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# Isotope archaeology

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ABSTRACT: The application of isotope geochemistry to archaeoiogical problems, especially the determination of the provenenance of the raw materials of archaeological artifacts but also the possibility to trace back the movement of individuals is described.

## 1 INTRODUCTION

It has long been recognized that it should be possible to use some form of geochemical fingerprinting to trace archaeological finds to their mineralogical source or, at least, to their production site. The first application was on archaeological metal finds (Göbel 1842) where the basic ideas were already described. However, the analytical methods were not advanced enough so that too much material was needed and not enough elements could be determined with sufficient sensitivity.

Since the advent of instrumental methods for chemical analysis in the 1930s large programs of analysis of prehistoric metal objects have been undertaken (e.g. Otto & Witter 1952; Pittioni 1957; Junghans et al. 1960). However, the relationship between a metalliferous ore and that of a metal object is much more complicated than originally assumed. Although the chemistry can be used to some extent for provenance studies (Pemicka 1999), the application of lead isotope abundance ratios in this field has provided a major breakthrough (Grögler et al. 1966; Brill & Wampler 1967). The method is neither confined to metal objects nor to lead isotope abundance ratios. Following is a short overview of various applications in archaeology.

## 2 METALS

### 2.1 Lead and silver

The basic rationale behind the application of lead isotope abundance ratios for provenance studies is quite simple. It is based on the natural radioactive decay of isotopes of uranium and thorium. in open systems like in magma chambers and in ore forming solutions all three elements (Pb, U, and Th) are associated with typical U/Pb and Th/Pb ratios of 0.1 and 0.4 respectively and, accordingly, the isotopic composition of lead continuously changes. At the time of lead ore formation, Pb is effectively separated from Th and U (typical U/Pb and Th/Pb ratios are far less than $10^{-6}$) and a particular lead isotope composition is virtually 'frozen in' to that lead ore. Hence the lead isotopic composition may be different from a number of deposits within a given area, so that the isotopic composition of lead in an archaeological lead artifact may be matched with a particular lead ore deposit.

Of course there may be complications when the ore formation did not occur in a single stage. In such cases the isotopic ratios vary along straight lines within an ore body or a mining district. Fortunately, at least in the so-called Old World (Europe with the Mediterranean and southwest Asia) such lead types are rare although they do exist in archaeologically important areas like Egypt. More often each mining district will be characterised either by a small range (in the order of a few tenths of a percent relative) of its lead isotopic composition.

This method has some desirable features, in that the isotopic composition of lead is not changed by extraction or refining processes applied to an ore to produce a metal, nor by the fabrication process, nor by any subsequent corrosion of the artifact. This fact gives the lead isotope method an important advantage over chemical analysis as a 'fingerprint' method in establishing the provenance of a metal.

in antiquity silver was almost exclusively produced from argentiferous lead ores by production of lead and subsequent cupellation. Since a few tenths of a percent of Pb remain in cupelled silver, this method is equally applicable to ancient silver objects. It also eliminates the problem of ensuring representativity in chemical analysis.

The most serious problem in the application of lead isotope ratios to archaeology is the re-melting and mixing of metals originating from different geographical areas. Such mixing will invalidate both chemical and isotopic analyses. This problem is particularly common with coinage, which has often been debased and later refined to gain the silver and strike new coins. On the other hand, so far there has been little indication that lead was regularly mixed except for lead solders (Wyttenbach & Schubiger 1974175).

A further difficulty is the possibility that lead ores from different geographical regions have lead isotope abundance ratios that are indistinguishable, even when the highest possible precision in measurement is obtained. In such cases a combination of lead isotope studies with trace element concentration may lead to further differentiation or one may have to use evidence of ancient mining or simple archaeological reasoning to eliminate some isotopically possible ore sources.

This combination of methods was highly successful in the study of silver used for early coinage in the Aegean (Gale et al. 1981). There are many texts that document that the ancient city state of Athens was in the possession of a rich silver mine at Laurion in the southeast of Attica. Less reliable seemed reports of ancient silver mining on the Cycladic island of Siphnos, because no silver occurrences were known there to modern geologists. A thorough field survey combined with geochemical analyses of lead ores and silver coins from the Aegean revealed not only that silver does occur on the island of Siphnos and that it was mined in the sixth and fifth centuries BC, contemporary with the issue of the analyzed coinage (Wagner & Weisgerber 1985).

A particularly instructive example is the study of Early Bronze Age lead and silver artifacts in the Aegean (Gale & Stos-Gale 1982). From the field work mentioned above it had been known that lead and silver ores were exploited on Siphnos from the Early Bronze Age on, i.e. from the beginning of the third millennium. Lead isotope analyses indicated that the same was true for Laurion also. And indeed, this suggestion was later confirmed by archaeological excavation.

Although Laurion and Siphnos apparently supplied a large share of the total lead and silver used in the third millennium on the Cyclades there must have been other sources as well as indicated by lead isotope ratios (Fig. 1) that may be in the Aegean but could also be located somewhere else. This is one serious limitation of geochemical provenance studies altogether in that only negative evidence is conclusive. Only if the lead isotopic composition of an artifact is different from an orefield one can safely conclude that it does not derive from there, while the reverse argument is not compelling as long as not all possible sources are known and analyzed.

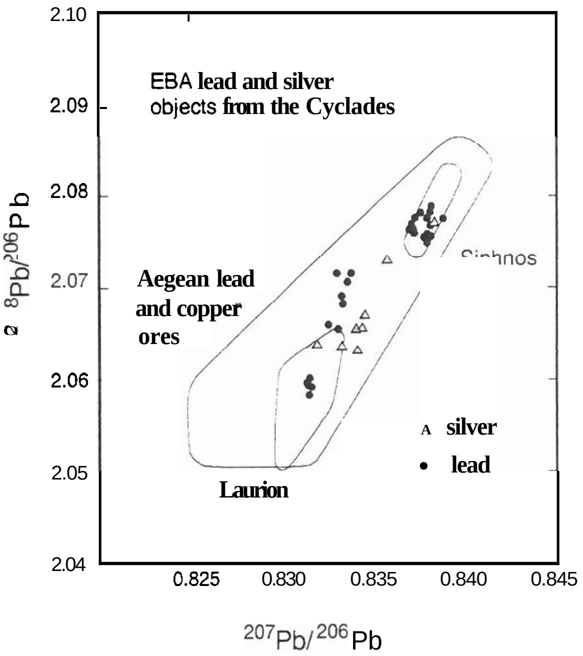

**Figure** I. **Lead isotope ratios of base** metal **ores in** the **Aegean** and **Early Bronze Age lead and silver** artifacts.

### 2.2 *Coppper and copper alloys*

For the application of lead isotope analyses to the provenance of copper it must be sure that in the ancient copper-based alloys studied the lead present is an accidental contamination coming from the copper ore and was not added intentionally to alter the properties of the metal.

It is difficult to provide a clear concentration limit for this distinction, but it is usually assumed that a few percent lead in copper-based alloys can derive accidentally from the copper ores themselves. More than 5% Pb are generally considered an intentional addition.

The most abundant copper alloy in prehistoric times was bronze, a copper alloy with about 10% tin. Interpretion of lead isotope ratios in such alloys in terms of provenance requires knowledge of the relative contributions of the alloying materials towards the lead budget in the metal. Fortunately, ancient tin is rather pure due to the fact that most probably cassiterite was exclusively used for its production in early periods and this mineral has notoriously low lead contents (Gmelin 1971).

Thus it is usually the source of copper that is determined by lead isotope ratios in copper-based alloys. There is, however, a further possible complication. In copper deposits the model assumption is not always fulfilled that no changes must have taken place of the isotopic composition since formation of the ores, because some copper combine low concentrations of lead with appreciable and highly variable concentrations of uranium that may even form uranium minerals. This situation has been observed in ores from two of the earliest copper mines identified so far, namely Rudna Glava in Serbia (Pernicka et al. 1993) and Rosen in Bulgaria (Pemicka et al. 1998).

Nevertheless, many important results have been obtained with this approach, like the observation that Rudna Glava may not have produced copper metal at all but that, indeed, already in the fifth millennium BC copper metal was transported.(traded?) over considerable distances in southeastern Europe. It was also shown that, contrary to archaeological exeption, in the Late Bronze Age copper was traded in the form of so-called oxhide ingots from Cyprus to Sardinia but that the same shape was also made from copper from other sources (Gale 1991).

All these data have been acquired with thermal ionization mass spectrometry which is a very accurate and precise method but also a very time consuming one. Recent improvements in mass spectrometry resulting in the introduction of inductively coupled plasma source magnetic sector multiple collector mass spectrometers (hereafter called multicollector ICPMS, Walder & Freedman 1992) have reduced the experimental effort considerably and opened up new isotopic systems for investigation.

Although a large mass discrimination effect occurs in the plasma source this fractionation is fixed and independent of time and of the chemical properties of the element measured. Instrumental mass discrimination can thus be corrected by using a second element of similar mass (e.g. zinc for copper) and measuring the mass bias. With this technique it has become possible to measure copper isotope ratios very precisely and detect small but significant variations in nature (Luck et al. 1999). Since copper is the major element in copper-based alloys it is not to be expected that the copper isotope abundance ratio should be altered by the pyrometallurgical production processes to a measurable extent so that it may provide useful information on the provenance of copper in the future.

## 2.3 *Tin*

The only variations that might exist in the isotopic composition of tin ores are such as they may have come about during the chemical processes involved in the formation of the ores. On theoretical reasons such effects are to be expected to be very small. Indeed, an earlier study (McNaughton & Rosman 1991) has shown that isotopic variation in tin must be sought at levels below 0.1% ($^{122}$Sn/$^{116}$Sn).

In a heating experiment Begemann et al. (1999) reported a change in $^{122}$Sn/$^{116}$Sn of c. 0.048% for a heated bronze which had lost 10% of its tin. In addition, a smaller but systematic enrichment of heavy tin isotopes by up to $\cong$0.02% per amu in ancient bronzes from Central Europe compared with bronzes from the Eastern Mediterranean was observed. These bronzes are quite likely to have received tin from different ore sources, which raises the question whether these preliminary data reflect different tin isotope compositions in the source ore or fractionation by metallurgical processes.

Both studies were performed with thermal ionization mass spectrometry. The new analytical possibilities will finally clarify this question and will open up new possibilities for the search of the tin sources used in the Early Bronze Age of the Near East and the eastern Mediterranean that has been going on for more than hundred years (von Baer 1876).

## 2.4 *Gold*

Although in principle much easier for provenance studies, because it does not require pyrometallurgical production processes, extensive trace element analyses of ancient gold artifacts (Hartmann 1970) have not yielded conclusive results. When it was discovered that ancient gold frequently contains inclusions of platinum group metals (Young 1972) it was hoped that if not their presence itself but their composition (roughly a mixture of indium, osmium and ruthenium) could be a guide to provenance. Unfortunately, this did not prove to be the case (Meeks & Tite 1980).

However, these inclusions contain osmium as major element that is one of the few heavy elements with variable isotopic composition due to radiogenic nuclides. $^{187}$Os is the decay product of $^{187}$Re with a half-life of 5 x $10^{10}$ years. Os and Re are fractionated strongly in the interior of the Earth with Os mainly residing in the core and Re in the crust resulting in a rather large variation of the $^{187}$Os/$^{188}$Os ratio between about 1 and 15. Until recently it has been extremely difficult to measure osmium isotope ratios with thermal ionization mass spectrometry. Even after the introduction of measuring negative ions of osmium it is still experimentally an extremely demanding procedure (Creaser et al . 1991).

In contrast, the multicollector ICPMS can be easily coupled with a laser sampling system with a focused laser beam of less than 50 µm diameter that evaporates a small sample volume. The sample vapour is transported with a carrier gas to the ICP flame where it is ionized and analyzed by the mass spectrometer. Thus even small inclusions of platinum group elements in gold artifacts can selectively (and almost non-destructively) be sampled and the isotopic composition of osmium be determined with a precision of better than 0.1% according to preliminary results (Junk & Pemicka in preparation).

## 3 OTHER MATERIALS

The same approach can in principle be applied to all other materials that contain elements that inherit their isotopic variation from their natural occurrence. With pottery sherds, the most abundant archaeological finds, the question of provenance emerges frequently although the site of production is usually of more interest than the actual location of the raw material(~).Many thousands of pottery samples have been analyzed by powerful multi-element methods such as neutron activation analysis and many production sites have thus been satisfactonly characterized.

Nevertheless, it sometimes happens that despite the large number of elements that are available for discrimination it is not possible to clearly distinguish between two production sites. This is, for instance, the case for Troia and Mycenae, an archaeologically particularly interesting pair of sites. In this case the application of Pb, Sr, and Nd isotope ratios allowed a clear differentiation (Knacke-Loy et al. 1995).

Historically, this information was sought in order to trace back the movement of people in prehistoric times. Nowadays the results of artifact analyses are usually discussed in terms of trade but the geochemical analysis of bones may provide actual evidence for the movement of individuals. Strontium with isotope ratios typical of their living regions are taken up by humans and animals and preserved in their bones. When they move into geologically (and isotopically) different regions the adaptation of the isotope ratios in bone takes a few years. Thus isotopic differences between skeletal remains and surrounding rocks indicate movement in a short time period before the death of an individual (Grupe et al. 1997).

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