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Copper isotopes as a means of determining regional metallurgical practices in European prehistory: A reply to Jansen (2018, J. Arch. Sci. 89)

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ABSTRACT

We present a detailed response to the critique by Mr. Jansen of the paper "*Digging Deeper: Insights into Metallurgical Transitions in European Prehistory through Copper Isotopes*". When we consider Cu isotope ratios of European Eneolithic and Early Bronze Age artifacts in the context of their local geological settings, climates, and archaeological contexts, Mr. Jansen's hypothesis that ^{63}Cu enrichment results from the adoption of fahlore ores is untenable. In both Serbia and Central Europe, the earliest copper production is associated with ^{65}Cu-enriched ores and subsequently produced artifacts yield lower ranges δ^{65}Cu. This shift in Cu isotopic composition correlates with the initial use of predominantly hypogene ores, not with variations in their trace element content. Essentially the expanded dataset supports the conclusions that were presented in the original paper—Cu isotopes are an effective means of delineating the transition from oxide-based smelting to methodologically more complex smelting of sulphide ores in prehistoric Europe with its relatively limited production and trade. Mixing did not mask the critical Cu isotope signatures in this setting. Therefore, Cu isotope compositions of artifacts can be used to interpret the mineralogical character of the ores from which they were produced, regardless of their provenance, as long as trade networks remained within a region of similar climatic history.

In "*Digging Deeper: Insights into Metallurgical Transitions in European Prehistory through Copper Isotopes*", Powell et al. (2017) investigated the Late Eneolithic metallurgical hiatus in Serbia, and the re-emergence of metal production in the region at the beginning of the Bronze Age. Based on a shift from ^{65}Cu-enriched to ^{65}Cu-depleted copper in artifacts across the Eneolithic-Bronze Age boundary at 2500 BCE, we concluded that the gap in metal production was due to the exhaustion of accessible near-surface oxide ores within the modern geographic region of Serbia. However, in his comment regarding this study ("*On the Use of Cu Isotopes in Archaeometallurgy*"), Mr. Jansen offered an alternative interpretation of our Balkan Cu-isotope dataset. Specifically, Jansen (2018) asserted that: 1) oxidized ore resources of Serbia were not deleted over the 4000-year interval of the Eneolithic and Bronze Age; 2) the observed shift in Cu isotope composition was driven by the widespread adoption of previously unexploited As-rich ores due to the introduction of a new preference for aesthetic and working properties; and 3) Cu isotope studies of artifacts can be interpreted only if ore provenance is known (e.g., Pb isotope fingerprinting).

In this reply, we address Jansen's misleading estimate of Serbia's prehistoric mineral wealth by discussing apparent misconceptions involving geological processes associated with the formation of both hypogene and supergene copper deposits. Secondly, we present new Cu isotope data from Bronze Age artifacts from Central Europe as a test of Jansen's hypothesis that a transition to fahlore

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ores is the causal factor in the lower δ^{65}Cu values in the European Early Bronze Age. Certainly, where possible, multiple independent analytical approaches should be brought to bear on the study of ancient metallurgical processes; compositional analysis of related metallurgical by products, direct evidence of mining activity, and isotopic provenance each provide valuable insight. Unfortunately, multiple lines of inquiry are not always possible due to a paucity of archaeological finds. In such cases (e.g., Serbia), we argue that the Cu isotopic system is robust enough that patterns in δ^{65}Cu alone can be used to elucidate trends in mining and smelting practices in pre-Iron Age Europe.

1. Climate and the development of supergene copper ores

Jansen (2018) asserts that Serbian copper oxide ore reserves could not have been exhausted over several millennia based on the volume of oxidized ore processed at sites such as Faynan (Jordan), where it is estimated that a minimum of 5000 tons of copper were produced during the Iron Age alone (Hauptmann, 2007). Without providing evidence, he implies that similar volumes of ore would have been available in Serbia, and would have been sufficient to supply Balkan metallurgical demands well into the Bronze Age. However, this is inconsistent with the character of Serbian ores and the geological processes by which they formed.

There is a marked difference between development of oxidized ores in the Levant and the Balkans that is due, in part, to the contrasting long-term climates of the two regions. Local climatic and geomorphological factors have been linked to supergene enrichment (Alpers and Brimhall, 1989; Chavez, 2000; Titley and Marozas, 1995; Vasconcelos, 2015). Most studies argue the need for semi-arid to arid conditions in which there are large fluctuations of the position of the water table that promotes extensive vertical migrations of copper. Such conditions that are conducive to extensive and deep oxidation exist in the Levant. However, palaeoclimatic proxies indicate that the Central Balkan region experienced persistent warm and humid conditions throughout the later Neogene (10 Ma) (Utescher et al., 2017), followed by humid glacial and more arid interglacial cycles during the Pleistocene (2.8 Ma) (Zech et al., 2013). Stable temperate, moist conditions have prevailed since the beginning of the Holocene (11.0 ka). Therefore, no extensive supergene oxide enrichment caps could have developed over Balkan copper orebodies. Instead, thin zones of Cu oxides formed in the narrow interval between the ground surface and the water table, and with incomplete oxidation, these ores would have contained considerable amounts of relict sulphide impurities (Fig. 1). This is supported by the work of Jovanovic and Ottaway (1976) who noted that oxides and sulfides were sorted from the ores of Rudna Glava in the Eneolithic. Whether this mine site was exploited for smelter-feed, at least in part (Jovanovic and Ottaway, 1976), or exclusively for ornamental malachite as Jansen states in his comment, is irrelevant; Rudna Glava provides an example of the composition, and most likely the upper size limit of the shallowly-worked Balkan copper mines that were exploited in the Eneolithic. Each of these small impure oxide bodies would have been sufficient only to serve local, small-scale metal production for a limited time.

2. The Early Bronze Age in Central Europe

Although small scale or experimental use of local copper resources in the Eneolithic has been documented, pre-Bronze Age copper in the Eastern Alpine region was likely imported from the Majdenpek area of Serbia (Höppner et al., 2005; Frank and Pernicka, 2010). Well documented examples of exploitation of Austrian copper deposits date to the Early Bronze Age (2150-1700 BCE, Stockhammer et al., 2015), associated with the production of copper with significant As and Sb impurities (Kienlin and Stöllner, 2009; Pernicka et al., 2016). Thousands of high-As copper ring ingots (Ösenringbarren; Early Bronze Age) and rib ingots (Spangenbarren; latest Early to Middle Bronze Age) having been discovered mostly in hoards from the western Alps to the Baltic Sea, and into the Carpathians, with the largest concentration in southern Germany, Austria and the Czech Republic (Junk et al., 2001; Chvojka and Havlice, 2009; Frána et al., 2009; Kienlin and Stöllner, 2009). The Cu-As-Sb-Ag ± Ni composition of ring ingots is consistent with their derivation from ores associated with minerals in the tetrahedrite-tennantite series (fahlore ores) that occur in the region (e.g., Schwaz Brixlegg).

Despite the abundance of metal artifacts from the Early Bronze Age in Central Europe, little evidence of mining and smelting has been uncovered from this time, and few settlements are related to mining and copper production, suggesting that mining occurred on a small scale, probably seasonally (Kienlin and Stöllner, 2009). Recently one mining settlement, which was coeval with Ösenringe production, was discovered in the Inn Valley of Austria, in association with the Cu-As-Sb-Ag mineralization of Brixlegg (Martinek, 2011). Finds from this site indicate that the ore consisted of a mix of oxides and sulphides which were co-smelted using a one-step process similar to that used to smelt oxide ore (both pure and mixed) in the Eneolithic (Martinek, 2011).

Although mining began in the region in Early Bronze Age with the exploitation of at least partially oxidized ores, it appears that these deposits were exhausted or of diminished importance by the Middle Bronze Age when industrial-scale mining of chalcopyrite ore was developed at Inn Valley sites, including Mitterberg (Höppner et al., 2005; Kienlin, 2013). The short duration of primarily oxide-based mining in the Alps relative to that which occurred in Serbia and the Levant is consistent with the climatic conditions of the region and the high elevation at which the ores occur. Pleistocene glaciation would have scoured away any pre-existing surficial oxide caps. With the Last Glacial Maximum ending approximately 20,000 years ago (Ehlers and Gibbard, 2004), Eastern Alpine ores would have been exposed to weathering processes for less than 15,000 years (Reuther et al., 2011). Therefore, oxidized zones would be poorly developed over Alpine copper deposits, being thin, only partially oxidized, and lacking a distinct enrichment zone of secondary sulphides (Fig. 1).

3. Comparison of Serbian and Central European artifact compositions

The range of δ^{65}Cu for 122 Serbian artifacts from the Eneolithic through the Bronze Age, as reported in Powell et al. (2017), is illustrated in Fig. 2a. The distinct shift from positive to negative δ^{65}Cu across the Bronze Age boundary is comparable to the δ^{65}Cu variation between local malachite and sulphide ores, including a significant component of enriched sulfide ore (Fig. 2b) (Lazarov et al., 2011; Lazarov and Horn, 2015).

Forty-four new copper isotope analyses of Central European artifacts are presented in Fig. 2c and Table 1. This new data set includes artifacts from the Salzburg region of Austria, and across the Bohemian region of the Czech Republic. Eneolithic Serbian artifacts and earliest Bronze Age artifacts from Central Europe exhibit an almost identical range of δ^{65}Cu (approximately 0 to +2‰) which is consistent with an oxide-based ore containing varying fractions of sulphide impurities. Independent archaeological data confirms such ore in the Eneolithic in Serbia (Radivojević et al., 2010) and the earliest Bronze Age in Central Europe (Martinek, 2011). Therefore, there is little doubt from both a geological and archaeological perspective that the earliest copper production in both localities involved simple reduction-based smelting methods involving

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