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Use of non-traditional heavy stable isotopes in archaeological research

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ABSTRACT

Recent analytical developments in the field of mass spectrometry have made possible accurate measurements of “non-traditional” isotopic ratios of elements such as Fe, Cu, Ag, Sn, Sb and Hg. The stable isotopes of these elements do not have any radioactive parents, but their ratios undergo limited fractionation from various causes, most of them mass-dependent. These effects can lead to variation in isotopic ratios of natural materials (minerals, rocks, ores, etc.) and in archaeological artifacts derived from them. Research since 2010 has investigated whether variation in these isotopic ratios can be used to infer the geological provenance of archaeological materials, including bronze and glass. Here we review recent research on these isotopic systems in archaeology, their principal applications, as well as expected future developments in their use. We conclude that none of these isotopic systems are likely to be very useful for provenance, mostly because of limited ranges of isotopic ratios and/or extensive overlap between the isotopic ratios of most geological sources. Copper isotope ratios are however a reliable method for inferring the type of ore (supergene versus hypogene) smelted to produce copper, and recent studies indicate that silver isotope ratios can also be applied to this effect.

1. Introduction

Isotopic analyses have a long history in archaeological science. Pb isotopes have been used for provenance of non-ferrous metals and glass since the late 1960's (reviewed by Killick et al., 2020) and light stable isotopes (H, C, O, N) have been used since the 1970's in reconstructions of past sea and air temperatures (e.g. Hays et al., 1976), and in inferring past diets (DeNiro, 1987; Jaouen and Pons, 2017; Makarewicz and Sealy, 2015; Tykot, 2004; Van der Merwe and Vogel, 1978). Sr isotopes have become very important since the early 1990's as a tracer of mobility in humans and animals (e.g. Bentley, 2006; Ericson, 1985), and more recently in tracing the geological provenance of ancient glasses, marble and turquoise (e.g. Brilli et al., 2005; Henderson et al., 2010; Thibodeau et al., 2015). Neodymium (Nd) isotopes have been recently shown to be a useful complement to Sr isotopes and chemical analysis for tracing glass to its primary region of manufacture (e.g. Degryse, 2014). There is also emerging interest in the use of osmium (Os) isotopes for provenance of iron and gold (e.g. Brauns et al., 2020; Jansen et al., 2016). All of these isotopic techniques (some radiogenic, and others stable isotopic systems) are considered “traditional” isotopes – even if

only recently used in archaeology – because they have a long history of use in geology, so their isotope systematics and ranges of natural variation are well understood (Faure and Mensing, 2005).

Unlike radiogenic isotopes, where an unstable parent nuclide decays to one or more stable daughter isotopes and the ratio of parent to daughter(s) decrease with time elapsed, differences in the relative abundance of “stable” isotopes are solely produced by physical, chemical, and biological processes. These processes can create slight imbalances between lighter and heavier isotopes of the same element (fractionation), and usually do so in proportion to the mass differences between them. Light stable isotopes are easily measured by gas-source mass spectrometers, and there are tens of thousands of individual measurements of these isotopes in the archaeological literature alone. Ratios of heavy stable isotopes are more difficult, and thus more expensive, to measure. Until the late-1990's the primary instrument used to measure ratios of these elements was Thermal Ionization Mass Spectrometry (TIMS), which remains the gold standard for high precision radiogenic isotopic measurement. However, TIMS instruments have a relatively low ionization efficiency and thus have not been particularly useful in studying the non-traditional stable isotopes discussed in this

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review. The development of the multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS)¹ in the late 1990's has significantly expanded the range of stable isotope analysis to include elements with mid-to high-atomic number (Z) and high ionization energies; these include Fe, Cu, Sb, Ag, Sn and Hg, which are of interest to this review. MC-ICP-MS instruments also use multiple detectors to simultaneously collect multiple isotopes, and thus limit effects from instability of the plasma source (Albarède and Beard, 2004; Rehkämper et al., 2001; Vanhaecke et al., 2009). Additionally, spikes/dopants of elements with a known isotopic composition can be added to help resolve isotopic fractionation where not enough natural isotopes are available, and to correct for isobaric interferences (Vanhaecke et al., 2009). They also have the advantage of excellent ionization of the sample in argon plasmas (often 100% compared to the typical 1–2% in TIMS), and therefore samples analyzed with MC-ICP-MS can be one-tenth as large as those required for analysis on other instruments (Albarède and Beard, 2004). The disadvantage is that mass fractionation in the instrument is poorly known and not constant (Albarède and Beard, 2004), and thus must be corrected by standard-sample-standard bracketing. In contrast, fractionation laws in a TIMS instrument are well known (Wasserburg et al., 1981).

The magnitude of fractionation between non-radiogenic isotopes depends in large part upon the mass differences between the isotopes of each element. Light elements such as hydrogen, carbon, nitrogen, oxygen, and sulfur have a relatively large percent difference in the masses of their isotopes. This accounts for their tendency to undergo substantial mass-dependent fractionation during equilibrium (e.g. changes in redox state) or kinetic reactions (e.g. photosynthesis). For example, carbon (Z = 6) has two stable isotopes (¹²C and ¹³C) with a mass difference of 8.33%, and an isotopic range of 120‰ in δ¹³C (values of +20‰ to –100‰; Hoefs 2018, 61). In contrast, copper (Z = 29) has two stable isotopes (⁶³Cu and ⁶⁵Cu) and a mass difference of only 3.17%. The published range of natural variation in δ⁶⁵Cu is less than 10‰ (from about +3‰ to –6‰; Klein et al., 2010). However, most values fall between +3‰ and –2‰ (Powell et al., 2017). Because most heavy elements undergo very limited mass-dependent fractionation, isotopic differences were essentially impossible to resolve prior to the development of MC-ICP-MS. In addition, some of the stable isotope fractionation effects seen in nature are mass-independent and related to other factors, such as photochemical reactions. This applies particularly to Hg isotopes (Bergquist and Blum 2007; Cooke et al., 2013, 4182).

In equilibrium fractionation, the isotopes of an element are allowed to openly equilibrate and exchange between two or more phases of a system, usually during changes in temperature, pressure, oxygen fugacity, or speciation. This results in the preferential gain or loss of certain isotopes and establishes an equilibrium in accordance to the change. The partitioning of isotopes during equilibrium fractionation is largely governed by the subtle difference in the properties of a lighter and heavier isotope (ex: ⁶³Cu and ⁶⁵Cu). In particular, there is a difference in the vibrational frequencies of each isotopic species at its zero, or ground state – lighter isotopes will have a slightly higher vibrational frequency and heavier isotopes will have a lower vibrational frequency. This makes it easier for the lighter isotope to preferentially leave with changes in the surrounding environment because the lighter isotope will have a slightly longer bond length (therefore requiring less energy to break). The ground state vibrational frequency of individual isotopes is referred to as the “Zero Point Energy” (ZPE) of an isotope, and the lighter isotope of an element always has a slightly higher ZPE than the heavier isotope because of its mass.

Though there are many factors that govern equilibrium fractionation, there are two particularly important rules (for a more expansive overview of other rules, see Schauble, 2004). First, the heavier isotope

will preferentially concentrate in the phase with a stiffer bond; this stiffer bond is correlated with a higher oxidation number (a higher ionic charge, for redox considerations), a lower bond coordination (less atoms bonded to the element in question), and shorter bonds (making the vibration between them shorter and requiring more energy to break). Second, equilibrium fractionation increases as temperature is decreased, roughly in accordance with 1/T² (Schauble, 2004). As we shall see in the review of each isotopic system, this rule explains both the low range of fractionation observed in most high temperature magmatic ore samples, and the much greater range of fractionation observed in low temperature supergene minerals. For the chalcophile (Cu, Ag, Sb, Hg) and siderophile (Fe) isotopes of interest to this review, low temperature processes (e.g. supergene enrichment) are particularly important, as redox equilibrium reactions transform minerals from hypogene sulfides and native metals to supergene oxides, carbonates, sulfides and other minerals (Schauble 2004). Interested readers should consult Schauble (2004), Hoefs (2018), Criss (1999), Blanchard et al. (2017), Shahar et al. (2017), and reference therein for additional information.

The other mass dependent mechanism typically responsible for stable isotope fractionation is kinetic fractionation. Unlike equilibrium fractionation, kinetic reactions are not open systems where isotopes can be exchanged between two or more phases until thermodynamic equilibrium is established. Instead, kinetic reactions are one way and incomplete, and usually operate on the difference in activation energy of lighter and heavier isotopes. Typically, a lighter isotope (e.g. ⁶³Cu) has a lower activation energy than a heavier isotope of the same element (e.g. ⁶⁵Cu). Therefore, in a kinetic process like evaporation/condensation, rapid crystal formation, and mineral dissolution, the lighter isotope reacts faster to form a new phase (e.g. the vaporization from liquid into gas) because it requires less energy for this change to be made. This usually has the effect of making the product phase of the reaction lighter in isotopic composition, while the reactant phase becomes enriched in heavy isotopes. Additional details are given in Schauble (2004), Hoefs (2018), Criss (1999), Watkins et al. (2017) and references therein.

The degree of fractionation exhibited by isotopes of an element as they are partitioned into different phases at various temperatures can also be predicted. This can be accomplished using empirical force field models or *ab initio* quantum mechanical calculations (for reviews of these techniques, see Blanchard et al., 2017 and Schauble 2004). These can predict the partitioning of light and stable isotopes by modeling vibrational frequencies as force fields (empirical force field models) or by assessing the electronic structure of a molecule (*ab initio* quantum calculations) at various temperatures, with various ligands, and in different systems (closed versus open). Theoretical fractionation factors can then be experimentally tested and used to better understand the nuances of isotopic fractionation. The *ab initio* approach has gained in popularity since 2000, as it allows for more straightforward calculations that can be tested against known properties of the molecules in question (Blanchard et al., 2017). For archaeological purposes, the modeling of isotopic behavior is important, as it affords a theoretical understanding of the natural fractionation of an isotope in specific ore forming environments, which can then be experimentally tested with ore samples (e.g. Fujii and Albarède, 2018). A review of empirical force field models and *ab initio* quantum calculations is far beyond the scope of this paper, but interested readers should consult Blanchard et al. (2017) and Schauble (2004). Both Blanchard et al. (2017, 38–40) and Schauble (2004, 102–111) also contain lists (organized by isotopic system) of studies of theoretical fractionation.

Geological and archaeological applications of stable isotopes of midrange (from Cl (Z = 17) through Zn (Z = 30)) and heavy (Z > 30) elements are still in the exploratory phase (Hoefs, 2018; Teng et al., 2017), but we have learned enough about them at this point to merit a

¹ For a review of MC-ICP-MS and TIMS instrumentation, see Albarède and Beard (2004).

² Provenance studies of low-fired ceramics still rely on the proven - and cheap - methods of trace element analysis and optical petrography.

review of archaeological applications. We and many others call these applications “non-traditional stable isotopes”, to distinguish them from “traditional” isotopes whose use is well established (H, C, N, O, S, Sr, Nd, Os, Pb). We discuss recent archaeological studies of the isotopes of the transition metals Fe, Cu, Ag, and Hg, the metalloid Sb, and the post-transition metal Sn. We list the relative global abundance of the isotopes of each element, the range and causes of fractionation (where known), notations and standards, and to what archaeological questions these have been applied.

Note also that we are interested here only in the use of these isotopes for provenance of inorganic artifacts, and for information of the type of resource utilized (e.g. supergene versus hypogene ores). The implications in variation of some of these same isotopes (and of others, like calcium, zinc and magnesium) in human and other animal tissues has been reviewed elsewhere (Jaouen and Pons 2017).

2. Principles of provenance analysis using isotopes

In archaeological sourcing studies the *provenance postulate* is the key concept (Weigand et al., 1977, 24; Neff, 2001). This rule specifies that to unambiguously match an archaeological object to a geological source, the chemical or isotopic variation within individual sources must be smaller than variation between them. If a study is predicated on a *reference group* approach (see Bishop et al., 1982; Glascock and Neff, 2003; Schneider et al., 1979) - where comparisons of unknowns are made to known production sites (e.g. pottery kilns) or to artifacts (e.g. potsherds that are assumed on archaeological criteria to have been locally manufactured), this rule still holds (Garrigós et al., 2001). Thus, great care must be taken to fully characterize the range of geochemical or isotopic variation within geological sources or reference groups (Baron et al., 2014; Budd et al., 1996; Garrigós et al., 2001; Ixer, 1999; Pearce, 2016). If geological sources or reference groups, cannot be distinguished from each other by chemical, mineralogical or isotopic data (or by combinations of them), then unique source attributions for archaeological samples cannot be credible.

Over the last 40 years, archaeologists have made increasing use of radiogenic isotopic ratios (e.g. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) to trace the origin of minerals, metals, glasses and glazes.² For these isotopes, archaeologists can draw upon the large number of relevant isotopic measurements in the geological literature to define, at least provisionally, the range of variation within potential sources.³ For example, Killick et al. (2020) provide a database of 11,884 lead isotope measurements on ore minerals. But there are as yet comparatively little data in the geological literature for “non-traditional” isotopes (such as Fe, Cu, Ag, Sn, Sb and Hg), because it has only been possible to acquire high-quality data for these since MC-ICP-MS became widely available in the 1990’s.

There are other uncertainties associated with the use of these newer isotopic systems for inferring the provenance of archaeological materials. Some elements, such as copper, tend to display more isotopic variability within ore deposits than between ore deposits. For copper this is because the low-temperature reduction-oxidation (redox) processes that form supergene ores from primary sulfides induce isotopic fractionation (Klein et al., 2010; see the Cu isotopes section below). A further concern that provenance studies must address is whether pyrotechnological processes (e.g. smelting of metals, or primary melting of glass) can alter the isotopic signatures of the raw materials. This usually occurs when an element is reduced or oxidized during a pyrotechnological process. Antimony isotopes, for example, were recently shown to fractionate when antimony sulfide (stibnite) was added as an opacifier for glass (Dillis et al., 2019; see the Sb isotopes section below). Studies

³ It should be noted, however, that provenance studies using radiogenic isotopes are often impeded by isotopic overlap, as was recently discussed by Killick et al. (2020).

should also investigate whether the laboratory procedures used to extract the isotopes may induce fractionation. This was recently demonstrated in tin isotopes as the methods of Yamazaki et al. (2013), involving low temperature dissolution and ion-exchange chromatography, significantly fractionate the tin isotopic signature of cassiterite (see Sn isotopes section below). Attention to fractionation effects is therefore critical for non-traditional stable isotopes and needs to be well understood before engaging in destructive analysis of scarce or valuable archaeological artifacts.

In situations where variation within sources exceeds variation between them and/or pyrotechnological processes alter the isotopic signature (thus invalidating their use for inferring provenance), non-traditional stable isotope systems can still be extremely useful and applied to better understand the technology and practices used to craft archaeological objects. (For example, copper isotopes, as noted below, provide important evidence about past selection of copper ores). This approach operates by reconstructing the “technological styles”⁴ and “*chaînes opératoires*”⁵ of past peoples in order to answer anthropologically driven questions including apprenticeship processes, interactions within and between communities, procurement practices and technologies used, materiality, scale, etc. Archaeologists commonly study these questions with various theoretical lenses to help integrate them with the broader archaeological record, and we find community of practice (Gosselain, 2000, 2010, 2017; Kiriatzi and Knappett, 2016; Lave and Wenger, 1991; Roddick and Stahl, 2016; Wallaert, 2012; Wenger, 1998) and social constructionist (Dietler and Herbich 1998; Dobres and Hoffman 1994; Hoffman and Miller 2014; Killick 2004) theories to be particularly helpful with this. It is beyond the scope of this article to further detail ways in which we can better integrate archaeometric data with an anthropological perspective and the archaeological record, but the reader can consult Freund (2013), Hughes (1998), Triadan et al. (2002), Zedeño (2002), Zedeño et al. (2003) for further discussion.

3. A review of non-traditional Isotopic Analysis and applications to archaeology

Though a wide variety of midrange and heavy stable isotopes have been applied in other fields of study, archaeological research with inorganic materials has primarily focused on the isotopes of copper (Cu), tin (Sn), iron (Fe), silver (Ag), antimony (Sb), and mercury (Hg). Our discussion here will highlight the nuances of each of these non-traditional isotopic systems utilized in archaeological research, including their geochemical and isotopic background; notations, standards, and uncertainties; causes of fractionation; how they have been applied to study archaeological objects; and what needs to be taken into consideration for any future application of these isotopic systems.

3.1. Cu isotopes

3.1.1. Geochemical and isotopic background

Copper ($Z = 29$) is a relatively rare metal (estimated abundance in the earth’s crust: 60 ppm) with usual valences of Cu^+ , Cu^{2+} , and Cu^0 . Native copper (Cu^0) is of archaeological importance in some regions, especially in eastern North America. Cu^+ and Cu^{2+} occur in sulfides (chalcocite, chalcopyrite, bornite, etc.), sulfosalts (e.g. tennantite, tetrahedrite), oxides (cuprite) and carbonates (azurite, malachite). Copper only has two stable isotopes (^{63}Cu – 69.1% and ^{65}Cu – 30.9%),

⁴ Technological style is defined as “culturally specific choices made between functionally equivalent production techniques which can actively or passively communicate social information, and which can be manifestations of cognitive processes,” (Hoffman and Miller 2014, 710).

⁵ *Chaîne opératoire* is defined here as the socially contextualized sequence of steps and practices used to produce an object, however it typically extends into the realm of use, reuse, and discard in archaeological discourse.

which poses issues with quantifying instrumental fractionation. Despite this limitation, copper isotopic values work well to identify material selection of metal and possibly vitreous raw materials (Klein et al., 2010, 51–52; Markl et al., 2006; Rodler et al., 2019), although they are inherently poor indicators of provenance for archaeological objects.

3.1.2. Notations, standards, uncertainties

Copper isotopic data is reported as $\delta^{65}\text{Cu}$, which quantifies the difference between experimentally derived (sample) and known (standard) isotopic values:

$$\delta^{65}\text{Cu}\text{‰} = \left[\frac{\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{Sample}}}{\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{Standard}}} - 1 \right] * 1000$$

The standard used in previous $\delta^{65}\text{Cu}$ analyses was NIST SRM 976, but this standard is no longer available. Standards currently in use are ERM-AE633 and ERM-AE647, which have been calibrated against NIST SRM 976 for comparability (Möller et al., 2012). Precision of $\delta^{65}\text{Cu}$ values is typically better than 0.1‰ (Jansen et al., 2017; Powell et al., 2017). $\delta^{65}\text{Cu}$ values for ore minerals typically range from +3‰ to –6‰, and

data on the range of measurement in sediments, river and ocean water, and in magmatic rocks can be found in Hoefs (2018), and studies cited therein.

3.1.3. Causes of fractionation

Copper isotopes are poor indicators of provenance because there is more fractionation within copper deposits than between them. Fractionation within copper deposits is produced by redox reactions. Most primary (hypogene) copper sulfide minerals (i.e. those formed during high-temperature magmatic processes) have very similar isotopic ratios (around 0‰) which is expected by equilibrium fractionation mechanisms, and these ratios are also similar to those of the mantle (Hoefs, 2018). Copper isotopic variation is largely created during low temperature redox processes at and above the water table. These convert hypogene sulfide ores to a wide array of supergene copper minerals, including native copper, supergene copper sulfides, and copper carbonates and oxides (Ehrlich et al., 2004; Larson et al., 2003; Mathur et al., 2010). Copper isotopes thus violate the provenance postulate, since variation within a single ore deposit is usually as large or larger than variation between deposits. Although copper isotopes are a poor indicator of provenance, Klein et al. (2010) argue in a pioneering paper

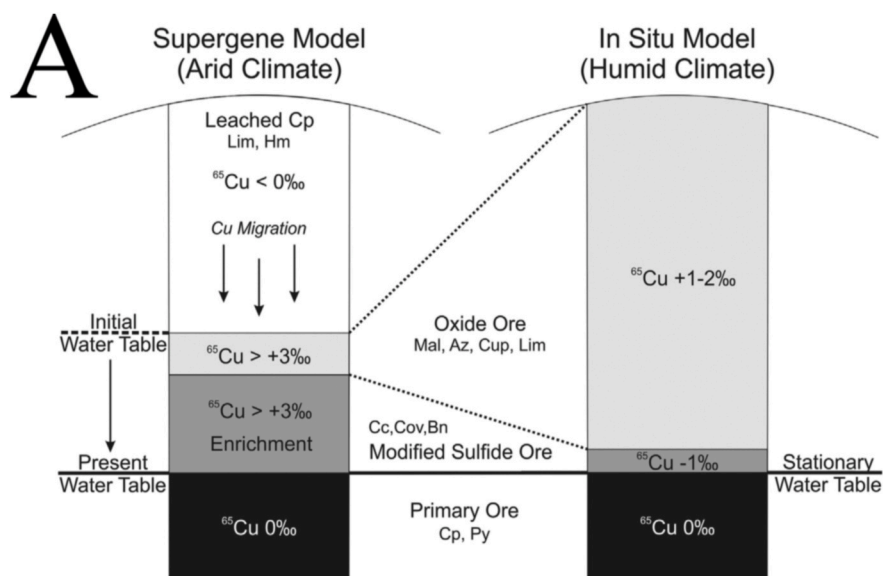
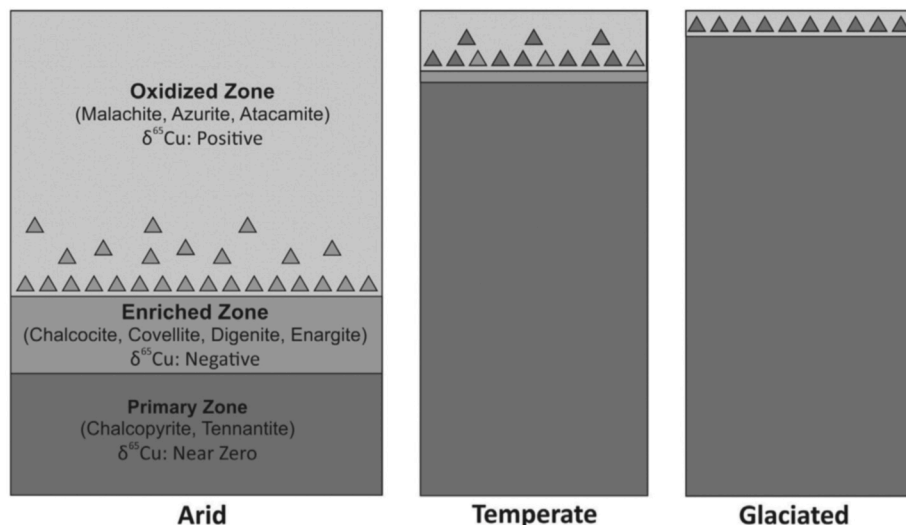


Fig. 1. Klein et al. (2010) and Powell et al. (2017) demonstrate that the fractionation of copper isotopes within a deposit is greater than between deposits, and that they pattern by stage in the weathering process of hypogene copper sulfides to supergene copper carbonates. The pattern established by Klein et al. (2010) holds for copper deposits formed in temperate climates, while copper deposits in arid climates behave by the pattern of Powell et al. (2017), Fig. 4. 1b reproduced from Powell et al., 2017, Fig. 4. 1b reproduced from Powell et al., 2018a, Fig. 1).



that they are useful indicators of the type of ore used to produce copper. They conclude that supergene carbonate/oxide copper deposits typically plot above the $\delta^{65}\text{Cu}$ value of 0.3‰, while primary sulfide deposits plot between $\delta^{65}\text{Cu}$ values of -0.4 to 0.3‰ and supergene sulfide deposits plot between $\delta^{65}\text{Cu}$ values of -1 to -0.4 ‰ (Fig. 1a).

Powell et al. (2017, 2018a) add several important points on how copper isotopic ratios vary according to environment of formation. They emphasize the importance of climate in development of classic supergene copper deposits with a gossan cap, enriched oxide layer, supergene sulfide enrichment layer, and primary hypogene deposit. Such supergene deposits are most fully developed in arid regions like Chile, Peru and the southwestern USA, where major changes in the level of the water table from the last glaciation to the present have promoted substantial vertical transport of copper ions throughout the deposit (Powell et al., 2017, 42). Consistently humid environments, like those of Europe, do not favor the formation of a gossan cap, and often only produce only a thin layer of copper oxides (Powell et al., 2017, 43). The environmental difference directly impacts the range of copper isotopic ratios. Partially formed supergene deposits in humid zones would follow the pattern outlined in Klein et al. (2010), while fully formed supergene deposits in arid zones would exhibit $\delta^{65}\text{Cu}$ values greater than +3‰ for supergene oxide and sulfides, and a value of 0‰ for primary sulfides (Fig. 1a). Archaeologists must therefore interpret copper isotope ratios with a full understanding of both the geology of potentially exploited deposits and the climate history of the region (Fig. 1b). We thus echo the suggestion by Jansen et al. (2017, 3) to pair copper isotopic analysis with a technique which could establish the provenance of the archaeological metal object, such as lead isotopic analysis. These would work in a complementary fashion to understand where the smelted ore originated and what mining and materials selection practices were used.

Ever since the experiments of Gale et al. (1999), it has been assumed that copper isotopes do not fractionate further in smelting or refining. However, recent work by Klein and Rose (2020) indicates that this issue is more complex than previously believed. They conducted experimental smelts with both malachite and copper sulfides to investigate: 1) if fractionation occurs between ore and metal in archaeologically relevant smelting conditions; and 2) the ratios of copper isotopes in various raw materials and products of smelting (slag, clay from the furnace lining and/or tuyères, matte, trapped copper prills, charcoal and wood fuel). They conclude that there is no fractionation between ore and metal in smelts that achieve clear separation of copper from slag, but in smelts that do not fully separate – forming prills trapped in slag – the isotopic ratios of ores may show additional fractionation (the latter reflects kinetic fractionation). They also show that smelting debris does not reliably reflect the original isotopic composition of the copper ore. Slag is a particular poor proxy and is typically enriched in ^{65}Cu . Klein and Rose (2020) therefore conclude that significant fractionation can occur in metal produced from 1) the reworking of copper slag or 2) the extraction of trapped metal prills from slag, therefore obscuring any isotopic signature of the original ore. Future studies should thus investigate the metallurgical technology used to produce archaeological copper metal in the region under investigation *before* undertaking a copper isotopic study. Future studies should also pair copper isotopes with microprobe or SEM chemical analysis on inclusions in the copper metal for a robust determination of the ore used (see Bugaj et al., 2019). For a thorough review of these and other mechanisms responsible for copper isotopic fractionation, see Moynier et al. (2017).

3.1.4. Applications

Copper alloys: For studies of copper and copper alloys, sampling procedures are particularly important because of the role redox processes play in copper isotopic fractionation. Care needs to be taken to only sample the uncorroded core, as the corrosion layer is typically enriched in ^{63}Cu (Bower et al., 2013; Mathur et al., 2014).

The first application of copper isotopes to copper and bronze objects was in the late 1990's (Gale et al., 1999; Woodhead et al., 1999), and

was taken further by Klein et al. (2004, 2010), who focused on Roman coinage from ca. 50 BCE to 250 CE. They used both copper and lead isotopic analyses to understand changes in mining practices and sources. These analyses work particularly well together; lead isotopes may provide clues about provenance, while copper isotopes show whether supergene or hypogene ores were used. In order to illustrate the use of copper isotopic analysis as an indicator of materials selection, they first analyzed supergene sulfides, hypogene sulfides, and carbonates/oxides to establish their model of fractionation among supergene and hypogene ore minerals. Analyses of a well seriated assemblage of Roman coins then allowed them to track the use of Iberian Copper Belt and Central Iberian Zone ores with a high degree of resolution. They concluded that an industrial scale mine was opened in the Central Iberian Zone during the reign of Augustus, which contributed both supergene carbonates and hypogene sulfides, and that new mines in the Iberian Copper belt contributed a large amount of copper smelted from supergene carbonates. (Previous Iberian Copper Belt copper production was primarily from supergene sulfides). Since 2010, there has been a surge of publications which apply copper isotopes, many of which focus on copper-based metallurgy in the Mediterranean.

Bower et al. (2013) followed the template of Klein et al. (2010) and used lead and copper isotopes to track changing mining practices and sources in the Levant through Judean coins. Their results indicate a shift from positive $\delta^{65}\text{Cu}$ values to negative $\delta^{65}\text{Cu}$ values in the Eastern Mediterranean during the 1st century CE, which they interpreted as a shift from a hydrocarbonate/oxide Cu source to a predominantly sulfide source for copper metal after the opening of an industrial mine at Faynan, Jordan.

Balliana et al. (2013) employed copper isotopic analysis in their study of pre-Roman and Roman bronzes from sites in Teruel and Huesca, Spain to test the feasibility of both tin and copper isotopic analyses in archaeological studies. They concluded that the pre-Roman and Roman bronzes were predominantly smelted from primary and supergene copper sulfides. Unfortunately, no further conclusions can be drawn, as they do not indicate which samples are from pre-Roman versus Roman contexts.

Jansen et al. (2017, 2018) applied copper and lead isotopic analyses to metals in the eastern Mediterranean Bronze Age, and Jansen et al. (2017) argued that copper isotopic data can complement lead isotopic analysis at the local level to help resolve areas of lead isotopic overlap

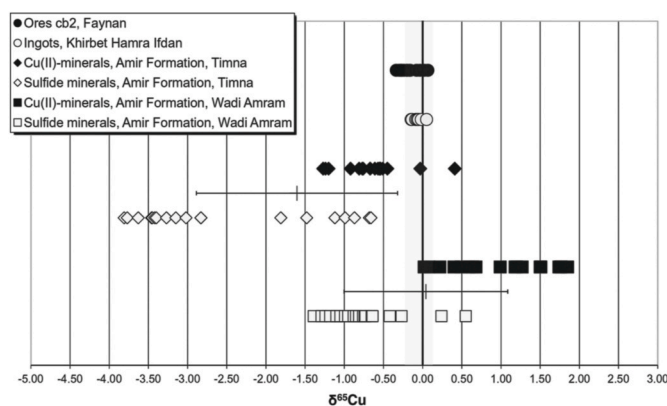


Fig. 2. Jansen et al. (2017) argue that copper isotopes can complement lead isotopes at the local level where lead isotopic overlaps exist. They test this at the Timna and Wadi Amram deposits within the Amir formation and show that some differences do exist between sulfide and carbonate copper isotope data from the two deposits. However, studies wishing to take a similar approach should first characterize the potential geological deposits with both lead and copper isotopes to confirm overlap (lead isotopes) and separation (copper isotopes), and complement their study with microprobe or SEM chemical analysis on inclusions in the copper metal to confirm the type of ore used (Bugaj et al., 2019) (Reproduced from Jansen et al., 2017, Fig. 6).

(8–11). There appears to be some merit to this argument (Fig. 2), but it requires sufficient sampling of prehistoric mines within the geological district identified by lead isotopic analysis. Jansen et al. (2017) also used this data to understand ore selection practices from the site of Khirbat Hamra Ifdan near Faynan, Jordan. $\delta^{65}\text{Cu}$ values from these ingots form a fairly tight distribution, matching the supergene oxide ore distribution from the Faynan deposit, so Jansen et al. (2017) concluded that supergene carbonate materials were the dominant type of ore for the production of copper ingots at this site. Jansen et al. (2017, 2018) also analyzed a large assemblage of copper ingots from sites across the Mediterranean Sea, which were previously matched to deposits in Cyprus using LIA (Stos-Gale et al., 1997; Gale, 1999). The authors included reinterpreted copper isotopic data from Gale et al. (1999) and Woodhead et al. (1999) to illustrate a clear shift in material selection of oxide to sulfide ores in the 13th century BCE.

In addition to their important contribution regarding the impact of climate on copper isotopic patterning, Powell et al. (2017) applied copper isotopic analysis in order to assess the change in mining and metallurgical practice over the *longue durée* in the Balkans, from the Eneolithic to the Late Bronze Age (5000–1000 BCE). Copper objects from the earlier Eneolithic (5000–3700 BCE) match the copper isotope signature of oxide ores. Powell et al. (2017) noted an apparent hiatus in copper production in the Balkans from about 3700 BCE until 2500 BCE, when the resumption of copper production marks the start of the Early Bronze Age (EBA). The renewed production of copper objects coincided with a shift to negative $\delta^{65}\text{Cu}$ values, which Powell et al. (2017) interpreted as evidence of a switch to the use of sulfide ores. They argued that the hiatus represented both the exhaustion of oxide ores and the inability of Eneolithic Balkan metallurgists to smelt sulfide ores. The resumption of smelting in the EBA reflects, in their view, introduction of new technology, likely brought into the Balkans from the Near East. Jansen (2018) rejected the argument for exhaustion of oxide ores, and instead suggested, following Pernicka et al. (1993), that the change reflected a shift in cultural preference for type of ore. Powell et al. (2018a), armed with data from an additional 44 samples, reaffirmed their earlier conclusions. We find their argument to be more persuasive than that of Jansen (2018).

Gold: Baron et al. (2019) combined lead, silver, and copper isotopes to investigate multiple generations of hypothermal gold mineralization within the French Massif Central. Specifically, they applied copper isotopes to try to resolve overlaps in lead isotope data for the two generations of gold mineralization. Baron et al. (2019) suggested that $\delta^{65}\text{Cu}$ data on gold mirrors the fractionation mechanism established through copper minerals (Klein et al., 2010), and that copper isotopes could be used to identify placer vs. hard rock gold mining. They also suggested that copper isotopes could be used in situations where gold coins were debased with copper. Recent work by Saunders et al. (2016) showed that copper isotopes can be applied to understand the metal source of copper-rich epithermal gold deposits. The data presented by Baron et al. (2019) mirrors that of Saunders et al. (2016) and suggests a magmatic metal source for analyzed hypothermal gold deposits in the French Massif Central. Future applications of copper isotopes to understand gold mineralization should focus on placer gold deposition. Brüggmann et al. (2019) recently applied silver isotopes to this effect (see section 3.4.4), and it is possible that copper isotopes are similarly affected by the detrital transport of gold grains.

Glass colorants: Copper was frequently used as a colorant in ancient glass. Lobo et al. (2014) tried to use copper isotopes for provenance of the copper in glass, but, as noted above, this tool is not suitable for this purpose. Our examination of their data (using the model established by Klein et al. (2010)) suggests that their glass samples from Bronze Age Egypt, Iron Age Georgia and Turkey, as well as most of the sampled glass from Bronze Age Mesopotamia, relied on colorants derived from supergene copper sulfides, although some Bronze Age Mesopotamian data does range into the hypogene sulfide field. Rodler et al. (2017, 2019) emphasized, however, that all interpretations of copper isotopic data in

glass must be considered tentative. Currently there is no understanding of how copper isotopes behave throughout the glass-forming and weathering process in vitreous materials. Recently, Dillis et al. (2019) proved that antimony isotopes are subject to redox fractionation during the opacification process of ancient glasses. Since copper isotopes are also subject to redox fractionation, and corrosion impacts the isotopic value of copper metal (Bower et al., 2013; Mathur et al., 2014), we cannot rule out similar shifts for copper colorants (particularly for the production of Egyptian blue which involves the oxidation of Cu^0 to Cu^{2+}).

Turquoise: A small suite of studies from the Southwestern USA attempted to use biplots of copper isotopic values against hydrogen isotopic values to infer the geological provenance of turquoise in archaeological sites (e.g. Hull et al., 2008; 2014; Hull and Fayek, 2012; Othmane et al., 2015). The attributions to source in these studies are not credible. Both copper and hydrogen isotopic ratios were measured by SIMS (Secondary Ion Mass Spectrometry), which has much lower precision for copper isotopes (1–2‰) than that of MC-ICP-MS. Matrix effects that fractionate the copper isotopic ratios are also difficult to account for when using SIMS, though Othmane et al. (2015) tried to develop a correction factor for turquoise. The most serious problem with these studies, however, is that this group made no attempt to establish the range of variation for copper isotopes within potential geological sources of turquoise. Most turquoise deposits in the Southwestern USA were formed by near-surface alteration of porphyry copper deposits. Mathur et al. (2010) reported a wide range in copper isotope ratios from the supergene zones of individual porphyry deposits in this region, and extensive overlap of values from different deposits, but Hull and collaborators appear in many cases to have analyzed only one reference sample for each geological deposit (Hull et al., 2018, Fig. 2).

3.2. Sn isotopes

3.2.1. Geochemical and isotopic background

Tin ($Z = 50$) has ten stable isotopes ($^{112}\text{Sn} - 0.97\%$, $^{114}\text{Sn} - 0.66\%$, $^{115}\text{Sn} - 0.34\%$, $^{116}\text{Sn} - 14.54\%$, $^{117}\text{Sn} - 7.68\%$, $^{118}\text{Sn} - 24.22\%$, $^{119}\text{Sn} - 8.59\%$, $^{120}\text{Sn} - 32.58\%$, $^{122}\text{Sn} - 4.63\%$, $^{124}\text{Sn} - 5.79\%$), and valences from -4 to $+4$, though -4 , $+2$ and $+4$ are the most common. Native tin (Sn^0) is extremely rare. Tin is most commonly found in the mineral cassiterite (SnO) – the only economic source of tin today – and less commonly as stannite ($\text{Cu}_2\text{FeSnS}_4$), although traces of Sn are found in many oxide ore minerals (Hoefs, 2018, 158–159). Tin is a rare element (2.3 ppm in the earth's crust), so geological processes must concentrate it by at least four orders of magnitude to form deposits that could be exploited by prehistoric metallurgists. Many regions have no viable tin sources, so their inhabitants have to obtain it by long-distance trade (Franklin, 1978; Muhly, 1973).

Despite the fact that tin has more stable isotopes than any other element, tin isotopic analysis saw little use in geology or archaeology until recently. This delay was largely caused by the difficulty of dissolving cassiterite – a problem that also accounts for scarcity of lead isotope measurements for this mineral. A solution was found by Hausstein et al. (2010, 819–823). They reduced cassiterite with KCN to form tin metal at 800°C , and then dissolved the tin metal concentrate using 6M HCl. This procedure was tested and further detailed by Brüggmann et al. (2017), Mathur et al. (2017), and Mason (2020), and yields sufficient Sn for isotopic analysis without altering the tin isotopic ratios of the sample. In contrast, Yamazaki et al. (2013, 24) dissolved cassiterite at low temperature (100°C) in solutions of HI and HCl before purifying the solution using ion-exchange chromatography. However, Brüggmann et al. (2017), Mathur et al. (2017), and Mason (2020) concluded that this procedure does not produce sufficient yields for isotopic analysis and can induce isotopic fractionation. The low temperature method detailed by Yamazaki et al. (2013) should therefore not be used to purify samples for tin isotopic analysis.

Berger et al. (2017) compared procedures for analyzing cassiterite,

tin metal, and bronze in the hope of finding an alternative to the toxic KCN method employed by [Haustein et al. \(2010\)](#). However, they concluded that the KCN method produces the most consistent and reliable results. These experimental tests will be discussed further below, as they detail several important mechanisms for the fractionation of tin isotopes during pyrometallurgical processes.

3.2.2. Notations, standards, uncertainties

As tin isotopic analysis is a developing technique, agreement on a common notation is still pending and scholars have applied ratios of the ten stable isotopes on a case by case basis. The majority of studies use ^{116}Sn as the reference isotope, but some ([Berger et al. 2017, 2018, 2019](#); [Brügmann et al., 2017](#); [Nessel et al., 2016](#); [Yamazaki et al., 2014](#)) use ^{120}Sn , as it is more abundant. [Bower et al. \(2019\)](#) also used the ^{120}Sn denominator, however they reported their data in $\delta\text{Sn}/u$ where u is the mass difference between the numerator and denominator tin isotopes. Unfortunately, most studies did not provide their data (whether for cassiterite or archaeological metal) in both formats, which severely limits the comparability of datasets. Future studies either need to agree on a common format to present data or should endeavor to publish their data in both formats, as was recently done by [Berger et al. \(2019\)](#). Calculations for the standard δ notation are made using the following equation:

$$\delta^{1XX}\text{Sn}\text{‰} = \left[\frac{\left(\frac{^{1XX}\text{Sn}}{^{116}\text{Sn}} \right)_{\text{Sample}}}{\left(\frac{^{1XX}\text{Sn}}{^{116}\text{Sn}} \right)_{\text{Standard}}} - 1 \right] * 1000$$

Standards used in tin isotopic studies also vary and include NIST 3161a and commercial solutions by SPEX (CLSN-2 and PLSN5). Several studies also used Puratronic grade tin metal foil (PSn) as a standard ([Berger et al., 2019](#); [Bower et al., 2019](#); [Haustein et al., 2010](#); [Nickel et al., 2012](#)). Solid leaded bronze reference material (BAM 211 and IARM 91D) has also been used for standardization purposes ([Balliana et al., 2013](#); [Brügmann et al., 2017](#)). Future studies should consult [Brügmann et al. \(2017\)](#) when conducting a tin isotopic investigation, as they analyzed most of the above standards to define standardized isotopic data which could be compared against. Future tin isotopic endeavors should also use an Sb dopant in order to correct for instrumental mass bias ([Haustein et al., 2010, 824](#); [Mathur et al., 2017, 702](#); [Nickel et al., 2012, 170](#)).

$\delta_{^{116}\text{Sn}}^{124}\text{Sn}$ typically varies between -1 and 2‰ in analyzed samples and errors range between 0.04 and 0.3‰ ([Brügmann et al., 2017](#); [Haustein et al., 2010](#); [Mason et al., 2016](#); [Mason 2020](#)). However, error ranges continue to decrease as a result of the use of an antimony dopant during sample analysis. Further, [Mathur et al. \(2017\)](#) and [Mason \(2020\)](#) were able to record a greater amount of $\delta_{^{116}\text{Sn}}^{124}\text{Sn}$ variation in cassiterite samples, hinting at the possibility for further discriminatory power. $\delta_{^{120}\text{Sn}}^{124}\text{Sn}$, on the other hand, varies between -0.5 and 1‰ with much lower error ($<0.01\text{‰}$ – 0.03‰) ([Berger et al., 2017, 9](#); [Berger et al., 2019](#); [Brügmann et al., 2017, 443–444](#)).

3.2.3. Causes of fractionation

[Berger et al. \(2017, 2018\)](#) recently contributed a great deal to our understanding of tin isotopic fractionation in archaeologically relevant pyrometallurgical processes. They used CO reduction, cementation, and co-smelting of cassiterite/stannite and various copper minerals/metal to assess if these traditional metallurgical processes fractionate the tin isotopic signature. The results of their experiments clearly illustrate that redox conditions do induce tin isotopic fractionation, particularly during CO reduction. [Berger et al. \(2017\)](#) conducted a CO experimental smelt of cassiterite and stannite under laboratory conditions, and the resulting tin bead was enriched in heavy tin ($\Delta_{^{120}\text{Sn}}^{124}\text{Sn} \cong 0.1\text{‰}$) as the lighter tin was

preferentially volatilized during the reduction process. The authors argued that the enrichment of reduced tin metal in heavy tin could be exacerbated by the presence of impurities in the tin ore, possibly resulting in increased evaporation rates of lighter tin. This result contradicts the assertions of [Gale \(1997\)](#), [Haustein et al. \(2010\)](#), and [Yamazaki et al. \(2014\)](#), who all argued that the reduction of tin ore to metal would not significantly fractionate the tin isotopic signature. The CO reduction results from [Berger et al. \(2017\)](#) were corroborated by [Berger et al. \(2018\)](#) using archaeological tin smelting techniques, and resulted in a $\delta_{^{120}\text{Sn}}^{124}\text{Sn}$ isotopic shift of 0.09 – 0.18‰ towards a heavier tin signal. This shift changed with degree of reduction, as an incompletely reducing atmosphere resulted in a more drastic isotopic shift ($\Delta_{^{120}\text{Sn}}^{124}\text{Sn} \cong 0.88\text{‰}$), while a completely reducing atmosphere resulted in less fractionation of the tin isotopic signature. Importantly, [Berger et al. \(2018\)](#) argued that the isotopic shift in completely reducing atmospheres is not drastic enough to obscure a source determination because the isotopic range of sources is usually much wider than the degree of fractionation during complete reduction.

In their bronze alloying experiments using the cementation technique,⁶ [Berger et al. \(2017\)](#) noticed a slight shift in tin isotopic signature ($\Delta_{^{116}\text{Sn}}^{124}\text{Sn} = 0.02$ – 0.03‰). They believe that this shift was caused by the purification of tin metal through ion exchange chromatography, rather than by the cementation procedure (see [Brügmann et al., 2017, 446](#)). This was also noted by [Yamazaki et al. \(2013, 2014\)](#). [Berger et al. \(2017\)](#) therefore concluded that cementation alloying should preserve the isotopic signature of the tin ore. Their co-smelting⁷ experiments also successfully resulted in a bronze alloy, but some of the metallic tin segregated from the bronze component. This segregation was reflected in isotopic composition, as the tin metal component was isotopically heavier than the bronze bead. However, [Berger et al. \(2017\)](#) argued that the average of the tin isotopic values for the bronze bead and tin metal should approximate that of the original cassiterite mineral. [Berger et al. \(2017, 24–25\)](#) also noticed a correlation between the variance of tin isotopic signatures and percentage of tin in archaeological bronzes. Their data show that low-tin bronzes (<3 wt % Sn) are more significantly affected by the preferential volatilization of lighter tin isotopes ([Fig. 3](#)). This behavior makes it difficult to support analysis of low-tin bronzes for archaeological provenance studies using tin isotopes.

Currently, it is unclear if casting bronze results in isotopic fractionation between core and surface. Both [Yamazaki et al. \(2014\)](#) and [Nickel et al. \(2012\)](#) detected a slight enrichment of heavy tin at the surface of cast bronze objects, and both interpreted this result as enrichment due to evaporation of lighter tin isotopes from the hot surface exposed to atmospheric oxygen. [Nickel et al. \(2012\)](#) detected no difference between body metal and corroded surfaces in archaeological samples but noticed a slight enrichment in artificially grown patinas. Therefore, tin isotopes could potentially be used to identify artificially-patinated forgeries in museums, but further testing is required on the fractionation of tin isotopes from techniques of traditional bronze casting.

Though the results of the above studies are extremely important in understanding and applying tin isotopic analysis to archaeological samples, they do raise several important issues to consider. 1) Completely reducing conditions did not significantly alter the tin isotopic composition, but complete reduction cannot be assumed for every archaeological smelt. 2) Although the average tin isotopic ratio of all co-smelting products is approximately equal to the isotopic ratio of the original cassiterite mineral, this experiment was conducted in laboratory conditions where one could recover both the bronze and unalloyed tin

⁶ Cementation alloying involves heating cassiterite with copper metal and charcoal in a crucible.

⁷ Co-smelting involves smelting cassiterite with copper oxide ores to produce a Cu–Sn alloy.

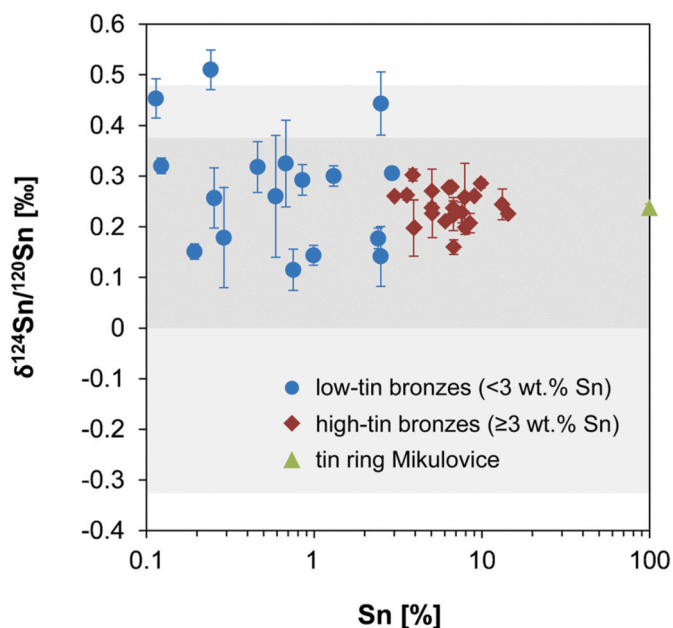


Fig. 3. Berger et al. (2017) demonstrate that low-tin bronzes are significantly impacted by the preferential volatilization of lighter tin isotopes in the bronze making process. This implies that low-tin bronzes are poor samples for tin isotopic analysis, and researchers are instead directed to the radiogenic isotopic methods employed by Berger et al. (2019) and Molofsky et al. (2014) (Reproduced from Berger et al., 2017, Fig. 16).

metal components. In archaeological situations the unalloyed tin metal component is unlikely to be recovered and would be almost impossible to match with its successful bronze component. Further, the remaining tin metal component could have simply been recycled into the next metal batch. 3) A difference was noted in tin recovery percentages from laboratory and archaeological smelts. Berger et al. (2018) addressed this difference by subtracting an isotopic value of 0.1‰ from the $\delta_{120}^{124}\text{Sn}$ value (or -0.2‰ for studies using $\delta_{116}^{124}\text{Sn}$; Mason et al. (2020); Mason (2020)). They argued that this should be the degree of isotopic fractionation during a smelt with 30% recovery and would thus account for low tin recovery and tin volatilization behavior. This fractionation correction value is lower than the variation observed in the orebodies of most interest to Berger et al. (2018), and subsequent studies have agreed that this correction factor helps to align archaeological and ore deposit data (Berger et al., 2019; Bower et al., 2019; Mason et al., 2020; Mason, 2020, 37; Powell et al., 2019). But it is nevertheless an arbitrary correction, and there can be no assurance that it would apply to all archaeological tin and bronze.

Subsequent geological studies have also added to our understanding of the fractionation of tin isotopes in geological environments. Yao et al. (2018) showed that redox processes enrich cassiterite minerals in heavy tin isotopes as they are precipitated from tin bearing fluids through the oxidation of Sn^{2+} to Sn^{4+} , thus providing a stronger bonding environment. Later forming (and much rarer) tin minerals, like stannite, exhibit a lighter tin isotopic signature because the prior precipitation of cassiterite has depleted the tin-bearing hydrothermal fluid in heavy tin isotopes (Yao et al., 2018). Thus, small deposits which formed quickly are expected to have a more homogenous distribution of tin isotopes while larger deposits, where the reaction front moves over time, exhibit a greater range of fractionation. Further, equilibrium fractionation in boiling tin bearing fluids has been observed and works to deplete these fluids in heavier tin isotopes by partitioning the heavier component to the gaseous SnCl_4 molecule in the vapor phase. This has a shorter Sn–Cl bond length and therefore a stronger bond (She et al., 2020; Wang et al., 2019). Thus, cassiterite deposits which crystallized slowly at depth, such

as cassiterite emplaced in pegmatites, exhibit more homogenous tin isotope values because no vapor phase was formed and redox reactions were the primary driver of isotopic fractionation (Wang et al., 2019). For deposits which formed at shallow depth, such as volcanic deposits, both redox reactions and the generation of a vapor phase via boiling produce tin isotopic fractionation. Thus, deposits formed at shallow depth generally display more tin isotopic heterogeneity and more positive $\delta_{116}^{124}\text{Sn}$ values⁸ (Wang et al., 2019). Variation in the tin isotopic signature of cassiterite minerals, therefore, appears to reflect the geological conditions under which they were formed, and Powell et al. (2018b, 2019) and Mason (2020) used this characteristic to discriminate between various European and west Asian tin deposits (Fig. 4).

3.2.4. Applications

Tin and Bronze Metal: Much effort, and much funding, has recently been devoted to tin isotopes because one of the major unsolved questions in the archaeology of western Eurasia is the source (or sources) of tin for the Bronze Age. This has been intensely debated for almost fifty years (Franklin 1978; Muhly 1973). Although lead isotope measurements are useful in provenance studies of pure tin, they are usually not applicable to the analysis of bronze because the small amount of lead in the tin is usually overwhelmed by the larger amount of lead in the copper with which it is alloyed. There has therefore been an extraordinary level of interest in the application of tin isotopic analysis to bronze objects and tin ore deposits in Europe, around the Mediterranean, and in western Asia (Balliana et al., 2013; Berger et al., 2019; Bower et al. 2013, 2019, 2019; Haustein et al., 2010; Mason et al. 2016, 2020; Mason 2020; Powell et al. 2018b, 2019; Yamazaki et al. 2013, 2014).

Earlier applications of tin isotopic analysis did not appreciate some of the difficulties discussed in the previous section, and so their conclusions should be viewed with some caution. Haustein et al. (2010) claimed to distinguish Cornwall (England) and Erzgebirge (Germany) tin sources with tin isotopes. However, isotopic differences between regions are slight at best, and often overlap one another. Mason (2020) and Powell et al. (2018b, 2019) have since shown that overlap between Cornwall and Erzgebirge tin are better resolved when the Erzgebirge data is broken down by geological pluton (east, west, and central; Fig. 4). Balliana et al. (2013) analyzed an assemblage of pre-Roman and Roman bronze metals from Spain using the same notation as Mason et al. (2016). Their data shows some clustering of isotopic values by source, but data produced by Mason et al. (2016) from the Balkans exhibits a similar isotopic distribution to that of Balliana et al. (2013). Tin from Spain and the Balkans cannot therefore be distinguished by any means other than context (Balliana et al., 2013, Fig. 3a; Mason et al., 2016, Fig. 4). Balliana et al. (2013) also conducted copper isotopic analysis on these bronzes, including an attempt to discriminate localities by plotting $\delta_{116}^{122}\text{Sn}$ vs. $\delta^{65}\text{Cu}$, but no discrimination is apparent in this plot.

Recent studies applying tin isotopes have predominantly originated from two camps: the U.S. group comprised of the American geologists Ryan Mathur, Wayne Powell, and Andrea Mason; and the German group headed by Ernst Pernicka. The U.S. group has focused on integrating statistics (distributional, multivariate, and Bayesian) and geological parameters to investigate the provenance of archaeological bronzes; particularly in objects from Austria, Bosnia and Herzegovina, Bulgaria, Czechia, Hungary, Romania, and Serbia dating to the Bronze and Iron Ages (Mason et al., 2020; Mason 2020; Powell et al., 2018b, 2019, Fig. 4). They have also significantly expanded the existing body of data for cassiterite ores. To understand the isotopic variation in European tin

⁸ It should be noted, however, that She et al. (2020) achieved opposite results (enrichment of liquid phase in heavy tin isotopes) at sub-boiling temperatures (96 °C) and attribute this result to the back-reaction of SnCl_4 at the liquid-vapor boundary. Thus, degree and type (equilibrium vs. kinetic) fractionation appears to be highly temperature dependent.

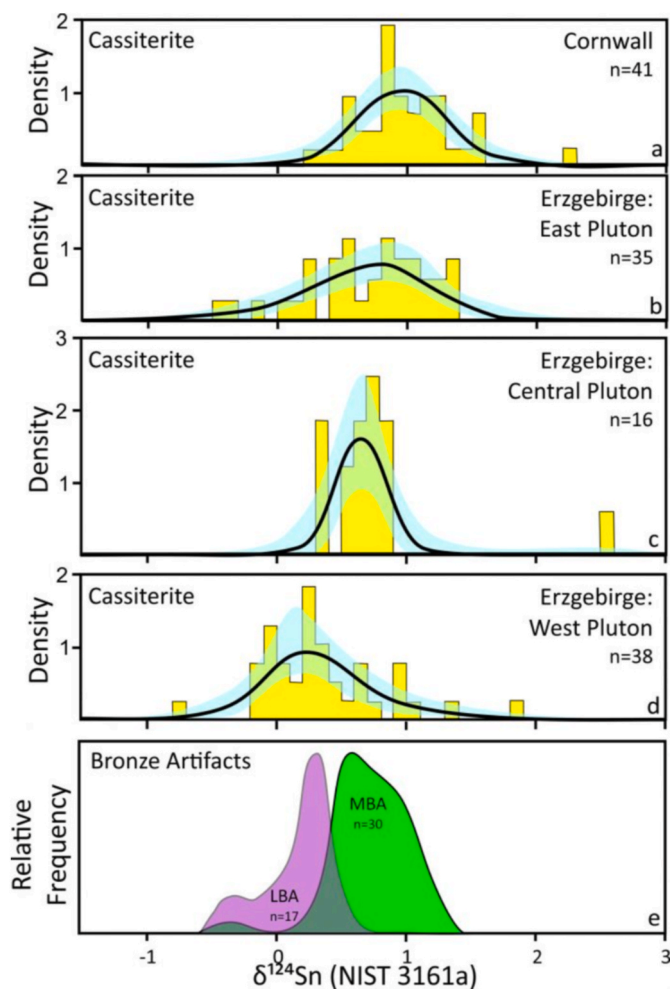


Fig. 4. Mason (2020) and Powell et al. (2018a, 2019) use recent understandings on the geological fractionation mechanism of tin (Wang et al., 2019; Yao et al., 2018) to map the isotopic distribution of tin deposits in England, Germany, and Serbia. Differences in tin isotopic distribution correspond to the scale and depth of tin mineralization, and these mechanisms appear to produce slight differences between various deposits in England, Germany, and Serbia. As is clear, overlaps still exist and Mason (2020) and Powell et al. (2018a, 2019) use the distance postulate and the archaeological record to assess the most likely tin source(s) for sampled objects. For a more expanded diagram, see Mason (2020, Fig. 9) (Reproduced from Powell et al., 2019, Fig. 3).

deposits, they relied on recent advances in the geological principles of tin isotopic fractionation (Yao et al., 2018; Wang et al., 2019) (Fig. 4). The integration of geological and statistical frameworks allowed them to assess the probability that archaeologically defined groups - organized regionally (Mason et al., 2020; Mason 2020; Powell et al., 2018b) or chronologically (Powell et al., 2019) - matched geological data at the level of individual ore deposits. However, this publication group also acknowledges that several limitations remain in tin isotopic analysis: 1) overlaps still exist, particularly between deposits formed under similar geological conditions (e.g. the Erzgebirge East Pluton and Cornwall); 2) there remains a need for further geological sampling, particularly of very small deposits which would be considered un-economical by modern mining standards; and 3) areas of overlap can at present only be resolved on the basis of which deposits are closest, or which make the most archaeological sense. The tin isotope data is not therefore a truly independent source of evidence for provenance.

Publications from the German team, meanwhile, have focused on the provenance of bronze and tin objects from Europe and the Mediterranean (Berger et al., 2019; Nessel et al., 2016). Nessel et al. (2016) used

both ^{116}Sn and ^{120}Sn as the denominator but were largely unable to assess where the tin in their German, Hungarian, Romanian, and Cretan samples originated. Berger et al. (2019) focused exclusively on the analysis of Late Bronze Age (LBA) tin ingots and objects from the Eastern Mediterranean and combined tin isotopic analysis with trace elements and lead isotopes. The tin isotopic data are inconclusive, but the lead isotopes for most of the ingots produced an isochron age consistent with the Variscan orogeny (320-280 My). This approach is consistent with previous studies on the provenance of tin using lead isotopes (e.g. Molofsky et al., 2014). Berger et al. (2019) then used tin isotopes and trace elements to narrow down the list of possible sources. LBA tin ingots from modern Israel most likely source to European tin deposits, and especially to those of Cornwall, while the oldest example (from Mochlos on Crete) might derive from tin deposits in either Afghanistan or Tadjhikistan.

The results presented above highlight the difficulty of working with tin isotope data. There is a very limited range of natural variation, the sources for which tin isotope data is available exhibit a wide degree of overlap, and there is no data as yet for many potential geological sources of tin. Informed interpretation of tin isotopes requires a detailed geological understanding of tin mineralization within each potential tin deposit. For future studies using tin isotopes, we urge scholars to (1) use the KCN reduction method highlighted by Brüggemann et al. (2017), Hausteiner et al. (2010), Mason et al. (2020), Mason (2020), and Mathur et al. (2017) and (2) to agree on a standard way of reporting results. Based on the state of tin isotopic analysis, we agree with Berger et al. (2019) that lead isotope analysis of tin metal should be considered the first line of analysis when conducting an investigation of tin provenance, with tin isotopes and trace elements in supporting roles.

3.3. Fe isotopes

3.3.1. Geochemical and isotopic background

Whereas copper and tin are relatively rare elements, iron ($Z = 26$) is geochemically abundant (5.63 wt % of the earth's crust) and can be found in many forms, including hydroxides, carbonates, oxides, silicates, and sulfides. The common valences are +2 and +3, and more rarely +6. Terrestrial native iron (Fe^0) is extremely rare, but forged iron-nickel meteorites are occasionally reported in archaeological contexts. Iron oxides, hydroxides, and carbonates were processed to produce ceramic, metal and glass objects, and used unprocessed as brown, yellow and red pigments in rock art.

Iron isotopic analysis is a common analytical method in the fields of geochemistry and paleoceanography, but has yet to see wide application in the field of archaeology (Hoefs, 2018, 129–136). Interest in iron isotopes in the fields of geochemistry and paleoceanography is a result of iron's high abundance in the natural world, and its role in high- and low-temperature geological processes (Hoefs, 2018). However, the influence of temperature and fluid history in the formation of iron isotopic ratios would make it difficult for iron isotopes to be used in provenance studies (Rose et al., 2019), because a single mineral (e.g. hematite) could have different isotopic signatures within an individual deposit because of complex histories of deposition and subsequent weathering (see Anbar 2004; Beard et al., 2003; Beard and Johnson, 2004). It is currently unclear how useful iron isotopes can be for archaeological inference, but Rose et al. (2019) outline potential alternative uses for iron isotopes. This is discussed further below.

3.3.2. Notations, standards, uncertainties

Iron has four stable isotopes ($^{54}\text{Fe} - 5.84\%$, $^{56}\text{Fe} - 91.76\%$, $^{57}\text{Fe} - 2.12\%$, $^{58}\text{Fe} - 0.28\%$), and isotopic variations are typically reported as $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values:

$$\delta^{\text{Fe}}\text{‰} = \left[\frac{\left(\frac{{}^{\text{Fe}}}{{}^{54}\text{Fe}} \right)_{\text{Sample}}}{\left(\frac{{}^{\text{Fe}}}{{}^{54}\text{Fe}} \right)_{\text{Standard}}} - 1 \right] * 1000$$

The standard most commonly used for this measurement is NIST IRMM-014. $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values typically range between -4 and $+2\text{‰}$ and can be measured with a precision of 0.05‰ (Craddock and Dauphas 2010; Hoefs 2018, 129; Milot et al., 2016a). Details on the range of plants, shales, river and ocean water, and magmatic rocks can be found in Hoefs (2018) and references therein.

3.3.3. Causes of fractionation

Fractionation of iron isotopes is largely caused by redox reactions. The more oxidized Fe^{3+} minerals and aqueous species are enriched in heavy isotopes of Fe, while Fe^{2+} minerals and species are typically depleted. However, the isotopic composition of iron minerals can vary at the mining district, deposit, vein, and even individual mineral-scale, and reflects the complex fluid alteration and precipitation processes to which the sample has been subjected (Horn et al., 2006; Markl et al., 2006). Given the role of fluid history in altering iron isotopic ratios and the ubiquity of iron minerals, we do not consider iron isotopes a viable indicator of provenance. We agree with Rose et al. (2019), who conclude that it is impractical and unfeasible to sample all potential iron deposits within a given landscape (or larger, if looking at wider networks of mobility and exchange).

Experimental reconstructions by Eerkens et al. (2014), Milot et al. (2016a), and Rose et al. (2019) have shown that iron isotopic fractionation from anthropogenic processes (smelting or firing) is minimal, though one bloomery smelting experiment from Milot et al. (2016a) did produce a more positive (heavier) $\delta^{57}\text{Fe}$ isotopic signature for the bloom than for slag, refined metal, and ore (16–17). They suggested that the difference in isotopic signature between bloom and other components could either have been a result of the incomplete nature of the smelt (lack of separation between bloom and slag) which resulted in kinetic fractionation of iron isotopic signature (though Milot et al. argue that this would result in a lighter, not heavier, isotopic signature), or that the high sulfur content of the 2009 bloom enriched it in heavy Fe and thus produced the higher $\delta^{57}\text{Fe}$ value (Milot et al., 2016a, 17). Additional data from experimental kiln linings indicate that minimal isotopic diffusion should occur between iron bloom/slag and the clay used for the furnace, though Milot et al. (2016a) admit that this could change if a high-iron clay was used in the construction of the furnace. Rose et al. (2019) also note that other processes (pH of the ore forming environment and intrusion of organic matter) can significantly enrich a mineral in heavy Fe isotopes.

It appears that iron isotopic fractionation between corrosion productions and iron metal in marine and oxidizing environments is also minimal (Rose et al., 2020). The authors of this study admit that more samples are needed before this hypothesis can be considered proven, however initial results appear promising and show that sample sizes of at least 1 mg minimize micro-fractionation from iron dissolution and produce data that is comparable to iron isotopic values of the core metal. In future studies, the authors also plan to investigate iron isotopic fractionation in acidic and anoxic soils. For a thorough review of other mechanisms responsible for iron isotopic fractionation, see Dauphas et al. (2017).

3.3.4. Applications

Chert: Chert is one form of a common silica mineral (chalcedony). It has a very fine grain size and was therefore much prized for flaking small stone tools. Chert may incorporate impurities that lend the mineral its color. Among these are goethite ($\text{FeO}(\text{OH})$), which gives chert a yellow color. Mathur et al. (2020) investigated the potential of iron isotopes as a method to provenance yellow cherts in the American Northeast. Their preliminary study focused on Bald Eagle chert in Pennsylvania, but also

investigated a number of other chert deposits in Canada, Massachusetts, New Jersey, and Rhode Island. They showed that there is some isotopic separation between natural deposits of yellow chert, but they have few samples from deposits other than Bald Eagle. These results are promising, and we look forward to seeing expanded sampling of other yellow chert deposits in the area to fully prove the provenance postulate.

Though chert was often used in its natural state, it was also common practice to heat-treat chert to improve its mechanical properties (Mathur et al., 2020). This had the added effect of transforming yellow chert to red chert, as goethite was converted to hematite (Fe_2O_3). Mathur et al. (2020) experimentally tested if this process fractionates the isotopic signature of the chert and concluded that any changes to the iron isotopic signature were not caused by redox processes, as iron remains in its Fe^{3+} state. Rather, it seems that the process of burying chert in the soil under a heat source is the primary contributor to iron isotopic fractionation. Mathur et al. (2020) showed that iron isotopes were exchanged between chert and iron-bearing soil to create a red chert that is typically 0.2‰ heavier than the original isotopic signature for yellow chert. However, their results also showed that iron fractionation is dependent on the type of soil (there was no isotopic shift when heated in soils with no measurable iron, while one soil type depleted the chert signature in heavy Fe).

Further work is needed to understand the exchange mechanism between soil and chert, and also to investigate the utility of this technique on other colors of chert. Future studies looking to apply this technique should understand the range of chert colors on a regional level and the likely composition of the soil where chert objects were heat treated.

Pigments and Clay: Iron plays a major role in materials used for ceramic manufacture, as a pigment, as part of a glaze, or as a component of the clay. Eerkens et al. (2014) applied iron isotopic analysis to ceramic paints in an attempt to discriminate and reconstruct the technological style of Peruvian ceramic producers between 1800 BCE – 1532 CE. They combined mineralogical, chemical, and isotopic analyses, and found that no fractionation of iron isotopes occurs due to firing temperature or kiln atmosphere. No isotopic diffusion was observed between the clay matrix and paint, either. The authors applied iron isotopic analysis to characterize both red (oxidized, Fe^{3+}) and black (reduced, Fe^{2+}) iron pigments, but only sampled nine hematite minerals from Peru. Thus, the explanatory power of their pigment analysis is limited, as iron isotopes can vary by mineral and fluid history, as the authors admit. Though their results intriguingly show that red and black pigments separate into distinct clusters (Eerkens et al., 2014, Fig. 4), the lack of an adequate geological sampling strategy and lack of understanding of the mechanisms of fractionation of iron isotopes makes their assignments to particular sources unconvincing.

Iron Metal: Milot et al. (2016a, 2016b) applied iron isotopic analysis in an attempt to infer the provenance of iron bars from the Les Saintes-Maries-de-la Mer Roman shipwreck, near the Montagne Noir massif. They assigned a local provenance (Montagne Noir) for most of these objects, and their groupings align with the conclusions that Baron et al. (2011) made using trace element analyses of slag inclusions in the same samples. However, this study has a number of important factors which make it perhaps an exceptional example of a provenance study. Not only were the archaeological mines known, still extant, and well understood from a mineralogical and fluid history standpoint, but these authors also possessed archaeological ores that could be matched to this mining area. They were also able to conduct their experimental smelts with ore from this region in order to study fractionation effects from the smelting process. The only unknowns left in their study were the isotopic variability of these ores (mostly gossans) at a micro- and macro-level

within the Montagne Noir massif, and the iron isotopic ratios for other possible areas of provenance.⁹ Milot et al. (2016a, 18) acknowledged this shortcoming and predicted that a regional scale approach would likely produce overlapping isotopic fields.

In a follow-up study focused on bog iron ore from Germany and central Europe, Rose et al. (2019) confirmed the issue of overlapping isotopic fields from different deposits. Their goal was to investigate iron isotopic fingerprints of bog ores, which were a major resource for much of central and northern Europe. Their experiments showed minimal fractionation during the smelting process and make valuable contributions to understanding the impact that organic matter has on the distribution of heavy and light iron isotopes. Rose et al. (2019) ultimately defined several data fields which would overlap with the archaeological iron bar samples analyzed by Milot et al. (2016a, 2016b) (Fig. 5). Thus, they concluded that isotopic overlap of potential sources violates the provenance postulate and makes iron isotopic analysis unsuitable as a method for establishing the provenance of archaeological iron. Rose et al. (2019) did admit that there is potential for this technique as a complimentary method to investigate intra-deposit zonation and exploitation, and landscape reconstruction, but only in support of other approaches, such as trace element and osmium isotopic analyses.

Non-ferrous Metals: Iron isotopes have also been tested as a complementary tracer to lead isotopes for non-ferrous archaeological metals (Milot et al., 2018). For this study, Milot et al. analyzed galena, slag from lead-silver smelting, and furnace linings from Imiter mine, Morocco with both lead and iron isotopes. As expected, there is overlap in the lead isotope data from the Imiter mine and other Moroccan ore deposits, but gossan ore and other geological materials from these deposits (including Imiter itself) were not characterized using iron isotopes. This was a controlled study where the provenance of these materials was previously known, however if this combination is to be applied in future archaeological scenarios then the proposed potential of the technique to resolve areas of lead isotopic overlap needs to be fully proven. This study has a number of other limitations, including a lack of experimental testing of the fractionation of iron isotopes throughout the non-ferrous metallurgical process, and restricted sampling – only metallurgical debris and

furnace linings were sampled. Milot et al. (2018) ultimately concluded that iron isotopic analysis is an adequate complimentary technique for determining the provenance of non-ferrous metallurgical remains. We are unconvinced.

It is clear that ubiquity of iron sulfides, oxides, carbonates, and hydroxides – and the potential for iron isotopic signatures to vary at the centimeter scale – inhibits the use of iron isotopic analysis for provenance of archaeological materials. Future studies should concentrate on first assessing this technique from a geological standpoint – by assessing the variation of iron isotopic data within the broader catchment of an archaeological study – before applying this technique to additional archaeological samples. Rose et al. (2019) also outlined several interesting avenues of future work which could make iron isotopic analysis a useful analytical technique, but at present it appears that osmium isotopic analysis is a better technique for provenance of iron (Brauns et al. 2013, 2020; Dillmann et al., 2017). But any advocate of isotopic or chemical methods for inferring the provenance of iron must at some point acknowledge the presence of the elephant in the room, which is the geochemical abundance of iron. While it is sometimes possible to distinguish between local deposits using these techniques (e.g. Dillmann et al., 2017), it seems extremely unlikely that any technique could convincingly establish the provenance of iron imported over long distances – the number of potential sources will inevitably make it impossible for archaeometrists to characterize them all. In this we find ourselves in disagreement with the optimistic predictions of Charlton (2015).

3.4. Ag isotopes

3.4.1. Geochemical and isotopic background

Silver ($Z = 47$) has two stable isotopes ($^{107}\text{Ag} - 51.4\%$ and $^{109}\text{Ag} - 48.6\%$). It is a very rare element, with an abundance in the earth's crust of only 0.05 ppm. It is found as a native metal (Ag^0) and as a natural alloy with gold (electrum). It is also found as silver sulfides, sulfoantimonides, and chlorides; the usual valence is Ag^+ . It substitutes readily for lead, and most silver production today is from the lead sulfide galena.

Interest in this isotopic system in archaeology and numismatics was fueled by hopes that it would be a better indicator of silver provenance than lead isotopes¹⁰ (Albarède et al., 2016, 130; Fujii and Albarède 2018, 38), and more recently, it has also been used in efforts to proveance archaeological gold.

3.4.2. Notations, standards, uncertainties

Silver isotopic variation was previously reported in epsilon notation (ϵ), which measures the difference between samples and standards in parts per 10,000 (Albarède et al., 2016; Baron et al., 2019; Desautly et al., 2011; Desautly and Albarède 2013):

$$\epsilon^{109}\text{Ag} = \left[\frac{\left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}} \right)_{\text{Sample}}}{\left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}} \right)_{\text{Standard}}} - 1 \right] \times 10,000$$

More recent investigation by Arribas et al. (2020), Chugaev and Chernyshev (2009), and Mathur et al. (2018) have expanded the isotopic range of silver isotopes. Therefore, these papers employ the delta notation, which measures the difference between samples and standards in parts per 1000 (‰):

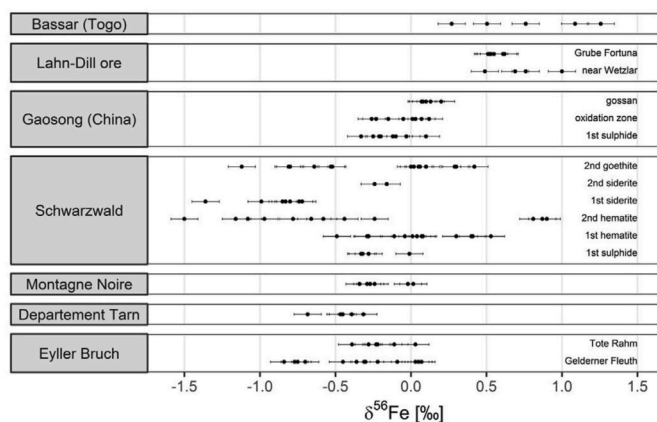


Fig. 5. Rose et al. (2019) test the ability of iron isotopes to provenance bog ore in central and northern Europe but show that the geological fractionation of iron is extremely varied. This creates wide overlaps between different iron deposits and prevents iron isotopes from being used to provenance iron objects (Reproduced from Rose et al., 2019, Fig. 6).

⁹ Baron et al. (2011) identified a group of iron bars whose trace elemental composition did not match the Montagne Noir massif, though some of these samples overlapped with the iron isotopic “fingerprint” for the Montagne Noir massif.

¹⁰ Silver purification technologies like cupellation often require the addition of lead, and thus complicate the application of lead isotopic analysis.

$$\delta^{109}\text{Ag}\text{‰} = \left[\frac{\left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}} \right)_{\text{Sample}}}{\left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}} \right)_{\text{Standard}}} - 1 \right] \times 1,000$$

The standard is typically NIST SRM978a, and $\delta^{109}\text{Ag}$ values vary between about from -1 to $+5\text{‰}$ with errors typically less than 0.015‰ (Arribas et al., 2020; Mathur et al., 2018).

3.4.3. Causes of fractionation

Several studies have investigated the isotopic variability of native silver and various other hypogene and supergene silver bearing minerals (including silver-sulfides, -sulfosalts, and -chlorides) from a large range of deposits and districts (Arribas et al., 2020; Desaulty et al., 2011; Desaulty and Albarède 2013; Mathur et al., 2018). Their results demonstrate that silver isotopes are primarily fractionated by redox processes, including the weathering of primary hypogene ores to more frequently exploited supergene minerals (Arribas et al., 2020, 9–12; Fujii and Albarède 2018, 40; Mathur et al., 2018), but solid-state ion conduction and other less well-studied processes can also result in natural fractionation of silver isotopes (Anderson et al., 2019). Redox fractionation behavior of silver isotopes is similar to that of copper isotopes, where oxidation of hypogene native silver and silver sulfide minerals typically results in the enrichment of ^{109}Ag because of the stronger bonding environment. Data presented in Arribas et al. (2020) is particularly enlightening and shows that hypogene native silver and silver sulfides center around 0‰ (with a range of -0.4‰ to $+0.4\text{‰}$). Supergene native silver also centers around 0 but with a larger overall range (at least -1‰ to $+2\text{‰}$; Fig. 6). Supergene halides typically plot above 0.5‰ . Thus, it appears that silver isotopic data within a single deposit varies based on the temperatures of mineralizing fluids. It is important to note that no patterns discriminate data by location, deposit type, or mineralization age, and thus all mined silver deposits will overlap with one another (Arribas et al., 2020). This precludes the use of silver isotopes as an indicator of provenance. Future studies should employ silver isotopes in a manner similar to current use of copper isotopes – to infer whether the ore was hypogene or supergene.

For archaeological purposes, there is no fractionation of Ag as a result of metallurgical processes so long as Ag yields are high (Desaulty et al., 2011). Luckily, silver was considered a precious metal, so past craftsmen usually made a concerted effort to keep silver yields as high as

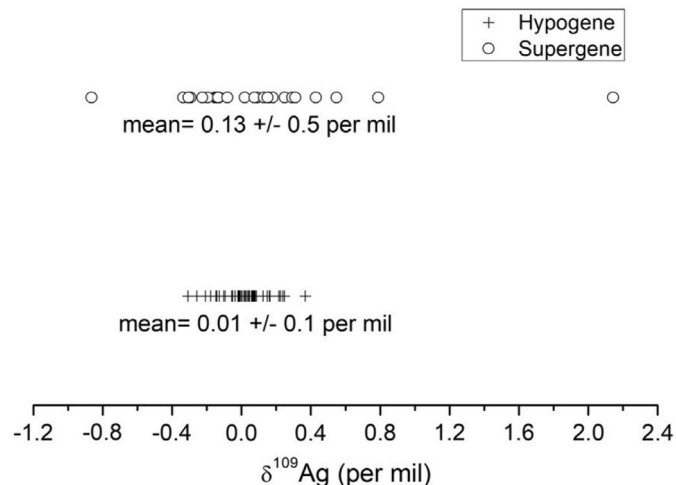


Fig. 6. Mathur et al. (2018) expand the known range of silver isotopes and illustrate that they behave similar to copper isotopes. Thus, as silver migrates from hypogene to supergene, its silver isotopic ratio fractionates. This suggests that silver isotopes can be applied to identify the type of ore selected for silver metallurgical activities (Reproduced from Mathur et al., 2018, Fig. 7).

possible (Desaulty et al., 2011, 9005). When processing samples for silver isotopic analysis, it is important to eliminate chlorine, as silver can complex with the Cl^- ion to precipitate AgCl and thus impact the $\delta^{109}\text{Ag}$ value (Baron et al., 2019; Fujii and Albarède 2018; Anderson et al., 2019).

3.4.4. Applications

Silver Metal: Applications of silver isotopes in archaeology prior to 2017 were spearheaded by Francis Albarède and colleagues at Université de Lyon (Desaulty et al., 2011; Desaulty and Albarède, 2013; Albarède et al., 2016). These studies took creative multi-isotopic approaches in efforts to not only provenance the silver and lead components of the silver metallurgical process, but also to investigate the discriminatory power of various isotopic combinations.¹¹ Initial results appeared promising, as all were able to illustrate a degree of separation between silver from Mexico, Peru and Europe. However, these studies were done before there was much data on variation in geological sources of silver or knowledge of the fractionation mechanism of silver isotopes, and differences between various categories were slight when only silver isotope data was plotted (Fujii and Albarède 2018) (Fig. 7). Subsequent work by Mathur et al. (2018), Fujii and Albarède (2018), and Arribas et al. (2020) have improved our understanding of natural variation in the silver isotopic system. It now appears that the data produced by Desaulty et al. (2011), Desaulty and Albarède (2013), and Albarède et al. (2016) match the range of variation in hypogene silver minerals and in supergene native silver. However, since these studies also employed lead

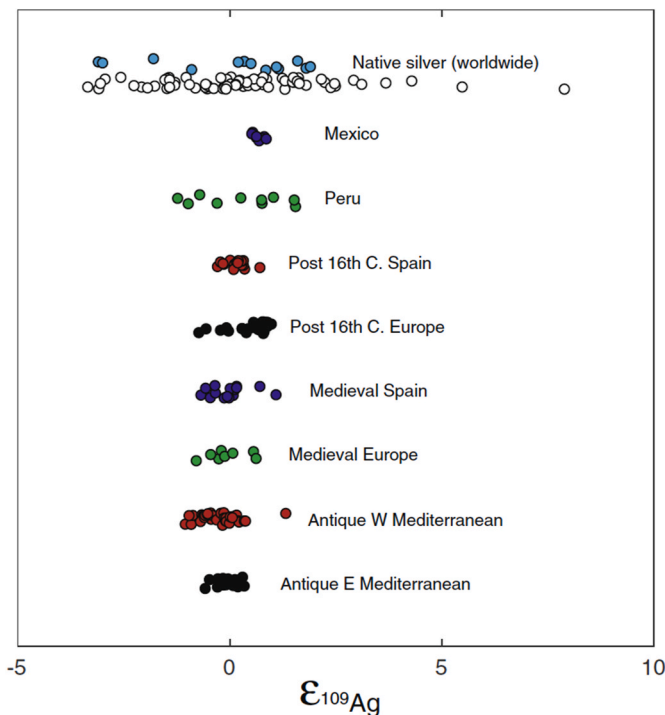


Fig. 7. Previous to Mathur et al. (2018), archaeological studies using silver isotopes produced data within a very narrow band and used $\epsilon^{109}\text{Ag}$ patterning to make provenance assessments. If reinterpreted based on the conclusions of Mathur et al. (2018) and Arribas et al. (2020), these data indicate the use of hypogene or supergene native silver (Reproduced from Fujii and Albarède, 20186 Fig.1).

¹¹ These studies used a combination of Pb, Cu, and Ag isotopes. Cu isotopes were included, as copper is often alloyed with silver metal to improve hardness.

isotopic analysis, many of their provenance conclusions are still valid.

Gold Metal: Since 2018, interest in silver isotopes has also focused on archaeological gold, as both silver and gold are transported by the same hydrothermal fluids at primary lode gold deposits and gold nuggets can host a wide range of silver concentrations (ppm to %). Mining of gold, both archaeological and current, has focused on primary hydrothermal deposits as well as secondary detrital placer deposits, which can be many hundreds of km from their primary source.

Baron et al. (2019) and Brüggmann et al. (2019) both tested silver isotopes as a potential tool for provenancing gold, and framed their studies as an initial investigation of if/how redox and low temperature processes fractionate silver isotopes in gold minerals across this mineralization process (primary to placer). Baron et al. (2019) used a combination of lead, silver, and copper isotopes to investigate multiple generations of primary gold mineralization within the French Massif Central and applied silver isotopes to try and resolve deposit overlaps within the two generations of mineralization defined by lead isotopes. However, their $\epsilon^{109}\text{Ag}$ data occupies an extremely narrow range consistent with other hypothermal ores (Mathur et al., 2018), is negatively correlated with $\delta^{65}\text{Cu}$, and does not pattern by groups established with lead isotopes. Therefore, Baron et al. (2019) concluded that the fractionation behavior of silver isotopes in gold is similar to that measured in silver minerals, and that the negative correlation of $\epsilon^{109}\text{Ag}$ and $\delta^{65}\text{Cu}$ can be explained by the higher mobility of copper during the gossan formation process. Silver, on the other hand, maintains its hypothermal signature in this primary deposit, regardless of stratigraphic position or generation of gold mineralization.

Brüggmann et al. (2019) added to these conclusions by sampling both primary hypothermal and secondary placer gold deposits, some many hundreds of km from the supposed primary source. Analyzed placer gold samples from Bolivia vary greatly and indicate that silver gain or loss in gold grains during their detrital transport can affect $\epsilon^{109}\text{Ag}$ values. Conversely, $\epsilon^{109}\text{Ag}$ values for placer gold samples from the Rhein river are homogenous, but Brüggmann et al. (2019) suggested that this homogeneity was produced from the mixing and deposition of gold from various sources. These issues illustrate the potential limitation of silver isotopic analysis to source gold, though integration with other isotopic systems could still lead to useful conclusions.

3.5. Sb isotopes

3.5.1. Geochemical and isotopic background

Antimony (Z = 51) has two stable isotopes (^{121}Sb – 57.21% and ^{123}Sb – 42.79%) (Hoefs, 2018, 159) and its abundance in the earth's crust is only 0.2 ppm. As an amphoteric metalloid, it has a very wide range of valences, from –3 to +5. Native antimony (Sb^0) is rare but has been recovered from archaeological contexts (Dillis et al., 2019). It is most commonly found as a sulfide (especially stibnite Sb_2S_3) or sulfosalt. The continuous solid solution series from tetrahedrite $\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{Sb}_4\text{S}_{13}$ to tennantite $\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{As}_4\text{S}_{13}$ is also of particular interest to archaeologists. Ore deposits dominated by these minerals are called fahlores, and smelting of them produced the copper/arsenic/antimony alloys that were important in the early history of metallurgy in western Eurasia (Dillis et al., 2019; Killick, 2014; Reguera-Galan et al., 2019). Antimony oxides were also used in prehistory as an opacifier and de-colorant in Greek, Roman, Egyptian, and Mesopotamian glass (Degryse et al., 2015; Lobo et al., 2013, 2014).

3.5.2. Notations, standards, uncertainties

Isotopic data is expressed as $\epsilon^{123}\text{Sb}$:

$$\epsilon^{123}\text{Sb} = \left(\frac{\text{corr} \left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}} \right)_{\text{Sample}}}{\text{corr} \left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}} \right)_{\text{Standard}}} - 1 \right) \times 10,000$$

Studies applying antimony isotopic analysis have all used in-house standards (such as SPC Science, F2-SB03010; Lobo et al., 2014) and revised Russell's law for mass bias correction (Degryse et al., 2015, 155; Lobo et al., 2012, 1305–1306; Lobo et al., 2013; Lobo et al., 2014). On present data, the range of natural variation of $\epsilon^{123}\text{Sb}$ values is 10‰ and the precision of measurements by MC-ICP-MS is typically less than 1‰. Details on the range of sediments, environmental samples, seawater, and magmatic rocks can be found in Rouxel et al. (2003).

3.5.3. Causes of fractionation

Fractionation among antimony isotopes is poorly understood but is thought to be caused by physicochemical and redox processes (Dillis et al., 2019; Lobo et al., 2012, 1305; Lobo et al., 2013). Rouxel et al. (2003) reported significant fractionation among various geological and environmental samples in differing redox environments and confirmed these results experimentally by reducing Sb^{5+} to Sb^{3+} . Dillis et al. (2019) also conducted several experiments to evaluate how significantly redox processes fractionate the $\epsilon^{123}\text{Sb}$ ratio. They make two important conclusions. 1) There is significant risk in inducing fractionation during the digestion of samples for antimony isotopic analysis, as many procedures involve transformation from Sb^{5+} to Sb^{3+} . Thus, for high Sb glass and metal, researchers should use digestion procedure 3 in Dillis et al. (2019, 5–6). No fractionation was observed from this procedure because antimony remains in the Sb^{5+} valence. This procedure does fractionate the isotopic signature of stibnite ore, however, as it transforms Sb^{3+} to Sb^{5+} during the initial digestion. 2) Pyrotechnological processes (smelting of metals and opacification of glass) do fractionate antimony towards lighter isotopic values (usually by 0.5–2.5‰), because stibnite is oxidized to its Sb^{5+} state. This does not necessarily happen every time a glass is opacified, but rather depends on how fully Sb^{3+} is oxidized to Sb^{5+} for glass, or reduced to Sb^0 for metal. Future studies should also consult Dillis et al. (2019, 9–10) for direction on processing samples with Sb > 10 wt %.

3.5.4. Applications

Glass: Antimony was added to glass as an opacifier and colorant from the Late Bronze Age in Mesopotamia and Egypt (Dillis et al., 2019). Lobo et al. (2013, 2014) and Degryse et al. (2015) applied antimony isotopic analysis in an attempt to source the Sb opacifier incorporated into Mesopotamian, Egyptian, and Roman glass. Data produced by these studies were comparable, and initial results showed differences between Late Bronze Age Mesopotamian and Egyptian objects (with negative $\epsilon^{123}\text{Sb}$ values) and Roman glass objects (which usually had positive values). Degryse et al. (2020) reevaluated these results against new stibnite data from Georgia, and existing stibnite data of Degryse (2014) and Lobo et al. (2012), to frame general conclusions regarding the provenance of antimony opacifiers. By applying a –3‰ $\epsilon^{123}\text{Sb}$ fractionation correction to account for fractionation during pyrotechnological processes, Degryse et al. (2020) argued that Mesopotamian and Egyptian glass opacifiers match ore deposits in the Racha-Lechkumi region of Georgia. These deposits are also associated with gold mineralization, and they argued that stibnite-opacified yellow glass could act as a skeuomorph for this material. However, the range of ore data from other stibnite deposits in the Mediterranean would also overlap this data with the –3‰ $\epsilon^{123}\text{Sb}$ fractionation (Fig. 8) (Degryse et al., 2020, Fig. 1). Given the demonstrated overlap of $\epsilon^{123}\text{Sb}$ values from Georgia, Italy and Spain (Fig. 8), the lack of isotopic data for many other antimony deposits, and the shifts in $\epsilon^{123}\text{Sb}$ produced in the making of glass and in the laboratory, we believe that the results of Lobo et al. (2013, 2014), Degryse et al. (2015) and Degryse et al. (2020) should be reframed as evidence for the technological processes used during the opacification of these glasses, rather than as proof of provenance. Mesopotamian and Egyptian glasses show negative $\epsilon^{123}\text{Sb}$ values as antimony was oxidized to its Sb^{5+} valence, while Roman glasses usually have antimony in its Sb^{3+} valence (Fig. 8).

Metal: Copper-antimony alloys are much less commonly found in

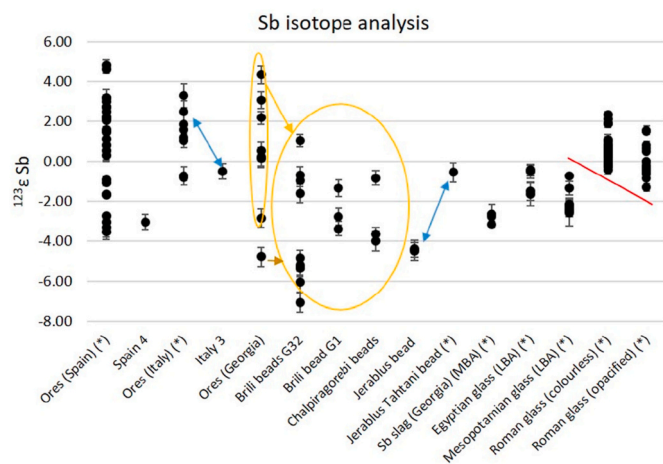


Fig. 8. Dillis et al. (2019) indicate that pyrotechnological treatment of stibnite can fractionate (usually by 0.5–2.5 $\epsilon^{123}\text{Sb}$) the antimony isotopic signature, as Sb^{3+} was commonly oxidized to Sb^{5+} during the glass making process and Sb^{3+} reduced to Sb^0 during the production of antimony metal. Dillis et al. (2019) and Degryse et al. (2020) argue that you can identify the provenance of glass and metal objects if you take a $-3 \epsilon^{123}\text{Sb}$ fractionation factor into account. We remain skeptical of this conclusion, however, due to isotopic overlaps between regions of interest, lack of isotopic data for many other antimony deposits, and potential for shifts in $\epsilon^{123}\text{Sb}$ during the making of glass and in the laboratory (Reproduced from Dillis et al., 2019, Fig. 8).

prehistory than are copper-arsenic alloys, but are well represented in the Early Bronze Age (EBA) of Anatolia (Dardeniz, 2020) and Italy (Dillis et al., 2019), and in the extraordinary Chalcolithic hoard of cast copper alloys from Nahal Mishmar Cave, Israel. The latter objects are remarkable for their technical excellence, their very early date (4200–4000 cal BCE) and for the absence of sources of antimony (or antimonial copper) ores in the Levant (Tadmor et al., 1995). Antimony deposits are reported from Georgia, Anatolia and Armenia (Dardeniz, 2020). There has been no Sb isotopic data yet published for Chalcolithic or EBA copper alloys from Anatolia, nor from Nahal Mishmar. Metallic antimony beads have been recovered from the Chalcolithic of central Italy, and from the Late Bronze Age (LBA) of Georgia and Armenia. Degryse et al. (2015) have analyzed antimony slag from Georgia and a metallic antimony bead from Syria, and these results have been reinterpreted by Dillis et al. (2019) based on conclusions made from their fractionation experiments. Dillis et al. (2019) sampled Sb-rich items of archaeological jewelry from the Caucasus region, and results showed the expected isotopic shift towards lighter $\epsilon^{123}\text{Sb}$ values because of the reduction of stibnite from an Sb^{3+} to Sb^0 state. Both Dillis et al. (2019) and Degryse et al. (2020) argued for a provenance match to Georgian ore deposits for at least half of the jewelry when the $-3 \epsilon^{123}\text{Sb}$ fractionation offset from reduction is taken into account (Fig. 8). While this is certainly a likely conclusion given the catchment of possible ore deposits within reach of these sites and their social networks, there is as yet insufficient antimony isotope data on other potential sources of antimony, especially those of Turkey (Dardeniz, 2020).

Reguera-Galan et al. (2019) also applied antimony isotopic analysis to complement their lead and copper isotopic study of Bronze Age Iberian arsenical copper samples. $\epsilon^{123}\text{Sb}$ values from their study appear to be randomly distributed and there are no $\epsilon^{123}\text{Sb}$ data on ores from this region to compare them to. It is unclear if this variation of $\epsilon^{123}\text{Sb}$ values is due to fractionation induced by procedural or metallurgical activities.

Following Dillis et al. (2019, 11), we conclude that interpretations of antimony isotope data as fractionation caused by technological practices of glass opacification and antimonial metallurgy seem much more secure than as indicators of provenance, when we know so little about the range of isotopic values within and between antimony ore deposits. We also need further studies of the extent to which laboratory

procedures and measurement may induce fractionation.

3.6. Hg isotopes

3.6.1. Geochemical and isotopic background

Mercury ($Z = 80$) has seven stable isotopes ($^{196}\text{Hg} - 0.15\%$, $^{198}\text{Hg} - 9.97\%$, $^{199}\text{Hg} - 16.87\%$, $^{200}\text{Hg} - 23.10\%$, $^{201}\text{Hg} - 13.18\%$, $^{202}\text{Hg} - 29.86\%$, $^{204}\text{Hg} - 6.87\%$) (Hoefs 2018, 164). It is a very rare element (crustal abundance: 0.08 ppm), and has valences of -1 , 0 , $+1$ and $+2$. Archaeologically, it is most often noted as the blood red cinnabar (HgS), which was valued as a pigment in many regions, but especially in China, Peru and Mesoamerica. In each of these regions it is found especially in elite tombs. It also occurs in nature as a native metal, as halides, and as sulfosalts. An important technological innovation in the use of mercury occurred in 1550's with the invention of the patio process in Mexico. This mixed liquid mercury with powdered ores of silver and gold. The mercury/silver/gold amalgam was easily recovered by washing away the silicate gangue, and the precious metals were then recovered by distilling off the mercury (Craddock 1995, 214–216; Nriagu 1993).

3.6.2. Notations, standards, uncertainties

Mercury stable isotopes are expressed in relation to the standard NIST SRM 3133 (Blum and Bergquist 2007). Reporting for this isotopic system is more complicated than for others, as natural materials may exhibit both mass-dependent and mass-independent variations in mercury isotope abundances. By convention, mercury isotope variations are reported in per-mil notation according to the equation below (where x is any mercury isotope with atomic mass between 199 and 204):

$$\delta^x \text{Hg} \text{‰} = \left[\frac{\left(\frac{x \text{Hg}}{^{198}\text{Hg}} \right)_{\text{Sample}}}{\left(\frac{x \text{Hg}}{^{198}\text{Hg}} \right)_{\text{Standard}}} - 1 \right] * 1000$$

By convention, $\delta^{202}\text{Hg}$ is used to denote mass-dependent fractionation. Mercury isotopes may also undergo mass-independent fractionation (MIF) by at least three different mechanisms (see Blum et al., 2014 for a review). Although mass-independent variations have been observed for all isotopes of Hg, most natural materials only preserve MIF of the two odd-numbered isotopes ^{199}Hg and ^{201}Hg . MIF of mercury isotopes is reported using the capital-delta notation, $\Delta^x \text{Hg}$, which is the difference between a measured $\delta^x \text{Hg}$ and the $\delta^x \text{Hg}$ value predicted by kinetic mass-dependent fractionation law. For values below 10‰, the following equation provides an adequate approximation of MIF¹²

$$\Delta^x \text{Hg} = \delta^x \text{Hg} - (\delta^{202}\text{Hg} \times Z)$$

For sediments and mercury ores, $\delta^{202}\text{Hg}$ values typically range between -4.5 and 2.5 ‰ with errors between 0.01 and 0.6‰, and $\Delta^{199}\text{Hg}$ typically ranges between -0.5 and 0.5 ‰ with errors less than 0.1‰ (Blum et al., 2014; Cooke et al., 2013, 4182; Hoefs 2018, 164–168). Details on the range of mercury isotopic values measured in fish, moss, lichen, coal, and volcanic emissions can be found in Hoefs (2018), and references cited therein.

3.6.3. Causes of fractionation

Mass-dependent fractionation of mercury isotopes may occur as a result of almost any physical, chemical, or biological process (Bergquist and Blum 2007; Blum and Johnson 2017; Cooke et al., 2013, 4182; Hoefs 2018, 165–166). Large MIF in natural materials is usually attributed to photochemical processes (Bergquist and Blum 2007; Blum and Johnson 2017; Cooke et al., 2013, 4182; Hoefs 2018, 165–166). For

¹² Z in the MIF equation is a scaling constant dependent on the mercury isotope under investigation. Constant values can be found in Bergquist and Blum (2007).

reviews, see [Blum and Johnson \(2017\)](#) and [Hoefs \(2018\)](#).

3.6.4. Applications

Cinnabar: [Cooke et al. \(2013\)](#) applied mercury isotopic analysis to cinnabar sprinkled as grave offerings, and used as a pigment on ceramic, metal, and wood objects from the pre-Inca period (pre 1400 CE) to the colonial period (1532–1821 CE). Initial results from this study are complex and require additional investigation. Cinnabar ore samples from the Huancavelica mine in Peru produce a linear array¹³ ([Cooke et al., 2013](#)) (Fig. 9a) and mostly plot away from samples from Bolivia, Chile, Columbia, Honduras, and other parts of Peru. However, these other locations were limited to one sample per mine. If each of these is as variable in mercury isotopic values as Huancavelica, then the provenance postulate would be violated. Both colonial and pre-Incan objects plot within the Huancavelica ore grouping, but Incan cinnabar samples appear to come from an un-sampled source (or sources). Until other sources are fully characterized, these attributions must be regarded as tentative. [Prieto et al. \(2016\)](#) and [Burger et al. \(2016\)](#) built on this initial work with additional analyses of Peruvian pre-Incan archaeological samples, but they still relied on the few cinnabar samples analyzed by [Cooke et al. \(2013\)](#) for their interpretations regarding provenance.

Mercury isotopic analysis has also been applied in the Old World, though not for analysis of inorganic materials. [Emslie et al. \(2015\)](#) used mercury isotopic analysis to investigate the high Hg concentrations observed in human bones from three Chalcolithic/Neolithic sites in southern Portugal. Their results matched the data field defined by [Gray et al. \(2013\)](#) for the Almadén mining district (Spain) and thus supported their argument that chronic exposure to mercury via mining and use of cinnabar can impart lasting biological markers in human bone. Importantly, data from the Almadén mining district overlaps that of the Huancavelica (Peru) field defined by [Cooke et al. \(2013\)](#) (Fig. 9b). Large quantities of mercury were exported from Almadén to South America during the Spanish colonial period ([Nriagu 1993](#)), so further work will be needed to see if these sources can be distinguished by other methods.

4. Conclusions

This paper reviews applications of non-traditional heavy stable isotopes in archaeological research on provenance and resource use. Accurate and precise measurement of these isotopes has only been possible since the advent of multicollector ICP-MS technology, and most of the papers reviewed here were published after 2010. Additional non-traditional stable isotopic systems of potential interest for archaeologists include $\delta^{26}\text{Mg}$, $\delta^{30}\text{Si}$, $\delta^{66}\text{Zn}$, $\delta^{98}\text{Mo}$ and $\delta^{60}\text{Ni}$. Thus far these isotopic systems have only been applied in geochemistry, though [Jaouen and Pons \(2017\)](#) have considered how non-traditional isotopes (including some from this list) might be used in bioarchaeology. [Devulder et al. \(2013, 2014\)](#) have attempted to use boron ($\delta^{11}\text{B}$) isotopic analysis to provenance natron sources in ancient glass. Their results were largely inconclusive, as there can be more than one source of boron in the glass making process (e.g. both sand and natron). It is beyond the scope of this paper to provide detailed information on these systems, but researchers seeking further information should consult [Hoefs \(2018\)](#).

None of the isotopic systems reviewed here have yet established themselves as reliable techniques for tracking the provenance of inorganic materials. We note a sharp contrast between the introduction of “traditional” isotopes for provenance studies in archaeology, and the introduction of the “non-traditional” isotopes. The former group were adopted in archaeology after they had been used for many years in geology, so their mechanisms of fractionation and ranges of natural variation were already well understood. The use of “non-traditional” isotopes in archaeology began before the range and causes of natural

variation in these systems had been established by geologists. Archaeologists also have to worry about fractionation induced by pyrotechnological processing of these materials, which must be estimated through experimental reconstructions of these processes. In some cases, there are not even accepted international standard reference materials for isotopic analysis.

There has been understandable excitement about the potential of these isotopic systems to answer long-standing archaeological questions that have resisted all other attempts to answer them. Tin isotopes were particularly attractive ([Gale 1997](#)) because they seemed to have the potential to solve a question that has been hotly debated in archaeology for more than fifty years. With the results from a well-funded European study now published ([Berger et al., 2019](#)) we can conclude that natural variation in tin isotopic ratios is not sufficient to allow tin isotopes to be used as a stand-alone method for provenance of tin and bronze, but that they are potentially a valuable complement to older methods, such as lead isotopes and trace elements ([Artioli et al., 2020](#)). Several studies cited in this review have conducted multi-isotopic investigations (e.g. [Albarède et al., 2016](#); [Baron et al., 2019](#); [Desautly et al., 2011](#); [Desautly and Albarède 2013](#); [Klein et al., 2010](#); etc.), and we believe that their creative combination of isotopic systems points the way towards the future role of non-traditional stable isotopes.

As far as copper and silver isotopes are concerned, we now know that variation within deposits (especially between hypogene and supergene mineral species) is greater than variation between them, so neither can be used to establish the provenance of archaeological or historical materials. Copper isotopes have however become an established method for inferring whether a given artifact was smelted from carbonate/oxide/hydroxide supergene ores, or sulfide ores from the zone of secondary enrichment (chalcocite) or the primary ores of the hypogene zone (chalcopyrite, bornite, etc.). This is a distinction of great importance for those who study prehistoric metallurgy ([Killick 2014](#)). It was recently shown that silver isotopes also fractionate during the weathering of hypogene to supergene ores, and we expect future silver isotopic studies to follow the lead of copper isotopic studies to infer the type of ore exploited for the manufacture of archaeological objects. Archaeometallurgists have also been frustrated by the lack of established methods for establishing the provenance of iron, but it does not appear that Fe isotopes offer a solution to the problem. Although osmium isotopes ([Brauns et al., 2020](#)), and laser-ablation ICP-MS chemical analysis of slag inclusions ([Charlton 2015](#); [Dillmann et al., 2017](#)) may be able to distinguish between a limited number of local deposits, we do not believe that there will ever be a method that can reliably track long-distance trade of iron. The number of potential iron ore deposits is far too great for archaeologists to characterize them individually, and some types of iron ore (e.g. laterites and banded iron formations) may extend continuously over hundreds of kilometers.

We are not yet in a position to judge whether antimony isotopes or mercury isotopes can become useful methods for archaeology. There is very little data as yet on the range of natural variation in Sb isotopic ratios, and there can be large fractionation effects when Sb is processed by pyrotechnology to make metal or glass. These effects are not yet fully understood. Mercury isotopes are certainly the most complex isotopic system of potential interest to archaeologists, as mercury forms a broad range of inorganic and organic compounds, and both mass-dependent and mass-independent fractionation occurs. We do not yet understand the implications of these for provenance, and in any case have very little data as yet on Hg isotopic variation within ore deposits.

In order for meaningful archaeological provenance conclusions to be drawn, the following criteria must apply. Firstly, geological ore deposits need to comply with the provenance postulate, that there be greater variation between potential sources than within them. Copper, silver and iron fail this requirement, and there is insufficient data on variation within and between the ore deposits of the other isotopic systems discussed here. Secondly, any fractionation produced by technological processes like smelting and glass making must be well understood

¹³ It should also be noted that many ore samples were procured from museum collections without detailed information on geological contexts.

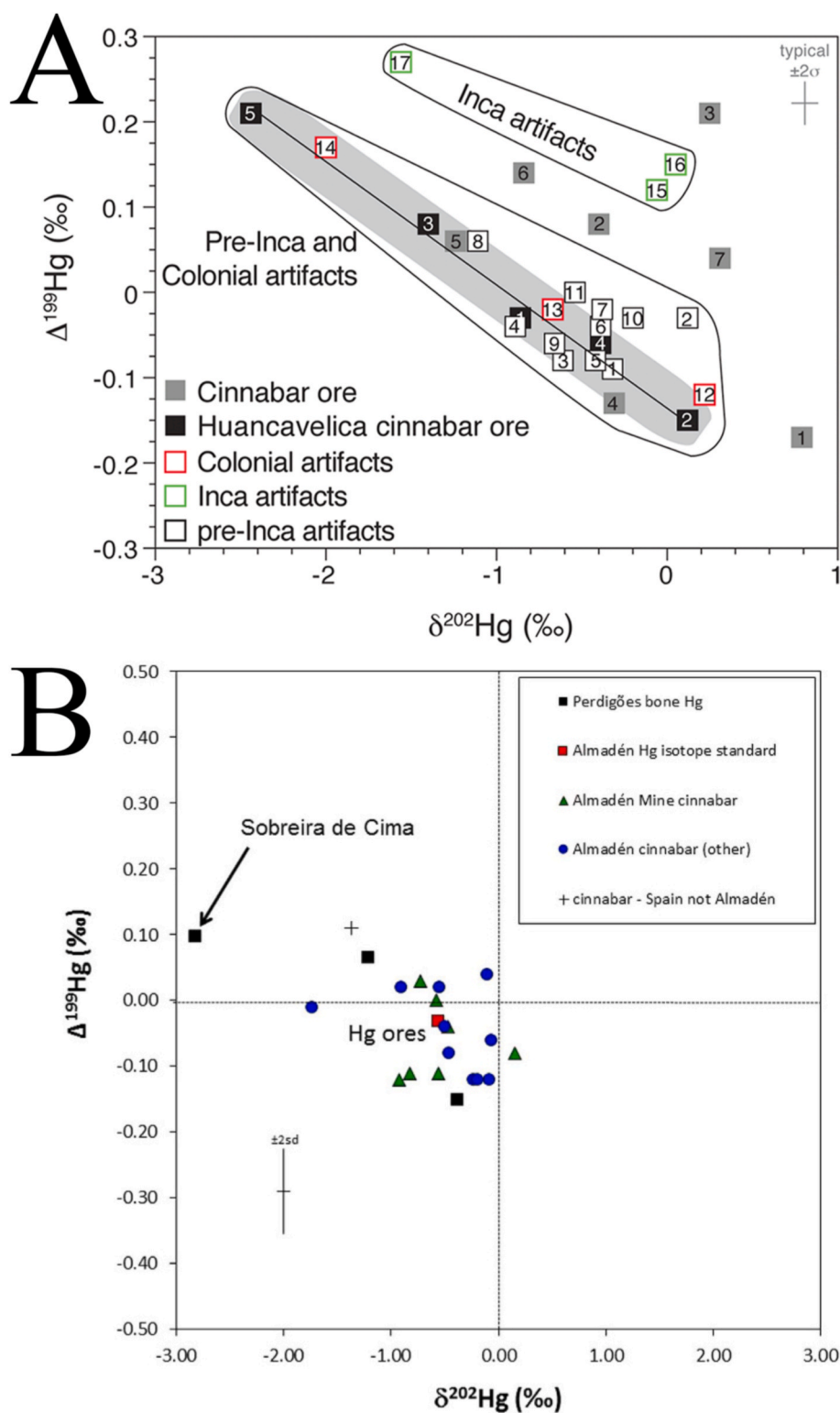


Fig. 9. Cooke et al. (2013) use mercury isotopic data to argue for the provenance of archaeological cinnabar in South America. However, they relied on very few geological datapoints for their conclusions and did not properly identify the mercury isotopic distribution for most cinnabar deposits. When compared against the data presented in Emslie et al. (2015) it is clear that Huancavelica, Peru ore field overlaps with Almadén Mine, Spain and calls the conclusions of Cooke et al. (2013) into question (12a reproduced from Cooke et al., 2013, Fig. 2. 12b reproduced from Emslie et al., 2015, Fig. 4).

through experimental reproduction of those technologies. Thirdly, the laboratory procedures employed in the purification of samples for isotopic analysis should not produce further fractionation, and fractionation within the ICP-MS instrument must be corrected for. Lastly, any inferences made about provenance, used of resources, or technology should be compatible with archaeological and other archaeometric evidence. None of the isotopic systems reviewed here yet meets all four of these requirements.

Our major conclusion from this study is that none of these techniques is yet firmly established as a reliable, independent, technique for inferring the geological provenance of archaeological materials, but that some may provide reliable evidence on the types of minerals procured, and on human technological practice. “Non-traditional” stable isotopes can be creatively combined with “traditional” stable and radiogenic isotopes (e.g. Pb, Sr, Nd, Os), and with archaeological materials science, to infer both the geological provenance of raw materials and

manufactured objects, and to more fully recreate human choices and technological abilities. In this sense, each approach is non-redundant, and all combine to afford a better understanding of the past. As more research floods into this new niche, we hope to see an influx of isotopic research engaging with anthropological questions aiming to reconstruct the social practices and technological styles of past miners, metalworkers, glassworkers, jewelers, and other craftspeople. These will complement provenance studies, which are better addressed with radiogenic isotopes and trace elements.

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.

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References

- Albarède, F., Beard, B., 2004. Analytical methods for non-traditional isotopes. *Rev. Mineral. Geochem.* 55 (1), 113–152. <https://doi.org/10.2138/gsrmg.55.1.113>.
- Albarède, F., Blichert-Toft, J., Rivoal, M., Telouk, P., 2016. A glimpse into the Roman finances of the Second Punic War through silver isotopes. *Geochemical Perspectives Letters* 2, 127–137. <https://doi.org/10.7185/geochemlet.1613>.
- Anbar, A.D., 2004. Iron stable isotopes: beyond biosignatures. *Earth Planet Sci. Lett.* 217 (3–4), 223–236. [https://doi.org/10.1016/S0012-821X\(03\)00572-7](https://doi.org/10.1016/S0012-821X(03)00572-7).
- Anderson, C., Mathur, R., Rakovan, J., Tremsin, A., 2019. Natural solid-state ion conduction induces metal isotope fractionation. *Geology* 47 (7), 617–621. <https://doi.org/10.1130/G45999.1>.
- Arribas, A., Mathur, R., Megaw, P., Arribas, I., 2020. The isotopic composition of silver in ore minerals. *G-cubed* 21, e2020GC009097. <https://doi.org/10.1029/2020GC009097>.
- Artioli, G., Canovaro, C., Nimis, P., Angelini, I., 2020. LIA of prehistoric metals in the Central Mediterranean area: a review. *Archaeometry*. <https://doi.org/10.1111/arcam.12542> (in press).
- Balliana, E., Aramendía, M., Resano, M., Barbante, C., Vanhaecke, F., 2013. Copper and tin isotopic analysis of ancient bronzes for archaeological investigation: development and validation of a suitable analytical methodology. *Anal. Bioanal. Chem.* 405 (9), 2973–2986. <https://doi.org/10.1007/s00216-012-6542-1>.
- Baron, S., Coustures, M.P., Béziat, D., Guérin, M., Huez, J., Robbiola, L., 2011. Lingots de plomb et barres de fer des épaves romaines des Saintes-Maries-de-la-Mer (Bouches-du-Rhône, France): questions de traçabilité compare. *Rev. Archéol. Narbonnaise* 44 (1), 71–97. <https://doi.org/10.3406/ran.2011.1820>.
- Baron, S., Tâmaş, C.G., Le Carlier, C., 2014. How mineralogy and geochemistry can improve the significance of Pb isotopes in metal provenance studies: the significance of Pb isotopes in metal provenance studies. *Archaeometry* 56 (4), 665–680. <https://doi.org/10.1111/arcam.12037>.
- Baron, S., Tâmaş, C.G., Rivoal, M., Cauuet, B., Télouk, P., Albarède, F., 2019. Geochemistry of gold ores mined during celtic times from the north-western French massif central. *Sci. Rep.* 9 (1), 1–15. <https://doi.org/10.1038/s41598-019-54222-x>.
- Beard, B.L., Johnson, C.M., Skulan, J.L., Neelson, K.H., Cox, L., Sun, H., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chem. Geol.* 195 (1–4), 87–117. [https://doi.org/10.1016/S0009-2541\(02\)00390-X](https://doi.org/10.1016/S0009-2541(02)00390-X).
- Beard, B.L., Johnson, C.M., 2004. Fe isotope variations in the modern and ancient earth and other planetary bodies. *Rev. Mineral. Geochem.* 55 (1), 319–357. <https://doi.org/10.2138/gsrmg.55.1.319>.
- Bentley, R.A., 2006. Strontium isotopes from the earth to the archaeological skeleton: a review. *J. Archaeol. Method Theor* 13 (3), 135–187. <https://doi.org/10.1007/s10816-006-9009-x>.
- Berger, D., Brüggmann, G., Pernicka, E., 2017. On smelting cassiterite in geological and archaeological samples: preparation and implications for provenance studies on metal artefacts with tin isotopes. *Archaeological and Anthropological Sciences* 11 (1), 293–319. <https://doi.org/10.1007/s12520-017-0544-z>.
- Berger, D., Figueiredo, E., Brüggmann, G., Pernicka, E., 2018. Tin isotope fractionation during experimental cassiterite smelting and its implication for tracing the tin sources of prehistoric metal artefacts. *J. Archaeol. Sci.* 92, 73–86. <https://doi.org/10.1016/j.jas.2018.02.006>.
- Berger, D., Soles, J.S., Giunilia-Mair, A.R., Brüggmann, G., Galili, E., Lockhoff, N., Pernicka, E., 2019. Isotope systematics and chemical composition of tin ingots from Mochlos (Crete) and other Late Bronze Age sites in the eastern Mediterranean Sea: an ultimate key to tin provenance? *PLoS One* 14 (6). <https://doi.org/10.1371/journal.pone.0218326>.
- Bergquist, B.A., Blum, J.D., 2007. Mass-dependent and-independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* 318, 417–420. <https://doi.org/10.1126/science.1148050>, 5849.
- Bishop, R.L., Rands, R.L., Holley, G.R., 1982. Ceramic compositional analysis in archaeological perspective. *Adv. Archaeol. Method Theor.* 5, 275–330. <https://doi.org/10.1016/B978-0-12-003105-4.50012-1>.
- Blanchard, M., Balan, E., Schauble, E., 2017. Equilibrium fractionation of non-traditional isotopes: a molecular modeling perspective. *Rev. Mineral. Geochem.* 82 (1), 27–63. <https://doi.org/10.2138/rmg.2017.82.2>.
- Blum, J.D., Bergquist, B.A., 2007. Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* 388, 353–359. <https://doi.org/10.1007/s00216-007-1236-9>.
- Blum, J.D., Sherman, L.S., Johnson, M.W., 2014. Mercury isotopes in earth and environmental sciences. *Annu. Rev. Earth Planet Sci.* 42 (1), 249–269. <https://doi.org/10.1146/annurev-earth-050212-124107>.
- Blum, J.D., Johnson, M.W., 2017. Recent developments in mercury stable isotope analysis. *Rev. Mineral. Geochem.* 82 (1), 733–757. <https://doi.org/10.2138/rmg.2017.82.17>.
- Bower, N.W., Hendin, D.B., Lundstrom, C.C., Epstein, M.S., Keller, A.T., Wagner, A.R., White, Z.R., 2013. “Biblical” bronze coins: new insights into their timing and attribution using copper and lead isotopes. *Archaeological and Anthropological Sciences* 5 (4), 287–298. <https://doi.org/10.1007/s12520-012-0113-4>.
- Bower, N.W., Lundstrom, C.C., Hendin, D.B., 2019. MC-ICP-MS analyses of tin isotopes in Roman-era bronze coins reveal temporal and spatial variation. *Archaeometry* 61 (4), 891–905. <https://doi.org/10.1111/arcam.12459>.
- Brauns, M., Schwab, R., Gassmann, G., Wieland, G., Pernicka, E., 2013. Provenance of Iron Age iron in southern Germany: a new approach. *J. Archaeol. Sci.* 40 (2), 841–849. <https://doi.org/10.1016/j.jas.2012.08.044>.
- Brauns, M., Yahalom-Mack, N., Stepanov, I., Sauder, L., Keen, J., Elyahu-Behar, A., 2020. Osmium isotope analysis as an innovative tool for provenancing ancient iron: a systematic approach. *PLoS One* 15 (3), e0229623. <https://doi.org/10.1371/journal.pone.0229623>.
- Brilli, M., Cavazzini, G., Turi, B., 2005. New data of 87Sr/86Sr ratio in Classical marble: an initial database for marble provenance determination. *J. Archaeol. Sci.* 32 (10), 1543–1551. <https://doi.org/10.1016/j.jas.2005.04.007>.
- Brüggmann, G., Berger, D., Pernicka, E., 2017. Determination of the tin stable isotopic composition in tin-bearing metals and minerals by MC-ICP-MS. *Geostand. Geoanal. Res.* 41 (3), 437–448. <https://doi.org/10.1111/gr.12166>.
- Brüggmann, G., Brauns, M., Maas, R., 2019. Silver isotope analysis of gold nuggets: an appraisal of instrumental isotope fractionation effects and potential for high-resolution tracing of placer gold. *Chem. Geol.* 516, 59–67. <https://doi.org/10.1016/j.chemgeo.2019.03.015>.
- Budd, P., Haggerty, R., Pollard, A.M., Scaife, B., Thomas, R.G., 1996. Rethinking the quest for provenance. *Antiquity* 70 (267), 168–174. <https://doi.org/10.1017/S0003598X00083034>.
- Bugaj, U., Nejbert, K., Ilnicki, S., Wiciński, P., Onyszczuk, T., Garbacz, H., Włodarczyk, P., 2019. Copper sulphosalts in early metallurgy (2600–1900 BC)—chemical-mineralogical investigation of artefacts from southern Poland. *Geol. Q.* 63 (2), 302–318. <https://doi.org/10.7306/gq.1473>.
- Burger, R.L., Lane, K.E., Cooke, C.A., 2016. Ecuadorian cinnabar and the prehispanic trade in vermilion pigment: viable hypothesis or red herring? *Lat. Am. Antiq.* 27 (1), 22–35. <https://doi.org/10.7183/1045-6635.27.1.22>.
- Charlton, M.F., 2015. The last frontier in ‘sourcing’: the hopes, constraints and future for iron provenance research. *J. Archaeol. Sci.* 56, 210–220. <https://doi.org/10.1016/j.jas.2015.02.017>.
- Chugaev, A.V., Chernyshev, I.V., 2009. Variations of ¹⁰⁷Ag/¹⁰⁹Ag isotope ratio in ore deposits by high-precision MC-ICP-MS. *Geochem. Cosmochim. Acta* 73, A225.
- Cooke, C.A., Hintelmann, H., Ague, J.J., Burger, R., Biester, H., Sachs, J.P., Engstrom, D. R., 2013. Use and legacy of mercury in the andes. *Environ. Sci. Technol.* 47 (9), 4181–4188. <https://doi.org/10.1021/es3048027>.
- Craddock, P., Dauphas, N., 2010. Iron isotopic compositions of geological reference materials and chondrites. *Geostand. Geoanal. Res.* 35, 101–123. <https://doi.org/10.1111/j.1751-908X.2010.00085.x>.
- Craddock, P.T., 1995. *Early Metal Mining and Production*. Edinburgh University Press, Edinburgh.
- Criss, R.E., 1999. *Principles of Stable Isotope Distribution*. Oxford University Press, Oxford, UK.
- Dardeniz, G., 2020. Why did the use of antimony-bearing alloys in bronze age Anatolia fall dormant after the early bronze age?: a case from resuloğlu (çorum, Turkey). *PLoS One* 15 (7), e0234563. <https://doi.org/10.1371/journal.pone.0234563>.
- Dauphas, N., John, S.G., Rouxel, O., 2017. Iron isotope systematics. *Rev. Mineral. Geochem.* 82 (1), 415–510. <https://doi.org/10.2138/rmg.2017.82.11>.
- Degryse, P., 2014. *Glass Making in the Greco Roman World: Results of the Archglass Project*. Leuven University Press, Leuven.
- Degryse, P., Lobo, L., Shortland, A., Vanhaecke, F., Blomme, A., Painter, J., Gimeno, D., Eremin, K., Greene, J., Kirk, S., Walton, M., 2015. Isotopic investigation into the raw materials of Late Bronze Age glass making. *J. Archaeol. Sci.* 62, 153–160. <https://doi.org/10.1016/j.jas.2015.08.004>.
- Degryse, P., Shortland, A.J., Dillis, S., van Ham-Meert, A., Vanhaecke, F., Leeming, P., 2020. Isotopic evidence for the use of Caucasian antimony in Late Bronze Age glass making. *J. Archaeol. Sci.* 120, 105195.
- DeNiro, M.J., 1987. Stable isotope and archaeology. *Am. Sci.* 75 (2), 182–191.

- Desautly, A.M., Telouk, P., Albalat, E., Albarède, F., 2011. Isotopic Ag-Cu-Pb record of silver circulation through 16th-18th century Spain. *Proc. Natl. Acad. Sci. Unit. States Am.* 108 (22), 9002–9007. <https://doi.org/10.1073/pnas.1018210108>.
- Desautly, A.M., Albarède, F., 2013. Copper, lead, and silver isotopes solve a major economic conundrum of Tudor and early Stuart Europe. *Geology* 41 (2), 135–138. <https://doi.org/10.1130/G33555.1>.
- Devulder, V., Degryse, P., Vanhaecke, F., 2013. Development of a novel method for unraveling the origin of natron flux used in Roman glass production based on B isotopic analysis via multicollector inductively coupled plasma mass spectrometry. *Anal. Chem.* 85 (24), 12077–12084. <https://doi.org/10.1021/ac403176c>.
- Devulder, V., Vanhaecke, F., Shortland, A., Mattingly, D., Jackson, C., Degryse, P., 2014. Boron isotopic composition as a provenance indicator for the flux raw material in Roman natron glass. *J. Archaeol. Sci.* 46, 107–113. <https://doi.org/10.1016/j.jas.2014.03.009>.
- Dietler, M., Herbich, I., 1998. *Habitus, techniques, style: an integrated approach to the social understanding of material culture and boundaries*. In: Stark, M.T. (Ed.), *The Archaeology of Social Boundaries*, Smithsonian Series in Archaeological Inquiry. Smithsonian Institution Press, Washington, D.C, pp. 232–263.
- Dillis, S., Van Ham-Meert, A., Leeming, P., Shortland, A., Gobejishvili, G., Abramishvili, M., Degryse, P., 2019. Antimony as a raw material in ancient metal and glass making: provenancing Georgian LBA metallic Sb by isotope analysis. *Star: Science & Technology of Archaeological Research* 1–15. <https://doi.org/10.1080/20548923.2019.1681138>.
- Dillmann, P., Schwab, R., Bauvais, S., Brauns, M., Disser, A., Leroy, S., Gassmann, G., Fluzin, P., 2017. Circulation of iron products in the North-Alpine area during the end of the first Iron Age (6th-5th c. BC): a combination of chemical and isotopic approaches. *J. Archaeol. Sci.* 87, 108–124. <https://doi.org/10.1016/j.jas.2017.10.002>.
- Dobres, M.A., Hoffman, C.R., 1994. Social agency and the dynamics of prehistoric technology. *J. Archaeol. Method Theory* 1 (3), 211–258.
- Eerkens, J.W., Barford, G.H., Vaughn, K.J., Williams, P.R., Leshner, C.E., 2014. Iron isotope analysis of red and black pigments on pottery in Nasca, Peru. *Archaeological and Anthropological Sciences* 6 (3), 241–254. <https://doi.org/10.1007/s12520-013-0151-6>.
- Ehrlich, S., Butler, I., Halicz, L., Rickard, D., Oldroyd, A., Matthews, A., 2004. Experimental study of the copper isotope fractionation between aqueous Cu(II) and covellite, CuS. *Chem. Geol.* 209 (3–4), 259–269. <https://doi.org/10.1016/j.chemgeo.2004.06.010>.
- Emslie, S.D., Brasso, R., Patterson, W.P., Valera, A.C., McKenzie, A., Silva, A.M., Gleason, J.D., Blum, J.D., 2015. Chronic mercury exposure in Late Neolithic/Chalcolithic populations in Portugal from the cultural use of cinnabar. *Sci. Rep.* 5, 14679. <https://doi.org/10.1038/srep14679>.
- Ericson, J.E., 1985. Strontium isotope characterization in the study of prehistoric human ecology. *J. Hum. Evol.* 14, 503–514. [https://doi.org/10.1016/S0047-2484\(85\)80029-4](https://doi.org/10.1016/S0047-2484(85)80029-4).
- Faure, G., Mensing, T.M., 2005. *Isotopes: Principles and Applications*. John Wiley & Sons, Hoboken.
- Franklin, A.D. (Ed.), 1978. *The Search for Ancient Tin*. Smithsonian Institution Press, Washington.
- Freund, K.P., 2013. An assessment of the current applications and future directions of obsidian sourcing studies in archaeological research. *Archaeometry* 55 (5), 779–793. <https://doi.org/10.1111/j.1475-4754.2012.00708.x>.
- Fujii, T., Albarède, F., 2018. ^{109}Ag – ^{107}Ag fractionation in fluids with applications to ore deposits, archeometry, and cosmochemistry. *Geochem. Cosmochim. Acta* 234, 37–49. <https://doi.org/10.1016/j.gca.2018.05.013>.
- Gale, N.H., 1997. The isotopic composition of tin in some ancient metals and the recycling problem in metal provenancing. *Archaeometry* 39 (1), 71–82. <https://doi.org/10.1111/j.1475-4754.1997.tb00791.x>.
- Gale, N.H., 1999. Lead isotope characterization of the ore deposits of Cyprus and sardinia and its application to the discovery of the sources of copper for late bronze age oxidized ingots. In: Young, S.M.M. (Ed.), *Metals in Antiquity*, BAR International Series 792. Archaeopress, Oxford, pp. 110–122.
- Gale, N.H., Woodhead, A., Stos-Gale, Z.A., Walder, A., Bowen, I., 1999. Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry. *Int. J. Mass Spectrom.* 184 (1), 1–9. [https://doi.org/10.1016/S1387-3806\(98\)14294-X](https://doi.org/10.1016/S1387-3806(98)14294-X).
- Garrigós, JB i, Kilioglou, V., Day, P.M., 2001. Chemical and mineralogical alteration of ceramics from a Late Bronze Age kiln at Kommos, Crete: the effect on the formation of a reference group. *Archaeometry* 43 (3), 349–371. <https://doi.org/10.1111/1475-4754.00021>.
- Glascock, M.D., Neff, H., 2003. Neutron activation analysis and provenance research in archaeology. *Meas. Sci. Technol.* 14 (9), 1516–1526.
- Gosselain, O.P., 2000. Materializing identities: an african perspective. *J. Archaeol. Method Theory* 7 (3), 187–217. <https://doi.org/10.1023/A:1026558503986>.
- Gosselain, O.P., 2010. Exploring the dynamics of African pottery cultures. In: Barndon, R., Engevik, A., Øye, I. (Eds.), *The Archaeology of Regional Technologies: Case Studies from the Palaeolithic to the Age of the Vikings*. Edwin Mellen Press, Lewiston, NY, pp. 193–224.
- Gosselain, O.P., 2017. A tradition in nine maps: un-layering Niger River polychrome water jars. In: Gori, M., Ivanova, M. (Eds.), *Balkan Dialogues: Negotiating Identity between Prehistory and the Present*, vol. 25. Taylor & Francis, pp. 85–108.
- Gray, J.E., Pribil, M.J., Higuera, P.L., 2013. Mercury isotope fractionation during ore retorting in the Almadén mining district, Spain. *Chem. Geol.* 357, 150–157. <https://doi.org/10.1016/j.chemgeo.2013.08.036>.
- Haustein, M., Gillis, C., Pernicka, E., 2010. Tin isotopy—a new method for solving old questions. *Archaeometry* 52 (5), 816–832. <https://doi.org/10.1111/j.1475-4754.2010.00515.x>.
- Hays, J.D., Imbrie, J., Shackleton, N.J., 1976. Variations in the earth's orbit: pacemaker of the ice ages. *Science* 194 (4270), 1121–1132.
- Henderson, J., Evans, J., Nikita, K., 2010. Isotopic evidence for the primary production, provenance and trade of Late Bronze Age glass in the Mediterranean. *Mediterranean Archaeology and Archaeometry* 10 (1), 1–24.
- Hoefs, J., 2018. *Stable Isotope Geochemistry*. Springer International Publishing AG.
- Hoffman, B.C., Miller, H.M.L., 2014. Production and consumption of copper-base metals in the indus civilization. In: Roberts, B.W., Thornton, C. (Eds.), *Archaeometallurgy in Global Perspective*. Springer Science & Business Media, pp. 697–727.
- Horn, I., von Blanckenburg, F., Schoenberg, R., Steinhöfel, G., Markl, G., 2006. In situ iron isotope ratio determination using UV-femtosecond laser ablation with application to hydrothermal ore formation processes. *Geochem. Cosmochim. Acta* 70 (14), 3677–3688. <https://doi.org/10.1016/j.gca.2006.05.002>.
- Hughes, R.E., 1998. On reliability, validity, and scale in obsidian sourcing research. In: Ramenofsky, A.F., Steffen, A. (Eds.), *Unit Issues in Archaeology: Measuring Time, Space, and Material*, Foundations of Archaeological Inquiry. University of Utah Press, Salt Lake City, pp. 103–115.
- Hull, S., Fayek, M., Mathien, F.J., Shelley, P., Durand, K.R., 2008. A new approach to determining the geological provenance of turquoise artifacts using hydrogen and copper stable isotopes. *J. Archaeol. Sci.* 35 (5), 1355–1369. <https://doi.org/10.1016/j.jas.2007.10.001>.
- Hull, S., Fayek, M., 2012. Cracking the code of pre-Columbian turquoise trade networks and procurement strategies. In: King, J.C.H., Carocci, M., Cartwright, C., McEwan, C., Stacey, R. (Eds.), *Turquoise in Mexico and North America: Science, Conservation, Culture and Collections*. Archetype Publications in Association with the British Museum London, pp. 29–40.
- Hull, S., Fayek, M., Mathien, F.J., Roberts, H., 2014. Turquoise trade of the ancestral puebloan: chaco and beyond. *J. Archaeol. Sci.* 45, 187–195. <https://doi.org/10.1016/j.jas.2014.02.016>.
- Ixer, R.A., 1999. Role of ore geology and ores in the archaeological provenancing of metals. In: Young, S.M.M. (Ed.), *Metals in Antiquity*, BAR International Series 792. Archaeopress, Oxford, pp. 43–52.
- Jaouen, K., Pons, M.L., 2017. Potential of non-traditional isotope studies for bioarchaeology. *Archaeological and Anthropological Sciences* 9 (7), 1389–1404. <https://doi.org/10.1007/s12520-016-0426-9>.
- Jansen, M., 2018. On the use of Cu isotope signatures in archaeometallurgy: a comment on Powell et al. *J. Archaeol. Sci.* 93, 211–215. <https://doi.org/10.1016/j.jas.2018.02.016>.
- Jansen, M., Aulbach, A., Hauptmann, A., Höfer, H.E., Klein, S., Kruger, M., Zettler, R.L., 2016. Platinum group placer minerals in ancient gold artifacts: geochemistry and osmium isotopes of inclusions in Early Bronze Age gold from Ur/Mesopotamia. *J. Archaeol. Sci.* 68, 12–23. <https://doi.org/10.1016/j.jas.2016.02.004>.
- Jansen, M., Hauptmann, A., Klein, S., Seitz, H.M., 2017. The potential of stable Cu isotopes for the identification of Bronze Age ore mineral sources from Cyprus and Faynan: results from Uluburun and Khirbat Hamra Ifdan. *Archaeological and Anthropological Sciences* 10 (6), 1485–1502. <https://doi.org/10.1007/s12520-017-0465-x>.
- Jansen, M., Hauptmann, A., Klein, J., 2018. Copper and lead isotope characterization of late bronze age copper ingots in the eastern mediterranean: results from gelidonya, gournia, enkomi and mathiati. In: Giunlia-Mair, A., Lo Schiavo, F. (Eds.), *Bronze Age Metallurgy on Mediterranean Islands*, Monographies Instrumentum 56, Editions Mergiol, pp. 552–578. Drémel-Lafage.
- Kilick, D.J., 2004. Social constructionist approaches to the study of technology. *World Archaeol.* 36 (4), 571–578. <https://doi.org/10.1080/0043824042000303746>.
- Kilick, D.J., 2014. From ores to metals. In: Roberts, B., C A (Eds.), *Thornton Archaeometallurgy in Global Perspective: Methods and Syntheses*. Springer, New York, pp. 11–46.
- Kilick, D.J., Stephens, J., Fenn, T., 2020. Geological constraints on the use of lead isotopes for provenance in archaeometallurgy. *Archaeometry* 62 (S1), 86–105. <https://doi.org/10.1111/arc.12573>.
- Kiriati, E., Knappett, C., 2016. *Human mobility and technological transfer in the prehistoric Mediterranean*. Studies in Greek Antiquity/British School at Athens. Cambridge University Press, New York.
- Klein, S., Lahaye, Y., Brey, G.P., Von Kaenel, H.M., 2004. The early Roman imperial aes coinage II: tracing the copper sources by analysis of lead and copper isotopes—copper coins of Augustus and Tiberius. *Archaeometry* 46 (3), 469–480. <https://doi.org/10.1111/j.1475-4754.2004.00168.x>.
- Klein, S., Brey, G.P., Durali-Müller, S., Lahaye, Y., 2010. Characterisation of the raw metal sources used for the production of copper and copper-based objects with copper isotopes. *Archaeological and Anthropological Sciences* 2 (1), 45–56. <https://doi.org/10.1007/s12520-010-0027-y>.
- Klein, S., Rose, T., 2020. Evaluating Copper Isotope Fractionation in the Metallurgical Operational Chain: an Experimental Approach. <https://doi.org/10.1111/arc.12564>. *Archaeometry* (in press).
- Larson, P.B., Maher, K., Ramos, F.C., Chang, Z., Gaspar, M., Meinert, L.D., 2003. Copper isotope ratios in magmatic and hydrothermal ore-forming environments. *Chem. Geol.* 201 (3–4), 337–350. <https://doi.org/10.1016/j.chemgeo.2003.08.006>.
- Lave, J., Wenger, E., 1991. *Situated Learning: Legitimate Peripheral Participation, Learning in Doing*. Cambridge University Press, Cambridge, England.
- Lobo, L., Devulder, V., Degryse, P., Vanhaecke, F., 2012. Investigation of natural isotopic variation of Sb in stibnite ores via multi-collector ICP-mass spectrometry – perspectives for Sb isotopic analysis of Roman glass. *J. Anal. At. Spectrom.* 27 (8), 1304. <https://doi.org/10.1039/C2JA30062A>.

- Lobo, L., Degryse, P., Shortland, A., Vanhaecke, F., 2013. Isotopic analysis of antimony using multi-collector ICP-mass spectrometry for provenance determination of Roman glass. *J. Anal. At. Spectrom.* 28 (8), 1213. <https://doi.org/10.1039/C3JA50018G>.
- Lobo, L., Degryse, P., Shortland, A., Eremin, K., Vanhaecke, F., 2014. Copper and antimony isotopic analysis via multi-collector ICP-mass spectrometry for provenancing ancient glass. *J. Anal. At. Spectrom.* 29 (1), 58–64. <https://doi.org/10.1039/C3JA50303H>.
- Makarewicz, C.A., Sealy, J., 2015. Dietary reconstruction, mobility, and the analysis of ancient skeletal tissues: expanding the prospects of stable isotope research in archaeology. *J. Archaeol. Sci.* 56, 146–158. <https://doi.org/10.1016/j.jas.2015.02.035>.
- Markl, G., von Blanckenburg, F., Wagner, T., 2006. Iron isotope fractionation during hydrothermal ore deposition and alteration. *Geochim. Cosmochim. Acta* 70 (12), 3011–3030. <https://doi.org/10.1016/j.gca.2006.02.028>.
- Mason, A.H., Powell, W.G., Bankoff, H.A., Mathur, R., Bulatović, A., Filipović, V., Ruiz, J., 2016. Tin isotope characterization of bronze artifacts of the central Balkans. *J. Archaeol. Sci.* 69 <https://doi.org/10.1016/j.jas.2016.04.012>, 110–107.
- Mason, A., Powell, W., Bankoff, H.A., Mathur, R., Price, M., Bulatović, A., Filipović, V., 2020. Provenance of tin in the Late Bronze Age balkans based on probabilistic and spatial analysis of Sn isotopes. *J. Archaeol. Sci.* 122, 105181.
- Mason, A.H., 2020. Provenance of Tin in the Late Bronze Age Balkans: Preparation of Cassiterite for Sn Isotope Analysis and the Probabilistic and Spatial Analysis of Sn Isotopes. Dissertation. The City University of New York.
- Mathur, R., Dendas, M., Tittley, S., Phillips, A., 2010. Patterns in the copper isotopic composition of minerals in porphyry copper deposits in the Southwestern United States of America. *Econ. Geol.* 105, 1457e1467. <https://doi.org/10.2113/econgeo.105.8.1457>.
- Mathur, R., Wilson, M., Parra, M.L., 2014. Challenges of using copper isotope ratios to trace the origin of native copper artifacts: an example from the Keweenaw Peninsula. *Ann. Carnegie Mus.* 82 (3), 241–245. <https://doi.org/10.2992/007.082.0304>.
- Mathur, R., Powell, W., Mason, A., Godfrey, L., Yao, J., Baker, M.E., 2017. Preparation and measurement of cassiterite for Sn isotope analysis. *Geostand. Geoanal. Res.* 41 (4), 701–707. <https://doi.org/10.1111/ggr.12174>.
- Mathur, R., Arribas, A., Megaw, P., Wilson, M., Stroup, S., Meyer-Arrivillaga, D., Arribas, I., 2018. Fractionation of silver isotopes in native silver explained by redox reactions. *Geochim. Cosmochim. Acta* 224, 313–326. <https://doi.org/10.1016/j.gca.2018.01.011>.
- Mathur, R., Burns, J., Powell, W., Boryk, R., Sheetz, B., D'Amico, P., Harney, P., 2020. Evaluation of Fe isotope values as a provenance tool for chert artefacts from the north-eastern United States. *Archaeometry*. <https://doi.org/10.1111/arc.12572>.
- Milot, J., Poitrasson, F., Baron, S., Coustures, M.P., 2016a. Iron isotopes as a potential tool for ancient iron metals tracing. *J. Archaeol. Sci.* 76, 9–20. <https://doi.org/10.1016/j.jas.2016.10.003>.
- Milot, J., Poitrasson, F., Baron, S., Coustures, M.P., Robion-Brunner, C., 2016b. Ancient iron metals tracing by iron isotopes analysis. *Crucible* 92, 3–4.
- Milot, J., Baron, S., Poitrasson, F., 2018. Potential use of Fe isotopes for ancient non-ferrous metals tracing through the example of a lead-silver production site (Imiter mine, Anti-Atlas, Morocco). *J. Archaeol. Sci.* 98, 22–33. <https://doi.org/10.1016/j.jas.2018.07.004>.
- Möller, K., Schoenberg, R., Pedersen, R.B., Weiss, D., Dong, S., 2012. Calibration of the new certified reference materials RRM-a633 and ERM-a647 for copper and IRMM-3702 for zinc isotope amount ratio determinations. *Geostand. Geoanal. Res.* 36 (2), 177–199. <https://doi.org/10.1111/j.1751-908X.2011.00153.x>.
- Molofsky, L.J., Killick, D., Ducea, M.N., Macovei, M., Chesley, J.T., Ruiz, J., Thibodeau, A., Popescu, G.C., 2014. A novel approach to lead isotope provenance studies of tin and bronze: applications to South African, Botswana and Romanian artifacts. *J. Archaeol. Sci.* 50, 440–450. <https://doi.org/10.1016/j.jas.2014.08.006>.
- Moynier, F., Vance, D., Fujii, T., Savage, P., 2017. The isotope geochemistry of zinc and copper. *Rev. Mineral. Geochem.* 82 (1), 543–600. <https://doi.org/10.2138/rmg.2017.82.13>.
- Muhly, J.D., 1973. Copper and tin: the distribution of the mineral resources and the nature of the metals trade in the Bronze Age. *Trans. Conn. Acad. Arts Sci.* 43, 155–535.
- Neff, H., 2001. Neutron activation analysis for provenance determination in archaeology. In: Ciliberto, E., Spoto, G. (Eds.), *Modern Analytical Methods in Arts and Archaeology*, vol. 155. Chemical Analysis Series, John Wiley & Sons, New York.
- Nessel, B., Brüggemann, G., Pernicka, E., 2016. Tin isotope ratios in early and Middle Bronze Age bronzes from central and southeastern Europe. *The Journal of the International Union of Prehistoric and Protohistoric Sciences* 2 (1), 1–11.
- Nickel, D., Hausteine, M., Lampke, T., Pernicka, E., 2012. Identification of forgeries by measuring tin isotopes in corroded bronze objects. *Archaeometry* 54 (1), 167–174. <https://doi.org/10.1111/j.1475-4754.2011.00598.x>.
- Nriagu, J.O., 1993. Legacy of mercury pollution. *Nature* 363, 589. <https://doi.org/10.1038/363589a0>.
- Othmane, G., Hull, S., Fayek, M., Rouxel, O., Geagea, M.L., Kyser, T.K., 2015. Hydrogen and copper isotope analysis of turquoise by SIMS: calibration and matrix effects. *Chem. Geol.* 395, 41–49. <https://doi.org/10.1016/j.chemgeo.2014.11.024>.
- Pearce, M., 2016. Archaeology and archaeometallurgy: some unresolved areas in the interpretation of analytical data. *Star: Science & Technology of Archaeological Research* 2 (1), 46–53. <https://doi.org/10.1080/20548923.2016.1160593>.
- Pernicka, E., Begemann, F., Schmitt-Strecker, S., Wagner, G.A., 1993. Eneolithic and Early Bronze Age copper artefacts from the Balkans and their relation to Serbian copper ores. *Prähistorische Z.* 68 (1), 1–54. <https://doi.org/10.1515/prz.1993.68.1.1>.
- Powell, W., Mathur, R., Bankoff, H.A., Mason, A., Bulatović, A., Filipović, V., Godfrey, L., 2017. Digging deeper: insights into metallurgical transitions in European prehistory through copper isotopes. *J. Archaeol. Sci.* 88, 37–46. <https://doi.org/10.1016/j.jas.2017.06.012>.
- Powell, W., Mathur, R., Bankoff, H.A., John, J., Chvojka, O., Tisucká, M., Bulatović, A., Filipović, V., 2018a. Copper isotopes as a means of determining regional metallurgical practices in European prehistory: a reply to Jansen. *J. Archaeol. Sci.* 93, 216–221. <https://doi.org/10.1016/j.jas.2018.02.015>.
- Powell, W., Bankoff, H.A., Mason, A., Mathur, R., Bulatović, A., Filipović, V., 2018b. Tin sources and regional trade in the Bronze Age of Southeast Europe: evidence from tin isotopes. In: Alexandrov, S., Dimitrova, Y., Popov, H., Horejs, B., Chukalev (Eds.), *Gold & Bronze: Metals, Technologies and Interregional Contacts in the Eastern Balkans during the Bronze Age*. Nacionalen Arheološki Institut s Muzej, Sofia, pp. 141–149.
- Powell, W., Mathur, R., John, J., Price, M., Bankoff, H.A., Tisucká, M., Godfrey, L., 2019. Unearthing Europe's Bronze Age mining heritage with tin isotopes: a case study from Central Europe. *Eur. Geol.* 48.
- Prieto, G., Wright, V., Burger, R.L., Cooke, C.A., Zeballos-Velasquez, E.L., Watanabe, A., Suchomel, M.R., Suescun, L., 2016. The source, processing and use of red pigment based on hematite and cinnabar at Gramalote, an early Initial Period (1500–1200 cal. BC) maritime community, north coast of Peru. *J. Archaeol. Sci.: Report* 5, 45–60. <https://doi.org/10.1016/j.jasrep.2015.10.026>.
- Reguera-Galan, A., Barreiro-Grille, T., Moldovan, M., Lobo, L., de Blas Cortina, M.Á., García Alonso Ji, 2019. A provenance study of early bronze age artefacts found in Asturias (Spain) by means of metal impurities and lead, copper and antimony isotopic compositions. *Archaeometry* 61 (3), 683–700. <https://doi.org/10.1111/arc.12445>.
- Rehkämper, M., Schönbacher, M., Stirling, C.H., 2001. Multiple collector ICP-MS: introduction to instrumentation, measurement techniques and analytical capabilities. *Geostand. Newsl.* 25 (1), 23–40. <https://doi.org/10.1111/j.1751-908X.2001.tb00785.x>.
- Roddick, A., Stahl, A., 2016. *Knowledge in Motion: Constellations of Learning across Time and Place*. University of Arizona Press.
- Rodler, A.S., Artioli, G., Klein, S., Petschick, R., Fink-Jensen, P., Brøns, C., 2017. Provenancing ancient pigments: lead isotope analyses of the copper compound of Egyptian blue pigments from ancient Mediterranean artefacts. *J. Archaeol. Sci.: Report* 16, 1–18. <https://doi.org/10.1016/j.jasrep.2017.09.008>.
- Rodler, A.S., Klein, S., Artioli, G., Brøns, C., 2019. Probing the provenance of archaeological glaze colorants: polychrome faunal reliefs of the Ishtar Gate and the processional way of Babylon. *Archaeometry* 61 (4), 837–855. <https://doi.org/10.1111/arc.12455>.
- Rose, T., Télouk, P., Klein, S., Marschall, H.R., 2019. Questioning Fe isotopes as a provenance tool: insights from bog iron ores and alternative applications in archaeometry. *J. Archaeol. Sci.* 101, 52–62. <https://doi.org/10.1016/j.jas.2018.11.005>.
- Rose, T., Télouk, P., Fiebig, J., Marschall, H.R., Klein, S., 2020. Iron and oxygen isotope systematics during corrosion of iron objects: a first approach. *Archaeological and Anthropological Sciences* 12 (6). <https://doi.org/10.1007/s12520-020-01072-8>.
- Rouxel, O., Ludden, J., Fouquet, Y., 2003. Antimony isotope variations in natural systems and implications for their use as geochemical tracers. *Chem. Geol.* 200 (1–2), 25–40. [https://doi.org/10.1016/S0009-2541\(03\)00121-9](https://doi.org/10.1016/S0009-2541(03)00121-9).
- Saunders, J.A., Mathur, R., Kamenov, G.D., Shimizu, T., Brueske, M., 2016. New isotopic evidence bearing on bonanza (Au-Ag) epithermal ore-forming processes. *Miner. Deposita* 51, 1–11. <https://doi.org/10.1007/s00126-015-0623-y>.
- Schauble, E., 2004. Applying stable isotope fractionation theory to new systems. *Rev. Mineral. Geochem.* 55 (1), 65–111. <https://doi.org/10.2138/gsrng.55.1.65>.
- Schneider, G., Hoffman, B., Wirz, E., 1979. Significance and dependability of reference groups for chemical determinations of provenance of ceramic artifacts. In: *Proceedings of the 18th International Symposium on Archaeometry and Archaeological Prospection*, vol. 10. 18th International Symposium on Archaeometry and Archaeological Prospection, Bonn, Bonn, pp. 269–283.
- Shahar, A., Elardo, S., Macris, C., 2017. Equilibrium fractionation of non-traditional stable isotopes: an experimental perspective. *Rev. Mineral. Geochem.* 82 (1), 65–83. <https://doi.org/10.2138/rmg.2017.82.3>.
- She, J.X., Wang, T., Liang, H., Muhtar, M.N., Li, W., Liu, X., 2020. Sn isotope fractionation during volatilization of Sn (IV) chloride: laboratory experiments and quantum mechanical calculations. *Geochim. Cosmochim. Acta* 269, 184–202. <https://doi.org/10.1016/j.gca.2019.10.033>.
- Stos-Gale, Z.A., Maliotis, G., Gale, N.H., Annetts, N., 1997. Lead isotope characteristics of the Cyprus copper ore deposits applied to provenance studies of copper oxide ingots. *Archaeometry* 39 (1), 83–123. <https://doi.org/10.1111/j.1475-4754.1997.tb00792.x>.
- Tadmor, M., Kedem, B., Begemann, F., Hauptmann, A., Pernicka, E., Schmitt-Strecker, S., 1995. The nahal mishmar hoard from the Judean desert: technology, composition, and provenance. *Atiqot* 27, 96–148.
- Teng, F.Z., Dauphas, N., Watkins, J.M., 2017. Non-traditional stable isotopes: retrospective and prospective. *Rev. Mineral. Geochem.* 82 (1), 1–26. <https://doi.org/10.2138/rmg.2017.82.1>.
- Thibodeau, A.M., Killick, D.J., Hedquist, S.L., Chesley, J.T., Ruiz, J., 2015. Isotopic evidence for the provenance of turquoise in the southwestern United States. *GSA Bulletin* 127 (11–12), 1617–1631. <https://doi.org/10.1130/B31135.1>.
- Triadan, D., Mills, B.J., Duff, A.I., 2002. From compositional to anthropological: fourteenth-century red-ware circulation and its implications for pueblo reorganization. In: Glowacki, D.M., Neff, H. (Eds.), *Ceramic Production and Circulation in the Greater Southwest: Source Determination by INAA and Complementary Mineralogical Investigations*. Monograph 44. Cotsen Institute of Archaeology at UCLA, Los Angeles, pp. 85–97.

- Tykot, R.H., 2004. Stable isotopes and diet: you are what you eat. Proceedings of the International School of Physics "Enrico Fermi." IOS Press.
- Van der Merwe, N.J., Vogel, J.C., 1978. ^{13}C content of human collagen as a measure of prehistoric diet in Woodland North America. *Nature* 276, 815–816. <https://doi.org/10.1038/276815a0>.
- Vanhaecke, F., Balcaen, L., Malinovsky, D., 2009. Use of single-collector and multi-collector ICP-mass spectrometry for isotopic analysis. *J. Anal. At. Spectrom.* 24 (7), 863. <https://doi.org/10.1039/B903887F>.
- Wallaert, H., 2012. Apprenticeship and the confirmation of social boundaries. In: Wendrich, W. (Ed.), *Archaeology and Apprenticeship: Body Knowledge, Identity, and Communities of Practice*. University of Arizona Press, Tucson, pp. 20–42.
- Wang, D., Mathur, R., Powell, W., Godfrey, L., Zheng, Y., 2019. Experimental evidence for fractionation of tin chlorides by redox and vapor mechanisms. *Geochem. Cosmochim. Acta* 250, 209–218. <https://doi.org/10.1016/j.gca.2019.02.022>.
- Wasserburg, G.J., Jacobsen, S.B., DePaolo, D.J., McCulloch, M.T., Wen, T., 1981. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochem. Cosmochim. Acta* 45 (12), 2311–2323. [https://doi.org/10.1016/0016-7037\(81\)90085-5](https://doi.org/10.1016/0016-7037(81)90085-5).
- Watkins, J., DePaolo, D., Watson, E.B., 2017. Kinetic fractionation of non-traditional stable isotopes by diffusion and crystal growth reactions. *Rev. Mineral. Geochem.* 82 (1), 85–125. <https://doi.org/10.2138/rmg.2017.82.4>.
- Weigand, P., Harbottle, G., Sayre, E., 1977. Turquoise sources and source analysis: mesoamerica and the southwestern USA. Exchange systems in prehistory 15–34. <https://doi.org/10.1016/B978-0-12-227650-7.50008-0>.
- Wenger, E., 1998. *Communities of Practice: Learning, Meaning, and Identity*, Learning in Doing. Cambridge University Press, Cambridge, U.K.; New York, N.Y.
- Woodhead, A.P., Gale, N.H., Stos-Gale, Z.A., 1999. An investigation into the fractionation of copper isotopes and its possible application to archaeometallurgy. In: Young, S.M.M. (Ed.), *Metals in Antiquity*. BAR International Series 792. Archaeopress, Oxford, pp. 110–122.
- Yamazaki, E., Nakai, S., Yokoyama, T., Ishihara, S., Tang, H., 2013. Tin isotope analysis of cassiterites from southeastern and eastern Asia. *Geochem. J.* 47, 21–35. <https://doi.org/10.2343/geochemj.2.0237>.
- Yamazaki, E., Nakai, S., Sahoo, Y., Yokoyama, T., Mifune, H., Saito, T., Chen, J., Takagi, N., Hokanishi, N., Yasuda, A., 2014. Feasibility studies of Sn isotope composition for provenancing ancient bronzes. *J. Archaeol. Sci.* 52, 458–467. <https://doi.org/10.1016/j.jas.2014.09.014>.
- Yao, J., Mathur, R., Powell, W., Lehmann, B., Tornos, F., Wilson, M., Ruiz, J., 2018. Sn isotope fractionation as a record of hydrothermal redox reactions. *Am. Mineral.* 103 (10), 1591–1598. <https://doi.org/10.2138/am-2018-6524>.
- Zedeño, M.N., 2002. Artifact design, composition, and context: updating the analysis of ceramic circulation at point of pines, Arizona. In: Glowacki, D.M., Neff, H. (Eds.), *Ceramic Production and Circulation in the Greater Southwest: Source Determination by INAA and Complementary Mineralogical Investigations*. Monograph 44. Cotsen Institute of Archaeology at UCLA, Los Angeles, pp. 74–85.
- Zedeño, M.N., Triadan, D., Bishop, R., 2003. Compositional analysis in American archaeology. *Patterns and Process: a Festschrift in Honor of Dr. Edward V. Sayre*. Smithsonian Center for Materials Research and Education, Suitland Md, pp. 27–55.