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Bismuth behaviour during ancient processes of silver–lead production

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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

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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; Tereygeol 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 (Tereygeol 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 XI3t). 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,

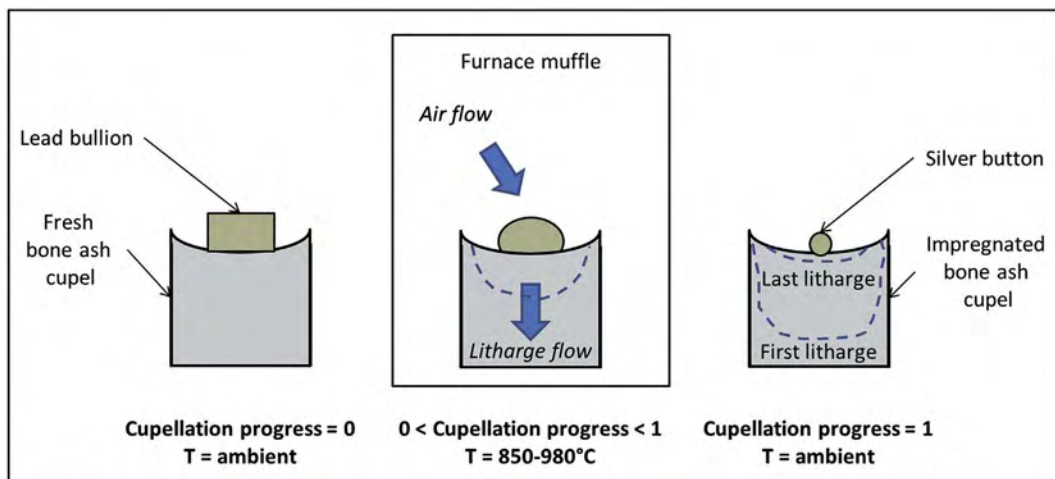


Fig. 1. Flowchart of the experimental cupellation process and experimental furnace used during the experiments.

and the bath was stirred with a small wooden spatula before final homogenisation for 30 min in the furnace. Eventually, the alloys were cast in ingots in a sand casting mould. 100 g of each alloy were prepared, which allowed performing four assays of approx. 20 g per batch. All Pb based alloys were characterised using ICP-MS (HR-ICP-MS) equipment by ALS laboratory.

2.2. Cupels composition

Cupels used for the present study are industrial bone ash cupels, with an inverted truncated cone shape and a weight of about 65 g. Their dimensions are as follows: external diameter is 5 cm on top and 4 cm at the bottom, height is 2.5 cm and the cavity has a diameter of 3.5 cm and is ~1 cm deep in the middle. A preliminary chemical characterisation of the cupels indicated no metal contamination.

Bone ash cupels are considered as inert material which does not react with litharge. In ancient times, however, textbooks as well as archaeological remains testify that, if the usual preference was indeed for bone ash, many other recipes were used depending on metallurgical traditions or more simply due to the availability of

Table 1

Composition of the processed Pb based alloys. The chemical characterisation was performed using ICP-SMS (HR-ICP-MS) by ALS laboratory.

Reference	Pb (wt.%)	Ag (ppm)	Bi (ppm)	Sb (ppm)	Sn (ppm)
XP1.1	94.9	7300	130	42 000	660
XP1.2	93.8	10 000	3000	42 000	6700
XP1.3	88.9	10 000	21 000	72 000	6500
XP2.1	98.0	10 100	9900	3.8	1.5
XP2.2	97.0	10 200	19 400	10.5	3.4
XP2.3	95.1	10 000	38 600	8.3	2.7
XP2.4	91.1	10 200	78 100	3.0	2.1

materials: wood ash, bone ash, a mixture of the two or even clay hearths topped with a non-siliceous lining (Agricola, 1556; Bayley and Eckstein, 2006; Biringuccio, 1540; Ercker, 1580; Hawthorne and Smith, 1979; Martín-Torres et al., 2008, 2009). All these materials may behave slightly differently during cupellation, and the formation of lead silicates or calcium–silica–phosphates is likely to diminish their capacity to absorb metallic oxides (Bayley and Eckstein, 2006; Rehren, 1998). Martín-Torres et al. (2008, 2009) however proved that whenever a top layer of bone ash is used, the separation of silver is just as easy as with an entirely bone ash cupel. These former studies on cupellation materials also showed that the composition of cupellation hearth has a negligible influence on the composition of the litharge cakes produced and on subsequent silver losses (Bayley and Eckstein, 2006).

2.3. Fire-assay of the Pb based alloys

Fire assaying was performed in a replica of fire-assay furnaces depicted by Agricola, 1556. The internal diameter of the furnace is 26 cm and the muffle in which the cupels were placed is 24 cm long, 13 cm wide and 9 cm in height. During the two campaigns, the assays were carried out one after another, in similar conditions, starting with the lowest Bi concentrations to prevent any pollution. The muffle temperature was monitored with a thermocouple. Prior to the start of experimental campaigns, the furnace was preheated for 150 min, until an adequate temperature was reached (~900 °C). Each fire-assay was then performed as follows: a fresh cupel containing the lead bullion was positioned in the centre of the muffle and the furnace door was closed until temperature stabilised and the alloy was melted. Then, the furnace door was slightly opened to let air in. Regular charcoal supply helped controlling the temperature inside the furnace: the thermocouple placed right above the cupel indicated a variation from 850 to 980 °C during the entire session. Finally, after the “blick”, the cupel was withdrawn and the next one placed inside the furnace. Each run lasted between 30 and 40 min and produced a silver button. Apart from the first fire-assay, escaping of the entrapped gases during cooling created cauliflowering aspect on the surface of the button.

2.4. Chemical characterisation of litharge impregnated cupels and silver buttons

Litharge impregnated cupels were analysed by SEM-EDS (scanning electron microscopy–energy dispersive spectroscopy) and microprobe. Elemental analyses were carried out for one cupel of each assay of XP 1, and concentration profiles through the cupels as well as elemental mappings were obtained. The silver buttons were analysed by LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) according to a protocol published elsewhere (Sarah et al., 2007). Reference materials whose compositions are close to the silver buttons (*i.e.* silver alloys containing up to 15 wt.% Cu doped with up to 2 wt.% Zn, Sn, Au, Pb and Bi) were used for normalisation. The composition of each silver sample was determined by calculating mean values on the homogeneous fraction of the signal.

An inter comparison between LA-ICP-MS and HR-ICP-MS analytical techniques was carried out on some lead and silver materials: the calculated analytical difference was less than 10% for all trace elements considered (Ag, Bi, Sn, Sb), which is on the same range as the intrinsic error of each analytical method.

2.5. Thermodynamic modelling of cupellation

Parallel to the experiments, a computational thermodynamics study was undertaken in order to model the chemical equilibria

involved during the cupellation process. For this purpose, the Equilibrium Module of the FactSage™ software (Bale et al., 2002) was used, taking into account the multicomponent system (Pb, Ag, Bi, Sb, Sn, O₂, N₂) and three major phases: a liquid metal phase (*i.e.* the lead bullion converted into a silver button), a liquid oxide phase (*i.e.* the PbO based litharge) and a gas phase (*i.e.* air).

The SGTE (Scientific Group Thermodata Europe, www.stge.org) Solution database was used to model the liquid metal phase, while air (a mixture of 20 mol.% O₂ and 80 mol.% N₂) was modelled with the SGTE Pure Substances database. No database was available for the liquid oxide phase, it was thus modelled as an ideal PbO liquid phase containing dilute amounts of AgO_{0.5}, SnO₂, SbO_{1.5} and BiO_{1.5}, using specific Henrian activity coefficients for each compound. Activity coefficients were assessed based on literature data from Ueda (2005, 2009). The selected activity coefficients are compiled in Table 2. With these parameters, the following major properties of the systems are well reproduced at 1000 °C: Ag solubility of about 5 wt.% both in PbO (Shao et al., 1993) and in Bi₂O₃ (Assal et al., 1999) in air, full miscibility of Bi₂O₃ and PbO (Diop et al., 2009), distribution ratio of Ag in Pb–PbO (Ueda et al., 2005), distributions ratio of Sn, Sb and Bi between Ag–Pb alloy and PbO (Ueda et al., 2009).

Given that, after preliminary calculations, Sn and Sb elements were found as the main elements to oxidise at the very beginning of cupellation, an additional ideal SnO₂–Sb₂O₃ solid solution described by Zaharescu (Zaharescu et al., 1991) was taken into account, while the liquid phase was considered as an ideal Sb₂O₃–PbO mixture (Kopyto et al., 2009).

In order to model the cupellation process, calculations were performed as follows:

- (i) the initial system was the lead bullion (100 g) at 1000 °C,
- (ii) a given amount of air (typically 1.25 mol, *i.e.* about 3.7 dm³) was added in the system and the equilibrium was computed,
- (iii) litharge, formed by reaction of the alloy with air, was removed from the system, in order to represent its flow into the cupel,
- (iv) steps (ii) and (iii) were repeated with the remaining metal phase until the oxidation reaction was completed.

Litharge and metal compositions were stored after each calculation step, in order to follow the evolution of composition of both phases during cupellation. Preliminary calculations using as benchmark the modelling of a modern industrial cupellation process, published by Swinbourne et al. (2003), gave satisfactory results regarding Ag recovery yield and final Pb content in the silver product.

In order to compare the calculations involving initial lead bullions of various Ag–Bi–Sb–Sn contents, a so-called “cupellation progress”, calculated as the amount (in mol) of O₂ added at a given step divided by the total O₂ addition, was chosen to represent the

Table 2
Input data for the model of the PbO based slag phase in the Equilibrium Module of FactSage™.

Compound (SGTE pure substance database)	Reference state	Form in PbO slag	New mixing particle	log (γ) at 1000 °C	References
PbO	liq	–	–	–	–
Ag ₂ O	s	AgO _{0.5}	2	–0.65	Ueda et al., 2005
Bi ₂ O ₃	liq	BiO _{1.5}	2	–0.70	Ueda et al., 2009
Sb ₂ O ₃	liq	SbO _{1.5}	2	0.46	Ueda et al., 2009
SnO ₂	liq	SnO ₂	1	1.50	Ueda et al., 2009

reaction advancement. With this convention, a cupellation progress of 0 represents the initial system (*i.e.* the lead bullion before the start of the reaction), while a cupellation progress of 1 represents the final system (*i.e.* silver button at the end of cupellation).

3. Results

In total, 28 fire-assays were carried out. A silver button was obtained for each of them. A summary of the experimental data is given in Table 3.

3.1. Macroscopic observation of the cupels after fire-assays

As evidenced on pictures presented in Fig. 2, an obvious difference between the batches is the presence of a brown ring at the initial periphery of the lead bullion for all fire-assays of XP1. As deduced from its location, the ring formed at the beginning of cupellation. No ring is observed for fire-assays of XP2, thus its formation is clearly not linked to the Bi content and can rather be attributed to the high Sb and Sn contents in lead bullions of XP1.

The major colour difference between the batches is located right around the silver button where a quite distinctive brownish oxide surrounded by a dark green circle appears in XP1-3 and all batches from XP2. XP1-2 also shows a slight colour change to a yellow brownish tint around the silver button, yet not as marked as on the other cupels. This feature clearly indicates a change in the oxide composition that penetrated the cupels at the end of the process, and concerns Bi rich batches.

3.2. Microscopic observation and chemical mapping with SEM-EDS

One cupel per batch of XP1 was crosscut in order to characterize and observe the distribution of metal oxides through the cupels. The three cartographic views presented in Fig. 3 show that Pb impregnated the entire cupels from the bottom to the top (*i.e.* from the first to the last litharge respectively). The distribution of the impurities (Bi, Sb, Sn), rather similar for each batch, is highly dependent on the nature of the element:

- Sb and Sn are mainly located in the brown rings and at the bottom of the cupels
- Bi is located at the top of the cupels, *i.e.* in the last litharge

3.3. Concentration profile of cupels using microprobe

Three chemical profiles, presented in Fig. 4, were obtained from the bottom to the top of the cupels from XP1, vertically to the location of the Silver button (see Fig. 3).

Ag and Bi exhibit a similar behaviour: their concentration is very low in most of the litharge, and at approx. $-2000 \mu\text{m}$ depth, a noticeable increase is observed. Ag concentration profiles are similar for each cupellation, which is consistent with a constant Ag initial concentration in the initial lead bullion. Bi content increases in the last litharge (0 to $-500 \mu\text{m}$ depth) according to its initial concentration in the lead bullion. In XP1.3, Bi content exceeds Pb content in the last litharge. Apart from this specific case, Pb content is rather constant and constitutes the major element of litharge.

Consistently with the chemical mapping presented in Fig. 3, microprobe analysis indicated very low Sb and Sn contents in the last litharge (values are scattered around the detection limits of respectively 0.010 and 0.015 wt.%) and a much higher content in the first litharge (notably above the quantification limits of respectively 0.10 and 0.15 wt.%). This confirms that most of Sb and Sn were confined in the brown ring.

Table 3

Summary of the fire-assays. Bi and Ag content were analysed by ICP-SMS (HR-ICP-MS).

Fire-assay identification	Mass of lead bullion (g)	Bi content (ppm)	Ag content (ppm)	Time (min)	Mass of silver button (g)	Ag yield (%) ^a
Experimentation 1 (XP 1)						
<i>Batch 1</i>						
XP1.1-1	20.72	130	7300	38	0.2564	169.5% ^b
XP1.1-2	21.2	130	7300	36	0.1481	95.7%
XP1.1-3	22.94	130	7300	31	0.1598	95.4%
XP1.1-4	16.74	130	7300	38	0.1186	97.1%
<i>Batch 2</i>						
XP1.2-1	20.15	3000	10 000	35	0.1928	95.7%
XP1.2-2	21.2	3000	10 000	40	0.2052	96.8%
XP1.2-3	22.13	3000	10 000	37	0.2093	94.6%
XP1.2-4	17.63	3000	10 000	30	0.1718	97.4%
<i>Batch 3</i>						
XP1.3-1	20.54	21 000	10 000	40	0.1912	93.1%
XP1.3-2	20.73	21 000	10 000	38	0.1927	93.0%
XP1.3-3	21	21 000	10 000	36	0.2003	95.4%
XP1.3-4	18.26	21 000	10 000	40	0.1520	83.2%
Experimentation 2 (XP 2)						
<i>Batch 1</i>						
XP2.1-1	18.75	9900	10 100	64	0.1775	93.9%
XP2.1-2	21.14	9900	10 100	36	0.1986	93.2%
XP2.1-3	22.35	9900	10 100	35	0.2135	94.8%
XP2.1-4	20.2	9900	10 100	30	0.1926	94.6%
<i>Batch 2</i>						
XP2.2-1	20.23	19 400	10 200	33	0.1917	93.0%
XP2.2-2	18.1	19 400	10 200	28	0.1695	91.9%
XP2.2-3	21.71	19 400	10 200	30	0.2042	92.3%
XP2.2-4	22.3	19 400	10 200	33	0.2154	94.8%
<i>Batch 3</i>						
XP2.3-1	22.34	38 600	10 000	34	0.2063	92.8%
XP2.3-2	19.38	38 600	10 000	32	0.1772	91.9%
XP2.3-3	19.7	38 600	10 000	32	0.1816	92.6%
XP2.3-4	23	38 600	10 000	37	0.2097	91.6%
<i>Batch 4</i>						
XP2.4-1	19.46	78 100	10 200	35	0.1789	90.6%
XP2.4-2	21.38	78 100	10 200	32	0.1972	90.9%
XP2.4-3	22.16	78 100	10 200	34	0.2052	91.2%
XP2.4-4	23.38	78 100	10 200	38	0.2099	88.5%

^a Yield = $Y = ((m(\text{Ag})_{\text{button}}/m(\text{Ag})_{\text{initial}})) \times 100$.

^b Such yield indicates that cupellation was not completed, which is consistent with the absence of gas expulsion observed for this sample (no cauliflowering). This run was disregarded in the results treatment.

3.4. Silver extraction yields

For each fire-essay, the silver extraction yield (Y) was calculated as the ratio of the silver button mass to the initial mass of silver

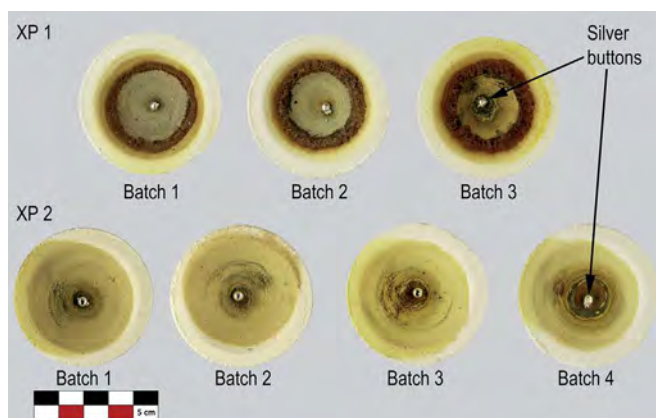


Fig. 2. Macroscopic view of the cupels seen from above after the seven fire-assays (one cupel per batch).

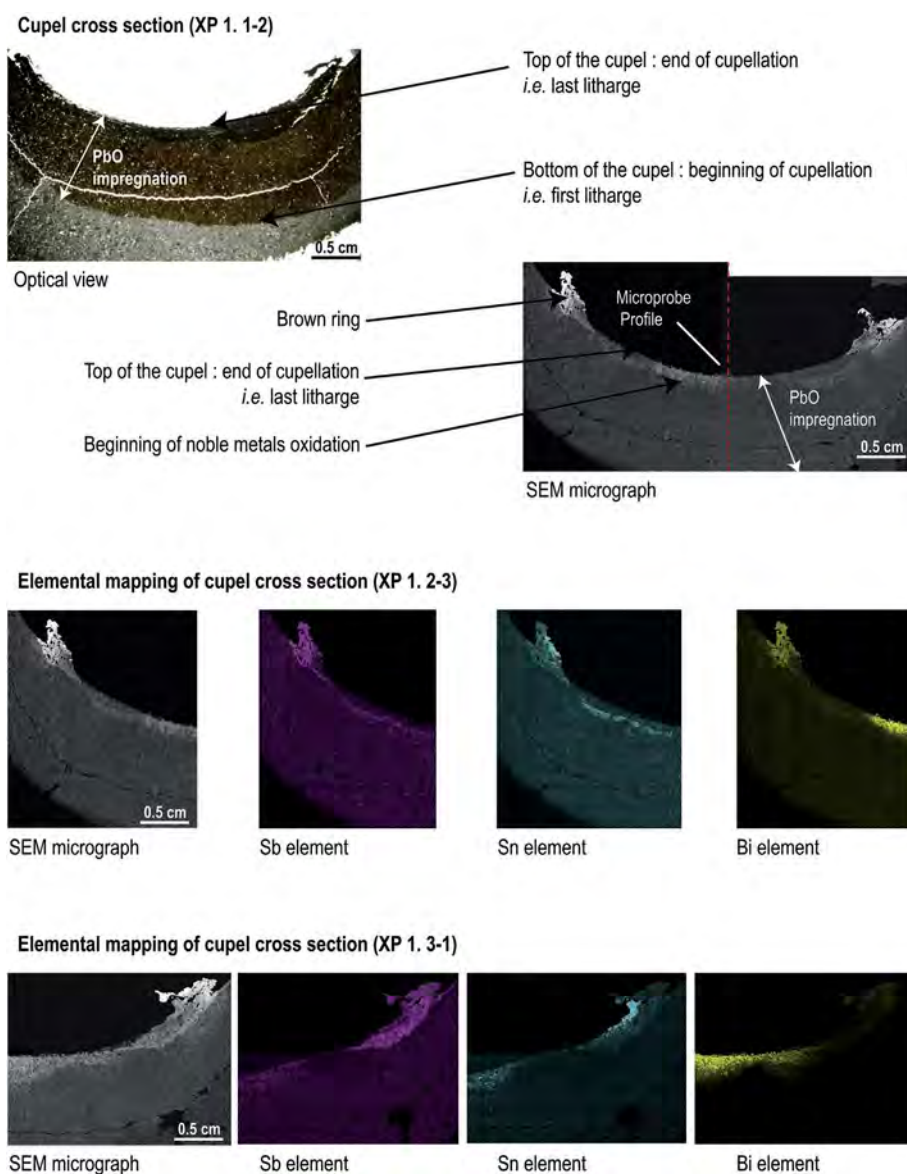


Fig. 3. Optical view and elemental mapping (acquired by SEM-EDS) of cupels from experiments XP1-1-2, XP1-2-3 and XP1-3-1.

present in the lead bullion (Table 3), assuming that silver buttons are composed of pure silver (see below “Chemical composition of the silver button”).

Silver extraction yields are reported in Fig. 5 versus the initial Bi content of lead bullions. A linear decrease of the yield – from average 96.1% for XP1.1 (130 ppm Bi) to average 90.3% for XP2.4 (7.8 wt.% Bi) – is evidenced.

3.5. Chemical composition of the silver button

Analyses of the silver buttons by LA-ICP-MS (Table 4) reveal that they are mostly composed of pure silver (>99.9%). Pb and Bi are the main impurities and other trace elements such as Sb and Sn are almost totally absent with concentrations below 1 ppm. Pb concentration is scattered between 2 and 25 ppm, with an average value of 15 ppm independent of the initial Bi content. Bi presents wider variations: it is logically absent for Bi poor batches XP1-1 (0.5 ppm in average) and rises up to 10–30 ppm for XP1.2, XP1.3, XP2.1 and XP2.2 and 100–200 ppm for XP2.3 and XP2.4. However,

no clear correlation was found between the Bi content of the final silver button and that of the initial lead bullion.

Yet, as illustrated in Fig. 6, despite a significant standard deviation in the Pb and Bi concentrations, a linear correlation between the Bi/Pb ratio in the silver button and the Bi content in the initial lead bullion was evidenced for both experimental campaigns.

3.6. Thermochemical calculations

The volatility of Bi element was evaluated as a preliminary calculation, in order to verify that Bi could be considered as a tracer. At 1000 °C, the vapour pressure of pure Bi is about $2 \cdot 10^{-3}$ bar, while the vapour pressure of pure Bi_2O_3 is $3 \cdot 10^{-6}$ bar. These low values indicate that negligible evaporation of the Bi element occurs. It is thus considered that, during the cupellation process, there is no loss of Bi in the atmosphere: either it stays in the button, or it oxidises in litharge.

Calculations related to cupellation reaction were performed for the seven lead bullion compositions processed in XP1 and XP2 (Table 1). Since very similar trends were obtained regarding the

individual behaviour of Sb, Sn, Pb, Bi and Ag, the results presented here are mostly focused on the case of XP1.2 (3000 ppm Bi, high Sn and Sb content) and XP2.2 (19 400 ppm Bi, low Sb and Sn content).

The evolution of the composition of the metal phase vs. cupellation progress is given in Fig. 7. Two plots (Fig. 7, top) represent the mass of each element left in the metal phase related to its initial mass, during the whole cupellation reaction. As the oxidation of bismuth and silver mostly occurs at the end of the reaction, a focus depicts the evolution of the mass of Pb, Ag and Bi in the metal phase for cupellation progress over 0.8 (Fig. 7, bottom).

The litharge phase composition is plotted in Fig. 8: the mass fraction of each element is indicated, and, again, a focus for cupellation progress over 0.8 is included.

It can be noted that, for high Bi initial content (which is typically the case of XP2.2), litharge contains more Bi than Pb at the very end of the reaction (cupellation progress > 0.95). This composition is thus outside the range of the model hypothesis, which considers a main PbO phase with diluted components.

The final Pb content in the silver button was calculated between 20 and 100 ppm, depending on the value of the calculation step (i.e.

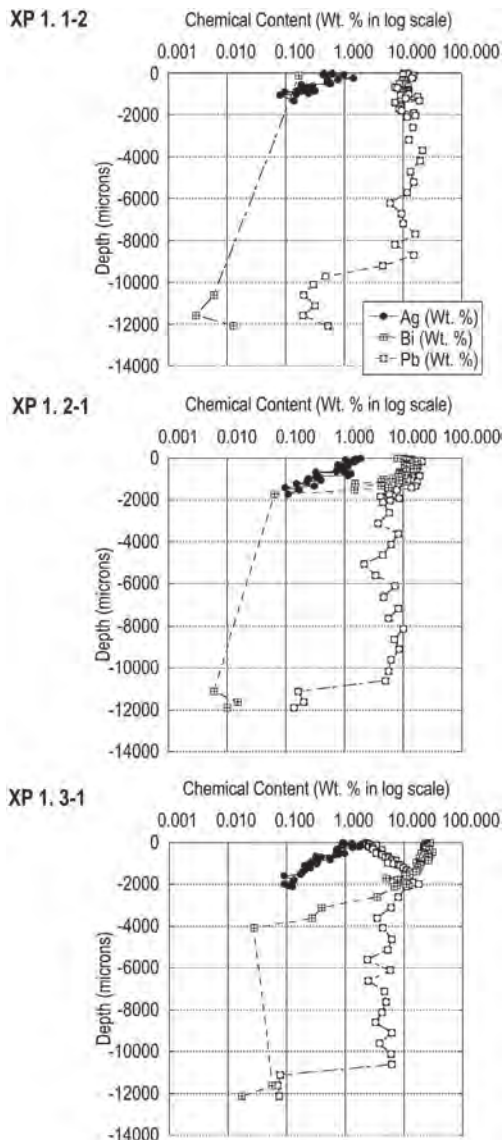


Fig. 4. Microprobe vertical profiles of three cupels from XP1 (1-2, 2-1 and 3-1) for Pb, Ag and Bi elements.

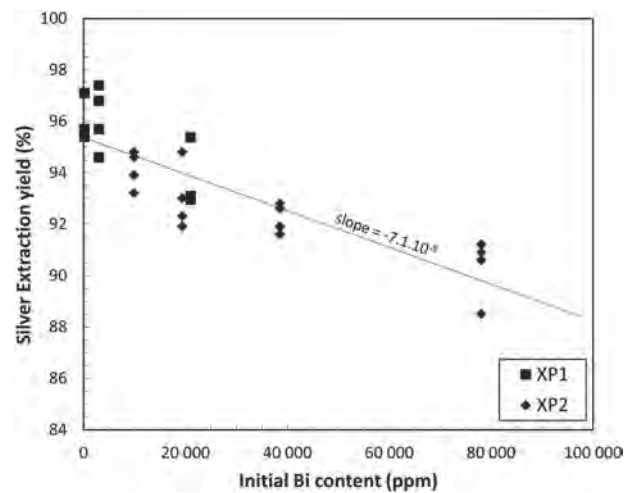


Fig. 5. Evolution of experimental silver extraction yield vs. Bi content in the initial lead bullion for all batches (except XP1-1-1 and XP1-3-4).

Table 4

Average composition of experimental silver buttons analysed by LA-ICP-MS.

Reference	Number of analyses	Ag (%)	Sn (ppm)	Sb (ppm)	Pb (ppm)	Bi (ppm)
XP1-1	5	99.99	<1	nd ^a	19 ± 10	0.5 ± 0.4
XP1-2	7	99.99	<1	nd	22 ± 10	11 ± 10
XP1-3	7	99.99	<1	nd	2 ± 2	9 ± 4
XP2-1	8	99.99	<1	<1	28 ± 7	27 ± 7
XP2-2	7	99.99	<1	nd	6 ± 4	24 ± 20
XP2-3	8	99.97	<1	<1	25 ± 27	209 ± 98
XP2-4	6	99.99	<1	nd	9 ± 10	70 ± 52

^a Not detected (nd) values are likely under 0.1 ppm.

the amount of air added in the system at each step). Similarly, the final Bi content in the silver button was highly dependent on the step value, while the Bi/Pb ratio was found much less sensitive to this calculation artefact. Fig. 9 shows the evolution of the Bi/Pb ratio in the metal phase for XP1-1, XP1-2, XP1-3 and XP2-2 during cupellation, together with the experimental ratio measured in the silver button.

Finally, the calculation of the Ag and Bi contents in an “average” litharge (i.e. calculated for a cupellation progress of 0.4), depending on the initial Ag and Bi content in the lead bullion, is presented in Fig. 10.

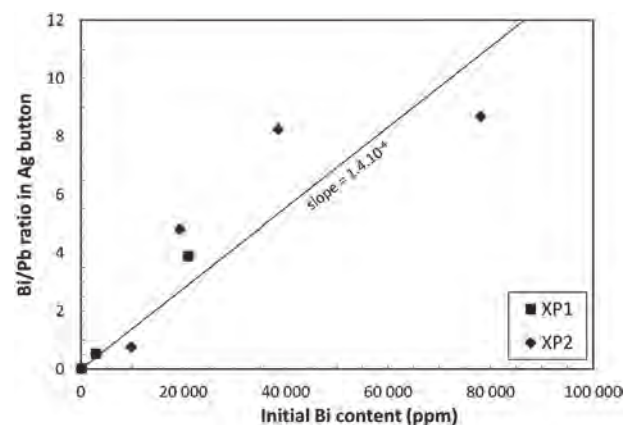


Fig. 6. Evolution of experimental Bi/Pb mass ratio in silver button vs. Bi content in the initial lead bullion.

4. Discussion

4.1. Chemical elements behaviour during cupellation

The combination of experimental results and modelling provides a clear picture of the behaviour of each element during the cupellation process. The major element of the system, Pb, oxidises during the whole process to form litharge, and the reaction stops when only traces of Pb are left in the silver button. Experimental data indicate a residual Pb concentration of 2–20 ppm in the silver button, while calculations lead to a higher concentration, in 20–100 ppm range, in good accordance with the model of Swinbourne (Swinbourne et al., 2003).

Sn, Sb and Bi also fully oxidise to litharge during the reaction. However, Sn and Sb oxidise at the beginning of cupellation (as a dross and in the first portions of litharge), while Bi oxidises mainly at the end of cupellation (in the last portions of litharge). A small proportion of silver finally oxidises at the very end of cupellation.

A discussion on the specific behaviour of each element is presented in this section. Former studies on archaeological cupels showed that cupellation hearth material does not affect the composition of the produced litharge nor the silver yield (see § 2.2). Thus, changes in its composition seem quite unlikely to distort radically neither the elemental behaviour of Bi nor the silver yield. Moreover, as silver losses and bismuth oxidation mainly occur at the end of the reaction they should not be greatly impacted by

reactions involving the lining taking place at the beginning of the cupellation. The following results are therefore valid for any kind of archaeological cupellation hearth material.

4.1.1. Behaviour of Sn and Sb

Calculations indicate that Sb and Sn elements oxidise at the beginning of the cupellation (Figs. 7 and 8). At the very beginning of cupellation, the formation of a solid $\text{SnO}_2\text{--Sb}_2\text{O}_3$ phase was computed in the case of XP1.2 and XP1.3, corresponding to Sn and Sb-rich lead bullions. For all XP1 compositions, it was also shown that, up to cupellation progress of about 0.2, litharge major component was Sb (Fig. 8). These calculations are experimentally supported by the presence of rings on the outer rim of cupels from XP1 (Fig. 2), where Sb and Sn were located by SEM-EDS exploration (Fig. 3). These rings are most probably composed of a mixture of $\text{SnO}_2\text{--Sb}_2\text{O}_3$, lead antimonate ($\text{Pb}_2\text{Sb}_2\text{O}_7$) and lead tin oxide (Pb_2SnO_4), which are stable compounds in the Sb–Sn–Pb–O system likely to separate as dross on the surface of the metallic bath (Schnabel, 1898). This matches with studies published by Pernicka et al. (1998), indicating that lead antimonates were observed in samples of archaeological litharges formed in the first stages of cupellation, with Sb contents up to 5 wt.% locally, near the surface of the litharge cake. The authors suspect this feature to be the remainder of such dross that has not completely molten and was not properly skimmed off from the cupellation bath. Mass et al. (2002) also report that these Sb-rich litharges and dross might

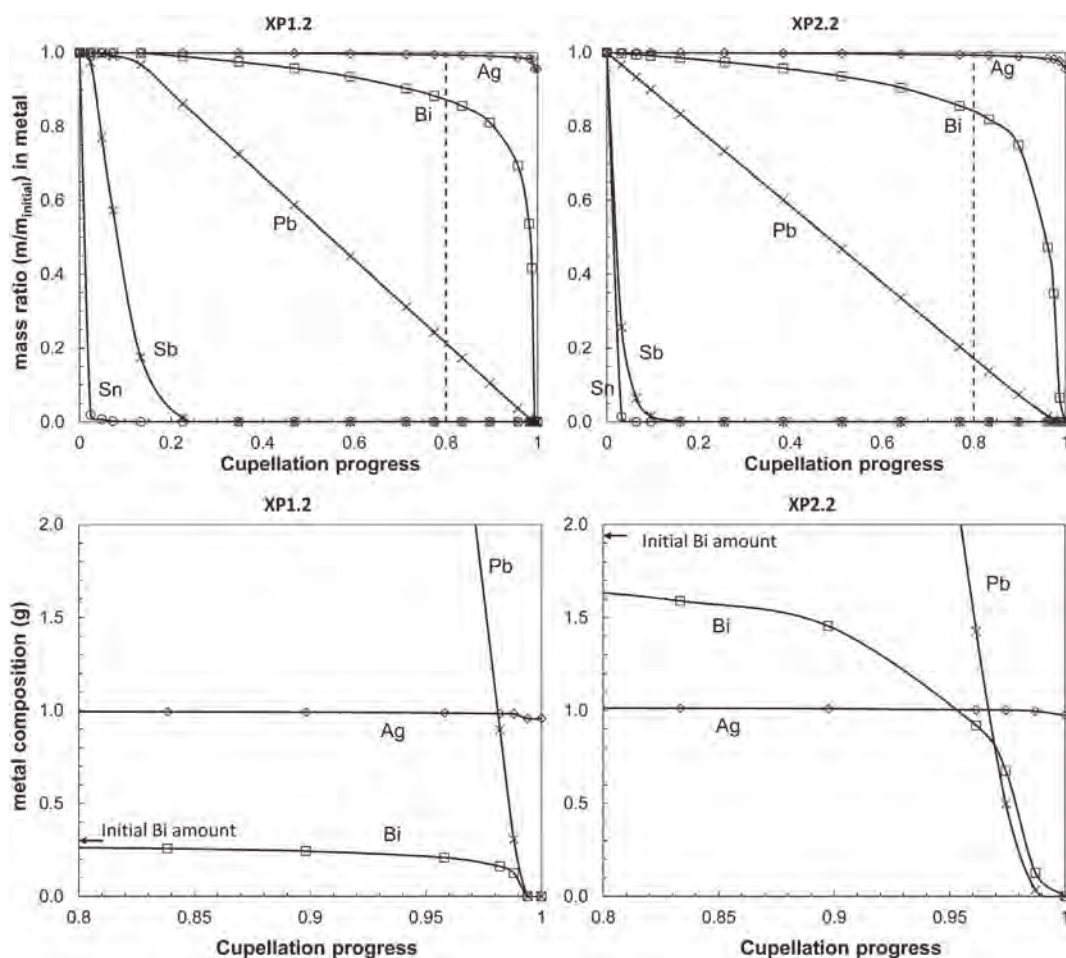


Fig. 7. Computed metal phase composition vs. cupellation progress for two initial compositions of the lead bullion (XP1-2 and XP2-2). Top: evolution of the mass ratio m/m_{initial} of each element during the whole reaction. Bottom: evolution of the metal composition (g for 100 g of lead bullion) for $0.8 < \text{cupellation progress} < 1$.

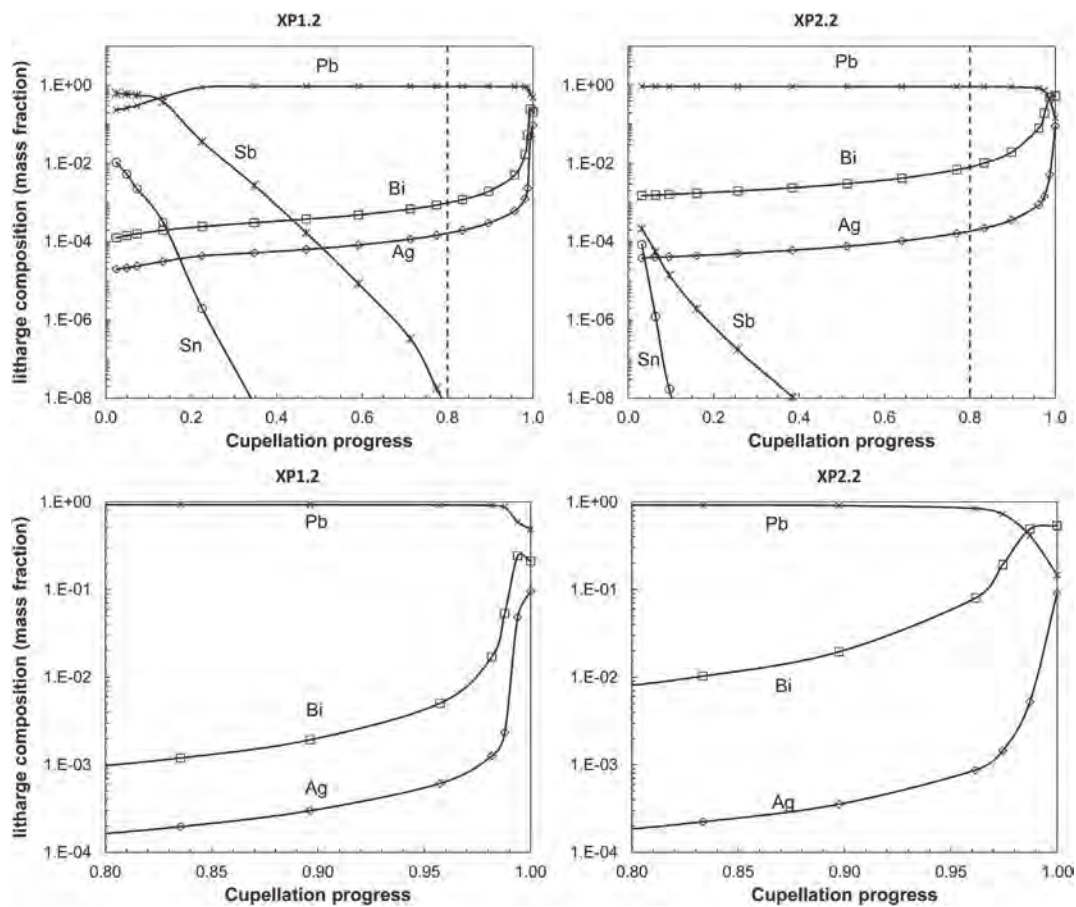


Fig. 8. Computed litharge phase composition (in mass fraction of elements) vs. cupellation progress for two initial compositions of the lead bullion (XP1-2 and XP2-2). Top: evolution of the litharge composition during the whole reaction. Bottom: evolution of the litharge composition for $0.8 < \text{cupellation progress} < 1$.

have been used in ancient yellow and green Roman glasses. Our experiments confirm that producing such lead antimoniate and separating it from the cupellation bath was natural when processing Sb-rich lead ores, due to dross formation in the early cupellation stages. Such valorisation and trade of this by-product should be looked for in future archaeological studies on regions with Sb-rich lead ores deposits.

Regarding litharge composition, it seems clear that, even if present in large proportions in the processed alloy, tin and

antimony will form solid dross rather than stay in solution in the litharge. Nevertheless, SEM-mapping and microprobe analyses of the experimental cupels testify that despite this behaviour a small proportion of both elements is still present in the first portions of litharge and thus in lead recovered from litharge resmelting.

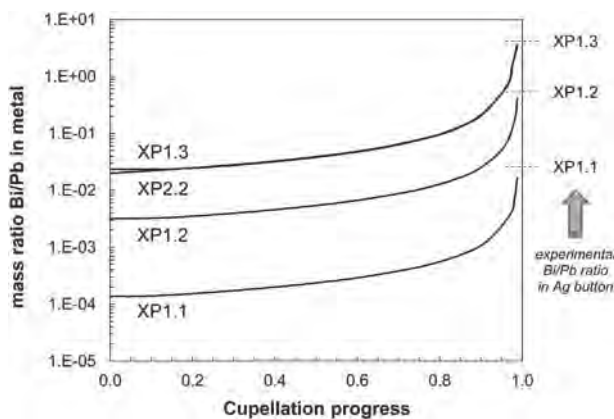


Fig. 9. Calculation of Bi/Pb ratio evolution in the metal phase vs. cupellation progress for four initial lead bullion compositions (XP1-1, XP1-2, XP1-3 and XP2-2). Comparison to experimental Bi/Pb ratio in silver buttons of XP1.

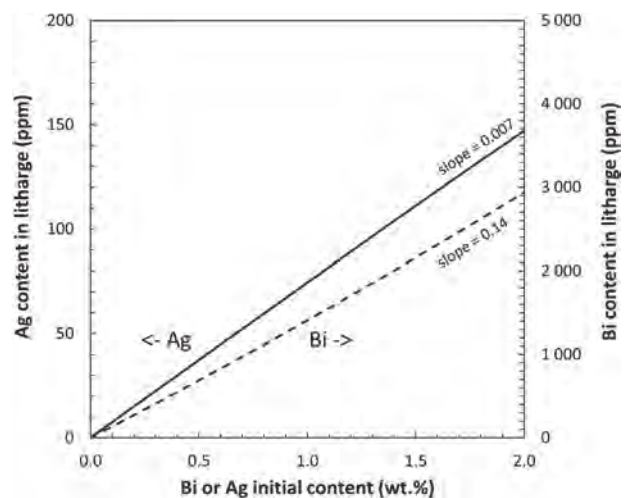


Fig. 10. Calculation of Ag (left y-axis) and Bi (right y-axis) content in an average litharge (cupellation progress = 0.4) depending on the initial Ag or Bi content in the lead bullion.

Estimating this proportion was however not possible with the present data.

Concerning the methodology of the present work and the fact that Sb and Sn oxidise at the beginning of cupellation, the great difference regarding Sb and Sn contents in the initial alloys between XP1 and XP 2 is believed to have no impact on Ag and Bi behaviours at the end of the cupellation.

4.1.2. Behaviour of Ag

Silver losses (about 2–5 wt.%) as measured in low Bi-content fire-assays are due to silver oxidation at the end of cupellation. Indeed, the concentration profiles in the cupels indicate a strong increase of Ag content in the last portions of litharge (Fig. 4). Accordingly, the present model shows that for lead bullions containing 1 wt.% Ag, litharge should bear about 50–100 ppm Ag during most of the reaction, while a content reaching up to a few wt.% is expected in the last portions of litharge (Fig. 8), leading to a silver reaction yield of about 96%. This result fits with experiments conducted at Pongibaud and quoted by Percy (1870) stating that Ag content in litharge is quite constant throughout the first stages of the process and reaches 4–8 g of silver in 100 kg of litharge (*i.e.* 40–80 ppm) for lead initially bearing as much as 6000 ppm Ag. The more recent work of Swinbourne *et al.* (2003), which focuses on modern industrial cupellation process confirms that silver losses in litharge occur at the end of the reaction. Moreover, the present thermochemical model demonstrates that the mean Ag content in “average” litharge (*i.e.* for cupellation progress = 0.4) is proportional to the Ag content in the initial lead bullion (Fig. 10), according to the relation: $\text{Ag}_{(\text{ppm in litharge})} = 0.007 \text{Ag}_{(\text{wt.\% in lead bullion})}$. This matches with previous experimental work (Berthier, 1834; Shephard and Dietrich, 1940) stating that in reproducible conditions silver loss is proportional to the initial Ag content. Available archaeological litharge analyses which could be compared with our data are however scarce in literature; first because few smelting sites were excavated and second because litharge cakes were likely to be reduced into metallic lead whereas the last portions of silver-rich litharge were reprocessed in order to recover the remaining silver. Litharge dated from the Bronze Age studied by Gale and Stos-Gale (1981) shows a Ag content usually below 50 ppm but reaching 200 ppm for a few samples. Syrian litharge dated from 3300 BC displays Ag content below 25 ppm for most samples but one reaching 3000 ppm (Pernicka *et al.*, 1998). These archaeological values vary widely; nevertheless, based on the present work, they seem to indicate that the present archaeological artefacts are coming from different steps of the cupellation process: silver-rich last portions of litharge (above 500 ppm) which could be retreated and silver-poor first portions of litharge (below 100 ppm) which could also be retreated or reduced to metallic lead.

4.1.3. Behaviour of Bi and influence of Bi content

Bismuth compounds are not volatile in the 900–1000 °C temperature range, as shown by thermochemical calculations. According to our experiments, Bi slightly oxidises at the beginning of the process and mostly at the end in the last portions of litharge alongside with Ag. This result matches with late 19th century treatises such as Percy (1870) and Schnabel (1898) endorsed by more recent works (Shephard and Dietrich, 1940; Pernicka and Bachmann, 1983). Furthermore, our experimental data allow evaluating the influence of the initial Bi concentration on the cupellation process, especially regarding the evolution of the silver extraction yields.

The decrease of the silver reaction yield with the increase of the initial Bi content is clearly evidenced by experimental results (Fig. 5). The thermochemical model does however not account for this fact, since constant silver yield of about 96% was computed for

all lead bullion compositions regardless of their Bi content. This is likely to be due to the description of the litharge phase used in the model: litharge is considered as a PbO phase including dilute amounts of Ag, Bi, Sb and Sn oxides. However, as shown by the concentration profile of XP1.3-1 (Fig. 4), the colour changes of cupels (Fig. 2) and the calculations (Fig. 8), the last portions of litharge in the case of high initial Bi contents are richer in Bi than in Pb. Thus, the model is not adapted for calculations at cupellation progress above 0.95–0.99, depending on the initial Bi content. The most likely explanation is that the model does not take into account a possible ternary interaction in the PbO–Bi₂O₃–Ag₂O system. Indeed, even if Bi₂O₃ and PbO dissolve Ag₂O roughly in the same proportion (about 5 wt.%), a PbO–Bi₂O₃ mixture might enhance Ag₂O solubility, and thus lead to an increase of Ag₂O loss with increasing Bi content. However, no thermochemical data was found to assess this assumption. Regarding material where bismuth is largely in excess, Berthier (1834) also registered enhanced silver loss and suggested that it mainly occurs by impregnation, as, according to him, bismuth oxide is more fluid than lead oxide and carries away more silver within the pores of the cupel. However, modern data rule out Berthier's hypothesis, since, at 1000 °C, the viscosity of PbO is 0.003 Pa s (Oliver, 1965) while the viscosity of Bi₂O₃ is 0.01 Pa s (Meshalkin and Kaplun, 2005).

Regarding the produced silver, experimental data show (Fig. 6) that the final Bi/Pb ratio in the silver button is increasing with the initial Bi content, while no clear tendency could be drawn from the final Bi content vs. the initial Bi content. As evidenced in Fig. 9, combining calculation and experimental results, the Bi/Pb ratio in the metal phase is clearly dependent on the initial Bi content during the whole process.

Regarding litharge, the thermodynamic model shows that Bi content in the first portions of litharge (“average” litharge) is directly proportional (by a factor of about 0.14) to the initial Bi content in the lead bullion (Fig. 10). For example, in XP1.2 (3000 ppm Bi in lead bullion), litharge should contain an average of 300–400 ppm Bi. The chemical analyses of the cupels (Fig. 4) do however not allow to discuss about the Bi content of the first portions of litharge (bottom of the cupel up to ~2000 μm depth) because of its low concentration, below the quantification limit (about 800 ppm). Furthermore, comparison with published Bi-rich litharge analysis is difficult owing to their scarcity.

4.2. Archaeological implications

These results provide new means for interpreting archaeological remains linked to lead and silver production. They also shed light on technological choices made by the ancient metallurgists when processing Bi-rich ores or lead bullions.

4.2.1. Silver materials

Both the model and the experimentations show that Bi does not stay in the silver bullion and mainly oxidises at the end of cupellation. The amount of Bi remaining in the silver button relies therefore on the final cupellation progress rather than on the initial Bi concentration of the lead bullion. This final cupellation progress depends on the type of process: whereas assaying tends to obtain pure silver, large-scale cupellation process does not. In order to avoid silver losses at the end of the process, large-scale cupellation was usually conducted in several steps (Agricola, 1556; Biringuccio, 1540; Ercker, 1580; Hawthorne and Smith, 1979). The operation was stopped several times (sometimes involving further addition of lead) and led to the production of unrefined silver containing varying amounts of lead and other impurities such as bismuth.

Table 5 gives more details on the metal phase composition and its evolution near the end of the process as well as of the (Bi/Ag)/

(Bi/Ag)₀ ratio according to our thermodynamic model. For an initial Bi concentration of 3000 ppm (XP 1.2), final Bi contents up to 8 wt.% can be expected in the silver depending on its refinement, whereas for 2 wt.% initial Bi (XP 2.2), unrefined silver containing up to 30 wt.% Bi and silver containing as much as 7 wt.% Bi can be produced. High Bi contents up to several percent found in archaeological unrefined silver (Craddock et al., 1985; Renzi et al., 2007) seem to be in very good agreement with our data.

Regarding the evolution of Bi contents throughout the reaction, experiments carried out by Pernicka and Bachmann (1983) state that the Bi/Ag ratio in the metal phase decreases by a ratio of about five to ten during cupellation. Our model shows that this order of magnitude is highly dependent on the reaction advancement as well as on the initial Bi content. During cupellation, the (Bi/Ag)/(Bi/Ag)₀ ratio changes from a relation of approximately four (1/0.3 for XP 1.1) to twenty (1/0.05 for XP 2.2) (Table 5), and is even likely to be much higher when quite “pure” silver (>95%) is to be obtained, largely amplifying the results proposed by Pernicka and Bachmann (1983). Large portions of Bi seem therefore in any case irremediably lost to litharge in the end of the process (see § 4.2.3).

Nonetheless, as the Bi/Pb ratio in the metal phase is clearly dependent on the initial Bi content throughout the whole reaction (Fig. 9), a more precise estimation of the initial Bi content of the lead bullion can be proposed using Fig. 6. The use of this ratio is likely to allow distinguishing between different silver–lead stocks regardless of the reaction advancement much rather than pure Bi concentrations. It should however not be forgotten that in many archaeological objects, further lead or copper addition, mixing of different metal sources in mints as well as frequent remelting and reminting of ancient coins might very much erase this signature. However, in a production context, computing this ratio provides estimations of the initial Bi concentration of the lead bullion processed by cupellation and therefore on the materials which were treated by ancient metallurgists and their recipes.

4.2.2. Lead materials

Further reflection on lead artefacts is linked to the hypothesis that lead coming from litharge resmelting would reflect the composition of an average litharge. This last comparison between resmelted lead and litharge compositions is however subject to caution, as metallic lead was not produced in our experiments. It is therefore impossible so far to assert whether litharge resmelting radically modifies the Bi content in lead materials or not. This specific point would require further experiments and investigations.

Nevertheless, assuming this hypothesis, Bi content in archaeological lead materials would mainly be a tracer of metallurgical processes as it should represent roughly 10–15% of its content in the initial lead bullion before cupellation (Fig. 10). This ratio is endorsed by experiments conducted by L’Héritier and Tereygeol (2010) who claim that lead coming from litharge resmelting is

10–30 times poorer in Bi than the initial lead bullion prior to the cupellation, i.e. 3–10% of the initial lead Bi content.

This result has a direct consequence on the identification means of desilvered lead, which were so far mainly based on Ag content only (Tylecote, 1986; Rehren and Prange, 1998; Asderaki and Rehren, 2006). According to our study, among all chalcophile elements, alongside silver, bismuth seems best to provide a new mean to estimate whether lead was desilvered or not. This potential discrimination remains of course highly dependent on the composition of the processed ores and the archaeological context.

For example, all lead ingots from the roman period analysed by Baron and Cochet (2003) would be coming from desilvered litharge resmelting. Most of them indeed exhibit very low Bi concentrations (<15 ppm) associated with low Ag content (<70 ppm) typical for this kind of lead. Even three ingots bearing respectively 100, 140 and 220 ppm of silver could be compatible with this hypothesis as no relevant difference in their Bi content could be highlighted.

Such reflexion led on much larger sets of lead artefacts might, in the near future, highlight the importance at a given time and place of simple fusion and desilvered lead.

4.2.3. Processing Bi-rich ores: a metallurgical challenge?

Results on silver loss during the cupellation of Bi rich silver lead bullions question as well the technical aspects of processing very rich Bi ores for silver production. One can suspect that metallurgists avoided such silver losses of 5–10% due to the presence of Bi during cupellation. For example, silver loss can be spared when processing Cu–Ag ores by the addition of an excess of lead, which prevents silver dilution in Cu₂O (Bayley and Eckstein, 2006). However, as Bi₂O₃ and PbO dissolve Ag₂O roughly in the same proportion, the present hypothesis favours a PbO–Bi₂O₃ interaction enhancing silver dilution. Lead addition might therefore not reduce silver losses as for the case of Cu–Ag ores. Such silver loss in litharge, alongside a fraction of bismuth, would seem here ineluctable when quite pure silver is to be obtained. These last silver and Bi rich portions of litharge were certainly retreated to improve the silver yield. Another challenge is to identify these technological decisions in archaeological remains. Very rich lead and bismuth material also containing silver from the Tartessian site of Peñalosa in Spain (Hunt Ortiz, 2003) could indeed match with the retreatment of such Bi-rich last portions of litharge and testify of the metallurgical choices improving the efficiency of the process. These archaeological examples are however scarce so far and future archaeological work should stress on this point to understand the technological decisions taken by the ancient metallurgists for processing this kind of ore and improve its efficiency. Comparison between the composition of both Bi-rich ore mining sources and lead and silver archaeological artefacts produced in the same regions should be investigated to highlight the frequency but also the technical aspects of processing such Bi-rich ores. Further archaeological investigations and fine analysis of silver and lead artefacts such as undergoing in the French site of Castel-Minier will be required to elucidate these interrogations.

5. Conclusions

This interdisciplinary approach focused on the behaviour of Bi, Sb and Sn during the cupellation process. Sb and Sn are carried away in the early stage of cupellation, and partially form solid compounds, but noticeable amounts of these elements are still likely to be present in the produced litharge cake. Bi is not volatile and distributes between the litharge and metal phase with an average ratio of one to ten during the first 80% of the reaction. It mostly oxidises at the end of the reaction and is finally present in very small proportions in the resulting silver button in assaying

Table 5
Evolution of Bi and Ag contents and of the (Bi/Ag)/(Bi/Ag)₀ ratio in the metal phase near the end of the cupellation process according to the thermodynamic model.

Cupellation progress	XP 1.2			XP 2.2		
	Ag (%)	Bi (%)	(Bi/Ag)/(Bi/Ag) ₀	Ag (%)	Bi (%)	(Bi/Ag)/(Bi/Ag) ₀
0.95	16	4	0.72	24	24	0.55
0.96	22	5	0.7	29	27	0.5
0.97	31	6	0.65	38	31	0.4
0.975	36	6	0.6	47	31	0.35
0.98	44	7	0.55	60	26	0.25
0.985	57	8	0.5	77	16	0.1
0.99	80	7	0.3	92	7	0.05

conditions. Moreover, the presence of Bi in the processed alloy has a detrimental effect on the silver yield.

Bi can be considered as an ore source tracer for silver material using the Bi/Pb ratio. Thermodynamic calculations assessed by experimental data offer predictive tools to estimate the initial quantities of Bi present in the lead bullions as well as the resulting Bi and Ag passing in litharge. These data will not be so useful for finished objects such as coins, in which the elemental signature is erased due to metal mixing and remelting, but could be used on metallurgical production sites, to study ore selection, recipes and technological choices as well as efficiency of the metallurgical processes.

Interpretations are more complex for metallic lead based artefacts which are likely to come from unrefined or desilvered lead, or mixed during recycling. However, should no important remobilisation of trace element between litharge and resmelted lead be assessed, Bi would also be a tracer of sources and metallurgical processes for archaeological leads. Low Bi contents could be explained by the use of Bi-poor lead ores as well as by their technological origin, *i.e.* desilvered lead coming from cupellation.

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