur Bronzezeit: Festschrift für Wilhelm Albert v. Brunn*, Mainz am Rhein, von Zabern: 419–445.

**Schmitt-Strecker, S., Begemann, F. 2005**. Kupfer- und bronzezeitliche Metallartefakte vom Westbalkan: Zur Frage nach den Quellen ihres Kupfers, *Prähistorische Zeitschrift* 80: 49–64.

**Scott, D. A. 1991.** *Metallography and Microstructure of Ancient and Historic Metals*, Marina del Rey, Getty Conservation Institute.

**Shennan, S. 2000.** Population, culture history, and the dynamics of culture change. *Current Anthropology* 41: 811–835.

**Šljivar, D., Kuzmanović-Cvetković, J., Živković, J. 2012.** Belovode, Pločnik: on copper metallurgy in the Vinča culture, *Zbornik Narodnog Muzeja* 20: 27–46.

**Smith, S. C. 1981.** On art, invention and technology, in: S. C. Smith (ed.) *A Search for Structure*, Cambridge (MA), The MIT Press: 325–331.

**Stech, T., Pigott, V. C. 1986.** The metals trade in southwest Asia in the third millennium BC, *Iraq* 48: 39–64.

**Stöllner, T., Samaschev, Z., Berdenov, S., Cierny, J., Doll, M., Garner, J., Gontscharov, A., Gorelik, A., Hauptmann, A., Rainer, H., Kusch, G. A., Merz, V.,**

**Riese, T., Sikorski, B., Zickgraf, B. 2011.** Tin from Kazakhstan - Steppe Tin for the West?, in: Ü. Yalçın (ed.) *Anatolian Metal V, Der Anschnitt*, Beiheft 24. Bochum, Deutsches Bergbau-Museum: 231–251.
**Tasić, N. 1982.** Naselja bakarnog doba u istočnoj Srbiji, *Zbornik radova Muzeja rudarstva i metalurgije u Boru* 2: 19–36.
**Thornton, C. P. 2007.** Of brass and bronze in prehistoric southwest Asia, in: S. La Niece, D. Hook, P. Craddock (eds.) *Metals and Mines: Studies in Archaeometallurgy*, London, Archetype Publications: 123–135.
**Thornton, C. P. 2009**. The Emergence of complex metallurgy on the Iranian Plateau: escaping the Levantine Paradigm, *Journal of World Prehistory* 22: 301–327.
**Thornton, C. P. 2014.** The Emergence of Complex Metallurgy on the Iranian Plateau. In: Roberts, B. W. & Thornton, C. P. (eds.) *Archaeometallurgy in Global Perspective*. New York: Springer, pp. 665-696.
**Todorova, H. 1995.** The Neolithic, Eneolithic and Transitional Period in Bulgarian Prehistory, in: D. W. Bailey, I. Panayotov, S. Alexandrov (eds.) *Prehistoric Bulgaria*, Madison, Prehistory Press: 79–98.
**Todorova, H., Vajsov, I. 2001.** *Der kupferzeitliche Schmuck Bulgariens*, Stuttgart: Steiner, Prähistorische Bronzefunde, Vol. 20, Band 6.
**Weeks, L. 1999.** Lead Isotope Analyses from Tell Abraq, United Arab Emirates: new data regarding the "tin problem" in Western Asia, *Antiquity* 73: 49–64.
**Weisgerber, G., Cierny, J. 2002**. Tin for ancient Anatolia?, in: Ü. Yalçın (ed.) *Anatolian Metal II, Der Anschnitt*, Beiheft 15, Bochum, Deutsches Bergbau-Museum: 179–187.
**Weninger, B., Lee, C., Rohling, E., Bar-Yosef, O., Böhner, U., Budja, M., Bundschuh, M., Feurdean, A., Gebe, H. G., Jöris, O., Linstädter, J., Mayewski, P., Mühlenbruch, T., Reingruber, A., Rollefson, G., Schyle, D., Thissen, L., Todorova, H., Zielhofer, C. 2009.** The impact of rapid climate change on prehistoric societies during the Holocene in the Eastern Mediterranean, *Documenta Praehistorica* 36: 7–59.
**Wertime, T. A. 1964**. Man's first encounters with metallurgy, *Science* 146: 1257–1267.
**Wertime, T. A. 1978.** The search for ancient tin: the geographic and historic boundaries, in: A. D. Franklin, J. S. Olin, T. A. Wertime (eds.) *The Search for Ancient Tin: a seminar organized by Theodore A. Wertime and held at the Smithsonian Institution and the National Bureau of Standards, Washington, D.C., March 14–15, 1977*, Washington, D.C., Smithsonian Institution Press: 1–6.
**Yener, K. A., Özbal, H. 1987.** Tin in the Turkish Taurus mountains: the Bolkardağ mining district, *Antiquity* 61: 220–226.
**Yener, K. A., Vandiver, P. B., Willies, L. 1993.** Reply to J. D. Muhly, "Early Bronze Age tin and the Taurus", *American Journal of Archaeology* 97: 255–264.

**Miljana Radivojević**
UCL Institute of Archaeology, London
**Thilo Rehren**
UCL Qatar, a partner of Hamad bin Khalifa University, Doha
**Julka Kuzmanović-Cvetković**
Museum of Toplica, Prokuplje
**Marija Jovanović**
Museum of Vojvodina, Novi Sad

## ZAŠTO NA BALKANU POSTOJE KALAJNE BRONZE U 5. MILENIJUMU P.N.E.?

Najstarija kalajna bronza na svetu potiče sa prostora Bliskog Istoka i datovana je u 3. milenijum p.n.e. Početak korišćenja ovog metala vezuje se za fenomen bronzanog doba i razvoj kompleksnih društava i intenzivnih ekonomskih kontakta na prostoru cele Evroazije. Kalajna bronza se smatra jednim od luksuznih sirovina koja je u to doba vlasniku davala prestiž i označavala statusni simbol. Međutim, danas se malo zna o tome kojom tehnologijom su proizvedeni najraniji nalazi od kalajne bronze i odakle potiče ruda od koje se dobijao kalaj. Studije su pokazale da je najverovatnije upravo kalajna ruda iz ležišta na području centrale Azije i Irana bila korišćena za legiranje sa bakrom kako bi se dobila kalajna bronza. Međutim, dokazi za tvrdnju o takvoj tehnologiji proizvodnje kalajne bronze još nisu pronadjeni.

U radu je predstavljen unikatan nalaz lima napravljenog od kalajne bronze, koji je otkriven na vinčanskom lokalitetu Pločnik i sigurno datovan u 4 650. godinu p.n.e. Analiza hemijskog sastava ovog nalaza pokazala je skoro 12% kalaja, ali i značajno učešće pratećih elemenata, kao što su kobalt, nikl, cink, gvožđe, arsenik i antimon, što ukazuje na tehnologiju izrade ovog predmeta od kompleksne bakarno–kalajne rude (kao što je stanit), a ne legiranjem dva metala. Metalografske analize su pokazale da ovaj predmet nije slučajno proizveden, pošto je tehnika topljenja bila složenija od one koja je bila potrebna za proizvodnju bakra, dominantog metala u upotrebi u vinčanskoj kulturi i ranom halkolitu Balkana.

Pronalazak ovog predmeta zahteva revidiranje našeg znanja o tehnologiji vinčanskih kovača od pre 6 500 godina. Zato smo uporedili ovaj predmet sa 14 nalaza od kalajnih bronzi, koji su samo uslovno datovani u 5. milenijum p.n.e. Ovih 14 nalaza potiče sa prostora Srbije i Bugarske i analize su pokazale da sadrže promenljivi sastav kalaja, od oko 2,5% do 10%. Oni potiču sa višeslojnih lokaliteta koji su imali halkolitski horizont, a zbog mogućnosti upada iz kasnijih kulturnih slojeva samo uslovno su proglašeni halkolitskim. Černih je tvrdio da su nalazi najverovatnije iz 5. milenijuma p.n.e i zbog toga što predmeti takvog sastava i tipoloških karakteristika nisu pronađeni u kasnijim metalnim dobima na Balkanu.

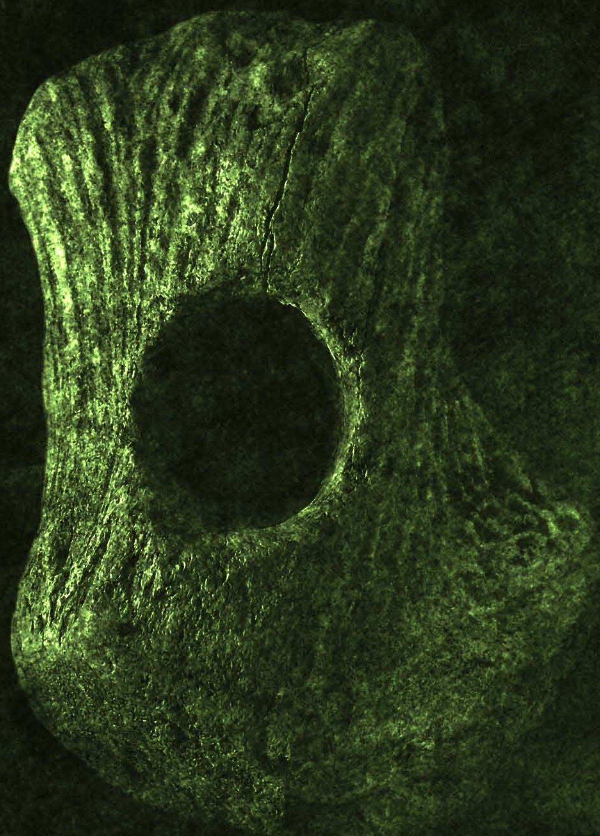
Uporednom analizom svih 15 kalajnih bronzi došli smo do zaključka da one pokazuju sličan geohemijski obrazac rude koja je korišćena za njihovo pravljenje, a koja je bila mešavina stanita i tetraedrita (falerz ruda). Upečatljiva karakteristika stanita je njegova prirodna crno–zelena boja, posebno važna zato što je bila presudna za početak prerade metala na lokalitetima vinčanske kulture. Naša pretpostavka je da su vinčanski metalurzi otkrili bronzu tako što su sakupljali rudu odredjene boje za topljenje i vremenom upoznali novi metal i njegova svojstva. Stoga mislimo da se ostale pomenute kalajne bronze, zbog hemijske sličnosti sa pločničkim nalazom, mogu, sa većom sigurnošću, svrstati u 5. milenijum p.n.e.

Na pitanje zašto se ona proizvodila naša pretpostavka je da je za proizvodnju kalajne bronze, pošto se radi o dekorativnom predmetu, bila presudna boja zlata. Poznato je da kalajna bronza koja u svom sastavu ima između 2 i 12 % kalaja dobija zlatastu boju, pa je možda imitiranje zlata i bila želja zanatlije koji je proizveo predmet. Veoma je zanimljivo primetiti da se kalajna bronza pojavljuje u isto vreme kada i prvi zlatni predmeti na Balkanu. Mišljenja smo da to nije slučajnost, već da su se objekti od kalajne bronze u to doba proizvodili da bi, možda, imitirali zlatne predmete.

Stoga nas proizvodnja bakra, zlata, kalajne bronze, zajedno sa upotrebom olova i srebra, navodi na pretpostavku da je 5. milenijum p.n.e. na Balkanu bio milenijum polikolora, odnosno proizvodnje metala sa ciljem da zadovolji i estetske i funkcionalne potrebe tadašnjih zajednica.

# ARCHAEOTECHNOLOGY

## *studying technology from prehistory to the Middle Ages*



**Editors**

*Selena Vitezović*

*Dragana Antonović*

# ARCHAEOTECHNOLOGY:
## studying technology from prehistory to the Middle Ages

**Editors:**
**Selena Vitezović**
**Dragana Antonović**

Belgrade, 2014

*Published by / Izdavač*
Srpsko arheološko društvo
Beograd, Čika-Ljubina 18-20

*For the publisher / Za izdavača*
Dragana Antonović

*Editors / Urednici*
Selena Vitezović
Dragana Antonović

*Reviewed by / Recenzenti*
Markó András (Hungary), Dragana Antonović, Krum Bacvarov (Bulgaria), Jacqueline Balen (Hrvatska), Marija Buzov (Hrvatska), Heidi Luik (Estonia), Ina Miloglav (Hrvatska), Dubravka Nikolić, Ben Roberts (United Kingdom), Perica Špehar

*Translation and proofreading / Prevod i lektura*
Ivan Bugarski, Jelena Vitezović, Selena Vitezović and individual authors

*Graphic layout / Grafička oprema*
Kristijan Relić

*Cover / Korica*
Mihajlo Vitezović

*Printed by / Štampa*
DC Grafički centar
Savski nasip 7, 11070 Novi Beograd

*Print run / Tiraž*
100

This book is published with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia.

**CONTENTS**
**SADRŽAJ**