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Julien Flament, Guillaume Sarah, Florian Téreygeol. Litharge cakes from Castel-Minier (Ariège, France): understanding strategies of the cupellation in a multi metals workshop from the 14th century. Montero Ruiz, Igniocio; Perea, Alicia. Archaeometallurgy in Europe IV, 33, Consejo Superior de Investigaciones Científicas, 2017, Bibliotheca praehistorica hispana, 978-84-00-10287-6. hal-01959856

HAL Id: hal-01959856

<https://hal.science/hal-01959856>

Submitted on 26 Jan 2023

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LITHARGE CAKES FROM CASTEL-MINIER (ARIÈGE, FRANCE): UNDERSTANDING STRATEGIES OF THE CUPELLATION IN A MULTI-METALS WORKSHOP FROM THE 14TH CENTURY

Julien Flament*, Guillaume Sarah*, Florian Téreygeol**

Abstract

Cupellation remains are among the most significant evidences of silver production for the Medieval period. However, these debris are rarely unearthed in archaeological context due to their fragility and their possible recycling. The exceptional corpus of cupellation remains from the metallurgical workshop at Castel-Minier (Ariège, France), dating from the XIVth century, provides the opportunity for a better understanding of the cupellation process for the late Middle Ages. Moreover, several pieces of earth lining impregnated with litharge entrapped metallic prills which were analysed using LA-ICP-MS. On the one hand our results highlight the quality of lead-silver bullion and silver produced in the workshop. On the other hand it is demonstrated how the distribution of metallic prills in the impregnated lining fragments reflects the manufacturing and recycling practices. Next, combining location of prills on linings' surface and their elemental composition, a thermodynamic model of the cupellation in Castel-Minier is proposed. Finally, LA-ICP-MS allows measurements of trace elements which are frequently used in provenance studies (bismuth, tin, antimony). Their behaviour during cupellation is studied and their relevance as ore tracers is discussed.

Key words: cupellation, silver production, litharge, impregnated earth lining, LA-ICP-MS, Pyrenees, Middle Ages.

Resumen

Los restos de copelación son una de las evidencias más significativas de la producción de plata durante el medievo, aunque raramente fueron descubiertos en contexto arqueológico a causa de su fragilidad y de su posible reciclaje. El corpus excepcional de fragmentos de cope-las halladas en el taller metalúrgico de Castel-Minier (Ariège, Francia), que data del siglo XIV, ofrece nuevas perspectivas para la comprensión de la copelación. Además, varias piezas contienen pepitas metálicas que fueron analizadas por LA-ICP-MS. Los resultados alcanzados destacan, por un lado, la calidad de lingotes de plomo de obra y de plata producidos en el taller. Por el otro, se ha demostrado cómo la distribución de las pepitas metálicas en los fragmentos de cope-la reflejan prácticas de fabricación y de reciclaje. Combinando la localización en las copelas y la concentración elemental de las pepitas, se propone a continuación un modelo termodinámico de copelación para el sitio de Castel-Minier. Por último, los análisis LA-ICP-MS permitieron efectuar mediciones de los elementos traza utilizados con frecuencia en los estudios de procedencia (bismuto, estaño, antimonio). Su comportamiento durante copelación se estudia y se discute su relevancia como trazadores de minerales.

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Palabras clave: copelación, producción de plata, copela, LA-ICP-MS, Pirineos, Medievo.

INTRODUCTION

The Medieval period in Western Europe is stressed by a large demand for noble metal particularly for coin minting. Since the establishment of silver monometallism from the late 7th century to the 8th century in this area, silver-rich ores became actively searched and mining extraction expanded rapidly. The economic development in Europe during the XIIIth and XIVth centuries is the culmination of this movement. For the Kingdom of France and during this period, the production of silver is estimated to several tons per year (Bailly-Maître and Benoit 1997). Over the last few decades, under the cover of new developments in archaeology and in materials analyses, a specific methodology was built-up for studying mining districts encompassing textual sources, archaeological data and experimental archaeology. It was applied fruitfully to several Medieval sites such as Brandes (Peloux *et al.* 2015), Paimpailly (Benoit 1997), Saint-Laurent-le-Minier (Bailly-Maître 2011) or Huneberg (Asmus 2012). Nevertheless, archaeological records of primary metallurgy operations are scarce and the few available sources are insufficient to sketch a realistic picture of silver production during the Medieval period. As a consequence, this part of the history of technology is often studied through the unique scope of metallurgical treatises from the early modern period for which Agricola's *De Re Metallica* is an eloquent example. The chaîne opératoire of silver production is frequently reduced to pyrometallurgical steps through a schematic tryptic encompassing roasting, smelting and refining. Cupellation is the most emblematic process of the refining step, however no related heating structure is recorded for the Medieval period. The discovery of numerous fragments of litharge impregnated earth linings undoubtedly related with primary silver production from a XIVth century workshop in Pyrénées (Castel-Minier, Ariège, France) marks an important watershed. Impregnated earth linings are cupellation wastes that give the opportunity to study this process through various scopes. First of all the manufacture of the bowl in which the process takes place can be studied. Then the quality of the lead-silver bullion processed at Castel-Minier can be highlighted as well as the purity of the silver produced. Finally our results could emphasise purposes of cupellation in Castel-Minier. They take part in larger thoughts about spatial and functional organisation of the site in order to reconstruct the silver chaîne opératoire active in this multi-metals workshop.

THE CUPELLATION PROCESS

Cupellation is a versatile metallurgical process defined by the porous bowl in which it takes

place. It is used to separate, by oxidation of a liquid mix, metals having differential affinity for oxygen. It has a wide range of applications, especially in extractive metallurgy, ore assaying, recycling and refining. These metallurgical processes involve different scales of cupellation and it is often referred to small scale cupellation for ore assaying or purity testing whereas large scale cupellation is related to extractive metallurgy or refining.

In the chaîne opératoire of primary silver production, cupellation is the last stage and it follows the smelting of argentiferous ores (of which the galena is the most common). Lead-silver bullion resulting from smelting is charged in a porous refractory hearth lining manufactured with bone and/or vegetal ashes. Once heated, lead-silver bullion starts to melt and transforms into litharge (PbO) under oxidizing conditions. Due to lower superficial tension, lead oxides are absorbed by the lining whereas silver remains metallic on the top at the end of the process. The used lining, full of lead oxides, is the most emblematic remain of this process but unfortunately rarely unearthed in excavations due to its degradation during burial. In addition, recycling practices in metallurgical workshops could also explain this scarcity. Cupellation by-products can be hard to identify and some disambiguation is required before studying them. Depending on the scale of the process, they do not have the same features and appropriate terminology must be defined. Concerning small scale cupellation, the term «used cupel» is proposed as it refers to the geometry of the bowl which is frequently preserved (White 2010). For cupellation at a larger scale, the expression «litharge cake» is consensual although an ambiguity remains between the impregnated earth lining and the lead oxide which could be removed from the furnace during cupellation. For this reason, we prefer to use «impregnated lining» to describe the fragments of large-scale bowl after it has absorbed lead oxides. This type of by-product can be identified by the nature of the material, the possible presence of a rim and metallic prills that can be trapped at its surface. As a consequence, it seems more appropriate to restrain the use of «litharge cake» to fragments of «pure» lead oxides collected either by immersion of bars or by the over-flowing method (Rehren *et al.* 1999).

STATE OF THE ART

As stated above and due to the absence of identification of heating structures linked to this process, by-products are often the only remains of cupellation available to understand the whole metallurgical process. The earliest evidences of

silver production by cupellation, dating from the late Uruk culture (around 3300 BCE), were discovered in Habuba Kabira (Syria) (Pernicka *et al.* 1998). It consists of hearths, made of calcareous clay or dolomitic marl, impregnated with lead oxides. For the Antiquity, cupellation is documented in relationship with large-scale production in mining and metallurgical districts. This is particularly true in ancient Greece where several litharge cakes from the Panormos workshop in the Laurion mining district were studied (Conophagos 1960; 1980). In Iberia several cupellation debris dating from the Tartessian period were unearthed. Impregnated linings and furnaces from the VIIth until the VIth century BCE were found in the Monte Romero workshop near the important mining district of Rio Tinto (Pérez Macías 1991). More recently it has been demonstrated that impregnated linings from La Fonteta (Alicante province) were manufactured to recover silver after the co-smelting of lead and argentiferous copper (Renzi 2013). Similar linings from the two sites of Huelva and El Cierro del Villar (Málaga) were also recorded (Rovira and Renzi 2013). One fragment of El Cierro del Villar entrapped a metallic prill whose analysis confirmed the cupellation of an argentiferous lead-copper mix. Later, several evidences of silver metallurgy were identified in many archaeological sites dating from the Roman period. Thus frequent finds of cupellation debris related to the refinement of debased silver were unearthed in British Roman sites (Bayley and Eckstein 1998). Similarly, hearth linings discovered during excavations in the Roman city of Ulpia Traiana (Xanten, Germany) demonstrated practices of silver refining from debased silver (Rehren and Kraus 1999).

The Medieval period suffers from a lack of archaeological evidences for cupellation. Nevertheless, some isolated debris are described for the Harz mountains district (Bartels *et al.* 2007), in the British Isles (Bayley and Eckstein 2004), in Saxony (Petr Hrubý *et al.* 2015) or in France within the Carolingian mining district of Melle (Téreygeol 2014). Silver metallurgy in Medieval Scandinavia is better documented with the discovering of cupellation debris (both cupels and impregnated hearths linings) in several sites dating from the VIIth to the XIIth century (Söderberg 2011). In the only scientific examination of a significant corpus published so far (Gribal 2011), 45 impregnated lining fragments from 12 archaeological sites dating from the Roman to the Medieval period were analysed with an attempt to correlate the time period and the nature of ashes used.

Finds of cupellation by-products increase for the early modern period but most of them are cupels dealing with ore assaying or purity testing—that is to say small scale cupellation. Thus,

cupels from the Tower of London, dating from the 16th century, were designed for the specific purpose of refining Ag-Cu alloys in close association with the Royal Mint (White 2010). Similarly, excavations of successive mints of archbishops of Trondheim provided 174 bone-ash cupels manufactured for metal testing (Ulseth *et al.* 2015). Small scale cupellation is also exemplified in the city of Montbéliard (France). Excavations provided a cupel, dating from the end of the 16th to the beginning of the 17th century, especially designed for the essay of argentiferous copper ore. Analyses revealed the use of a mix of vegetal and bone ashes (Martinon-Torres *et al.* 2008). Finally, among the by-products from the 16th century laboratory of Oberstockstall (Austria), some cupels were identified (Mongiatti 2009). In France, excavations of the early modern mint of La Rochelle provided a fragment of impregnated lining related to large scale cupellation for silver refining (Guirado *et al.* 2011).

This brief state of the art illustrates both the lack of archaeological evidences of large scale cupellation for the Medieval period and the absence of trapped metallic prills in the impregnated linings recorded. Extractive metallurgy of silver is underrepresented and impregnated linings found in archaeological contexts are scarce. They are often isolated pieces and no sizeable corpus from a unique site is known. In most cases metal was absent from impregnated linings, or not visually detected, hence previous studies focused on the morphology, typology and manufacture of the bowl. In order to identify raw materials some pieces have undergone microanalyses. Nevertheless, one should be aware of methodological limitations. In particular, some difficulties are often encountered in establishing the original composition of the lining, especially the distinction between vegetal and bones ashes.

CUPELLATION DEBRIS FROM CASTEL MINIER, NEW RESEARCH IN PROSPECT

Recent excavations in Castel-Minier (Ariège, France) provide an exceptional corpus of cupellation by-products which could partially fill lacks for the Medieval period. It is the most important corpus for Western Europe with 53 fragments of impregnated lining recovered so far. Moreover, several pieces contain metal as microscopic prills trapped at their surface. This last feature is exceptional and allows to go further in our understanding of the cupellation process as it was practised in the late Middle Ages. On the one hand, focusing on the elemental composition of metallic prills, the quality of raw materials and products of cupellation could be discussed. On the other hand, correlation between spatial

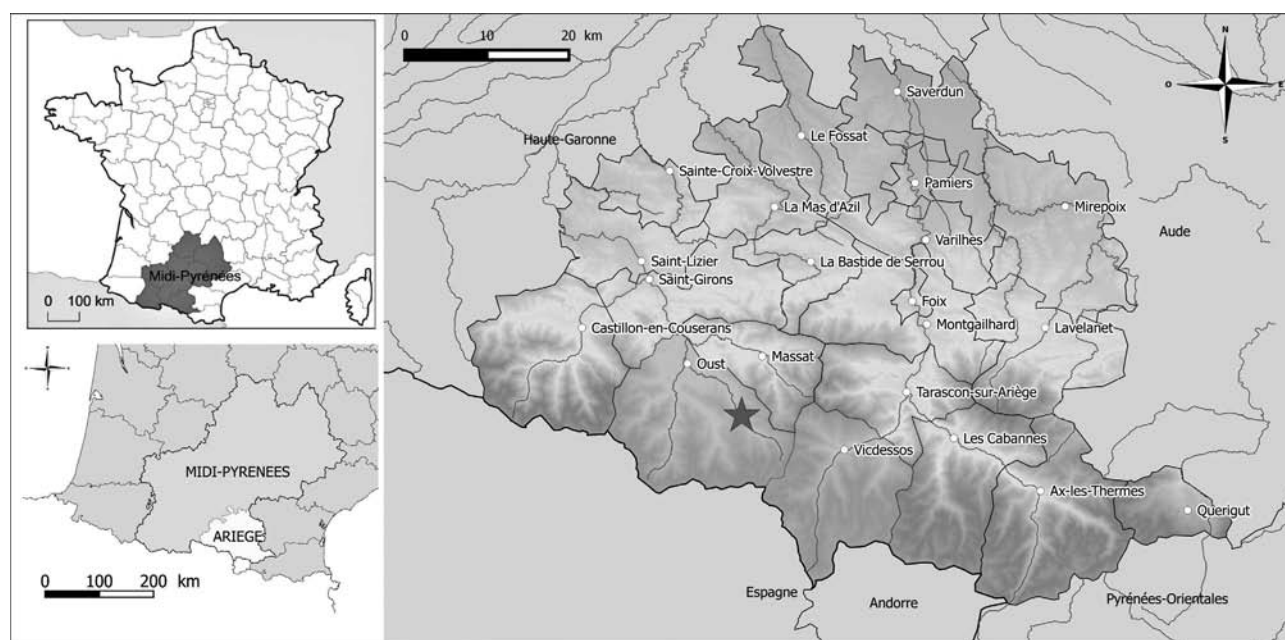


FIGURE 1: *Localization of Castel-Minier.*

distribution of prills on the lining's surface and their composition provides better understanding of the conduct of cupellation. In addition thermodynamics parameters of the system are discussed.

Castel-Minier is an archaeological site excavated yearly for more than a decade. The understanding of cupellation activities which took place there, among a wide variety of poly-metallic chaînes opératoires during several centuries, requires preliminary explanations. Located in the viscounty of Couserans in the central Pyrenees (Fig. 1), Castel-Minier associates mining and metallurgical activities. The orogeny of these mountains is complex with different events which entailed the formation of various mineralizations at different ages. As a consequence, several non-ferrous ores (such as galena, chalcopryrite and bournonite) were available to the Medieval miners. They were processed in a multi-metal workshop which was in activity from the late XIII to the XV century. Moreover in the course of the XV century, and until the end of the XVI century, iron production started at Castel-Minier. A metallurgical technology specific to the Pyrenees using hydraulic blowing and hammering-a mouline-was built in for this purpose (Téreygeol and Heckes 2012). As a consequence of the multi-metal nature of the workshop, the wide range of remains recovered in Castel-Minier are not easily discernible and attributable in such or such step of the chaîne opératoire. Various ores were encountered during excavations and several semi products, wastes and intermediate products are related to non-ferrous metallurgy.

Among them impregnated linings is the most emblematic evidence of cupellation. 53 fragments were discovered between 2012 and 2015. Except for one stock which was retrieved, probably stored for recycling, no spatialization could be enlightened and no heating structure can be associated. Nevertheless, all fragments exhibit a stratigraphic coherence as they were all found in levels dating from the 14th century.

DESCRIPTION OF THE CORPUS

The corpus of cupellation debris is composed of 53 fragments of impregnated lining. They are pulverulent and must be manipulated and conserved with care. Due to their specific nature, they are difficult to identify for someone little accustomed with the practice of cupellation or with metallurgical treatises from the early modern period.

The first identifying criteria of this debris is its density which is extremely high due to the presence of lead oxides. Then, the colour of the impregnated lining is a relevant evidence of the metallurgical process. Oxidation of lead during the cupellation entails the formation of lead oxides whose presence in the lining is revealed by a red or yellow coloration¹ at the surface. Concerning the corpus of Castel-Minier, lead oxides were identified whereas copper oxides were absent, suggesting that the debris recovered so far derive

¹ Red for litharge and yellow for lead monoxide (which forms above 600 °C).

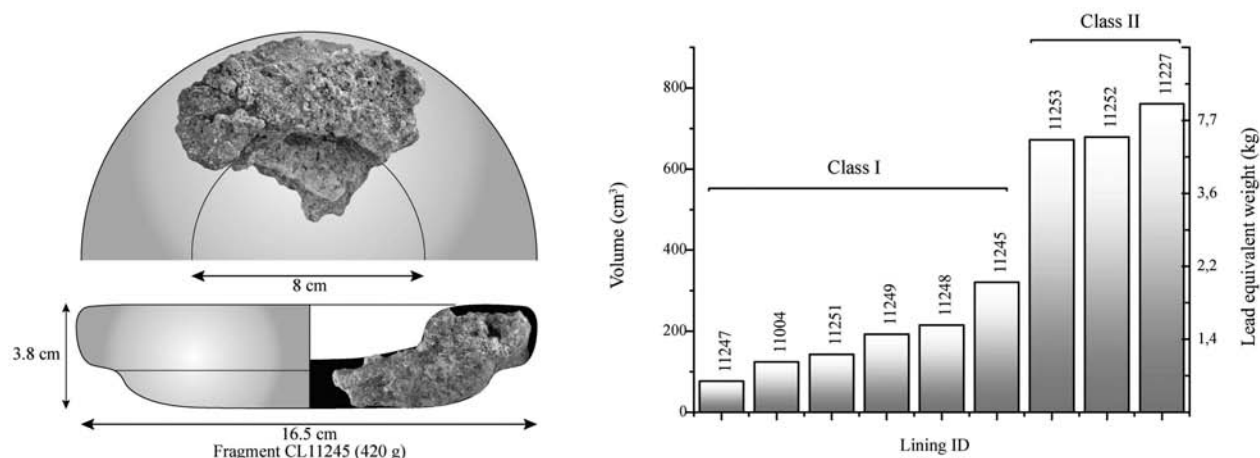


FIGURE 2: Typical geometry of impregnated lining (left). Classification of impregnated linings from Castel-Minier (right).

mostly from the processing of lead-silver bullion. Next, the texture and aspect of the impregnated linings are specific and should be described. The original lining is made of ashes which explains its porous nature and its grey colour once heated. From the observations based on the debris recovered so far, it can be stated that the lining used at Castel-Minier was made of non-washed vegetal basic ashes, probably wood ashes.²

The shape of the linings is concave, allowing better concentration of the refined metal (Fig. 2). Some large pieces present a rim³ which confines the pool and prevents from overflowing. There is a high variability in the geometry of the linings: although their thickness, ranging from 1.2 to 2.5 cm, is relatively homogenous, their diameters,⁴ on the contrary, vary from 9 to 24 cm. Thanks to these measurements, calculation of the lining's original maximum volume is possible. The estimated values range from 100 cm³ to 850 cm³ and permit distinction of two classes (Fig. 2) with corresponding maximum mass of lead-silver bullion between 800 g and 8 kg. These observations clearly demonstrate that at least two scales of cupellation were practiced at Castel-Minier.

ANALYTICAL METHODOLOGY

The analyses of the metallic prills trapped on linings' surface require a specific methodology

² Analysis of the ashes are not discussed here as they are still in progress. Nevertheless it is the first time that a corpus of impregnated linings made of wood ashes is highlighted. In the literature, analysis of such samples always revealed bone ashes or a mix of bone and presumed vegetal ashes.

³ The depth of the rim increases during cupellation as the metallic pool trims the lining (Téreygeol et al. 2013).

⁴ Measurable only for 9 large fragments of impregnated lining which original shape can be reconstructed.

suited to their microscopic size. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) appeared well-fitted and relevant to analyse these specific by-products. The Centre Ernest-Babelon (Orléans, France) has a long experience of archaeomaterials analyses by LA-ICP-MS in particular for glass and obsidian matrix (Gratuze 2014) as well as various metallic alloys (Sarah *et al.* 2007; Baron *et al.* 2014). Laser ablation allows micro sampling of metallic prills in situ without any preparation, preserving the integrity of archaeological artefacts. Furthermore pre ablation prevents from surface corrosion or depletion phenomena. This method allows quantitative measurements of a wide range of major and trace elements with low detection limits.⁵ For each element of interest, isotopes must be chosen carefully so as to avoid spectroscopic and atomic interferences. Elemental composition calculation is based on internal and external standardisation (Gratuze 1999) and requires reference materials specially designed for lead-silver artefacts studies.⁶

Archaeological objects are placed in an ablation cell and sampled by an excimer laser (ArF*, 193 nm). Its energy varies from 0.1 to 15 mJ and its frequency can be adjusted from 0.1 to 300 Hz.⁷ In addition, a wide range of ablation craters sizes are available (from 2 µm to 100 µm). These parameters must be carefully adjusted in order to maximize sensitivity and avoid inter elemental fractionation (Zhongxing 1999). During the ablation, the material is carried to the injector by means of argon flux where it is dis-

⁵ Below ppm for most of metallic elements measured in this study.

⁶ Elements measured are Ni, Cu, Zn, As, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Os, Au, Hg, Pb, Tl, Bi.

⁷ In our study, energy and frequency were respectively set to 4 mJ and 7 Hz.

sociated and ionized. Then ions are focused and sorted out according to their mass/charge ratio. Finally, ions are converted into electrons, using dynodes, and counted. For each sample, a background signal is measured prior to ablation. Reference materials whose composition is similar to the samples are analysed frequently during the session. Background is deducted from the signal which was then corrected, according to the isotopic abundance of the chosen isotopes, and normalized using internal standards. A relative response factor is calculated for each element present in the reference materials. Assuming that the sum of the elements concentration in the object is 100 %, it is possible to calculate each of them by using response factors.

PRODUCTS OF THE CUPELLATION

A total of 95 analyses were carried out on 88 metallic prills⁸ using LA-ICP-MS (Table 1). Elemental compositions range from the raw material (lead-silver bullion), to the final product of the cupellation (silver) with various intermediate compositions (Fig. 3), illustrating the different stages of the process. Among prills corresponding to lead-silver bullion several silver contents were measured. Indeed, it is linked to the quality of the argentiferous ore but also to the metallurgical process. Thus, lead is enriched in silver during reduction as a part of desilvered lead passes into the slag. Based on previous work (Rehren and Prange 1998) the minimum silver content of lead-silver bullion was fixed to 600 ppm which is the limit of economic desilvering for Roman times whereas analyses of few lead artefacts from Castel-Minier, obtained from reduction, suggested an upper limit of 1 500 ppm. Further works carried on archaeological ores and lead artefacts from the site will probably clarify this point. Copper was found as an impurity in the lead-silver bullion (below one percent) for most of the linings. This absence reveals that these pieces are linked to the processing of galena only. For metallic prills with higher copper content (for example CL 12113 in Table 1), it could be suggest that lead-copper-silver bullions were obtained by smelting of a composite ore (mix of galena and grey copper). Such ores were already unearthed in Castel-Minier, it consists of inclusions of tetrahedrite (with silver content ranging from 15.0 to 22.2 wt. %) in a galena matrix. One should notice the high degree of refining reached by ancient metallurgists with silver contents frequently above 99.0 wt. % – even though the composition of the final silver produced from galena at

Castel-Minier may not match the highest values determined for the metallic prills.

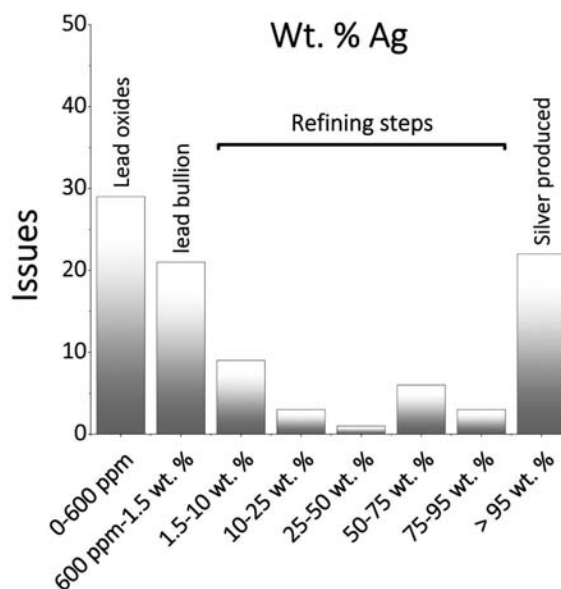


FIGURE 3: Classification of prills.

These analyses were then coupled to a spatial approach by a comparison between the composition of the prills and their position in the lining's surface⁹. This firstly allows to investigate the progress of cupellation and its efficiency. It is noticeable that the metallic silver is concentrated in the centre of the lining while lead partially enriched in silver is located at its periphery (Fig. 4). This distribution could be explained by pool fractionation caused by overflowing of the lining's rim. It can be proposed that silver could not concentrate in the centre while the decreasing temperature at the periphery resulted in the solidification of the metal. Finally metallic droplets, partially enriched in silver, remain. This behaviour does not mean that cupellation was unsuccessful. Pool fractionation is unavoidable during the process and experimental cupellations conduct frequently to the same result (Téreygeol and Guirado 2013). Finally, residual metallic prills could be easily withdrawn from the impregnated lining for later refining. In addition intermediate compositions are underrepresented in the centre of the lining that demonstrate the process efficiency.

THERMODYNAMICS OF THE SYSTEM

For each impregnated hearth lining, elemental composition of metallic prills are variable and

⁸ Between 2 and 18 prills per impregnated lining were analysed.

⁹ When the size and shape of the lining allows this investigation.

TABLE 1: Elemental compositions of impregnated hearth linings from Castel-Minier obtained by LA-ICP-MS. Unless otherwise specified data are in ppm. CL: laboratory code; US: stratigraphic unit.

CL	US	Ag	Cu	Pb	Au	Bi	Zn	Sn	Ni	As	Ru	Rh	Pd	Cd	In	Sb	Te	Os	Tl	Hg
10841_1	3082	259	98	99,96%	-	4	10	-	1	3	-	4	35	-	-	2	-	-	3	1
10841_2	3082	45	646	99,92%	-	5	7	-	1	3	-	6	52	-	-	2	-	-	3	1
10841_3	3082	46	99	99,52%	-	6	33	1	2	5	-	5	48	-	-	6	-	1	3	1
10841_5	3082	72,87%	239	27,04%	401	51	94	4	5	7	-	2	15	8	-	12	-	96	1	17
10841_6	3082	18,28%	71	81,70%	69	40	27	-	1	10	-	5	47	2	-	7	-	1	2	2
10841_6_1	3082	50,78%	147	49,17%	160	85	2	-	-	2	-	3	29	5	-	3	-	-	2	3
11004_1	2299	95,46%	2282	4,29%	7	120	3	1	3	3	-	1	15	13	-	6	3	33	1	4
11004_2	2299	91,67%	2225	8,08%	6	133	27	1	1	2	-	1	11	11	-	5	1	15	1	2
11004_3	2299	97,44%	449	2,50%	7	2	44	1	4	3	-	1	10	12	-	11	1	8	1	3
11004_4	2299	97,37%	5926	2,02%	7	121	5	1	2	1	-	1	5	11	-	2	2	16	2	3
11004_5	2299	63,34%	2298	36,41%	5	145	28	1	2	5	-	3	29	8	-	13	1	8	2	2
11229_1	2342	182	973	99,84%	-	5	249	7	10	20	-	12	106	1	-	69	-	2	4	1
11229_2	2342	275	1330	99,77%	-	6	217	2	7	18	-	8	76	1	-	87	-	258	4	1
11234_1	2348	2,86%	120	97,11%	-	20	-	-	1	-	-	13	115	1	-	-	1	11	4	1
11234_2	2348	1,92%	94	98,05%	-	16	-	-	1	-	-	12	116	1	-	-	1	12	4	1
11246_1	2351	99,36%	44	6350	9	-	-	-	-	-	-	-	1	17	-	-	-	-	-	4
11246_10	2351	275	1065	99,81%	-	7	277	5	25	15	-	173	58	2	-	211	1	-	-	8
11246_12	2351	99,61%	28	4142	10	-	-	-	1	-	-	-	1	17	-	-	-	-	5	4
11246_13	2351	99,45%	68	5447	9	-	-	-	-	-	-	-	1	17	-	-	-	-	4	7
11246_14	2351	150	174	99,94%	-	8	85	1	7	9	-	1034	56	-	-	28	-	-	-	1
11246_2	2351	99,20%	61	8226	9	-	1	-	-	-	-	-	1	16	-	-	-	-	4	4
11246_3	2351	1,08%	2164	97,92%	5	35	6837	81	256	202	-	21	83	56	1	578	15	1	2	122
11246_4	2351	3677	2088	99,93%	-	42	4293	35	265	150	-	10	46	5	0	200	1	-	-	10
11246_5	2351	103	117	99,96%	-	17	44	-	2	7	-	242	45	1	-	17	1	-	-	4
11246_6	2351	39	1089	99,85%	-	15	113	136	9	12	-	258	19	-	-	69	-	-	-	2
11246_7	2351	32	712	99,90%	-	23	194	-	4	5	-	438	50	1	-	28	-	-	-	1
11246_8	2351	184	268	99,94%	-	43	45	-	1	4	-	988	58	-	-	8	-	-	-	1
11246_9	2351	25	292	99,96%	-	7	3	-	2	1	-	1861	56	-	-	4	-	-	-	1
11247_1_1	2351	99,22%	42	8222	29	3	11	-	1	3	-	-	2	13	-	1	-	-	11	3
11247_2_2	2351	99,09%	46	9621	30	6	9	1	1	2	-	-	2	13	-	1	-	-	12	3
11247_4	2351	99,03%	137	1,01%	63	21	26	1	2	2	-	-	2	14	-	2	2	-	24	12
11247_5	2351	2795	399	99,68%	19	31	2	1	-	1	-	283	16	-	-	-	-	-	9	1
11247_7	2351	1365	685	99,79%	-	23	4	1	-	1	-	501	24	-	-	4	-	-	-	3
11247_8	2351	1,38%	102	98,58%	-	99	28	1	-	8	-	106	24	1	-	4	-	-	-	3
11248_1_1	2351	99,37%	78	6123	11	4	21	-	-	3	-	-	1	13	-	2	1	3	-	1
11248_2	2351	822	803	99,76%	3	80	373	3	10	49	-	7	66	2	-	207	1	4	4	1
11248_3_1	2351	98,88%	81	1,11%	12	2	12	-	-	1	-	-	2	14	-	5	1	3	-	2
11248_4	2351	98,04%	78	1,94%	13	14	45	-	2	5	-	-	3	14	-	5	1	4	-	2
11249_1	2351	220	202	99,91%	-	36	110	67	6	43	-	952	122	1	-	50	1	-	-	4
11249_2	2351	3082	241	99,67%	-	32	1	1	2	1	-	1073	123	-	-	-	1	-	-	9
11249_3	2351	166	699	99,87%	-	29	87	103	4	25	-	297	123	-	-	120	2	-	-	10
11249_4	2351	27	1000	99,87%	-	21	67	68	2	18	-	1015	111	-	-	75	-	-	-	2
11249_5	2351	2215	885	99,67%	-	9	3	1	1	-	-	14	129	-	-	1	-	2	5	1
11249_6	2351	2400	781	99,67%	-	8	5	1	1	1	-	13	124	-	-	5	-	3	4	1
11249_7	2351	660	445	99,87%	-	26	-	-	1	-	-	13	123	-	-	-	1	11	4	1

CL	US	Ag	Cu	Pb	Au	Bi	Zn	Sn	Ni	As	Ru	Rh	Pd	Cd	In	Sb	Te	Os	Ti	Hg
11249 8	2351	84	194	99,95%	-	62	11	4	1	8	-	14	131	-	-	7	-	7	4	1
11250 1	2351	176	236	99,93%	-	242	22	4	1	14	-	199	19	-	-	12	-	-	-	1
11250 1.1	2351	98,53%	239	1,54%	31	4	2	1	2	1	-	-	3	12	-	1	3	-	12	15
11250 2	2351	98,75%	257	1,30%	32	1	1	1	2	1	-	-	2	13	-	-	2	-	12	14
11250 2.1	2351	142	480	99,89%	-	5	256	4	6	24	-	56	24	3	-	166	2	-	-	7
11250 3	2351	59	253	99,94%	-	6	111	1	12	9	-	141	30	2	-	73	-	-	-	4
11251 1	2351	25	316	99,95%	-	9	28	9	1	7	-	474	34	-	-	15	-	-	-	2
11251 2	2351	16	455	99,94%	-	8	37	13	1	10	-	1120	38	-	-	19	-	-	-	1
11251 3	2351	28	654	99,91%	-	8	49	35	5	14	-	491	41	-	-	40	-	-	-	2
11251 5	2351	647	572	99,87%	-	32	-	-	-	-	-	743	48	-	-	-	-	-	-	3
11251 7	2351	15	277	99,96%	-	22	11	3	3	6	-	1278	55	-	-	3	-	-	-	1
11253 1	2351	839	429	99,86%	-	10	9	-	1	2	-	10	88	-	-	3	-	5	4	1
11253 2	2351	9273	1,19%	97,52%	33	23	74	70	105	83	19	16	68	21	5	31	204	2633	-	219
11253 3	2351	75	4147	99,48%	-	5	640	2	47	15	-	11	101	2	-	163	1	13	5	2
11253 4	2351	345	381	99,90%	-	10	80	-	2	4	-	11	98	-	-	13	-	2	4	1
11269 1	2299	98,84%	44	1,16%	5	-	1	-	-	-	-	-	2	10	-	1	-	1	-	3
11269 2	2299	99,10%	54	8936	6	-	8	-	-	1	-	-	2	12	-	-	4	1	3	-
11269 3	2299	97,71%	57	2,28%	6	-	4	-	-	-	-	-	3	12	-	7	-	2	-	2
11269 4	2299	92,68%	4020	6,91%	5	59	4	-	-	-	-	1	11	11	-	8	-	3	1	2
11269 5	2299	327	677	99,88%	-	16	68	-	-	3	-	12	107	1	-	13	-	-	4	1
11269 6	2299	25,61%	2249	74,14%	1	146	8	-	-	1	-	9	78	3	-	7	-	-	3	1
11269 8	2299	99,01%	47	9803	8	-	3	-	-	-	-	-	3	12	-	1	-	1	-	3
11269 9	2299	98,53%	170	1,45%	13	-	3	1	1	1	-	-	2	11	-	4	1	3	-	3
11494 2	2387	8158	646	98,86%	-	50	1780	12	48	186	-	13	117	9	1	179	1	15	5	4
11914 1	3125	98,85%	211	1,12%	6	-	1	-	1	1	-	-	2	15	-	-	2	17	-	4
11914 2	3125	642	404	99,86%	-	73	67	-	-	7	-	13	117	1	-	32	-	1	4	1
11914 3	3125	68	453	99,92%	-	6	45	-	-	4	-	13	116	1	-	45	-	2	4	1
11914 4	3125	98,33%	5894	1,07%	5	20	1	1	1	1	-	-	2	15	-	1	3	18	1	2
11957 3	3014	64	740	99,90%	-	33	34	-	2	2	-	8	71	-	-	4	-	1	4	1
11995 1	3126	2726	4628	99,23%	-	48	122	-	-	1	-	12	103	1	-	11	-	-	4	1
11995 2	3126	3651	4226	99,16%	2	51	323	1	-	2	-	13	117	2	-	24	-	1	4	1
11995 3	3126	6023	878	99,27%	-	67	5234	1	3	21	-	15	138	26	-	66	-	2	5	1
11995 5	3126	1343	1237	99,63%	-	24	923	-	1	2	-	13	119	2	-	6	-	-	4	1
11995 6	3126	137	572	99,90%	-	81	7	-	1	1	-	14	133	-	-	4	-	1	5	1
11995 7	3126	84,51%	3669	15,11%	11	5	47	1	5	3	-	5	41	17	-	35	5	32	1	7
12113 1	3074	1,91%	2,15%	94,70%	2	24	8945	7	47	299	-	15	129	37	-	2833	10	67	4	11
12113 2	3074	1,15%	7768	97,52%	-	5	2962	8	6	186	128	23	-	2212	2	12	2	12	5	2
12113 3	3074	5,95%	7330	92,95%	-	61	3283	1	26	33	-	14	118	10	-	133	2	11	5	2
12113 4	3074	5,95%	1,19%	92,23%	14	62	5797	2	54	40	-	13	113	31	-	150	2	16	5	2
12113 5	3074	10,78%	1317	89,04%	1	50	245	-	1	11	-	11	99	4	-	22	-	2	4	1
12113 7	3074	1262	2,84%	96,72%	1	15	2749	2	38	25	-	14	129	9	-	183	7	31	5	3
12661 1	3001	13,10%	1892	86,68%	1	60	44	-	2	1	-	12	107	1	-	7	-	-	4	1
12661 2	3001	5,19%	1268	94,65%	-	50	116	-	4	3	-	13	118	1	-	10	-	-	5	1
12661 3	3001	3,49%	563	96,43%	-	81	6	-	1	-	-	14	130	-	-	3	-	-	5	2
12661 4	3001	1,66%	685	98,25%	-	49	8	-	1	-	-	14	126	-	-	3	-	-	4	1
12661 5	3001	7,16%	1355	92,68%	-	56	1	-	1	-	-	14	127	1	-	2	-	1	4	2
12703 1	3194	59,14%	6870	40,12%	3	423	23	-	-	6	-	6	55	5	-	13	-	1	2	2
12703 2	3194	57,14%	6959	42,11%	2	365	62	-	-	4	-	6	56	6	-	11	-	-	2	1

TABLE I:

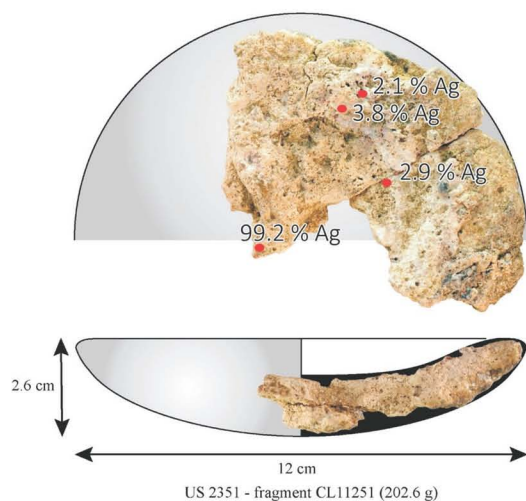


FIGURE 4: Distribution of silver content on lining's surface: pool fractionation evidence.

seems to be depend of their position on the lining. Thus, combining the spatial distribution of prills and their elemental composition it is possible to investigate the thermodynamic parameters of the system. The success of cupellation involves two major thermodynamic parameters: temperature and air flux. Indeed oxygen is required for lead oxidation and litharge formation. In addition, an elevated temperature must be maintained in the furnace to keep the litharge liquid so it can be absorbed by the porous lining. These requirements could not be fulfilled for the entire surface of the lining as we illustrated previously on lining's periphery or as experimental archaeology has demonstrated. For several impregnated linings from Castel-Minier only reduced areas where cupellation was carried until its conclusion could be defined. As expected, higher silver contents are encountered in prills located at the centre of the lining and lower content at its periphery (Fig. 5). According to these observations, a precise location of the air inlet can be suggested. Moreover, the elemental composition of the metallic prills helps identifying and drawing a thermic gradient on the lining's surface. Combining these two parameters a partial thermodynamic model was established for one impregnated fragment. It is important to notice that the effective area of cupellation is reduced and does not match with the whole lining. In absence of furnace remains we can just argue that forced blowing used for cupellation results in a highly localized hot spot. Similar behaviour was observed during experimental cupellation that tends to validate our theory (Guirado *et al.* 2010).

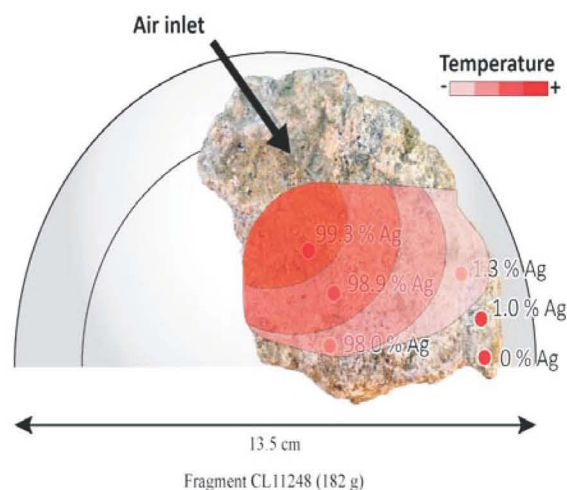


FIGURE 5: Thermodynamic model of cupellation in Castel-Minier.

RECYCLING AND REUSING OF IMPREGNATED LININGS

To go further in the understanding of the cupellation process, some impregnated linings were cut to study cross-sections. In particular, we focused on the presence and the distribution of metallic prills. This study aims distinguishing two kinds of metal trapping in the cake during cupellation. The first kind is the filling of the lining's cracks. Metallic prills are easily identified near the surface of the lining (Fig. 6). Cracks at this location are consequences of flaw of the lining. In particular, ashes insufficiently grinded or badly compacted during manufacturing entail cracking due to heat shrinkage.

The second kind of trapping is due to lining reshaping. After a first cupellation, the earth was reshaped and a new lining was manufactured above the first. Thus metallic prills, unremoved from the first cupellation, remained entrapped at the interface between the two linings. There are many evidences of such practice of reusing. The first one is the presence of metallic prills on the whole lining (Fig. 7), suggesting that several cupellations were conducted successively. Indeed, the trapping metal so deep in the lining during a single operation is highly unlikely.

The second clue for lining reshaping is given by the distribution of the metallic prills in cross-sections of impregnated linings. Prills are not distributed randomly but regularly organised in such a way that they define a limit which separate two different linings (Fig. 7). These linings correspond to two different cupellations hence their dissimilar aspect. Indeed litharge crystals from upper and lower linings are different in size as well as in growing directions suggesting that liquid litharge was absorbed at different

times. Thus it is possible to propose functional interpretation of some impregnated linings. A first lining is manufactured with vegetal ashes and a first cupellation is conducted. At the end of the process, a second lining is shaped on the first one and a new cupellation takes place. The practice of lining reusing and reshaping was recently tested experimentally in order to discuss its feasibility and efficiency.¹⁰ Positive results were obtained in all cases with successful production of silver. Moreover, experimental impregnated linings exhibit the same facies. In particular, the interface between the two linings is clearly visible from the prills' distribution (Fig. 7).

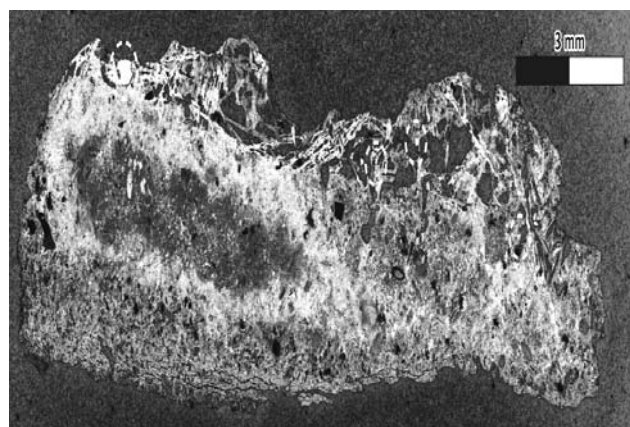


FIGURE 6: Prills filling cracks in an impregnated lining.

One could be surprised by the relative high quantity of metallic prills found in the impregnated linings from Castel-Minier demonstrating that their removal was not systematized. This could be simply explained by recycling practices in Castel-Minier. According to metallurgical treatises from the early modern period, impregnated linings could be grinded and loaded in the smelting furnace. Litharge acts as a melting agent increasing the fusibility of ores. Another argument strengthens this hypothesis. Impregnated linings discovered at Castel-Minier represent a production of few kilograms whereas in the beginning of the xiv, according to rare textual sources,¹¹ 1 250 kg of silver were produced annually. Relatively to this production, the scarcity of impregnated linings in Castel-Minier demonstrates recycling practices.

¹⁰ These experiments were conducted in summer 2015 on the international site dedicated to experimental paleometallurgy in Melle (France).

¹¹ We refer to Paolo Girardi, in charge of the mines of the Kingdom of Navarre in the first half of the xiv century. Silver production of Castel-Minier is mentioned in his dissertation for the king Philip III, dating from 1340 (Muguetta Moreno 2004).



FIGURE 7: Archaeological (top) and experimental (bottom) lining reshaping.

TOWARD A BETTER UNDERSTANDING OF TRACE ELEMENTS BEHAVIOUR DURING THE CUPELLATION

Quantitative measurements of trace elements in metallic prills were carried out using LA-ICP-MS. These elements are frequently used in various studies in particular for distinguishing groups of artefacts or provenancing. The understanding of both the metallurgical processes involved and the behaviour of trace elements are nonetheless very important to use them fruitfully. Pioneer studies were conducted for iron metallurgy in particular the distribution of trace elements between slags and semi products (Leroy *et al.* 2012). Non-ferrous metallurgy is also involved in such researches. For example, the study of trace elements fingerprinting in copper permitted defining relevant elements for provenancing or technological studies (Pernicka 1999). Recently, the evolution of the platinum-group metals versus gold ratios during gold refining was studied and their stability was demonstrated (Blet-Lemarquand *et al.* 2014). Unfortunately silver production, as it is a complex metallurgy with several steps, did not benefit from the same consideration. The chaînes opératoires are diverse and complex with many particularisms according to ores qualities, technologies involved or level of skill.

The analyses of metallic prills trapped in impregnated linings from Castel-Minier contribute to this debate. Although this study does not intend to examine the behaviour of all trace elements during silver production. For the example of Castel-Minier it only aims to provide some guidelines for understanding the cupellation process in Medieval times. Some trace elements identified during LA-ICP-MS analyses (tin, antimony and bismuth) were selected and their behaviour during this metallurgical process was studied. As presented above, the determina-

tion of the elemental composition of metallic prills allowed us to identify lead-silver bullion, silver produced and various intermediate compositions. Thus, all steps of cupellation are represented and consequently the evolution of trace elements concentrations during the entire process could be investigated.

Bismuth behaviour is chosen to illustrate our results as its content is extremely variable in silver artefacts and often used as an ore tracer. Until recently, no specific work had been done to understand bismuth behaviour during cupellation. L'Héritier *et al.* (2015) investigated the evolution of bismuth content during cupellation and partitioning between lead and silver. They pointed out the distribution of Bi at the top of the cupel i.e. in the litharge formed at the end of the cupellation, suggesting that Bi was removed from lead-silver bullion at this moment. Although the process cannot be fully compared due to differences in scale production, similar behaviour was observed for impregnated linings from Castel-Minier. At the beginning of the cupellation, Bi content is quite stable (Fig. 8). Small variations are due to different qualities of lead-silver bullion and possible enrichment or depletion phenomena during smelting. Following the process, Bi enrichment started around 25.0 wt.% silver. Around 97,5 wt.% Ag, a threshold from which Bi is removed is clearly identified. At this point, this metal is absorbed by the lining. Similar evolution was observed for Sb and Sn but with lower threshold values. These thresholds represent the starting of the oxidization. It varies for each element as they do not have the same affinity for oxygen.¹²

¹² A study of Ellingham diagram demonstrates it: Gibbs's energy required for oxides formation are different.

Finally, trace elements concentration in the final product is highly dependent on the silver concentration. From one quality of silver to another, Bi could be present or absent. This variability is not related to the ore nature but to the metallurgical process, in particular the moment at which cupellation stopped.

CONCLUSIONS

With 53 pieces¹³ the corpus of impregnated lining from Castel-Minier is among the most exceptional recorded so far. For the first time, metallic prills were identified in several fragments and analysed. This particularism allowed studying cupellation in an original way focusing not only on the impregnated lining but also on metals from different steps of the process: lead-silver bullion, intermediate states and final products. This study using quantitative measurements by LA-ICP-MS provides new lights for the understanding of cupellation. Firstly the quality of the lead-silver bullion and silver produced were defined. In particular, one should notice the wide range of silver qualities obtainable for a same workshop. This variability has a crucial implication on trace elements contents in the final product in particular for Bi. Secondly, based on correlation between elemental composition of metallic prills and their distribution in the lining's surface, the conduct of the process was highlighted. Thus, pool fractionation was identified and a partial thermodynamic model of cupellation (combining temperature and oxygen flux) have been proposed. Finally, part of

¹³ The corpus increases each year as excavations are still in progress.

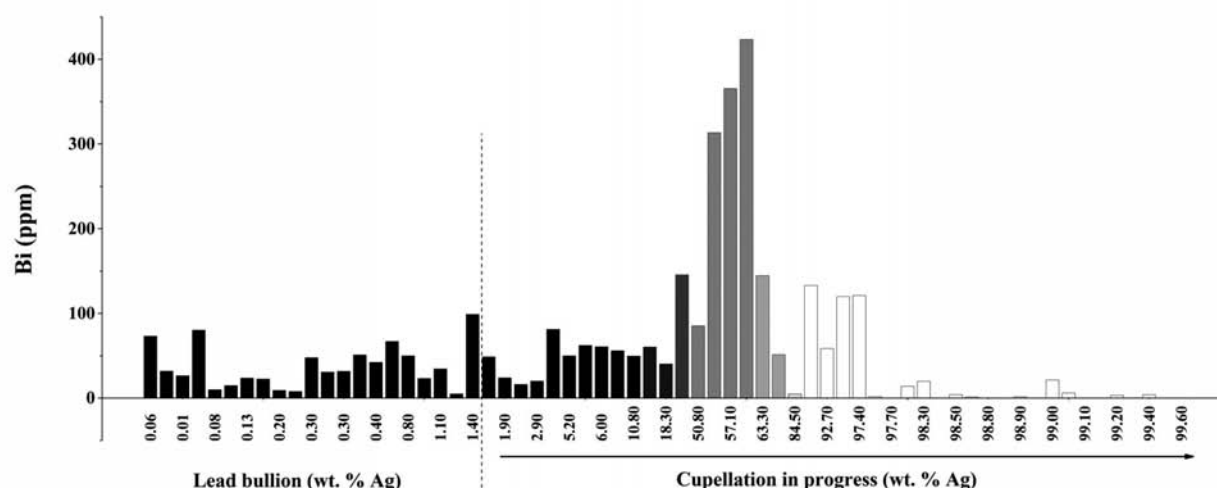


FIGURE 8: Evolution of bismuth behaviour during cupellation.

the chaîne opératoire at work in Castel-Minier has been defined, in particular reusing practices with reshaping of the lining to conduct new cupellation.

However, some aspects of cupellation are still unclear and need further works. Thus, the scale of cupellation is a challenging problem. Diameters of initial lining suggest no litharge removing during cupellation whereas some «pure» litharge (up to 1 kg), with Pb-Ag prills trapped inside, were discovered during excavations in Castel-Minier. They clearly testify another scale of cupellation more suited to mass silver production as suggested by textual sources from the early modern period.

The first results on trace element behaviour (Bi, Sb and Sn) during cupellation are encouraging. Even if they cannot be extended to all silver artefacts they highlight how trace elements concentrations are strongly process-dependent. Based on these observations careful consideration should be given to conclusions drawn solely with trace elements concentrations. Taking into account influence of metallurgical process could prevent from misinterpretations in provenance studies.

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