Archaeometallurgy of the Vinča culture: a case study of the site of Belovode in eastern Serbia

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ABSTRACT: The site of Belovode came to fame within the archaeological community with the discovery of the earliest metallurgy so far known. The evidence is several pieces of copper slag dated to c5000 BC (Radivojević et al 2010). Extensive compositional, microstructural and provenance analyses of this material showed a consistent smelting technology over the c400 years of the site's occupation. This paper provides a detailed analytical account of 12 further samples from Belovode indicating copper mineral use and archaeometallurgical activities. Particular emphasis is given to production debris from the 'metallurgical' Trench 3, although other significant metallurgical contexts are also included. The overall aim is to investigate technological relationships between the specimens presented here and those previously published by Radivojević et al (2010). Their technological associations provide a more coherent image of the archaeometallurgical activities in this part of Eurasia at the dawn of metallurgy.

Introduction

The site of Belovode (*c*5350-4650 BC) is located in eastern Serbia and belongs to the Vinča culture, a Late Neolithic/Early Chalcolithic phenomenon which lasted for nearly a millennium in a large part of the northern and central Balkans (Fig 1). The Vinča culture material shows strong links to the contemporaneous Karanovo culture (phase III through to Kodžadermen-Gumelniţa-Karanovo VI) in Bulgaria, Precucuteni-Tripolye A in Moldavia and Ukraine, and Dimini in Greece. The most distinctive links, amongst others, are in settlement patterns, pottery production and the earliest mass-production of metal objects in this part of the world. Almost five tonnes of extant copper implements from the 5th millennium BC Balkans are known today, comprising *c*4300 objects preserved in modern museum archives (Chernykh, 1978; Pernicka *et al* 1997; Ryndina 2009). These artefacts occur in typologically distinctive shapes and are made from copper from several Balkan deposits (Pernicka *et al* 1993; 1997).

Figure 1: The Danube basin showing the location of Belovode and the Ždrelo and Rudna Glava mines. Base map © Zentai László, 1996

The periodisation of the Vinča culture has been developed by several scholars; the one followed here was

Table 1: The copper mineral and archaeometallurgical collection from Belovode.

No	Analytical No	Field label	Field context	Relative chronology	Type of material	EPMA	Fig
1	Belovode 3	Trench 13, spit 14	Household	Vinča B1	Copper mineral		4a, 5a
2	Belovode 30a	Trench 3, spit 5	(Building) waste pit	Gradac Phase	Slagged ceramic sherd	X	6a, 9a
3	Belovode 30c	Trench 3, spit 5	(Building) waste pit	Gradac Phase	Slagged ceramic sherd		
4	Belovode 31a	Trench 3, spit 6	(Building) waste pit	Gradac Phase	Slagged ceramic sherd	X	6b, 9b, 12b
5	Belovode 31b	Trench 3, spit 6	(Building) waste pit	Gradac Phase	Slagged ceramic sherd	X	3c, 6b, 10, 11, 12a
6	Belovode 33b	Trench 14, spit 15	Household	Vinča B1	Copper mineral		5b, 19
7	Belovode 34a	Trench 14, spit 3	Household	Gradac Phase	Copper mineral		
8	Belovode 40	Trench 9, spit 18	Household - pits	Gradac Phase	Lead-based slag cake		
9	Belovode 131	Trench 3, spit 6	(Building) waste pit	Gradac Phase	Copper slag	X	17
10	Belovode 134	Trench 3, spit 7	(Building) waste pit	Gradac Phase	Copper slag	X	3b, 15, 16
11	Belovode 136	Trench 3, spit 5	(Building) waste pit	Gradac Phase	Copper slag		
12	Belovode M6	Trench 3, spit 10	(Building) waste pit	Gradac Phase	Copper metal droplet	X	18
13	Belovode M10	Trench 3, spit 19	Household	Vinča B1	Copper mineral		4b
14	Belovode M14	Trench 9, spit 11	Household	Gradac Phase	Copper metal droplet		
15	Belovode M20	Trench 3, spit 2	(Building) waste pit	Gradac Phase	Copper slag	X	
16	Belovode M21	Trench 3, spit 4	(Building) waste pit	Gradac Phase	Copper slag	X	
17	Belovode M22a	Trench 3, spit 5	(Building) waste pit	Gradac Phase	Copper slag	X	
18	Belovode M22b	Trench 3, spit 5	(Building) waste pit	Gradac Phase	Copper slag	X	
19	Belovode M23	Trench 3, spit 7	(Building) waste pit	Gradac Phase	Copper slag	X	

Notes: Samples 14-19 have already been studied by Radivojević *et al* 2010.
All samples have been studied by optical microscopy (OM) and SEM-EDS. Those analysed by EPMA are marked X.

established by Milojčić (1949) using alphabetic letters (Vinča A-D, with subdivisions). The start of the Vinča A phase is recognised as *c*5400/5300 BC, while Vinča B starts around 5200 BC. The latest date for Vinča B1 is *c*5000/4950 BC; this marks the beginning of the Gradac Phase, which probably lasted for *c*50-100 years. Vinča C lasts from *c*4900 to *c*4850/4800 BC, while the abandonment of the Vinča culture settlements at the end of Vinča D falls around 4650/4600 BC (Borić 2009, 234).

The estimated duration of the Vinča culture is therefore between *c*5400-4600 BC, with metallurgical activities starting around *c*5000 BC, or just at the beginning of the Gradac Phase (or Vinča B2) (Radivojević *et al* 2010). This is also the period when copper mining activities in the Rudna Glava mine intensify (Borić 2009, 205-206), suggesting that the Gradac phase was very significant for the adoption of metallurgy among Vinča culture communities. This particular phase was not an isolated event; relevant changes in pottery and figurines making, or settlement patterns noticeable across the Balkans, prompting Garašanin (1995) to argue that such changes announced the beginning of the Chalcolithic (or Eneolithic) in the region, most likely initiated by the synchronous emergence, adoption and transmission of copper metal making and subsequent consumption.

The site of Belovode has thus far yielded the best quality material for the study of the dawn of the Chalcolithic in the Balkans, or the beginnings of metallurgy in this area. There are nineteen samples indicating copper mineral use and metallurgical activities (Table 1), of which only six have previously been published (Radivojević *et al* 2010).

The assemblage studied here includes copper minerals, ores, slags, slagged sherds and a metal droplet, twelve samples in total (Table 1). The lead-based cake (Belovode 40) is only recorded here as part of the evidence for archaeometallurgical activities but will be addressed in a separate publication. This paper provides nuanced technological details that are presented here for the first time, although publication elsewhere is under consideration. The terms *copper mineral* and *copper ore* distinguish material intended for use for bead or pigment making (‘cold’ processing) from that used for metal smelting (‘hot’ processing). Microstructural and compositional analyses of these provide a more complete account of copper mineral use and archaeometallurgical activities at the site of Belovode and also demonstrate one of the methodological approaches to the future studies of early metallurgical assemblages worldwide. This micro-study aims to provide a coherent picture on the interrelation of copper-based samples from Belovode, address the

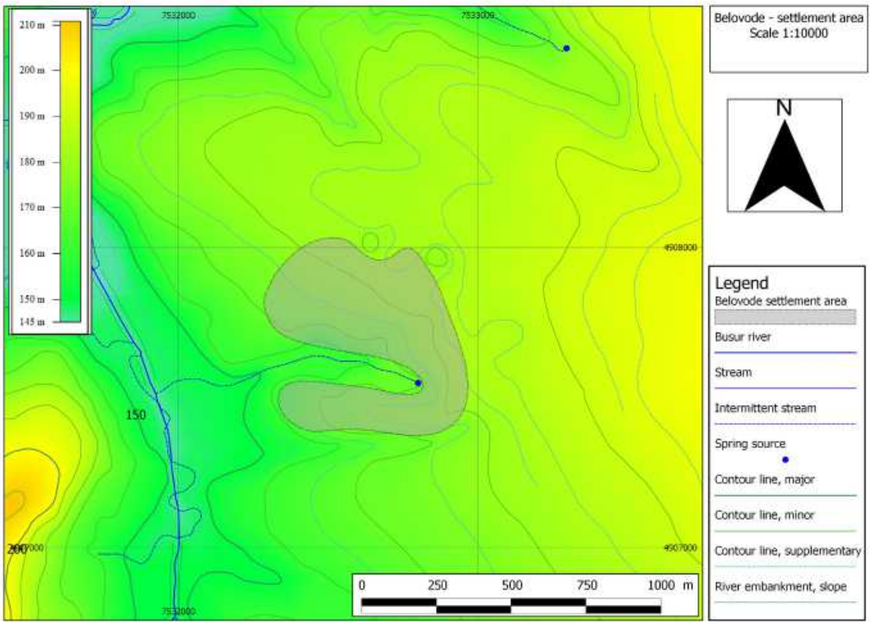

Figure 2: The central shaded area is the site of Belovode (drawing by J Pendic).

presence of potential workshops and aid reconstruction of metal production practices in this settlement. Such technological study is expected to aid understanding of otherwise insufficiently contextualised specimens; this is partly due to the lack of recognition during the Belovode excavations, and partly because a large part of the field documentation is as yet unpublished.

Copper mineral use and metallurgical activities

The site of Belovode (Fig 2) lies around a spring, near the village of Veliko Laole *c*140km southeast of Belgrade. Its location is typical for Vinča culture settlements: it sits on a large ellipsoidal plateau at an altitude of *c*200m, surrounded by land suitable for agricultural activities, cattle breeding and pastures (Šljivar *et al* 2006, 251-252). It has been excavated since 1993 by the National Museum of Belgrade and the Museum in Požarevac (Šljivar and Jacanović 1997; 1996a; 1996b; Jacanović and Šljivar 2003; Šljivar *et al* 2006). Within an estimated 100 hectares covered by up to 3m of cultural layers, four building horizons were recognized (Belovode A-D), correlating with the entire Vinča culture sequence (*ibid*, 251). By 2009, *c*400m^2 was excavated through 14 trenches, usually 25m^2 in size, all of which are concentrated in the southern part of this settlement. The nearby Mlava River runs deep into the volcanic mountain range called Homolje, which belongs to the zone of primary copper mining and metallurgy (Krajnović and Janković, 1995).

The Vinča culture sequence of Belovode was established on the basis of distinctive ceramic typology (Garašanin 1951; 1973), including locally recognised pottery variations (Arsenijević and Živković 1998; Šljivar and Jacanović 1996b). At its earliest stages, Belovode was most likely inhabited by Early Neolithic Starčevo groups, as indicated by occasional finds of late Starčevo pottery. This potential brief occupation was followed by the Vinča culture occupation, which ended around the mid 5th millennium BC. By the end of the 4th millennium BC a section of this site was briefly re-occupied by the Late Chalcolithic Kostolac culture but this is limited to a single intrusion in a zone avoided in this study (Borić 2009, 208).

Animal bones from Belovode have recently provided nine AMS radiocarbon dates, which confirmed the expected Vinča culture dating (Borić 2009; Gläser 1996). The probability distribution for the beginning of the Vinča occupation indicates a date of *c*5350 BC, while the end of the Vinča culture use of the site is *c*4650 BC. Of particular significance here is the dating of the earliest stratigraphic evidence for the extractive metallurgy in Belovode, which starts around 5000 BC; this is currently the earliest secure date for copper metal production anywhere (Radivojević *et al* 2010).

As already mentioned, it coincides with the intensive mining activities in Rudna Glava, at around *c*5000 BC (Borić 2009, 206). However, Rudna Glava does not appear to have been exploited by the inhabitants of Belovode as another copper source discovered in Ždrelo, *c*10km away from Belovode, makes the most likely candidate according to lead isotope analysis (Radivojević *et al* 2010, 2781, Figure 10). Nine Vinča culture settlements have been found in the area around

Figure 3: Finds from Belovode. a) Typical black and green minerals, b) slag 134, c) slagged sherd 31b. Image widths 45, 11 and 60mm respectively.

Belovode prompting scholars to propose their association with the mining and metallurgical activities in eastern Serbia (Šljivar and Jacanović 1996b), although this remains to be explored in future research.

Copper mineral use

Malachite beads, pendants and lumps of copper minerals appear from the earliest occupation of Belovode, and continue throughout all building horizons. The highest concentrations are usually found mixed with ash and pieces of charcoal. Other contexts include house floors, storage jars, ceramic sherds (malachite adhering to them), or workshops within a household. Two such areas in Trenches 12 and 13 together yielded *c*2.5kg of copper minerals in all the building horizons, almost one third of the total weight of malachite discovered at this site.

Four samples from the copper minerals group have been selected for this study; one comes from the 'metallurgical' Trench 3, while the rest are from various household contexts (Table 1; Fig 3a). The small size of these minerals (*c*10-30mm) may imply that they were beneficiated. Two stone mallets with a groove in the middle discovered in the context of workshops in Trenches 1 and 7 (Šljivar *et al* 2012, 259, plate I/4) offer clues to the tools used for this process. Similar tools may also have been used for mining by analogy with similar finds from Rudna Glava (cf Jovanović 1982).

Installations/slagged sherds

Charred surfaces with malachite (copper mineral) powder adhering to fragmented ceramic sherds and grooved stone mallets are common in household contexts in Belovode. There are also a few small conical pottery vessels of coarse fabric from Trenches 7 and 8 (Vinča B1 horizon) which had green minerals attached to their outer surfaces; however, technological analyses have shown that these were not crucibles (Radivojević 2007).

Two shallow pits rimmed with ceramic sherds and a burnt layer of clay from Trenches 10 and 13 (a Vinča B1 building horizon) are identified as furnaces by the excavator, based on comparison with similar small-sized hearths discovered in the region in the late fifth millennium BC (Šljivar *et al* 2006, 253, 260, plate II/4; Dimitrov 2002). Elongated cylindrical ceramic forms (so-called 'chimneys') with a diameter of about 200mm and a reconstructed height of up to 800mm, open at both ends, have been tentatively linked to these rimmed pits and thus the smelting operation (Šljivar 2006; Šljivar *et al* 2006, 253). Nevertheless, neither of these chimneys showed convincing traces of use in the smelting process (Radivojević *et al* 2010, 2779).

Smelting activities in the site of Belovode are only represented by eight individual copper slag samples and four slagged ceramic sherds from Trench 3, all of which demonstrated sustained smelting activities at the outskirts of this site (Table 1). These materials were usually discovered in areas filled with ash, charcoal, charred wood or stone constructions and mainly represent an outdoor activity. Another metallurgical area was recovered in Trench 9; both are presented in more detail below.

Trench 3 (8m x 2m) yielded evidence for copper smelting activities throughout the final, D horizon of occupation of Belovode, which coincides with the entire Gradac Phase starting at *c*5000 BC (Radivojević *et al* 2010). This phase of the Vinča culture is known to last longer in the Morava Valley settlements than in those situated nearer to the Danube (Jovanović 1994), and at this site most likely covers the entire late Vinča culture sequence, dated at *c*5000-4650 BC (Jacanović and Šljivar 1995). The Belovode D horizon, represented in this Trench by materials from a waste pit (Šljivar and Jacanović 1996a), includes all finds coming from spits 1-11, and amongst others various archaeometallurgical debris (slags only from spit 7). Thousands of ceramic finds were unearthed in this horizon alone, many of which are diagnostic for the Gradac Phase in general (Arsenijević and Živković 1998; see also Schier 1996; Schier 2000).

The eight free slag pieces collected from this trench are vitreous, strongly magnetic green-stained droplets, not exceeding 10mm in size (*eg* Fig 3b). They appear to have been highly viscous and very rich in copper metal, but with no signs of crushing in pursuit of copper metal prills. This may have been due to their small size and weight, since all samples in total weigh below 10g. Given that these slag pieces resemble (green) malachite as a result of the corrosion of the copper metal prills entrapped in them, it is possible that the green colour facilitated their recognition in the excavations, leading to a recovery biased in favour of more copper-rich pieces and overlooking those without green staining (cf Radivojević *et al* 2010, 2779).

The green staining on four fragmentary slagged sherds comes from the contact of these samples with metallurgical slag. The slagged mass is next to heavily vitrified areas, which appear along the edges of studied samples (Fig 3c) but also extend across their cross-sections. The latter implies that these sherds were most likely used as fragments during the metallurgical process. Samples 30a and 30c are two body sherds of similar thickness, *c*15mm, and not exceeding 20mm in the longest section, possibly belonging to the same ceramic vessel. This probably applies to a flat body sherd (Belovode 31a) and a vessel rim (Belovode 31b), which were discovered together. Both samples (31a/31b) are heavily vitrified and topped with a grey mass which contains small green-stained droplets. It is noteworthy that they have an almost triangular shape, with the longest section bloated from contact with temperatures higher than the initial clay firing.

A copper metal droplet was found stratigraphically beneath the slag samples (M6; Table 1) and represents one of two copper metal pieces from the site. All metallurgy-related materials were discovered sealed by a collapsed building, with the remains of daub, domestic pottery and animal bones. Notably, in spit 10, which belongs to this building horizon, two shallow rock-lined constructions, indicated as fireplaces, were potentially linked with metallurgical debris in the excavation records. The stratigraphic evidence related to the earliest slag piece is dated to *c*5000 BC; the smelting evidence, according to the excavation reports (Radivojević and Kuzmanović-Cvetković forthcoming), continues until the abandonment of the site, at *c*4650 BC.

Pyrometallurgical activities are also recorded in Trench 9 (5m x 5m) (Jacanović and Šljivar 2003). The use of copper minerals occurs regularly throughout this trench (except in the Belovode D horizon). Of particular interest here is spit 11, which yielded a copper metal droplet (M14), already published in Radivojević *et al* (2010). It was discovered in the context of regular appearance of ceramic pedestal bowls, typical of the Vinča A to Gradac Phase. Chronologically and in relative stratigraphic terms, this droplet is possibly contemporary with the start of metallurgical activities in Trench 3.

An unusually large round slag cake was unearthed in spit 18 (Belovode 40, Table 1), and is argued as firmly stratified within the Vinča B1 phase (Šljivar *et al* 2012, 33-34, plate VIII/1). Preliminary analyses conducted by the author of this paper revealed that this piece has significant concentrations of lead, which may suggest production of this metal; however, future analysis is expected to shed more light on this unusual archaeometallurgical evidence and will be addressed elsewhere. In terms of absolute dating, the metal droplet (M14) could be dated at *c*5000 BC, while the slag cake (Belovode 40) may be ascribed the date of *c*5200 BC.

Copper mineral and copper metal artefacts

Malachite beads occur throughout all horizons in Belovode and vary in size, from 4-15mm in diameter, with an exceptional piece, a deltoid pendant with perforation, found in Trench 1 (Vinča A1 horizon; Šljivar et al 2006, plate II/1). Malachite beads occur as whole artefacts or fragmented, implying the potential presence of a bead workshop at this site. The analysis of these artefacts will be addressed in detail in a separate publication.

Besides copper metal droplets M6 and M14 (Table 1), two copper artefacts have been identified as belonging to the Vinča culture occupation of Belovode, a copper chisel and a bun-shaped metal ingot (Šljivar et al 2006, 252, 269, plate I/1, 2). Since these were found in the vicinity of the site, they could belong to the Late Chalcolithic occupation, as already indicated by the late 4th millennium BC dates from the top horizon in a defined area of this settlement (Borić 2009, 208).

Materials and methods

Twelve samples have been selected for this study (Table 1). Of these, eight are metal production evidence and the rest are copper minerals. All the copper minerals studied here are recognised as archaeological since they originate from archaeological sites (not geological minerals that come from mines). Although the bead minerals and ores in this study are both typically malachite, the rationale for a distinction between them has been developed in the previous study on material from

Belovode (Radivojević *et al* 2010) and refers to their different technological treatment. In comparison with the amount of technological debris (and slags in particular) in later prehistoric periods, the sample size in this study appears small by any standard. However, it targets the crucial period for the evolution of metallurgy in Europe, and as a coherent assemblage is unprecedented in size and quality.

Analytical work was conducted at the Wolfson Archaeological Science Laboratories at the UCL Institute of Archaeology, London, for their composition and microstructure (see Table 1). The samples were cut to size where necessary, mounted in epoxy resin discs, ground using abrasive discs (1200 and 2400 grit) and polished using diamond pastes (1μm and ¼μm). They were examined by reflected light microscopy (OM, Leica DMLM and Olympus BX60) prior to scanning electron microscopy with energy dispersive spectrometry (SEM-EDS; Philips XL30ESEM, Superprobe JEOL-JXA-8600) and electron probe micro analysis (EPMA; Superprobe JEOL-JXA-8100). Both SEM-EDS and EPMA used an accelerating voltage of 20kV, with average dead-time of 35-40% and working distance of 10mm. All data are presented as normalized weight percent, with oxygen calculated by stoichiometry, if not otherwise stated. The total iron content is presented as FeO, regardless of real valency. The elements checked by EPMA were Se, Zn, Cu, Fe, As, Ag, Cl, Te, S, Au, Sn, Bi, Co, Sb, Ni, Mn, and Pb. Data from EPMA are presented as measured (*ie* not normalised) as wt% and ppm, with trusted values established at ≥10ppm.

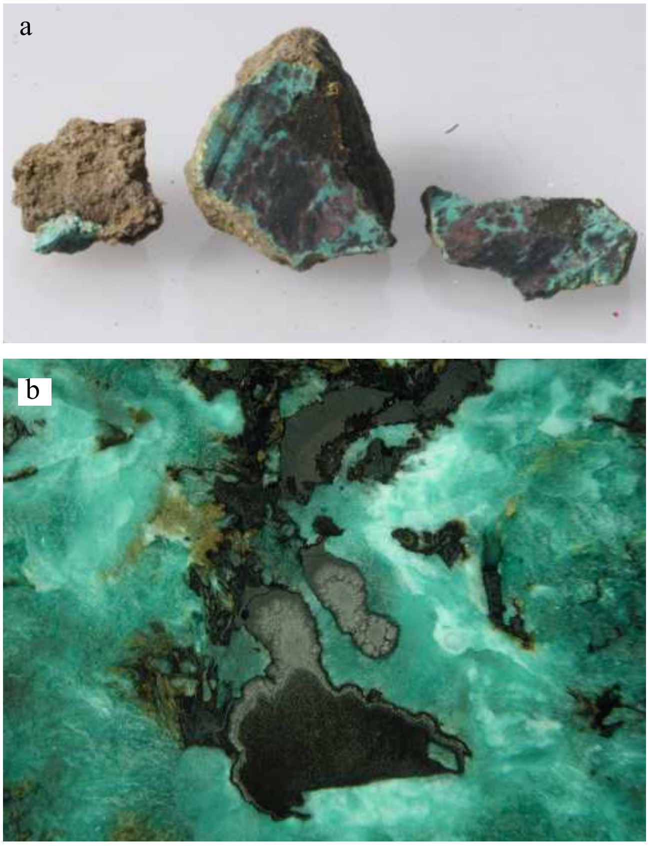

Figure 4: a) copper mineral 3; b) copper mineral M10 under cross-polarised light. Note the two phases: bright green and dark/grey oolithic. Image widths 50 and 3.2mm respectively.

Results

The early metal smiths in Belovode needed to possess two distinctive skills: to correctly identify and acquire appropriate copper minerals for smelting, and to master the control over redox conditions during the extraction process.

Minerals

Compositional analyses of the copper minerals reveal two distinctive groups within the studied assemblage, oxidic (34a, M10) and sulphidic (3, 33b) minerals. The oxidic minerals contain two phases: bright green crystals and dark oolithic structures (Figs 3a, 4b); while the former is mainly based on copper oxide and most likely represents copper carbonate, the latter exhibits a more complex chemical structure (Table 2). Both M10 and 34a contain significant levels of MnO (56.5wt% and 25.7wt% respectively), as well as copper oxide in different concentrations; the main difference is in the presence of PbO in M10.

The sulphidic minerals (3 and 33b; Fig 4a) appear more solid than the green-and-black oxidic minerals, although they too have distinctively-coloured cross-sections in shades of green and grey with metallic lustre. Both samples are composed of a light grey 'blocky' phase surrounded by grey drossy areas and a dark grey spongy matrix, which appears red and green under cross-polarised light (Fig 5). In this study the drossy areas refer to copper oxide-based phases with varying Cu:O ratios, and include a wide range of newly formed, residual and post depositional formations. All the drossy areas in these samples are therefore copper-oxide-based, while light grey 'blocky' crystals in Belovode 3 and 33b are compositionally closest to covellite (CuS) (Table 3).
Both oxidic and sulphidic minerals present a common feature: their colour is distinctively black/dark and

Table 2: SEM-EDS data for oolithic structures in copper minerals (wt%).

	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	MnO	FeO	CuO	ZnO	PbO
M10	0.0	1.8	3.3	0.6	0.3	56.5	1.7	9.4	1.5	24.7
34a	0.5	8.5	6.2	1.3	0.7	25.7	0.7	55.9	0.6	0.0

Note: All values are averages of 2-13 analyses.

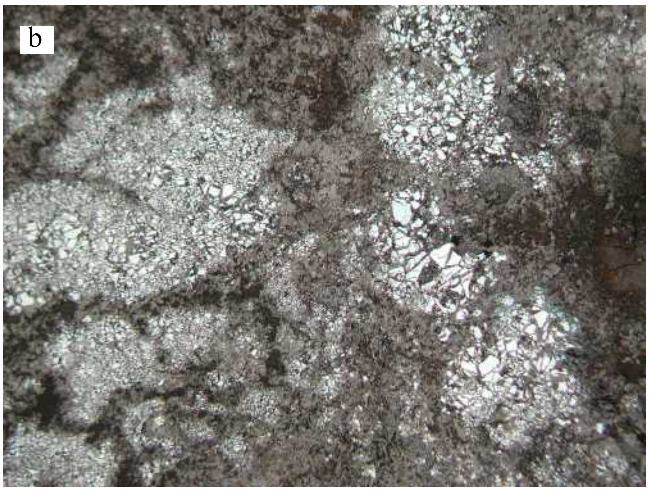

Figure 5: Copper minerals: a) 3, plane-polarised light, image width 0.85mm; b) 33b, plane-polarised light, image width 3.2mm. Note the similarity in phases with light grey 'blocky' crystals surrounded by grey drossy areas and dark grey spongy matrix.

green, which could be an intentional colour choice of the Belovode occupants. Significantly, the only other group of minerals that can be found on this site are pure green minerals (malachite), which were used only for bead making (cf Radivojević *et al* 2010, 2780ff). Although the geological environment of eastern Serbia contains more than one kind of copper mineral (Janković 1997), the choice of the Belovode craftsmen seems to have been restricted to pure green or black/dark and green minerals.

Table 3: SEM-EDS data for optically drossy grey and 'blocky' light grey phases in copper minerals (at%).

		O	S	Mn	Fe	Cu	Zn
3	grey phase O 75/Cu 25	77.6	0.3	0.0	0.0	22.0	0.1
3	grey phase O 65/Cu 35	63.7	0.1	0.0	0.0	36.1	0.0
3	grey phase O 45/Cu 55	45.1	0.0	0.0	0.0	54.7	0.0
3	covellite	1.1	41.5	0.0	0.0	57.4	0.0
33b	grey phase O 75/Cu 25	77.0	0.4	0.0	0.1	22.0	0.5
33b	covellite	1.0	41.5	0.0	0.0	57.5	0.0

Note: All values are averages of 3-12 analyses.

Production evidence

The so-called metallurgical Trench (No 3) yielded a total of thirteen samples indicating copper smelting activities, five of which have been analysed previously and published (Radivojević *et al* 2010) (Table 1). The samples presented here include four slagged ceramic sherds and three free slag samples, all of which were discovered scattered across three archaeological spits (5-7, each *c*100 mm thick), with no clear physical connection recorded in the excavation records, except for the slagged sherds Belovode 30a/c and 31a/b (Radivojević and Kuzmanović-Cvetković forthcoming). Significantly, given that the outer appearance of these slags resembles copper minerals due to the corrosion of the copper metal entrapped in them, the main feature leading to the recognition of slag during the Belovode field campaigns was its distinctive colour. Thus one could assume that more slag samples may have gone unnoticed in the dark brown soil in the field (Radivojević *et al* 2010, 2779).

All slag-based samples appear very heterogeneous under the microscope with dross areas (copper-oxide-based phases) dominating the microstructure. Other major phases are metal prills, spinels and delafossite, all of which are embedded in a glassy matrix.

Slagged sherds

Judging by the field evidence, the Belovode slagged sherds (30a/c, 31a/b) were used as fragmented pieces of ceramics in the same metallurgical process (Fig 3c). Bulk chemical analyses of the ceramic bodies indicated the use of similar clays for all samples (Table 4). The consistent ratio of silica to alumina (approx 4:1) and similar values for iron oxide, potash, lime and manganese suggest a common origin for the clay. Nevertheless, the variations in composition imply that 30a and 30c could be part of one vessel, and 31a and 31b fragments of another. The contamination with copper (up to 0.4wt%) and manganese (0.1wt%) oxides in the bloated and vitrified areas points towards their utilisation in metallurgical activities.

The ceramic fabric of 30a/c and 31a/b is optically dark grey, well kneaded and tempered with abundant fine-grained quartz grains and crushed calcite, amounting to around 50vol% (Fig 6). The orientation of clay minerals is parallel to the surfaces; the pores tend to be elongated, indicating a low firing temperature of the vessel. The dense paste looks 'dry', with little indication of potential collapse. Most of the quartz grains closer to the area of intense vitrification have lost their angularity and decomposed; this is accompanied by coarse bloating pores. Optical microscopy and SEM-EDS analyses revealed

Table 4: SEM-EDS data for ceramic bodies of slagged sherds (normalised wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO
30a	0.9	1.9	15.9	63.0	0.2	3.3	2.4	1.0	0.0	11.3	0.0	0.0	0.0	0.0
30c	1.0	1.6	16.0	65.0	0.8	3.6	2.0	0.8	0.0	9.2	0.0	0.0	0.0	0.0
31a	1.5	1.5	15.8	65.4	0.4	3.7	1.8	0.7	0.1	8.8	0.0	0.0	0.4	0.0
31b	1.1	1.4	14.7	67.7	1.4	3.6	2.0	0.8	0.1	7.0	0.0	0.0	0.0	0.0

Note: All values are averages of 5-18 analyses.

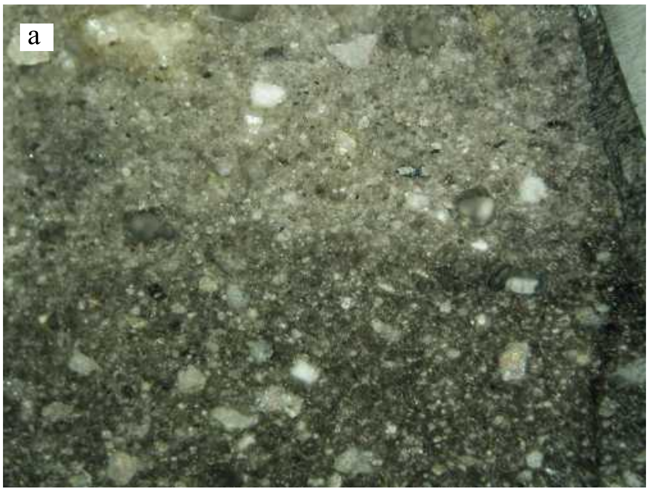

Figure 6: Ceramic bodies of slagged sherds: a) 30a, cross-polarised light, image width 3.2mm; b) 31b, cross-polarised light. Note crushed quartz grains and calcite, image width 3.2mm.

an extremely heterogeneous structure of slag and copper-rich materials in 30a, 30c, 31a and 31b. All samples are dominated by copper oxide and copper metal prills with the main components of the slag matrix being copper 'dross', delafossite, iron-rich spinels, leucite and the pyroxene group phase, all present to different extents throughout the samples and embedded in a glassy matrix. The bulk chemical analyses of the glassy matrix were conducted in areas relatively free of copper-based components, with the aim of understanding its genesis (Table 5). The chemistry of the green-stained and bloated outer surface of all the slagged sherds revealed significant contamination with fuel ash (elevated readings of P_2O_5 and MgO) and copper (with relevant levels of ZnO and MnO), clearly different from the bulk ceramic composition

These data correlate well with the already published slag samples from Belovode, which include significant quantities of MnO and ZnO, and to an extent FeO (Radivojević *et al* 2010, 2782, table 1). Thus, these elements, and in particular manganese and zinc oxides, define the 'metallurgical' slag within the Vinča culture context. In Table 5 the values of MnO, ZnO and FeO vary, with the highest being for Belovode 31b. Furthermore, the silica to alumina ratio in this sample (*c*7:1) stands out from values for other slagged sherds, which at *c*4:1 are closer to the ceramic composition (cf Table 4). This implies that sample 31b was closer than the other sherds to the metallurgical slag formation in a process that took place in Trench 3. However, the combination of the silica to alumina ratio of the ceramic body and the fuel ash and ore impurities still describe samples 30a, 30c and 31a as vitrified ceramics fused with elements of metallurgical slag. It appears that not all samples were exposed to this metallurgical process with the same intensity. This is illustrated by various levels of MnO and ZnO in all glassy matrices, which – particularly in Belovode 31b – are detected in higher concentrations than in slag matrices in other slagged sherd samples, thus indicating the composition of gangue minerals in the exploited ore body (Table 5).

In order to explore the origin of the iron in the slag matrix, *ie* whether or not it comes from the ceramic, iron oxide values are plotted together with likely ore contamination oxides MnO and ZnO (Fig 7). This figure shows two data clusters: ellipse 1 contains points with higher FeO values (average 11.4wt%, sd 4.8) and less MnO and ZnO while ellipse 2 has higher MnO and ZnO levels and less FeO (average 8.5wt%, sd 3.1) . While the first cluster indicates slag matrix areas with dominant FeO content similar to that in the ceramic body (Table 4) and low or zero values of MnO and ZnO, the second seems indicative of the chemical composition of gangue minerals in an ore body used for smelting here. Although measurements in the glassy matrix of 31b appear to indicate the dominance of the ore signature (ellipse 2),

Table 5: SEM-EDS data for the glassy slag matrix of slagged sherds (normalised wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O5	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO
30a	0.0	2.9	8.9	38.5	1.4	3.9	23.0	0.6	1.1	6.4	0.0	0.0	13.2	0.1
sd 30a	*0*	*1.3*	*2.4*	*2.1*	*1.5*	*2.2*	*4.3*	*0.3*	*0.7*	*2.3*	*0.0*	*0.0*	*5.3*	*0.3*
30c	0.0	2.5	9.8	40.1	1.7	3.6	12.5	0.5	2.0	5.6	0.1	0.0	21.2	0.4
sd 30c	*0*	*1.0*	*2.8*	*4.2*	*1.6*	*1.3*	*7.9*	*0.3*	*1.0*	*2.5*	*0.2*	*0.0*	*7.3*	*0.3*
31a	1.8	1.7	16.3	50.1	1.4	3.0	7.9	0.7	0.4	7.5	0.0	0.0	9.0	0.1
sd 31a	*1.3*	*1.1*	*5.6*	*6.2*	*1.9*	*1.5*	*4.7*	*0.5*	*0.8*	*3.3*	*0.1*	*0.0*	*8.2*	*0.2*
31b	0.8	1.6	6.0	40.4	3.9	1.8	15.0	0.3	8.4	12.7	0.5	0.0	7.3	1.4
sd 31b	*0.6*	*0.8*	*2.6*	*7.4*	*1.6*	*1.2*	*6.5*	*0.3*	*5.2*	*4.4*	*0.4*	*0.0*	*14.2*	*0.9*
Ceramics	1.1	1.6	15.6	65.3	0.7	3.6	2.1	0.8	0.0	9.1	0.0	0.0	0.0	0.0
sd	*0.3*	*0.2*	*0.6*	*1.9*	*0.5*	*0.2*	*0.2*	*0.1*	*0.0*	*1.8*	*0.0*	*0.0*	*0.0*	*0.0*

Notes: All values are averages and standard deviations of 7-49 analyses of each sample.
The ceramics values are averages of the data in Table 4.

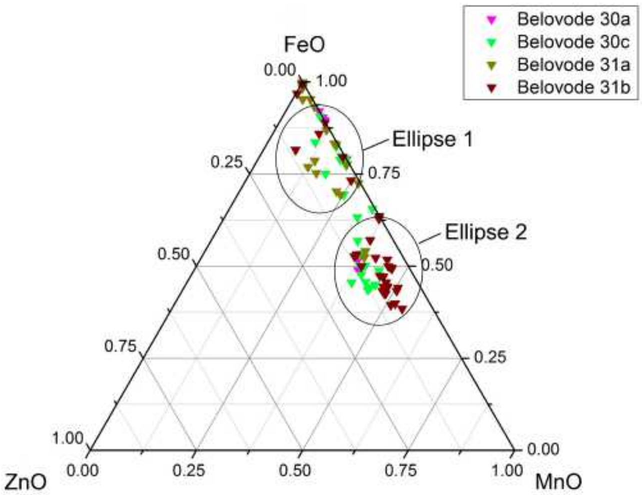

Figure 7: Ternary plot of MnO-FeO-ZnO for the slag matrices of 30a, 30c, 31a and 31b.

the clustering of data from all other samples (30a, 30c, 31a) within this group indicates that some areas within them contain metallurgical slag as well. These results reinforce the assumption of a twofold origin of iron in the glassy matrix, namely from both vitrified ceramic and the ore. It is noteworthy that areas of all four slagged sherds fall into both ellipses (although MnO and ZnO levels are variable), so could indicate the presence of different ore batches in the smelt, leading to a poorly homogenised slag matrix.

In order to test the origin of MnO in relation to the plausible fuel contamination of the slag, the composition of Mn-rich beech ash has been plotted with the slag matrix data for the slagged sherds (Fig 8). This figure does not indicate the inclusion of Mn-rich ashes in the smelt, hence potentially implying that the strong correlation of lime and MnO in the slag matrix could have originated instead from gangue minerals in an ore body. This is well illustrated on the MnO-CaO axis, where values plot away from the plausible fuel ash composition. Thus, this strong signature with dominant manganese and lime content further suggests the type of ores used for making metal at Belovode and also indicates that the primary production of metal was a main activity. Also, given the extent of the metallurgical slag presence in these sherds, defined by the significant intake of manganese and zinc oxides and elevated readings of iron oxides (Radivojević *et al* 2010, 2782, table 1), it appears that not all samples were exposed to this process with the same intensity.

Copper-rich phases in the slagged sherds

As mentioned above, copper oxides are the most common phase in the glass matrix in all four samples, varying from cuprite and tenorite to copper corrosion products (Fig 9). Iron spinels are recognised as characteristic grey cubic crystals embedded in a glassy matrix, corresponding to the general formula $A^{2+}B_2^{3+}O_4^{2-}$. In both 31a and 31b, these newly formed phases are found intergrown

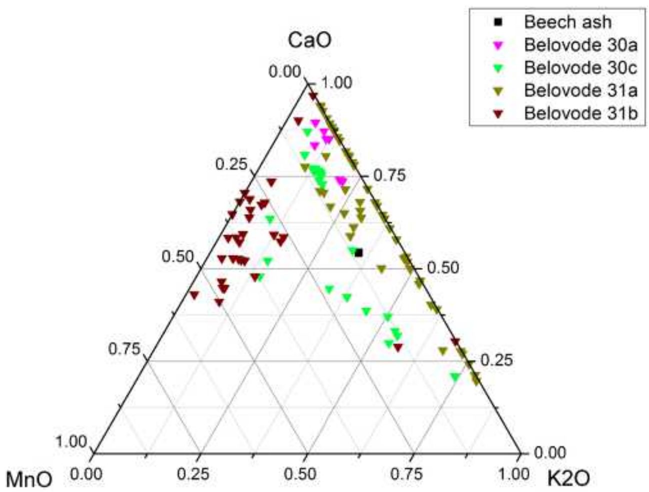

Figure 8: Ternary plot of K_2O-CaO-MnO for the slag matrices of 30a, 30c, 31a, 31b. Beech ash data from Jackson and Smedley 2004, table 4.

Table 6: SEM-EDS data for delafossite in slagged sherds (at%).

	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	O
30a	0.0	0.8	5.3	2.8	0.0	1.5	0.5	0.6	13.9	0.1	0.1	21.3	0.1	52.9
30c	0.1	0.6	1.1	0.2	0.0	0.2	0.8	1.8	22.9	0.2	0.0	23.3	0.0	48.7
31b	0.6	1.9	4.1	0.3	0.2	1.9	0.2	3.8	17.3	0.2	0.0	18.5	0.0	50.8

Note: All values are averages of four to eleven analyses.

with convoluted agglomerations of cuprite (Fig 10a). Belovode 31b contains magnetite with significant Mn, Zn and Co contents, similar to the composition of the mineral franklinite, $(Fe,Mn,Zn)(Fe,Mn)_2O_4$.

Delafossite, $Cu^{1+}Fe^{3+}O_2$, is usually recognised optically as straight laths embedded in the glassy matrix (Table 6; Fig 10b). In nature, this mineral usually forms near the base of the oxidised zone of copper deposits, however it is less commonly found as a primary mineral. The association of delafossite and cuprite in the slag usually indicates fairly oxidising conditions in the melt, around the partial oxygen pressure required to reduce copper from cuprite (Müller *et al* 2004, 40). The debate on

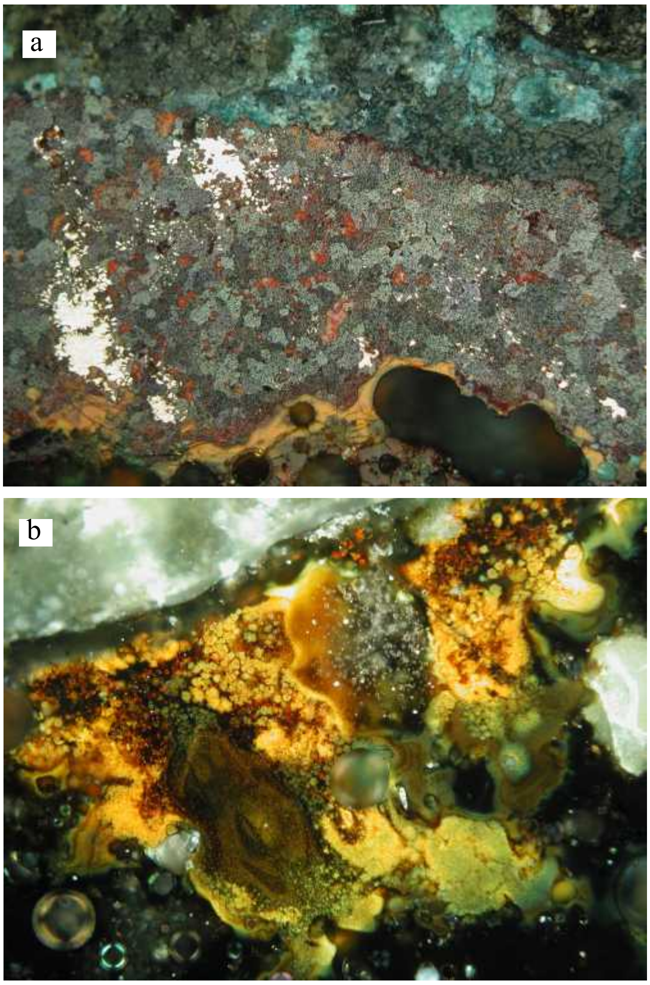

Figure 9: a) copper metal (bright) surrounded by copper-oxides with variable Cu:O ratios in slagged sherd 30a, cross-polarised light, image width 3.2mm; b) copper-rich area (yellow) in slagged sherd 31a, cross-polarised light, image width 0.85mm.

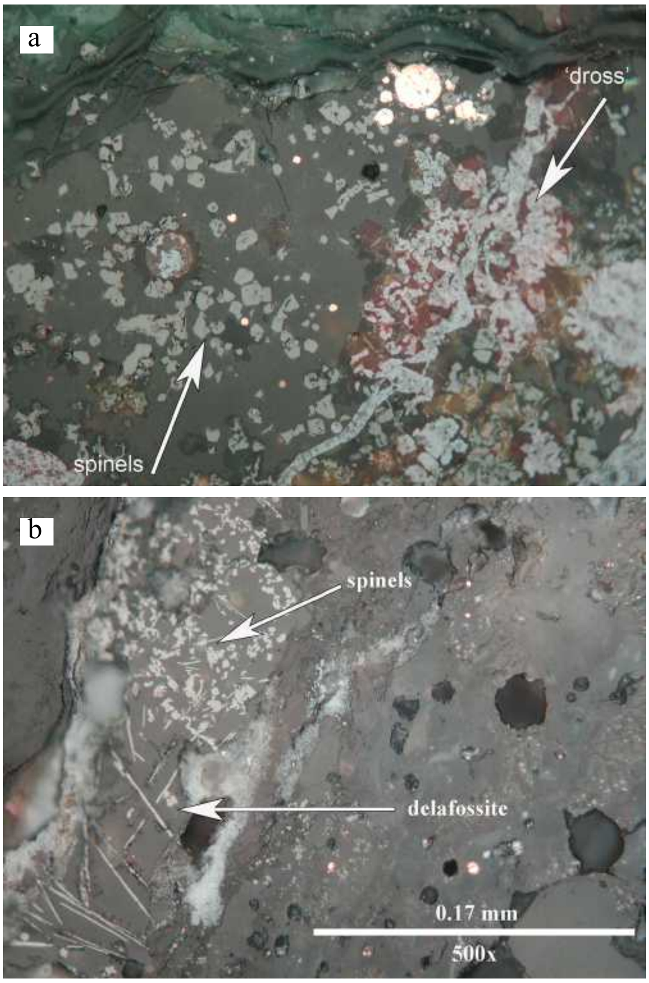

Figure 10: Glassy matrix of slagged sherd 31b: a) iron spinels (grey cubic crystals) and dross, plane-polarised light; b) delafossite and magnetite, plane-polarised light; image widths both 0.34mm.

whether the presence of delafossite represents evidence of either melting or smelting has yielded a substantial body of evidence in support of both arguments (for melting see Bachmann1982, 16; and for smelting Hauptmann *et al* 1993, 566; Hauptmann 2000, 147); these will be discussed in more detail below. Silicates are optically visible in Belovode 31b as polyhedral crystals within the glassy matrix, with forms ranging from platy crystals to dendrites. Two distinct phases formed from the glassy matrix of 31b (Fig 11), leucite ($KAlSi_2O_6$) and a phase from the pyroxene group, close to the composition of hedenbergite ($CaFeSi_2O_6$).

The conditions of this smelt were moderately reducing,

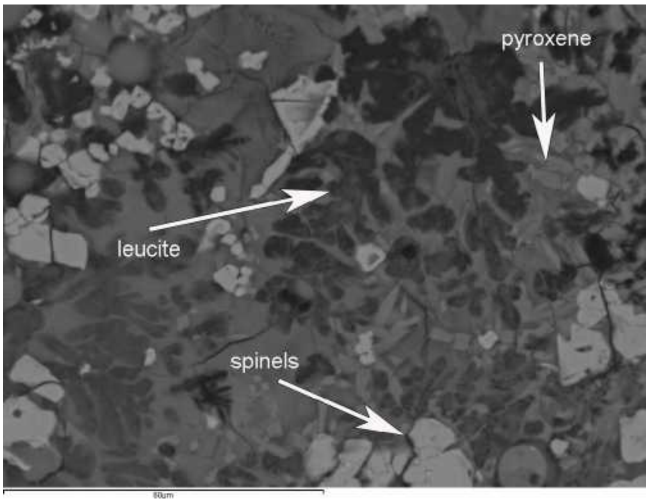

Figure 11: BSE image of platy pyroxene, leucite and iron spinels in glassy matrix of 31b, image width 120µm.

an aspect which is determined by the valency of the newly-formed copper and iron phases in the glassy matrices of slagged sherds, cuprite (Cu_2O) and delafossite ($CuFeO_2$). The formation of spinels with significant levels of manganese, cobalt, nickel and zinc strengthens the argument for copper smelting, but is also further indicative of the composition of gangue minerals in the smelted ores.

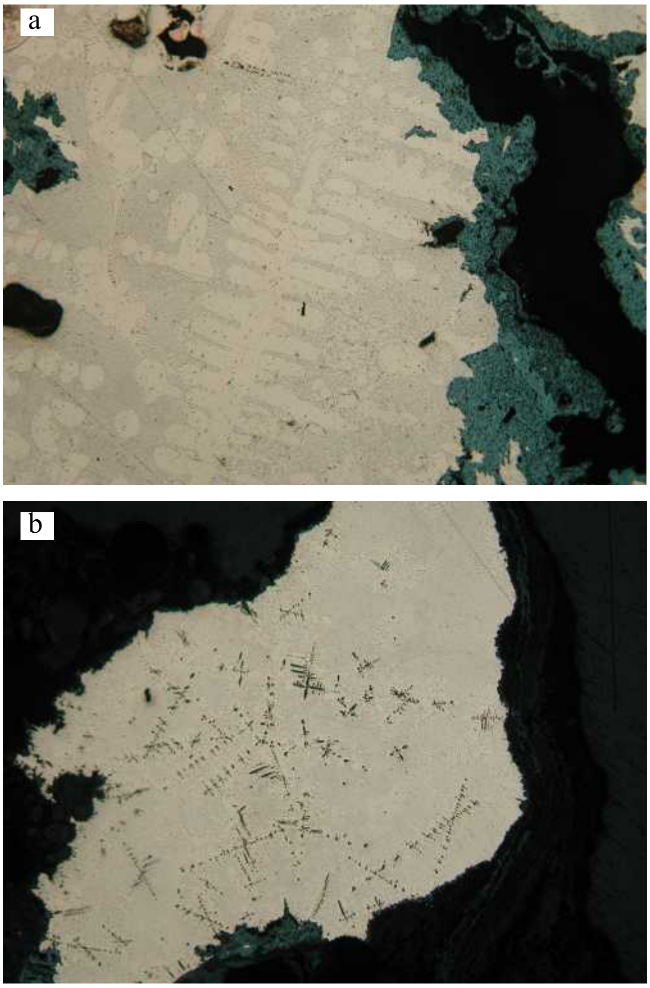

Figure 12: Copper metal in slagged sherds: a) 31b, plane-polarised light, image width 1.6mm; b) 31a, plane-polarised light, image width 3.2mm.

Copper metal in the slagged sherds

The copper metal phase in 30a, 31a and 31b solidified from a fully molten state, demonstrated by the as-cast structure (Fig 12). In 30a and 31b, large alpha copper grains are fully formed in the ($Cu+Cu_2O$) eutectic, indicating gradual cooling prior to their crystallisation (Fig 12a). In comparison with the developed dendrites (α phase) in 31b, the smaller size of dendritic structures in Belovode 31a might indicate a faster cooling rate in this sample (Fig 12b). In metallic areas, the α copper grains take up to 50vol%, implying that the melt had about half the eutectic amount of oxygen, *c*0.22wt% (Fig 13). This is significant for the working temperature of the system, where such an oxygen content indicates a working temperature of *c*1075°C (cf Neumann *et al* 1984).

EPMA examination of pure copper metal phases in the slag matrices of 30a, 31a and 31b yielded an interesting trace element pattern (Table 7). Particularly noteworthy are iron readings, established as significant only above the 10ppm level: concentrations of metallic iron vary from 16 to 36ppm in 30a and 31b, while in 31a it is detected only in a single measurement (16ppm) and hence is not a reliable value. The same is true for the manganese content in 31b, which appears as a single measurement at 17 ppm. However, more significant manganese readings are detected in 31a (17 and 27ppm), though not paired with iron, thus potentially suggesting different origins for their presence in the copper metal

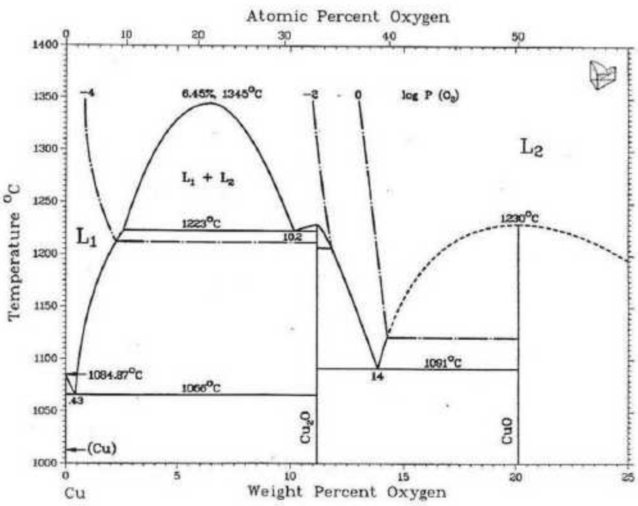

Figure 13: Phase diagram for Cu-O. Note the eutectic at 1066°C, 0.43wt% oxygen, a reference point for estimating the temperature of smelting in slagged sherds 30a, 31a and 31b; after Neumann et al 1984.

Table 7: EPMA data for copper prills in the slag matrices (selected significant trace element values in ppm).

	S	Mn	Fe	Ni	Zn	As	Sn	Au	Bi
Belovode 30a	bdl	bdl	16	70	bdl	bdl	bdl	200	bdl
	bdl	bdl	16	50	bdl	55	bdl	bdl	bdl
	bdl	bdl	bdl	80	bdl	55	bdl	bdl	bdl
	bdl	bdl	bdl	90	bdl	45	bdl	bdl	bdl
	bdl	bdl	bdl	50	bdl	25	bdl	bdl	bdl
	12	bdl	16	80	bdl	bdl	70	bdl	bdl
	12	bdl	16	90	bdl	bdl	bdl	32	bdl
	bdl	bdl	16	50	bdl	bdl	bdl	bdl	bdl
	bdl	bdl	bdl	70	bdl	55	bdl	bdl	bdl
	12	bdl	26	50	bdl	bdl	bdl	bdl	bdl
Belovode 31a	12	27	bdl	50	bdl	93	bdl	bdl	bdl
	12	bdl	bdl	50	bdl	bdl	bdl	bdl	20
	bdl	bdl	bdl	40	bdl	bdl	bdl	bdl	30
	bdl	bdl	bdl	50	bdl	23	bdl	bdl	bdl
	12	17	bdl	60	bdl	bdl	bdl	bdl	50
	12	17	bdl	40	bdl	bdl	20	160	bdl
	bdl	bdl	bdl	70	bdl	bdl	bdl	120	40
	12	bdl	16	60	bdl	bdl	bdl	150	30
	22	17	bdl	100	bdl	bdl	bdl	360	bdl
Belovode 31b	20	bdl	16	70	bdl	bdl	bdl	bdl	bdl
	20	bdl	16	70	bdl	bdl	bdl	bdl	bdl
	12	bdl	26	70	bdl	bdl	30	50	bdl
	30	bdl	26	80	bdl	bdl	bdl	50	20
	12	17	bdl	70	bdl	bdl	bdl	110	bdl
	40	bdl	16	70	bdl	bdl	bdl	270	bdl
	12	bdl	bdl	70	bdl	85	bdl	20	bdl
	12	bdl	36	60	bdl	bdl	bdl	70	bdl
	30	bdl	16	80	bdl	bdl	20	230	bdl
	20	bdl	bdl	90	bdl	bdl	40	140	30
	20	bdl	16	60	bdl	bdl	50	340	40

Note: Reliable values established as >10ppm, all others indicated as below detection limit (bdl).

phase. Measurable iron contents appear regularly in ancient copper (Tylecote *et al* 1977, 309; Craddock and Meeks 1987), while the manganese could have originated from the Mn-rich flux used in the smelting process (Tylecote *et al* 1977, 313- 314, table 7) or have been detected in the area immediately surrounding the copper, due to the effective analytical volume excited by the electron beam. The presence of metallic iron in pure copper phases has significant implications for the understanding of the slagging process, as well as of the redox conditions during the melt, see below.

It is worth mentioning that the EPMA revealed significant nickel, 60-70ppm on average throughout 30a, 31a and 31b, paired with consistent gold levels, *c*200ppm on average, and sulphur, which is present in the highest concentrations in 31b (up to *c*40ppm). Some arsenic and tin are present in a few readings in all samples, as well as bismuth, which goes up to *c*50 ppm in 31a. The absence of zinc in the copper metal phase is notable, and it seems that all the zinc from the ores dissolved in the slag matrix, with the highest readings in 31b, at 1.4wt% on average (see Table 5). The opposite is true for nickel, which is known from experiments to contribute to the pattern of copper metal impurities (Tylecote *et al* 1977, 323).

Free slag samples

Microstructural and compositional analyses of the three free slag samples (Belovode 131, 134 and 136) revealed an exceptionally heterogeneous composition of slag matrices and newly developed phases within them. These samples consist essentially of copper 'dross', iron spinels, leucite and fayalite crystals (Belovode 131 only), all embedded and relatively evenly distributed throughout a glassy matrix.

The bulk slag composition, which includes all present phases, shows that major oxides (silica, alumina, iron and copper oxides) add up to *c*77wt% on average (Table 8). These are followed by lime, potash, magnesia and phosphorus oxide at *c*15wt% average sum, with phosphorus and lime contents, in particular in samples 131 and 136, contrasting with the Belovode ceramic compositions. The elements unlikely to come from the ceramic body (MnO, ZnO and CoO) add up to another *c*7wt% average sum, with all three highest in Belovode 136. The bulk slag composition of all three samples is clearly not a product of a fused ceramic body, see below. In all three samples the glassy slag matrix contains elevated copper levels and significant amounts of iron, manganese and zinc, clearly different from the average

Table 8: SEM-EDS data for bulk analyses of free slags in areas of c100x100µm (normalised wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO
131	0.1	1.2	10.0	54.5	4.6	0.0	2.5	8.8	0.5	2.8	8.8	0.2	0.0	5.6	0.5
134	0.0	1.0	8.3	38.0	2.8	0.7	0.7	4.4	0.1	4.5	13.6	0.6	0.0	24.3	0.9
136	0.1	1.6	6.7	31.9	2.6	0.0	2.7	12.0	0.2	9.6	21.1	0.9	0.1	8.6	1.9
Ceramic	1.1	1.6	15.6	65.3	0.7	0.0	3.6	2.1	0.8	0.0	9.1	0.0	0.0	0.0	0.0

Notes: All values are averages of five to six analyses of each sample. The ceramics values are averages of the data in Table 4.

Table 9: SEM-EDS data for the glassy matrix of free slags (normalised wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO
131	0.1	1.7	8.9	46.8	4.3	0.0	1.7	8.6	0.4	7.1	17.0	0.2	0.0	2.6	0.6
sd 131	*0.4*	*1.6*	*2.9*	*9.0*	*1.6*	*0.0*	*1.2*	*6.4*	*0.2*	*6.8*	*9.2*	*0.2*	*0.0*	*3.9*	*0.7*
134	0.9	1.9	7.3	41.6	3.5	0.3	0.9	13.6	0.2	7.4	10.1	0.3	0.0	10.9	1.1
sd134	*0.7*	*1.0*	*1.4*	*4.7*	*0.8*	*0.5*	*0.8*	*7.7*	*0.2*	*2.7*	*4.7*	*0.3*	*0.0*	*12.0*	*0.5*
136	0.5	1.6	6.9	36.4	3.2	0.0	2.5	16.8	0.2	9.8	12.0	0.7	0.0	7.5	1.8
sd136	*0.4*	*0.4*	*0.6*	*4.3*	*0.6*	*0.0*	*1.0*	*6.2*	*0.2*	*0.4*	*7.6*	*0.3*	*0.1*	*8.0*	*0.4*
Ceramics	1.1	1.6	15.6	65.3	0.7	0.0	3.6	2.1	0.8	0.0	9.1	0.0	0.0	0.0	0.0
sd	*0.3*	*0.2*	*0.6*	*1.9*	*0.5*	*0.0*	*0.2*	*0.2*	*0.1*	*0.0*	*1.8*	*0.0*	*0.0*	*0.0*	*0.0*

Notes: All values are averages and standard deviation of 13-29 analyses. The ceramics values are averages of the data in Table 4.

ceramic composition (Table 9). These values are associated with high lime and phosphorus levels, like those observed in glassy matrices of the slagged sherds (Table 5) but they are not accompanied by increased potash or magnesia levels, which would suggest fuel ash intake. The ratio of silica to alumina in the free slag pieces is between 5:1 and 6:1 (Table 9), which is higher than the 4:1 ratio observed for the ceramic body composition of the slagged sherds (Table 4). This indicates that the glassy matrix in the free slag samples did not derive from the vitrification of a ceramic body, but represents a metallurgical slag. Nevertheless, similarly to the glassy matrices in slagged sherds, not all areas analysed in samples Belovode 131, 134 and 136 bear characteristics of metallurgical slag.

With the intention of discriminating the ore signature in samples Belovode 131, 134 and 136, CaO, MnO and K_2O values (averages presented in Table 9) are plotted in Figure 14, together with the slagged sherd data (Fig 8) and slag data from Radivojević *et al* (2010). The data clusters on the two axes, K_2O-CaO and CaO-MnO, the former (ellipse 1) associated with fuel ash and the latter (ellipse 2) with the ore signature. It is interesting to note that the majority of readings from the slagged sherds (30a, 30c, 31a) fall into the fuel ash category (ellipse 1), while the free slag pieces, along with 31b, contain a significantly higher ore signature. The presence of trace elements from the ore signature, such as Mn, Zn, Co and Ni (Table 9), strengthens the assumption that these slags represent debris from the primary copper extraction process.

All the free slag samples contain relatively large areas rich in copper 'dross': copper-rich phases varying from newly formed tenorite and cuprite to corrosion products. Distinguished by its typical bright red or orange internal reflection, cuprite is mostly present as convoluted agglomerations, like the pink or violet phases of newly formed tenorite (Fig 15). Interestingly, Belovode 131

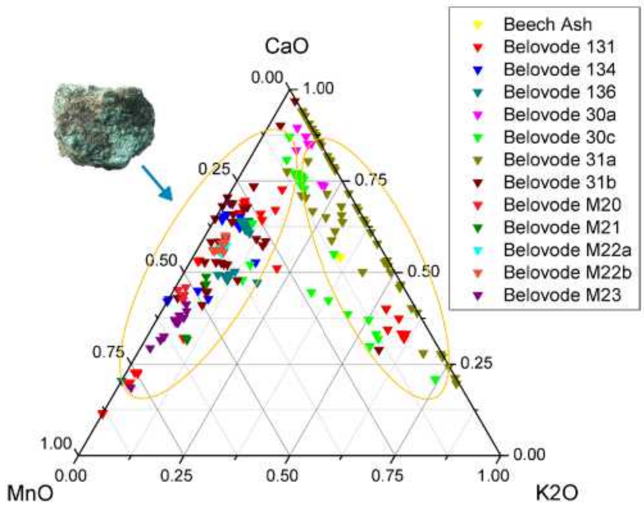

Figure 14: Ternary plot of K2O-CaO-MnO for slag matrices in samples Belovode 30a, 30c, 31a, 31b, 131, 134 and 136 with data from Radivojević et al 2010. Beech ash data from Jackson and Smedley 2004, Table 4.

shows up to 7.7at% sulphur in the copper dross phase (Radivojević 2012), hence possibly indicating the presence of primary copper ore from the charge. This sample also contains Mn-rich dross, with high concentrations of manganese (*c*30wt% average) and Fe (*c*18wt% average), but also silica and alumina with a 4:1 ratio (*ibid*). This particular phase could well be residual, with silica and alumina readings possibly implying a reaction with an (as yet undiscovered) crucible used in the process, or possibly a lump of clay in the ore charge.

Iron spinels occur throughout all the free slag samples as characteristic grey cubic crystals embedded in the glassy matrix, packed with copper dross (Fig 16a). Belovode 131 contains magnetite with 92.6wt% FeO, higher than in the other free slag pieces (134 and 136) (Table 10); however, Zn, Co, Cu and Mn contents are three to ten times lower than in the other samples. In samples Belovode 134 and 136, significantly higher readings of Mn, Zn and Co most likely indicate a crystal which resembles franklinite, $(Fe,Mn,Zn)(Fe,Mn)_2O_4$.

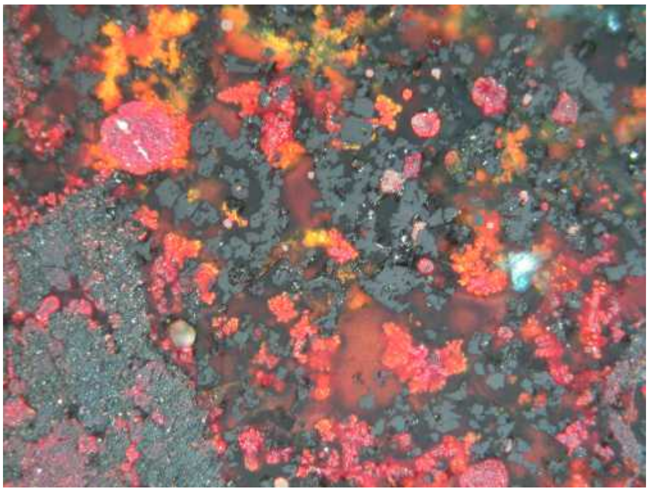

Figure 15: Dross-rich area in free slag 134, cross-polarised light, image width 0.85mm. Note grey rhombic spinels in the glass matrix.

The compositional discrepancy between Belovode 131, and Belovode 134 and 136 on the other hand is further underlined by the formation of different silicates in their glassy matrices. Silicates in Belovode 131 belong to the family of olivines, found here in the form of fayalite crystals (Fe_2SiO_4) with significant levels of Mn, Zn, Mg, and Ca (Table 11, Fig 16b). These newly formed crystals of fayalite are detected as optically dark and light grey, clearly differentiated by the levels of Mn and Mg. The presence of fayalite indicates more reducing smelting conditions for sample 131. Another silicate, leucite ($KAlSi_2O_6$), has been detected analytically in samples 134, 136 and 31b.

The copper metal phases in all the free slag samples is smaller in volume than those observed in the slagged sherds, and thus do not provide detailed information on their microstructure. Nevertheless, the presence of a pure copper metal phase itself confirms a high temperature process in the range of 1100°C. EPMA of copper metal phases in Belovode 131 and 134 indicate

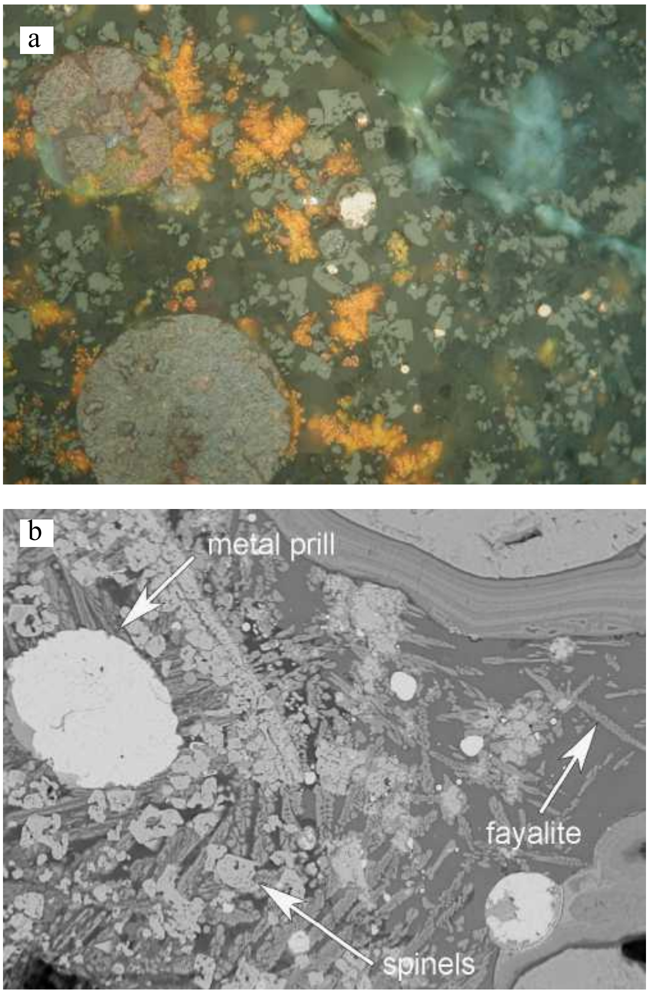

Figure 16: Copper slags: a) iron spinels and dross in glassy matrix in free slag 134, cross-polarised light, image width 340µm; b) BSE image of fayalite, iron spinels and copper metal prills embedded in glassy matrix in free slag 131, image width 250µm.

significant traces of both iron and manganese (Table 12). While elemental iron is most likely present as metal dissolved in the copper metal phase, manganese most likely found its way into this phase as the oxide. Since iron and manganese levels are significant in the slag

Table 10: SEM-EDS data for iron spinels in free slags (normalised wt%).

	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO
131	0.0	2.5	0.9	0.2	0.0	0.0	1.0	92.6	0.7	0.0	1.1	0.9
134	3.2	7.0	0.5	0.0	0.2	0.1	11.9	67.6	3.1	0.3	3.0	3.1
136	1.5	3.5	0.2	0.0	0.4	0.1	13.0	69.8	3.1	0.4	4.4	3.5

Note: Values are averages of 7-13 analyses.

Table 11: SEM-EDS data for fayalite in free slag 131 (at%).

	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Co	Ni	Cu	Zn	O
131 dark	0.0	2.1	0.2	13.5	0.5	0.1	0.9	2.4	25.3	0.2	0.0	0.3	0.2	54.1
131 light	0.1	4.5	1.0	13.4	0.8	0.1	1.9	6.1	15.5	0.7	0.0	0.2	0.3	55.4

Note: Values are averages of 4-7 analyses.

Table 12: EPMA data for copper prills in the free slag matrix (ppm). Note the very similar values of the Fe/Mn ratio (except for one analysis of sample 131 where metallic iron is most likely dissolved in the copper metal phase).

	Fe	Mn	Fe/Mn
Belovode 131	50400	340	148
	21340	10400	2
	49900	11300	4.5
	22860	10550	2
Belovode 134	bdl	bdl	-
	10330	3430	3
	bdl	bdl	-
	bdl	bdl	-
	14400	4800	3
	12400	4300	3
	9980	3420	3
	21130	5150	4
	23180	5900	4

Note: Reliable values established as >10ppm, all others indicated as below detection limit (bdl).

matrix and oxides bordering the copper metal phase, the assumption is that the presence of some iron and manganese in the latter could have derived from the immediate surroundings as a result of the effective analytical volume excited by the electron beam.

The presence of metallic iron in Belovode 131 (3.6wt% average) is demonstrated by the presence of optically pale metal prills with exceptionally high iron (*c*80at% average) and cobalt (*c*6at%) readings, and significant levels of copper (*c*5at% average) (Fig 17). These prills must have formed under temperatures higher than those required for smelting copper, but below the melting temperature of iron (1535ºC). Their presence further strengthens the validity of the assumption concerning the strongly reducing conditions of the smelt; it fits with the suggested presence of metallic iron in copper, as well as with the crystallisation of fayalite in the same sample. It therefore follows that Belovode 131 was formed under more reducing conditions than Belovode 134 and 136.

Table 13: EPMA data for copper prills in the slag matrix (selected significant trace element values in ppm).

	S	Co	Ni	Zn	As	Sb
Belovode 131	bdl	bdl	bdl	260	810	600
	14	10100	1440	5610	bdl	bdl
	30	20060	1070	730	bdl	bdl
	16	10150	1280	5250	bdl	bdl
Belovode 134	bdl	bdl	bdl	bdl	bdl	bdl
	bdl	50	bdl	bdl	bdl	bdl
	10	bdl	bdl	bdl	bdl	bdl
	14	bdl	bdl	bdl	bdl	bdl
	bdl	70	bdl	bdl	bdl	bdl
	bdl	65	bdl	bdl	bdl	bdl
	bdl	bdl	bdl	bdl	bdl	bdl
	bdl	1000	bdl	160	bdl	bdl
	bdl	1090	bdl	370	bdl	bdl

Note: Reliable values established as >10ppm, all others indicated as below detection limit (bdl).

There are significant amounts of other trace elements in samples 131 and 134 Levels are lower in 134 than in 131 with fewer elements detected (Table 13). Interestingly, Zn and Co are both present in the slag matrices of samples Belovode 131 and 134, unlike Ni, which could suggest that the smelted ore contained a geological association of the former two elements.

Copper metal droplet

The copper metal droplet M6 was initially thought to be a copper mineral until the cross-section revealed a dark-red phase surrounded by a thick light green layer. Compositional analysis revealed a complex structure of copper-based compounds, made predominantly of dross, followed by a copper metal phase that emerges in amorphous islands within the dross, a dark grey copper-rich matrix, and light grey chalcocite minerals (Table 14; Fig 18). It is worth noting that all except the latter appear as either a secondary, heat-treated phase (metal, dross) or corrosion products (dark grey matrix). In particular, the amorphous shape of the metal phase indicates that this sample was once molten copper; however, it is now heavily corroded, due to post-depositional processes. This droplet most likely cooled rapidly, as indicated by porosity holes and cracks throughout the polished sections.

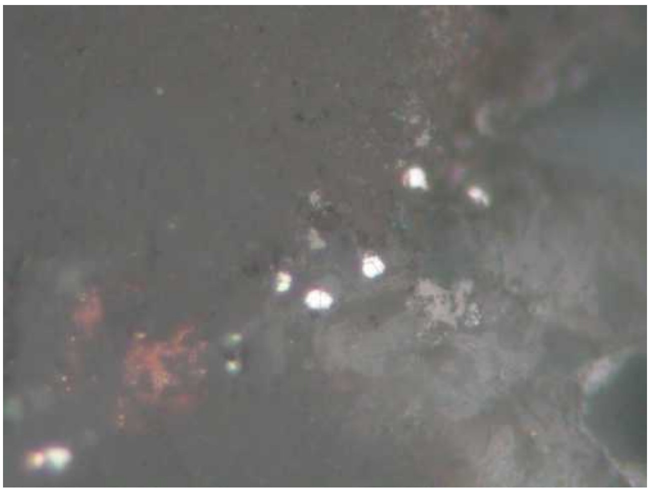

Figure 17: Iron-rich bright metal prills (average c80at%) in glassy matrix of free slag 131, plane-polarised light, image width 100µm.

The presence of chalcocite is particularly intriguing. While blocky grey crystals of chalcocite are mainly found in the grey corroded copper-rich matrix, its round phases are firmly embedded in the dross of sample M6. The latter formations are of particular interest here as their morphology could possibly originate from a heat treatment. Also, slightly less angular chalcocite phases in the grey matrix of M6 (Fig 18b) could be interpreted as only partially decomposed due to heat treatment. The copper minerals Belovode 3 and 33b reveal a similar pattern of areas of copper sulphides surrounded by copper oxides (Fig 19) to that observed in Belovode M6. Although a significant amount of metallic copper is present only in the latter, all three share significant analogies on a qualitative level. This comparison may prove informative in terms of what types of minerals could have been selected for processing in Belovode (3 and 33b) and the likely outcome of their smelting (M6).

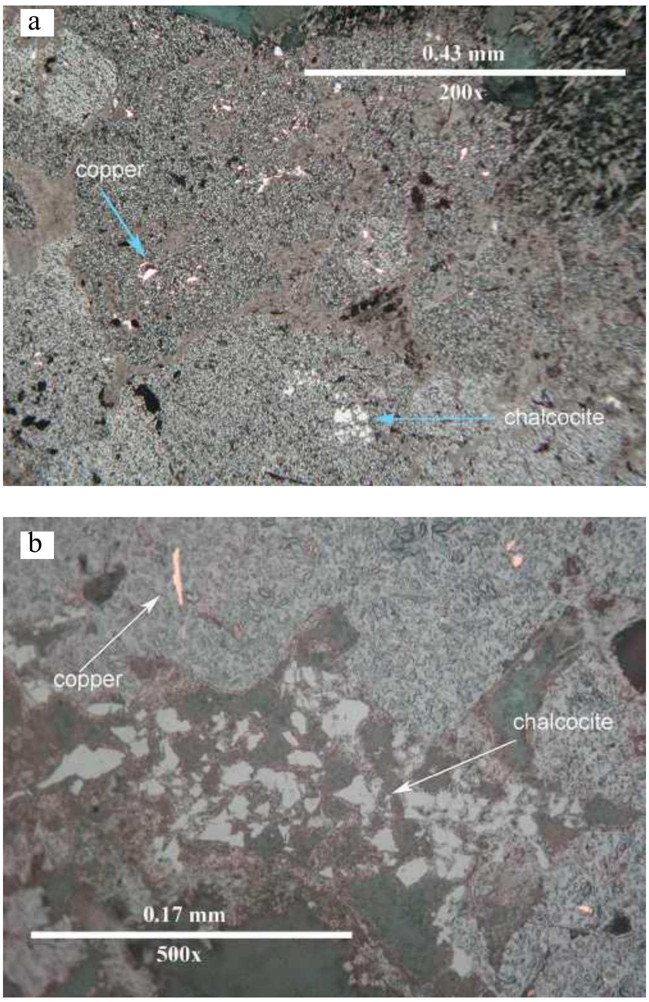

Figure 18: Copper droplet M6, plane-polarised light. a) Note the copper metal phase, the grey dross and the chalcocite embedded in it, image width 0.85mm; b) Note the copper metal droplets embedded in the grey dross and the partially decomposed chalcocite, image width 0.34mm.

Table 14: SEM-EDS data for copper-rich phases in copper droplet M6 (at%).

Belovode M6	O	S	Cu
metal phase	0.6	0.0	99.4
dross	16.3	0.0	83.8
tenorite	45.5	0.0	54.4
grey matrix	38.9	0.2	60.9
chalcocite	0.0	34.3	65.8

Note: All values are averages of 3-10 analyses.

Figure 19: Copper mineral 33b, cross-polarised light. Note the similar association of copper oxides (green) with copper sulphides (light grey) to that in Figure 18, image width 3.2mm.

Discussion

Extensive microanalytical examination of copper minerals and production debris indicate that they form a coherent assemblage, largely linked through significant manganese and zinc content, which came from the gangue minerals in the copper deposit. Internal discrepancies among the production evidence in particular, reflected in the presence of distinct inclusions, are assumed here to demonstrate the variability of factors surrounding the choices in preparing and carrying out a high-temperature treatment, see below.

The occurrence of different phases throughout the studied slag (both free slag and slagged sherds) reflects a poor homogenisation of the slag during the high-temperature process. This feature has already been noted by Tylecote *et al* (1977, 311), who recognised heterogeneous slags as a common feature of early smelting processes. The identification of the slag as products of smelting is further corroborated by the significant presence of trace elements throughout all slag components, indicating a strong presence of gangue minerals from the ore body, typical for primary metal production. Another indication supporting primary metal production is the presence of metallic iron in the copper, which is known to be co-reduced during smelting operations, and has been linked to a slag-forming process (Cooke and Aschenbrenner 1975; Tylecote *et al* 1977; Craddock and Meeks 1987; Craddock 2001). In Table 12 variable iron contents that are mainly well above the detection limit can be seen, of which the value of *c*5wt% in sample Belovode 131 appears most convincing, since it is not analytically not paired with MnO, which is argued above as a possible analytical 'contamination'. In discussing the redox conditions in the Belovode samples, the absence of delafossite in the free slag specimens, as opposed to their presence in the slagged sherds, is noteworthy. The association of delafossite and cuprite in the slag matrix has already been noted as indicative of the fairly oxidising conditions of the process. Thus, the presence of delafossite in the slagged sherds could indicate their exposure to more oxidising conditions then those prevailing during the formation of the individual slag specimens. This could imply that Belovode samples were situated in different locations during the smelt, provided that they were part of the same process.

With regard to the working temperature of the system, an estimate is based on the Cu-O phase diagram, where the presence of the ($Cu+Cu_2O$) eutectic in *c*50:50 ratio points towards a temperature of at least *c*1075°C (Figs 12 and 13). The Cu-O binary system is preferred here to ternary diagrams as it is free of the uncertainties included in projecting complex compositional data into the latter. The presence of iron-rich prills in sample 131 is noteworthy. These must have formed under temperatures greatly exceeding the general estimate of *c*1075°C, as indicated by the copper-iron equilibrium diagram (Daniloff 1948, 1198). This does not imply that reaching higher temperatures during the smelt was a rule but rather an indicator of variable smelting conditions. A certain degree of overheating is a plausible scenario and already argued in the previous study of Belovode smelting evidence (Radivojević *et al* 2010, 2783).

The chemical fingerprint of the ore used for smelting is best illustrated in Fig 14 and Tables 5-13, which indicate that the smelted ore had a strong chemical association of Mn and Zn, with some Co, Ca and Fe. Although a plausible ore signature may be ascribed to the association of copper, zinc, manganese, cobalt, lime and iron, it is noteworthy that not all of these elements partition in the slag matrix, but some instead into copper (cf Tylecote *et al* 1977, 330). The signature of the ores appears more strongly in the free slag samples (131 and 134), in which the metal prills are dominated by significant amounts of Fe, Zn, S, Au, Co and Ni. Therefore it is likely the ores used could have been a geological mixture of copper-zinc-manganese minerals, with some other elements coming from the attached primary copper sulphide mineralisation (such as S, Fe) or gossan. Their inclusion in the ore charge may not have been intentional, but most likely evolved as a natural consequence of the stratigraphy of weathered copper sulphide ore bodies (cf Rostoker *et al* 1989, 85).

Given this body of evidence, the inhomogeneity in the structure and chemistry of Belovode samples could be due to two factors, arising before or during the smelting operation. The pre-smelting factor is selecting a very heterogeneous ore charge, with an uneven distribution of gangue minerals within it. This ore batch could have disintegrated in situ during the smelt, only just reaching liquid conditions and therefore not mixing thoroughly, hence resulting in areas crystallising differently. The second factor would be variable temperatures during the smelt, which were generally just about the melting temperature of copper, but not sufficiently constant to allow for a fully liquefied state throughout. Both factors could have occurred separately, or very likely, follow each other.

When it comes to field interpretation, it is noteworthy that all the metallurgical debris originates from the last building horizon (Belovode D), in the 'metallurgical' Trench 3. The production (slag) evidence was discovered scattered throughout spits 2-7 in Belovode D, dated between *c*5000-4650 BC (Borić 2009, 209), thus implying the continuity of copper smelting throughout this period. Nevertheless, the majority of this production evidence appears clustered in spits 4-7 (Table 1) which could suggest that they were related to a single smelting episode. This possibility is further strengthened by the strong resemblances these samples bear to each other in terms of composition, particularly with regard to their Mn and Zn content (Tables 5-6, 8-11) (cf Radivojević *et al* 2010, 2782, table 1), the fact that they represent smelting debris, but also their likelihood of originating from the same type of copper ores (which contained a strong signature of MnO/ZnO/CoO and included lime and iron oxide). Sample M20 is also characterised by the presence of MnO; however, the elevated phosphorus content (Radivojević *et al* 2010, 2782, table 1) and the fact that it comes from the top spit and contextually unrelated to the samples from spits 4-7 may indicate a separate smelting event in Trench 3.

If the working hypothesis is that the eleven samples from spits 4-7 were related to a single smelting episode, the difference in their chemical composition could be due to their different locations within the smelt. For instance, looking at the shape of the slagged sherds, it can be noted that 30a and 30c could have had different functions from 31a and 31b. This idea comes from heavily vitrified sections of these sherds (30a, 30c) which indicates their fragmentation prior to the metallurgical process, and hence their potential function as hearth lining. Samples 31a and 31b, on the other hand, have a distinctive triangular shape, where slag is positioned only on one edge, leaving the rest of the body 'cold' and seemingly unaffected by the metallurgical process. Such a distinctive shape and slag position could imply that 31a and 31b had different locations from 30a and 30c in the assumed hearth lining, or that they were possibly used in procedures that involved closer contact with the metallurgical slag, as observed in 31b.

All eight free slag droplets are very similar; they are amorphous, highly viscous, rounded, and do not exceed 20mm across. Despite the small size of these samples, they show no broken surfaces and so were not crushed in a search for the trapped copper metal; they are most likely as they were at the end of the smelting event in Trench 3, about 7000 years ago. Thus, if these samples represented a single smelting episode, they imply the presence of a small workshop, with the smelting installation or hearth lined with sherds, and slag scattered around. The assumption is that the (raw) metal was further refined to remove impurities (cf Tylecote *et al* 1977, 308), which must have taken place in some other location in Belovode. The (casting) metal droplet M14 from Trench 9 makes it a likely candidate location for such a process in this site (Radivojević *et al* 2010, 2780).

The sulphur-rich copper metal droplet (Belovode M6) also bears morphological characteristics similar to those of Belovode M14, thus potentially indicating that similar courses of action produced them. However, the microstructures of Belovode M6 exhibits remnants of chalcocite in the form of residual and post-depositional phases, the former of which are commonly encountered in smelting rather than melting. The microprobe examination, on the other hand, did not detect significant iron levels, which would have indicated primary metal production (cf Tylecote and Boydell 1978; Craddock and Meeks 1987). However, the absence of iron in Belovode M6 does not rule out the possibility of this droplet being produced in a smelting event. This sample indicates that Vinča culture smiths in Belovode were producing copper in both slagging and non-slagging processes, depending on the chemistry of the smelted ores.

Theoretically, primary copper ores could be directly reacted to produce metallic copper by oxidising the sulphides to elemental copper and ferrous oxide, provided that iron is present in the ores (Davenport *et al* 2002, 57). However, given the evidence presented for Belovode M6, it may be assumed that the smelted ore was originally a mineral combination of copper sulphides (chalcocite) and oxides (or carbonates). This assumption is also corroborated by the presence of a similar mineral combination in Belovode (3 and 33b), which suggests that it was these types of 'mixed' minerals that were included in smelting activities at the site.

The original mineral from which M6 derived was most likely smelted at temperatures exceeding 700°C. However, the residual chalcocite in it indicates that there was not enough oxygen in the system to completely remove the sulphur from the copper. This process would also be dependent on the duration of the smelt, which was possibly insufficient to produce a fully liquefied state throughout. Another important observation is that smelting an ore charge of the assumed composition (copper oxides and chalcocite) would not produce much slag.

Conclusion

One of the most significant outcomes of the analyses presented here is the demonstration of the potential of a materials science approach for integrating insufficiently contextualised materials into one technological narrative. The analytical highlights underlying this narrative are the compositional connection of copper minerals and production debris from Trench 3 through Mn-rich copper ores, the potential presence of a minimum of three separate smelting events in Trench 3 and identification of both slagging and non-slagging events in the earliest context of metallurgical development in the site of Belovode.

The black and green minerals (both oxidic and sulphur-rich) selected by the Belovode miners predate the earliest documented smelting event in this site, indicating that they were potentially experimented with in the first centuries of the site's occupation. This experiment, although probably unsuccessful, could be recognised in sample M6, which contains molten copper, but also some residual sulphur-rich phases. The distinctively coloured copper minerals became copper ores only at the dawn of the 5th millennium BC, and their smelting is attested by the strong presence of manganese and zinc in the chemical signatures of glassy slag matrices as well as in other newly-formed phases in the metal production samples. Nevertheless, the copper minerals presented here may not have been the only copper ores used in the smelting process, since the analysed slag samples contain cobalt, iron and traces of nickel and gold, as well as manganese and zinc (Tables 5-13).

The combination of analytical and the available fieldwork data facilitated recognition of potentially three separate smelting events in Trench 3, one of which, represented by M6, was most likely unsuccessful. Firstly, the data demonstrates sustainable smelting activities during at least the latest building horizon in Belovode (*c*5000-4600 BC), while sample M6 was produced earlier. Secondly, the data shows a similar technological principle for the slagging events, but also highlights that the early beginnings of metallurgy were not producing slag, as previously assumed by Craddock (2001). Still, it was not long before the Belovode metal smiths optimised metal extraction by producing minute concentrations of slag, documented at the turn of the 5th millennium BC (Radivojević *et al* 2010).

It appears that Belovode metal smiths were aware of the properties of black and green copper minerals, the knowledge of which possibly developed over the course of a few centuries. This knowledge was not only about manganese-rich copper minerals, but of sulphur-rich ones as well, indicating that it was the distinctive colour of the minerals that prompted their selection and subsequent smelting. The colour appeal of copper ores has already been argued as probably the most significant sensory aspect of the early metallurgical activities (Radivojević *et al* 2010; 2013) and the Belovode case stands out as the earliest currently known in the line of evidence assembled within the Vinča culture (Radivojević 2012).

The task for future research is to check for consistency of black and green ores during the course of early metallurgical evolution; this is essential given the small scale of the excavated areas of Belovode, but is equally applicable to other Vinča culture sites with traces of early metallurgical activities (ie Vinča, Pločnik, Gornja Tuzla). Importantly, the scale of the production evidence presented here is still too small to be compared with the vast numbers of massive contemporary copper implements, and the question remains how representative a few grams of slag are of the overall 5th millennium BC Balkan metallurgy. It may be hypothesised that excavators failed to recognise the majority of the slag in the field, or it is still waiting to be uncovered, as is the case with most of the (very ephemeral) pre-Bronze Age production evidence across Europe and the Near East (Bourgarit 2007).The general absence of slag speaks indirectly of the prevalence of malachite smelting for metal extraction, which is the scenario discussed at length for the early development of metallurgy (*eg* Wertime 1964; Craddock 2001). However, the consistency in selecting the black and green minerals to be used as ores by the Belovode craftsmen over the course of *c*700 years of the site's entire occupation suggest a practice that was almost religiously followed in this community. Therefore, the quality and analytical resolution of the evidence presented demonstrates a unique technological narrative for the evolution of metallurgy in this part of the world, and currently stands as a model, as well as a challenge, for similar research in the future.

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