Journal of Archaeological Science 57 (2015) 56–68

Contents lists available at ScienceDirect

Journal of Archaeological Science

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

Bismuth behaviour during ancient processes of silver–lead production

Maxime L'Héritier [a, *], Sandrine Baron [b, c], Laurent Cassayre [d, e], Florian Téreygeol [f]

[a] Université Paris 8, EA 1571, Centre de Recherches Historiques: Histoire des Pouvoirs, Savoirs et Sociétés, 2 rue de la Liberté, 93526 Saint-Denis Cedex, France
[b] Université de Toulouse Jean-Jaurès, Laboratoire TRACES, Maison de la Recherche, 5 allées Antonio-Machado, F-31 058 Toulouse Cedex 09, France
[c] CNRS, Laboratoire des Travaux et Recherches Archéologiques sur les Cultures, les Espaces et les Sociétés, F-31058 Toulouse, France
[d] Université de Toulouse, INP, UPS, Laboratoire de Génie Chimique, 4 Allée Emile Monso, F-31030 Toulouse, France
[e] CNRS, Laboratoire de Génie Chimique, F-31030 Toulouse, France
[f] Institut de Recherches sur les Archéomatériaux (IRAMAT), CNRS UMR 5060, LMC – LAPA, Bat 637 CEA – Saclay, 91191 Gif-sur-Yvette Cedex, France

ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form
29 January 2015
Accepted 3 February 2015
Available online 12 February 2015

Keywords:
Cupellation
Fire-assay
Thermodynamics
Experimental archaeology
Trace elements
Silver
Lead

ABSTRACT

Bismuth is one of the main trace elements found in archaeological lead and silver material in very variable contents. As silver refining by cupellation involves the redistribution of some trace elements contained in the initial lead bullion into the litharge and silver phases, an interdisciplinary approach has been carried out to understand the behaviour of bismuth during this process. Twenty-eight fire-assays were processed with seven different Pb–Bi–Ag alloys of various Bi content. A chemical characterization of all products was carried out. Parallel to the experiments, a thermodynamic approach was undertaken. The combination of experiments and modelling shows that the Bi/Pb ratio can be used as a tracer in silver material throughout the whole cupellation process. Bi and Ag contents in metallic lead might as well highlight the metallurgical process used to obtain lead. High Bi contents in silver–lead bullions are shown to notably reduce the silver extraction yield.

1. Introduction

The present work places specific attention on the behaviour of bismuth (Bi) in ancient processes of silver–lead production. Bi content is extremely variable in both lead and silver archaeological artefacts reported in literature. Regarding silver material, most Carolingian deniers (silver coins) contain a few hundreds ppm Bi (Sarah et al., 2008; Sarah, 2012). Yet, some authors also cite oriental silver coins containing up to several percent of Bi (Mac Kerrel and Stevenson, 1972; Cowell and Lowick, 1988). Sarah (2012) reports as well silver dirhams with up to 0.6 wt.% Bi. Likewise in prehistoric and ancient Spain, data summed up by Hunt Ortiz (2003) show that Bi content in silver is usually low (<0.1 wt.%), yet a sample of unrefined silver (91 wt.%) from Rio Tinto dated from the Roman period and analysed by Craddock et al. (1985) bears as much as 4.6 wt.% Bi.

Regarding lead artefacts, very high Bi concentrations ranging from several hundred ppm up to a few thousand ppm are observed in Egyptian net sinkers (Rehren and Prange, 1998) and in diverse material coming from ancient Thrace and from the Black Sea (Kuleff et al., 1995, 2006). Kuleff et al. (2006) even report a lead anchor from the Euxine exceeding 2 wt.% Bi. However, most archaeological lead artefacts are below 100 ppm and very often below 10–20 ppm Bi, *e.g.* medieval and modern stained-glass joints dated from the 8th to the 17th centuries (Cuzange and Texier, 2000). Among 40 lead objects from Nuragic Sardinia more than a third have less than 1 ppm Bi, the maximum recorded being 80 ppm (Atzeni et al., 2003; Cincotti et al., 2003). The Bi content of Hellenistic lead ingots, sheets and trephines are scattered between 30 and 45 ppm (Asderaki and Rehren, 2006). For lead objects excavated in Rhineland and Westphalia from Augustan–Tiberian military camps (Bode, 2008) it is usually lower than the detection limit of their analytic procedure (10 ppm). All Roman lead ingots analysed by Baron and Cochet (2003) are likewise below 10 ppm Bi. Eventually, despite some very rich artefacts, most objects reported by Kuleff et al. (1995, 2006) have a very low Bi content (<20 ppm).

These compositions offer a stunning paradox with the known characteristics of contemporary lead metallurgy: at the present day, bismuth extraction from the lead bullion is a real challenge with

* Corresponding author.
E-mail address: maxime.l_heritier@univ-paris8.fr (M. L'Héritier).

http://dx.doi.org/10.1016/j.jas.2015.02.002
0305-4403/

standard refining techniques, such as pyrolysis or electrorefining (Ramachandra Rao, 2006). As the presence of Bi lowers mechanical properties and corrosion resistance of Pb based alloys, bismuth purification is a crucial operation in many domains, which actually became one of the metallurgical challenges during the 20th century. Several treatments (basically by the addition of alkaline elements or antimony) were developed to reduce Bi content in lead materials down to 60 ppm on average (Kroll, 1922; Betterton and Lebedeff, 1936; Kroll, 1938; Evers, 1949; Defonte, 1964) and improved to reach the level of 10 ppm Bi in lead bullion (Ng and Siviour, 1994; Lu et al., 2011), which is common in most archaeological materials. However, before the identification of the element Bi by French and German chemists Claude Geoffroy the Younger and J. H. Pott in the mid 17th century (Pott, 1738; Grandjean de Fouchy 1757), debismuthizing according to the above-mentioned processes could certainly not be used by ancient metallurgists. Ancient lead production processes must therefore be investigated to shed light on such compositions.

Lead was then mostly a by-product of silver production. On the one hand, galena, *i.e.* lead sulphide, was among the main silver ores processed before the modern times. On the other hand, high amounts of lead were also required to retrieve silver from any polymetallic ore – *e.g.* jarosite in Rio Tinto (Anguilano et al., 2010) – and, in particular, from low grade copper ores with the liquation and drying process which was developed in the end of the Middle Ages (Suhling, 1976, 1994; L'Héritier et al., 2010). Details about the ancient lead–silver *chaîne opératoire* are reported elsewhere (Tylecote, 1976; Baron et al., 2009). Lead and silver were then separated via the cupellation process, used in ancient and medieval times to retrieve silver from argentiferous lead ingots (Tylecote, 1976; Téreygeol and Thomas, 2003). This process involves the oxidation of the silver-containing lead bullion in air at a temperature of about 900–950 °C, producing silver metal and lead oxide (also called litharge) as separate phases. The trace elements contained in the initial lead bullion are separated according to their affinity with oxygen: noble elements tend to stay in the silver button, whereas elements which oxidise end up in litharge and therefore in the resulting metallic lead obtained after litharge resmelting (Téreygeol and Thomas, 2003). The impact of the cupellation process on the chemical repartition of trace elements and specifically Bi should thus be questioned.

Discussions regarding Bi behaviour during silver refining have been contradictory. In the 19th century, elemental Bi was considered as strongly volatile by French assayer Chaudet (1818) and mining engineer Berthier (1834), later endorsed by Matthey (1887). Berthier (1834) also registered a higher silver loss when using bismuth instead of lead for cupellation. Metallurgical treatises from the end of the 19th century claim on the other hand that Bi, like noble metals, has a small affinity for oxygen and therefore stays concentrated in the metal phase (Percy, 1870; Schnabel, 1898). Taking the example of Bi-rich litharge derived from lead ores of the Upper Harz, Percy (1870) even adds that Bi oxidises at the end of the operation, just shortly before the "blick" *i.e.* with the last litharge. This last theory was endorsed in the 20th century by several works (Shepard and Dietrich, 1940; Pernicka and Bachmann, 1983; Raub, 1995). Yet, if the general behaviour of bismuth during cupellation is by no means controversial anymore, the precise conditions of bismuth partitioning between lead oxide and silver and its influence on cupellation products remain largely understudied. Experiments carried out by Pernicka and Bachmann (1983) show that bismuth oxidizes after lead. According to them, when 99.9% of the lead has already oxidised, 50% of the bismuth is still present in the silver bead. Yet, they give no interpretation about the influence of the initial Bi content on the silver yield nor on the lead and silver materials produced. Regarding this last point, L'Héritier and Tereygeol (2010) state that Bi content is ten to thirty times lower in lead resmelted from litharge collected during cupellation than in the initial lead–silver bullion. There is however no further interpretation of Bi content in ancient artefacts: this point has never been fully discussed and Bi is usually only considered as an ore source tracer (Cuzange and Texier, 2000; Baron and Cochet, 2003; Kuleff et al., 2006; Forel et al., 2010) despite all issues linked to ore or metal mixing and remelting (*e.g.* Anguilano et al., 2010). Thus, there is a need to estimate the impact of the cupellation process on the impurities dispersion between lead and silver button as well as the role of the ores elemental composition.

The question eventually comes down to: Is Bi a tracer for metallurgical process rather than a tracer for ores sources? And how are technological choices and archaeological remains impacted by the treatment of such Bi rich ores? These crucial historical questions are also linked to the use of lead ores and the trade of unrefined lead produced in certain European countries where lead–silver production was important. It was therefore necessary to focus on understanding Bi behaviour during the cupellation process. For this purpose, the approach included:

- Fire-assaying (*i.e.* cupellation) of "home-made" lead ingots processed on the international site dedicated to experimental paleometallurgy in Melle (France), according to the flowchart presented in Fig. 1. The Bi content of the ingots ranged from 130 ppm to 78 000 ppm: some of these materials were notably much richer in Bi than most archaeological ores, since the purpose was to verify the potential effect of Bi on the cupellation process.
- Chemical characterisation of all products *i.e.* "home-made" initial alloys, cupels impregnated with litharge and silver buttons.
- A modelling of the chemical equilibrium involved in the cupellation process, using computational thermodynamics and modern data. This approach was driven by a model aiming at sharpening the prediction of process performances proposed by Swinbourne et al. (2003), in the frame of the improvement of the modern industrial cupellation technology.

2. Materials and methods

2.1. Pb based alloys preparation

In order to evaluate the influence of the initial Bi content on the behaviour of the other elements and on the cupellation products, two experimental cupellation campaigns (XP1 and XP2) were carried out, using as starting material Pb–Bi–Ag–Sb–Sn alloys of various compositions. Overall, seven different Pb based alloys were prepared, with constant (1 wt.%) Ag content (representative of silver-rich lead bullions, *e.g.* obtained from galena smelting) and Bi contents ranging from 130 ppm to 78 000 ppm. All alloys were prepared using pure silver powder (Goodfellow AG006021/2 at 99.99%) and bismuth (>99% as analysed by portable XRF Thermo Scientific Niton Xl3t). The lead source was slightly different between the two campaigns. As evidenced in Table 1, which summarizes the composition of each Pb based alloy, the ingots used in XP1 present higher Sb and Sn content than ingots used in XP2. These "home-made" ingots can be considered as archaeological lead analogues with different impurities reflecting the lead production of different mining districts.

As the Pb based alloys melt at ca. 300 °C, they were prepared in a laboratory furnace at 450 °C. First, lead was heated in a lidded graphite crucible for 30 min. Then, silver and bismuth were added,