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Digging deeper: Insights into metallurgical transitions in European prehistory through copper isotopes

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A B S T R A C T

Southeastern Europe is the birthplace of metallurgy, with evidence of copper smelting at ca. 5000 BCE. There the later Eneolithic (Copper Age) was associated with the casting of massive copper tools. However, copper metallurgy in this region ceased, or significantly decreased, centuries before the dawn of the Bronze Age. Archaeologists continue to be debate whether this hiatus was imposed on early metal-working communities as a result of exhaustion of workable mineral resources, or instead a cultural transition that was associated with changes in depositional practices and material culture. Copper isotopes provide a broadly applicable means of addressing this question. Copper isotopes fractionate in the near-surface environment such that surficial oxide ores can be differentiated from non-weathered sulphide ores that occur at greater depth. This compositional variation is transferred to associated copper artifacts, the final product of the metallurgical process. In the central Balkans, a shift from 65Cu-enriched to 65Cu-depleted copper artifacts occurs across the metallurgical hiatus at the Eneolithic-Bronze Age boundary, ca. 2500 BCE. This indicates that the reemergence of metal production at the beginning of the Bronze Age is associated with pyrotechnical advancements that allowed for the extraction of copper from sulphide ore. Thus copper isotopes provide direct evidence that the copper hiatus was the result of exhaustion of near-surface oxide ores after one-and-a-half millennia of mining, and that the beginning of the Bronze Age in the Balkans is associated with the introduction of more complex smelting techniques for metal extraction from regionally abundant sulphidic deposits.

1. Introduction

The extent to which humans manipulated and used Earth's rock and mineral resources forms the basis for the classic subdivisions of prehistory (stone, bronze, and iron ages). Here we focus on the transition of technologies associated with the smelting of copper ores and their relationship to the beginning of the Bronze Age in southeastern Europe. The copper mineral malachite ($Cu_2CO_3[OH]_2$), with its intense green color, has been used to manufacture beads since the dawn of agriculture 10,000 years ago (Bar-Yosef Mayer and Porat, 2008). However, the first instance of intentional extraction of copper from this mineral through pyrotechnology appears to have occurred at 5000 BCE by the Vinča culture of Serbia (Radivojević et al., 2010). There the Eneolithic began with the production of small jewelry pieces and rapidly progressed to the casting of massive copper shaft-hole axes (Fig. 1) for approximately 1500 years (Jovanović, 2009; Sava, 2015). However, copper metallurgy ceased, or dramatically decreased, in the mountains of southern Serbia and the adjacent Pannonian Plain (Vojvodina, Hungarian Plain, Romanian Banat) in the mid-fourth millennium (Sava, 2015), centuries before the Bronze Age began (O'Brien, 2014; Sherratt, 1997; Spasić, 2010; Tasić, 2003) (Fig. 2). A similar hiatus in

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Fig. 1. Variation in form and size of typical axes from the Eneolithic to the Early Bronze Age of Serbia.

copper production occurred at the end of the Eneolithic and Early Bronze Age in southwest Spain (Rothenberg and Blanco-Freijeiro, 1981), and the Adige Valley of northeastern Italy during the Middle Bronze Age (Cierny et al., 1998). Whether any, or all, of these lulls in metal production were the result of a cultural shift or depletion of mineral resources due to extended periods of mining remains a subject of debate (Kienlin, 2014, 2016; O'Brien, 2014).

Eneolithic cultures in Serbia appear to have relied on oxide ores: malachite fragments and beads are common in settlements of that age (Glumac and Trigham, 1990; Radivojević and Kuzmanović-Cvetković, 2014); sulphide minerals were intentionally sorted from oxide ores at Eneolithic mine sites (Jovanović and Ottaway, 1976); rare Eneolithic slag fragments are compositionally consistent with malachite-bearing ore (Glumac and Todd, 1991; Radivojević et al., 2010). Smelting of copper oxides is a relatively simple, potentially slagless process that can be conducted in a modified hearth-like structure (Craddock, 2001; O'Brien, 2014; Timberlake, 2007), as has been found in several Balkan sites (Radivojević and Rehren, 2016; Rehren et al., 2016). The same pyrotechnology can be used to extract copper from mixed oxide-tetrahedrite (fahlore) ore (Bourgarit, 2007). This form of copper production supplied much of the copper of central Europe in the Early Bronze Age (Höppner et al., 2005), and may have been employed at European Eneolithic sites where fahlore ores ($[Cu,Ag]_6Cu_4(Fe,Zn]_2[As,Sb]_4S_{13}$) were present (Bougarit, 2007). However, this is not the case in Serbia where such deposits are rare, and the vast majority of early copper artifacts lack the As-Sb-Ag-bearing composition that is indicative of a fahlore ore source.

The production of copper from the far more plentiful, purely sulphidic ore (predominantly chalcopyrite; $CuFeS_2$) is a more complex, multi-stage process that requires contrasting oxidation conditions, specialized furnaces, and the controlled inclusion of fluxing agents (Bourgarit, 2007; Craddock, 2001). The earliest definitive evidence for multi-stage chalcopyrite smelting in continental Europe is associated with the ore deposits of Mitterberg, Austria in the Middle Bronze Age (1600-1200 BCE) (Stöllner, 2009, as cited in O'Brien, 2014; Pernicka et al., 2016) where "*the scale of production achieved during the Middle Bronze Age was at a level that can arguably be described as industrial*" (O'Brien, 2014, p.164). However, the presence of slag with copper matte inclusions from Eneolithic sites in Bulgaria (Ryndina et al., 1999) suggest that mixed malachite-chalcopyrite ores may have been exploited to some extent at that time. Whether such mixed ores were processed by repeated cycles of crushing and smelting (Bourgarit, 2007), or the first introduction of a two-step, roasting and smelting process (Ryndina et al., 1999) is uncertain.

It has been speculated that the marked reduction in metal production in southeastern Europe in the latest Eneolithic may have been due to social forcings (Kienlin, 2013; Weninger et al., 2009), or alternatively, to the exhaustion of surficial oxide-bearing ores and the technical inability to smelt the underlying sulphide minerals (Papalas, 2008; Sherratt, 1997). However, definitive archaeological evidence associated with metallurgical processes (e.g., slag, crucibles) at the Eneolithic-Bronze Age transition in the Balkans is exceedingly rare, and so this hypothesis has remained conjectural and disputed. Although "*lowly slag is rarer than gold*" (Papalas, 2008, p. 93), an estimated 4.7 tonnes of Eneolithic copper artifacts survive in the Balkan region (Pernicka et al., 1997). Advances in our understanding of copper isotopes and their variance with respect to copper ore mineral composition provides a new approach to investigating ancient mining practices through analysis of copper artifacts, the final product of the metallurgical process. Copper isotope analysis of 120 artifacts (Table 1) from across Serbia, and adjacent sites in Bosnia and the Romanian Banat (Fig. 3), spanning a 3500-year age range from the middle Eneolithic to the Early Iron Age, indicate that not only were local copper oxide ores depleted by the end of the Eneolithic, but that the critical pyrotechnological advancement of the smelting of

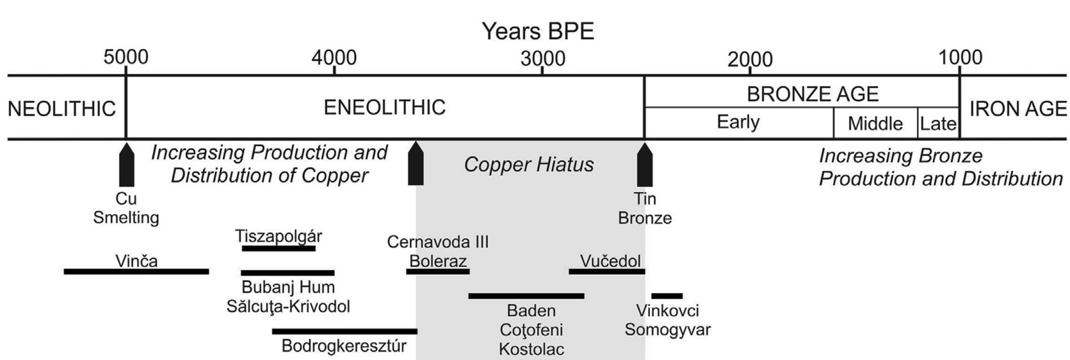

Fig. 2. Chronological framework for the study area comprising Serbia, including the Vojvodina and the contiguous Romanian Banat. Data compiled from Filipović (2013), Kalafatić (2006), Pătroi (2013), Sava (2015), and Tasić (2003).

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