Journal of Archaeological Science 98 (2018) 22–33

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: www.elsevier.com/locate/jas

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)

Jean Milot[a,b,*], Sandrine Baron[a], Franck Poitrasson[b]

[a] Travaux et Recherches Archéologiques sur les Cultures, les Espaces et les Sociétés, UMR 5608 Centre National de la Recherche Scientifique - Université de Toulouse, Maison de la Recherche, 5 allées Antonio Machado, 31 058, Toulouse Cedex 09, France

[b] Géosciences Environnement Toulouse, UMR 5563 Centre National de la Recherche Scientifique - Université de Toulouse - Institut de Recherches pour le Développement, 14-16, avenue Edouard Belin, 31400, Toulouse, France

ARTICLE INFO

Keywords:
Non-ferrous metals
Slag characterization
Fe isotopes
Pb isotopes
Provenance

ABSTRACT

Determining the provenance of non-ferrous metals is a major issue in archaeology and history. The classical method using Pb isotopes shows several limitations, and new isotopic tracers need to be developed in archaeometallurgy. Recently, Fe isotopes were found to be promising for iron metal tracing. In this context, we evaluated the pertinence of Fe isotopes as a new tool for provenance studies of non-ferrous metals. We collected slag and furnace lining samples from the Imiter silver mine in Morocco (Anti-Atlas), where many archaeological remains attest ancient lead-silver production. Their mineralogical composition was investigated by optical microscopic observations, SEM-EDS and EPMA. Besides, we measured both Pb and Fe isotope compositions of these samples by high resolution MC-ICP-MS after wet sample decomposition and purification chemistry. The occurrence of Ag, Pb, Cu and Ag/Pb metallic beads in the slag samples and their high Fe content suggests that these metallurgical materials result from the exploitation of Ag-rich polymetallic ores associated with gossan formations. Isotopic analyses of these slags highlighted their heterogeneous Pb isotope compositions and homogeneous Fe isotope composition. This points to the exploitation of two distinct ore sources with different Pb but similar Fe isotope compositions, despite the Fe isotope variability often encountered in metallic ores worldwide. Hence, Fe isotopes provide a complementary approach to trace lead-silver products from Imiter. Overall, the combination of Pb and Fe isotope analyses constitutes a promising method for further provenance investigations of non-ferrous metals.

1. Introduction

Non-ferrous metals, such as lead, copper, tin, silver or gold played a major role in most ancient societies. They were generally used to produce prestige objects and coins. For instance, the power of ancient monarchs during medieval times was directly linked to their coins minting capacity. Therefore, the extraction of non-ferrous metals constituted a regalia right. For these reasons, the study of production and exchange of non-ferrous metals represents a crucial issue in archaeology and history as it helps to understand the economic organization of past societies and to characterize ancient trade networks (e.g., Junk and Pernicka, 2003; Baron et al., 2006; Desaulty et al., 2011). Moreover, the restitution of ancient metallurgical techniques provides information on the level of technological advancement of past civilizations, or on the mode of currency devaluation or appreciation adopted for coin production (e.g. Roux and Guerra, 2000; Desaulty and Albarède, 2013; Corsi et al., 2016). In addition to a purely archaeological approach, geochemical tools are now essential for provenance studies of metallic artefacts and for the understanding of ancient *chaîne opératoire* in a given area. Ancient metals tracing is based on the mineralogical, chemical and isotopic characterization of archaeological remains (ores, reduction slags and metals) in order to identify geochemical tracers which are preserved all along the *chaîne opératoire* (e.g. Baron et al., 2014).

Lead isotopes have been the most commonly used isotopic tracer for provenance studies of non-ferrous metals so far. However, some case studies have shown that using of Pb isotopes only is not sufficient to discriminate between sources. As a result, the current trend in

* Corresponding author. Géosciences Environnement Toulouse, UMR 5563 Centre National de la Recherche Scientifique - Université de Toulouse - Institut de Recherches pour le Développement, 14-16 avenue Edouard Belin, 31400, Toulouse, France.
E-mail address: jean.milot@get.obs-mip.fr (J. Milot).

https://doi.org/10.1016/j.jas.2018.07.004
Received 19 January 2018; Received in revised form 10 July 2018; Accepted 13 July 2018

archaeometallurgy is to develop new, complementary isotopic tracers such as the isotopic compositions of Cu, Ag or Os (e.g. Junk and Pernicka, 2003; Klein et al., 2004, 2009; Desaulty et al., 2011; Desaulty and Albarède, 2013; Jansen et al., 2016). Recently, Milot et al. (2016) illustrated the promising use of Fe isotopes for ancient ferrous metal tracing. However, several examples in the literature highlighted the occurrence of sizeable amounts of Fe (from tens to thousands ppm) even for non-ferrous materials (e.g. Moreno-Suàrez et al., 2015; Vasilescu et al., 2015; Charalambous, 2016; Rademakers et al., 2017). We thus investigate in this contribution the potential use of Fe isotopes as a new tool for non-ferrous metal tracing, focusing on the example of an ancient lead-silver production site in Morocco (the Imiter mine, Anti-Atlas).

1.1. Silver production in ancient times

The *chaîne opératoire* of silver production during ancient times depended on the nature of the exploited ores. Different Ag-bearing ores are not necessarily associated with the same gangue or the same metals. Generally, ancient miners preferentially exploited the richest ores, in particular supergene enrichment zones formed by chemical weathering of the superficial part of mineralized veins, and mainly associated with iron gossan formations (e.g., Velasco et al., 2013; Yesares et al., 2014; Andreu et al., 2015). This may explain the usual occurrence of iron and many other metals in non-ferrous ores and thus, in non-ferrous metals. Silver could be associated with gold in electrum, with hydrous sulfates of potassium and iron in jarosite, with copper in grey copper, or with several metal-bearing minerals in polymetallic ores. Archaeological evidence for Ag extraction from the latter types of ores is scarce, thus these *chaînes opératoires* are usually not well known.

In contrast, galena ores (PbS, with at least 0.1% Ag content) are the most abundant Ag-bearing ores in nature and they have been intensively exploited during ancient times. This exploitation has left archaeological evidence (mine tailing heaps, slags, by-products, ingots …) allowing a better understanding and a restoration of the *chaîne opératoire* in a given regional and social context. The general principle is that galena ores were reduced to obtain a Pb-Ag bullion from which silver was further separated from lead. Thus, lead may be considered as a by-product of silver production (Domergue, 2008; Baron et al., 2011). The study of some archaeological sites enabled to determine the theoretical *chaîne opératoire* of Ag-bearing galena reduction, in particular for medieval times, although the exact processes may vary depending on the archaeological context (e.g. Téreygeol and Happ, 2000; Mahé-Le-Carlier et al., 2011; Ettler et al., 2015; Gauthier et al., 2015).

Generally, after a first step of ore sorting and concentration, a possible roasting under oxidizing conditions allowed galena oxidation (and ore weakening). The roasted ore was then reduced in a smelting furnace at about 1000 °C and under reducing conditions where CO and C reducing agents enabled metallic Pb production. Treated ores could also be directly reduced in a smelting furnace, without any roasting. This process required the use of different additions to improve the extraction of lead and precious metals from the ore by increasing the silicate slag formation (e.g. Baron et al., 2009; Mahé-Le-Carlier et al., 2011; Liu et al., 2015; Wood et al., 2017). For example, metallic iron addition allows sulfur segregation from galena. Overall, the addition of Fe, K, Ca or Na silicates, or lime (CaO) allowed a better extraction of lead during reduction processes (e.g. Mahé-Le-Carlier et al., 2011). More detailed explanations about lead-silver ores treatment and reduction are given in Ploquin et al. (2004), Baron et al. (2009), Mahé-Le-Carlier et al. (2011) or Liu et al. (2015).

During the smelting process, the metallic Pb went through a liquid state and could be molded into ingots since the high temperature of the furnace (about 1000 °C) exceeds the lead fusion point (327 °C). At this stage, silver and other impurities were still associated in the lead metallic bullion, and a subsequent cupellation step was needed to separate silver from lead. During this process, the bullion was melted at high temperature (900–950 °C) to remove lead by preferential oxidization, forming litharge (PbO), while silver remained in the smelting bath (e.g. Conophagos, C., 1980; Téreygeol and Thomas, 2003; L'Héritier et al., 2015).

1.2. Methods and limitations of non-ferrous metals tracing

In contrast to iron materials which stays in a "semi-solid" state during reduction, non-ferrous materials reduction normally goes through a liquid phase which enables the incorporation of impurities in the metallic phase. Thus, following the cooling of a lead ingot, the elemental concentrations could be highly heterogeneous (Baron and Cochet, 2003). Furthermore, potential additives may further disturb the elemental composition, masking the compositional signature and potentially hampering provenance links between metallic artefacts and a specific ore source (e.g. Baron and Coustures, 2015).

Lead isotopes have been used for tracing non-ferrous materials tracing since their natural variability may allow sources distinction. Accordingly, the radiogenic nature of three of the four lead isotopes (^{208}Pb, ^{207}Pb and ^{206}Pb are radiogenic, ^{204}Pb is stable) induce different Pb isotope compositions between terrestrial reservoirs (e.g. Faure and Mensing, 2005; Albarède et al., 2012). Hence, since the pioneering study of Brill and Wrampler in 1965, this method has been widely employed for non ferrous metals tracing (e.g. Gale et Stos-Gale, 1982; Stos-Gale et al., 1997; Niederschlag et al., 2003; Durali-Müller et al., 2007; Trincherini et al., 2001, 2009; Baron et al., 2009; Huelga-Suarez et al., 2014; Ling et al., 2013, 2014).

However, as for many tracers (elemental and isotopic), several factors may limit provenance determination using Pb isotopes. For example, the possible variations of composition in a single mining district or similar compositions between distinct districts may prevent their use for source discrimination (e.g. Yener et al., 1991; Stos-Gale et al., 1995, 1996; Gales et al., 1997; Baron et al., 2014). Moreover, the use of mixtures of ores, or additions during the reduction process (e.g. Mahé-Le-Carlier et al., 2011), with distinct Pb amounts and signature may increase isotopic differences between the silicate and metallic phases of the produced slags. This is due to different mixing proportions and contrasted distribution of chemical elements between both phases (e.g. Baron et al., 2009; Rademakers et al., 2017). This is particularly the case for tin production where the metallurgy is conducted in a Pb-poor system (Molosfsky et al., 2014). For the same reasons, mixing metals with potentially distinct lead isotope signature for bronze and other Cu-based alloys production could also complicate provenance determinations (e.g. Gouchet et al., 1976; Torrisi et al., 2016; Rademakers et al., 2017).

Consequently, other isotopic tracers have been developed to overcome these limitations. In this endeavor, several new isotopic systems have been used, including: (i) Cu isotopes on ores and metallic artefacts (e.g. Klein et al., 2004, 2009; Jansen et al., 2017; Powell et al., 2017), (ii) Sn isotopes on ores and slags (e.g. Haustein et al., 2010; Yamazaki et al., 2014; Mason et al., 2016; Berger et al., 2018), (iii) Ag isotopes on silver coins and galena (e.g. Desaulty et al., 2011; Desaulty and Albarède, 2013) or (iv) Os isotopes on gold coins and artefacts (Junk and Pernicka, 2003; Jansen et al., 2016). The present study offers a contribution to this trend by exploring the combination stable Fe isotopes coupled with Pb isotopes as a provenance tracer. The combination of several isotopic tracers on the same batch of archaeological materials actually appears to be the most promising approach for future metal provenance studies.

1.3. Potential use of Fe isotopes for non-ferrous metals tracing

Recently, Fe isotopes have been tested as a potential new tool for ancient ferrous metal tracing. The demonstration of the absence of any Fe isotopes fractionation during bloomery process (Milot et al., 2016), combined with the previously observed isotopic variability of