Journal of Archaeological Science 118 (2020) 105123

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Research Papers

Pyrotechnological connections? Re-investigating the link between pottery firing technology and the origins of metallurgy in the Vinča Culture, Serbia

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ARTICLE INFO

Keywords:
Pyrotechnology
Late Neolithic
Vinča culture
Ceramic technology
Dark-burnished pottery
Graphite decoration
Early metallurgy

ABSTRACT

The present paper re-examines the purported relationship between Late Neolithic/Early Chalcolithic pottery firing technology and the world's earliest recorded copper metallurgy at two Serbian Vinča culture sites, Belovode and Pločnik (c. 5350 to 4600 BC). A total of eighty-eight well-dated sherds including dark-burnished and graphite-painted pottery that originate across this period have been analysed using a multi-pronged scientific approach in order to reconstruct the raw materials and firing conditions that were necessary for the production of these decorative styles. This is then compared to the pyrotechnological requirements and chronology of copper smelting in order to shed new light on the assumed, yet rarely investigated, hypothesis that advances in pottery firing technology in the late 6th and early 5th millennia BC Balkans were an important precursor for the emergence of metallurgy in this region at around 5000 BC. The results of this study and the recent literature indicate that the ability to exert sufficiently close control over the redox atmosphere in a two-step firing process necessary to produce graphite-painted pottery could indeed link these two crafts. However, graphite-painted pottery and metallurgy emerge at around the same time, both benefitting from the pre-existing experience with dark-burnished pottery and an increasing focus on aesthetics and exotic minerals. Thus, they appear as related technologies, but not as one being the precursor to the other.

1. Introduction

Pyrotechnology is defined as the "deliberate process utilising the control and manipulation of fire" (McDonnell, 2001, p. 493), or put simply, the use of fire as a tool (Bentsen, 2014). The term is commonly used in connection with high temperature processes including cooking, heating, illumination and particularly the production of synthetic materials such as plaster, ceramics, metals and glass (Roberts and Radivojević, 2015, p. 300). The emergence of metallurgy in particular is seen as an important advance in the history of humankind and has been the focus of historical narratives explaining the evolution of social complexity, amongst others (*e.g.* Childe, 1944; Craddock, 1995; Renfrew, 1973; Wertime, 1964). Debate has focused on the questions of *when* and *where* ancient humans first learned to use fire to extract metal from naturally occurring ore (Gourdin and Kingery, 1975; Jovanović and Ottaway, 1976; Jordan and Zvelebil, 2009; McDonnell, 2001; Roberts et al., 2009; Wu et al., 2012 and literature therein). One of the most influential studies on this topic is by Childe (1944), who asserted that the Near Eastern prehistoric communities were the sole inventors of extractive metallurgy, which then spread to other parts of the globe. This view was challenged by Renfrew (1969), who argued instead for multiple inventions of metallurgy in different independent centres across Eurasia, basing the argument largely on artefact typology and C14 dates.

Recent excavations at the 7000 year old Vinča culture site of Belovode in eastern Serbia (Fig. 1) and laboratory analysis of unearthed archaeometallurgical artefacts revealed the earliest evidence for copper smelting in Eurasia (Radivojević et al., 2010; Radivojević, 2013). At Pločnik, a Vinča culture settlement in the south of the country, the recovery of a well-contextualised tin bronze foil dated to c. 4650 BC has also suggested the presence of a very early but short-lived tin bronze making tradition in the Balkans, technologically linked to the early copper making by Vinča culture communities (Radivojević et al., 2013).

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https://doi.org/10.1016/j.jas.2020.105123
Received 10 August 2019; Received in revised form 23 January 2020; Accepted 3 March 2020
Available online 30 April 2020

Both discoveries reinforce the theory of multiple independent centres of metallurgy invention in Eurasia, with Iran and possibly the Iberian Peninsula as other likely contemporary metallurgy heartlands alongside the Balkans. Radivojević and Rehren (2016) have suggested that the evolutionary trajectory of copper metallurgy in this part of the world is connected to the knowledge of material properties of black and green manganese-rich copper minerals, which feature as raw materials for both copper and tin bronze making. Such knowledge emerged locally and was subsequently transmitted across the Balkans over the course of c. 2000 years, starting in the late seventh millennium and continuing into the mid to late fifth millennium BC (Radivojević and Rehren, 2016, p. 228).

Advances in pottery firing technology, which predates metallurgy in many parts of the world, have been proposed as precursors to the emergence of metal extraction (Wertime, 1964 and literature therein). According to this theory, metallurgists gained transferrable skills from potters, including the ability to reduce metal oxides (Wertime, 1964, pp. 1264–1266). This appears to be supported by archaeological evidence from the Balkans, where together with other forms of decoration (*e.g.* cinnabar, calcite, black-topped) dark-burnished and graphite-painted pottery (Fig. 2) are typical productions. The high firing temperatures of about 1000 °C or above and predominantly reducing atmosphere that were assumed to be necessary for the production of dark-burnished and graphite-painted decoration were taken to indicate that potters of the Late Neolithic Balkans already possessed a sophisticated understanding of pyrotechnology and the behaviour of naturally occurring inorganic materials at high temperatures (Gimbutas, 1976, pp. 173–176; Kaiser et al., 1986; Renfrew, 1969) by the time that metallurgy emerged, arguing that this knowledge and skill must have featured as a crucial prerequisite for the development of copper smelting technology.

Whilst this is an attractive and convenient interpretation, it has never been rigorously tested. In particular, an in-depth understanding of the technology involved in the production of dark-burnished and graphite-painted pottery in the Vinča Culture is lacking, especially in the context of most recently reported detailed technological studies on the emergence and evolution of metallurgy in this culture (*e.g.* Radivojević et al., 2010 and literature therein). The present paper addresses this gap in our knowledge by studying in detail a total of eighty-eight well-dated sherds that include a relevant selection of dark-burnished and graphite-painted sherds from Belovode and Pločnik (Table 1). Using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), thin section petrography and traditional macroscopic observations, the raw materials, pyrotechnological conditions and procedures required to produce the ceramics' distinctive decoration have been reconstructed. This has then been compared to the contemporary knowledge of copper production technology at the two studied sites and the Vinča culture in general in order to shed more light on the relationship between pottery making and the emergence of metallurgy, as well as the likelihood that the former was a key precursor to the latter in this part of the world. The study represents a significant contribution to the study of the late

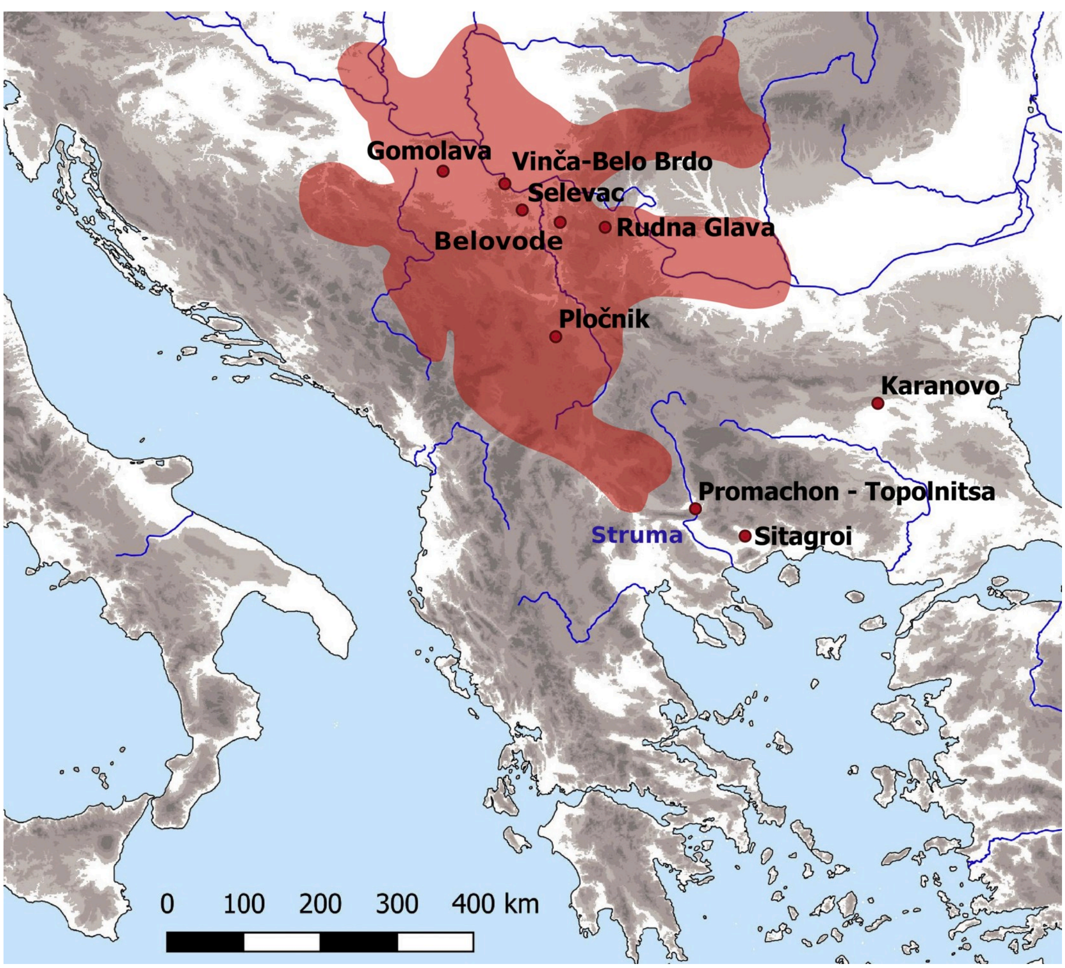

Fig. 1. Distribution of the Vinča culture throughout all its periods (shaded) and location of sites mentioned in this study (map by Lars Heinze and Jugoslav Pendić).

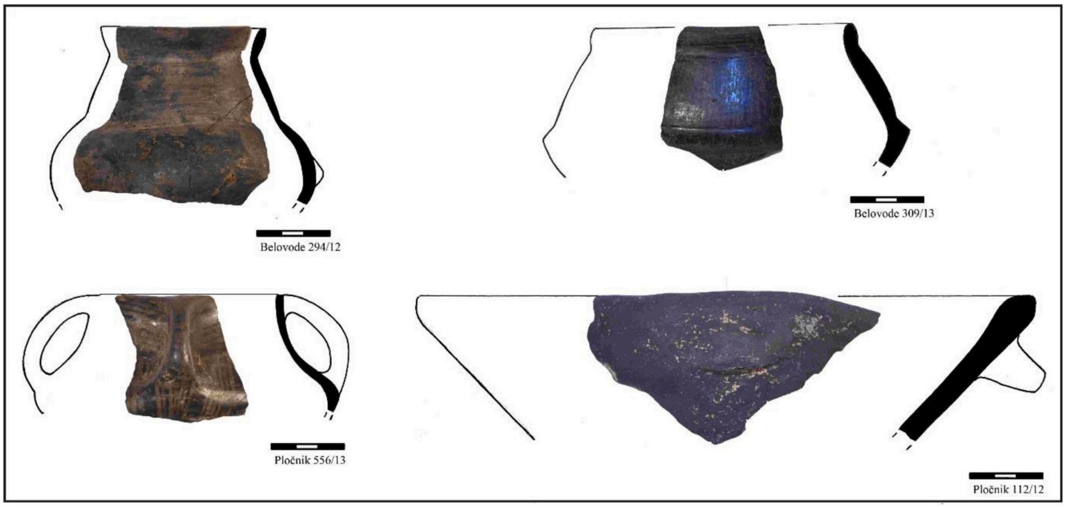

Fig. 2. Dark-burnished and graphite-painted pottery sherds from the Vinča culture sites of Belovode and Pločnik (copyright 'Rise of Metallurgy in Eurasia' project at the UCL Institute of Archaeology).

Neolithic and early Chalcolithic in the Balkans at a time of remarkable craftsmanship and pyrotechnological advancements by the communities in this region.

1.1. Archaeological background

The Vinča culture is a Neolithic/Chalcolithic phenomenon that covered a vast area comprising parts of the northern and central Balkans, including North Macedonia, Serbia, northeast Bosnia, the Vojvodina, southern Transdanubia, the Banat, Oltenia, west Transylvania, and the lower Tisza valley (Fig. 1). This cultural phenomenon has been the subject of intense research, including key studies by Chapman (1977, 1981), Garašanin (1951, 1979), Jovanović (1971), Marić et al. (2016), Radivojević (2012), Renfrew (1970), Schier (1996) and Tasić et al. (2015). According to published absolute dates, the estimated duration of the Vinča culture ranges from c. 5350 to c. 4600 BC (Breunig, 1987; Ehrich and Bankoff, 1992; Schier, 2000; Whittle et al., 2016) and has been divided into different phases according to the observable stratigraphic sequences and typological developments within the ceramic material culture, with the most widely used divisions based on Garašanin (1951, 1979, 1993) and Milojčić (1949) (supplementary materials).

In this study we focus on the Gradac Phase, which starts at the beginning of the fifth millennium BC (Garašanin, 1994/95; Jovanović, 1993/1994, 2006; Schier, 1996; Whittle et al., 2016) and lasts for around a century in the northern part of the Vinča culture phenomenon (defined as Gradac I-II) or until its end in settlements of the Morava valley and its tributaries in central and south Serbia, termed as Gradac I, II and III (the end varies between c. 4600 and c. 4400 BC, see Radivojević and Grujić, 2018; Radivojević et al., forthcoming). The Gradac Phase has been broadly correlated with the expansion of metallurgy and mining activities in the Vinča culture, particulary at the site of Rudna Glava (Jovanović, 1980, 1993/1994), as well as Belovode and Pločnik (Radivojević and Kuzmanović-Cvetković, 2014).

According to Jovanović (1993/1994) developments corresponding to the appearance of the Gradac phase clearly denote significant social changes at the time that he linked with the beginning of the Chalcolithic period in the Vinča culture and the entire Balkans. Garašanin (1994/95) also noted that this phase in the broader cultural and geographic context of this region belongs to a clearly distinguished and important period. Therefore, the influence which the appearance of metal had played within the Vinča culture is an important matter of debate, as much as its origin. To address themes such as invention, innovation and cultural change, a closer look into the material culture with a technological approach that includes archaeometric analysis seems to be particularly important. The study of the sites of Belovode and Pločnik offers the opportunity to approach these themes by investigating the archaeological records from two sites that gave important evidence for metallurgical activities and accordingly could have played a major role in the invention and adoption of metallurgy in Europe.

The site of Belovode is situated on a plateau located close to the village of Veliko Laole, c. 140 km southeast of Belgrade (Fig. 1). It has yielded the earliest known evidence for copper smelting in the world, dated at around 5000 BC (Radivojević et al., 2010). Pločnik in southern Serbia lies on a fertile floodplain on the left bank of the Toplica River (Fig. 1). It yielded the world's earliest known tin-bronze object, dated to approximately 4650 BC, alongside more than 40 massive copper implements (*e.g.* Radivojević et al., 2013; Radivojević and Kuzmanović-Cvetković, 2014). In both sites abundant pottery finds were unearthed, including dark-burnished pottery (Fig. 2) coming from different features recognised during the excavations (*e.g.* dwellings, pits) that belong to building horizons corresponding to different Vinča culture phases (Radivojević et al., forthcoming). In Pločnik graphite-painted sherds emerge in the Gradac phase concurrently with metallurgy, as seen in the case of a copper chisel from Trench 14 that is dated to the context associated with 5040–4860 BC (95% probability, Radivojević and Kuzmanović-Cvetković, 2014, p. 18).

1.2. Dark-burnished and graphite-painted pottery

Dark-burnished pottery, also known as black-burnished ware, is a pottery tradition with a widespread distribution during the Late Neolithic across the Balkans (Bonga, 2013, pp. 133–178; Chapman, 2006, 2007, p. 296; Holmberg, 1964). According to Garašanin (1954), this pottery type may have originated in Anatolia due to the finds of aesthetically similar pottery, however their technological link to the Balkan examples has never been thoroughly investigated.

Nevertheless, other scholars argue that it could have evolved independently in the Balkans (Chapman, 2006; Childe, 1936/1937, p. 29) based on a few convincing arguments. Dark-burnished pottery was one of the main features of Vinča material culture and is found from its earliest development (c. 5350 BC). Also, its colour and brightness well match the Neolithic Balkan visual identity based on striking and dark colours (Chapman, 2006, 2007). Besides pottery, other examples for this aesthetical preference include black and green ores used for copper smelting, and obsidian (Radivojević and Rehren, 2016).

The distinctive black or dark grey decoration of the Balkan dark-burnished pottery could have been produced in several different ways

Table 1
Details of eighty-eight pottery samples from the Vinča culture sites of Belovode and Pločnik analysed in the present study with indication of building horizons and corresponding Vinča culture chronological phases (DB = dark-burnished; GP = graphite-painted).

Sample	Chronological Horizon	Shape	Fabric	DB	GP	Colour of the Core	Colour of the Edges	Surface Colour	SEM
BEL 31	1 (C–D)	Spherical bowl	BEL–D	X		Grey	Grey	Very dark grey	
BEL 46	1 (C–D)	Pithos	BEL–A1			Light grey	Light red	Light red	X
BEL 52	1 (C–D)	Pot	BEL–B2			Dark grey	Dark grey	Dark grey	
BEL 68	1 (C–D)	Spherical bowl	BEL–A1	X		Light grey	Dark grey	Very dark grey	Refiring
BEL 94	1 (C–D)	Biconical bowl	BEL–A2	X		Light grey	Very dark grey	Very dark grey	Refiring
BEL 95	1 (C–D)	Spherical bowl	BEL–A1	X		Dark grey	Very dark grey	Very dark grey	Refiring
BEL 101	1 (C–D)	Biconical bowl	BEL–B2	X		Very dark grey	Very dark grey	Very dark grey	
BEL 109	1 (C–D)	Biconical amphora	BEL–A2	X		Very dark grey	Very dark grey	Very dark grey	
BEL 115	1 (C–D)	Pot	BEL–B1			Grey	Yellow	Grey to yellow	X
BEL 116	1 (C–D)	Pot	BEL–B1			Yellow	Yellow	Yellow	X
BEL 118	1 (C–D)	Amphora	BEL–A2	X		Light reddish brown	Very dark grey	Very dark grey	Refiring
BEL 123	1 (C–D)	'Chimney'	BEL–A1			Light red	Light red	Light red	X
BEL 132	1 (C–D)	Pithos	BEL–B1			Grey	Grey	Grey	Refiring
BEL 162	2 (Gradac–C)	Biconical bowl	BEL–A2	X		Dark grey	Dark grey	Very dark grey	
BEL 163	2 (Gradac–C)	Biconical bowl	BEL–A2	X		Yellow	Light red	Reddish grey	
BEL 169	1 (C–D)	Conical plate	BEL–A2	X		Very dark grey	Very dark grey	Very dark grey	
BEL 176	2 (Gradac–C)	Amphoretta	BEL–A2	X		Dark grey	Dark grey	Dark grey	
BEL 198	2 (Gradac–C)	Biconical bowl	BEL–A2	X		Reddish brown	Very dark grey	Very dark grey	
BEL 219	2 (Gradac–C)	Amphoretta	BEL–A2	X		Very dark grey	Very dark grey	Very dark grey	
BEL 221	2 (Gradac–C)	Pot	BEL–B1			Light red	Light red	Pale brown	
BEL 224	2 (Gradac–C)	'Chimney'	BEL–A1			Light grey	Light red	Light red	X
BEL 288	4 (A)	Pot	BEL–F			Dark grey	Dark grey	Light brown	X
BEL 289	3 (B1–B2)	Conical bowl	BEL–A2	X		Light reddish brown	Dark grey	Dark grey	
BEL 290	4 (A)	Conical bowl	BEL–A1			Dark grey	Dark grey	Reddish yellow	
BEL 295	4 (A)	Pot	BEL–A1			Very dark grey	Reddish yellow	Light red to very dark grey	X
BEL 299	3 (B1–B2)	Biconical bowl	BEL–A1	X		Light red	Very dark grey	Very dark grey	
BEL 300	3 (B1–B2)	Conical plate	BEL–A1	X		Reddish yellow	Grey	Grey	
BEL 303	5 (Starčevo/A)	Undetermined	BEL–C			Very dark grey	Reddish yellow	Reddish yellow	X
BEL 334	5 (Starčevo/A)	Biconical bowl	BEL–C			Very dark grey	Reddish yellow	Reddish yellow	X
PL 21–2	1 (Gradac II–III)	Conical bowl	PL–A1	X		Very dark grey	Light grey	Very dark grey	
PL 21–5	1 (Gradac II–III)	Pot	PL–A1			Grey	Reddish yellow	Reddish yellow	
PL 21–11	1 (Gradac II–III)	Biconical bowl	PL–A1	X		Reddish yellow	Very dark grey	Very dark grey	
PL 21–21	3 (Gradac I)	Amphora	PL–A1	X		Grey	Very dark grey	Very dark grey	X
PL 21–27	3 (Gradac I)	Conical bowl	PL–A2			Reddish brown	Reddish brown	Reddish brown	
PL 21–47	1 (Gradac II–III)	Conical bowl	PL–A2	X		Yellowish red	Dark grey	Very dark grey	Refiring
PL 21–49	1 (Gradac II–III)	Conical bowl	PL–A2	X		Reddish yellow	Light grey	Dark grey to reddish yellow	Refiring
PL 21–55	1 (Gradac II–III)	Biconical bowl	PL–A2	X		Dark grey	Yellowish red	Very dark grey	Refiring
PL 21–56	1 (Gradac II–III)	Biconical bowl	PL–B	X		Yellowish red	Very dark grey	Very dark grey	
PL 20–63	1 (Gradac II–III)	Biconical bowl	PL–J			Pale brown	Pale brown	Pale brown	
PL 20–69	1 (Gradac II–III)	Amphoretta	PL–E			Light red	Light red	Light red	X
PL 24–15	1 (Gradac II–III)	Biconical bowl	PL–A1	X		Dark brown	Dark brown	Dark brown to reddish yellow	
PL 24–23	1 (Gradac II–III)	Undetermined	PL–F			Light reddish brown	Grey	Grey	X
PL 24–32	1 (Gradac II–III)	Beaker	PL–I			Reddish yellow	Light grey	Very dark grey	
PL 24–34	1 (Gradac II–III)	Biconical beaker	PL–B			Reddish grey	Reddish yellow	Reddish grey to reddish yellow	
PL 24–54	1 (Gradac II–III)	Undetermined	PL–B			Brown	Brown	Brown	
PL 24–70	1 (Gradac II–III)	Undetermined	PL–B	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–73	1 (Gradac II–III)	Conical bowl	PL–A2			Reddish yellow	Grey	Reddish yellow	
PL 24–74	1 (Gradac II–III)	Undetermined	PL–A1			Reddish yellow	Reddish brown	Reddish brown	
PL 24–75	1 (Gradac II–III)	Undetermined	PL–B			Reddish yellow	Reddish yellow	Reddish yellow	
PL 24–83	1 (Gradac II–III)	Conical bowl	PL–A1			Grey	Grey	Light reddish brown	X
PL 24–101	2 (Gradac I)	Biconical bowl	PL–A1	X		Light reddish brown	Light reddish brown	Very dark grey	
PL 24–103	2 (Gradac I)	Bowl	PL–A1		X	Light reddish brown	Very dark grey	Very dark grey	X
PL 24–107	2 (Gradac I)	Undetermined	PL–A1	X		Light reddish brown	Very dark grey	Very dark grey	
PL24–113	2 (Gradac I)	Undetermined	PL–J			Reddish yellow	Grey	Grey	

(*continued on next page*)

Table 1 (*continued*)

Sample	Chronological Horizon	Shape	Fabric	DB	GP	Colour of the Core	Colour of the Edges	Surface Colour	SEM
PL 24–124	2 (Gradac I)	Conical bowl	PL–A2		X	Very dark grey	Very dark grey	Very dark grey	X
PL 21–129	2 (Gradac I)	Conical bowl	PL–A2		X	Very dark grey	Very dark grey	Very dark grey	X
PL 24–132	2 (Gradac I)	Conical bowl	PL–A1	X		Light grey	Light grey	Light grey	
PL 24–145	2 (Gradac I)	Conical bowl	PL–A2	X		Light grey	Light grey	Grey	
PL 24–157	3 (Gradac I)	Conical bowl	PL–A2	X		Reddish brown	Grey	Grey to reddish brown	Refiring
PL 24–161	3 (Gradac I)	Undetermined	PL–A2	X		Very dark grey	Very dark grey	Very dark grey	Refiring
PL 24–179	3 (Gradac I)	Biconical bowl	PL–A1			Ligh grey	Reddish yellow	Red	
PL 24–186	3 (Gradac I)	Conical plate	PL–A2	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–204	3 (Gradac I)	Amphora	PL–A1	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–209	4 (B2)	Undetermined	PL–A1	X		Reddish yellow	Reddish yellow	Very dark grey	
PL 24–211	4 (B2)	Conical bowl	PL–F	X		Grey	Grey	Grey	
PL 24–215	2 (Gradac I)	Amphora	PL–A2		X	Light reddish brown	Light reddish brown	Very dark grey	X
PL 24–247	3 (Gradac I)	Beaker	PL–A2		X	Light reddish brown	Very dark grey	Very dark grey	X
PL 24–263	3 (Gradac I)	Undetermined	PL–A1	X		Very dark grey	Very dark grey	Very dark grey	
PL 24–267	3 (Gradac I)	Biconical bowl	PL–A2	X		Light grey	Light grey	Light grey	
PL 24–275	4 (B2)	Conical bowl	PL–A1	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–287	4 (B2)	Biconical bowl	PL–A1			Reddish yellow	Grey	Very dark grey	
PL 24–288	4 (B2)	Conical bowl	PL–A2	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–299	4 (B2)	Pot	PL–A1			Reddish yellow	Reddish yellow	Reddish brown	
PL 24–303	4 (B2)	Amphora	PL–A1	X		Grey	Grey	Very dark grey	X
PL 24–307	4 (B2)	Amphora	PL–A2	X		Ligh grey	Light grey	Dark grey to grey	
PL 24–313	5 (A2–B1)	Biconical bowl	BEL–A1			Reddish yellow	Grey	Reddish yellow to grey	X
PL 24–314	5 (A2–B1)	Conical bowl	PL–A2	X		Light grey	Light grey	Very dark grey	
PL 24–315	5 (A2–B1)	Amphora	PL–D	X		Light grey	Light grey	Light grey	
PL 24–318	5 (A2–B1)	Conical bowl	PL–A1			Reddish yellow	Reddish yellow	Reddish brown	
PL 24–319	5 (A2–B1)	Conical bowl	PL–B	X		Reddish yellow	Very dark grey	Very dark grey	
PL 24–320	5 (A2–B1)	Pot	PL–A1	X		Reddish yellow	Reddish yellow	Very dark grey	
PL 24–323	5 (A2–B1)	Pot	PL–A1			Light grey	Reddish yellow	Reddish yellow	
PL 24–324	5 (A2–B1)	Undetermined	PL–A2			Light red	Light red	Light red	
PL 24–328	5 (A2–B1)	Undetermined	PL–B			Reddish yellow	Light grey	Ligh grey	
PL 24–329	5 (A2–B1)	Conical bowl	PL–A2	X		Very dark grey	Very dark grey	Very dark grey	
PL 24–331	5 (A2–B1)	Conical bowl	PL–A1	X		Reddish yellow	Grey	Grey	
PL 24–332	5 (A2–B1)	Conical bowl	PL–A2	X		Very dark grey	Very dark grey	Very dark grey	
PL 24–333	5 (A2–B1)	Biconical bowl	PL–B			Light grey	Light grey	Light grey to very dark grey	

including iron reduction, the application of manganese, the deposition of carbon as soot, or painting with graphite pigment. The iron reduction technique fires iron-rich clay above 500 °C under reducing conditions (Cuomo di Caprio, 2007, p. 121; Jones, 1986, p. 762; Maritan, 2004; Noll, 1991, p. 121). A reducing atmosphere is achieved during firing when little or no 'free oxygen' is available due to restricted air supply or the addition of excess fuel. In this situation, the iron in the clay is reduced to 'ferrous' minerals such as magnetite (Fe_3O_4), and carbonised amorphous organic matter in the clay is not burnt off, giving the pottery a grey or black colour. Manganese black decoration is formed by the presence of manganese-rich mineral phases such as pyrolusite which are applied to pottery as a pigment or within a clay-rich slip, then fired in oxidising conditions (Jones, 1986, p. 762; Noll, 1991, p. 140; Spataro, 2019).

Carbon black decoration is typically produced by adding organic material and firing under reducing conditions, resulting in the formation of a layer of charcoal or soot (Jones, 1986, pp. 763–764; Letsch and Noll, 1978, 1983; Noll, 1991, p. 175). A typical method involves 'smudging' (Jones, 1986, pp. 763–764), that is the deposition of carbon on the surface of a vessel and within open pores during the firing process, for example by smothering the pots with fine-textured fuel at the end of the firing. The coating is composed of a very fine crystalline or amorphous carbon (Jones, 1986, p. 763) producing a shiny 'Glanzkohlenstoff' (lustrous carbon) finish (Letsch and Noll, 1978, 1983). Significant technological skill is required to produce carbon black as timing is crucial and it is essential to maintain reducing conditions in order for the coating not to be burnt off. Letsch and Noll (1978) argued that the black finish on Neolithic and Bronze Age pottery from the Balkans, Anatolia, the Near East and Egypt is due to the deposition of carbon primarily from the smudging, but also from the organic matter contained within the clay body.

Painting pottery with graphite pigment is another method of achieving a highly reflective black surface finish (Jones, 1986, p. 768). Vessels with geometric patterns painted in graphite are found across the fifth millennium BC Balkans (*e.g.* Gaul, 1948, pp. 98–99; Leshtakov, 2005; Martinon, 2017; Todorova, 1986, p. 107). The earliest documented use of graphite decoration is considered to come from Promachon-Topolnica (Fig. 1) in the Struma valley and is dated to the beginning of the fifth millennium (Vajsov, 2007). Within the Vinča culture it appears for the first time during the Gradac phase (Perić, 2006, p. 238). Graphite is a crystalline form of carbon that occurs naturally in highly metamorphic rocks such as marble, schist and especially gneiss. It was ground to a fine powder, mixed with water and perhaps clay, then applied, often onto a burnished surface. The reduction during the firing should be well controlled to preserve the graphite layer (Kreiter et al., 2014).

It has been suggested that the use of graphite decoration on pottery was closely related to the emergence of early metal production. Its light-reflective qualities produce a metallic sheen that may have been aesthetically appealing to prehistoric communities (Todorova, 1981). The acquisition of graphite would have required the participation in specialist trade networks comparable to those required for copper exploitation (*e.g.* Leshtakov, 2005; Radivojević and Grujić, 2018). Another link that has been proposed, as will be discussed below, is that the high temperatures necessary for copper metallurgy (around and exceeding c. 1100 °C) could also have been required to produce graphite-painted pottery (Renfrew, 1969).

Noteworthy, the nature of the relationship between the emergence during the Gradac phase of the Vinča Culture of graphite-painted pottery and extractive metallurgy has never been properly investigated.

1.3. Previous analytical studies

The earliest investigation of the pyrotechnological link between pottery and metallurgy in the Balkans was carried out by Frierman (1969), who analysed a late fifth millennium BC dark-burnished sherd

Table 2
Munsell codes corresponding to the colours provided in Table 1.

Colour	Munsell Code
Light red	(2.5 YR 6/8 – 10R 7/8)
Dark grey	(5 YR 3/1)
Reddish brown	(5 YR 1/3)
Yellowish red	(5 YR 4/6–5/4)
Reddish grey	(5 YR 5/2)
Grey	(5 YR 6/1)
Light reddish brown	(5 YR 6/3–6/4)
Light grey	(5 YR 7/1)
Reddish yellow	(5 YR 7/6)
Dark brown	(7.5 YR 3/1)
Brown	(7.5 YR 5/3)
Very dark grey	(10 YR 3/1)
Pale brown	(10 YR 6/3)
Yellow	(10 YR 7/6)
Red	(10 R 4/8)

Table 3
Petrographic fabrics corresponding to the abbreviations used in Table 1.

Fabric	Description
Pločnick	
PL–A1	Sedimentary rock fabric, coarse
PL–A2	Sedimentary rock fabric, fine
PL–B	Micaschist rock fabric
PL–D	Phyllite fabric
PL–E	Epidote fabric
PL–F	Volcanic rock fabric
PL–I	Serpentinite fabric
PL–J	Amphibole fabric
Belovode	
BEL–A1	Metasedimentary rock fabric, coarse
BEL–A2	Metasedimentary rock fabric, fine
BEL–B1	Fossiliferous fabric coarse
BEL–B2	Fossiliferous fabric fine
BEL–C	Chaff tempered fabric
BEL–D	Very fine fabric
BEL–F	Metamorphic fabric with weathered plagioclase

decorated with graphite from the site of Karanovo in Bulgaria (Karanovo VI) by determining its fusion point via thermal analysis. He estimated that the sample had been fired to a temperature around 1050 °C in a strongly reducing atmosphere. The latter was beneficial for graphite application, since under oxidising conditions graphite burns off above c. 725 °C. Frierman (1969) therefore suggested that firing took place in a kiln, given the high temperature and prolonged period of reduction required to produce this type of pottery. This finding was taken forward by Renfrew (1969, p. 38) who suggested that "refractory technology in the south-east European Chalcolithic had evolved sufficiently in the firing of pottery to provide the conditions required for smelting and casting of copper". However, a few years later Kingery and Frierman (1974) re-fired the same sherd at 700, 800, 900 and 1000 °C in reducing conditions and concluded that it had in fact been subjected to a maximum temperature of $<$800 °C, and possibly as low as 700 °C.

Kaiser et al. (1986) studied the firing temperature of dark-burnished pottery and other pottery types from the Vinča culture sites of Selevac and Gomolava in Serbia via thermal expansion (also Kaiser and Lucius, 1989) and SEM to document the vitrification microstructure. This indicated that the ceramics they studied were variously fired between 850 and 1000 °C under oxygen-poor conditions. Despite this variability, the authors concluded that potters of the western Balkans were routinely capable of achieving temperatures of 1000 °C under reducing atmospheres, and that this pointed to a sophisticated knowledge of the firing process, including managing the required resources of labour, fuel and time. Since the pottery came from different contexts at these two relatively distant sites (c. 100 km), it may be inferred that this knowledge was widely shared between Vinča culture communities at the time and

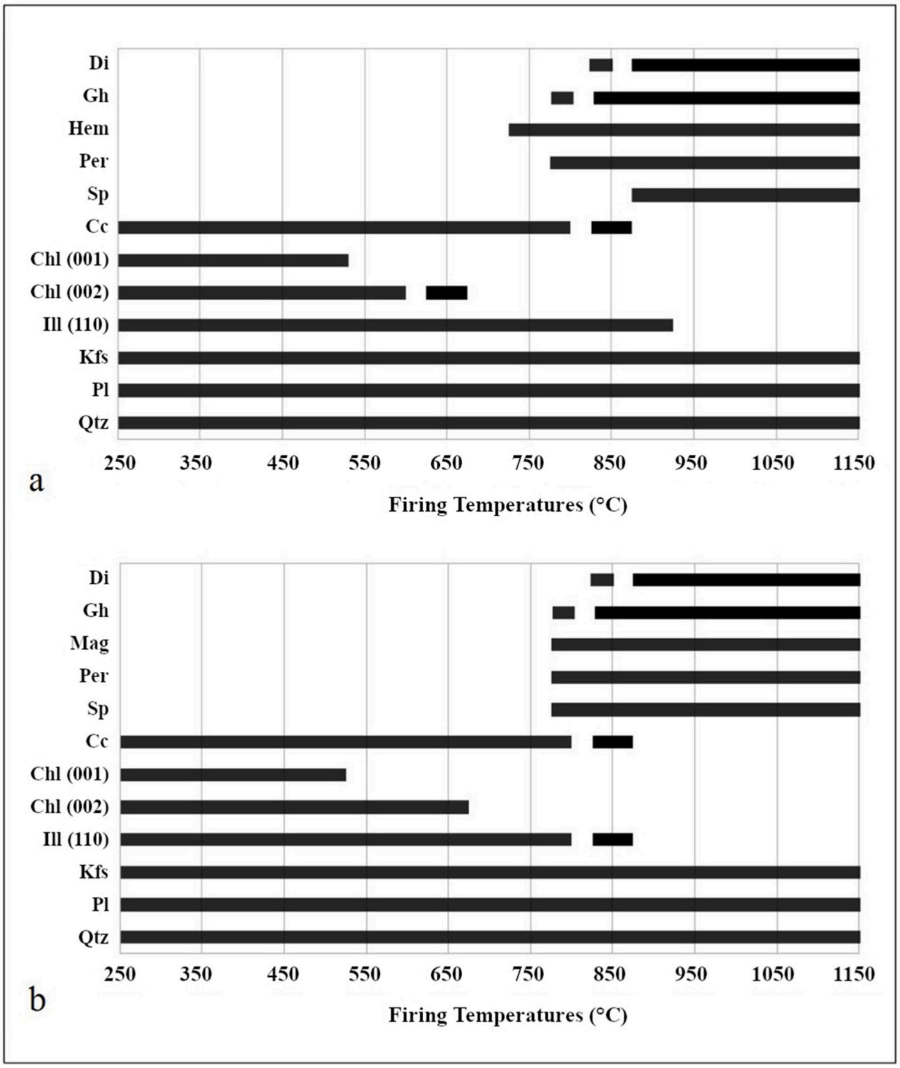

Fig. 3. Bar diagrams documenting the mineralogical changes that take place during the firing of earthenware ceramics in oxidising (a) and reducing (b) atmosphere (modified after Maritan 2004, p. 304, Fig. 7). Mineral abbreviations: Di = diopside; Gh = gehlenite; Hem = hematite; Mag = magnetite; Per = periclase; Sp = spinel; Cc = calcite; Chl = chlorite; Ill = illite; Kfs = potassium feldspar; Pl = plagioclase; Qtz = quartz.

could have been transferred to craftspeople who specialised in other pyrotechnologies, such as the smelting of copper metal.

Other studies on the firing of dark-burnished and graphite-painted pottery from the Balkans and Greece include those by Gardner (1978, 1979, 2003), Goleanu et al. (2005), Maniatis and Tite (1981), Perišić et al. (2016), Spataro (2014, 2017, 2018) and Yiouni (1995, 2000, 2001). Among these, Perišić et al. and Spataro focused especially on Vinča pottery. Perišić et al. (2016) analysed ten samples from Pločnik, but only a few were dark-burnished, and their typology and chronology were not contextually secure. The research of Spataro (2018) includes the materials from the eponymous site of Vinča Belo Brdo, originating from contexts excavated between 1930 and 1936 by Miloje Vasić, which have no direct association with metal artefacts from this site. All these studies applied a wide range of techniques including thin section petrography, SEM, re-firing tests, FTIR, XRPD and thermo-analytical studies. These investigations revealed that firing temperatures were highly variable, and unlike the findings of Frierman (1969) and Kaiser et al. (1986), did not appear to have exceeded 900 °C. Gardner (1978, 2003, p. 289) observed that graphite-painted vessels from Phases III from the site of Sitagroi in Greece (Fig. 1) have a red core, suggesting that the firing process involved two steps. This may have included an initial firing step under oxidising conditions below 700 °C, followed by a second smoky reduction phase.

Thus, considerable uncertainty surrounds the topic of Late Neolithic/Chalcolithic ceramic pyrotechnology in the Balkans, particularly the conditions required to achieve dark-burnished and graphite-painted decorations and their role in the inception of early metallurgy. It appears that too much emphasis has been placed on firing temperature and not enough attention has been given to other pyrotechnological parameters such as the redox conditions and length of firing. The former is of crucial importance to the process of smelting copper (Gardner, 1979, pp. 20–21; Rehren, 1997), as a reducing environment is necessary for the formation of metallic copper, the chemical change starting at temperatures as low as 700 °C, whilst a more oxidising environment and a rise in temperatures up to the melting point of pure copper at 1083 °C are required to initiate the physical change from solid to liquid metal (Pollard et al., 1991; Radivojević et al., 2010).

2. Materials and methods

Eighty-eight Vinča culture pottery sherds were selected from the sites of Belovode and Pločnik in order to investigate the pyrotechnology necessary to produce dark-burnished pottery and graphite decoration (Table 1). Twenty-nine of these were chosen from the assemblage of

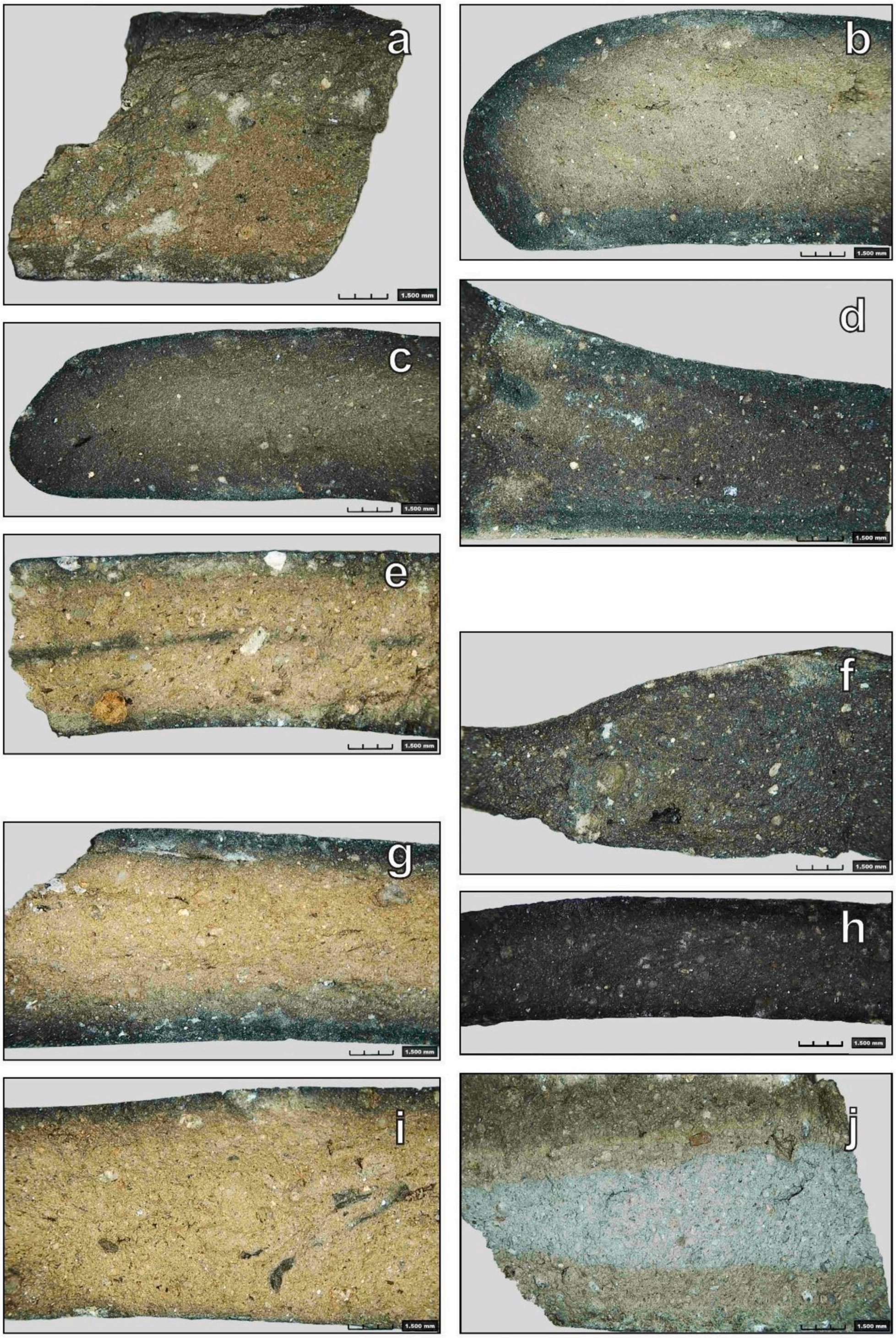

Fig. 4. Selected dark-burnished and graphite-painted pottery sherds from the Vinča culture sites of Belovode seen in fresh break, revealing the fired colour of their fabric and the presence of firing horizons: a) BEL 289; b) BEL 94; c) BEL 162; d) BEL 219; e) BEL 299; f) PL 24–129 (graphite-painted); g) PL 24–107; h) PL 24–124 (graphite-painted); i) PL 24–288; j) PL 24–145. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Trench 18 in Belovode, while at Pločnik fifty-nine samples were taken from Trenches 20, 21 and 24. The selected samples come from different features recognised during the excavations (*e.g.* dwellings, pits), represent various types of pottery found within the excavated assemblages, and come from different building horizons (1–5) corresponding to different Vinča culture phases of the settlements (Radivojević et al., forthcoming). Horizon 1 is the youngest, while horizon 5 belongs to the earliest layers of occupation in both sites. Also, both sites share the similarity of the youngest (horizon 1) showing a possible evidence for abandonment and destruction. In Belovode horizon 1 belongs to Vinca C-D, horizons 2 and 3 to Gradac and Vinca B1-B2, horizon 4 and 5 to Vinca A and Starčevo. While dark-burnished pottery spread throughout, dark-burnished pottery spread throughout is not known from this site. In Pločnik, horizon 1 is related to Gradac II and III, horizons 2 and 3 to Gradac I, horizon 4 to B2 and horizon 5 to Vinca A2-B1. All graphite-painted pottery come from horizons 2 and 3, which is the beginning of the Gradac phase on this site, concurrent with the appearance of the earliest metal artefacts as well.

The raw materials and technology involved in the production of the eighty-eight sherds and their decorative finishes was investigated in

Table 4
Summary of the XRD results (DB = dark-burnished; GP = graphite-painted). The presence/absence of montmorillonite or chlorite is not reported due to the weak main 001-intensity at app. 6°2θ (see also information given in the text).

Sample	Chronological Horizon	DB	GP	Optical Activity	Qtz	Fsp	Cc	Am	Ill	Msc	Hem	Cri	Spl	Temp
BEL 31	1 (C–D)	X		high	X	X			X					<900 °C
BEL 46	1 (C–D)			absent	X	X					X	X	X	>1000 °C
BEL 52	1 (C–D)			weak	X	X	X		X					<900 °C
BEL 68	1 (C–D)	X		moderate	X	X			X					<900 °C
BEL 94	1 (C–D)	X		moderate	X	X			X					<900 °C
BEL 95	1 (C–D)	X		high	X	X			X					<900 °C
BEL 101	1 (C–D)	X		high	X	X	X		X					<900 °C
BEL 109	1 (C–D)	X		weak	X	X		X	X					<900 °C
BEL 115	1 (C–D)			moderate	X	X	X		X					<900 °C
BEL 116	1 (C–D)			high	X	X	X		X					<900 °C
BEL 118	1 (C–D)	X		weak	X	X			X					<900 °C
BEL 123	1 (C–D)			absent	X	X					X	X	X	>1000 °C
BEL 132	1 (C–D)			weak	X	X	X		X					<900 °C
BEL 162	2 (Gradac–C)	X		moderate	X	X		X	X					<900 °C
BEL 163	2 (Gradac–C)	X		high	X	X			X					<900 °C
BEL 169	1 (C–D)	X		weak	X	X			X					<900 °C
BEL 176	2 (Gradac–C)	X		weak	X	X			X					<900 °C
BEL 198	2 (Gradac–C)	X		weak	X	X			X					<900 °C
BEL 219	2 (Gradac–C)	X		moderate	X	X		X	X					<900 °C
BEL 221	2 (Gradac–C)			absent	X	X	X		X					<900 °C
BEL 224	2 (Gradac–C)			absent	X	X					X	X	X	>1000 °C
BEL 288	4 (A)			absent	X	X			X					<900 °C
BEL 289	3 (B1–B2)	X		moderate	X	X			X					<900 °C
BEL 290	4 (A)			absent	X	X			X					<900 °C
BEL 295	4 (A)			weak	X	X			X					<900 °C
BEL 299	3 (B1–B2)	X		moderate	X	X			X					<900 °C
BEL 300	3 (B1–B2)	X		high	X	X	X		X					<900 °C
BEL 303	5 (Starčevo/A)			weak	X	X			X					<900 °C
BEL 334	5 (Starčevo/A)			weak	X	X			X					<900 °C
PL 21–2	1 (Gradac II–III)	X		moderate	X	X			X					<900 °C
PL 21–5	1 (Gradac II–III)			moderate	X	X			X					<900 °C
PL 21–11	1 (Gradac II–III)	X		weak	X	X			X					<900 °C
PL 21–21	3 (Gradac I)	X		weak	X	X			X					<900 °C
PL 21–27	3 (Gradac I)			moderate	X	X			X					<900 °C
PL 21–47	1 (Gradac II–III)	X		moderate	X	X			X					<900 °C
PL 21–49	1 (Gradac II–III)	X		absent	X	X			X					<900 °C
PL 21–55	1 (Gradac II–III)	X		weak	X	X			X					<900 °C
PL 21–56	1 (Gradac II–III)	X		weak	X	X			X					<900 °C
PL 20–63	1 (Gradac II–III)			weak	X	X		X	X	X	X	X		>1000 °C
PL 20–69	1 (Gradac II–III)			absent	X	X		X	X	X	X	X		>1000 °C
PL 24–15	1 (Gradac II–III)	X		moderate	X	X			X					<900 °C
PL 24–23	1 (Gradac II–III)			moderate	X	X		X		X		X		>1000 °C
PL 24–32	1 (Gradac II–III)			weak	X	X			X					<900 °C
PL 24–34	1 (Gradac II–III)			moderate	X	X			X?	X?				<900 °C
PL 24–54	1 (Gradac II–III)			absent	X	X			X					<900 °C
PL 24–70	1 (Gradac II–III)	X		weak	X	X			X					<900 °C
PL 24–73	1 (Gradac II–III)			absent	X	X			X					<900 °C
PL 24–74	1 (Gradac II–III)			absent	X	X			X					<900 °C
PL 24–75	1 (Gradac II–III)			absent	X	X			X					<900 °C
PL 24–83	1 (Gradac II–III)			absent	X	X	X		X					<900 °C
PL 24–101	2 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–103	2 (Gradac I)		X	moderate	X	X			X					<900 °C
PL 24–107	2 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–113	2 (Gradac I)			high	X	X		X	X					<900 °C

(continued on next page)

Table 4 (*continued*)

Sample	Chronological Horizon	DB	GP	Optical Activity	Qtz	Fsp	Cc	Am	Ill	Msc	Hem	Cri	Spl	Temp
PL 24–124	2 (Gradac I)		X	weak	X	X			X					<900 °C
PL 24–129	2 (Gradac I)		X	weak	X	X			X					<900 °C
PL 24–132	2 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–145	2 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–157	3 (Gradac I)	X		weak	X	X	X		X					<900 °C
PL 24–161	3 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–179	3 (Gradac I)			weak	X	X			X					<900 °C
PL 24–186	3 (Gradac I)	X		moderate	X	X			X					<900 °C
PL 24–204	3 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–209	4 (B2)	X		weak	X	X			X					<900 °C
PL 24–211	4 (B2)	X		moderate	X	X		X	X					<900 °C
PL 24–215	2 (Gradac I)		X	weak	X	X			X					<900 °C
PL 24–247	3 (Gradac I)		X	weak	X	X			X					<900 °C
PL 24–263	3 (Gradac I)	X		weak	X	X			X					<900 °C
PL 24–267	3 (Gradac I)	X		high	X	X			X					<900 °C
PL 24–275	4 (B2)	X		absent	X	X	X		X					<900 °C
PL 24–287	4 (B2)			moderate	X	X			X					<900 °C
PL 24–288	4 (B2)	X		high	X	X			X					<900 °C
PL 24–299	4 (B2)			high	X	X			X					<900 °C
PL 24–303	4 (B2)	X		weak	X	X			X					<900 °C
PL 24–307	4 (B2)	X		weak	X	X			X					<900 °C
PL 24–313	5 (A2–B1)			weak	X	X			X					<900 °C
PL 24–314	5 (A2–B1)	X		weak	X	X			X					<900 °C
PL 24–315	5 (A2–B1)	X		weak	X	X		X	X					<900 °C
PL 24–318	5 (A2–B1)			weak	X	X	X		X	X				<900 °C
PL 24–319	5 (A2–B1)	X		moderate	X	X		X	X					<900 °C
PL 24–320	5 (A2–B1)	X		weak	X	X			X					<900 °C
PL 24–323	5 (A2–B1)			moderate	X	X			X					<900 °C
PL 24–324	5 (A2–B1)			absent	X	X			X					<900 °C
PL 24–328	5 (A2–B1)			moderate	X	X			X?	X?				<900 °C
PL 24–329	S (A2–B1)	X		moderate	X	X			X					<900 °C
PL 24–331	5 (A2–B1)	X		weak	X	X			X					<900 °C
PL 24–332	5 (A2–B1)	X		weak	X	X			X					<900 °C
PL 24–333	5 (A2–B1)			moderate	X	X			X					<900 °C

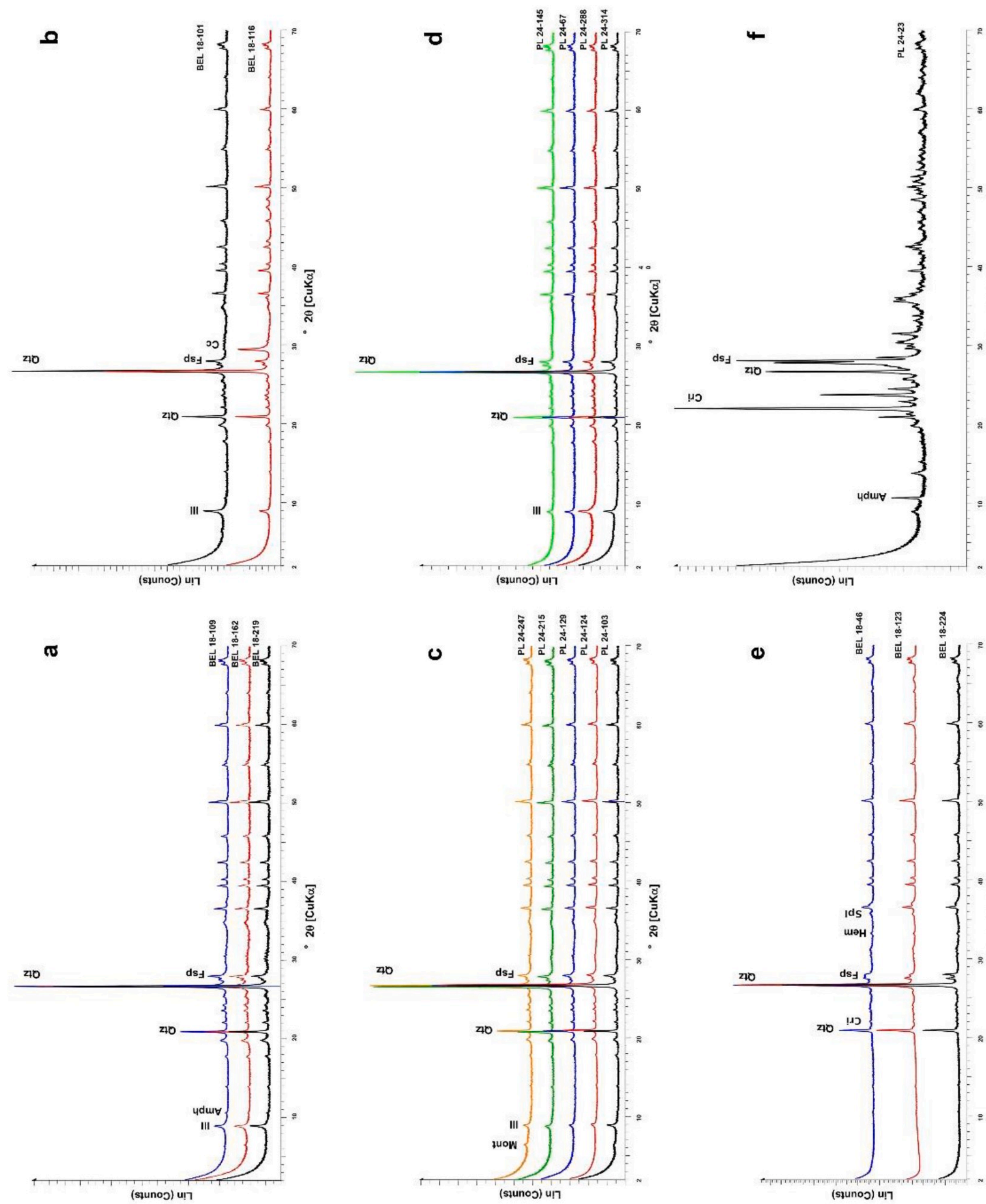

Fig. 5. X-ray diffractograms of selected pottery sherds from the Vinča culture sites of Belovode and Pločnik in this study. Mineral abbreviations: Amph = amphibole; Cc = calcite; Cri = cristobalite; Hem = hematite; Ill = illite; Fsp = feldspar; Mont = montmorillonite; Qtz = quartz; Spl = spinel: a) dark-burnished pottery from Belovode, fabric A2; b) dark-burnished pottery from Belovode, fabric B2; c) dark-burnished pottery from Pločnik, fabric A2; d) graphite-painted pottery from Pločnik, fabric A2; e) and f) sherds from Belovode and Pločnik containing high temperatures phases.

detail using a combination of macroscopic and instrumental analyses, including thin section petrography, XRPD and SEM. The colour variability within individual sherds was recorded using a Munsell colour chart (Table 2) in order to shed light on their atmosphere of firing (Mentesana et al., 2017; Rice, 2015, pp. 276–290). The birefringence or 'optical activity' of the sherds in section under the polarising light microscope was used to determine the degree to which they had undergone vitrification during firing (Quinn, 2013, p. 190; Whitbread, 1995, p. 382).

The mineralogical composition of the ceramic body was determined via XRPD and used to reconstruct their original firing temperature ('archaeothermometry', Rice, 2015, pp. 99–116; Quinn and Benzonelli, 2018). This method makes use of the presence/absence of mineral phases that form or disappear at specific temperatures and atmospheric conditions, as determined experimentally and reported in 'bar diagrams' (Maggetti, 1982, p. 128; Maritan, 2004, p. 304; Maritan et al., 2007, p. 533; Nodari et al., 2007, p. 4668) (Fig. 3).

For XRPD analysis, the surface layer of each sherd was removed with a tungsten carbide drill and discarded, and c. 1 g from the body were ground to a fine powder and dried for 12 h at 110 °C. Initial characterisation of all samples was performed using a Rigaku MiniFlex 600 X-ray diffractometer equipped with a Cu-X-ray tube running at 40 kV/30 mA and a graphite primary monochromator. This was used to select specific samples (Fig. 5) for more detailed analysis using a Bruker D8Advance powder diffractometer with a Cu-X-ray tube running at 40 kV/20 mA, with a Goebel mirror optic, a 0.2 mm divergence slit, a fixed knife edge to suppress air scatter, sample rotation and a VÅNTEC-1 detector. Mineral identification was performed by matching the

Table 5
Summary of the results of the SEM analysis (IV = initial vitrification 750–800 °C; V = extensive vitrification 900–950 °C; C = continuous vitrification 1000–1050 °C; DB = dark-burnished; GP = graphite-painted).

Sample	Chronological Horizon	DB	GP	Fabric	Refiring	Degree of vitrification
BEL 46	1 (C–D)			BEL–A1		C
BEL 68	1 (C–D)	X		BEL–A1	X	IV
BEL 94	1 (C–D)	X		BEL–A2	X	IV
BEL 95	1 (C–D)	X		BEL–A1	X	IV
BEL 115	1 (C–D)			BEL–B1		IV
BEL 116	1 (C–D)			BEL–B1		IV
BEL 118	1 (C–D)	X		BEL–A2	X	IV
BEL 123	1 (C–D)			BEL–A1		C
BEL 132	1 (C–D)			BEL–B1	X	IV
BEL 224	2 (Gradac–C)			BEL–A1		C
BEL 288	4 (A)			BEL–E		IV
BEL 295	4 (A)			BEL–A1		IV
BEL 303	5 (Starčevo/A)			BEL–C		IV
BEL 334	5 (Starčevo/A)			BEL–C		IV
PL 21–21	3 (Gradac I)	X		PL–A2		IV
PL 21–47	1 (Gradac II–III)	X		PL–A2	X	IV
PL 21–49	1 (Gradac II–III)	X		PL–A2	X	IV
PL 21–55	1 (Gradac II–III)	X		PL–A2	X	IV
PL 20–69	1 (Gradac II–III)			PL–E		IV
PL 24–23	1 (Gradac II–III)			PL–F		V
PL 24–83	1 (Gradac II–III)			PL–A1		IV
PL 24–103	2 (Gradac I)		X	PL–A1		IV
PL 24–124	2 (Gradac I)		X	PL–A2		IV
PL 24–129	2 (Gradac I)		X	PL–A2		IV
PI. 24–157	3 (Gradac I)	X		PL–A2	X	IV
PL 24–161	3 (Gradac I)	X		PL–A2	X	IV
PL 24–215	2 (Gradac I)		X	PL–A2		IV
PL 24–247	3 (Gradac I)		X	PL–A1		IV
PL 24–303	4 (B2)	X		PL–A1		IV
PL 24–313	5 (A2–B1)			PL–A1		IV

diffractograms against the 2006 International Centre for Diffraction Data-Joint Committee of Power Diffraction Standards (ICDD-JCPDS) database.

Selected samples from Belovode (n = 14) and Pločnik (n = 16) (Table 1) were also examined in fresh fracture under the SEM. The vitrification microstructure of the clay matrix was compared to published studies including Faber et al. (2009), Maniatis and Tite (1975, 1981) and Tite and Maniatis (1975a, 1975b) to provide an alternative assessment of firing temperature. Subsamples of five dark-burnished pottery sherds from each site (Table 1) were re-fired at 700, 750, 800, 850, 900, 950, 1000, 1050 and 1100 °C, respectively, for 1 h under reducing conditions, then studied in the SEM and their vitrification compared to the original specimens (Wolf, 2002). The samples were all gold coated and the analysis was carried out on a HITACHI S-3400N SEM using an accelerating voltage of 5 kV and an operating current of 110 µA with a variable working distance.

Non-destructive and locally resolved characterisation of the decoration of five 'graphite-painted' sherds from Pločnik was performed via X-ray microdiffraction (µ-XRD^2) using a Bruker D8 Discover-GADDS microdiffractometer with a Co-X-ray tube running at 30 kV/30 mA, a graphite primary monochromator and a 500 µm monocapillary X-ray optic with a 300 µm pinhole at the exit and a large 2-dimensional VÅNTEC-500 detector covering app. 40° in °2Θ and °Chi. (Berthold et al., 2015; Berthold and Mentzer, 2017; He, 2018). Micro-Raman spectroscopy was also performed using a Renishaw InVIA Reflex Raman microscope with a 532 nm laser for excitation and a 50× objective to discriminate between the different carbon modifications (Cuesta et al., 1998).

3. Results

The majority of the pottery from Belovode has a pale yellow to reddish yellow surface colour that indicates firing under oxidising conditions (Amicone, 2017, p. 152). Only those vessels with burnished/-polished surfaces appear to have been fired under reducing conditions, resulting in a darker light grey to very dark grey/black colour. Few of these display a homogenous very dark grey/black colour across their surface. In contrast, at Pločnik approximately 60% of the sherds from all five horizons exhibit grey and black shades associated with burnishing/polishing and more rarely with graphite decoration (Amicone, 2017, p. 190). These originate from bowls, pithoi, amphorae, amphorettae and other larger pots. This preference for dark pottery persists into Horizon 1 (Gradac III), although there is only rare evidence for burnishing at this point. Some black-topped sherds occur at both sites, for example in Horizons 4 and 5 (Vinča A2–B2). The colour of most of the examined sherds varies in cross section, indicating variable atmospheric conditions during firing and/or a short firing duration (Fig. 4). Fragments from Pločnik decorated with graphite exhibit a relatively homogeneous dark to light grey fabric in cross section (Fig. 4 f and h).

The petrographic composition of the ceramics (Table 3) from both sites and its comparison with the bedrock geology and raw material field samples indicates that the vast majority of specimens were locally produced with non-calcareous clay pastes (Amicone, 2017, pp. 154–160 and 192–198). The degree of optical activity of the clay matrices of the sherds under the microscope in crossed polarisers varies from sample to sample (Table 4). Some specimens especially those originating from layers in horizon 1 of both sites are optically inactive, suggesting firing above 900 °C. The majority of specimens exhibit weak to high optical activity indicating lower firing temperatures.

X-ray powder diffraction revealed a mineralogical assemblage of quartz and feldspar and less frequently amphibole. The majority of the samples also shows illite (Table 4; Fig. 5), though the identification of this clay mineral is hindered when muscovite is present due to the overlap between the main illite and muscovite peaks. Some samples exhibit a weak diffraction peak corresponding to a d-value of approximately 14 Å (Fig. 5 c), which points to either chlorite or probably montmorillonite.

The presence of clay minerals indicates that the maximum firing temperature of the majority of the analysed pottery samples must have been below 850–900 °C, at which their crystalline structure is destroyed

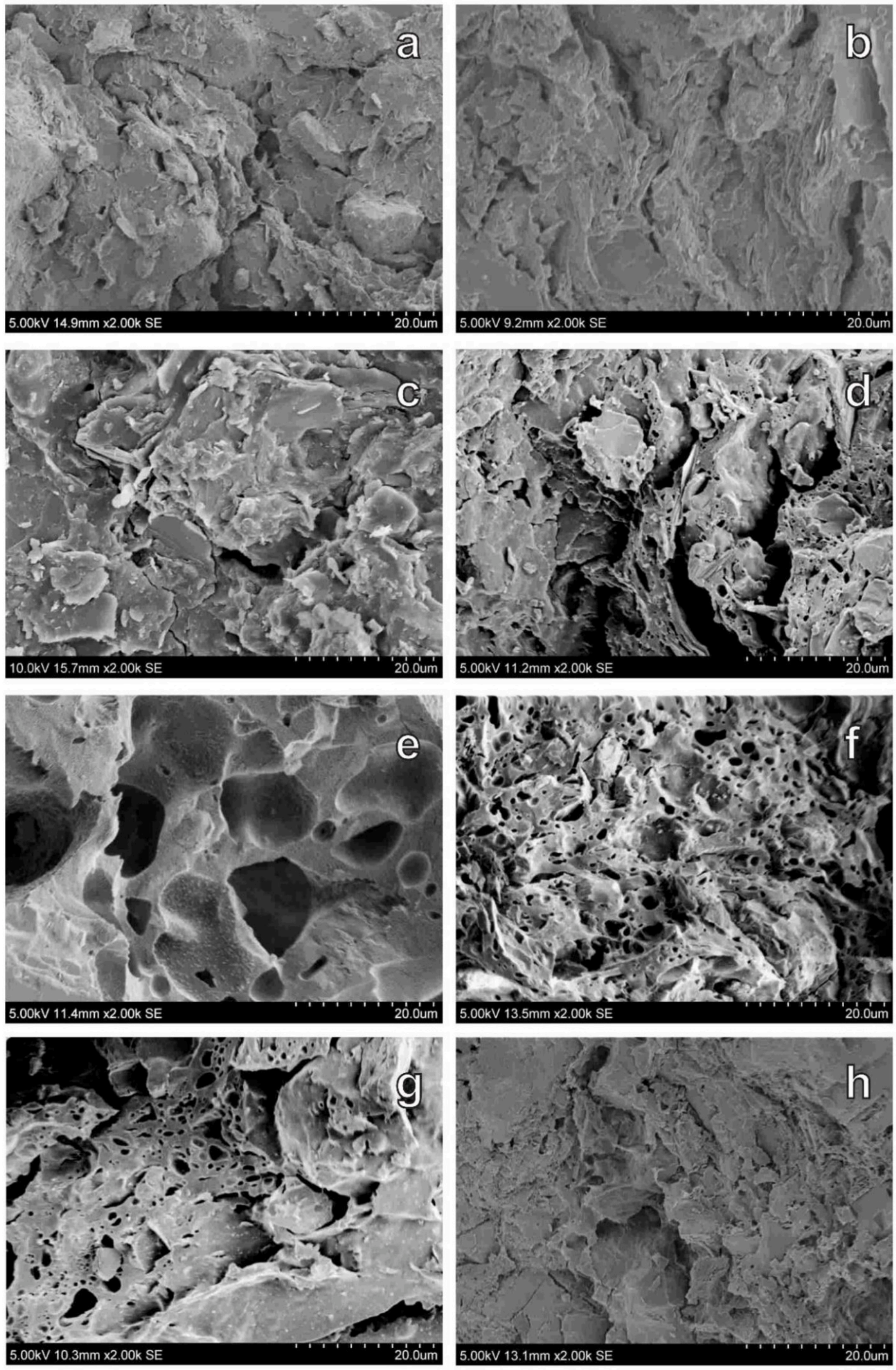

Fig. 6. Vitrification microstructure of selected pottery sherds from the Vinča culture sites of Belovode and Pločnik, as seen in the SEM under secondary electron imaging: a) BEL 118; b) PL 21–55; c) PL 24–215 (graphite-painted); d) PL 24–247 (graphite-painted); e) BEL 46; f) BEL 123; g) BEL 224; h) PL 24-23). See Table 5 for interpretation of vitrification stage and firing temperatures.

(Kulbicki, 1958; Maggetti, 1982). In addition, some samples contain calcite (d = 3.04 Å), which decomposes between 750 and 850 °C (Maggetti, 1982; Maritan, 2004).

The mineralogical composition of the ceramics suggests that most sherds, including the dark-burnished and graphite-painted pottery, were probably fired to a maximum temperature of between 750 and 850 °C. However, few sherds from Belovode and Pločnik (Fig. 5 e and f) contain high temperature neo-phases including cristobalite and spinel, recognisable from a broad reflection at d = 2.44 Å and d = 4.14 Å. These samples do not show presence of clay minerals, but contain hematite, which was not detected in any other of the sherds analysed. In non-calcareous clay pastes fired under oxidising conditions this mineral could begin to nucleate at about 700 °C. It may be below the limits of detection in the majority of samples given their relatively low concentration of iron (c. 6% Fe_2O_3) (Amicone, 2017, pp. 161–170 and 199–208) and their lower firing temperature.

The microstructure of thirty samples examined in fresh fracture in the SEM indicates that initial vitrification had taken place (Table 5; Fig. 6). This is compatible with an equivalent firing temperature of 800–850 °C in an oxidising atmosphere and 750–800 °C in a reducing atmosphere in both calcareous and non-calcareous clay (Maniatis and Tite, 1981, p. 61). One sherd decorated with graphite (PL 24–247)

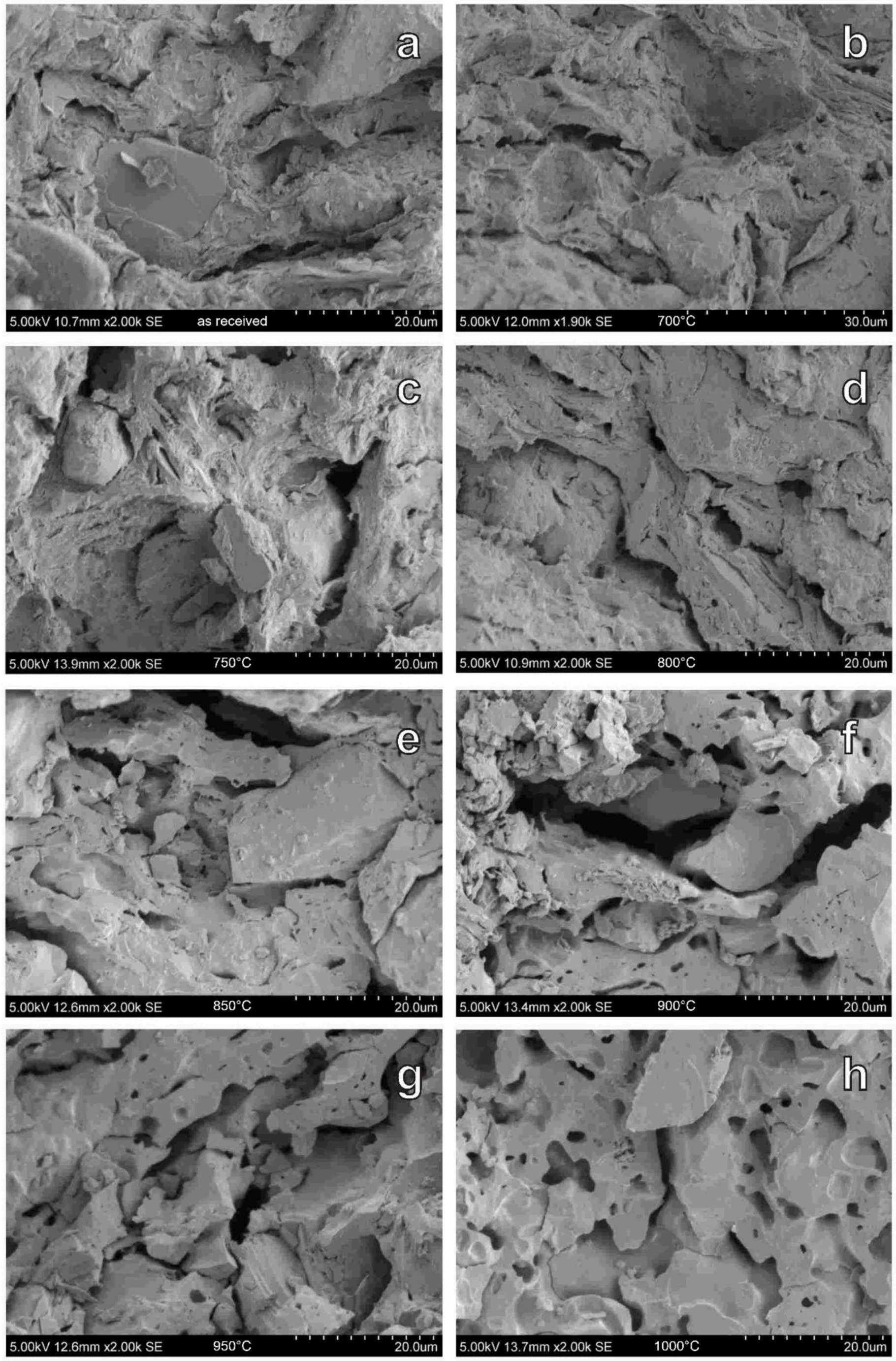

Fig. 7. Vitrification microstructure as seen in the SEM under secondary electron imaging of a dark-burnished (BEL 94) sherd from the Vinča culture site of Belovode, refired in reducing atmosphere at different temperatures: a) as received; b) 700 °C; c) 750 °C; d) 800 °C; e) 850 °C; f) 900 °C; g) 950 °C; h) 1000 °C.

revealed a microstructure more vitrified and with fine bloating pores that is compatible with more reducing conditions (Maniatis and Tite, 1981, p. 61). The re-fired dark-burnished sherds indicated a change in the vitrification microstructure between 750 and 800 °C (Fig. 7), thus confirming the above firing temperature estimate. Additionally, few samples from both sites that contain high temperature neo-phases exhibit an extensive or continuous degree of vitrification with or without bloating pores (Fig. 6 e-h), and could have been fired as high as 1000 °C. These sherds were not dark-burnished or graphite-painted and were either recovered from possible destruction layers or were examples of so-called 'chimneys' that were initially interpreted as connected to smelting activities. The 'chimney' theory was discarded after chemical analysis of these objects showed no contamination with metallic elements (Radivojević and Kuzmanović-Cvetković, 2014).

Analysis of the surfaces of the graphite-painted sherds from Pločnik via μ-XRD[2] indicates that both the undecorated and decorated areas contain quartz. However, in the diffractograms recorded on the decoration there is in most cases a small shift in the position of the quartz_{104} peak and significant increase in intensity that seems to signify the presence of graphite (Fig. 8). The latter has its main peak at almost the same angle as quartz, hindering secure discrimination between the two phases (Letsch and Noll, 1978, p. 1983). Analysis via μ-Raman spectroscopy (Fig. 8) confirmed that the graphite decoration in four specimens analysed consists of perfect crystalline and well textured flaky

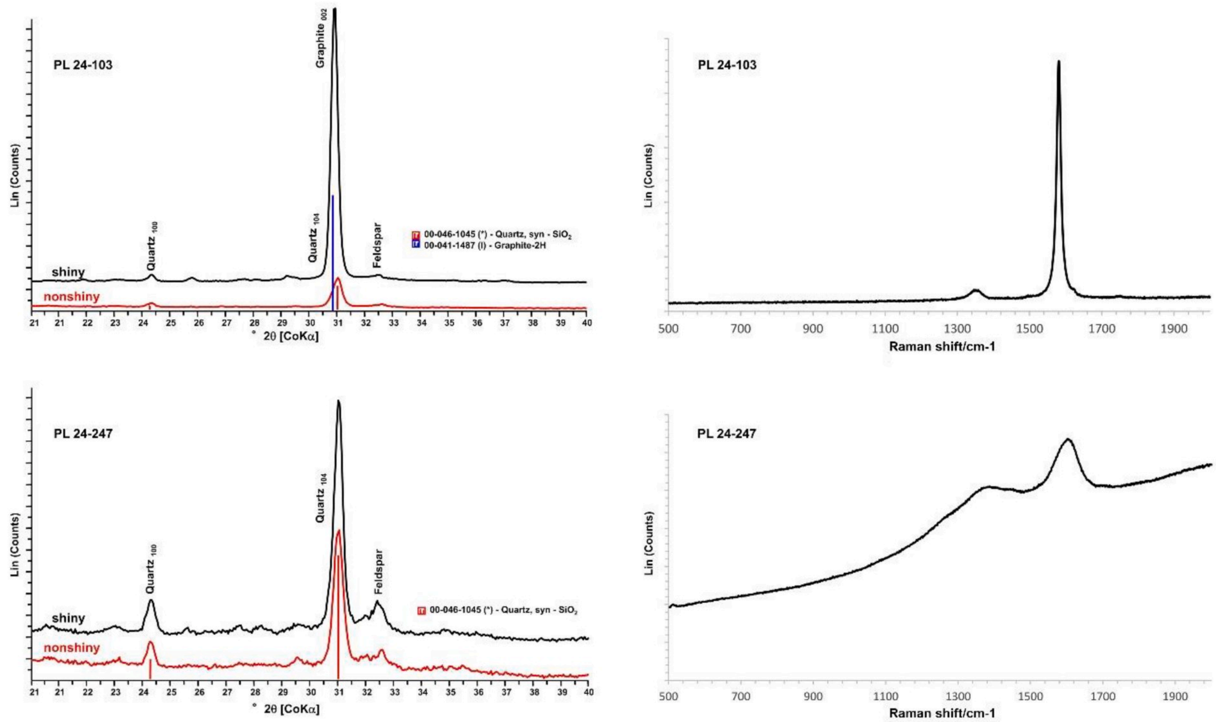

Fig. 8. Diffractograms and spectra revealing the mineralogical composition of the surface of selected graphite-painted pottery sherds from the Vinča culture sites of Pločnik in this study, collected via μ-XRD^2 (on the left) and μ-Raman (on the right).

graphite that is likely to come from a natural source. In one sample (PL 24–247), however, μ-Raman analysis suggests that the decoration consists of poorly crystalline carbon black (Fig. 8). This is the same type of carbon black pigment that is found on the undecorated dark-burnished ceramic.

4. Discussion

No secure evidence exists to provide information about the firing technology of Vinča pottery, such as kilns, workshops or wasters (Vuković, 2018), and it is not possible to exclude that ceramics were fired in bonfires or pits (Amicone and Berthold, 2019; Svoboda et al., 2004/2005; Vuković, 2018), which often leave no trace in the archaeological record. Nevertheless, the results of this archaeometric study on the fired pottery sherds together with the recent literature mentioned above helps to identify important aspects of Vinča ceramic pyrotechnology.

4.1. Reconstructing black pottery production

The surface colour of dark-burnished pottery could have been achieved in several possible ways, including iron reduction, manganese black or the carbon black smudging technique. Mineralogical analysis via XRPD analysis did not record the presence of magnetite nor manganese on the surface of any of the analysed sherds from either site, thus ruling out the first two methods of producing black pottery (see above, 1.2). However, carbon was detected on the surface of several dark-burnished sherds from both Pločnik and Belovode via μ-Raman analysis, suggesting that their lustrous black surfaces were the result of the carbon black smudging technique.

As most of the samples have a reddish core and dark margins, it is possible to propose a two-step firing procedure in which vessels were initially fired in an oxygen-rich atmosphere at which the maximum firing temperature was achieved and sintering started to take place, giving the ceramics their rigidity. Following this, as the temperature was decreasing towards the end of the firing process, a reducing atmosphere was created, probably by covering the firing installation and possibly adding some sort of readily combustible fine-textured organic material. This second step would have resulted in an increase in smoke and the deposition of carbon on the surface of the pottery. The absence of magnetite in the sherds indicates that the reducing phase was rather short and probably took place at the end of the firing. This is also indicated by the reddish core of the majority of the samples, suggesting a rather superficial penetration of carbon into the body of these vessels. Variation in the colour or the dark finish from black through light grey and yellow suggests that potters may not have been able to entirely control the firing atmosphere during the smudging phase. The presence of a small amount of free oxygen would have burnt off some of the carbon or prevented its deposition in places.

Graphite-painted Vinča pottery may also have been fired in a two-step firing procedure, with a longer reducing process given the relatively homogeneous dark to light grey colour of most of these sherds in thin section. The reducing phase would have started earlier in the process than in the production of black-burnished pottery, certainly before the initial oxidising phase would have reached a temperature of about 700 °C, at which point the graphite would have begun to burn off relatively quickly (Kreiter et al., 2013, p. 176, 2014). Despite the predominantly reducing conditions for most of the firing, sintering has been achieved, with estimated firing temperatures of most samples between 750 and 800 °C; the presence of bloating pores in one sherd (Fig. 6 d) indicated more reducing conditions (Maniatis and Tite, 1975).

Analysis of the ‘graphite’ painted decoration of one out of five selected samples using μ-XRD^2 and μ-Raman revealed that it was actually decorated with a type of artificial carbon black pigment which achieved a very similar metallic lustre to mineral graphite (the ‘Glanzkohlenstoff’ of Letsch and Noll, 1978, 1983), where the distinction from graphite painting is difficult to make by naked eye. This finding suggests that the same ‘graphite’ decorative effect on Vinča pottery could have been produced using several alternative technological processes that well show the technological advancements reached by the potters. Equally, it exhibits innovative solutions to decorate the pottery with metallic lustre, which also confirms distinctive metal-like appearance as one of the linking components between the metal and pottery technologies in the presented case.

Overall, the combination of petrographic, XRPD and SEM analyses of the Belovode and Pločnik sherds suggest that they were fired at a range of temperatures between 750 °C and 900 °C, with the majority of samples falling between 750 and 800 °C. Firing temperatures did not exceed c. 900 °C on a regular basis and only the two so-called 'chimney' fragments (which were not dark-burnished or graphite-painted) and few other sherds from possible destruction layers were heated to temperatures above 1000 °C.

4.2. Deconstructing the link between pottery production and metallurgy

Based upon the above reconstruction of Vinča culture ceramic pyrotechnology, it is possible to re-examine its purported link to the emergence of copper smelting in the Balkans, prominently proposed by Renfrew (1969), Kaiser et al. (1986), and others. In order to achieve the various decorative finishes applied to Vinča ceramics, potters were able to control the redox conditions of the firing process. The production of both dark-burnished and graphite-painted pottery would have been achieved by opening and closing the firing installation and thus varying the air to fuel ratio. Potters also seem to have added relatively moist organic matter, such as straw and leaves which combusted quickly and used up free oxygen while depositing soot, as well as perhaps ash.

This manipulation of firing atmosphere, particularly the ability to obtain and sustain reducing conditions, could have been an important precursor to the development of early metallurgy, which requires a predominantly reducing atmosphere to smelt copper from its ore before more oxidising conditions are introduced to reach the melting point of pure copper. It is certainly possible to envisage the transfer of this knowledge of manipulating and varying temperatures and redox conditions from ceramic production to another technological domain such as metallurgy.

The term invention is often defined as the discovery of a new idea, a new material or a new process (*e.g.* Lienhard, 2006; Radivojević, 2015; Renfrew, 1978). This can be a completely new product (Weber et al., 1993), or, alternatively, involve the recombination of pre-existing technological components for a new purpose (Fleming and Sorenson, 2004; Henrich, 2010), as appears to have been the case here. Even if the matter is still debated (*e.g.* Kaiser, 1984; Vucović, 2011; Spataro, 2018) and it is not possible to exclude that a certain degree of specialisation in pottery production existed among Vinča potters, no convincing arguments have been brought in thus far that demonstrated that this craft was a highly specialised activity carried out by professional figures that had privileged access to resources and technology. The stated argument is further corroborated by the fact that metalworking during its inception was most probably a non-specialised household activity, as already suggested in Radivojević and Rehren (2016). According to this scenario, craft knowledge was not segregated within certain specialised groups and could have been easily transferred from pottery making to other technological domains or vice versa.

The wider appearance of graphite decoration in particular seems to be contemporary with the emergence of metallurgy during the start of the fifth millennium BC across the Balkans (Bailey, 2000, p. 227; Vajsov, 2007) and requires a similarly strongly reducing atmosphere for much of the firing cycle as is required in copper smelting, as presented above. Based on current dating evidence placing graphite painted decoration in Pločnik at the onset of the fifth millennium BC, it is possible to suggest a parallel development or even reverse trajectory of transmission in which the production of a graphite-painted decoration was influenced by early metallurgy and they were both benefitting from the pre-existing experience with dark-burnished pottery.

Nevertheless, while graphite-painted decoration and metallurgy emerge in the Balkans at broadly the same period it is important to bear in mind that the current evidence seems to suggest that the earliest emergence of the two are geographically unrelated, with graphite-painted pottery probably first appearing in the Struma Valley (Vajsov, 2007), outside the Vinča Culture (Fig. 1), which was home to the earliest metallurgy (Radivojević et al., 2010).

At the same time, as a rare naturally occurring substance with a strong visual appeal, the use of graphite by potters across such a wide region could indicate that they participated in or benefitted from specialist trade networks; these networks may not have been the same as those of copper supply for the mentioned sites (Radivojević and Grujić, 2018) though they must have required similar cooperation patterns to meet the (high) demand.

Given all the above, to investigate better these themes more work focused on the study of graphite deposits in the Balkans, graphite circulation and on the origin and technological development of this decorative technique needs to be done.

5. Conclusion

The results of the present study suggest that the potters in the sites of Belovode and Pločnik were not normally using firing temperatures in excess of 750–800 °C, which were sufficient to produce functional pots, but not enough to melt copper metal. This clearly contrasts with the much higher temperatures proposed in early previous studies such as Frierman (1969; but see Kingery and Frierman, 1974) and Kaiser et al. (1986), and is instead more in line with the findings of Gardner (1978, 1979, 2003), Goleanu et al. (2005), Maniatis and Tite (1981), Perišić et al. (2016), Spataro (2014, 2017, 2018) and Yiouni (1995, 2000, 2001). While the firing temperatures to which the analysed samples were subjected would have been sufficient for solid-state reduction of oxidic copper minerals to copper metal (Pollard et al., 1991, p. 133; see Radivojević et al., 2017 for a detailed discussion of this phenomenon from an experimental context), the pottery firing installations would not have supplied enough energy to effectively smelt copper from its ore, or facilitate physical change from solid to liquid metal. This requires not only sufficiently reducing conditions, but a sustained temperature well in excess of 1000 °C to melt the micro-prills of copper metal formed at lower temperatures, and coagulate them to useable quantities of metal. Whilst it is possible that Vinča potters could have achieved higher maximum temperatures and energy levels within their firing installations, the analysis of sherds from Belovode and Pločnik do not record any clear evidence for this. The early over-estimation of ceramic firing temperatures by previous authors appears to have subsequently been over-interpreted to explain the very early appearance of copper smelting in this region. Our own work, building on more recent moderate temperature estimates from various sites across the Balkans (see references above), expands them with a systematic study of a large number of samples from two key Vinča sites for the emergence of metallurgy. In conjunction with more recent dating evidence for the emergence of graphite-painted pottery (Vajsov, 2007) and early metallurgy (Radivojević and Kuzmanović-Cvetković, 2014), respectively, this now makes a chronological sequence of the two phenomena less likely, let alone a causal technological sequence of metallurgy emerging directly from the firing technology used to produce black pottery.

Nevertheless, the results of this study and the recent literature indicate that Vinča pottery firing technology shares some significant similarities with the pyrotechnology of copper smelting, namely the ability to exert sufficient control over redox atmosphere of the firing process to produce a consistently shiny black appearance of dark-burnished and graphite-painted pottery.

Noteworthy, the technique that appears to have the strongest link with copper smelting is the graphite decoration, as it is the one that relies the most on a nuanced understanding of the balance of redox conditions and of the two-step principle of alternating between reduction and oxidation stages during firing. The latter applies to both graphite decorating and metal smelting, albeit in different order. With this in mind, the two crafts are likely to have been generally linked, making them 'close cousins' rather than one being the precursor to the other.

Tantalisingly, graphite is also visually appealing as a lustrous black mineral, and as such may have been part of the same supply chain and conceptually included by early prospectors in the suite of black-and-green minerals that lies at the heart of the earliest metallurgy in the Balkans (Radivojević and Rehren, 2016). This supply chain is only one of the building blocks of this connection; the main output of aesthetically appealing materials with high brilliance certainly fits the practices of exceptional craftsmanship (Chapman, 2011) and even more importantly, the increased demand for it at the time.

Author contributions

Silvia Amicone: conceptualisation, investigation, methodology, archaeometric analyses and their interpretation, writing (original draft). Miljana Radivojević: funding acquisition, project administration, conceptualisation, investigation, supervision, editing and reviewing (original draft). Patrick Quinn: investigation, methodology, supervision, validation, writing, editing and reviewing (original draft). Christoph Berthold: investigation, methodology, supervision (XRD and Raman analyses), validation, editing and reviewing (methods and results sections). Thilo Rehren: funding acquisition, conceptualisation, investigation, supervision, editing and reviewing (final draft).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are indebted to all those who contributed to the archaeological excavation of Belovode and Pločnik settlements during the summer excavations seasons in 2012 and 2013. Financial support for this research has been generously provided by the Arts and Humanities Research Council (AHRC), the Institute for Archaeo-Metallurgical Studies (IAMS), and the Funds for Women Graduates (FfWG). We would like to thank Julka Kuzmanović-Cvetković, Gordana Grabez, Dusko Sljivar, and the National Museum in Belgrade for securing access to materials. We are also indebted to Enrica Bonato, Michael Charlton, Annette Flicker, Lars Heinze, Tobias Kiemle, Tobias Kienlin, Evangelia Kiriatzi, Frieder Jakob Lauxmann, Neda Mirković-Marić, Miroslav Marić, Lionello Morandi, and Jugoslav Pendić for their help and feedback. Silvia Amicone and Christoph Berthold would like to express their gratitude to the Excellence Initiative of the Eberhard Karls Universität Tübingen and the Ministry for Science, Research and Art of Baden-Württemberg for their support during the preparation of this article. Constructive comments by reviewers and the editor helped us strengthen the paper, and are much appreciated. All remaining shortcomings are ours.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jas.2020.105123. The data that support the findings of the study (sample pictures, SEM micrographs and XRPD measurements) are openly available at https://doi.org/10.7910/DVN/YLZVJC.

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