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On the use of Cu isotope signatures in archaeometallurgy. Some considerations on “Digging deeper: Insights into metallurgical transitions in European prehistory through copper isotopes” by W. Powell et al. / Journal of Archaeological Science 88, pp. 37–46

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A B S T R A C T

Cu isotope characterization of copper-based artifacts is a powerful tool used in recent decades to investigate the types of ore smelted in ancient metal production. Within a larger sample set, Powell et al. (2017) have identified a shift from positive δ^{65}Cu values obtained for Eneolithic artifacts in the Balkans (5000–3600 BC) to more moderate and negative δ^{65}Cu values of Bronze Age artifacts (2500–1000 BC), with a so-called “copper hiatus” between these two periods. Powell et al. concluded that accessible oxidized ore sources in this region were totally exhausted by the end of the Eneolithic period, directly leading to a “hiatus” in copper production. After the “hiatus”, starting with the Early Bronze Age, they proposed that sulfide ores were smelted using the Mitterberg process. The current paper addresses some weaknesses of the arguments put forth by Powell et al. and instead argues that Cu isotope ratios must be jointly considered with additional archaeometallurgical and archaeological investigations. Selective changes in preference for metal alloys likely affected the Cu isotope composition. Metallurgical operations using distinct Cu isotope reservoirs can alter the univariate Cu isotope ratio (^{65}Cu/^{63}Cu). Key points that must be considered are the transition from pure copper in the Eneolithic to arsenical copper in the Bronze Age, the co-smelting of distinct ore types, and the co-melting of metals derived from multiple smelting operations or from re-used metal artifacts. Moreover, there is no archaeological evidence for the Mitterberg smelting process in the Balkans during the Early Bronze Age.

1. The investigation of Cu isotopes in archaeometallurgy

Cu isotopes in archaeometallurgy were first studied in the mid-1990s by members of the Isotrace Laboratory in Oxford (Gale et al., 1999; Woodhead et al., 1999). Since then, several scholars have investigated the potential of Cu isotopes in archaeometallurgy (Artioli et al., 2008; Balliana et al., 2013; Bendall, 2003; Bower et al., 2013; Desaulty et al., 2011; Durali-Müller, 2005; Jansen et al., 2017; Klein et al., 2002, 2004, 2007, 2009, 2010; Markl et al., 2006; Mathur et al., 2009a, 2014). A brief overview of these studies is given by Jansen et al. (2017).

The investigation by Powell et al. (2017) provides the first comprehensive dataset for copper-based artifacts from the Balkans and presents Cu isotope composition information to identify the types of ore used for the primary production of copper, i.e. if primary (hypogene) or secondary ore sources like oxidized or supergene sulfide ore minerals were smelted. The idea to characterize archaeological copper-based artifacts and determine their ore types was first postulated by Klein et al. (2009, 2010). For sourcing with isotopes, the isotopic composition must not be altered due to metallurgical operations. Fractionation of Cu isotopes was not detected during experiments using technology available in ancient times (Gale et al., 1999) and modern copper production (Mathur et al., 2009a), since these are high-temperature processes and Cu isotope fractionation occurs at low temperature, e.g. due to weathering processes (Mathur et al., 2009a). However, recent laboratory experiments showed that fractionation processes during smelting could occur even at higher temperatures and might be

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controlled by parameters other than temperature (Rose et al., 2016). Copper from the late stage of smelting and slagged ore derived from this experiment showed lower δ^{65}Cu values than the starting composition of the ore, making further research necessary. Hence, especially the study of Cu isotope composition of slag to characterize types of ore used in ancient smelting operations as presented in our previous study (Jansen et al., 2017) may result in faulty interpretations.

In this paper, the main conclusions of the work by Powell et al. are disputed: First, it was postulated that a “copper hiatus” (basically a decrease of copper artifacts in the archaeological record) at the end of the Eneolithic was caused by a total exhaustion of accessible oxidized ores (p. 44). Second, it was postulated that the Mitterberg process was introduced in the Early Bronze Age for the production of copper from sulfide ores (p. 44).

1.1. Cu isotopes and the balkans

Powell et al. analyzed 120 copper-based artifacts from the Balkans for their Cu isotope composition. The artifacts were divided by their age into five groups: Eneolithic, Early Bronze Age, Middle Bronze Age, Late Bronze Age, Iron Age (Table 1 and Fig. 5 in Powell et al.). Based on the mean and distribution of δ^{65}Cu values, shifts in ore types were discussed. First, it is worth mentioning that there is an overlap between the distribution of all groups (Fig. 5 in Powell et al.), indicating that the same ore mineral types (oxidized, and supergene and hypogene sulfide ores) could have been used in any of the periods.

Higher δ^{65}Cu values and a higher mean were detected in the Eneolithic artifacts than in the later periods. At the end of the Eneolithic in the Balkans, the number of copper artifacts in the archaeological record decreases but not fully ceases. This period of approximately a millennium is indicated by Powell et al. as the “copper hiatus”. After this period, more moderate and negative δ^{65}Cu values of Bronze and Iron Age artifacts were detected. The authors concluded that the accessible oxidized ore sources (characterized by more variable and higher δ^{65}Cu values) were totally exhausted during the preceding Eneolithic, causing the so-called “copper hiatus” since “oxide-based smelting techniques would have failed to produce metal from this ore (sulfide ore)” (Powell et al. p. 44).

1.2. Full exhaustion or cultural choice?

The study of Powell et al. presented that in the Eneolithic most probably a larger portion of oxidized ores was used than in the Bronze Age. One of the potential origins of oxidized ores for the Eneolithic artifacts discussed by Powell et al. (p. 44) are the Eneolithic mines of Rudna Glava (Serbia). A major problem is that these mines have already been excluded as a source for Eneolithic copper from Serbia and Bulgaria based on previous analysis by Pernicka et al. (1993, 1997) and Gale et al. (2003). Hence, Rudna Glava should not be discussed in the context of metallurgy in the Eneolithic period. While the deposit of Aibunar (Bulgaria) was also mentioned by Powell et al. (p. 44), additional deposits require consideration: Rosen (Bulgaria), Majdanpek (Serbia), and as-of-yet unidentified ore deposits recognized through Pb isotope analysis in combination with trace element fingerprinting of Serbian artifacts by Pernicka et al. (1993, 1997). Aside from some early tin bronzes of the Vinca culture likely made from complex tin-copper-bearing ores (Radivojevic et al., 2013), the copper of the Balkan Eneolithic is very pure and unalloyed. Pure copper may originate from smelting oxidized ores or melting native copper which is in agreement with the δ^{65}Cu values presented by Powell et al.

It was shown by Pernicka et al. (1993, 1997) that copper in the Balkans was smelted from ores of multiple deposits. In total, 4700 kg of copper-based artifacts from the second half of the 5th and the first half of the 4th millennium BC has been found in South-Eastern Europe (Pernicka et al., 1997). Needless to say, this does not represent the entire amount of copper that was smelted during this early period, but it is hard to believe that exploitation of ores for an amount of copper in this order could, as proposed by Powell et al. have resulted in a complete exhaustion of accessible oxidized ores from multiple copper deposits. Just to give an impression but geographically and chronologically un-related to the Eneolithic Balkans, 50,000 to 60,000 tons of slag were found at the Iron Age smelting site of Khirbat en-Nahas in Jordan (Hauptmann, 2007, pp. 127–130). Giving a metal to slag ratio of 1:10, this single smelting site produced thousand times more metal using the oxidized ore sources from Faynan than the amount which is recorded from the Eneolithic Balkans.

So, are Powell et al. correct in proposing an exhaustion of oxidized ore sources based on shifting Cu isotope ratios? By putting the artifacts within the context of previous archaeometallurgical studies, an alternative interpretation can be made. There are substantial differences between earlier Eneolithic copper and the copper of the Baden culture and the Early Bronze Age, when the use of arsenic-rich copper arose. Pernicka et al. (1993) have demonstrated that copper with higher amounts of arsenic and impurities such as antimony is typical for the Baden culture at the end of the Eneolithic period (during the “copper hiatus”) and for Early Bronze Age Serbia. Arsenical copper, as well as the so-called fahlore copper (which contains arsenic, antimony, silver and nickel in varying amounts), is characterized by a silver color, a greater hardness than pure copper (which can be drastically increased by cold working), and improved casting properties (e.g. lower melting point).

The production of arsenical copper is a heavily debated topic in archaeometallurgy. Smelting of sulfide ores like fahlore (tennantite) and enargite may result in such “dirty” copper, as well as complex copper-mineralization bearing minerals like chalcopyrite and arsenopyrite, co-smelting of oxidized ores with such sulfide components (see discussion below), or the intentional adding of speiss (byproduct of sulfide smelting) or realgar and oripigment to molten copper (for a recent overview on production of arsenical copper, see Boscher, 2016). The selection of these ores and adapted smelting technologies were no doubt rooted in a preference for specific aesthetic and working properties. In conclusion, the general shift in Cu isotope composition from the Eneolithic to the Early Bronze Age copper likely stems from larger cultural shifts that are at least in part related to preferences for the appearance and workability of copper rather than the complete exhaustion of oxidized copper in the Balkans. Given the overlap in δ^{65}Cu values, notably the positive values, it is very likely that some oxidized copper production continued well into the EBA.

1.3. Homogenization of Cu isotope compositions through metallurgical processes

It is apparent that archaeological copper-based artifacts presented in numerous studies have a much more moderate and homogenous Cu isotope composition than was found for secondary copper ores of deposits. For example, only five out of the 120 artifacts presented by Powell et al. do not cluster within δ^{65}Cu = -1 to +1‰, which is the typical range found for primary ores (Mathur et al., 2009b). Why do we not find such extreme ratios, e.g. identified for secondary ores like δ^{65}Cu = -16 to +12‰ by Mathur et al. (2009b), or δ^{65}Cu = -2.92 to +2.41‰ by Markl et al. (2006)? If metallurgical operations do not fractionate Cu isotopes (Gale et al., 1999; Mathur et al., 2009a), this might be a result of mixing and homogenizing Cu isotope reservoirs during different metallurgical

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