Der Anschnitt, Beih. 50, pp.87 – 104, 2023, https://doi.org/10.46586/DBM.264.395

George D. Papadimitriou

Cupellation and litharge in their technological context at Laurion, Attika (Greece) – From Prehistoric to Hellenistic and early Roman periods

ABSTRACT: *The extraction of silver and lead at Laurion started in prehistoric times and reached its peak in the classical period, it passed through crises and recoveries during the Hellenistic period and finally ceased permanently in the beginning of the Roman period. During this long period of time, the techniques used for silver extraction were adapted to the raw material available and the production scale. Among them, cupellation variants of argentiferous lead for silver production were evidenced at many locations of the wider area of Laurion, as it is shown from findings of different types of litharge and cupel forms and sizes, located close or at a greater distance from the source of the ore.*

In the present work, the process of cupellation is described from a scientific and technical point of view and an attempt is made to interpret the remains that were preserved on the surface or found in excavations, with regard to their technological context. The technology of the cupel of the classical period at Laurion is examined and compared with the corresponding technology of the prehistoric period and with cupels made from porous ceramics of the Middle Ages in Europe. Litharge, the waste of the cupellation process, is also thoroughly examined, since it plays a key role in the performance of the process for minimizing silver losses. But this material, even after its removal from the furnace, remained still useful in applications of technological or economic importance, to which reference or brief description is also made in the text.

KEYWORDS: CUPELLATION, LITHARGE, FURNACES, LAURION, ANCIENT METALLURGY

Introduction

The old-world mining and metallurgical history of the wider area of Laurion, also known as Lavreotiki, extends from the Late Neolithic to the Roman and early Byzantine period. In recent times, after a long period of inactivity, mining and metallurgy have been resumed from about the middle of the 19th to the middle of the 20th century AD. (Kordellas, 1867; Ardaillon, 1897; Conophagos, 1980).

In the old technological history, there are, however, intermediate gaps, most probably due to lack of evidence as opposed to the absence of activities in the corresponding periods.

The most imperfectly known aspect of Laurion is its technological path through prehistoric times, which extends further until the end of the Archaic period. This is due mainly to the rarity of relevant findings. The failure to find prehistoric metallurgical remains inside the central mining zone of Laurion, has been attributed to the fact that older residues were recycled, moved or covered with newer ones during periods of intense mining and metallurgical activity, so that today it is difficult to isolate and identify them. Nevertheless, it is now confirmed that copper, silver and lead had begun to be produced at Laurion since the end of the Neolithic era, thanks to the isotopic analysis of lead contained in prehistoric metal objects, which proved that a significant number of them had been produced from silver and copper from Laurion (Gale and Stos-Gale, 1981, p.211 – 13; Stos-Gale, 1989, pp.287 – 88).

Prehistoric remains of silver metallurgy (mainly litharge and lead pieces, fragments of cupels and smelting slags) associated with Laurion, have been identified at Thorikos, in a settlement near the top of Velatouri hill, where silver production was evident from cupellation residues (Servais, 1967, pp.24 – 7) and on the islands of Makronissos (Spitaels, 1982a, p.158) and Keos (Gale and Stos-Gale, 1981, p.191; Gale and Stos Gale 1984). Significant concentrations of litharge and other residues of the prehistoric period that are clearly related to silver production were found more recently in Mesogeia, at the site of Lambrika-Koropi, at Koropi and other nearby areas (Kavogianni, et al., 2008, p.58 – 62). In particular at Lambrika, along with pieces of litharge, a large number of broken shallow bowls were discovered and have been characterized as a particular type of litharge, but in my opinion are certainly prehistoric cupels. These indicate the existence of an argentiferous lead cupellation workshop which, according to the dating, was active in phase I of the Early Bronze Age (Kakavogianni, et al., 2006).

Findings concerning copper metallurgy have been identified at Raphina (Theocharis, 1952; Theocharis, 1954) and on the island of Keos (Coleman, 1977).

The sites above are located at the wider periphery of the mining zone, with the exception of Thorikos and Makronisos which are close to Laurion.

Mining activity in Lavreotiki during the prehistoric era is known from the hill Ovriokastro of Keratea, on the southern slope of which there are mining traces in the first metalliferous contact, outcroppings on the surface, as well as obsidian blades and fragments of vessels of the Final Neolithic period (3500 – 3000 BC) and from the Early Bronze Age I (3000 – 2800 BC) (Kakavogiannis and Kakavogianni, 2001, pp.55 – 85).

But the only prehistoric mining work that has been thoroughly studied so far is the Mine 3 at the foot of Velatouri hill, west of the Thorikos Theatre (Spitaels, 1984). It dates back to the 3rd millennium BC and was opened for the extraction of lead ore from a vein outcropping on the surface. There have not been remains of silver metallurgy at this place, but fragments of litharge of the same period, were found in the prehistoric settlement of Provatsa in the near-by Makronisos island (Lambert, 1972; Spitaels, 1982a).

In Thorikos the production of silver continued during the Late Bronze Age (Mycenaean period), as evidenced by the presence of fragments of Mycenaean vessels in Mine 3 (Spitaels, 1982b).

During the Classical period, well organized mines, ore dressing plants and metallurgical furnace compounds were active, producing silver and lead. The relevant technology is mainly known from archaeological excavations (Conophagos, 1980; Jones, 1982; Tsaïmou,1988; Kakavogiannis, 2001) as well as from an important number of archeometallurgical studies. Iron production from local ores has been, also, documented in the same period (Conophagos and Papadimitriou 1982, p.363).

During the Hellenistic times the number of active mines was reduced, due to political instability. Mining experienced long periods of crisis, but during the 2nd century BC mining activities resumed. During this period the exploitation of ores in deeper horizons (the so called “third contact”) was intensified by means of mining shafts. The ores extracted from them included sulphides very rich in silver; for example in the regions of Ari and Soureza contents up to 5,000 g Ag/t Pb were found. At Demoliaki, which is situated near to Ari, Hercules Katsaros located a few years ago, the first roasting furnace for sulphides (Papadimitriou and Katsaros, 2019) which allowed roasted sulphides to be smelted in the conventional smelting furnaces. In the same period, a new technology for recycling of old stocks of litharge was developed due to the discovery of, high productivity, circular mills, which enabled fine and uniform grinding of the material (Papadimitriou, 2015, 2016).

There is no information on possible production of silver at Laurion after the Hellenistic era, except from Strabo (9,1,23), reporting on recycling of old waste stocks for production of silver. Then the eclipse of Laurion is attested by Pomponius Mela (II,3,46) in 40 AD and is confirmed by Pausanias in the 2nd century AD (1,1,1). However, some activities are confirmed later, at the beginning of the Byzantine period, as evidenced by the discovery of coins of the 4th century AD (Cordella, 1894, p.239; Conophagos 1980, p.385). There is, also, a reference by Silentarius Paulus to the Inauguration of the church of Hagia Sophia in Constantinople in 563 AD, according to which the decoration of the church was made with silver from the Mines of Pangaion and Laurion (Corpus Scriptorum Historiae Byzantinae, 26, pp.679 – 80).

From the previous review it is clearly seen that cupellation was the technique continuously employed, from the Final Neolithic period and onward, since remnants of litharge have been identified in sites of either period of prehistoric and then of historical times until the end of the Hellenistic period. Furthermore, the cupellation findings scattered across various locations, near or in the periphery of the source of the ore, are an indication that the process of cupellation was practiced also as a small-scale metallurgical process, independent of smelting and mining. These reasons could justify possible local variations of the process, and adaptations to the production scale. Unfortunately, no place is known until now where a cupellation furnace along with its workshop and relevant remains are still preserved and studied. For this reason, many issues of cupellation of argentiferous lead remain open, so that discussion continues with much interest, especially for the prehistoric period, where the interpretation of some archaeological findings, still remains controversial.

In the present paper the cupellation process is described and discussed, with emphasis given to its operation at Laurion, based mainly on the study of local findings. In the same context a brief description is given for the roasting and smelting processes which are stages of the production chain of silver and lead, prior to cupellation.

Special sections are devoted to the technology of cupels and to the metallurgical properties of litharge, since both of them are of main concern for the good performance of the process for avoiding/minimizing silver losses. A particular section is also devoted to the cupellation process of the prehistoric period attempting to interpret the exact role of the cupels in the form of shallow bowls with depressions at their bottom, which were found at many places of Laurion and more recently in a large number at Lambrika-Koropi.

Litharge, after it was discarded from the cupellation furnace, was not a real waste, since it became later a source of revenues from production of silver and commercial lead after recycling. Furthermore, due to its special properties it was used in many different applications such as waterproofing mortars for cisterns (Conophagos and Papadimitriou, 1978; Papadimitriou and Kordatos, 2001) and ceramic fabrics for making cupels. These issues are also mentioned or briefly described.

The present work is limited as far as possible to technological issues, without extending to archaeological ones, for which there is a significant number of archaeological studies available (see Andrikou, 2015, Kakavogiannis, 2005).

Ore smelting

The first stage of silver production process from ore at Laurion was smelting. The charge smelted comprised mainly cerussite with possible addition of galena up to 20 percent (Conophagos, 1980, pp.278 – 79). It is of course known that there is a possibility of a combined process of roasting and reduction of the ore in one single stage in the reduction furnace, as described by Hauptmann, et al. (1988, p.110 – 11) for Thassos, but so far it remains open whether it was used at Laurion (Bachmann, 1982, pp.248 – 51). In any case, the product obtained from smelting was argentiferous lead, an alloy of lead containing silver at a ratio varying between 1,000 and 4,000 g Ag/ t Pb, depending on the ore used. The most common average silver content was around to 2,000 g Ag/t Pb.

Fig. 1: Remains of the Megala Pefka smelting furnace at Legrena, Laurion). The semi-circular supporting wall of the furnace shaft with the air inlet stone-built channel at its base. (Photo: G.D. Papadimitriou).

Fig. 2: Remains of a smelting furnace at Ari (Laurion). The shaft was based on two stone boulders, carved internally in a circular cross-section of 1 m diameter. The air inlet was through a vertical stone-built channel at the back of the furnace. (Photo: G.D. Papadimitriou).

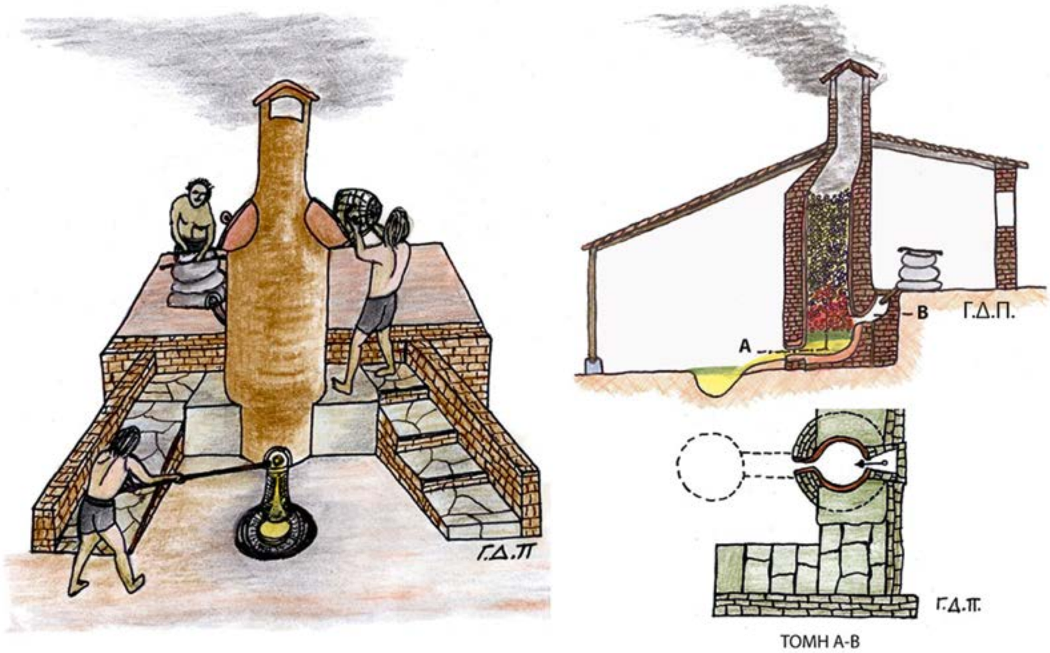

Fig. 3: Schematic representation of the smelting furnace at Ari (Laurion). (Drawing: G.D. Papadimitriou).

Smelting was done in shaft furnaces using charcoal as heating and reducing agent. Photographs of remains of smelting furnaces at Laurion in the areas of Megala Pefka and at Ari are shown in Fig. 1 and 2. A schematic reconstruction of a typical smelting furnace, based on the previous remains, ancient texts (Diosc. 5,85) and Attic vase paintings (Chatzidimitriou, A., 2005, tab. X2, X12, X13) is shown in Fig. 3 (Papadimitriou, 2018).

The internal diameter of the furnace is about 1m and the height is estimated at 2 – 2.3 m. Three consecutive levels serve the operation of the furnace: the ground level, where the furnace is based and where liquid lead and slag are concentrated in a pit, the second level accessible by a staircase, from which a worker charged the furnace with ore and charcoal and the upper level, behind the furnace, where one or two workers operated skin-bellows for furnace blowing, Fig.2. The air blown was directed through a vertical stone-built channel and entered at the back of the furnace. No residues of ceramic channels were found during excavations.

In order to have a proportion of sulphides higher than 20 % in the charge, the miners had to expose the sulphides to an oxidizing roasting environment, in order to convert them to oxides before smelting.

Roasting was certainly known and practiced in the antiquity using stalls or roasting furnaces, however, only one

Fig. 4: Remains of a roasting (or calcination) furnace for galena (PbS) at Demoliaki (Laurion). (Photo: G.D. Papadimitriou).

Fig. 5: Schematic representation of a roasting furnace during the charging phase with galena and a small proportion of charcoal. (Drawing: G.D. Papadimitriou).

roasting furnace has been discovered so far. This furnace has been at Dimoliaki and discovered by Hercules Katsaros.The furnace is contemporary to the smelting furnaces at Ari (Papadimitriou and Katsaros, 2019), belonging to the Hellenistic period (Tsaimou, et al., 2015). It is a strong construction with 0.9m thick stone-walls, having the form of an inverted truncated cone, broadening upward with a slope of about 10 degrees, with a height of 2.2m and, an unusually large, diameter of about 2.5m, compared to the smelting furnaces which had an internal diameter of only 1m. Few slag foams remain attached on the wall near the furnace mouth, indicating that during operation the furnace was filled up to its top and that temperatures of 800 – 900 °C prevailed, locally, at this uppermost zone, leading to melting of the most fusible ore components. This is certainly due to the abundance of free air available near the wide furnace mouth.

A photograph of the remains and a reconstruction of the roasting furnace are presented in Fig. 4 and 5 respectively.

If the ores containing silver (or in other cases gold) were not ores of lead, but –for example- oxidized ores of iron, then they were subjected to leaded smelting (Hauptmann, 2020, p.338). They were smelted in the presence of a quantity of lead, so that silver was again dissolved in lead, giving argentiferous lead from which the precious metals were extracted by cupellation. As a matter of fact, lead is an extremely efficient scavenger of silver and gold. This technique was probably used in ancient times in the region of Pangaion mountain in Macedonia and in Chalcidique during the Byzantine period but nothing so far indicates its application at Laurion.

In 1864, about 30 heaps of ancient smelting slags were identified at different mining locations of Laurion by Kordellas, who recorded them on behalf of the State. About half of them were by the sea and the rest in the hinterland. Their reserves amounted to 1.5 – 2 million tons and were smelted by the Greek Metallurgical Company for lead production between 1865 and the beginning of the 20th century.

Assuming that each heap of slags was created from one complex of furnaces, we must accept the existence of at least 30 furnace complexes active in antiquity (from the Archaic to the Hellenistic period). However, only in six places remains of furnaces have survived and four of them have been excavated. Most furnaces were probably constructed during the Archaic and Classical period for the production of argentiferous lead intended for production of silver by cupellation, but their last period of operation should be placed in Hellenistic and Roman times. These were mainly used for the production of commercial lead from litharge and low content ore wastes (ekvolades), possibly aided by the addition of a small quantity of old slag relatively rich in lead. This was the case with furnaces at “Ari”, as confirmed by radiocarbon dating of charcoal samples that gave a calibrated date (2σ) of 246-03 BC (Tsaïmou, et al., 2015, p.118).

Cupellation at Laurion in the Classical period

In order to separate and recover silver from argentiferous lead produced in the smelting stage, only a unique method was known: “cupellation”.

Cupellation is a process separating silver and lead by the selective oxidation of lead from an alloy of predominantly lead and silver composition (argentiferous lead).

The method consists in melting the argentiferous lead in a cupel placed inside a reverberatory furnace by burning wood or charcoal and blowing air on the surface of the bath by means of bellows (Fig. 6).

During this process lead is selectively oxidized to form litharge (lead oxide, PbO) which is immiscible with lead and has a lower density, so it floats as a thin liquid layer on top of the bath of lead.

As soon as the layer of litharge reaches a thickness of about 1 – 2 mm, it is somehow removed from the surface of the melt, so that, by continuing air blowing, the quantity of lead in the cupel diminishes and silver content increases progressively in the bath. The temperature should be maintained around 900 °C, given that litharge melts at 880 °C. Pure silver melts at 962 °C, but remains in solution in the liquid alloy almost to the end of the process, namely until the liquid alloy content reaches 90 % of silver. Then it begins to solidify and, therefore, the temperature should be increased to about 1000 °C, so that the alloy remains in a liquid state for as long as necessary to complete the removal of lead and impurities.

When almost all lead is oxidized and removed, silver remains in the bottom of the cupel, as an alloy of silver containing mostly lead and copper as impurities (in actual metallurgical jargon this alloy is called a “doré”). Then with further oxidation of the last impurities, silver becomes superclean, its melting point increases sharply leading, eventually, to its solidification. This is the end of cupellation

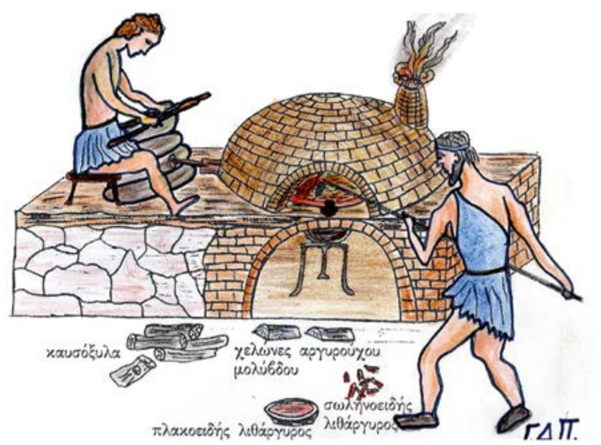

Fig. 6: Virtual reconstruction of a cupellation furnace of the classical period at Laurion. (Drawing: G.D. Papadimitriou).

Fig. 7: Very shallow cupel of the classical period at Laurion, from the collection of K. Konophagos (Author's modification from Conophagos, 1980, p.315, fig.12-4).

Fig. 8: Deep Cupel of conical form from Megala Pefka (Legrena, Laurion), Classical to Hellenistic period. (Photo: G.D. Papadimitriou).

and it is clearly perceived from the characteristic "glancing of silver". This is attributed to the latent heat that is abruptly released from the solidification of silver.

However, the description above is rather simplified from a technical point of view. In practice, the process of cupellation was certainly done in two successive stages in order to limit losses of silver withdrawn inside the rejected litharge. This issue is described below.

It should not be disregarded that during cupellation a small fraction of silver oxidizes as Ag_2O and dissolves into the mass of liquid litharge. As a matter of fact, liquid litharge which forms on the surface of the metallic bath is a sort of slag and chemical elements and oxides such as CaO, SiO_2 and Cu/Cu_2O, including silver, are partitioning between the metal and the slag. Modern experiments show that the quantity of the silver lost in litharge as silver oxide, would cause silver losses of the order of 1–3 % (Swinbourne, et al., 2003, C73; Ulseth, et al., 2015, p.269). It is not possible to avoid completely these "chemical" losses, but it is possible to reduce them by applying cupellation temperature which is as low as possible. The control of this process requires however a deep metallurgical knowledge and a strict control of temperature, something that was certainly beyond the skills of ancient metallurgists. However, a more practical means for reducing this kind of losses is by removing the litharge as soon as possible from the surface of the bath, before it becomes saturated in Ag_2O. Removal of litharge from the surface of the bath is also advantageous because it allows direct contact of air with the lead, accelerating thus the oxidation process.

In the Classical period, litharge was aided to flow over the rim of the cupel and run out of the furnace, by the impact of the air blown on the bath. Alternatively, it was removed from the surface of the cupel by means of a scraper. At the same time, the volume of litharge removed was replaced by a corresponding addition of argentiferous lead in the form of ingots. During the removal of litharge from the cupel, small masses of liquid argentiferous lead were inadvertently entrapped in litharge and were carried away, forming solid inclusions inside the litharge mass after its solidification. This was a second type of silver loss, a "mechanical loss", which was more important than "chemical loss" described above, in particular, when the cupellation process had advanced and the lead bath had become very rich in silver.

For resolving this problem, the metallurgists conducted cupellation in two successive stages. Between the two stages, they probably transferred the content of the cupel in use to a second one. The technique of using two cupels is mentioned by Pliny, but it is not quite clear how it was practiced, in the case it was actually applied during the classical years at Laurion.

Nevertheless it is certain that in the second stage of cupellation, the removal of litharge from the cupel was no longer done as previously, but by dipping in the bath the edge of iron rods, on which litharge was selectively attached and drawn out of the furnace. After solidification it had the form of small tubes, Pliny (n.h. 32) and is known as tubular litharge. Argentiferous lead was not attached on the iron rods, since there is neither wetting, nor reaction between iron and lead.

The application of this method was confirmed after identification of tubular litharge pieces at Laurion. This was a very smart technique, but since it suffered from low productivity, it was applied only as a second stage, when lead had become relatively rich in silver. This technique was shown to be applied during the classical years in Laurion during excavations (Conophagos, 1959), but it was also applied industrially in the 19th century AD, for example at Kongsberg (Girardin and Lecoq, 1826, pp.280–82).

Two cupels were identified at Laurion so far (Fig. 7. 8). They have not exactly the same form. The first one (Fig. 7) from the collection of K. Konophagos (Conophagos, 1980, p.315, fig. 12-4) was shallow with a large surface area in relation to its depth, in order to accelerate the cupellation process. The form of this cupel seems quite adapted for the first stage of cupellation, when the silver content of the bath was still relatively low and the removal of litharge from the cupel was done in one of the ways described earlier in this section. Then litharge was poured out of the furnace, either on the ground or in molds with a flat bottom, where it solidified taking the form of lumps or plates a few centimeters thick, respectively.

The second cupel (Fig. 8) was like a cone with a large surface area, but it was deeper than the previous one and therefore it was more convenient for dipping the edge of the iron bars into the bath. (Papadimitriou, 2012, p.810, fig. 3).

An estimation of the silver content in argentiferous lead, at the time when the removal of litharge started using iron rods, was done by examining an important number of samples of plate litharge using EDS microanalysis in Scanning Electron Microscopy (SEM). It was found that the inclusions of argentiferous lead in litharge contained usually 2.5 – 2.8 % Ag and in some cases up to a max. 5 %. Tubular litharge produced in the next stage of cupellation was practically exempted of measurable argentiferous lead inclusions.

Our knowledge on the form and size of the cupellation furnaces of the classical period at Laurion is limited. The only authentic testimony available is due to Kordellas, who wrote that: "Tracks of cupellation furnaces found at Lavrion testify that they were round, low, hollow in their middle and made of clay materials full of litharge" (Cordellas, 1890). This description clearly suggests that they were vaulted furnaces and that at least a portion of litharge was raked from the cupel on the bottom of the furnace. Conophagos represented a cupellation furnace as a vaulted furnace (Conophagos, 1980, p.307, fig. 12-1; p.315 fig. 12-4) in agreement with Agricola's depictions (1950, p.481) and in accordance to verbal information of old miners who had seen remains of ancient cupellation furnaces in the early 20th century.

Many years ago, I saw a vaulted cavity in the area of Bertseko, near the so-called "archaic washeries" of the excavations of E. Kakavogiannis. It had a diameter of about 0.8 m and was dug on a slope of the ground, inside a circular stone-walled enclosure of about 2.5 m diameter (Fig. 9). I considered it to be most likely a cupellation furnace, because of glazing and soot evidence on its vault and of its location in an area rich in metallurgical remains (lead smelting slags, fragments of litharge and burnt ceramic pieces. H. Katsaros, a resident of Lavrio, and passionate explorer of the mining area, found recently one similar furnace close to the previous one inside a rectangular enclosure of about 2×2.5 m, and probably another hidden in vegetation.

The presence of these furnaces situated close to each other, in an area where smelting and cupellation activities certainly took place, suggests that they are actually cupellation furnaces. However, it is astonishing that their construction looks like primitive, compared to smelting furnaces, washeries and other industrial constructions of the classical period that have been found so far at Laurion. In particular, it seems that they were fully operated by the door and neither chimney nor inlet for air blowing are present. It is thus probable, that they are older than classical, taking also into account that they are in proximity of the so-called archaic washeries, which according to Kakavogiannis (2001) are dated to the end of the archaic period. These washeries are also dug into the ground, their channels and water tanks have no waterproof lining and are irregular in shape and rather irrational from an ergonomic point of view.

Fig. 9: Cupellation furnace from the area of Bertseko (Legrena, Laurion) near the so-called "archaic washeries of Kakavogiannis" at Vrissaki of Kamariza. (Photo: G.D. Papadimitriou).

I suppose that cupellation furnaces attached to the Classical and Hellenistic furnace complexes were built more diligently, resembling rather to those of Agricola (Agricola, 1950, p.481). In this respect, it is worth noting that in the areas of "Oxygen" and "Megala Pefka" at Laurion, where the remains of important complexes of smelting furnaces survived, conical piles of stones are present, for which the most probable interpretation based to their shape and position is that they were once bases of stone-built cupellation furnaces.

Litharge

The oldest litharge pieces in the Helladic space and in particular at Laurion go back to the Late Neolithic and Early Bronze Age (Lambert, 1972; Spitaels, 1982a; Servais, 1967; Kakavogianni, et al., 2008; Papadopoulos, 2008). Then litharge is found in much more important quantities until the classical and Roman years. Although its persistence may seem singular, it is not unexpected, considering that cupellation was, in a global scale, the unique technique used for the extraction of precious metals from a melt of lead from the prehistoric through the classical, Roman, Byzantine and medieval times, until the early 19th century, when it was replaced by Pattinson's more economical method. But even today, although the industrial application of cupellation has ceased, the method continues to be used by goldsmiths for refining

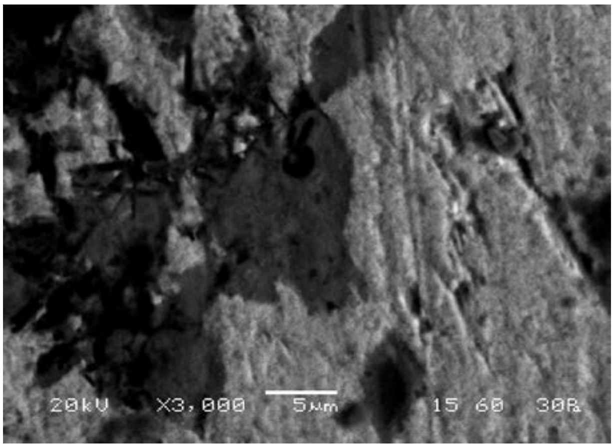

Fig. 10. Backscattered electron image from a section of a fragment of a platy litharge. Yellow litharge in light grey, red litharge in dark grey. Black needles are calcium-magnesium silicates, probably merwinite ($Ca_3Mg[SiO_4]_2$). (SEM micrograph: G.D. Papadimitriou).

and controlling the purity of gold, as an analytical tool for gold and silver determination, as well as in some special technological applications. Cupellation is thus, among the most resisting metallurgical techniques throughout the time. This allows us to deal with cupellation and litharge as a global issue, since the basic fundamentals of the method remain unchanged with the exception of technological details.

The name of litharge comes from the Greek λιθάργυρος, given by Dioscorides (50 AD) to a material obtained in the process of separating lead from silver. Litharge, in Greek, means literally "stony silver", certainly implying a useless form of silver, as if it was a "poor" stone. In Latin it is referred to by Pliny as spuma argenti, i.e. "silver foam" (Plin. n.hg. 32,106), a name that refers to the way it is produced, because during cupellation it floats on the bath from which it is removed by skimming. It is also mentioned by the name galena, essentially identified by Pliny with (non-silvery) galenite, i.e. an ore that can be used solely for lead production (Plin. n.h. 34,159). Therefore, all three names – Greek or Latin – are very expressive and contain important technological information.

Litharge (lead II oxide, lead monoxide, PbO) occurs in two crystal forms. The first one, massicot, has an orthorhombic structure, is yellow, and is stable at high temperatures. The rsecond crystal form has a tetragonal structure, is red in colour and is stable for $\theta < 540\,°C$. With rapid cooling from high temperature, the yellow form is maintained at the ambient temperature, but with even faster cooling the amorphous (glassy) state can be also obtained. Red litharge is obtained by slow cooling down to the temperature of the environment. All forms of litharge have a high specific gravity, the yellow 9.53 t/m^3, the red 8 t/m^3, and the amorphous 9.2 – 9.5 t/m^3, versus 11.34 t/m^3 of lead.

The chemical composition of litharge corresponds to 92.8 % lead and 7.2 % oxygen, so it can be considered as an extremely rich material for commercial lead production. Litharge obtained as a by-product of lead metallurgy in Laurion contained various impurities, mainly Fe, Ca, Si, As, etc. Among them the silver content ranges from 20 to 100 g Ag/t Pb (0.002-0.01 %), while the rest of metallic elements do not exceed 0.5 – 2 % in total. However, the silver content may reach 800 – 1,000 g/t Pb if many inclusions are present.

By examination of litharge samples from Laurion by means of X-ray diffraction and scanning electron microscopy associated to EDS microanalysis it is found that they consist mainly of a mixture of red and yellow litharge. Over time, a quantity of these was converted into lead carbonate (cerussite) and hydrated lead carbonate (hydrocerussite) under the influence of carbon dioxide and atmospheric moisture. Lead silicates and calcium-lead silicates that also contain magnesium, are also recognized either in massive or in needle-like form (Fig. 10).

Fragments of litharge of Laurion exhibit three different forms in terms of shape: plate litharge as slabs, a few centimeters thick, tubular pieces 3 – 5 cm long and 2 – 3 cm in diameter and lumps, i.e., masses without any specific shape. Their particular forms depend on the way litharge was extracted from the cupel and to subsequent solidification. It should be emphasized that litharge is also found at Laurion as residue of fine-ground material, usually of grain size either under 2mm or under 0.5mm. Their difference of fineness is due to the grinding equipment which was used in each case, namely reciprocating Olynthus mills in the old ore washery compounds and circular mills in the corresponding compounds, respectively. This issue will be addressed further in the section "Litharge during the Hellenistic period at Laurion".

The reason why litharge flowing out of the furnace was poured into molds with a flat bottom is, in my opinion, the following: during cooling and before solidification, the inclusions of argentiferous lead contained in the melt, settled near the bottom due to their higher specific gravity. After solidification many of them were visible on the outer surfaces of the plate and their concentration allowed metallurgists to judge which of the plates were rich in silver. Such plates were redirected in the smelting furnace to recover the metal. In the photograph of Fig. 16, a piece of litharge with many inclusions visible near their bottom is shown. The pieces of litharge in the form of lumps may have come from the earliest stages of the cupellation process, when the bath was still poor in silver. They were therefore poured into the ground or into small cavities before being disposed or stored for some other use. As a matter of fact, litharge could be used for the production of commercial lead, for the preparation of medicines, for the production of the waterproof coatings of water cisterns and possibly for other special applications.

Cupels

Two technical issues are directly related to the construction of a cupel: its shape and the material. Both of them

Fig. 11: Optical micrograph of the material of the cupel of Fig. 8, showing a kind of breccia microstructure characteristic of material produced by a mortar. It consists of angular fragments of broken litharge embedded in a fine-grained matrix. (Optical micrograph: G.D. Papadimitriou).

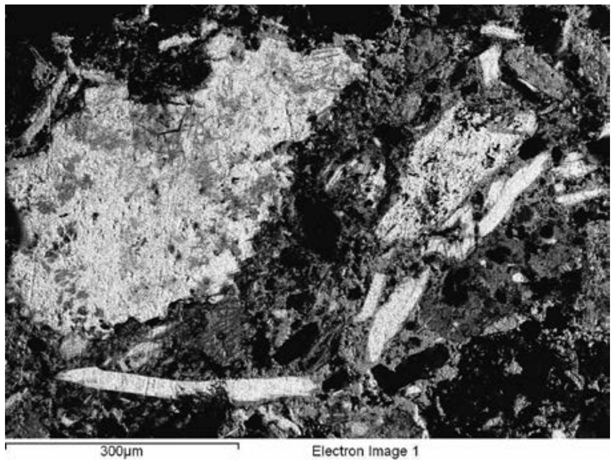

Fig. 12: Scanning electron micrograph of the material of the cupel of Fig. 8. Angular fragments of ground litharge are readily recognized. Light grey grains are PbO-yellow, dark-grey material is PbO-red, whereas grains of black material are mainly calcite, kaolinite and illite. (SEM micrograph: G.D. Papadimitriou).

are crucial in limiting silver losses during cupellation. The material of the cupel should not be wetted by liquid silver, otherwise some silver would be absorbed and lost in cracks and pores of the cupel.

The first choice of material that was most probably used for making cupels in prehistoric times at Laurion should be clay, since metallurgists were already familiar with clay from their standard metallurgical practice, namely for making ceramic walls of furnaces, refractory linings, crucibles and molds for casting. But clay was certainly judged not quite satisfactory in the case of cupellation, since it might absorb silver (Nezafati and Pernicka, 2012, p.41) leading thus to losses. In fact, wetting of ceramic materials from silver is a well-known physical property and is for example applied in modern technology brazing of ceramic materials, such as alumina and quartz, by means of silver as a filler metal. With regard to cupellation, it is known that materials consisting mainly of SiO_2 and CaO with some Al_2O_3 and minor concentrations of MgO, K_2O and P_2O_5, but without using bone ash, were used from the 4th millennium BC in East Anatolia for making cupels (Hess, et al., 1998, p.63–64). Also cupels made of ceramic materials were used in the Middle Ages before the 13th century, but there were not satisfactory, because litharge reacted with the silica contained in them, forming a glassy layer to which silver was mechanically attached (Bayley, 2008, p.138).

Prehistoric metallurgists certainly noticed the penetration of silver in cracks and pores of clay materials in their cupellation furnaces, and that's probably why they turned to the use of litharge for the manufacture of cupels, since they knew from experience that litharge and silver are not mutually wetted. For making cupels, the well-known technique used for ceramics was certainly applied. Litharge was ground to fine powder and mixed with the appropriate amount of lime as binding material and a small amount of clay as plasticizing agent with the necessary quantity of water for making a plastic mass. Then the cupels were shaped manually, from the plastic mass obtained.

Fig. 11 is an optical micrograph of the material of the cupel of Fig. 8, showing a kind of breccia microstructure consisting of angular fragments of broken litharge embedded in a fine-grained compact matrix.

The scanning electron micrograph (SEM; Fig. 12) shows that the mass of the cupel is compact and consists of rather angular grains of yellow litharge (light grey) and red litharge (dark gray), bound to each other with clay and calcium and lead carbonates that formed respectively from lime and PbO, under the influence of carbon dioxide and moisture of the atmosphere. The clay minerals are identified as kaolinite, illite, chlorite and quartz by means of EDS microanalysis and x-ray diffraction (Fig. 13). It is clearly seen that all of them serve as binding agents and form an almost continuous network around the grains of litharge (materials in black in the SEM photograph (Fig. 12). They also fill the voids of the material. The presence of other secondary minerals which usually accompany lime and clay are present in small quantities (dolomite, magnetite).

This form of microstructure clearly proves that the material was produced in the way we described earlier.

Similar results are obtained with a fragment of another broken cupel. Somewhat different was the x-ray diffraction spectra of powder taken from the inner surface of the cupel, showing the presence of an increased quantity of lead carbonate and kaolinite, meaning probably that a plaster of clay was applied on the internal surface of the cupel.

A question arises, however, for what reason ground litharge has been used for making cupels, since litharge could eventually melt in the temperature of the cupellation. At first, it should not be disregarded that the binding material used to consolidate litharge is refractory and should encompass the low melting point of litharge. On the other hand, one could object that during most of the time of the cupellation process the bath remains at temperatures around 900 °C and therefore the underlying wall of the cupel remains unaffected. The real problem could arise only at the final stages of cupellation, when the silver content in the bath reaches about 90 % Ag. Above this content, temperatures up to 960 °C are needed to melt the alloy which becomes progressively richer in silver. Even in this case, the presence of impurities lowers the melting point of silver. In the extreme case where some melting of the cupel would occur, this melting would be only at the surface and the underlying mass of the cupel would remain intact.

Positive arguments for using litharge are that it is a clean material and does not cause contamination of the bath, as it would, certainly, occur if the cupel was made of clay. Silver does not wet litharge and is not absorbed by it, contrary to the ceramic materials known at the time. The cupels produced by mixing litharge with refractory binders are strong and resist thermal shocks without cracking, as opposed to the common ceramics. Lastly, one may wonder, what other choices of materials could be available, taking into account the limited number of materials available at that time?

It is worth noting that with an almost identical material was produced the water proofing plaster of the ancient water cisterns, during the Classical period at Laurion, having excellent water proofing properties as well as an astonishing strength and resistance to time (Conophagos and Papadimitriou, 1978; Papadimitriou and Kordatos, 1995). Its composition in a number of samples from Soureza was found to contain 30 – 40 % CaO, 45 – 53 % PbO, 10 – 13 % SiO_2, 0.80 – 1.70 % FeO and 2 – 2.4 % Al_2O_3. It was applied on the walls of the cisterns in multiple layers, as a suspension of very finely ground litharge in lime, by means of a brush. Litharge grains were in an amorphous (glassy) condition bound with lime, which after drying transformed to calcite, as it was confirmed from relevant micrographs and X-ray diffraction. The excellent water proofing properties of the material were confirmed by standard hydraulic tests (Conophagos and Badekas, 1974)

During the Middle Ages, a completely different logic prevailed in Europe for removing litharge from the cupel. Instead of discarding litharge out of the furnace, they left it in the cupel, until it was absorbed completely from the porous material of the cupel. For this purpose, highly porous materials were needed, which were able to selectively absorb in their mass the entire amount of litharge as well as the base metals carried in solution (Martinon-Torres, et al., 2008; Ulseth, et al., 2015). These cupels were formed from a mixture of marl with wood and bone-ashes. They are readily recognized from the presence of fragments of bones and by their high content of phosphates. Their manufacture strictly followed specific recipes, because it was not enough for the cupels to simply absorb litharge, but they had to be able to absorb the entire quantity of litharge produced during the cupellation process. That's why they had to have a large and open porosity, so that

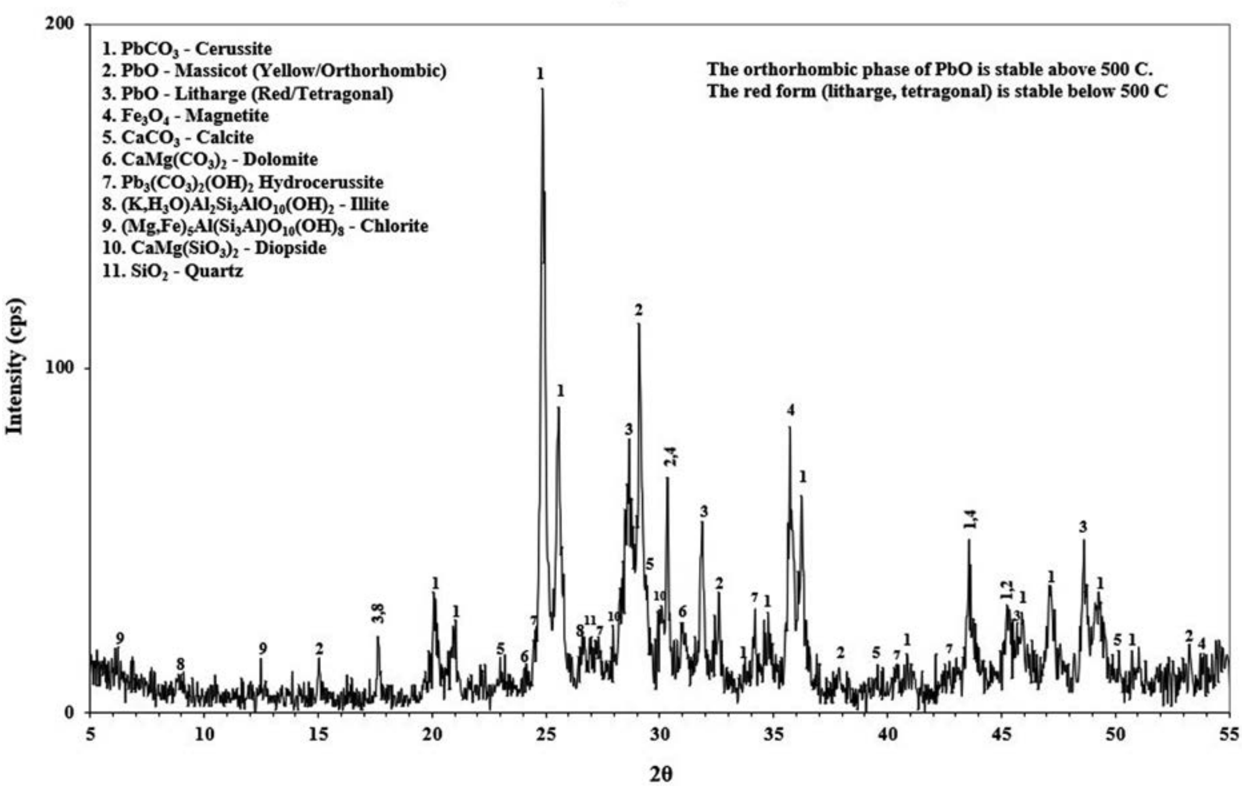

Fig. 13: X-ray diffraction diagram of a sample from the cupel of Fig. 8. The most frequent phases identified are listed in the diagram. (X-ray diffraction diagram: G.D. Papadimitriou).

litharge could penetrate to a great depth from the bottom of the cupel by capillary action. Simple clay did not have this capability, so suitable mixtures had to be used, mainly from calcium-rich marl mixed with wood ash and bone ash.

With regard to Laurion, there has not been any indication of using this kind of porous cupels so far. It is not excluded, however, that they have been used in some period of time, for example for cleaning of the bullion to make blanks for coining.

Prehistoric Cupellation

Prehistoric sites in the area of Laurion, where pieces of litharge were identified, have so far been characterized as potential metallurgical sites for production of silver from argentiferous lead by means of cupellation, considering that litharge is the characteristic by-product of the process. In some of these places were also found fragments of shallow bowls with a flat or slightly concave surface at their bottom, whose role was not obvious and became, therefore, the object of discussion and conjectures. Similar bowls have been found previously in other prehistoric areas of Greece, for example in Thasos (Papadopoulos, 2008) and more recently at Lambrika-Koropi and other places in Attika, as cited in the introduction.

A second variant of bowls very similar to the previous one, but having multiple small depressions at the bottom was identified only at Laurion (Fig. 14). C. Conophagos first investigated this type of bowls with depressions and interpreted them as small cupels serving for melting and refining weighted silver quantities for silver coining in the classical years (Conophagos, 1980, p.367, fig. 16.4; p.369). Since then, these findings have been characterized unambiguously as belonging to prehistoric times (Papadopoulos, 2008, p.64; Kakavogianni, et al., 2008, p.47), therefore this observation needs now to be revised with regard to coining. Nevertheless, the statement of Konophagos that it is a cupel remains valid. As a matter of fact, the chemical analysis performed on a dozen of similar objects coming from Lambrika (Kakavogianni et al, 2006, p.81, Tab. 1) along with careful visual observation of their form and shape suggest that they are made just like the cupels of the classical period, i.e. modeled as ceramics, from a plastic mixture consisting of finely ground litharge mixed with a quantity of lime as binding agent and a small amount of clay as plasticizing additive. As a matter of fact, analyses of twelve samples gave the following results: PbO ~83 %, CaO ~4 %, Al_2O_3 ~2 %, SiO_2 ~7 %, FeO ~1 % and MgO = 1.5.

In terms of their shape, they have a large area compared to to their depth, but, as it is expected, they have much smaller dimensions and capacity in comparison to cupels of the classical period.

These characteristics suggest that the bowls represent actually cupels which were in use during the prehistoric era and their size was adapted to the scale of production of the corresponding period. This is confirmed by the fact that no function other than a cupel could be attributed to this kind of bowl and inversely no other sherds with geometrical characteristics required for a cupel have been identified in the areas, where pieces of litharge and other findings characteristic of lead and silver metallurgy are present.

It is worth mentioning that the large number of litharge lumps and fragments of plate-shaped litharge found at Lambrika suggest clearly that the well-known technique of cupellation, as it was practiced during the classical period at Laurion, was already in use since the prehistoric times. Namely, litharge, was removed from the cupel and was cast out of the cupellation furnace in cavities on the ground or in molds, where it solidified forming lumps and pieces of plate-like litharge respectively.

According to Papadopoulos (2008, p.64), the remains of the bowls found at Limenaria, which seem to be among the oldest ones in the Aegean (Final Neolithic), have a diameter of about 15 cm and a depth of 1 – 2 cm and do not have depressions. In Lambrika their diameter varies between 10 and 14 cm and their height between 1 and 2 cm. The depressions have a diameter of 1 – 2cm. and a depth from 2 – 4 mm. The sole intact example found at Lambrika weighs 500 g.

Now, since the silver content in the argentiferous lead is extremely small (in the best case it could be about 5,000 g Ag/t Pb, but it was usually 2,000 g Ag/t Pb or lower at Laurion), in order to obtain on the bottom of the bowl a quantity of silver of about 15 g at the end of the process, one should treat at least a quantity of 7 – 8 kg of argentiferous lead. This quantity of lead could not be added in the cupel at once, but progressively, as the lead was oxidized and skimmed out. Therefore, repeated removal of litharge from the cupel was necessary, as in the case of cupellation in the classical period. Since the cupel with its content was not too heavy, it was drawn easily out of the furnace and liquid litharge was poured out by slightly tilting the cupel. Litharge was possibly poured straight into a cavity in the ground, in front of the cupellation furnace. Such cavities were found in the excavations of Lambrika, covered internally with a white layer of lead carbonate ($PbCO_3$), which came over time from transformation of litharge under the influence of the CO_2 of the atmosphere. These cavities had the form of a funnel to collect at their bottom any argentiferous lead that was inadvertently carried away with litharge from the cupellation furnace.

A practical problem relevant to the small quantity of silver obtained in the cupel should occur at the end of the process, when the last litharge formed should be removed, leaving the quantity of silver free at the bottom of the cupel. This was most probably done by tilting slightly the bowl and paying attention to avoid withdrawal of silver along with litharge. It was, certainly, a difficult task and the presence of a rim of semi-circular cross section on the bowl, reported by Papadopoulos (2008, p.64), is an argument for the actual existence of the problem. But a more efficient way to avoid loss of silver, was certainly the presence of depressions in

Fig. 14: A prehistoric cupel in the form of a shallow bowl, with multiple depressions at its bottom, from the collection of K. Konophagos (Author's modification from Conophagos, 1980, p.367, fig.16-4).

Fig. 15: A prehistoric cupel fragment from Lambrika-Koropi (Author's modification from Kakavogianni et al., 2008, p.54, fig.14).

the bottom of the cupels, that is probably an invention of the metallurgists of Laurion. In this case it is evident that the mass of silver was divided into a number of individual spherical bodies lodged in the depressions and this way impeding them to run out with litharge, when the bowl was tilted (Papadimitriou, 2012). This remark seems to be confirmed by the photograph of a small cupel (Kakavogianni, et al., 2008, p.54, fig. 14 here fig. 15). This photograph shows clearly the local melting in the form of craters, which has been produced by the hot silver spherulites lodged in the depressions on the underlying litharge. This local surface melting, is however not a problem for the cupel as a whole. One may also observe that the silver spherulites are not of the same size, as they certainly come from coalescence of very small drops of silver.

In addition, splitting the mass of silver to small usable quantities could be practical, avoiding cutting (Papadimitriou, 2012). Furthermore, one could speculate that the division of silver to flans of equal mass could breed later the idea of coins and in this respect, the hypothesis of Conophagos about the use of the shallow bowl with depressions for melting silver and preparing blanks for coining appears valid.

It is interesting to know how much silver was produced in a cupel during a complete cupellation cycle as well as the corresponding amount of argentiferous lead used for it. An approximate estimate of these quantities was possible thanks to the cupel (Fig. 15) accompanied by its scale. The cupel has a diameter of about 10 cm and is broken, but missing parts are located along its periphery, so that probably only one cavity is missing. The cupel was slightly overheated during its use, so that it was softened and slightly deformed. At the same time, the silver beads that had settled on its bottom caused local melting of the substrate and sank to some extent in its soft mass, leaving behind them clearly visible imprints. The imprints of twelve silver beads were detected after magnifying the photograph, of which ten were inside the cavities of the cupel and two outside. After measuring their diameter, their volume and then their weight was calculated, as it is seen in Table 1. Finally, their total weight was found to be 11.09 g.

From this quantity of silver, the quantity of argentiferous lead used during a complete cupellation cycle could be estimated. For the value of 2000 g Ag/t Pb which is usually considered as most representative for the silver content in argentiferous lead, a quantity of 6 kg of argentiferous lead was found.

Furthermore, given that a cupel with a diameter of 10 cm and a depth of 2 cm has approximately a capacity of 155 cm^3, which can accommodate only 1650 g of melted lead, the quantity of argentiferous lead used in one cupellation cycle (i.e., 6 kg), could not be added at once in the cupel. This means that the well-known technique of removing litharge from the cupel and replacing it progressively with argentiferous lead was actually practiced and confirmed from the presence of lumps and plate litharge pieces in the workshop. From the above it is concluded that the design of the cupel was made in such a way that the depressions help to coalescence the silver droplets into larger coarse drops, so that they could not be scattered again and to fit 10, maybe 20 g of silver in the cupel at the end of a cupellation cycle.

The form and size of the cupel changes with time as the production scale increases. As a matter of fact,

No of cavity	Spherulite diameter mm	Spherulite volume mm^3	Spherulite weight g
Mean value		88.0	0.92
1	7.5	220.9	2.32
2	6.65	154	1.62
3	4.15	37.40	0.39
4	5.81	102.7	1.08
5	6.64	153.3	1.61
6	4.15	37.4	0.39
7	3.32	19.16	3.85
8	7.47	218.25	2.29
9	4.15	37.42	0.39
10	4.15	37.42	0.39
11	3.32	19.16	0.20
12	3.32	19.16	0.20
Sum		1056.27	11.09

Tab. 1: Calculation of the quantity of silver produced in a complete cycle of cupellation. (Measurements and calculations: G.D. Papadimitriou).

in prehistoric years mining was limited and the furnace size for the extraction of the argentiferous lead from ore was certainly small, producing perhaps some kilograms at most. For the cupellation of such quantities of lead the cupels in the form of small shallow bowls were sufficient. In the classical years, however, and possibly even earlier, a change in the scale of production has occurred. Systematic underground mining, ore dressing plants and high-capacity reduction furnaces have emerged. Under these circumstances the cupel could not be anymore the small shallow bowl, which continued probably to exist only for assaying purposes. To the opposite, a sizeable recipient with a capacity of the order of 100 kg of lead, as the one shown from the collection of Konophagos (Fig. 7) or the one whose bottom is examined in this investigation (Fig. 8) should be needed. These cupels may have a diameter of at least 0.5m and do not bear depressions any more, but the principle of protecting silver in a depression is preserved as a narrow bottom, away from the surface.

With regard to the prehistoric cupellation furnaces, nothing is known. It is, however, most probable that they were of the type from the region of Bertseko (Fig. 9).

Concluding some discussion should be made relevant to the interpretation that has been proposed by Kakavogianni, et al. (2008) and Georgakopoulou, et al. (2020) for the cupellation technique used in the excavated cupellation workshop at Lambrika and for the origin of the shallow bowls with impressions at their bottom, that were characterized as a new type of litharge and named "bowl shaped litharge".

With regard to the cupellation method, Georgakopoulou, et al. (2020, p.188–89) stated that "the cupellation technology of Prehistoric Attica is different from that of Classical Laurion, at least on the basis of how litharge was removed from the melt" and suggested that the removal of litharge was done by absorption from the lining of the cupellation hearth, i.e the bowls were "litharge-impregnated cupellation hearth linings" as those studied from Pernicka, et al. (1998) at Habuba Kabira Syria and from Hess, et al. (1998) at Fatmali-Kalecik, East Anatolia. For this hypothesis they were based on the presence of a number of cavities of conical form carved in the ground (Kakavogianni, et al., 2008, p.49, fig. 5), having a diameter of 19 cm on the surface and a depth of 10 cm, and bearing remains of a white lining in their interior (Kakavogianni, 2005, p.46). According to them, the dimensions of intact shallow bowls (10 – 14 cm diameter) correspond to the dimensions of the above cavities (19 cm diameter at their upper end on the surface), and therefore they should be considered as cupellation hearths. Clearly, the presence of these cavities alone is not a strong argument, since there are no indications suggesting that these cavities were actually cupellation hearths, but could be probably used for pouring litharge extracted from the cupel. Moreover, this assumption conflicts with the actual fact of the presence of a significant number of pieces of plate litharge and lumps at Lambrika and other places, suggesting that the only technique for which we can safely claim that it was applied at Lambrika is the technique of the classical period, in which litharge was discarded from the furnace and cast in molds or poured into cavities on the ground, giving after solidification, pieces of plate -shaped litharge or lumps, respectively.

Furthermore, shallow bowls found at Lambrika are not pieces of litharge solidified after absorption from a porous material, but they are actually cupels, i.e. handmade artifacts modeled like a ceramic vase from a plastic mass, as evidenced by their net contours and strictly symmetrical shape, reproduced as a standard form in all cupels. This is also confirmed from the smoothness of their surface, and from fine details, such as the uniform rim on the periphery of the bowl and the depressions in their bottom. It is, certainly, possible to obtain a crude bowl form by absorption of litharge into a porous cupel having a hemispherical bottom, like those used for cupellation in the Middle Ages, but it is quite unlikely to obtain a perfect shape from the spontaneous penetration of litharge into a porous material.

It is also worth repeating that a shallow bowl, found intact at Lambrika, had a weight of 500 g (Kakavogianni, et al., 2006, p.79, fig. 3).

If we accept as a hypothesis that litharge was removed by absorption from the hearth material and that the weight of litharge absorbed during a cupellation cycle was about 500 g, then this would correspond to about 375 g of argentiferous lead, from which – for a silver content of 2,000 g Ag/t Pb – only 0.75 g of silver could be produced. This quantity is far less than the quantity of 11 g which, according to a previous calculation, had been concentrated in the cavities of the cupel (Fig.15). The limited ability of

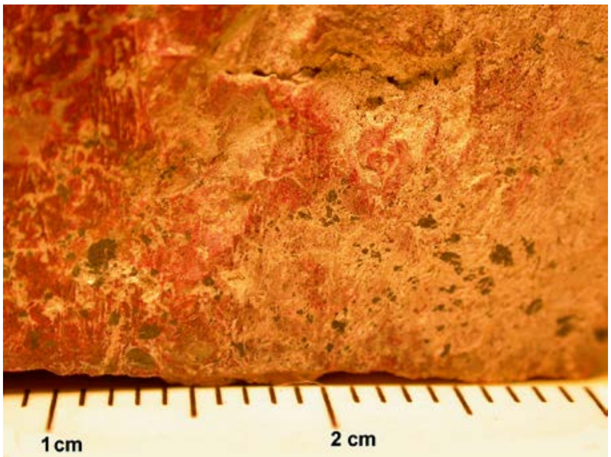

Fig. 16: Macrograph of plate litharge containing inclusions of a lead-silver alloy with impurities near its bottom. The matrix is mainly red litharge, whereas some yellow litharge is also present at some places. (Macrograph: G.D. Papadimitriou).

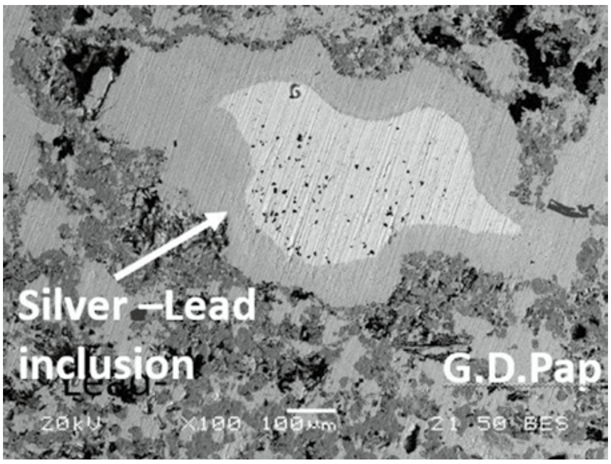

Fig. 17: Scanning electron micrograph of a lead-silver inclusion in a matrix of yellow and red litharge. (SEM micrograph: G.D. Papadimitriou).

Fig. 18: A pile of finely ground litharge in the corner of the enclosure of a circular mill at Ari-Lavrion and in the embedded photo a piece of agglomerated ground litharge, certainly serving as a feed material for the smelting furnaces producing commercial lead. (Photo: G.D. Papadimitriou).

the cupel to absorb more than 500 g of litharge, brings us back to the assumption of the classical technique, characterized by repeated removal of litharge from the cupel and simultaneous replacement by a corresponding amount of argentiferous lead, until a significant amount of silver was concentrated in the depressions of the cupel.

Litharge during the Hellenistic period at Laurion

During the Hellenistic and early Roman period (3rd to 1st century BC), the operation of the mines fell into decline mainly due to political instability. As a solution, production of silver and lead from ores was partially substituted from recycling of stocked mining and metallurgical waste materials of the classical period (Strabo 3,2,9). Among these materials, was litharge, which was recycled for its rich-in-silver, lead-silver inclusions (Papadimitriou, 2020).

Mechanical inclusions consisting mainly of lead and silver with some impurities, such as Cu, Ca, and As are the most important ones and are present in lumps and plates of litharge. Some of them are observed by naked eye as dark grey particles inside red litharge near the bottom of the plates (Fig. 16). Apparently, they precipitated to the bottom of the plate, while litharge was still in the liquid state, due to their higher density. Some of them have an equivalent diameter of 1 mm or even higher, but most of them are smaller than 0.5 mm. These inclusions, were certainly perceived by the ancient metallurgists on the surface of litharge or of broken pieces. Actually, not all pieces of plate litharge contained important inclusions, and this was presumably depending on the skill of the metallurgists in removing effectively litharge from the bath of argentiferous lead.

Tubular forms of litharge are free of mechanical inclusions, and this seems plausible with regard to the corresponding separation technique by means of iron bars.

Inclusions in plate litharge are shown in the SEM micrograph (Fig. 17) and in most litharge samples contain 2.5 – 5 % silver in lead.

For recovering inclusions, the ancient metallurgists followed the same technique, as for beneficiation of silver bearing lead ores in the washeries, namely they subjected the litharge pieces to fine grinding (in the present case under 0.5 mm), in order to liberate the inclusions from the surrounding mass and then recovered them by hydromechanical processing in the washeries as a concentrate (heavier fraction). From this concentrate, silver was presumably obtained by means of cupellation, after eventual addition of a quantity of lead and some charcoal powder in order to reduce any silver oxide which was eventually present. The lighter fraction of the separation in the washery consisted of the mass of ground litharge having a low silver content (called for brevity desilvered litharge).

This fraction was subjected to agglomeration and then smelted in shaft furnaces for production of commercial lead, which was in great demand at the time.

Fig. 20: Representation of a circular mill in operation (Drawing: G.D. Papadimitriou).

Initially the processing described above was certainly done in the old ore washery compounds of the classical period, where crushing and grinding equipment was available. This is evidenced by the presence of ground litharge residues identified in many of them (Conophagos, 1980, p.273; Rehren, et al., 1999, pp.299 – 308). Finally, it was found associated with the circular mills of Laurion (Papadimitriou, 2015; Papadimitriou, 2016; Nomicos, 2021, p.50 – 57) (Fig. 18).

In particular, during excavations in the Asklipiakon washery at Soureza, residues of ground litharge from both a) a quantity stocked in a room adjacent to the washery and b) a small pile abandoned just outside the washery were identified. After sampling and chemical analysis, it was found that the first sample contained 65.75% Pb and 601 ppm Ag, whereas the second one contained 66.6 % Pb and only 134 ppm Ag. These figures suggest that ground litharge was processed in the washery for recovering silver inclusions and that the first sample belonged to the feeding material, whereas the second one was the waste (light fraction) of the concentration process. Unfortunately, we do not have any evidence of the concentrate (heavy fraction of the separation), but we may assume that it consisted from a fine powder of lead-silver inclusions with some middlings and that about 470 g of silver had been recovered in the concentrate from each ton of ground litharge processed.

In a later period, during the 2nd century BC, when mining and metallurgical activities resumed, new workshops for the recovery of silver from litharge were already in operation near old furnaces. In these workshops grinding of litharge was performed by means of the "circular mills of Laurion", which had been discovered in the meantime. A circular mill consists of a vertical millstone, freely mounted on a long horizontal axle which turns around a vertical shaft in the center of the structure. The millstone revolves in a circular path inside a trough, crushing the material which should be reduced in size. The mill is driven manually or most probably from a donkey (Fig. 19 – 20).

It should be emphasized that the circular mill of Laurion was the ideal device for grinding litharge, due

Fig. 19: A well-preserved circular mill at Ari-Lavrion (Ari-II), used for fine grinding of litharge. (Photo: G.D. Papadimitriou).

to its high productivity and strict control of the fineness of the material produced. The older attrition devices of Laurion, i.e. boulders on which crushing was done by means of hammers and reciprocating Olynthus mills for grinding were not satisfactory, due to their inability to grind the material finer than 0.5 mm and to their low productivity. Yet, large quantities of litharge, of the order of 1 – 1.5 million tons, had probably been abandoned in more ancient times near the furnaces as waste, so that high-capacity grinders were necessary for their treatment.

To date, remains of eleven circular mills have been identified, considered previously as helicoidal washeries or mixing devices of ore (Tsaïmou, 2005). All of them are near old stocks of smelting slag and one of them at Ari which is preserved in a good condition, is representative of an integrated recycling compound, comprising one circular mill, one washery and five or six smelting furnaces. It was still active in the Hellenistic or Early Roman period, as shown by radiocarbon dating of charcoal samples coming from the furnaces of the compound that gave a calibrated date of 246-03 BC (Tsaïmou, et al., 2015, p.118).

The operation of the circular mills was apparently very successful. Certainly, for this reason, their technology was transferred to the gold mines of the Eastern Desert of Egypt in the time of Ptolemies (Klemm and Klemm, 2013, p.167, fig. 5. 109), where they probably served in the process of recovering gold from old waste of gold bearing quartz (Papadimitriou, 2020)

Conclusions

The subject explored in this paper is cupellation, as a silver production technique in Laurion. The conclusions we reach are the following:

In Laurion the production of silver lasted from the Final Neolithic until the end of the Hellenistic period, with a production scheme that includes two basic metallurgical processes: smelting and cupellation.

For all phases of this long period of 3000 years, the main evidence, and at the same time source for studying the early technology, are fragments of cupels and pieces of litharge, which prove that the technique of producing silver from lead was steadily cupellation. In particular, the common presence of two typical forms of litharge, in lumps and plates, proves that the basic technique of using a cupel from which litharge was mechanically removed and solidified outside the furnace, was applied throughout the aforementioned time period.

The study of cupels in terms of form and size proves that the technology of both the prehistoric and the Classical-Hellenistic periods is determined by the scale of production. In terms of material, it turns out that the cupels were made with the technique of ceramic materials from ground litharge to which a small amount of lime and clay had been added.

The main concern of the metallurgists of all times was to limit the losses of silver during the removal of litharge from the furnace, along which a quantity of argentiferous lead was carried away. In prehistoric times at Laurion this problem was resolved by printing hemispherical cavities at the bottom of the cupel, where silver was concentrated in thick drops, and its re-dispersion was prevented when the cupel was tilted. During the classical period, large cupels of conical form were used and a technique for removal of litharge in two stages was adopted. During the second stage, the removal was done by immersing the end of iron rods in the cupel, where litharge was selectively attached forming a short tube around the bar. This is evidenced by the existence of tubular litharge pieces.

During the Hellenistic and early Roman periods, litharge stocks were recycled in order to recover silver from the silver inclusions they contained. The litharge was ground into very fine material on the circular mills and inclusions were recovered in the washeries. Silver was finally obtained from the concentrate by cupellation, whereas the desilvered litharge was driven to the smelting furnaces for production of commercial lead.

Bibliography

Agricola G., 1556 (1950). *De Re Metallica*. New York: H. Dover Publications.

Andrikou, E., 2020. Thorikos in Context: The Prehistory. In: N. Papadimitriou, J.C. Wright, S. Fachard, N. Polychronakou-Sgouritsa and E. Andrikou, eds., 2020. *Athens and Attica in Prehistory. Proceedings of the International Conference, Athens, Greece, 27 – 31 May 2015*. Oxford: Archaeopress, pp.19 – 28.

Ardaillon, E., 1897, *Les mines du Laurion dans l'antiquité*. Paris: Fontemoing.

Bachmann, H.-G., 1982. Archäometallurgische Untersuchungen zur antiken Silbergewinnung in Laurion, II: Charakterisierung von Bleiverhüttungsschlacken in Laurion. *Erzmetall*, 35 (5), pp.246 – 51.

Bayley, J., 2008. Medieval precious metal refining: archaeology and contemporary texts compared. In: M. Martinon Torres and Th. Rehren, *Archaeology, history and science: integrating approaches to ancient materials*. Walnut Creek: Left Coast Press, pp.131 – 50.

Chatzidimitriou, A., 2005. *Performances of Workshops and Commerce in Iconography of the Archaic and Classical Period.* Athens: Archaeological Resources Fund.

Coleman, J., 1977. Kephala, a late Neolithic settlement and cemetery, Keos I. Princeton, N.J.: American School of Classical Studies.

Conophagos, C.E., 1959. *Une méthode ignorée de coupellation du plomb argentifère utilisée par les anciens Grecs. Annales géologiques des pays Hélleniques*, 11 pp.137 – 49 pl.I-V.

Conophagos C. and Badekas, E., 1974. Αι δεξαμεναί ύδατος της Αρχαίας Μεταλλουργίας εις το Λαύριον και το ειδικόν στεγανοποιητικόν επίστρωμα τούτων. *Πρακτικά Ακαδημίας Αθηνών*, 49, pp.251 – 61.

Conophagos, C. and Papadimitriou, G., 1978. On the waterproofing plaster of ancient Greek cisterns of Lavrion. *Comptes Rendus de l' Académie des Sciences de Paris*, pp.287 – 89.

Conophagos, C., 1980. *Le Laurium antique et la technique grecque de la production de l'argent.* Athens: Ekdotike Héllados.

Conophagos, C., and Papadimitriou, G., 1982. La métallurgie du fer et de l'acier en Grèce, pendant la période classique. In: J.D. Muhly, R. Maddin and V. Karageorghis, eds., *Early metallurgy in Cyprus 4000–500 BC*. Larnaca*, Cyprus 1 - 6 June 1981*. Acta of the International Archaeological Symposium Nicosia: The foundation, pp.363–72.

Cordellas, A., 1869. *Le Laurium*. Marseille: Cayer.

Cordellas, A., 1890. Το Λαύριον και ο ελληνικός Άργυρος. Lecture at «Parnassos» Society, Athens.

Cordellas, A. and Wolters, P., 1894. Λαυρεωτικαί αρχαιότητες. *Mitteilungen des Kaiserlich-Deutschen Archäologischen Institut,* 19, pp. 238–47.

Gale N.H. and Stos-Gale, Z.A., 1981. Cycladic lead and silver metallurgy. *The Annual of the British School at Athens,* 76, pp.169–224.

Gale N.H., Z.A. Stos-Gale and Davis, J., 1984. The provenance of lead used at Ayia Irini, Keos. *Hesperia*, 53, pp.386–406.

Georgakopoulou, M., Douni, K., Ginalas, M., Kakavogianni, O. and Bassiakos, I., 2020. Recent Finds from Final Neolithic and Early Bronze Age- Silver Production Sites in Southeastern Attica. In: N. Papadimitriou, J.C. Wright, S. Fachard, N. Polychronakou-Sgouritsa and E. Andrikou, eds., 2020. *Athens and Attica in prehistory. Proceedings of the International Conference, Athens, Greece, 27–31 May 2015.* Oxford: Archaeopress, pp.185–92.

Girardin, J. and Lecoq, H., 1826. *Éléments de Minéralogie appliquée aux sciences chimiques*. Paris: Libairie Thomine.

Hauptmann, A., Pernicka, E. and Wagner, G., 1988. Untersuchungen zur Prozesstechnik und zum Alter der frühen Blei-Silbergewinnung auf Thasos. In: G.A. Wagner and G. Weisgerber, eds., *Antike Edel- und Buntmetallgewinnung auf Thasos.* Der Anschnitt, Beiheft 6. Bochum: Deutsches Bergbau-Museum, pp.88–112.

Hauptmann, A., 2020. *Archaeometallurgy, Materials Science aspects.* Berlin: Springer.

Hess, K., Hauptmann, A., Wright, H. and Whallon, R., 1998. Evidence of fourth millennium BC silver production at Fatmali-Kalecik, East Anatolia. In: Th. Rehren, A. Hauptmann and J. Muhly, eds., *Metallurgica Antiqua, In Honour of Hans-Gert Bachmann and Robert Maddin.* Der Anschnitt, Beiheft 8. Bochum: Deutsches Bergbau-Museum, pp.57–67.

Jones, J.E., 1982. The Laurion silver mines: a review of recent researches and results. *Greece and Rome*, 29 (2), pp.169–83.

Kakavogianni, O., 2005. Εργαστήριο μεταλλουργίας αργύρου της Πρωτοελλαδικής Ι Εποχής στα Λαμπρικά Κορωπίου. *Αρχαιολογία και τέχνες,* 94, pp.45–8.

Kakavogianni, O., K. Douni, F.Nezeri, M.Georgakopoulou, I. Bassiakos, 2006. Απόπειρα τεχνολογικής προσέγγισης της παραγωγής αργύρου και μολύβδου κατά την τελική νεολιθική και πρωτοελλαδική Ι περίοδο στα Μεσόγεια. In: G. Kazaze, ed., *2ο Διεθνές Συνέδριο Αρχαίας Ελληνικής Τεχνολογίας: πρακτικά = 2nd International Conference on Ancient Greek Technology: proceedings. Αθήνα: 17–20 Οκτωβρίου 2005.* Αθήνα: Τεχνικό Επιμελητήριο Ελλάδας, pp.77–83.

Kakavogianni, O., Douni, K. and Nezeri, Ph., 2008. Silver Metallurgical Finds Dating from the End of the Final Neolithic Period until the Middle Bronze Age in the Area of Mesogeia. In: I. Tzachili, ed., 2008. *Aegean Metallurgy in the Bronze Age. Proceedings of an International Symposium Held at the University of Crete. Rethymnon, Greece, 19–21 November 2004.* Athens: Ta Pragmata. pp.45–57.

Kakavoyannis, E., 2001. The silver ore processing workshops of the Lavrion region. *The Annual of the British School at Athens*, 96, pp.365–80.

Kakavogiannis, E., 2005. *Μέταλλα Εργάσιμα και Συγκεχωρημένα. Η οργάνωση της εκμετάλλευσης του ορυκτού πλούτου της Λαυρεωτικής από την Αθηναϊκή Δημοκρατία*. Athens: Archaeological Resources Fund.

Kakavogiannis, E. and Kakavogianni, O., 2001. Τα μνημεία της περιοχής Οβριόκαστρο-Δάρδεζα-Ποτάμι-Σταθμός Δασκαλιού του Δήμου Κερατέας. In: *Πρακτικά Η΄ Επιστημονικής συνάντησης ΝΑ Αττικής = Proceedings of the 8th Scientific Meeting of the SE Attica, Κερατέα Αττικής, 30 Οκτωβρίου - 2 Νοεμβρίου 1997: αφιέρωμα στους Πάνο Π. Παναγιώτου, Τάσο Χατζή, Χρίστο Ενισλείδη*. Κερατέα Αττικής: Σύνδεσμος Πνευματικής και Κοινωνικής Δραστηριότητας Χρυσή Τομή Κερατέας, pp.55–85.

Klemm R. and D. Klemm, 2013. *Gold and gold mining in ancient Egypt and Nubia: geoarchaeology of the ancient gold mining sites in the Egyptian and Sudanese eastern deserts*. Berlin-Heidelberg: Springer.

Lambert, N., 1972. Vestiges préhistoriques dans l'île de Macronissos. *Bulletin de Correspondence Hellénique,* 96, p.873–81.

Martinon-Torres, M., Thomas, N., Rehren, Th. and Mongiatti, A., 2008. Some problems and potentials of the study of cupellation remains: the case of post-medieval Montbelliard, France. *ArchaeoSciences, Revue d' Archaeométrie*, 32, pp.59–70.

Nezafati, N., and E. Pernicka, 2012. Early silver production in Iran. *Iranian Archaeology,* 3, pp 38–45.

Nomicos, S., 2021. Laurion. Montan- und siedlungsarchäologische Studien zum antiken Blei-Silberbergbau. Der Anschnitt, Beih. 44 (= Veröffentlichungen aus dem Deutschen Bergbau-Museum Bochum, Nr. 244). Bochum u. Rahden/Westf.: Marie Leidorf.

Papadimitriou, G. and Kordatos, J., 1995. The brown waterproofing plaster of the ancient cisterns in Lavrion and its weathering and degradation. In: Y. Maniatis, N. Herz and Y. Bassiakos, eds., *The Study of marble and other stones in antiquity*. London: Archetype, pp. 277–284.

Papadimitriou, G.D, 2012. Litharge: Waste or useful raw material? An intriguing material revisited. Λιθάργυρος: Απόρριμα ή χρήσιμη πρώτη ύλη; Ενα ενδιαφέρον υλικό επανεξετάζεται. In: N. Zacharias, M. Georgakopoulou, K. Polykreti, G. Fakorellis and Th. Vakoulis, eds., *Πρακτικά 5ου Συμποσίου Ελληνικής Αρχαιομετρικής Εταιρείας. 5th Symposium of the Hellenic Society of Archaeometry, 8–10 October 2008*, Αθήνα:: Papazissis, pp.799–819.

Papadimitriou, G., 2015. Μία νέα άποψη για τα λεγόμενα Ελικοειδή Πλυντήρια του Λαυρίου και τις μεταλλουργικές διεργασίες που συνδέονται με αυτά, In: A.D. Stefanis, ed., *Πρακτικά ΙΕ΄ Επιστημονικής Συνάντησης ΝΑ Αττικής: Καλύβια Θορικού Αττικής 17–20 Οκτωβρίου 2013 = Proceedings of the 15th Scientific Meeting of SE Attica, Koropi (17–20 Oct. 2013).* Καλύβια Θορικού: Εταιρεία Μελετών Νοτιοανατολικής Αττικής, pp.149–57.

Papadimitriou G.D., 2016. The so called "helicoidal ore washeries of Laurion": their actual function as circular mills in the process of beneficiation of silver and lead contained in old litharge stocks, in E. Photos-Jones, ed., *Proceedings of the 6th Symposium of the Hellenic Society for Archaeometry, Athens 16–18 May 2013.* BAR International Series 2780, Oxford: British Archaeological Reports Ltd., pp.113–18

Papadimitriou G.D., 2018. Λειτουργία και Τεχνολογία των αρχαίων καμίνων της Λαυρεωτικής υπό το φως των ανασκαφών, των αρχαίων απεικονίσεων και κειμένων. In: N. Papagiannakos, ed., *Πρακτικά ΙΖ' Επιστημονικής Συνάντησης Ν.Α. Αττικής = Proceedings of 17th Scientific Meeting of SE Attika, Μαρκόπουλο Αττικής, 3–7 Οκτωβρίου 2018.* Καλύβια Θορικού: Εταιρεία Μελετών Νοτιοανατολικής Αττικής (in prep.).

Papadimitriou G.D. and H. Katsaros, 2019. Discovery of an ancient roasting furnace in Lavreotiki and the problem of the exploitation of galenite for silver production. In: *Πρακτικά 7ου Συμποσίου Ελληνικής Αρχαιομετρικής Εταιρείας. 7th Symposium of the Greek Society of Archaeometry, 9–12 October 2019*, Byzantine and Christian Museum, Athens (in prep.). Book of abstracts: http://archaeometry.org.gr/index.php?option=com_content&view=article&id=3&Itemid=110 (Zugriff 25.05.2022).

Papadimitriou, G.D., 2020. *Landscape reconstruction in the Ergastiria of Lavreotiki during the decline period of the mines* *(after 300 BC), Proceedings of the 4th Arch_RNT, Archaeological Research and New Technologies, Wednesday, 1 October, 2014 to Friday, 3 October, 2014*. Kalamata: University of the Peloponnese, pp. 13 – 23.

Papadopoulos, S., 2008. Silver and copper production practices in the prehistoric settlement at Limenaria, Thasos. In: I. Tzachili, ed., 2008. *Aegean Metallurgy in the Bronze Age. Proceedings of an International Symposium Held at the University of Crete. Rethymnon, Greece, 19 – 21 November 2004*. Athen: Ta Pragmata. pp.59 – 67.

Pernicka, E., Rehren, Th. and Schmitt-Strecker, S. 1998. Late Uruk silver production by cupellation at Habuba Kabira, Syria. In: T. Rehren, A. Hauptmann and J. Muhly, eds., *Metallurgica Antiqua: in Honour of Hans-Gert Bachmann and Robert Maddin*. Der Anschnitt, Beih. 8. Bochum: Deutsches Bergbau-Museum Bochum,, pp.123 – 34.

Rehren, Th., Vanhove, D., Mussche, H.F. and Oikonomakou, M., 1999. Litharge from Laurion, A medical and metallurgical commodity from South Attika. *L' Antiquité Classique,* 68, pp.299 – 308.

Servais, J., 1967. Les fouilles sur le haut du Vélatouri. In: H.F. Mussche, J. Bingen, J. Servais, J. de Geyter, T. Hackens, P. Spitaels and A. Gauthier, eds., *Thorikos 1965. Rapport préliminaire sur la troisième campagne de fouilles*. Bruxelles – Brussel: Comité des fouilles belge en Grèce, pp.9 – 30.

Stos-Gale, Z.A., 1989. Cycladic copper metallurgy. In: A. Hauptmann, E. Pernicka and G.A. Wagner, eds., *Old World Archaeometallurgy.* Der Anschnitt, Beih. 7. Bochum: Deutsches Bergbau-Museum Bochum, pp.279 – 91.

Tsaïmou, C.,1988. *Εργασία και Ζωή στο Αρχαίο Λαύριο σε εγκατάσταση εμπλουτισμού μεταλλευμάτων τον 4ο αιώνα π.Χ.* Unpublished PhD, National Technical University of Athens.

Tsaïmou, C., 2005. Αρύ Λαυρεωτικής. *Αρχαιολογικόν Δελτίον*, 60, A, pp.183 – 90.

Tsaïmou, C., P.E.Tsakiridis and P. Oustadakis, 2015. Analytical and technological evaluation of ancient lead slags from Lavrion, Attika, Greece. *Mediterranean Archaeology and Archaeometry*, 15 (2), pp.113 – 27.

Spitaels, P., 1982a. Provatsa in Makronisos. *Αρχαιολογικά Ανάλεκτα εξ Αθηνών*, XV, pp.155 – 58.

Spitaels, P., 1982b. An unstratified Late Mycenean deposit from Thorikos mine gallery no. 3, Attica. In: P. Spitaels, ed., Studies in South Attica I. Miscellanea Graeca 5. Gent: Comité des fouilles Belges en Grèce, pp.83 – 96.

Spitaels, P., 1984. The Early Helladic period in Mine 3 (The Theater sector). In: H. F. Mussche, J. Bingen, J. Servais and P. Spitaels, eds., *Thorikos VIII 1972/1976*. Gent: Comité des fouilles Belges en Grèce, pp.151 – 74.

Swinbourne, D.R., Yan, S., Hoang, G. and Higgins, D., 2003. Thermodynamic modelling of cupellation: activity of AgO0.5 in molten PbO at 1000° C, Mineral Processing and Extractive Metallurgy. T*ransactions of the Institutes of Mining and Metallurgy*, 112, C69-C74.

Theocharis, D.R., 1952. Ἀνασκαφὴ ἐν Ἀραφῆνι. *Πρακτικά της εν Αθήναις Αρχαιολογικής Εταιρείας*, pp.129 – 51

Theocharis, D.R., 1954. Ἀνασκαφὴ ἐν Ἀραφῆνι. *Πρακτικά της εν Αθήναις Αρχαιολογικής Εταιρείας*, pp.104 – 13

Ulseth, P., Lohne, O., Risvaag, J.A., Lohne, J., and Ervik, T., 2015. Late Medieval bone-ash cupels from the archbishop's mint in Trondheim. *Fornvännen, tidskrift för svensk antikvarisk forskning*, 110 (4), pp.267 – 79.

Author

George D. Papadimitriou – National Technical University of Athens (NTUA), School of Mining and Metallurgical Engineering, Laboratory of Physical Metallurgy (Metallognosia), Zografou Campus, Athens, Greece, gpapadimitriou@metal.ntua.gr

Correspondence and material requests should be addressed to: gpapadimitriou@metal.ntua.gr