



Iridium to provenance ancient silver



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ABSTRACT

Trace levels of iridium in ancient silver artefacts can provide information on the sources of silver-bearing ores as well as the technologies used to extract silver. A geographically and chronologically disparate legacy dataset, comprised of Near Eastern objects from the Sasanian and Byzantine Empires (1st Millennium AD) and coins circulating around the Mediterranean in the mid-1st Millennium BC, shows that Ag-Au-Ir log-ratio plots can help identify silver derived from the same mining areas, as well as broadly differentiating between the ore types exploited. Combining trace element and lead isotope analyses through the Pb crustal age of the ore, further delimits interpretations on the compositions and locations of silver ore sources. Furthermore, it is shown that silver artefacts of Near Eastern origin have exceptionally high iridium levels, suggesting a unique silver-bearing ore source, potentially in the Taurus mountain range of southern Anatolia. The wide range of crustal ages identified for ancient Greek coins and Near Eastern objects suggest that the addition of exogenous lead as a silver collector during smelting was common practice in the Near East as early as 475BCE. The practice of mixing silver from different sources has also been identified by triangulating the log-ratio subcomposition plots, Pb crustal ages of the ore from which the silver derived and absolute values of trace levels of gold and iridium in silver artefacts.

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1. Introduction

Metal ores are unevenly distributed over large areas, which suggests some kind of long-distance transport is required to explain the geographical distribution of artefacts in the archaeological record (Pernicka, 2014). Tracing the ore source of ancient metal artefacts can complement any investigations based on style and iconography, thereby providing information on the movement of the materials that culminated in final deposition of the object.

Provenancing silver objects has been attempted since the 19th century using elemental analyses and more recently using lead isotope ratios (for a review, see Pernicka, 2014). In order to determine the trajectory of a silver object from its ore source, a metallurgical signature needs to be identified and measured (Randle et al., 1973; Meyers et al., 1975). Establishing a relation between chemical analyses on ancient silver objects and mineralogical sources of silver requires not only knowledge of the composition of the ores, but also of how the composition changes during smelting and cupellation (a selective oxidation process where silver is

separated from its less-inert lead host) (Pernicka et al., 1998). For example, a silver-bearing ore, such as galena (PbS) or cerussite (PbCO₃), contains, in addition to lead, a small amount of silver but a large number of impurities. Some of these elements are retained in the silver, while others are partially or completely removed into slag or fumes during the smelting and refining processes (McKerrel and Stevenson, 1972; Pernicka and Bachmann, 1983; L'Heritier et al., 2015). Furthermore, contamination can occur from materials used in furnaces, fuel and fluxes. Deliberate additions to the system, such as alloying elements or recycled silver from other sources, contain their own associated impurities which can also contribute to the final composition of the silver object, thus potentially blurring further the provenance signature. Exogenous lead, added as a silver collector during extraction from lead-poor silver-bearing ores, affects the lead isotope signature derived from the silver and may render the provenancing of archaeological silver even more challenging than for other materials (Murillo-Barroso et al., 2016).

The complexity of the processes involved in the production and alloying of silver makes determining a parent-ore indicator extremely challenging, especially when it is considered that any indicator needs to have significant variability between ore sources.

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In other words, not only does an indicator need to survive the smelting, cupellation and alloying operations, but also the variability within a single ore source must be small compared to variations in geographically separated ore sources (Pollard and Bray, 2015).

Trace levels of gold in silver have been considered associated solely with silver sources, as they tend to be virtually absent in any other material in the system and they are not significantly altered by the smelting and cupellation processes (Gitler et al., 2009). Variability in gold concentrations between silver artefacts has been applied successfully to differentiate between lead ore types (the main source of ancient silver), with an empirical value of 0.1 wt% Au in silver objects being the upper limit for galena ore sources (Pernicka, 1981). Iridium (Ir), like gold, is an inert siderophile element (Alard et al., 2000). Traces of iridium have been found in ancient silver artefacts, suggesting that this metal with its high melting point (2447 °C) and similar atomic size to silver survives the smelting and cupellation process (Ogden, 1977). Furthermore, gold and iridium are unlikely to enter the system in any significant amount due to alloying (i.e. copper, the main alloying metal is poor in these elements and rarely exceeds more than 5 wt% of the silver alloy) or to be associated with any non-argentiferous lead (a chalcophile) added as an exogenous silver collector in the smelting of lead-poor silver-bearing ores. Hence gold and iridium are potential proxies to provenance silver from ore to object.

This paper aims to further this hypothesis through the re-analysis of a legacy dataset of 283 analyses on silver objects together with published data on ores. We propose that Ag-Au-Ir log-ratio plots are useful to discriminate silver deriving from different ore types, hence contributing to provenance studies, and that sometimes iridium levels alone can be very diagnostic of individual sources. In addition, we explore new ways of combining this information with lead isotopic data, leading to more robust approaches to the identification of exogenous lead additions for silver extraction, silver mixing through recycling, and metal fingerprinting generally.

2. Legacy data and re-analysis

Although iridium is not measured routinely in archaeometallurgy, some studies have measured iridium without using it explicitly as a discriminator (Gale et al., 1980). Other investigations, especially those associated with Pieter Meyers, were quite successful at grouping silver artefacts using iridium, often with an aim of assessing the authenticity of silver objects in museum collections (Harper and Meyers, 1981; Meyers, 1992). Meyers' experimental analysis on Sasanian silver (Harper and Meyers, 1981) measured major, minor and some trace elements (including iridium) in 38 objects from several museums around the world. Although unprovenanced, these objects are made of silver from potentially a single ore source (see Section 2.2). Similarly, a study on ecclesiastical Byzantine silver provides compositional data from 69 objects dated between the 4th and 7th centuries AD (Meyers, 1992). Several of these objects were later analysed for lead isotopes (LIA) in a study with two other artefacts in order to investigate their authenticity as ancient objects (Scott, 1990). A numismatic study on the Asyut hoard (pre-475BCE) measured iridium concentrations in 283 coins, 102 of which have associated LIA data (Gale et al., 1980; Stos-Gale and Gale, 2009). The mints of some of these coins have been suggested, which provide a potential indication of the ore source of silver, since silver from the Athenian mint is generally accepted to have come from the mines at Laurion on the Attic peninsula.

The following re-analysis has simply pooled this data with no particular archaeological question: our hypothesis is largely

methodological, even if our results may be useful for later archaeological discussion (which is not attempted here). We believe this data set includes the majority of analyses in which iridium was measured for archaeological silver, some of which have associated LIA measurements. The focus is on the ore sources which, in some cases, may have been the same, irrespective of the period. Hence, we believe that the use of an archaeologically disparate dataset is justified. All compositional legacy data presented in the current study were measured using neutron activation analysis (NAA) or inductively coupled plasma mass spectrometry (ICP-MS). All compositional and LIA data used can be found in Supplementary Table 1.

Fig. 1 presents histograms of Au and Ir concentrations for this chronologically and geographically disparate dataset. The gold distribution appears to be bi-modal. The gold concentration in silver is often used to differentiate silver which originated from non-galena (>0.1 wt% Au) and galena ore (<0.1 wt% Au) sources (Pernicka, 1981). Iridium has a skewed distribution with a median value of 44 ppb.

A re-analysis of this legacy data has been conducted treating the system as a series of sub-compositional components, by transforming the data to a log-ratio scale (Aitchison, 1986, 2005). This approach removes the effects of the constant sum constraint (which compels the data to lay between 0 and 100%) in order to eliminate any 'spurious correlations' (Chayes, 1949). In essence, it considers from the outset that the interest lies in the relative magnitudes and variations of components, instead of in their absolute values. A multivariate analysis was performed of the full chemical data set using the Compositions package in R created by van den Boogaart (2013), applying Aitchison's geometry (i.e. the centred log-ratio transformation) to the raw compositional data. After using the variation matrix to measure the spread in the compositional data, the subcomposition Ag-Au-Ir was identified as providing the ratios

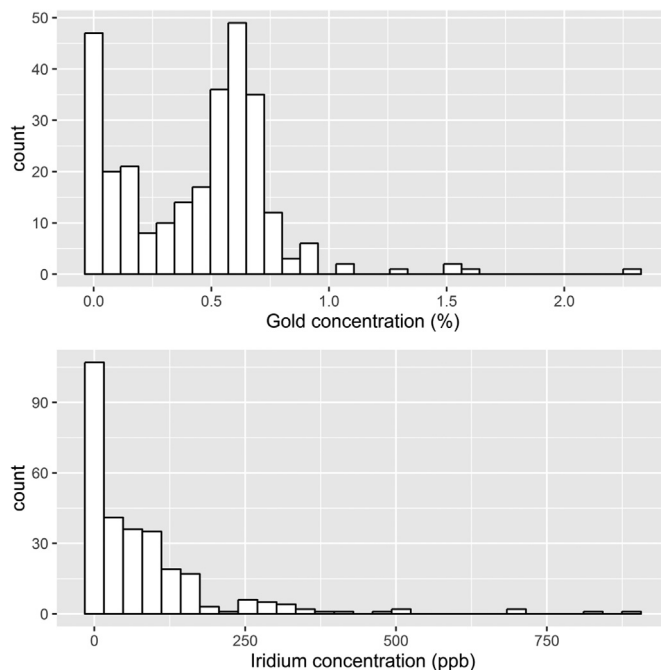


Fig. 1. Frequency distribution histograms of the iridium (ppb) and gold (wt%) concentrations of the full dataset. The bin width was set using the Freedman-Diaconis rule (Freedman and Diaconis, 1981). Note that some objects were measured more than once because they had more than one part (e.g. foot, rim etc.). The histograms show that the gold concentration is bi-modal and that the iridium concentration has a skewed distribution with a median value of 44 ppb.

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