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On the use of Cu isotope signatures in archaeometallurgy: A comment on Powell et al.

Moritz Jansen

Center for the Analysis of Archaeological Materials, University of Pennsylvania Museum of Archaeology and Anthropology, 3260 South Street, Philadelphia, PA 19104, USA

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ABSTRACT

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 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

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E-mail address: moritzj@upenn.edu.

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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 processes.

Powell et al. proposed the introduction of the so-called Mitterberg process in the Early Bronze Age Balkans, which is well-documented for Middle and Late Bronze Age smelting sites in the Alps (Eibner, 1982; Cierny, 2008), but not for the Balkans at all. In this process, sulfide ores were sorted, crushed and enriched through panning. They were partly oxidized by roasting in a bonfire prior the smelting process using open furnaces. Both rich supergene (secondary) sulfides as well as hypogene (primary) sulfides can be used in such processes. Following the values by Powell et al. the produced metal would end up in a homogenized composition of between $\delta^{65}Cu = -1$‰ (supergene sulfides) to 0‰ (hypogene sulfides).

An alternate to previous roasting of ores is the co-smelting of oxidized ores with hypogene or copper-rich supergene sulfide ores. The co-smelting process was not named, but was alluded to by Powell et al. (p. 38, 43 and 44) in discussing the occurrence of relics of sulfide ore in oxidized ores. Given the values by Powell et al. oxidized ores with $\delta^{65}Cu = +1$ to +2‰ were mixed with hypogene sulfides with $\delta^{65}Cu = 0$‰ and/or supergene sulfides with $\delta^{65}Cu = -1$‰. The result is a homogenized metal with $\delta^{65}Cu$ balanced between -1 and +2‰ (depending on portion of each ore source and its copper content).

In other words, having a source of oxidized ores with positive $\delta^{65}Cu$ values and rich supergene sulfides with negative $\delta^{65}Cu$ values would result in an intermediate composition, clustering and scattering between the extreme Cu isotope ratios of both ore sources as visible for the Bronze Age artifacts analyzed by Powell et al. Such metal could be misinterpreted as deriving from primary ores. Hence, the moderate Cu isotope composition of the Bronze Age artifacts presented by Powell et al. does not necessarily mean that only sulfide ore minerals were smelted using the Mitterberg process, but could alternatively be the result of mixing oxidized and sulfide ores, either as relics in the exploited mineralization or by intentional mixing of oxidized ores and sulfide ores at smelting sites. Only the use of solely oxidized or solely supergene sulfide ore in a smelting process allows a discrimination of these ore sources through extreme Cu isotope ratios of archaeological copper-based artifacts. For moderate compositions, also mixed sources with oxidized and sulfide ores must be taken into account.

In addition to co-smelting, co-melting occurred at Bronze Age smelting sites. Evidence comes from crushed slag found at many Bronze Age smelting sites in the Alps but is also well-documented in the Near East (Hauptmann, 2007). In ancient smelting operations, small copper prills were trapped within slag that was subsequently crushed and washed out for the remaining metal. The prills were then collected and re-melted forming larger portions of copper (e.g. ingots). If the metal was derived from multiple smelting charges of various ore sources (oxidized vs. sulfide ores) with distinct Cu isotope reservoirs, the final Cu isotope composition would have been a homogenized metal balanced between the initial Cu isotope composition of the ores. Additionally, the reuse of metal artifacts by melting down and mixing with fresh metal or metal from other artifacts can homogenize extreme $\delta^{65}Cu$ values, potentially masking the copper as deriving from primary sulfide ores.

The statement by Powell et al. (p. 44) that "Metals from the Middle Bronze Age through the Early Iron Age were extracted predominantly from larger tonnage non-weathered sulphide ores, as is evident from the tighter clustering and nearly identical means of the copper isotope values around -0.3‰" could alternatively have been caused by homogenization due to various metallurgical operations.

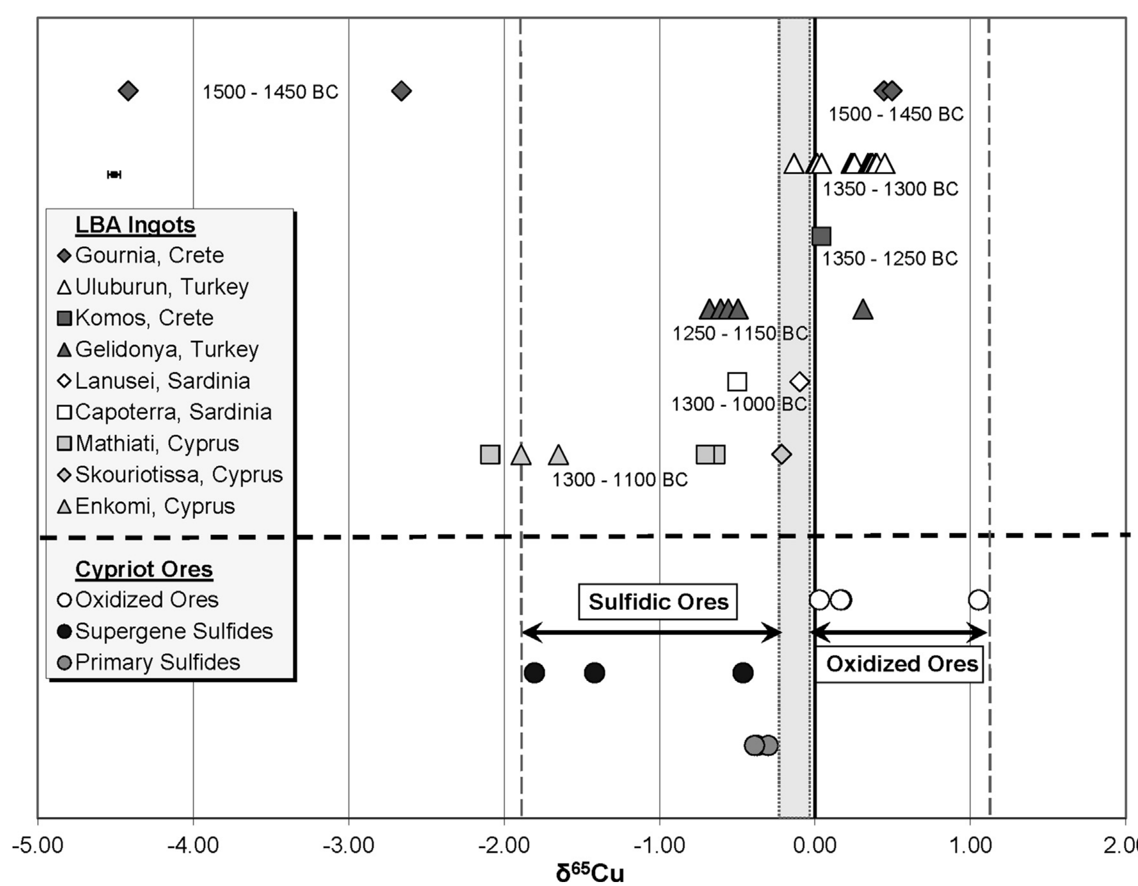

Fig. 1. Comparison of the Cu isotope composition ($\delta^{65}Cu$ [‰]) of Late Bronze Age ingots produced from Cypriot ore sources to the Cu isotope composition of ores from Cyprus. The starting composition of the primary ore was determined as $\delta^{65}Cu = -0.4$‰. A gradual shift from oxidized ore sources to sulfide ore sources occurred after 1300 BC (from M. Jansen, A. Hauptmann, S. Klein, forthcoming. Copper and lead isotope characterization of Late Bronze Age copper ingots in the Eastern Mediterranean: results from Gelidonya, Gournia, Enkomi and Mathiati).

1.4. Suggestions for the use of Cu isotopes

One of the major problems of the use of Cu isotopes in archaeometallurgy was addressed by Powell et al. (p. 44): “For any given deposit, the copper isotope values in all three reservoirs are controlled by the starting composition of the nonweathered ore, degree of weathering, and mineral species being weathered. This degree of variability from numerable ore deposits would likely result in the overlap of copper isotope composition between populations of artifacts.” I therefore propose that Cu isotope ratios of archaeological artifacts should be used in tandem with other archaeometallurgical techniques rather than standing alone.

A previous study of ore samples from the prehistoric mining district of Faynan with its sedimentary deposits demonstrated that oxidized ores mined in the Early Bronze Age cluster between $\delta^{65}Cu$ = -0.4 to +0.1‰ (Jansen et al., 2017). Without knowing the provenance, copper from Faynan could be incorrectly interpreted as deriving from hypogene sulfide ore based on the Cu isotope composition.

Hence, the ideal case for an archaeometallurgical approach of Cu isotopes is knowledge about the exact deposit where a copper artifact derived from, which of course is a challenging task in archaeometallurgy. It is proposed that additional methods like Pb isotope analysis should be applied to identify the provenance of artifacts first. After the identification of the geological origin of the copper, ores from its source can be directly compared to artifacts. This addresses the issue of identifying the starting composition of primary ores. We carried out such an approach by comparing Bronze Age ingots deriving from ores of Cyprus (Jansen et al., 2017). Fig. 1 shows a comparison of Late Bronze Age copper ingots from the Mediterranean. These ingots were studied for decades by Gale and Stos-Gale at the former Isotrace Laboratory in Oxford and assigned to Cypriot ore deposits (Stos-Gale and Gale, 2009). A general trend for ingots dating before 1300 BC with positive $\delta^{65}Cu$ values to negative $\delta^{65}Cu$ values for ingots dating after 1300 BC is visible. By a direct comparison with ore sources from Cyprus and a starting composition for the primary ores of about $\delta^{65}Cu$ = -0.4‰, the older ingots can be assigned to oxidized ore sources while the younger ingots were smelted from sulfide ores. By a combination of traditional Pb isotope characterization of artifacts, the deposits can be identified, and non-traditional Cu isotope ratios can be used to identify the ore types within such a deposit. Only through the previous long-lasting investigation of the Pb isotope composition and the assignment to ores from Cyprus, it was possible to get deeper insights into the mining history in Cyprus.

2. Conclusions

The interpretation of the Cu isotope composition of archaeological artifacts is a challenging task. Pb isotope studies have demonstrated that Eneolithic and Bronze Age copper artifacts from the Balkans derive from multiple ore deposits (Pernicka et al., 1997). A major difference between the Eneolithic and Bronze Age artifacts are the types of metal used (Pernicka et al., 1993): pure copper in the Eneolithic and arsenical copper in the Early Bronze Age. The shift from higher $\delta^{65}Cu$ values in the Eneolithic to moderate $\delta^{65}Cu$ values in the Bronze Age rather might reflect the selective use of sulfide ores to produce new types of copper in the Early Bronze Age than the complete exhaustion of accessible oxidized ore sources. Instead of technological needs, the decrease in the use of copper between the Eneolithic and the Early Bronze Age was likely caused by cultural changes affecting the use and/or deposition of copper-based artifacts.

Powell et al. mentioned that the starting composition of the primary ores can differ between deposits. To identify the ore types used in ancient metal production, knowledge about the geological origin of the copper artifacts is necessary to compare Cu isotope ratios of artifacts to Cu isotope ratios of ores. Within the simplicity of two Cu isotopes lies their complexity for archaeometallurgy, since the univariate Cu isotope ratio can be substantially altered by mixing different reservoirs of Cu (e.g., co-smelting of oxidized and sulfide ores). Reconstruction of specific metallurgical technologies like the introduction of the Mitterberg process in the Early Bronze Age Balkans as proposed by Powell et al. is not possible, and moreover not supported by archaeological evidence. Cu isotopes should be interpreted in tandem with other archaeometallurgical proxies like Pb isotopes and the chemical composition of copper-based artifacts.

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