



On the origins of extractive metallurgy: new evidence from Europe

Miljana Radivojević^{a,b,*}, Thilo Rehren^{a,*}, Ernst Pernicka^{c,d}, Dušan Šljivar^e, Michael Brauns^d, Dušan Borić^f

^a Institute of Archaeology, University College London, 31-34 Gordon Square, London WC1H 0PY, UK

^b Centre for Research in Archaeological Materials, Department of Archaeology, Faculty of Philosophy, Ćika Ljubina 18-20, Belgrade, Serbia

^c Institut für Ur- und Frühgeschichte und Archäologie des Mittelalters, Eberhard Karls Universität Tübingen, 72070 Tübingen, Germany

^d Curt-Engelhorn-Zentrum Archäometrie gGmbH, An-Institut der Universität Tübingen, C5 Zeughaus, 68159 Mannheim, Germany

^e Department of Prehistory, National Museum Belgrade, Trg Republike 1a, Belgrade, Serbia

^f School of History and Archaeology, Cardiff University, Cardiff CF10 3EU, UK

ARTICLE INFO

Article history:

Received 29 April 2010

Received in revised form

14 June 2010

Accepted 15 June 2010

Keywords:

Copper metallurgy

Smelting

Copper slag

Malachite

Bead

Vinča culture

Belovode

Serbia

Balkans

Eurasia

Chalcolithic

Lead-isotope ratios

Trace element analysis

ABSTRACT

The beginnings of extractive metallurgy in Eurasia are contentious. The first cast copper objects in this region emerge c. 7000 years ago, and their production has been tentatively linked to centres in the Near East. This assumption, however, is not substantiated by evidence for copper smelting in those centres. Here, we present results from recent excavations from Belovode, a Vinča culture site in Eastern Serbia, which has provided the earliest direct evidence for copper smelting to date. The earliest copper smelting activities there took place c. 7000 years ago, contemporary with the emergence of the first cast copper objects. Through optical, chemical and provenance analyses of copper slag, minerals, ores and artefacts, we demonstrate the presence of an established metallurgical technology during this period, exploiting multiple sources for raw materials. These results extend the known record of copper smelting by more than half a millennium, with substantial implications. Extractive metallurgy occurs at a location far away from the Near East, challenging the traditional model of a single origin of metallurgy and reviving the possibility of multiple, independent inventions.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The invention of extractive metallurgy, its location, timing, and origins, are among the restlessly argued matters in prehistoric archaeology. The introduction of metallurgy to prehistoric communities has provided an important chronological backbone for the later prehistory worldwide and has been widely discussed throughout the work of influential scholarship, and recognized as essential for the emergence of complex societies. Such ideas can be traced to the work of Childe (1944: 205, 209, 1958), who saw

the Near Eastern prehistoric communities as the single inventors of extractive metallurgy. The concept of a single origin was challenged by Renfrew (1969) who argued for multiple inventions of metallurgy in independent centres throughout Eurasia. This debate has since received new field and analytical data, which helped understanding the geological, technological and/or social factors involved in various cultural manifestations of emerging metallurgical activity (cf. Roberts et al., 2009). However, due to the lack of direct evidence of actual smelting from any of the suggested regions of invention, the origins of extractive metallurgy remain hotly contested (Roberts et al., 2009; Thornton et al., 2010).

Importantly, in the studies of ancient metallurgy, metal artefacts have received the lion's share of the scholarly attention. The structural, chemical and isotopic analysis of artefacts can respectively show the ancient technology of their working and making, and the suggested geological origins of the metal used. However,

* Corresponding authors. Institute of Archaeology, University College London, 31-34 Gordon Square, London WC1H 0PY, UK. Tel.: +44 207 679 1536.

E-mail addresses: m.radivojevic@ucl.ac.uk (M. Radivojević), th.rehren@ucl.ac.uk (Th. Rehren), ernst.pernicka@cez-archaeometrie.de (E. Pernicka), sljivard@yubc.net (D. Šljivar), michael.brauns@cez-archaeometrie.de (M. Brauns), boricd@cardiff.ac.uk (D. Borić).

the story of finished artefacts is only a relatively small part of the whole *chaîne opératoire* of metallurgy; a typical prehistoric metallurgical site would normally contain a set of various stone tools, ores, charcoal, fragments of technical ceramics and installations (furnaces, crucibles, tuyères) and various types of slag and other waste products (cf. Rehren and Pernicka, 2008). For a more comprehensive understanding of the technology of metal production and its cultural transmission, the full range of technological debris needs to be analysed and incorporated in archaeometallurgical research (cf. Bachmann, 1982; Craddock, 1995 and literature therein, Renzi et al., 2009; Thornton and Rehren, 2009; Thornton et al., 2009).

This paper contributes to the debate on the origins of extractive metallurgy by presenting remains of copper smelting discovered recently in Belovode, a Vinča culture site in Eastern Serbia. Chemical, structural and provenance analyses of numerous finds including copper slag, geological and archaeological minerals, a copper metal droplet, and several malachite beads demonstrate consistent and coexisting metal smelting and malachite bead manufacturing activities at the site. Significantly, the analyses indicated that different sources were exploited for raw materials for copper smelting and bead making, respectively, suggesting a good knowledge of their relevant material properties. The first smelting event so far documented at Belovode occurs at c. 5000 BC, which makes it the earliest securely dated record of extractive metallurgy, anywhere. This event occurs at a location far from the Near East and in a region exceptionally rich in early metal artefacts, thereby challenging the model of a single origin of extractive metallurgy.

2. Development of copper metallurgy in Eurasia

The use of geological copper sources is known from two technologically rather independent industries: minerals such as native copper, malachite and azurite were used for millennia for bead and pigment making using ‘cold’ lithic technologies, before the ‘hot’ metallurgical production of copper metal by smelting/melting began. Indeed, the earliest interest in copper minerals was due to their distinctive optical properties: the use of green and blue beads and pigments goes back to the eleventh millennium BC, as documented from the Shanidar Cave in northern Iraq and Rosh Horesha in Israel (Bar-Yosef Mayer and Porat, 2008; Solecki et al., 2004). Close to the end of the 9th millennium BC, native copper was worked in Çayönü Tepesi in eastern Turkey, where metallographic analyses showed indications of annealing (Maddin et al., 1999). In the following millennia, copper mineral use became common among the prehistoric communities in the Near and Middle East. However, most of these objects were produced by cold working or using temperatures not exceeding a few hundred degrees Celsius. As such, they are firmly rooted in the technology of the Neolithic, which already included similar heat treatment of flint to improve its properties (Robins et al., 1978). This “cold” processing of minerals stands in stark contrast to the radical *change of material properties*, such as in smelting/melting events, and separates transformative, “hot” metallurgy from the manufacture of copper minerals into artefacts involving “cold” technologies such as carving, cutting, grinding, and hammering or rolling of native copper, as well as the lower temperature heat treatment mentioned above.

The first cast copper artefacts, dependent in their production on controlled temperature use exceeding 1000 °C emerge throughout Eurasia in the early 5th millennium BC (e.g. the copper chisel from Mersin layer XVI, Garstang, 1953; Yalçın, 2000; Yener, 2000), concurrent with the earliest European copper mining at Rudna Glava in Eastern Serbia (Borić, 2009; Jovanović, 1980). These

artefacts appear almost a millennium earlier than the first known evidence for copper smelting in Jordan (Hauptmann, 2007) and Bulgaria (Ryndina et al., 1999). A possible exception is Tal-i Iblis in southeastern Iran, with numerous slagged crucible fragments from a large dump layer dated broadly between the late sixth and the late fifth millennium BC (Pigott, 1999).

At Çatal Höyük in Layer VI (dated to about 6500 BC) (Cessford, 2005: 69–70), Neuninger et al. (1964) reported ‘copper slag’, suggesting local processing of copper metal, but not necessarily its local smelting. Our interpretation of their detailed description of the relevant samples (Neuninger et al., 1964: 100–107) agrees with their identification of the non-magnetic copper oxide slag as dross, that is burnt metal, a typical by-product of metal melting and casting. The interpretation of the magnetic slag particles, not exceeding 4 mm in length, as possibly related to copper metallurgy is less clear. We agree with their identification of a limonitic core of these fragments, akin to gossan or other geological material, and a ‘hot’ outer skin reflecting sufficiently high temperatures to form rounded porosity, and possibly delafossite from the reaction of limonite and malachite. However, the small size of these particles and the limited penetration of the ‘hot’ zone into their core suggest a very short-lived thermal impact, not consistent with a well-mastered attempt to smelting. Although intentional heating could be suggested, in this context it is relevant to note that Layer VI is characterised by a large destructive fire (Mellaart, 1964: 115).

In Europe, researchers arguing for multiple origins of extractive metallurgy pointed to reports of copper smelting slag in Cerro Virtud in southeast Spain (Ruíz Taboada and Montero-Ruiz, 1999), questionably dated to the fifth millennium BC (Roberts, 2008), and the copious evidence for late sixth and fifth millennium BC copper ore mining in Rudna Glava and Ai Bunar, in the Balkans (Chernykh, 1978; Jovanović, 1971). The occurrence of the distinctive type of cast tools in this region during the early fifth millennium BC was cited as a strong indication for an independent metallurgical “industry” (Renfrew, 1969), hosted by several contemporaneous cultural groups, including the Vinča culture and the Kodžadermen-Gumelnița-Karanovo cultural complex. Significantly, the surviving amount of copper circulating the Balkans throughout this period was estimated to about 4.7 tons altogether (Pernicka et al., 1997), which is equal to about 4300 copper implements. Noteworthy, the total number of contemporaneous cast copper artefacts in the entire Near East does not exceed three hundred (Ryndina, 2009). Such discrepancy led many to suggest a large-scale local production of copper in the Balkans. Firm support for this interpretation is provided by trace element and lead-isotope analyses (Pernicka et al., 1993) demonstrating that the copper artefacts from this region can be convincingly related to numerous ore deposits in Serbia and Bulgaria. However, actual smelting sites were lacking, which stifled an informed debate of their production origin.

3. Early copper smelting

The identification of early smelting evidence is fraught with difficulties. Craddock (1995, 2009) presents the idea of ‘slagless’ metallurgy based on very pure copper carbonate ores which, in principle, may leave virtually no slag, and summarises the evidence for the earliest European copper smelting with ‘slag heaps’ weighing in the tens of grams in total. Bourgarit (2007:10) further explores this concept arguing that “slagless” metallurgy usually occurs in domestic contexts, while the evidence for advanced control of the slagging process is usually found in more specialised Chalcolithic sites. This trend seems to continue even within the EBA, where mass production of metal stands in contrast to small-scale domestic production, reflecting different levels of organisation of metal production.

It has been suggested that early smelting can be separated into two discrete steps; the reduction of copper ore to copper metal which requires reducing conditions and temperatures from c. 700 °C upwards (Budd, 1991), and the melting of the copper metal, which requires temperatures in excess of 1080 °C, but has fewer constraints on the redox conditions. In this model, the reducing stage is characterised by the necessarily incomplete burning of charcoal which results in limited heat generation and may lead to the reduction of some copper oxide to copper metal. This metal would form in a finely dispersed form intergrown with any gangue components such as iron oxides or silicates that come together with the copper mineral; it is speculated that such a low-temperature process is unlikely to leave vitrified material such as typical slag. However, depending on the nature of air delivery into the reaction zone, probably by blow pipe, there may well have been pockets of higher temperature directly in front of the blow pipes that led to localised fusion and partial formation of slag and molten metal. Any copper formed in this hypothetical process would then have to be melted in order to collect it, and for casting into artefact shape.

To do this one would have to raise the temperature above 1084 °C, the melting point of copper, which undoubtedly would convert at least part of the gangue into slag. This hypothetical scenario, however, is rather unrealistic in its separation of the practical process into two discrete steps. There are several physical–chemical and practical arguments against it: i) Reduction of copper to metal is much more efficient in the liquid phase due to much higher diffusion rates. ii) The reducing agent is gaseous carbon monoxide in all cases, which is produced when there is an excess of carbon dioxide in contact with the burning charcoal. This so-called Boudouard equilibrium of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ is on the right side only above ca. 800 °C. Below this temperature the reduction efficiency would be very low so that the postulated solid-state reduction at such a moderate temperature would be very slow. iii) Finally, it would be very difficult for the smelter to keep the temperature relatively low throughout the reaction vessel, due to inevitable temperature gradients from the tip of the blow pipe to areas further away. While locally temperatures of 1200 °C and higher were relatively easy to obtain, the use of blow pipes with their provision of humid and carbon dioxide-rich air would have limited the available thermal energy considerably (Rehder, 1999). In effect, it would be difficult to control the temperature in the region between 800 and 900 °C, if one would be determined to reduce copper at such a low temperature. Therefore, it is highly unlikely that the early smelter consciously aimed at such a two-step process; instead, the two discrete aspects of copper smelting – chemical reduction and physical melting – may well have blended into one process. The suggestion of a purely solid-state and “slag-less” copper production remains hypothetical at best, even for the earliest periods of metallurgy, as we will show by the presentation of proper copper slag, containing previously molten copper metal, and dated to c. 5000 BC (see below).

Unfortunately, the archaeologically visible remains of melting copper do not necessarily differ between re-melting existing copper metal, and the final stage of smelting copper from ores. The strongest criterion to identify smelting is thought to be a slag rich in transition metals other than copper. Slag from simple re-melting, in contrast, would mostly consist of fused ceramic material contaminated with fuel ash and varying amounts of copper metal and copper oxides, but would not have increased concentrations of typical ore elements such as iron, manganese and other base metals often associated with copper ores.

Obtaining reducing conditions by incomplete burning of fuel requires a controlled environment with limited air access, while the relatively high temperatures necessary to melt the copper require

an installation which retains and concentrates the heat generated from the fuel within the reaction container (Rehren, 2003). This container can for both processes be a dedicated ceramic vessel such as a crucible or furnace, or a simple hole in the ground with little identifiable structure. For melting of copper, the temperature around c. 1100 °C needed to be maintained for a certain amount of time to allow fully molten conditions to be reached throughout the charge; at this temperature, some of the ceramic material from the crucible or furnace will also melt and be mixed with the gangue and the ash from the fuel to form liquid slag which separates relatively cleanly from the liquid copper.

4. Vinča culture and copper metallurgy

The Vinča culture is a later Neolithic/early Chalcolithic phenomenon which lasted for 700 years in the largest part of the northern and central Balkans, spreading across an area which includes present-day Serbia, the Romanian Banat, parts of Romanian Oltenia, western Bulgaria, northern Macedonia and eastern parts of Slavonia and Bosnia (Garašanin, 1973). It shows strong links with the contemporaneous Kodžadermen-Gumelnița-Karanovo VI cultural complex in Bulgaria and Dimini V in Greece, particularly in the sphere of material culture including the use of heavy copper implements. In absolute dates, the estimated duration of the Vinča culture ranges from c. 5300 to c. 4600 BC (Breunig, 1987; Ehrich and Bankoff, 1992; Schier, 2000). The periodisation of the Vinča culture divides it into an early sequence, Vinča Tordoš (A–B1) and the later Vinča Pločnik (C1–D2), with an intermediate phase called Gradac (Vinča B2/C1) (Garašanin, 1951; Milojević, 1949). Of particular interest here is the Gradac phase, which lasts until the end of the Vinča culture in the Morava valley settlements (central Serbia), and appears related to the expansion of metallurgy and mining activities in Rudna Glava (Jovanović, 1980, 1994). Borić (2009: 234–238) chronologically identified the Gradac phase as starting at the turn of the fifth millennium BC and, in the central Serbian Morava valley sites, lasting until c. 4600 BC.

Copper mineral use in the Balkans emerged with the early Neolithic cultures; mostly for malachite bead making, although two metal artefacts, a double-pointed copper awl (Vlassa, 1969: 514) and a copper fish hook (Lazarović, 1970: 477) are reported in settlements in Transylvania and the Danube Gorges. Vinča groups continued to use copper for jewellery making: more than 400 sites were located within easy access to copper mineral deposits, of which the majority belonged to the belt rich in copper mineralisation cutting across Bulgaria and Serbia (Chapman, 1981; Krajnović and Janković, 1995). From the late sixth and early fifth millennium BC malachite beads and copper minerals were being used in settlements including Pločnik, the type-site Vinča and Selevac, while the latest use was recorded in Divostin and the burial site Gomolava (Antonović, 2006; Brukner, 1980; McPherron and Srejović, 1988; Tringham and Krstić, 1990) (Fig. 1).

The most impressive illustration of metallurgical craftsmanship within the Vinča culture is 45 massive copper implements found in Pločnik (Grbić, 1929; Stalio, 1960, 1962). The assemblage consists of the distinctive ‘Pločnik type’ of copper hammer-axes in the typology of metal artefacts in Europe (Schubert, 1965 and literature therein), chisels and a massive armband. All artefacts were made of high-purity copper (Junghans et al., 1968); of the 17 analysed so far for their geological provenance, the metal is most likely to come from various deposits across Bulgaria, Macedonia and possibly Serbia (Pernicka et al., 1997: 93–94). The resumed excavations at Pločnik confirmed the Vinča culture provenience for these implements (Šljivar and Kuzmanović-Cvetković, 1998), rejecting earlier views which suggested these finds to belong to later periods (Garašanin, 1973).

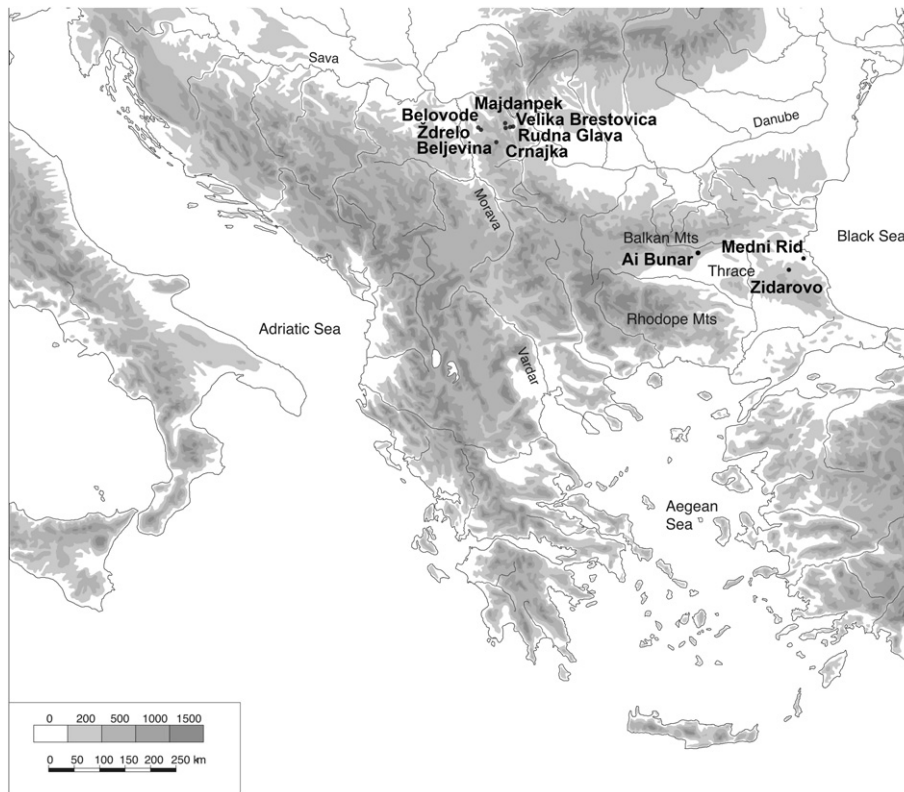


Fig. 1. Map showing the location of sites providing smelting evidence (Belovode) or samples for lead-isotope analysis reported in this paper.

In contrast to the large number of copper minerals and metal artefacts used by the Vinča groups, little is known about the production evidence. Individual slag pieces are reported from Selevac, Vinča, Gornja Tuzla, Anzabegovo IV and Stapani, of which only Selevac and Gornja Tuzla samples were analysed (Glumac and Todd, 1991: 11–12). The analysis of the Gornja Tuzla sample suggested the presence of melting rather than smelting slag. On the other hand, the Selevac sample revealed a copper–calcium–iron silicate matrix in which round copper metal prills with iron (0.18 wt %) and silver (0.29 wt %) were suspended. This slag sample is dated to the mid fifth millennium BC, making it one of the earliest known so far. Against this background, the recent discovery, in Belovode, of several levels within the Vinča culture occupation yielding copper smelting slag, copper minerals and ores, and a droplet of copper metal, dating from as early as 5000 BC and continuing to c. 4650 BC, gains particular significance.

4.1. Belovode

The site of Belovode lies on a windy plateau with the eponymous spring running through the settlement, located near the village of Veliko Laole, the city council of Petrovac on the Mlava River, c. 140 km southeast of Belgrade. It has been excavated since 1993 by the National Museum of Belgrade and the Museum in Požarevac (Šljivar and Jacanović, 1996 and literature therein). Within an estimated 100 hectares covered by up to 3 m of cultural layers, four building horizons were recognized, all of which belong to early and middle phases of the Vinča culture, namely Vinča Tordoš (A–B1) and the Gradac phase. By the end of the 4th millennium BC a section of this site was briefly re-occupied by the bearers of the late Chalcolithic Kostolac culture; their remains are limited to a single trench which has been excluded in its entirety from our analysis here, to avoid any doubt about possible

contamination of the studied material by later finds. By 2009, c. 400 m² had been excavated through 14 trenches, usually 25 m² in size.

Nine recent accelerator mass spectrometry (AMS) radiocarbon dates obtained from animal bones from Belovode confirm the expected Vinča culture chronological span (Borić, 2009; Gläser, 1996). These dates were modelled within the Bayesian statistical framework (Buck et al., 1996) by imposing constraints of the stratigraphic sequences for each of the trenches respectively. The model produced acceptable agreement indices (>90 and 100 percent) (Fig. 2).

The probability distribution for the starting boundary of the Vinča occupation (equivalent to the *terminus post quem*) was 5465–5311 cal. BC (68 percent probability) with the highest probability associated with 5350 cal. BC. The probability distribution representing the boundary for the end of the Vinča culture use of the site (the equivalent to the *terminus ante quem*) was 4710–4539 cal. BC (68 percent probability) with the highest probability of 4650 cal. BC. Of particular importance for our argument is that the earliest stratigraphic evidence for the extractive metallurgy on the site points at around 5000 cal. BC, which is the earliest secure date for copper metal production anywhere. Slag finds continue through to layers dating to the last use of the settlement around 4650 BC.

Thus, Belovode was occupied by Vinča groups from c. 5350 to 4650 BC, and coincides fully with the mining activities in Rudna Glava (Borić, 2009). Besides Rudna Glava, situated about 50 km from the site, a further copper source that could have been suitable for the inhabitants of Belovode was discovered in Ždrelo, c. 10 km away. Malachite beads, pendants and ‘green’ copper minerals date from the earliest occupation of the settlement, and continue throughout all building horizons. Charred surfaces with malachite, copper mineral powder adhering to fragmented ceramic sherds and grooved stone mallets are common finds in household contexts

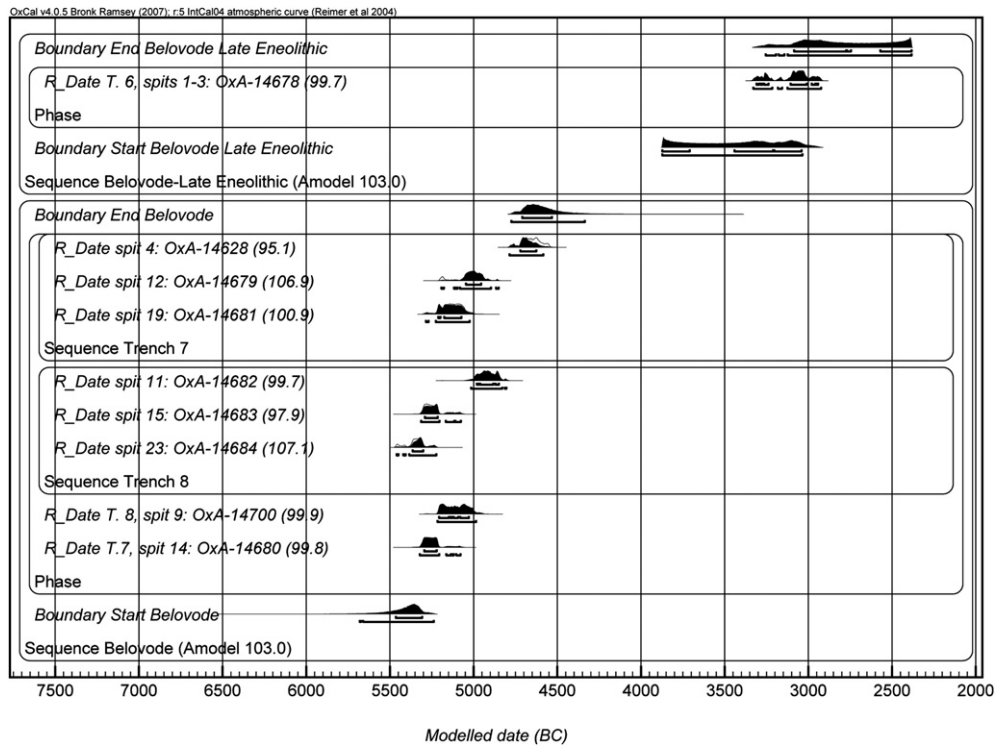


Fig. 2. Probability distributions of dates from Belovode. OxA-14680 and OxA-14700 are excluded from the constraints of stratigraphic sequences in trenches 7 and 8 respectively. The outline distributions show the likelihoods derived only from the calibration of dates. OxA-14678 dates the Late Eneolithic presence at the site and is made on a sample that came from the first three spits in Trench 6. The solid distributions show results when the stratigraphic constraints are imposed. The bars underneath distributions show the 68.2 and 95.4 percent ranges from the analysis.

in Belovode. Their diversity presumably suggests that various technological sequences of the *chaîne opératoire* of copper mineral exploitation are here represented; however, smelting installations with traces of the required temperature (i.e. ~ 1100 °C) have not yet been found. Elongated cylindrical ceramic forms with a diameter of about 20 cm and a reconstructed height of up to 80 cm, open on both ends, have been tentatively linked to the smelting of copper (Šljivar, 2006), however, no adhering slag, copper contamination or excessive vitrification of the ceramic has been found on these during our more recent investigation.

Several copper slag pieces were excavated from Trench No. 3, located in the South Sector, demonstrating sustained smelting activities in Belovode (see below). They were found distributed throughout a wide and deep depression, mixed with several thousand fragments of ceramic sherds, bones and charcoal, and sealed by a layer of building waste, daub. The ceramic material they were associated with belongs to the beginning of the Gradac Phase (Vinča B2). The stratigraphic evidence related to the earliest slag piece is dated to c. 5000 BC; the smelting evidence, according to the excavation reports, continues until the latest layers in this context, possibly finishing with the abandonment of the site, c. 4650 BC. This sequence corresponds well with intensified activities in Rudna Glava at the beginning of the fifth millennium BC (Borić, 2009: 206). The metallurgical finds from this Trench form the focus of this study.

5. Materials and methodology

5.1. Materials: selection and sampling

All materials discovered in the Belovode excavation, including the geological source nearby this site, were subject to selection

conducted in the Depot for Prehistory at the National Museum Belgrade. Out of c. 400 samples we initially selected 34 and grouped them on the basis of their macroscopic characteristics as slags, geological and archaeological minerals (Belovode and Ždrelo), copper ores, artefacts (numerous malachite beads and a droplet of copper metal) and green-stained ceramic sherds.

The slag pieces are vitrified, strongly magnetic and green-stained droplets, not exceeding 2 cm in length (Fig. 3).

They solidified from a highly viscous melt into amorphous, grey samples with light-green stains, which weigh up to 4 g. The outer appearance of slag samples resemble copper minerals, due to the patination of the copper metal entrapped in them; in our opinion, this was the main reason for these to be recognized in the field excavation, and slag fragments without corroded copper prills on their surface may have gone unnoticed in the dark brown soil.

In the selection of copper minerals and ores, we distinguished two main groups: geological and archaeological minerals. Geological minerals originate from two shafts in Ždrelo, discovered in the field survey near Belovode; the samples we selected have green and blue mineral veins of copper carbonates running through the silica-rich host rock. The archaeological mineral group consists of finds coming from cultural layers in Belovode; further sub-division separated bead minerals from ores. The term “bead mineral” stands for minerals clearly formed into beads and identified by their perforation; they are visually pure malachite. On the other hand, we perceive ore as a culturally defined term, which refers to agglomeration of minerals from which the extraction of one or more metals is seen as a profitable action. Thus, we restrict the use of the term ‘ore’ to minerals found in secure smelting contexts. Within the artefact group, we selected samples that were ‘cold’ (beads) and ‘hot’ worked (formerly molten metal). A droplet of molten metal was initially thought to be a mineral, because of the

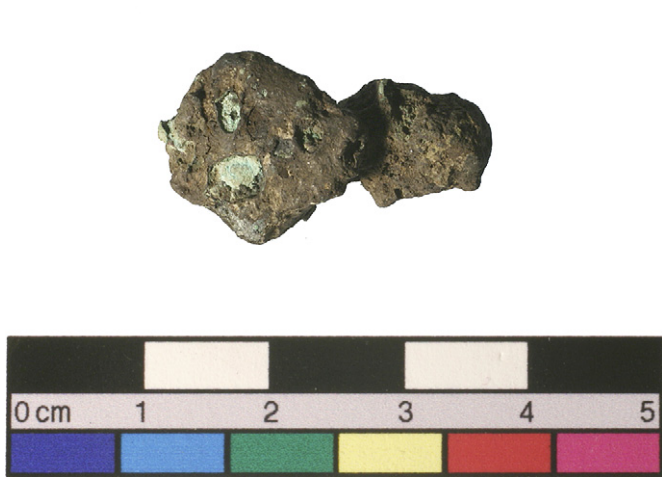


Fig. 3. Copper slag from Belovode (sample No. 21).

light-green patina on the surface; the dark red section revealed upon cutting identified it as metal (Fig. 4).

The green-stained ceramic sherds are fragments of domestic pottery, with green mineral particles attached to their walls. In most cases, the green colour was coming off the walls during the examination, indicating the mere presence of copper minerals near these sherds in the soil rather than a hot temperature treatment.

5.2. Methods

The material was examined at the Wolfson Archaeological Science Laboratories at the UCL Institute of Archaeology, London, UK (structural and chemical analysis) and the Curt-Engelhorn-Center for Archaeometry in Mannheim, Germany (chemical and provenance analysis). We aimed to compositionally characterize the materials indicating metallurgical activities, to explore their technological significance, and their geological relation to each other and with the locally available copper resources.

From each group apart from the Ždrelo ores, samples were mounted in epoxy resin and polished with diamond paste to $\frac{1}{4}$ μm for optical microscopy (OM), Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) and Electron Probe Micro Analysis (EPMA). OM (Leica DM LM) and SEM-EDS (Hitachi S-3400N with Inca software) were used to assess smelting conditions in the slag, determine the nature and spatial arrangement of phases present, to reconstruct the chemical and redox environments during their formation, and to delineate original parameters from post-depositional processes. Similarly, the artefacts were studied to determine the technology of their making and working, and their relation to the slag, mineral and ore samples from the site. Ceramic samples were analysed in search for indications of metallurgical processes carried out in them and to evaluate whether they were particularly refractory. For SEM-EDS analysis samples were coated with carbon and analysed using secondary electron (SE) and backscattered electron (BSE) imaging. The Environmental Scanning Electron Detector in VP-SEM (vacuum) mode was applied for analyses of malachite beads to avoid having to carbon-coat them. The accelerating voltage during Energy Dispersive Spectrometry was 20 kV, with an average dead-time of 35–40% and working distance of 10 mm. The compositional analyses of siliceous matrix and metal prills in the slag samples were obtained by EPMA (JEOL JXA-8100), using 20 kV accelerating voltage and a beam current of 60 nA.



Fig. 4. Copper metal droplet from Belovode (sample No. 14).

Two samples from Ždrelo minerals were ground to homogeneous pellets and prepared for Polarised Energy Dispersive X-Ray Fluorescence (PED-XRF) analysis. The pellets were analysed qualitatively with a three-target method (Turbo Quant-0261a) using a Spectro X-Lab 2000 instrument. The hardness of the copper ingot was tested using Vickers method (HV), with an attachment for microhardness testing under 50 g load (Vickers Instruments, UK). The indenter was calibrated using a standardized steel block (148 HV).

A total of 11 samples (geological and archaeological minerals, metal prills extracted from slags, and one malachite bead) were selected for provenance analysis. Lead-isotope (LI) analyses were conducted to establish relation between slag metal and minerals, using Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Measurements were performed on 1.5 ml of a 200 ppm Pb solution using an Aridus (Cetac) to inject the sample. Each sample was measured once, where a measurement includes 3 runs. For correction of internal fractionation in the instrument, thallium was added to the measuring solution (Niederschlag et al., 2003). Instrumental Neutron Activation Analysis (INAA) determined trace element composition of copper prills in slag, following procedures described in Pernicka (1984) and Kuleff and Pernicka (1995). Neutron irradiations were performed in the TRIGA reactor of the Institut für Kernchemie, University of Mainz.

6. Results

6.1. Composition and structure of slag

All slag samples from Belovode show consistency in their mineralogy, presenting various newly formed phases: prills of metallic copper, cuprite, spinels and delafossite in a mostly glassy siliceous matrix. The copper metal is free of metallic impurities above c. 0.1 wt% and solidified from a fully molten stage, as indicated by the formation of large alpha copper dendrites with the copper–copper oxide eutectic in the interstices (Fig. 5).

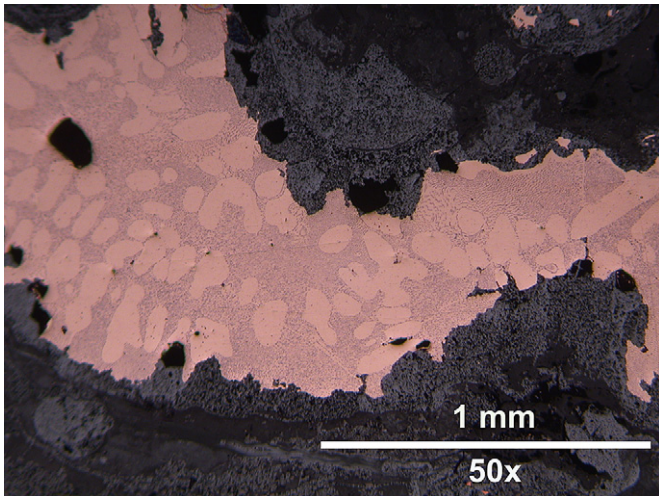


Fig. 5. Photomicrograph of copper metal embedded in glassy matrix and dross in sample No. 21, taken under plane polarised light. Large dendrites of copper alpha grains in copper–copper oxide eutectic indicate gradual cooling of the melt.

Larger areas of massive cuprite, most likely formed from re-oxidising metallic copper, indicate limited control over the redox conditions at the final stage of smelting (Fig. 6).

Although this type of “dross” is mostly found associated with melting processes (Bachmann, 1982), the microanalyses found a consistently high iron, manganese, zinc and cobalt content in the slag which cannot be explained from re-melting copper metal, but most likely derived directly from ores in a smelting process. The siliceous part in all samples is fundamentally similar, with some variation in copper, iron, manganese, silicon, calcium and potassium content, probably reflecting slight changes in ore composition and fuel consumption (Table 1).

According to its structure, the glassy siliceous matrix was fully liquefied during smelting. Upon cooling, the metal oxides cuprite, spinel and delafossite crystallised before the silicate melt solidified into two phases: leucite, $KAlSi_2O_6$, forming polyhedral crystals, and a pyroxenitic glass (Fig. 7).

The differences among the samples in concentrations of particular elements indicate that the samples originate from

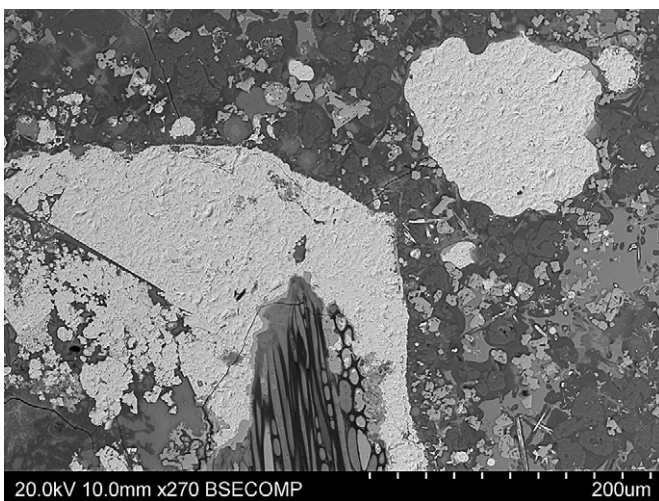


Fig. 6. Backscattered electron image of areas of cuprite (bright) embedded in glassy matrix of sample No. 22a together with various slag crystals (medium grey) and a piece of charcoal (centre bottom).

separate smelting events, while their basic similarity indicates that they were all based on the same technological principle, and using a similar ore. Significant levels of MnO (9.4 wt%), FeO^t (12 wt%), ZnO (2.4 wt%) and CoO (1 wt%) in the slag demonstrate that it derives from ore smelting and not from re-melting of copper metal. This assumption is further corroborated by the presence of spinels and delafossite, which are typical for smelting processes under less reducing to partially oxidising atmosphere (Müller et al., 2004) (Fig. 8).

The spinels in particular concentrate the transition metals in their crystal lattice, making them very distinct from geologically occurring magnetite, and they are very unlikely to form during re-melting copper metal from fused ceramic and fuel ash alone (Table 2).

The analysis of malachite samples from the site showed considerable levels of manganese oxide (up to 40 wt%) as well as lower levels of iron and zinc oxide, but no noticeable cobalt oxide (Table 3).

A comparison of these malachite samples with the slag composition shows general similarity in the transition element ratios, but with the absence of cobalt and lower readings in zinc oxide in the analysed minerals than in the slag.

The geological minerals from Ždrelo, a copper mineralisation several kilometres from Belovode, had significant levels of copper as well as the gangue oxides (particularly silica, alumina, magnesia and iron oxide) in qualitatively similar ratios to those found in slags (Table 4).

The absence of cobalt oxide in these minerals matches the mineral composition from the archaeological malachite excavated at Belovode, while significantly lower readings in manganese oxide (only up to 2.2 wt%) argue against Ždrelo as a possible source for copper smelting in Belovode.

A small droplet of molten metal, weighing just over two grams and initially mistaken for malachite due to its green colour, was discovered in a household context in Trench No. 9, in an area away from the slag findings and therefore possibly indicating different activity areas within the settlement for smelting and casting of copper. The pure copper metal matrix of this piece has abundant casting porosity and is heavily corroded (Fig. 9).

6.2. Provenance analysis

Eleven stratified samples covering all groups of materials (slag, a fragmented malachite bead, and archaeological and geological minerals) were analysed for lead-isotope abundance ratios, and compared with the existing data for copper deposits from Serbia and Bulgaria. Lead-isotope analysis (LIA) identified three distinctive groups, linked to different sources of exploitation (Fig. 10; Table 5).

Lead-isotope group *Belovode A* consists of a malachite bead and two archaeological mineral samples from Belovode; their LI ratios match closely the Majdanpek field (Eastern Serbia), and to some extent also copper minerals from Zidarovo (Eastern Bulgaria).

Group *Belovode B* consists of three mineral samples from Ždrelo and a single manganese-rich mineral batch from the settlement (Fig. 10a).

The most important feature of this group is that it potentially links the mine to the settlement, identifying Ždrelo as one of the deposits possibly exploited for copper production by the inhabitants of Belovode.

Group *Belovode C* comprises all slag samples and forms an elongated array of lead-isotope ratios, typical of high and variable U/Pb ratios in the ore (Fig. 10b).

Groups of chemically similar artefacts with highly variable lead-isotope ratios have been found in Serbia and Bulgaria (Pernicka et al., 1997). Copper ores of highly variable lead-isotope ratios are

Table 1
EPMA compositional data for glass matrices in slag samples.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	FeO ^a	CoO	ZnO	BaO	Cu ₂ O ^a
Average slag 20	0.0	1.7	16.1	37.1	14.4	1.8	7.0	0.5	5.7	13.0	0.7	1.7	0.4	27.8
Average slag 21	0.0	1.9	9.8	38.0	5.3	3.1	11.1	0.2	9.7	16.7	0.9	3.1	0.4	12.6
Average slag 22a	0.0	1.6	13.6	48.2	5.6	3.9	9.1	0.4	6.8	8.8	0.7	1.2	0.3	10.9
Average slag 22b	0.0	1.8	14.4	41.8	3.7	7.2	10.5	0.3	8.0	9.9	0.8	1.3	0.3	10.1
Average Slag 23	0.0	1.7	9.8	39.6	1.3	1.5	9.9	0.2	17.0	11.8	1.9	4.8	0.4	19.5
Average all	0.0	1.7	12.7	40.9	6.1	3.5	9.5	0.3	9.4	12.0	1.0	2.4	0.4	
Average ceramic composition	1.0	1.7	16.9	64.9	0.9	4.3	2.1	1.0	0.0	7.2	0.0	0.0	0.0	

Oxide compositions are given in weight percent as average values of several small area analyses (120 × 80 μm²) and normalised to 100 wt% without copper. Slag sample numbers are each representing a different excavation layer. FeO^f is total iron as FeO.

^a The original copper content prior to normalization.

known in the region, such as Rudna Glava, Crnajka, Beljevina and Velika Brestovica, although Rudna Glava can be ruled out by its lower ²⁰⁸Pb/²⁰⁶Pb ratio. However, copper deposits in eastern Bulgaria, including Medni Rid and Zidarovo have also radiogenic lead, and such ores are therefore generally better differentiated by their trace element patterns.

Trace element analysis of copper prills extracted from two slag samples of this LIA group perfectly match a trace element pattern that is defined by a group of 16 late Neolithic and Chalcolithic artefacts from Serbia and Bulgaria (Pernicka et al., 1993, 1997) (Fig. 11).

Lead-isotope ratios of this artefact group are also consistent with slag samples forming Group C from Belovode. Group C is, however, different from the copper minerals from Rudna Glava in trace element pattern, so that it probably derives from an as yet unidentified ore source. Unfortunately, no trace element analyses are yet available from Beljevina and Velika Brestovica, the two eastern Serbian sites whose LIA show the closest match to Group C samples.

An important feature of the new data is the evidence for several deposits supplying Belovode with copper-rich minerals for different purposes, including bead making and copper smelting. This corresponds well with the field evidence for spatial craft specialisation: a small droplet of copper metal, most probably lost during casting, was found in a different area than the smelting slag. It is further corroborated by the discovery of malachite for bead making, both as working waste and artefacts, in separate contexts across the Vinča culture sequence in Belovode.

7. Discussion

Our results present new insights into the beginning of extractive metallurgy. The identification of smelting activities in the Vinča culture settlement Belovode provides the earliest documented proof of pyrometallurgical copper extraction to date, at the turn of the sixth to the fifth millennium BC.

This is more than half a millennium earlier than previously published secure evidence for copper smelting from the Near East and the Balkans (Hauptmann, 2007; Ryndina et al., 1999). Importantly, the results cover the entire *chaîne opératoire* of extractive metallurgy in close proximity, from the acquisition of ores and minerals from local and regional sources, through smelting and casting, to the production of finished objects. Aspects of the geographic origin of the various raw materials and their relationship to the finished objects from across the Vinča culture form the topic of ongoing research; here, we focus on the new technological information about the earliest copper smelting.

7.1. Smelting conditions at Belovode

The data presented above allows for a tentative reconstruction of the early copper smelting practices at Belovode. The compositional and provenance analyses indicated consistency of smelting technology, ore composition and supply over the c. 300 years represented by the finds. The temperature, slag composition and level of fluidity achieved throughout this period suggest routine mastery of the smelting process, while the absence of any technical ceramic pieces, such as crucible or furnace fragments, is noteworthy.

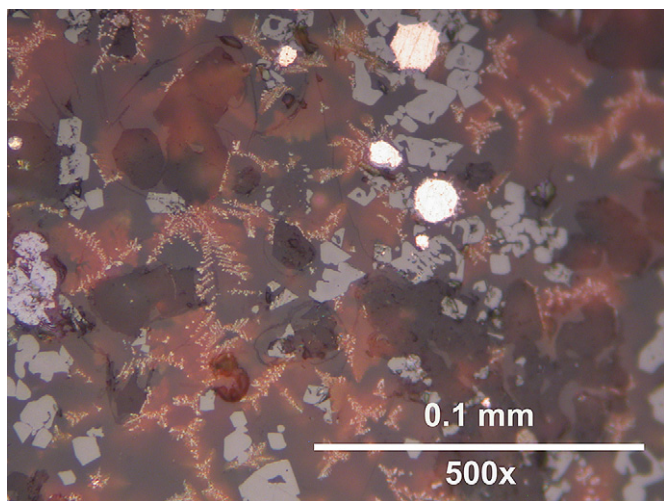


Fig. 7. Photomicrograph of spinel (angular inclusions), copper metal (prills) and cuprite (dendritic structures) embedded in glassy matrix of leucite (black crystals) and pyroxenitic glass (sample No. 22a, plain polarised light).

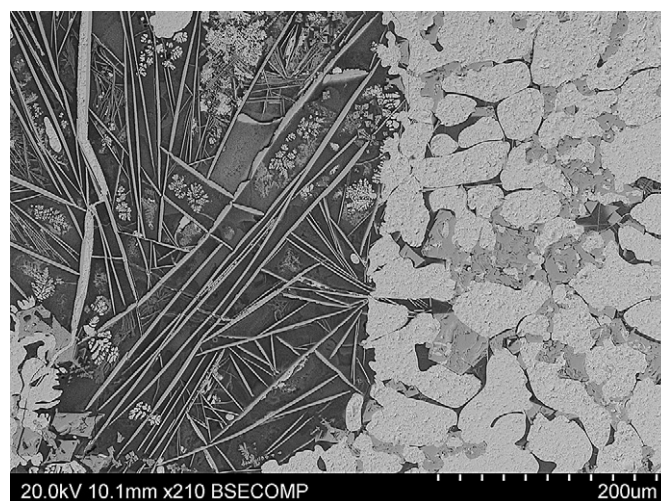


Fig. 8. Backscattered electron image of delafossite (straight lathes), spinels (mid grey) and area rich in cuprite (right) in dark glassy matrix of sample No. 21.

Table 2
SEM-EDS compositional data of spinels in all slag samples in Belovode.

	MgO	Al ₂ O ₃	TiO ₂	MnO	FeO ^t	CoO	NiO	ZnO
Average slag 20	3.0	12.4	0.3	15.7	56.6	2.6	0.8	8.5
Average slag 21	1.3	5.0	0.0	15.6	70.9	1.0	0.1	6.1
Average slag 22a	3.6	13.5	0.3	17.7	54.1	4.4	0.7	5.6
Average slag 22b	2.7	11.0	0.6	17.4	58.1	4.2	1.0	4.9
Average slag 23	1.2	10.3	0.2	18.0	53.5	6.5	1.2	9.0

All values are given in weight percent as averages of oxides, without copper content and normalised to 100 wt%. FeO^t – total iron.

So far, all slag samples found at Belovode are individual pieces, and it is hard to distinguish where exactly they formed during the process. From the bulk analyses we can recognize a strong ore signature, including typical gangue components rich in manganese, zinc or cobalt, and a considerable fuel ash contribution as seen in the elevated levels of potash, lime and phosphorus oxide.

In order to estimate the liquidus temperature of the slag we explored the individual small area analyses from the five slag samples. We added the measured concentrations of alkaline earth and transition metal oxides to iron oxide and phosphate to alumina, and plotted the resulting three-component composition into the FeO–Al₂O₃–SiO₂ system (Fig. 12).

Most compositions fall into or very near the ternary eutectic area between the tridymite, hercynite and mullite stability fields, with nominal melting temperatures in the pure three-component system of 1100–1200 °C. Several individual small areas plot along the main cotectic troughs leading towards this area, with even higher nominal melting temperatures. However, an estimation of real melting temperatures needs to consider that the data is based on a rather complex multi-component system, and that as a general rule any additional oxide will initially lead to a reduction of the true melting temperatures. On the other hand, a certain degree of overheating will have to be allowed for; even though in the case of the small slag droplets studied here this is likely to have been not a large amount. For the time being we estimate the smelting temperature to have been around 1100 °C, and certainly above the copper–copper oxide eutectic of c. 1070 °C.

The dominance throughout all slag samples of well-crystallised spinels and delafossite formed from an apparently fully molten siliceous matrix indicate that the smelting temperature was held for some time, while the chemical heterogeneity on a microscale observed from the individual area measurements point to limited fluidity and hence only limited overheating. The concentration in the slag of manganese oxide reaches on average almost the level of iron oxide (see Table 1). This is highly significant since manganese-rich systems form liquid slag over a much wider range of CO/CO₂ ratios than the more common iron-rich systems (Hauptmann, 2003). The compositional and redox conditions documented here are in good agreement with assumptions of early smelter's practice,

Table 3
SEM-EDS compositional data of copper minerals in Belovode.

	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	CaO	MnO	FeO ^t	Cu ₂ O	ZnO
Minimum mineral 9	0.0	3.9	18.6	1.3	2.6	26.7	1.2	29.8	0.0
Maximum mineral 9	0.0	6.2	26.5	2.5	3.4	34.7	7.5	38.1	2.1
Average mineral 9	0.0	4.9	21.6	1.9	3.0	30.9	3.7	33.2	0.8
St. Deviation	0.0	0.83	2.87	0.47	0.27	3.31	2.16	2.53	0.88
Number of analysis = 8									
Minimum mineral 12	0.0	0.0	13.1	0.0	2.1	24.7	0.0	37.4	0.0
Maximum mineral 12	0.7	3.8	25.0	2.1	3.0	40.0	3.4	43.8	0.0
Average mineral 12	0.3	1.7	18.3	1.4	2.4	34.9	0.7	40.4	0.0
St. Deviation	0.4	1.4	4.5	0.8	0.4	6.2	1.5	2.5	0.0
Number of analysis = 5									

All values given as minimum, maximum and average of oxides, and normalised to 100 wt%. FeO^t – total iron.

Table 4
(PIED)-XRF compositional data for ores from Ždrelo (samples ZdrC1 and ZdrC2).

	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	P ₂ O ₅ (%)	SO ₃ (%)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	MnO (%)	Fe ₂ O ₃ (%)	CuO (%)	Cl (ppm)	V ₂ O ₅ (ppm)	Cr ₂ O ₃ (ppm)	CoO (ppm)	NiO (ppm)	ZnO (ppm)	As ₂ O ₃ (ppm)	SrO (ppm)	Y (ppm)	Ba (ppm)	Ce (ppm)	PbO (ppm)	Total (%)
ZdrC1	6.2	9.0	47.7	0.2	0.5	1.1	16.1	0.3	0.2	11.7	6.9	143	74	87	188	79	560	54	74	0	44	0	156	91.31
ZdrC2	1.5	31.2	36.5	0.1	0.6	1.4	3.5	0.1	2.2	4.2	15.6	0	0	0	632	330	29,232	229	100	213	0	192	1383	65.84

All values given in weight percent and parts per million, and normalised to 100 wt%. Column "Total" shows analytical total prior to normalization.

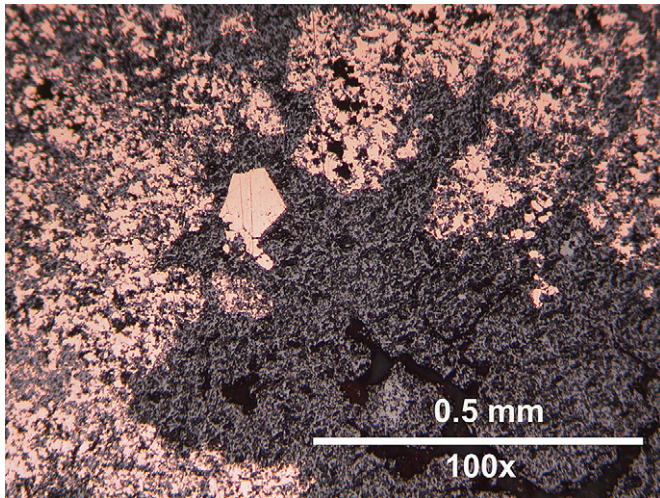


Fig. 9. Photomicrograph of copper metal droplet taken under plane polarised light, sample No. 14.

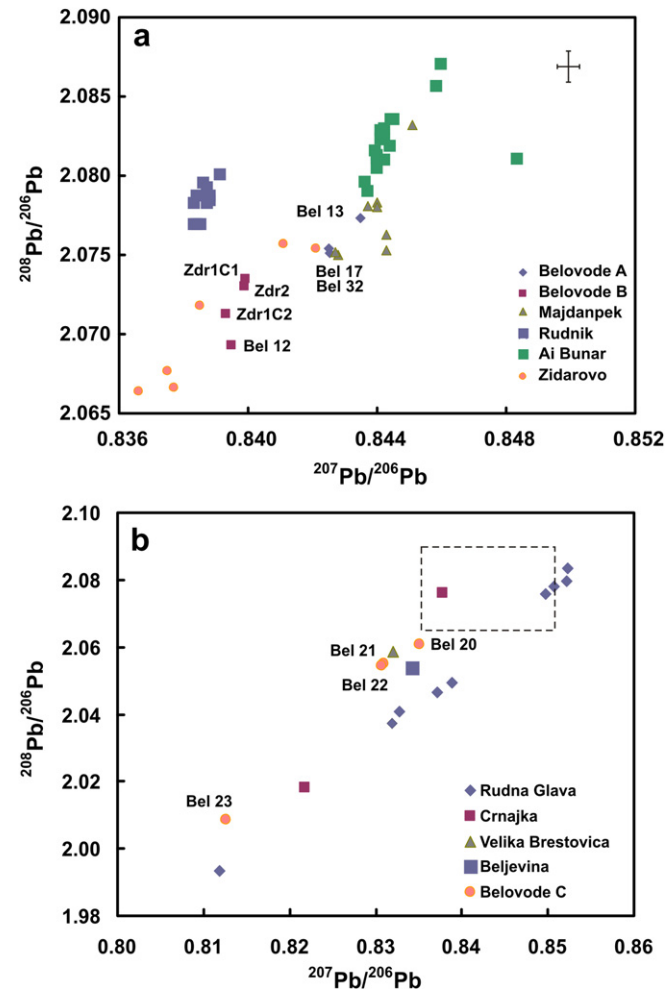


Fig. 10. Lead-isotope abundance ratios of groups Belovode A, B and C in relation to Serbian and Bulgarian copper ores, native copper and copper slag. a) Belovode A and B in relation to Serbian and Bulgarian deposits; b) Belovode C in relation to Serbian deposits (selected data for Rudna Glava and Crnajka). The slashed quadrangle shows the field in the isotope plot below. Error bars are smaller than the symbols (b) and shown in the upper right hand corner (a). Labels are abbreviated as follows: Bel = Belovode, Zdr = Ždrelo.

smelting rather rich and carefully selected ore batches while operating at the edge of their technological skills, reflected in unstable or locally heterogeneous firing conditions with somewhat variable redox ratios and temperatures.

The mineral ore being smelted in Belovode is most probably oxidic copper ore, such as malachite, with significant levels of manganese and zinc oxide, and varying concentrations of cobalt and nickel.

7.2. Selecting the right source: cold lithic technology vs. hot metallurgy

The most striking feature of the isotope data is the variety of copper sources exploited by Belovode inhabitants: the bead mineral, probably selected for its visual quality, is indicated to come from Majdanpek, while the ore minerals for smelting originate from an as yet unknown source, but different from the bead making deposit; their chemistry and visual appearance show a high level of contamination particularly with dark manganese-rich material.

Given the strong indication that selection, mining and manipulation of copper minerals were based on their particular qualities, we can assume that the Belovode craftsmen were well aware of the material properties these minerals bore. The distinction between different mineral properties is also recognized in the spatial distribution of activities across Belovode, suggesting bead making across the site, but more limited and separate smelting and casting areas. A *cold* mineral use is recognized here as bead making, including drilling and/or polishing of malachite beads into their final shape. Metallurgical use refers to the high temperature treatment of copper ores and metal, represented at Belovode by both smelting and casting. Such a specific selection and technical treatment ascribed to a particular quality of copper mineral allows us to argue a degree of specialisation within the copper-centred activities conducted at the site. The limited extent of our evidence, however, does not allow us to suggest whether these activities were performed seasonally or all year round, or whether metallurgical activities were a regular part of the subsistence strategy of the inhabitants of Belovode.

7.3. Belovode metallurgy within its wider context

In summary, we can argue for a regular use of a particular type of manganese-rich copper minerals that was technologically suited for the prevailing smelting conditions with variable redox conditions, and which co-existed with the exploitation of a different source of malachite for bead making. In this differentiation we see two distinctive cultural traits: on the one hand the established habit of copper mineral use as part of the so-called “Neolithic package” (cf. Needham, 1970; Sherratt, 2005), probably brought along with the migration of Neolithic groups from the East and evidenced from such early sites as Lepenski Vir and others, and on the other hand the independent development of copper smelting as part of the regional Vinča culture. Notably, the “Neolithic package” model has long been challenged by various scholars who advocated regional specificities in developing sedentism or agriculture (e.g. Barker, 1975; Whittle, 1996) or pottery (Barnett and Hoopes, 1995) independently from the package deal.

The claim for an independent development in this part of Eurasia is supported by the very early dates for smelting activities in Belovode, spanning from c. 5000 BC to c. 4650 BC and thus matching or even pre-dating much of the evidence for copper smelting in the Near East. The increased mining activity at Rudna Glava at this time, and the strong prevalence of copper implements in the Balkans, outweighing by an order of magnitude similar finds

Table 5
Lead-isotope abundance ratios in material from Belovode and Ždrelo.

Group	Sample	Pb (ppm)	$^{208}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ
A	Belovode 13	9.0	2.0771	0.0004	0.84338	0.00006	18.480	0.009
A	Belovode 17	254	2.0754	0.0002	0.84249	0.00010	18.491	0.012
A	Belovode 32	94	2.0751	0.0004	0.84252	0.00016	18.490	0.008
B	Ždrelo 1C1	730	2.0735	0.0001	0.83991	0.00008	18.620	0.012
B	Ždrelo 1C2	1290	2.0713	0.0005	0.83931	0.00013	18.617	0.018
B	Ždrelo 2	1120	2.0730	0.0001	0.83988	0.00006	18.623	0.020
B	Belovode 12	5.7	2.0693	0.0017	0.83947	0.00033	18.585	0.031
C	Belovode 20	3.2	2.0610	0.0010	0.83512	0.00018	18.675	0.018
C	Belovode 21	4.3	2.0550	0.0004	0.83089	0.00004	18.831	0.084
C	Belovode 22	1.2	2.0546	0.0001	0.83065	0.00010	18.870	0.003
C	Belovode 23	1.6	2.0088	(1 run)	0.81254	(1 run)	19.296	(1 run)

The standard deviations (2σ) are given in absolute figures. Thus the precision of the measurements varies between 0.005 and 0.05% for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ and between 0.02 and 0.25% for $^{206}\text{Pb}/^{204}\text{Pb}$. Samples are labelled as follows: Ždrelo stands for ores originating from this mine; Belovode 12 is a fine-grained black and green mixed ore; Belovode 13 and 17 are dark ores: Belovode 13 was thermally treated, as indicated by the presence of both tenorite and cuprite, while Belovode 17 has minor sulphide minerals (pyrite, chalcocite and covellite) in a copper carbonate-rich matrix; Belovode 32 is a cold-worked malachite bead; Belovode 20, 21, 22, 23 are slag samples.

from the Near East, further suggests that the Vinča metallurgy was anything but secondary.

Although the provenance analysis of smelting slag from Belovode rules out Rudna Glava as the source of the ore smelted here, the likely source can be assumed to be in the wider region around this location. Rudna Glava, however, stands as the only known late

Neolithic mine in Eastern Serbia not obliterated by the large-scale mining operations carried out in the Roman period and until the present day. Bearing in mind the abundance of copper mineralisation in this area, one can assume that there were more prehistoric mining locations such as Rudna Glava which did not survive later mining activities. The analysis of 17 of the 45 metal artefacts found at Pločnik point to at least five different geological sources scattered across Bulgaria, Macedonia and eastern Serbia that provided the metal for these typologically homogenous artefacts (Pernicka et al., 1997: 93–94, 105–106, Table. 3); it appears that the foundry at Pločnik routinely obtained metal from a range of sources. Conversely, the lead-isotope signature of the 16 late Neolithic and Chalcolithic artefacts that isotopically and chemically closely correspond with the Belovode slag samples, but which originate archaeologically from several sites in Serbia and Bulgaria along the lower Danube (Pernicka et al., 1997: 106, 112), imply an extensive use of a particular source/mine during this period. Our data show that Belovode metalworkers were among the first to smelt this metal. The fact that this as yet unidentified source was apparently exploited even after Belovode was abandoned in the mid fifth millennium BC shows that by then metallurgy was further disseminated throughout the area, and possibly beyond.

8. Conclusion

The research presented here documents the earliest sound evidence for copper smelting known so far, anywhere, consisting of slag droplets rich in typical gangue elements together with molten copper metal. We note the absence of dedicated ceramic vessels such as crucibles or furnace installations from our observations, leaving room for a potential ‘hole in the ground’ model for the predominantly solid-state reduction step (represented here by the small droplets of slag which may have formed in front of the blow pipes), followed by melting and casting elsewhere in the settlement (as indicated by the droplet of metal found away from the slag).

Another interesting and potentially important observation is the separation into two discrete crafts here, both based on copper minerals: ‘cold’ bead making using established Neolithic technologies, and ‘hot’ copper smelting, using newly developed metallurgical skills. The evidence from Belovode suggests that bead making was practised across the site, while copper smelting evidence is so far restricted to a single trench. Ongoing work addresses the question of the geological origin of the various minerals used, which at present appears to indicate a clear separation of geological sources between the two crafts. This gains further significance in view of the complex supply networks which are visible in the

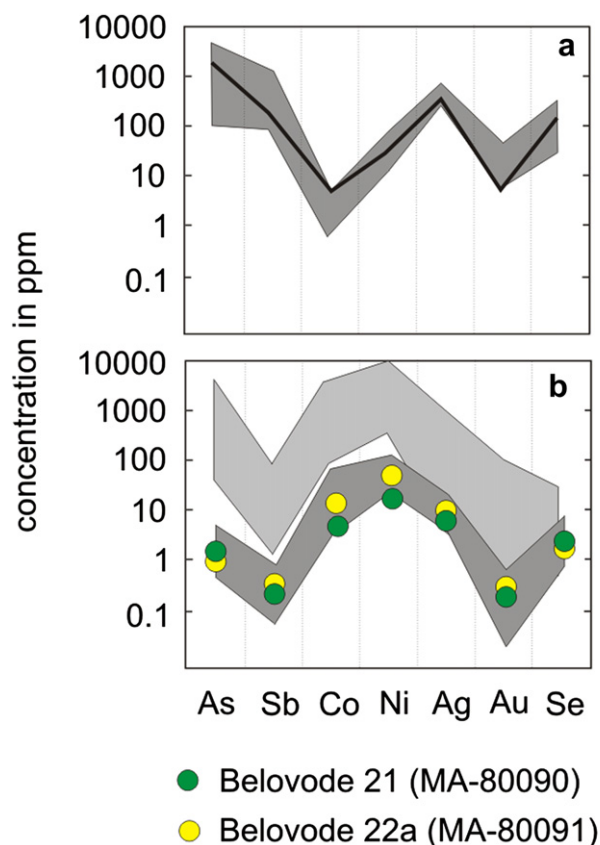


Fig. 11. Trace element patterns for Chalcolithic copper artefacts and copper mines in Serbia and Bulgaria. a) Trace element pattern of 40 Chalcolithic copper artefacts from Serbia and Bulgaria (shaded field) with trace element pattern of the copper mine Ai Bunar in Bulgaria (black line); b) trace element pattern of 16 Chalcolithic copper artefacts from Serbia and Bulgaria with yet unidentified source (dark shaded area) matching the trace element pattern of Belovode slag samples (green and yellow dots). This pattern differs from the trace element pattern of Rudna Glava in Serbia (light shaded area) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

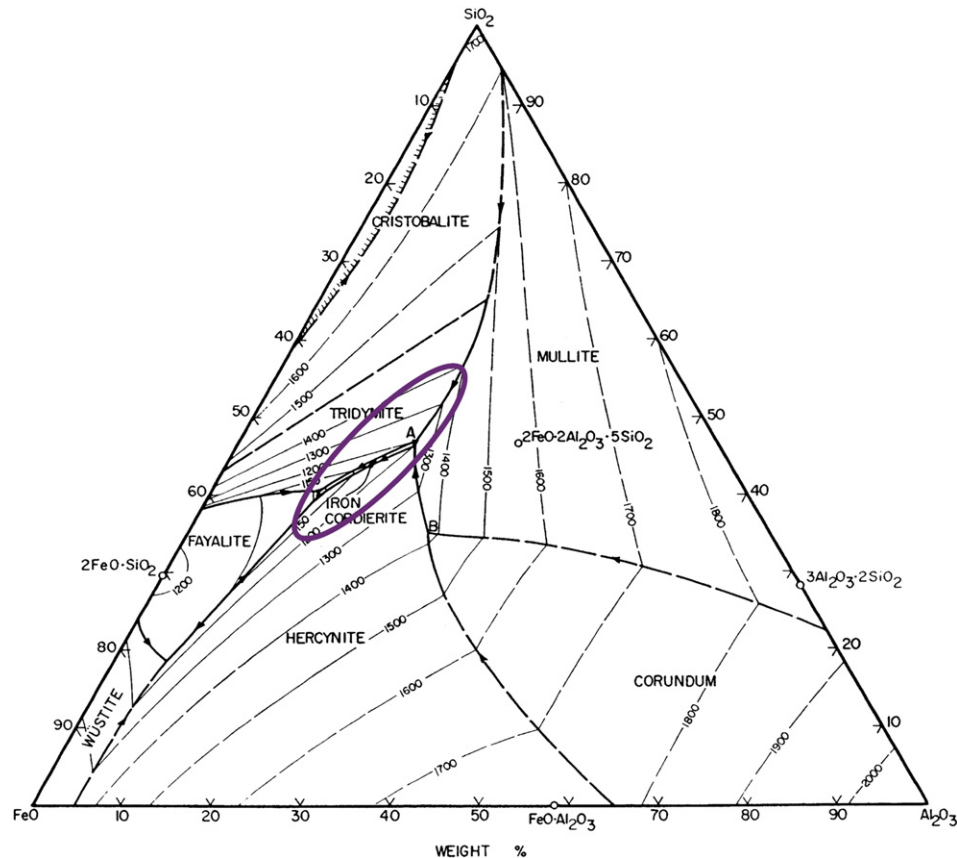


Fig. 12. Ternary diagram of the FeO–Al₂O₃–SiO₂ system, showing the working temperature for Belovode slag samples (ellipse). Alkali earth and transition metal oxides are added to iron, and phosphorus to alumina content. The melting temperature in the pure ternary system would be in the range of 1200–1400 °C; however the presence of minor metal oxides brings it down to c. 1150 °C.

multi-source origin of the stylistically homogenous Pločnik artefacts, and the multi-consumer exploitation of a single ore source as seen in the so far un-provenanced but isotopically and chemically well defined group of 16 Late Neolithic and Chalcolithic artefacts found along the Danube.

In summary, our results are significant for several reasons: first, they provide the earliest secure dates for copper smelting, taking its early history back to the very end of the 6th millennium BC, and placing it into a developed network of multiple resource exploitation and consumer choice. Second, they indicate the existence of different, possibly independent centres of invention of metallurgy, challenging the model of a single place of invention within Eurasia. Although the use of copper minerals and native copper within a lithic technology occurs with the spread of farming across Eurasia during the Neolithic, the Belovode evidence indicates that extractive metallurgy may have multiple origins across Eurasia, rooted within but independent from the Neolithic package.

Acknowledgements

The initial work was done as part of MR's MSc in Technology and Analysis of Archaeological Materials, which is continuing as doctoral research at the UCL Institute of Archaeology. ThR and MR acknowledge with gratitude the substantial financial support of this research first from the European Union for the Marie Curie action project IoASCA, under contract MEST-CT-2004-514509, Tokyo Foundation, and the Republic of Serbia (Fund for Young Talents, Ministries of Science and of Culture), and more recently from the EPSRC and Freeport McMoRan and IAMS as part of her DHPA scholarship, and substantial research support funds from the

OSI-Soros Foundation and the Exit Foundation. The support of K. Reeves and S. Groom in the UCL Wolfson Archaeological Science Laboratories and of T. Schifer in the Curt-Engelhorn-Centrum Archäometrie has been invaluable. M.R. thanks M. Martínón-Torres, C.P. Thornton, B. Roberts, J.K. Cvetković and B. Jovanović for comments, and D. Kovačević, A. Rico, Lj. Radivojević, E. Blakelock, D. Popović, G. Petković and Radivojević and Rajkovača families for other assistance. The authors are solely responsible for any mistakes.

References

- Antonović, D., 2006. Malachite finds in the Vinča culture: evidence for early copper metallurgy in Serbia. *Metallurgija – Journal of Metallurgy* 12, 85–92.
- Bachmann, H.-G., 1982. *The Identification of Slags from Archaeological Sites*. Institute of Archaeology, London.
- 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.
- Barker, G., 1975. Early neolithic land use in Yugoslavia. *Proceedings of the Prehistoric Society* 41, 85–104.
- Barnett, W.K., Hoopes, J.W., 1995. *The Emergence of Pottery: Technology and Innovation in Ancient Societies*. Smithsonian Institution Press, Washington, DC.
- Borić, D., 2009. Absolute dating of metallurgical innovations in the Vinča Culture of the Balkans. In: Kienlin, T.L., Roberts, B.W. (Eds.), *Metals and Societies. Studies in Honour of Barbara S. Ottaway*. Verlag Dr. Rudolf Habelt GmbH, Bonn, pp. 191–245.
- Bourgarit, D., 2007. Chalcolithic copper smelting. In: La Niece, S., Hook, D., Craddock, P. (Eds.), *Metals and mines: studies in archaeometallurgy. Archetype in association with the British Museum*, London, pp. 3–14.
- Breunig, P., 1987. ¹⁴C-Chronologie des vorderasiatischen, südost- und mitteleuropäischen Neolithikums. Kommission bei Böhlau, Köln.
- Brukner, B., 1980. Naselje vinčanske grupe na Gomolavi (neolitski i ranoeneolitski sloj). *Izveštaj sa iskopavanja 1967–1976.god. Rad Vojvodanskih muzeja* 26, 5–55.

- Buck, C.E., Cavanagh, W.G., Linton, C.D., 1996. Bayesian Approach to Interpreting Archaeological Data. John Wiley & Sons, Chichester.
- Budd, P., 1991. Eneolithic arsenical copper – heat-treatment and the metallographic interpretation of manufacturing processes. In: Pernicka, E., Wagner, G.A. (Eds.), *Archaeometry '90: International Symposium on Archaeometry*. Birkhäuser Verlag, Heidelberg, pp. 35–44.
- Cessford, C., 2005. Absolute dating at Çatal Höyük. In: Hodder, I. (Ed.), *Changing materialities at Çatalhöyük: Reports from the 1995–99 Seasons*. McDonald Institute Monographs, British Institute at Ankara, Cambridge, London, pp. 65–100.
- Chapman, J., 1981. Vinča Culture of South-East Europe: Studies in Chronology, Economy and Society. British Archaeological Reports, Oxford.
- Chernykh, E.N., 1978. Gornoe delo i Metallurgiya v dreivneishei Bolgarii. Bolgarskoj Akademii Nauk, Sofia.
- Childe, V.G., 1944. Archaeological ages as technological stages. *Journal of the Royal Anthropological Institute of Great Britain and Ireland* 74, 7–24.
- Childe, V.G., 1958. *The Prehistory of European Society*. Pelican, London.
- Craddock, P.T., 1995. *Early Metal Mining and Production*. Edinburgh University Press, Edinburgh.
- Craddock, P.T., 2009. Evidences for the earliest smelting processes in western Europe, *Archaeometallurgy in Europe: 2nd International Conference, Associazione Italiana di Metallurgia, Aquileia, Italy*, pp. 3–11.
- Ehrich, R.W., Bankoff, H.A., 1992. Geographical and chronological patterns in east central and southeastern Europe. In: Ehrich, R.W. (Ed.), *Chronologies in Old World Archaeology*. University of Chicago Press, Chicago, pp. 375–392.
- Garašanin, M., 1951. *Hronologija vinčanske grupe*. (Chronology of the Vinča group). Univerza v Ljubljani, Ljubljana (in Serbian).
- Garašanin, M., 1973. *Prastorija na tlu Srbije*. (Prehistory in Serbia). Srpska Književna Zadruga, Belgrade (in Serbian).
- Garstang, J., 1953. *Prehistoric Mersin*. Oxford University Press, Oxford.
- Gläser, R., 1996. Zur absoluten Datierung der Vinča-Kultur anhand von C-14 Daten. In: Draşovean, F. (Ed.), *The Vinča Culture, its Role and Cultural Connections*. The Museum of Banat, Timisoara, pp. 141–162.
- Glumac, P.D., Todd, J.A., 1991. Early metallurgy in Southeast Europe: the evidence for production. In: Glumac, P.D. (Ed.), *Recent Trends in Archaeometallurgical Research, MASCA Research Papers in Science and Archaeology*. University of Pennsylvania, Philadelphia, pp. 9–19.
- Grbić, M., 1929. *Pločnik, eine prähistorische Ansiedlung aus der Kupferzeit*. Nationalmuseum Belgrad, Belgrade.
- Hauptmann, A., 2003. Developments in copper metallurgy during the fourth and third millennia BC at Feinan, Jordan. In: Craddock, P.T., Lang, J. (Eds.), *Mining and Metal Production through the Ages*. The British Museum Press, London, pp. 90–100.
- Hauptmann, A., 2007. *The Archaeometallurgy of Copper: Evidence from Faynan*. Jordan. Springer, Berlin.
- Jovanović, B., 1971. *Metallurgy in the Eneolithic Period in Yugoslavia*. Archaeological Institute, Belgrade.
- Jovanović, B., 1980. The origins of copper mining in Europe. *Scientific American* 242, 152–167.
- Jovanović, B., 1994. Gradac-phase in the relative chronology of the Late Vinča culture. *Starinar (New Series)* 43–44, 1–12.
- Jungmans, S., Sangmeister, E., Schröder, M., 1968. *Kupfer und Bronze in der frühen Metallzeit Europas, Studien zu den Anfängen der Metallurgie*. Mann, Berlin. Band 2.
- Krajnović, D., Janković, S., 1995. Copper mineralization as potential raw material source of ancient copper metallurgy in Serbia. In: Jovanović, B. (Ed.), *Ancient Mining and Metallurgy in Southeast Europe*. Archaeological Institute, Museum of Mining and Metallurgy, Gornji Milanovac.
- Kuleff, I., Pernicka, E., 1995. On the instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry* 191, 145–161.
- Lazarovici, G., 1970. *Cultură Vinča A in Banat*. Acta Musei Napocensis (Romania) 7, 475–488.
- Maddin, R., Muhly, J.D., Stech, T., 1999. Early metalworking at Çayönü. In: Hauptmann, A., Pernicka, E., Rehren, Th., Yalçın, Ü. (Eds.), *The Beginnings of Metallurgy*. Deutsches Bergbau-Museum, Bochum, pp. 37–44.
- McPherron, A., Srejović, D., 1988. *Divostin and the Neolithic of Central Serbia*. University of Pittsburgh, Pittsburgh.
- Mellaart, J., 1964. Excavations at Çatal Höyük, 1963: third preliminary report. *Anatolian Studies* 14, 39–119.
- Milojević, V., 1949. *Chronologie der jüngeren Steinzeit Mittel- und Südosteuropas*. Mann, Berlin.
- Müller, R., Rehren, Th., Rovira, S., 2004. Almirazaque and the early copper metallurgy of Southeast Spain: New Data. *Madrid Mitteilungen* 45, 33–56.
- Needham, J., 1970. *Clerks and Craftsmen in China and the West*. Cambridge University Press, Cambridge.
- Neuninger, H., Pittioni, R., Siegl, W., 1964. *Frühkeramikzeitliche Kupfergewinnung in Anatolien*. *Archaeologia Austriaca* 35, 98–110.
- Niederschlag, E., Pernicka, E., Seifert, T., Bartelheim, M., 2003. The determination of lead isotope ratios by multiple collector ICP-MS: a case study of Early Bronze Age artefacts and their possible relation with ore deposits of the Erzgebirge. *Archaeometry* 45, 61–100.
- Pernicka, E., 1984. *Multi-Elementanalyse archäologischer Kupfer- und Bronzeartefakte: Ein Methodenvergleich*. *Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz* 31, 517–531.
- 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., 1999. A heartland of metallurgy: neolithic/chalcolithic metallurgical origins on the Iranian Plateau. In: Hauptmann, A., Pernicka, E., Rehren, Th., Yalçın, Ü. (Eds.), *The Beginnings of Metallurgy*. Deutsches Bergbau-Museum, Bochum, pp. 107–120.
- Rehder, J.E., 1999. High temperature technology in Antiquity – a sourcebook on the design and operation of ancient furnaces. In: Hauptmann, A., Pernicka, E., Rehren, Th., Yalçın, Ü. (Eds.), *The Beginnings of Metallurgy*. Deutsches Bergbau-Museum, Bochum, pp. 304–316.
- Rehren, Th., 2003. Crucibles as reaction vessels in ancient metallurgy. In: Craddock, P.T., Lang, J. (Eds.), *Mining and Metal Production Through the Ages*. The British Museum Press, London, pp. 207–215.
- Rehren, Th., Pernicka, E., 2008. Coins, artefacts and isotopes-archaeometallurgy and Archaeometry. *Archaeometry* 50, 232–248.
- Renfrew, C., 1969. The autonomy of the south-east European Copper Age. *Proceedings of the Prehistoric Society* 35, 12–47.
- Renzi, M., Montero-Ruiz, I., Bode, M., 2009. Non-ferrous metallurgy from the Phoenician site of La Fonteta (Alicante, Spain): a study of provenance. *Journal of Archaeological Science* 36, 2584–2596.
- Roberts, B., 2008. Creating traditions and shaping technologies: understanding the earliest metal objects and metal production in Western Europe. *World Archaeology* 40, 354–372.
- Roberts, B.W., Thornton, C.P., Pigott, V.C., 2009. Development of metallurgy in Eurasia. *Antiquity* 83, 1012–1022.
- Robins, G.V., Seeley, N.J., McNeil, D.A.C., Symons, M.R.C., 1978. Identification of ancient heat-treatment in flint artifacts by ESR spectroscopy. *Nature* 276, 703–704.
- Ruiz Taboada, A., Montero-Ruiz, I., 1999. The oldest metallurgy in Western Europe. *Antiquity* 73, 897–903.
- Ryndina, N., 2009. The potential of metallography in investigations of early objects made of copper and copper-based alloys. *Historical Metallurgy* 43, 1–18.
- Ryndina, N., Indenbaum, G., Kolosova, V., 1999. Copper production from poly-metallic sulphide ores in the northeastern Balkan eneolithic culture. *Journal of Archaeological Science* 26, 1059–1068.
- Schier, W., 2000. Measuring change: the Neolithic pottery sequence of Vinča-Belo Brdo. *Documenta Praehistorica* 27, 187–197.
- Schubert, F., 1965. *Zu den südosteuropäischen Kupfererzten*. *Germania* 43, 274–295.
- Sherratt, A., 2005. Settling the Neolithic: a digestif. In: Bailey, D.W., Whittle, A., Cummings, V. (Eds.), *(Un)settling the Neolithic*. Oxbow, Oxford, pp. 140–146.
- Šljivar, D., 2006. The earliest copper metallurgy in the Balkans. *Metallurgija – Journal of Metallurgy* 12, 93–104.
- Šljivar, D., Jacanović, D., 1996. Veliko Laole-Belovode, the settlement of the culture of Vinča. *Journal of Serbian Archaeological Society* 12, 55–60.
- Šljivar, D., Kuzmanović-Cvetković, J., 1998. Najstarija metalurgija bakra na Pločniku kod Prokuplje, naselju vinčanske kulture. (The oldest copper metallurgy at Pločnik near Prokuplje). *Archaeometallurgy (Belgrade)* 6, 1–8 (in Serbian).
- Solecki, R.S., Solecki, R.L., Agelarakis, A.P., 2004. *The Proto-neolithic Cemetery in Shanidar Cave*. Texas A&M University Press, Texas.
- Stalio, B., 1960. *Pločnik-Prokuplje-naselje*. (Pločnik-Prokuplje-settlement). *Arheološki pregled (Belgrade)* 2, 33–36 (in Serbian).
- Stalio, B., 1962. *Pločnik, Prokuplje-naselje vinčanske grupe*. (Pločnik, Prokuplje – the Vinča group settlement). *Arheološki pregled (Belgrade)* 4, 19–25 (in Serbian).
- Thornton, C.P., Rehren, Th., 2009. A truly refractory crucible from fourth millennium Tepe Hissar, Northeast Iran. *Journal of Archaeological Science* 36, 2700–2712.
- Thornton, C.P., Rehren, Th., Pigott, V.C., 2009. The production of speiss (iron arsenide) during the Early Bronze Age in Iran. *Journal of Archaeological Science* 36, 308–316.
- Thornton, C.P., Golden, J., Killick, D., Pigott, V.C., Rehren, Th., Roberts, B.W., 2010. A Chalcolithic error: rebuttal to Amzallag 2009. *American Journal of Archaeology* 114, 305–315.
- Tringham, R.E., Krstić, D., 1990. *Selevac: A Neolithic Village in Yugoslavia*. UCLA, Los Angeles.
- Vlassa, N., 1969. Einige Bemerkungen zu Fragen des Neolithikums in Siebenbürgen. *Studijne Zvesti AUSA* 17, 513–540.
- Whittle, A.W.R., 1996. *Europe in the Neolithic: the Creation of New Worlds*. Cambridge University Press, New York.
- Yalçın, Ü., 2000. *Frühchalkolitische Metallfunde von Mersin-Yumuktepe: Beginn der extraktiven Metallurgie?* *TÜBA-AR* 3, 109–128.
- Yener, K.A., 2000. *The Domestication of Metals: the Rise of Complex Metal Industries in Anatolia*. Brill, Leiden.