

From copper to silver: Understanding the *saigerprozess* through experimental liquation and drying

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ABSTRACT: The liquation and drying process is used to separate low amounts of silver from coppers, which spread in Europe at least from the 15th century onwards. Agricola was the first to describe extensively this new process in Book 11 of his De re metallica. A few metallurgical treatises from modern times evoke it as well, yet owing to the lack of archaeological data very little is known about this process and its products. Hence, several experiments reproducing the whole liquation and drying sequence were conducted on the experimental platform at Melle (France). Products and by-products were analysed by several methods (XRF, LA-ICP-MS, LIBS) so as to create a first reference corpus. This paper aims to present these experimental results and to compare them with analyses of copper-lead alloys coming from French archaeological sites, providing a new perspective on this process at the end of the Middle Ages.

Introduction

The liquation and drying process, also known as the *saigerprozess* or *Seigerhüttenprozess*, its German names, is an ancient metallurgical process used to extract silver from copper-silver alloys which developed in Europe since the Middle Ages. It relies on silver's strong affinity for lead, and on copper and lead liquid-liquid separation at high temperature. Practically, once reduced, the silver-containing black copper is mixed with great amounts of lead and cast into cakes. During cooling, the copper and lead phases separate while silver passes from copper to lead. These cakes are then heated up in a reducing atmosphere, above the fusion point of lead (327°C) but below that of copper (1083°C), so that the silver-rich lead would flow out leaving the copper behind. This first stage is called liquation. However, the separation is incomplete as the 'exhausted liquation cakes' still retain some silver-rich lead. Thus, they are re-treated in a so-called drying furnace under an oxidizing airflow which purifies them from the remaining lead. This is the drying stage. Eventually, the metallurgist has separated copper from the argentiferous lead which can be cupelled to retrieve pure silver.

Saigerprozess in history and archaeology

Even though *saigerprozess* is 'an antiquated process' by the end of the 19th century, metallurgical treatises such as Schnabel's *Handbook of metallurgy* still describe it for it was 'formerly in very general use for extracting silver from copper-silver alloys' (Schnabel 1898, 497).

Indeed, the liquation and drying process seems to have spread in Europe at least from the 15th century onwards (Blanchard 1994). Until then, most silver came from reduction and refining of argentiferous lead ores or very rich silver-copper ores. However, at the end of the Middle Ages, many great silver-rich lead mines in Central Europe were depleted though the demand for silver was stable and that for copper was increasing, thus use of argentiferous copper ores containing less than 2wt% silver became profitable. Suhling (1994) links the 500% rise in silver production in Germany between 1450 and 1540 with the blossoming of the 'art' of liquation.

The first evidence of this process in historical sources goes back as far as 1453 in Nurnberg, Germany, with the mention of a '*saiger-offen*' in the city's archive (Suhling 1994). A few years later, the city houses at least four *Hütten* treating raw copper coming from the surrounding

regions, and between 1460 and 1480, eight more can be identified in the Thuringian forest. These late-medieval archives evoke a well-mastered fully-developed process and it seems reasonable to assume that these techniques were developed long before this rapid expansion. Yet, as there is no clear earlier evidence for liquation and drying in either historical or archaeological sources, this precise point is still in debate. If Sisco and Smith (1951) believe that the liquation process was invented in the 15th century, Suhling (1994) himself thinks that there are enough clues in chemical, technical or alchemical treatises from the 12th–14th centuries to conclude that the method of liquation was already known by the end of the 14th century. In particular, it was suggested that treatises referring to copper and lead separation by melting such as Theophilus' *De diversis artibus* (Hawthorne and Smith 1979) in AD 1150 could be at the origins of *saigerprozess*. Yet as Hoover and Hoover (1950, 494) rightly point out, silver is never involved in these descriptions, which therefore cannot be interpreted as the first evidences of liquation. Eventually, according to Dungworth and Nicholas (2004), the abundance of vessels made of 'antimony bronze containing low levels of silver shows that the liquation process was in use in Europe by at least the 13th century'.

As mentioned before, there is so far no excavated example of a liquation or drying furnace, and debris linked to this process is also very scarce. Suhonen (1998) mentions a large oval 16kg ingot from the site of Mulli, Finland (980–1220 AD), which contained 14% lead, 86% copper and 0.36% antimony. Its dimensions (550 x 370 x 70mm) and composition could fit with an exhausted or a dried liquation cake if it contained at least 1000ppm silver, which was below the detection limit of the SEM-EDS analysis. It seems that only three other specimens of such large lead-bronze cakes were found in Scandinavia, two of them linked to the metallurgical site of Rausi, Latvia, dating from the 11th and 12th centuries. These examples are too few to demonstrate the existence of the liquation process in these regions during the High Middle Ages.

Metallurgical treatises

Due to the lack of archaeological data, liquation and drying are so far mainly known from metallurgical treatises, the earliest being Biringuccio's *La Pirotechnia* of 1540 (Smith and Gnudi 1990, book III) although his description is very incomplete. In the later 16th century, Agricola's *De re metallica* of 1556 (Hoover and Hoover 1950, book XI) and Ercker's *Treatise on ores and assaying* of 1574 (Sisco and Smith 1951, book III) give much more precise accounts on the

whole process. Besides these early records, many later authors, including Barba (1640), Schlüter and Hellot (1750), Karsten (1832), Dumas (1893), Percy (1870; 1880) and Schnabel (1898), also had an interest in liquation and drying that continued until the end of the 19th century. Thanks to this important theoretical documentation, the principles of *saigerprozess* are still well known. Yet things are different when it comes to practical knowledge, and one might suspect that the general ignorance of liquation and drying wastes, products and structures could already have led to a certain misreading of archaeological finds.

Hence, in July 2008 and January 2009 two experimental campaigns reproducing the whole liquation and drying sequence were conducted on the experimental platform at Melle in France. They were mostly based on Agricola's description in *De re metallica*, book XI which, besides being among the earliest, is also the most accurate available for the whole process. In the present paper, all references to Agricola's work come from Hoover and Hoover's translation in 1912, taken from the 1950 edition.

These experiments aimed at rediscovering ancient procedures and the necessary thermodynamic conditions to perform this metallurgical operation. They also created a reference database for liquation and drying products and by-products, which could afterwards be compared with archaeological finds, such as copper-lead alloys coming from metallurgical sites or lead from joints in medieval monuments.

Analytical methods

All products and by-products (see Appendix) were analysed using several methods to determine their major and trace element composition, especially for silver (Ag), copper (Cu) and lead (Pb) which are the main elements involved in the *saigerprozess*.

Lead samples were analysed by XRF on the rotating anode tube of the LRC DSM01-27 available at the SIS2M laboratory in Saclay, France. A one-hour analysis time was chosen to give a good definition of the peaks with a 2mm analysis spot. This method gives a good analysis for Cu (8.0keV) after calibration with reference samples: lead comes from stained-glass panels previously analysed by ICP-AES, whose composition is available in Cuzange and Texier (2000). However, in a lead matrix, many sum peaks above 10.5keV prevent any precise analysis by XRF for elements with higher-energy lines such as silver (22.1keV). Thus, lead samples were

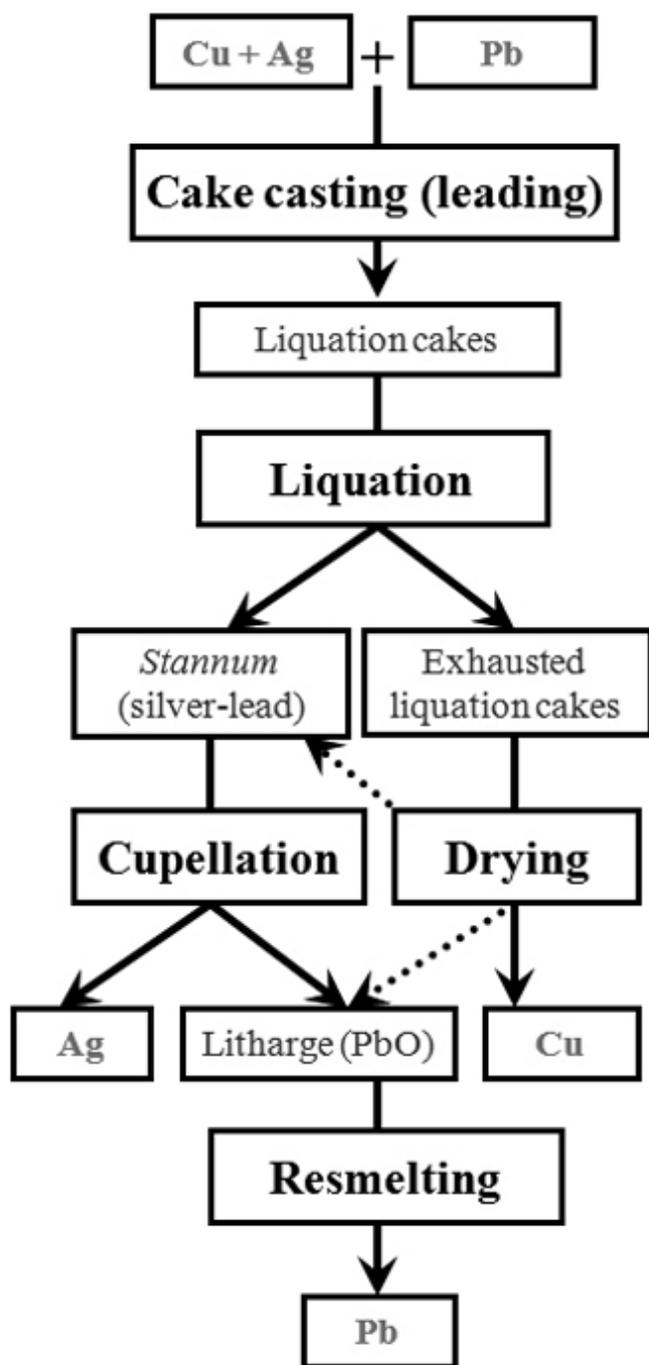


Figure 1: Diagram of the saigerprozess.

also analysed by LA-ICP-MS, using the same reference samples as internal standards. Analyses were performed at IRAMAT, Centre Ernest-Babelon in Orléans; for details on method see Gratuze *et al* (2001). Unlike XRF, LA-ICP-MS gives good results for heavy elements such as Ag, As, Bi, Sn and Sb but not for lighter ones such as Cu or Zn. In all cases, lead homogeneity and the reproducibility of the results were checked by performing at least three analyses on the same sample.

Silver prills were also analysed by LA-ICP-MS accord-

ing to a method published by Sarah *et al* (2007). Other by-products such as litharge and cake fragments are much more heterogeneous and required a bulk rather than a point analysis. This was performed with a portable XRF (Fondis, Niton XLt), a tailor-made device for the analysis of solid metals and alloys, ores and soils. The device was calibrated with reference bronzes and a 60 second analysis time was chosen with a 5mm spot. The entire surface of each sample was analysed to give an average composition. This method was sufficient to provide a rough estimate of Pb/Cu ratios in the samples but was inappropriate for minor and trace elements such as Ag or Bi. The analytical results are given in the Appendix.

Experimental work

The following sections describe the experiments in the order the *saigerprozess* was carried out: cake casting, liquation and drying (Fig 1). Eventually, to retrieve both silver and lead, cupellation and litharge resmelting experiments were also carried out on the silver-rich lead produced. It is necessary to stress the fact that every operation was performed at a smaller scale than was described in metallurgical treatises. ‘The cakes were generally two and one-half to three and one-half inches [65–90mm] thick and about two feet [0.6m] in diameter and weighed 225 to 375lbs [100–170kg]. This size was wonderfully persistent from Agricola down to modern times; and was no doubt, based on sound experience’ (Hoover and Hoover 1950, 504). Moving such big cakes would have required the use of a crane and it was indeed not appropriate to process hundreds of kilograms of metal for these first experiments. Nonetheless, all size and composition ratios stated in Agricola’s *De re metallica* were preserved. However, one has to bear in mind that some parameters such as operating times will *de facto* be different.

Cake Casting

Most authors describe several ways of making the so-called liquation cakes in which the argentiferous copper is mixed with lead. First, different copper qualities could be used: rich copper, black copper (also called *reguli*) or even already-exhausted liquation cakes. Many waste or by-products such as litharge, liquation thorns, impregnated cupels or any kind of lead slags could also partially or sometimes totally replace fresh metallic lead. Liquation therefore appears as a process used to recycle any cuprous or lead residues as long as their silver content is not too low. In all treatises, different types of ‘alloys’ are precisely described as well as the expected amount of silver eventually extracted. These recipes differ from one author to another, mostly

Table 1: Composition of the commercial lead used in the experiments (LA-ICP-MS)

Pb	Bi	Cu	Ag	Sn	Zn	Sb
99.7 %	2700 ppm	500 ppm	22 ppm	10 ppm	tr	tr

depending on the available ores in the mining region in question. However, in all cases, the easiest way to make a liquation cake is simply to use silver-rich copper and metallic lead, sometimes argentiferous, according to the copper fineness. The experiments were based on these last types of alloys.

Copper ore reduction was not carried out to make sure of the processed alloy quality and composition. Liquation cakes were therefore directly cast from pure copper and pure silver prills (99.99%) and leaded with commercial lead whose composition is given in Table 1. We chose an average Pb:Cu mass ratio of 10:3 on which most authors agree from the 16th–19th centuries: 3:1 according to Barba (1640, 180), an average of 10:3 as reported by Ercker (Sisco and Smith 1951, 235), 11:3 for Schlüter (1750, 479) and between 10:3 and 11:3 according to Dumas (1833, 410). Schnabel (1898) also states that the Pb:Cu ratio should be smaller than 11:3 to prevent a great loss of copper in the lead and that the Pb/Ag ratio should be higher than 500 to extract all the silver. All authors except Agricola seem to agree on this last condition. Even Ercker, writing only 25 years after Agricola, claims that for a profitable operation, four cakes made of 0.75centner copper and 2.5centner lead each should not bear more than 74lot silver in total, *ie* Pb/Ag > 470, as 16lot = 1mark = 1/200centner (Sisco and Smith 1951, 235). Agricola instead recommends ratios varying from 8:3 to 12:3 for argentiferous coppers containing a moderate proportion of silver, *ie* 0.7–1.2wt% (as calculated by Hoover and Hoover (1950) based on Agricola's use of

Roman units, *ie* 1libra = 12unciae, and 1centumpondium = 100librae); the richer the copper is, the more lead will be required (Agricola 1556, 405–6). Copper, lead and silver ratios in the successive alloys described by Agricola were sometimes misread by previous authors because of wrong translations or conversions; therefore the original Latin edition was consulted to make sure of the quantities processed. Hence, according to Agricola, the Pb/Ag ratio is quite stable around 350 whatever the alloy (Table 2). It even drops below 150 for very rich copper ores, containing up to 3librae of silver to the centumpondium, *ie* around 2–3wt%.

Regarding silver contents, comparisons between Agricola and Ercker prove quite confusing. The latter seems to have copied Agricola's alloys for moderate coppers, although the proportion of silver he gives is lower by one third (between 12 to 21 lot of silver per cake, *ie* 0.14–0.17% compared with 0.19–0.23% for Agricola). As mentioned above, ancient metallurgical treatises are based on practical experience of known ores: their silver content and thus the silver content in the liquation recipes may therefore vary from one region and author to another. Whether Ercker has adapted Agricola's charges to the reality he was describing, or whether Agricola was more systematically using the German centner weighing approximately 146 Roman librae instead of the Roman centumpondium of 100librae (see Table 2) is not certain. Computed with this new value, Agricola's first four 'alloys' would fit with Ercker's. Further investigation is required on this aspect. Nevertheless, this Pb/Ag ratio is not likely to affect the operation but only its yield regarding silver extraction. As Ercker states: 'the liquation lead may advantageously be as rich in silver as it wants to be; and even if the spent liquation cakes remain comparatively rich in silver, they can be used later as the addition to other, richer kinds of copper' (Sisco and Smith 1951, 229). Given that mass silver production was not the

Table 2: Composition of the liquation cakes according to Agricola (calculations are based on Roman units)

	Coppers containing a moderate proportion of silver					Rich coppers				
	1st alloy	2nd alloy	3rd alloy	4th alloy	5th alloy*					
Copper	¾ cent.	27.2%	¾ cent.	24.9%	¾ cent.	21.4%	¾ cent.	20.0%	1 cent.	24.8%
Silver	6–6.75 unciae	0.19%	7.5–8 unciae	0.22%	9–9.5 unciae	0.22%	10–10.5 unciae	0.23%	2.3–3 librae	0.74%
Lead	2 cent.	72.6%	2 ¼ cent.	74.8%	2 ¾ cent.	78.4%	3 cent.	79.8%	3 cent.	74.4%
Cu/Pb ratio	3/8		3/9		3/11		3/12		3/9	
Pb/Ag ratio	355–400		338–360		347–367		343–360		100–133	
Ag/Pb ratio	0.25–0.28%		0.28–0.30%		0.27–0.29%		0.28–0.29%		0.77–1%	
Ag/Cu ratio	0.67–0.75%		0.83–0.89%		1.00–1.06%		1.11–1.17%		2.3–3%	

Note: For the 5th alloy, Agricola mentions that a centumpondium of copper can weigh 133 or 146.6 librae (Agricola 1556, 408). Taking this into account, the Ag/Cu ratio would drop to 1.5% and the Pb/Ag ratio rise to 200, though remaining significantly lower than 500.

Table 3: Composition of experimental liquation cakes.

	Casting 98-1		Casting 98-2		Casting 99-3	
Cu	1133g	22.64%	1133g	22.61%	1020g	22.78%
Pb	3855g	77.04%	3862g	77.08%	3444g	76.91%
Ag	15.6g	0.31%	15.7g	0.31%	14.2 g	0.32%
Total	5003.6g	100%	5010.7g	100%	4478.2 g	100%
Pb/Ag	247		246		243	
Ag/Pb	0.40%		0.41%		0.41%	
Ag/Cu	1.38%		1.39%		1.39%	

primary goal in these experiments, and to make sure some silver would be retrieved in the end, we chose to process a rich copper with 1.4wt% silver.

Agricola describes casting as a 9–10 hour working day where 30 cakes can be made, the charge of each cake being weighed and melted separately (Hoover and Hoover, 1950, 508). These parameters seem quite persistent in time: Ercker speaks of casting forty cakes in 'eight or nine hours' (Sisco and Smith 1951, 240) and according to Schnabel (1898, 498) 'in successful work, a fresh liquation cake is made every 7 or 8 minutes', which would be about 60 per day. Only Schlüter and Hellot (1750, 526) give a significantly lower rate of 36 cakes in 20 hours, although their description of casting is identical to that of Agricola.

In the experiments, only five liquation cakes were cast in three successive operations: their composition is

Table 4: Mass (in grams) of the experimental liquation cakes

	Casting 98-1	Casting 98-2	Casting 99-3
Cake A	2058	2723	4478
Cake B	2212	2040	-
Total	4270	4763	4478
Loss	833 (14.7%)	247 (4.9%)	0 (0%)

Table 5: Comparison of Agricola's liquation furnace with experimental ones

	Agricola	Liquation 1	Liquation 2	Liquation 3
Furnace materials	Sole: stones and copper plates Sides: iron plates covered with lute, brick rear wall		Sole: bricks, iron plates Sides: bricks	
Furnace inner size	3 feet 3 palms 2 digits long ($\approx 1.15\text{m}$) 2 feet 1 palm 3 digits wide ($\approx 0.75\text{m}$)		200x450mm	
Channel width	1 foot wide at the back and 1 foot 1 palm wide at the front ($\approx 300\text{--}370\text{mm}$)		60mm	
Receiving pit	1 foot wide ($\approx 300\text{mm}$) and 3 palms deep ($\approx 220\text{mm}$)		300mm wide and 150mm deep	
Number of cakes	4–5	2	2	1
Lead beginning to flow out	$\approx 15\text{mn}$	13mn	7mn	11mn
Operation time	$\approx 2\text{h}$ (4 liquations/day)	1h 18mn	58mn	43mn
Temperature	?	550–700°C	700–800°C	700–850°C

presented in Table 3. The copper and lead were melted separately in two crucibles. Silver was then added to the molten copper, creating the argentiferous copper alloy to be processed. The molten lead was then poured into this crucible, the mixture was stirred and quickly cast into a sand mould, whose dimensions varied between 15–25mm thick and 120–150mm in diameter. The liquation cakes produced weighed 2–4.5kg (Fig 4; Table 4), which is about 50 times lighter than regular liquation cakes. Once the cakes have cooled, silver has already passed from the copper to the lead. The silver-rich lead now has to be separated from the de-silvered copper in the liquation and drying furnaces.

Liquation

Agricola precisely describes the liquation furnaces as those in 'which silver mixed with lead is separated from copper' (Hoover and Hoover 1950, 515). He depicts them as oblong open hearths operated under natural air-draught. The cakes are placed on the copper plates of the furnace and held in a standing position by iron blocks and charcoal. A sloping channel set beneath the furnace leads to a receiving pit in front, so that the 'argentiferous lead alloy which liquates from the cakes can flow into [it]' (Hoover and Hoover 1950, 516). The experimental furnace reproduces Agricola's depiction at a smaller scale and with modern materials (Fig 2). As in Schnabel's drawing (1898, 499), angled iron plates replace the copper ones to help the cakes stand and form the passage underneath. The characteristics of the furnaces are compared in Table 5.

Three liquation experiments were carried out with one or two cakes at a time. Each time, the furnace was preheated for about an hour before starting the operation, *ie* replacing the cakes in the hearth and covering them with live charcoals. A temperature of 600–800°C was easily reached and lead started flowing out approximately ten minutes after setting the fire, which is a



Figure 2: Liquation furnaces. Agricola's representation (left) and the experimental furnace before use (right).

similar order of magnitude to Agricola's fifteen minutes for much bigger cakes. Then, the lead flow was steady, although clearing the channel with a rabble was some-

times necessary when cold coals were trapped inside. All through the experiment, fuel was regularly added on top of the cakes to keep a reducing atmosphere and prevent lead loss by oxidation.

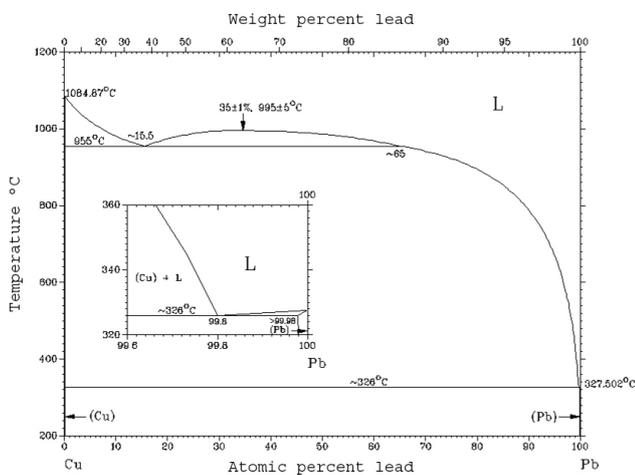


Figure 3: Copper-lead phase diagram.

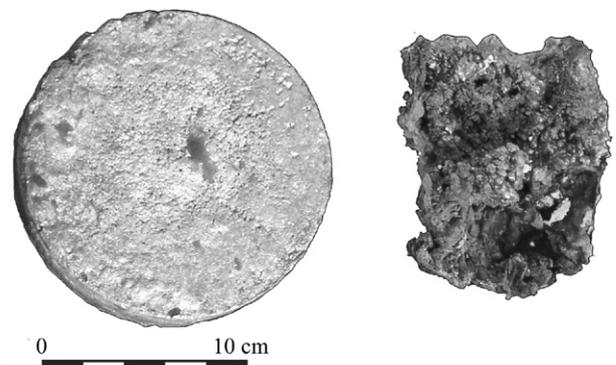


Figure 4: Experimental liquation cakes. As-cast (left) and exhausted (right).

Table 6: Mass balance for the experimental liquations (weights in grams)

	liquation 1		liquation 2		liquation 3	
Initial weight cake A	2058		2723		4478g	
Initial weight cake B	2212		2040		-	
Total cake weight	4270		4836		4478g	
Final weight cake A	504	24.5%	1417	52%	1410g	31.5%
Final weight cake B	536	24.2%	1257	61.6%	-	
Lead in the receiving pit	1237		1092		2401g	
Lead in the canal	914		376		49g	
Total extracted lead weight	2151	65%	1468	39%	2450g	71.1%
Waste	47		153		276g	
Total weight	3238	75.8%	4295	88.8%	4136g	92.4%

No authors give any information about the adequate temperature for this operation. Dumas (1833, 411) speaks of 'rising temperature to a given point' so that lead would be liquid and copper would not. Yet, considering the theoretical composition of liquation products can help estimating this 'given' temperature. The average copper content for the argentiferous lead extracted is 2–3wt% (Table 8) and, according to the copper-lead phase diagram, such alloys melt between 700–800°C (Fig 3). We therefore tried to work in this range, but controlling temperature was not easy in such an open hearth operated under natural air-draught. In liquations 1 and 2, where two cakes were processed at a time, the temperature seemed much lower next to the rear cake than around the front one. Similar issues are reported by Schlüter and Hellot (1750, 536) who suggests covering the cakes which do not shrink with more coals.

Each operation was stopped when lead stopped flowing out. For each experiment several cake fragments

were sampled, and the extracted argentiferous-lead was homogenised and cast into ingots before sampling for a global analysis as it proved quite heterogeneous.

Table 6 gives mass balances for the three experimental liquations. For liquation 1 and 3, approximately two-thirds of the initial lead weight was extracted, which is only a little below Agricola's or Ercker's estimates (75–83%) or Schnabel's 87%. On the other hand, with a 40% yield liquation 2 was certainly incomplete, which is confirmed by the analysis of exhausted cake 2A where more than 50% lead remained (Table 7). According to Hoover and Hoover (1950, 520), who summarise data from various authors, lead content in exhausted liquation cakes should be 25–33%. In the experiments, only exhausted cake 3A matches this composition, whereas exhausted cake 1A is almost depleted in lead and 1B still retains about 50% (Table 7). This last result illustrates the temperature gradient which was observed in the liquation furnace between the rear and front cakes. Sb and Zn were not present

Table 7: Average composition (wt%) of exhausted liquation cakes by portable XRF.

Exhausted cake no	No of analyses	Pb	Cu	Zn	Sb
1A	3	7	93	<0.5	nd
1B	4	47	51	1	<0.5
2A	12	46	52	1	<0.5
2B	0	-	-	-	-
3A	20	34	61	1	3

Table 8: Average copper content of the liquated lead (XRF on a rotating anode tube)

	Liquation 1	Liquation 2	Liquation 3	Agricola	Dumas/Karsten	Schnabel
Number of analyses	5	4	6	-	7	-
Average Cu content (wt%)	2.7	1.1	0.5	-	2.4	-
Min-Max Cu content (wt%)	0.1–3.3	0.1–1.3	0.3–2.8	2.2–4.8	2.1–2.8	2–3
Yield (% of lead extracted)	65	39	71	75–83	-	87
Temperature (°C)	550–700	700–800	700–850	?	?	?



Figure 5: Experimental drying furnace with the exhausted cake before the operation. Scale 400mm.. Inset, the dried cake at the end of the experiment with the flowed out oxides below. The cake is 100mm across.

in the initial copper/silver/lead system and therefore came from the furnace structure (cast iron plates, bricks, casting sand). Yet, in all the experiments, the composition of the liquated lead agrees with the values given by Agricola (Hoover and Hoover 1950), Schnabel (1898) and Karsten (1832) (Table 8), and does not seem to be linked to the yield of the liquation operation.

Only the last of among the three experiments, where one single cake of greater dimensions was processed, totally agrees with expected theoretical data. Temperature control in the open hearth and the thinness of the cakes, which sometimes ended up as fragments, seem to be mostly responsible for the relative failure of the first two liquations. One must also note that no residues such as 'liquation thorns' were found in the furnace at the end of the operation. These 'liquation thorns' should represent about 5% of the overall charge (Dumas 1833, 409) and up to 16% (Hoover and Hoover 1950, 512–13), which would be about 200 to 600g in these experiments. Metal losses, however, greatly exceed these values. Waste products are mostly partially-liquated cake fragments and lead pieces stuck inside the channel, although sometimes mixed with a few cuprous and lead oxides.

The *stannum* or silver-rich lead can then be carried directly to the cupellation furnace, whereas the exhausted liquation cakes have to be dried. Exhausted cakes 2B and 3 were collected for the drying experiments.

Drying

In ancient treatises the drying operation appears to be much more complex than liquation and 16th-century authors describe the drying phase more briefly than liquation; Biringuccio simply omits it. As Biringuccio is the first metallurgical account about liquation, we cannot completely rule out the possibility that drying might not have been common practice at that time although liquation was already well developed. Indeed, 15th-century records of the liquation process only mention *saiger-offen*, which translated in English refers to the liquation furnace. However, knowing that Agricola is giving a fairly exhaustive description of drying only 10 years later, it seems more likely that Biringuccio made an omission. Ercker's account is also quite short as he barely mentions the furnace and how drying should be conducted. Indeed, Agricola does not give many details of the operation itself. He speaks of a four-day work, but stresses the first two days where the master has to clean the exhausted cakes and arrange rows of bricks in the furnace on which to place the cakes. Only the third day is dedicated to the 'principal operation' and the fourth one to collecting the metallic residues in the furnace.

The principles of drying can be explained as extracting the remaining lead from the cakes and purifying the copper by oxidizing its impurities. Hence, unlike liquation, an oxidizing atmosphere is required in the furnace, at least for a time. The drying furnace is a huge reverberatory which seems to be a constant feature from

the 16th to the 19th century, although the fuel changes in time from charcoal to 'cheaper fuel' (Schnabel 1898, 500), probably coal. It has a tall chimney and several air holes at the back to control the atmosphere and provide access 'to see whether the cakes are properly "dried"'. It is closed on the front side by a huge sliding iron door. Inside, the exhausted cakes are laid next to one another on benches or rows of bricks. Reproducing all these features at a smaller scale required some adjustments. The experimental furnace was built solely out of bricks. Its inner dimensions are 20x25cm. The hearth was covered with casting sand and four small limestone blocks were used to support the exhausted cake (Fig 5). At the rear, to provide the desired oxidizing atmosphere, the vent-holes and the chimney were replaced by a small electric blower.

Most authors do not give much detail about the sequence of events after placing the cakes and setting the fire. Although Agricola does not mention it, it seems that a little silver-rich lead starts dripping out of the cakes after a certain time. This is quickly followed by what the authors refer to as 'slags', 'thorns' or 'oxides'. Schnabel (1898, 501) even distinguishes two types of oxides: the *darrost*, rich in lead (75–85%) and the *darrlinge*, poor in lead (15%). The most accurate description is given by Dumas (1833, 413–14) who clearly explains how the air-holes were used: they were opened and closed in several successive phases to oxidize the cakes and liquefy the oxide produced without losing too much copper (Table 9). Was the process conducted identically in the 16th century or has the art of drying really evolved in time? For the present, this question remains unanswered. In the experimental drying, we mainly focused on obtaining the required oxidizing atmosphere at the right temperature.

As for liquation, the metallurgical treatises give no specific information on the required temperature for drying, yet some useful clues help in estimating it quite precisely. Agricola states that the cakes 'become incandescent in an hour and a half' and that the 'slags begin to flow' shortly afterwards. He also insists on the

fact that the cakes should not melt. Schnabel evokes a 'high temperature' necessary 'to liquate the residues'. Assuming that the 'slags' or residues are mostly lead oxides, the temperature would therefore have to be above 890°C. Guillot and Benoit (1994) suggest that to extract the maximum lead it has to be 'close to the melting point of copper' (1083°C). However, the copper-lead phase diagram (Fig 3) clearly shows that above 955°C it is possible to melt copper with as little as 37% lead, which is irrelevant as the exhausted cakes have to remain in a solid state whilst drying. Combining this information seems to show that drying should be conducted between 900–950°C.

The first drying experiment was carried out with exhausted cake 2B at around 950°C. The cake was placed inside the furnace after 15 minutes preheating with live coals. Charcoal was then regularly added throughout the experiment. After one and a half hours the cake was fragmented. Some lead had flown out and solidified in the hearth. Light non-metallic porous residues and small lead prills were also found around the limestone blocks. Light elements, such as silicon or aluminium which mostly come from interactions with the furnace components, have been excluded from the analytical results for the residues from liquation and drying. Materials used in these experiments such as refractory bricks and casting sand are not likely to be comparable with a 16th-century furnace. Light non-metallic products were therefore not characterised at all. The analysis of the dried cake shows that it still retains great quantities of lead (Table 10), while the expelled lead is very rich in copper (10–35%) showing that the critical fusion point of 955°C was locally exceeded.

The second drying experiment was therefore carried out at a lower temperature with exhausted cake 3A. The operation lasted for two hours and temperature was measured and recorded with a thermocouple (Fig 6). On the first part of the graph, before the blower was shut down, the temperature inside the hearth was recorded. Afterwards, the probe was placed on the cake itself to measure the temperature of the metal. During the last hour,

Table 9: Comparison of the drying process according to various authors.

	Agricola	Ercker	Schlüter	Karsten/Dumas	Schnabel	Experimental
Processed cake weight	2.5–5 tons but might be less	6 tons	≈2–3 tons (36–48 exhausted cakes)	15–30 tons	?	0.5–1.5kg
Time	1 day (≈12h)	12–14hr	20–24hr	25–26hr	24hr	2hr
Number of stages	1	1	3	4	1	1
Products	Dried cakes, slags, thorns	Fresh lead, thorns, spent liquation cakes	Silver-rich lead, lead slags, dried cakes	Silver-rich lead (impregnated in the hearth), lead slags, dried cakes	Lead, Darrost, Picksheifer, Darrlinge (oxides)	Dried cake, lead oxide

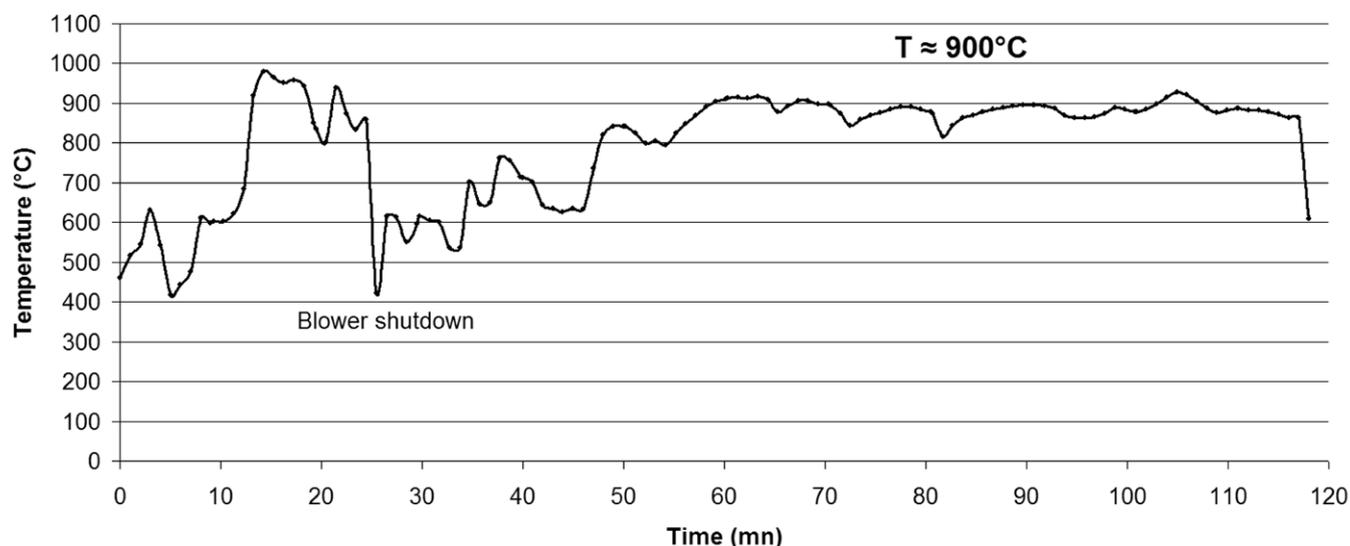


Figure 6: Temperatures recorded during the second drying experiment.

maintaining a stable temperature between 850 and 900°C without changing the air-blower output proved possible only by refuelling the hearth with charcoal on top of the cake every 10–15 minutes. In the end, the cake was also fragmented yet it was still in place and the bottom of the hearth was covered with dark red oxide (Fig 5). Separating the cake from the oxide was difficult, so the measured weights should be taken with caution. The dried cake contained only 9–14% lead, and the oxide 78% lead and 17% copper on average (Tables 10 and 11). These compositions match quite well with Karsten's (1832) data, which proves that the required conditions for drying were reached during this last experiment. Additional XRF analyses were made under helium flow to estimate the contribution of lighter elements in these drying residues

and provide a mass balance for the experiments. They give an average of 12% silicon, 2% phosphorus and traces of aluminium, with the average lead and copper contents dropping to 66% and 14% respectively. This last composition is still close to Karsten's (77–85% lead oxide, 4–8% cuprous oxide, 9–14% silica and 1–2% alumina). According to the experimental mass balance, 10% of the overall matter was lost. Although the calculation cannot be very accurate due to the approximate weights mentioned above, it seems that mostly lead was lost, the copper loss being negligible (Table 12).

The liquation and drying sequence stops here. The silver-rich lead oxide can be smelted to produce argentiferous lead or used to add lead to more silver-poor copper cakes,

Table 10: Range and average composition (wt%) of experimental dried liquation cakes (analysis by portable XRF).

Dried cake No	No of analyses	Pb		Cu		Zn		Sb	
		range	(average)	range	(average)	range	(average)	range	(average)
2B	2	31–39	(35)	59–67	(63)	1	(1)	nd	
3A	15	6–23	(12)	73–89	(84)	1–4	(2)	1–4	(2)
Karsten	5	9–17	(14)	83–91	(86)	-	-	-	-

Table 11: Average composition (wt%) of the oxide created during the experimental drying (analysis by portable XRF; light elements are not taken into account).

Sample No	No of analyses	Pb	Cu	Zn	Sb
mel09 LR1	2	91	3	1	3
mel09 LR2	3	75	20	1	3
mel09 LR3	2	77	18	1	3
mel09 LR4	2	80	14	1	3
mel09 LR5	11	77	18	1	3
Average	20	78	17	1	3



Figure 7: An 8th-10th century litharge cake from Melle (left) and a small experimental one (right).

whereas the dried liquation cakes can be refined for pure copper, or might even have been used as they were to produce coarse coppers among which are 'yellow copper' and *caldarium* (Dungworth and Nicholas 2004) or even lead bronzes. The silver-rich lead then enters another process: cupellation.

Cupellation

The objective of these experiments was to separate silver, lead and copper, the three metals that were mixed in the liquation cakes, in order to analyse their final composition at the end of the process and compare it with their initial composition. Thus, the primary aim of the experimental cupellation was to retrieve silver and litharge to be refined rather than testing archaeological or technical hypotheses. More information

about this process can be found in Guirado *et al* (this volume).

About one kilogram of silver-containing lead from liquations 1 and 3 were sent to the cupel in two successive operations. The furnace was built out of bricks according to Biringuccio's clay plate cupellation furnace (Smith and Gnudi 1990, 167). The hearth crucibles were made out of wood ash and preheated once before starting the operation. Then, the alloy was placed inside the crucible and fire was set, first with live coals and then refuelled with dry wood. During the first experiment, it was possible to rake-out some litharge forming on the top of the molten alloy with a rabble. The small litharge cakes which were produced clearly recall archaeological finds described by Conophagos (1981) and those found on the site of Melle (Fig 7). During the second experiment, all the litharge was absorbed by the cupel and consequently mixed with the ashes. Both experiments were stopped before oxidizing all the lead.

As both cupellations failed to retrieve the silver, two fire-assays were also carried out on silver-containing lead from liquation 3. Lead was oxidized and absorbed by the bone-ash cupel and each fire-assay produced a small silver prill (Table 15).

Resmelting the litharge

Copper was retrieved by drying the cakes, and silver by refining the silver-containing lead. Thus, the experiments ended with resmelting the lead oxide produced. Two resmelting experiments were carried out, using

Table 12: Mass balance for the second drying experiment (weights in grams).

	Lead (%)	Lead (wt)	Copper (%)	Copper (wt)	Total wt
Exhausted liquation cake	37	444	59	709	1201
Exhausted cake fragment	16	18	80	91	114
Dried liquation cake	12	83	84	580	~690
Oxide	66	195	14	41	~296
Total products	-	296	-	712	1100
Loss	33%	147	0%	-3	101 (9%)

Table 13: Parameters for litharge refining experiments.

	Litharge refining 1	Litharge refining 2	Litharge refining 3
Litharge weight (g)	50	50	33
Coal dust	Mixed + on top	on top	none
Time	47min	24min	22min
Number of castings	2	3	1
Weight of lead produced (g)	15.5	12.2	4.7
Yield	31%	24%	14%

Table 14: Analyses (ppm) of experimental silver prills by LA-ICP-MS.

	Ag (%)	Cu	Au	Bi	Cd	Hg	Pb	Pd	Ru	Sb	Sn
AG01	99.96	150	6	3	11	109	77	18	2	0	0
AG02	99.97	60	6	0	11	148	24	18	1	0	1

'pure' litharge from the first cupellation and litharge mixed with ash from the second cupellation.

For the first experiment, the lead oxide was crushed and placed inside a small crucible with or without coal dust (Table 13). The crucible was then heated in an open hearth above the litharge melting point (890°C). Eventually, the lead produced was cast. According to these first results, the use of coal dust seems to help reduction although it is not essential. However, in all cases, the operation yield is quite bad compared to Agricola who states that 'usually from 133librae of litharge only 100librae of lead are made' (Hoover and Hoover 1950, 505), expecting a yield of 75%. This yield is confirmed by both Ercker (Sisco and Smith 1951, 232) and Schlüter and Hellot (1750, 522–3) converting 130–135lbs of litharge to 100lbs of lead and 140lbs of litharge to 116lbs of lead respectively.

For the second experiment, the mixture of ash and litharge was crushed and sorted then placed inside a crucible with coal dust. No casting could be carried out after 45 minutes heating though some metallic lead prills were found inside the crucibles at the end of the operation. The XRF analysis shows that all except one of the lead prills are de-silvered, so we can expect that they come from litharge reduction.

These experiments were therefore successful in parting silver from copper by the liquation and drying process. Lead samples were collected after each sequence of the liquation and drying experiments to follow some of the trace elements' behaviour through the whole process. Our interest will now focus on three of them: silver and copper which are part of the system, and bismuth which

Table 15: Mass balance for the fire assays of silver-containing lead from liquation 3.

	Assay 1	Assay 2
Weight of argentiferous lead (g)	15.2	15.4
Weight of silver prills (g)	0.05	0.05
Silver content of lead (%)	0.33	0.32
Initial silver content of lead (%)	0.41	0.41
Experimental yield for silver extracted into the argentiferous lead	80%	79%

was present in significant amounts in the original lead. All analyses indeed showed that no other relevant elements were introduced into the system during the experiments.

Changes in lead composition during liquation and drying

Copper content

The interest in tracing copper into the lead is to determine whether or not this process has an influence on composition of the lead or litharge produced. The initial lead had an intermediate copper content compared to archaeological lead (about 500ppm) (Wytttenbach and Schubinger 1973; Rehren and Prange 1998; Cochet 2000; Cuzange and Texier 2000; Baron and Cochet 2003). After liquation, regardless of the yield of the operation, the lead was enriched in copper, containing 0.5–3wt% on average, which is consistent with metallurgical treatises and can be explained by the temperature reached during liquation. Between 700–800°C, lead containing up to 2% copper is indeed liquid. At these levels, copper nodules are visible on a polished cross-section. Lead produced during the first drying operation is richer in copper than the liquated lead. However, this operation was not carried through and might not be representative.

Finally, once cupelled and re-smelted, the lead is even richer in copper (Fig 8). The silver prills analysed confirm that copper does not remain with the silver but rather passes into the lead oxide (Table 14). As no copper was added during these last phases, only a significant loss of lead can explain this second enrichment in copper. Lead volatility as well as the poor yield of the litharge refining experiments can be cited here to explain such a loss. However, as the copper loss is not likely to be higher than that of lead during refining, the produced lead is not likely to contain less copper than the work-lead, *ie* 0.5–3% in these experiments. Thus, lead coming from the liquation and drying process will always be copper-rich at the level of a few thousand ppm up to a few percent.

Silver content

The changes in the silver content of the lead characterise the operational success and the experimental yield. The initial lead had a very low silver content (22ppm). After liquation, XRF analysis of the lead

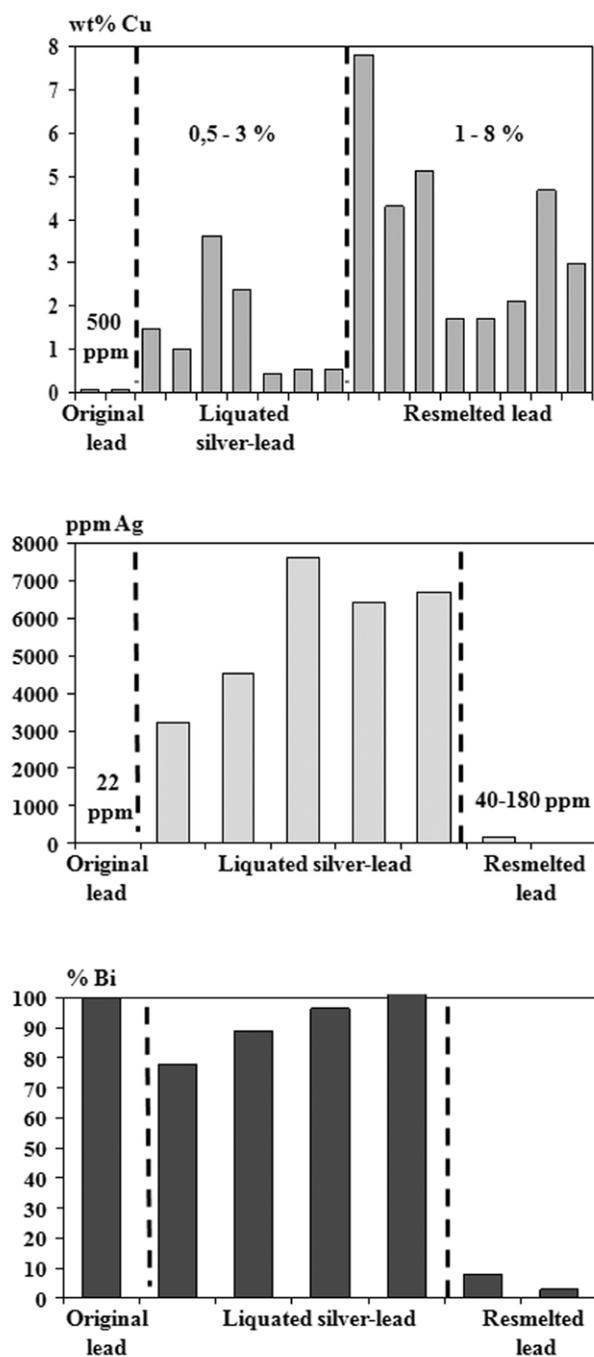


Figure 8: Changes in the copper (wt%), silver (ppm) and bismuth (% normalised to the original lead Bi concentration) content of lead throughout the experiments.

detected silver in all samples, proving that some of the silver had passed into the lead during casting as the cakes were cooling down. Complete LA-ICP-MS analysis was only carried out on samples from the first experiment. Before homogenisation, the silver content of the lead ranged from 0.45–0.76wt%, which is above the theoretical concentration. Indeed, if all the silver to the liquation system had passed into the lead, it would only have 0.41wt%. Agricola states that some of the silver remains in the copper and the liquation residues.

This extreme heterogeneity of the liquated lead has already been identified in ancient metallurgical treatises (Campredon 1909). Lead coming from the drying phase is also very heterogeneous as the single analysis exceeds the theoretical value too.

Finally, after cupellation and litharge refining, the re-processed lead contains only 40–180ppm silver (Fig 8), which matches the data for de-silvered lead (Rehren and Prange 1998). Hence, even though it was not carried through to completion, the large-scale cupellation was successfully conducted. The fire assay carried out on the lead from liquation 3 gives the average silver content as 0.32–0.33wt%. The experimental yield for silver extraction into lead therefore averages slightly below 80% (Table 15), which is very similar to Agricola’s or Ercker’s data: 71–85% depending on the amount of lead and on the copper:lead ratio (Hoover and Hoover 1950, 506–9; Sisco and Smith 1951, 226). Later, Percy (1880, 322) mentions a similar figure of 87% for silver extraction, a yield which ‘will vary according to the degree in which the liquation of the lead has been effected’. This final result proves that at least liquation 3 was brought to fruition.

Bismuth content

Bismuth was unintentionally added to the initial system with the commercial lead used in the experiments. Despite the possible lead heterogeneity, the bismuth content does not seem to change during liquation or drying. On the other hand, the re-smelted lead contains 30 times less bismuth (Fig 8). Bismuth did therefore not oxidize in the sampled litharge but it did not remain in the silver prills produced by fire assay either. Cupellation seems to have acted as a filter for this element. Is it volatile? Did it oxidize at the end of the process? Can it be retained in the silver? Many contradictory records exist in the literature about the behaviour of bismuth (Chaudet 1818; Berthier 1834, 612; Raub 1995) and oriental silver coins with high amounts of bismuth are also sometimes recorded (McKerrell and Stevenson 1972; Cowell and Lowick 1988). Further experiments will have to be carried out to understand the behaviour of bismuth.

Experimental conclusions and archaeological perspectives

These two experimental campaigns have produced a lot of information about the liquation and drying process.

First, regarding temperature, 700–800°C seems to be suitable for liquation although a slight variation is acceptable during this process. On the other hand, the drying temperature has to be much more precisely con-

trolled and kept within the 900–950°C range; below 900°C, the oxide produced would not be likely to flow out and above 950°C the exhausted cakes would melt.

Second, regarding yield, it was greatly enhanced in the third experiment. Our technical knowledge of the process might have improved, but another parameter must be cited: size. Processing a single bigger cake was much easier for two reasons: it avoided a temperature gradient inside the furnace leading to heterogeneous liquation and prevented the cake crumbling into pieces when lead flowed out. Lead losses were, however, still considerable, totalling about 40%: 8% during liquation then 33% during drying. In the 19th century, Karsten (1832) and Percy (1880, 338) note a 13–16% lead loss throughout the whole process, the greatest part occurring during drying and copper refining. Yields were probably much worse in the early modern period, as according to Ercker '1½ centners are lost out of every 10 centners of lead' only during leading and liquation (Sisco and Smith 1951, 232), Schlüter and Hellot's record was even worse, with the loss of at least one quarter and up to one third of the lead, this time for the entire process (1750, 518). The poor experimental yield must be mostly responsible for the absence of *spinae* or 'liquation thorns' in the residues, although a few of lead and cuprous oxide, always closely attached to bigger metallic fragments, could be identified. Processing a greater quantity of metal might also enhance their formation: 20kg of cakes should produce at least 1kg of thorns. Beside these residues, all other liquation and drying products and by-products could be chemically characterised.

Copper-based products are likely to contain high amounts of lead (up to 20%) which could have been used as leaded bronzes, as suggested by Dungworth and Nicholas (2004). As for lead-based products, they are highly influenced by both *saigerprozess* and the following cupellation. Copper is entrapped during liquation and drying (several percent on average) and cupellation seems to remove both silver and bismuth, but not copper. Hence, in the end, the litharge and lead are copper rich, and low in silver (and bismuth). The silver composition does not seem to be affected by liquation and drying, as copper remains within the litharge during cupellation.

Archaeological artefacts from metallurgical sites can now be compared to this reference database. A new interpretation of an oblong furnace at the La Rochelle royal mint dating from the 15th century has already been made due to the characterisation of copper-lead waste found inside it which resembled cake fragments obtained during these experiments (L'Héritier *et al* 2011).

Their analysis showed that this furnace was partly used to retrieve silver from silver-rich copper waste or even low-grade billon processed on the site, which is so far the earliest archaeological evidence for the liquation process, but much cruder than Agricola's description 100 years later. Such archaeological evidence of liquation in a mint is a new discovery for the 15th century, although the practice was described 300 years later by Delaguerre for the mint of Strasbourg (Bibl Nat France, no date).

In parallel with these experiments, hundreds of lead samples from joints in medieval monuments (among which are Auxerre, Metz and Strasbourg cathedrals, Vincennes castle and the palace of Charles the Great in Aachen) are being analysed to see whether the emergence of *saigerprozess* can be traced via the copper content of the lead.

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Appendix

List of experimental samples

Sample No	Description	No of specimens analysed
MEL08 PB1	Resmelted lead	1
MEL08 PB2	Resmelted lead	1
MEL08 PB3	Resmelted lead	1
MEL08 PB4	Resmelted lead	1
MEL08 PB5	Original lead ingot before experimentation	1
MEL08 PB6	Liquated lead (liquation 1) homogenised	1
MEL08 PB7	Liquated lead (liquation 1) homogenised	1
MEL08 PB8	Liquated lead (liquation 1) before homogenisation	1
MEL08 PB9	Liquated lead (liquation 1) before homogenisation	2
MEL08 PB10	Liquated lead (liquation 2) homogenised	1
MEL08 PB11	Liquated lead (liquation 2) homogenised	1
MEL08 PB12	Liquated lead (liquation 2) before homogenisation	1
MEL08 PB13	Liquated lead (liquation 2) before homogenisation	1
MEL08 PB14	Silver-rich lead from drying 1	1
MEL08 PB15	Silver-rich from drying 1	1
MEL09 PB1	Original lead ingot before experimentation	1
MEL09 PB2	Liquated lead (liquation 3) before homogenisation	4
MEL09 PB3	Liquated lead (liquation 3) homogenised	3
MEL09 PB4	Lead residues on top of the pit hole (liquation 3)	4
MEL09 PB5	Lead residues inside the passage (liquation 3)	4
MEL09 PB6	Lead residues inside the passage (liquation 3)	8
MEL09 PB7	Revivified lead prill	6

Composition of experimental leads (XRF on a rotating anode tube; results in ppm if not shown as %)

Sample No	Cu	Ag	Sn	Sb	Sample No	Cu	Ag	Sn	Sb
MEL08 PB1	11.8%	< 1500	< 1500	1100	MEL09 PB4a	1700	> 1500	< 1500	4000
MEL08 PB2	7.1%	< 1500	< 1500	< 200	MEL09 PB4b	1.1%	> 1500	< 1500	5300
MEL08 PB3	3.9%	< 1500	< 1500	< 200	MEL09 PB4c	39.8%	> 1500	< 1500	1.4%
MEL08 PB4	4.6%	< 1500	< 1500	< 200	MEL09 PB4d	5.4%	> 1500	< 1500	6900
MEL08 PB5	450	< 1500	< 1500	< 200	MEL09 PB5a	910	> 1500	< 1500	3700
MEL08 PB6	3.3%	> 1500	< 1500	600	MEL09 PB5b	1000	> 1500	< 1500	3800
MEL08 PB7	2.1%	> 1500	< 1500	500	MEL09 PB5c	930	> 1500	< 1500	3800
MEL08 PB8	2500	> 1500	< 1500	1200	MEL09 PB5d	4.0%	> 1500	< 1500	6100
MEL08 PB9a	3000	> 1500	< 1500	1400	MEL09 PB6a	3200	> 1500	< 1500	4300
MEL08 PB9b	1300	> 1500	< 1500	1300	MEL09 PB6b	6.4%	> 1500	< 1500	5600
MEL08 PB10	1.3%	> 1500	< 1500	400	MEL09 PB6c	39.4%	> 1500	< 1500	13300
MEL08 PB11	9100	> 1500	< 1500	300	MEL09 PB6d	42.0%	> 1500	< 1500	10500
MEL08 PB12	1900	> 1500	< 1500	700	MEL09 PB6e	23.0%	> 1500	< 1500	6700
MEL08 PB13	1400	> 1500	< 1500	700	MEL09 PB6f	37.7%	> 1500	< 1500	13600
MEL08 PB14	9.4%	> 1500	< 1500	600	MEL09 PB6g	64.9%	> 1500	< 1500	18600
MEL08 PB15	35.9%	> 1500	< 1500	900	MEL09 PB6h	62.0%	> 1500	< 1500	21200
MEL09 PB1	410	> 1500	< 1500	< 200	MEL09 PB7a	1.7%	< 1500	< 1500	5000
MEL09 PB2a	890	> 1500	< 1500	2900	MEL09 PB7b	1.7%	< 1500	< 1500	7900
MEL09 PB2b	2600	> 1500	< 1500	2300	MEL09 PB7c	2.1%	< 1500	< 1500	900
MEL09 PB2c	2.9%	> 1500	< 1500	5400	MEL09 PB7d	9100	> 1500	< 1500	2300
MEL09 PB2d	5000	> 1500	< 1500	2600	MEL09 PB7e	1300	< 1500	< 1500	2600
MEL09 PB3a	4200	> 1500	< 1500	2900	MEL09 PB7f	4.7%	< 1500	< 1500	600
MEL09 PB3b	5200	> 1500	< 1500	2800	MEL09 PB7g	3.0%	< 1500	< 1500	1900
MEL09 PB3c	5200	> 1500	< 1500	2800					

Appendix (cont)*Composition of some experimental leads by portable XRF.*

Ssample No	Pb	Cu	Sb
MEL08 PB1	88.3%	11.1%	< LOD
MEL08 PB2	91.8%	7.5%	< LOD
MEL08 PB3	94%	5.3%	< LOD
MEL08 PB4	93.4%	6%	< LOD
MEL08 PB5	99.1%	< LOD	< LOD
MEL08 PB6	93.6%	5.3%	< LOD
MEL08 PB7	95.9%	3%	< LOD
MEL08 PB8	97.8%	1.1%	< LOD
MEL08 PB8	98.1%	0.7%	< LOD
MEL08 PB9a	98.1%	0.6%	0.2%
MEL08 PB9b	98.5%	0.3%	< LOD
MEL08 PB10	97.1%	1.8%	< LOD
MEL08 PB11	97.4%	1.5%	< LOD
MEL08 PB12	98.1%	0.5%	< LOD
MEL08 PB12	98.5%	0.3%	< LOD
MEL08 PB13	98.1%	0.6%	< LOD
MEL08 PB14	89.3%	9.6%	< LOD
MEL08 PB15	68.8%	30.3%	< LOD
MEL09 PB3a	97.9%	0.7%	0.3%
MEL09 PB3b	97.8%	0.8%	0.3%
MEL09 PB3c	98%	0.7%	0.3%
MEL09 PB6a	98.1%	0.4%	0.4%
MEL09 PB6c_1	63%	34.8%	1.4%
MEL09 PB6c_2	62.2%	35.6%	1.3%
MEL09 PB6d	63.5%	34.9%	0.8%
MEL09 PB6e	76.5%	21.9%	0.6%
MEL09 PB6f	61.6%	36%	1.5%
MEL09 PB7a	96.9%	1.8%	0.4%
MEL09 PB7g	96.9%	2.1%	0.3%

Note: < LOD = below level of detection.

Composition of some experimental leads (LA-ICP-MS analyses; results in ppm if not %)

Sample No	Cu	As	Ag	Sn	Sb	Bi	Pb
MEL08 PB3	2.4%	< 1	180	< 1	150	220	97.6%
MEL08 PB4	2.6%	< 1	39	< 1	320	80	97.4%
MEL08 PB5	500	< 1	22	12	1	0.27%	99.7%
MEL08 PB9a	0.15%	< 1	0.45%	10	0.12%	0.21%	99.1%
MEL08 PB12	600	< 1	0.76%	24	800	0.24%	98.9%
MEL08 PB13	600	< 1	0.64%	17	760	0.26%	99.0%
MEL08 PB14	0.20%	< 1	0.67%	5	130	0.29%	98.8%