



## Research Article

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# The Presence of Au and Ag in Pb-rich Slags from Hellenistic Pistyros, N. Greece: Some Observations

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## Abstract

Pistyros, in NE Greece, is a small fortified urban settlement founded by Thasians on the mainland in the 7<sup>th</sup> c. BCE; it displays, uniquely for the region, a considerable amount of well contextualized and dated (4<sup>th</sup>-3<sup>rd</sup> c. BCE) metallurgical waste (in excess of 1.2 tons); further, the Pb-based metallurgical waste displays presence of Au and Ag. In an area famous, both on historical and geological grounds, for its base (Cu, Pb, Fe) and precious (Au, Ag) metals deposits, there exists, still today, no good evidence for their routine extraction and processing and on a large scale. The questions that arise are related to what was urban Pistyros' main function. Was it intent on making metals and which ones? Was it making only metals or metal derivatives (oxides or carbonates) as well? We have at this stage no definitive answers.

In this paper we focus on the presentation of EPMA (Electron Probe Micro Analysis) results from three slag sample-types (silicate slag, iron arsenides, lead oxides). We examine the presence and distribution of Au and Ag within, and suggest that the two metals probably play a secondary role to the site's main involvement, i.e. Pb-based metallurgy; be it for the production of antimonial lead and its 'purification' for the production of lead oxide and/or for the further processing of iron arsenides. Pistyros polymetallic metallurgical waste interpretation requires careful assessment of what it means to carry out high temperature metallurgical activities for the purpose of acquiring not just metals but possibly, also, metallic mineral derivatives within urban centers; such centers tend to be rare, nuanced, and certainly challenge us to look beyond the 'precious metal-for-coinage' axis we have been accustomed to.

**Keywords:** Pistyros, Thasos, Skapte Hyle, metallurgy, gold, silver, lead, EPMA**Abbreviations:** Th: Thucydides, *History of the Peloponnesian War*, Zen: Zenobius Paroemiographus, *Epitome collectionum Lucilli Tarrhaei et Didymi*, Arist: Aristoteles Philosophus Stagiritis, *Fragmenta*, Str: Strabo, *Geographia*, D.S: Diodorus Siculus, *Bibliotheca historica*. App: Appianus Historicus Alexandrinus, *Bella Civilia*

## Introduction

Ongoing excavation (2014-2022) of a Thasian fortified settlement, associated with ancient Pistyros, near Kavala in Northern Greece provided, for the first time, a rare opportunity to study large-scale metallurgical activities *within* an urban context, in the Hellenistic period (4<sup>th</sup>-3<sup>rd</sup> c. BCE). Pistyros was a Thasian colony established at the foothills of the Lekani mountain range (Figure 1) in the late 7<sup>th</sup> c. BCE and was inhabited until the 1<sup>st</sup> c. BCE [1-3]. It

displayed the characteristics of a *polis* (small urban settlement) with both civic (sanctuary) and 'agricultural/industrial' buildings (granary/winery). The weighed amount of recovered slag from excavated contexts is c. 1.2 tons, while an undisclosed amount is still waiting examination; further to the above, there are areas in the immediate vicinity of slag heaps waiting further excavation. These findings are significant as they represent the first, securely dated evidence for urban metallurgical practices in this region.

Although there are several mentions in ancient literary sources of the extraction of precious metals in this region of NE Greece, the actual chronology for mining and smelting activities on the Lekani massif remains unclear and as such is in much need of further investigation. Literary sources refer to a particularly rich mining area that the Thasians had under their control on their mainland territory (Thasian continent or *Peraia*) that was called *Skapte Hyle* (dug forest), the exact location of which still remains a matter of debate. Such historical documents are useful to consider as they tie in the archaeological evidence with significant events of the region's economic history. Pistyros with its wealth of well contextualized finds resulting from metallurgical activities and secure chronological framework, is in a unique position to bring together four already existing data sets, in a coherent way, a task that was not possible to achieve before. These data sets include a. the well-researched geology/minerals resources of the area, b. the associated ancient mining activities, c. historical sources and d. the various studies of pyrometallurgical remains belonging to unspecified/broadly outlined periods in the vicinity of the mining sites (Figures 1 & 2). We examine, in brief, each one of these data sets (Figure 2).

### Skapte Hyle and other metalliferous areas in the vicinity of Pistyros

The mines on Eastern Macedonia were always the goal behind attempts by the Athenians to break up the Thasian hegemony in that region and in the process colonise the area. They eventually did succeed in gaining control and founded a colony, Amphipolis, only to lose it at the start of the Peloponnesian war (430 BCE). The earliest literary reference concerning *Skapte Hyle* could be found in Herodotus *Histories*, dated 493 BC<sup>1</sup>. Allegedly, this mining region was so rich that the Thasians earned between 80 and 200 or even 300 talents per year, an enormous sum that is considered with

some skepticism by modern researchers.

Eventually Skapte Hyle came under Athenian control with the expedition of Cimon between 465 and 463 BCE. Plutarch<sup>2</sup>, at the end of the conflict between Thasos and Athens in 463 BCE a significant mining region that was exploited by the Thasians passed into the hands of the Athenians. Although the name of the region in question is not given, it has been suggested that the mines mentioned in this context should be identified with those of Skapte Hyle [5].

It should be also mentioned that. Thucydides locates the emporia coordinating such mining activity opposite of Thasos<sup>3</sup>, which excludes Mount Pangaion and the Strymon region. Along the same lines, Plutarch refers to mines beyond, or opposite the island<sup>4</sup>. The gold mines of Krenides-Philippi on the western Lekani massif are mentioned for the first time in the 360s BCE, when the exiled Athenian politician Kallistratis persuaded the exiled Athenians of the region to settle on the opposite shore of the lake, at the Thasian settlement of Krenides, by alluring them with the area's gold riches<sup>5</sup>.

When Philip II founded Philippi<sup>6</sup> in 356 BCE at the exact location of Krenides, the mines of the region passed under Macedonian control. At the time of Philip II, Aristotle mentions the auriferous veins of the mining region near Philippi while the later testimonies by Strabo<sup>7</sup> and Diodorus Siculus<sup>8</sup> give an account of the policy of Philip II and his desire to exploit the mining areas near Philippi. Both authors mention the immense income that Philip II was able to obtain through the exploitation of these mines. Interestingly later historical sources refer to this mining region with its Latin name, *Skaptensule*, and as a silver producer in addition to gold<sup>9</sup>. Lastly, Appian writing in the second c. AD mentions the gold mines near Philippi under the name *Asyla*<sup>10</sup> (lingual alteration from *Skaptesyala*?). The above literary references show the long history of gold mining in the region of Lekani covering at least from the mid-5<sup>th</sup> c. BCE up to the 2<sup>nd</sup> c. AD.

<sup>1</sup> Herodotus, *Histories* VI.46.3: "Their revenue came from the mainland and from the mines. About eighty talents on average came in from the gold-mines of Skapte Hyle, and less from the mines of Thasos itself, yet so much that the Thasians, paying no tax on their crops, drew a yearly revenue from the mainland and the mines of two hundred talents on average, and three hundred when the revenue was greatest"

<sup>2</sup> Plutarch, *Cimon* 14.2: "And after this, when the Thasians were in revolt from Athens, he defeated them in a sea-fight, captured thirty-three of their ships, besieged and took their city, acquired their gold mines on the opposite mainland for Athens, and took possession of the territory which the Thasians controlled there"

<sup>3</sup> Th. I 100.2: χρόνω δὲ ὕστερον ξυνέβη Θασίουσ αὐτῶν ἀποστήναι, διενεχθέντας περὶ τῶν ἐν τῇ ἀντιπέρας Θράκη ἐμπορίων καὶ τοῦ μετάλλου ἃ ἐνέμοντο.

<sup>4</sup> Plutarch, *ibid.* "τὰ χρυσεῖα τὰ πέραν"

<sup>5</sup> Zen. IV 34: Καλλίστρατος γὰρ ὁ ῥήτωρ ἐκπεσῶν Ἀθήνηθεν ἔπεισε τοὺς Ἀθηναίους τὴν ἀντίπεραν γῆν οἰκῆσαι, λέγων ὅτι καὶ χρυσεῖα μέταλλα ἔχει, καὶ γῆν ἄφθονον, καὶ ὕλην ἀρίστην etc.

<sup>6</sup> Arist. F 255 Rose ([Arist.], *Mir.* 833a): περὶ Φιλίππου τῆς Μακεδονίας εἶναι λέγουσι μέταλλα, ἐξ ὧν τὰ ἐκβαλλόμενα ἀποσύρματα αὐξάνεσθαι φασιν καὶ φύειν χρυσίον, καὶ τοῦτ' εἶναι φανερόν.

<sup>7</sup> D.S. XVI 8.6-7: "After this he [Philip] went to the city of Krenides, and having increased its size with a large number of inhabitants, changed its name to Philippi, giving it his own name, and then, turning to the gold mines in its territory, which were very scanty and insignificant, he increased their output so much by his improvements that they could bring him a revenue of more than a thousand talents".

<sup>8</sup> D.S. XVI 8.6-7: "After this he [Philip] went to the city of Krenides, and having increased its size with a large number of inhabitants, changed its name to Philippi, giving it his own name, and then, turning to the gold mines in its territory, which were very scanty and insignificant, he increased their output so much by his improvements that they could bring him a revenue of more than a thousand talents".

<sup>9</sup> Lucretius VI 808-810: 'denique ubi argenti venas aurique secuntur terrae penitus scrutantes abdita ferro qualis expiret Scaptensula subter odores' and Fest. Ed. Lindsay, 442-443: 'Scaptensula locus, ubi effoditur argentum in Macedonia'

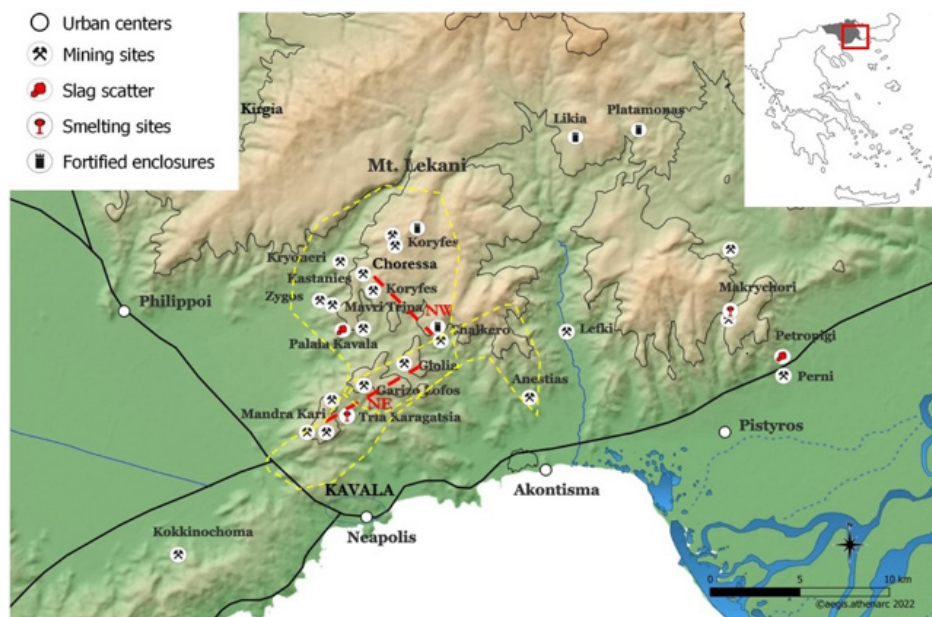
<sup>10</sup> App., *BC* IV 13.106 : Φιλίππων μὲν οὖν ἔστιν ἕτερος λόφος οὐ μακρὰν, ὃν Διονύσου λέγουσιν, ἐν ᾧ καὶ τὰ χρυσεῖα ἔστι τὰ Ἄσυλα καλούμενα.

## Brief outline of regional geology/ minerals resources

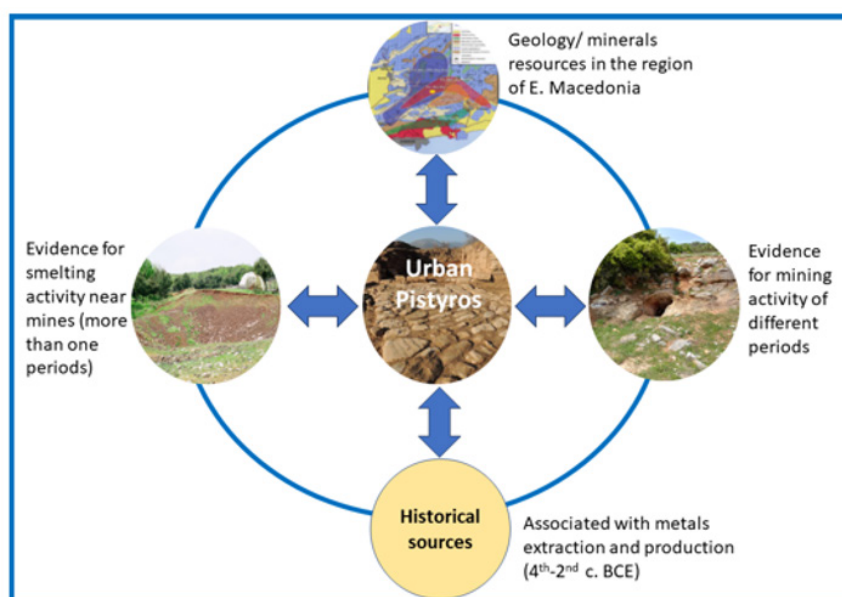
Over the years, there have been a number of studies regarding the region of Palaia Kavala (Figure 1) and its diachronic exploitation for Au/Ag in antiquity and in later periods. In the early 1980's Spathi and co-authors [6] drew a broad outline around that area which includes the villages of Palaia Kavala, Zygos, Kirgia and Makrychori (Figure 1). The authors reported that the area consists of schists with marbles and granitic offshoots. The mineralization occurs at the contact of marbles and mica schists and is developed along two zones, i.e., along a NE and NW direction. The former follows the line of occurrences at the sites Mandra Kari, Garizo Lofos and Giolia, while the NW occurrence is evident at the village of Chalkero and the site of Choressa (see Figure 1 for the direction

of this mineralization).

Interestingly, they suggested that the two directions of mineralization are quite distinct in both chemical and mineralogical terms. In the NE the iron manganese ores are associated with Pb, Zn and Ag, while in the NW it is associated with Cu and Au and occasionally Bi. Arsenic is present in both. More recently Fornadel and co-authors [7] refined on the observations of Spathi and co-authors [6] and highlighted 150 minor Fe-Mn (Pb ± Zn ± Ag), Fe-Mn-Au, Fe-As-Au, Fe-Cu-Au, and Bi-Te-Au occurrences that occur primarily in quartz-calcite-sulfide veins [7]. As we shall demonstrate below the Pistyros slags demonstrate presence, apart from Au and Ag also Ta, Pt and Hg (see Tables 1-3) which point to other sources as well, yet to be researched.



**Figure 1:** Map of the area showing the locality of Pistyros and other urban centers (Philippoi, Neapolis, Akontisma, Pistyros), mining (numerous sites of unspecified/ multiple periods) and smelting sites (Palaia Kavala, Tria Karagatsia, Petropigi, Makrychori). The directions of mineralization are indicated in yellow dotted lines (after Fornadel et al 2011) and red dashed lines (after Spathi et al 1982)



**Figure 2:** Graphic illustration of the existence of available datasets for the study of metals extraction in E. Macedonia in the Classical/ Hellenistic periods and the central role of Pistyros in processing one or more of them for a variety of markets.

## The largely undated pyrometallurgical activities near the mines

There is already substantial research that has focused on mining sites and the voluminous slag deposits away from urban centers tentatively dated to the Classical/Hellenistic periods, as deduced from associated pottery [8-12]. For example, near the modern villages of Perni and Petropigi (Figure 1) and only about 2.5 km to the NE of Pistyros there is evidence for mining galleries of square profiles, usually attributed to the Classical period; also evidence for small scale smelting activities [5, 8]. Further north, near the village of Makrychori, not far from mining galleries, the hills are covered by voluminous slag heaps across an extended area. Based on surface pottery, these slag deposits are conventionally dated from the 4<sup>th</sup> to the 2<sup>nd</sup> centuries BCE [9]. Therefore, Pistyros with its excavated metallurgical finds, securely dated to the Hellenistic period is, as of now, the single most important site to illuminate ancient metals extraction practices in the broader NE Greek territories.

### Archaeological evidence for urban metallurgy at Pistyros

During the course of excavations at Pistyros (2014 to present), the excavator, S. Papadopoulos, gradually brought to light primarily Hellenistic levels [3]. Hellenistic Pistyros is characterised by a range of civic (sanctuary-Figure 3, VIII) and industrial buildings (granary-Figure 3, VII/winery-Figure 3, III). Yet the central part of the site (which still awaits excavation) is largely dominated by a substantial amount of metallurgical waste. We maintain that it is unlikely that such a large amount of slag has been brought in the fortified settlement, in order to be used as foundation material, and instead,

was left there unused. Although there is so far no clear evidence for furnace(s) or hearths, nevertheless, furnace wall fragments and stones with slag adhering on their surface were recovered from the street and its adjacent open courtyard in square BΨ (IV in Figure 3). So, whether ores were being smelted within the site or not has to remain, for now, an open question. There are further issues:

- a. Evidence for charcoal is rather modest (it has not been quantified), given the large quantity of slag.
- b. Slag size is relatively small (c. 98% of the slag measures between 1 and 5 cm in diameter) suggesting breaking, presumably to release metallic inclusions within. There is at present no evidence for working floors or relevant tools which would indicate extensive manual slag-processing on site, let alone hearths, which may have been associated with secondary heating. So again, secondary manual processing (slag break-up) remains an open question.
- c. The majority of slag is found in the immediate proximity of the 'winery' which although likely to have been in operation on a seasonal basis, could in principle have been affected (building facilities and equipment) from the metalworking furnaces, if they turn out to have indeed been located nearby.
- d. The fortified site is relatively small (it covers c. 4 acres or 15000 square meters) with private houses and public places (granary/winery/sanctuary); this means that space must have been tight particularly since a large portion of the site has been taken up by the slag heap.



**Figure 3:** Aerial photo of the site with the main excavated buildings indicated in roman numerals. I: building attached to the fortification wall, II building with benches, III: 'winery', IV: building west of the street, V: large Hellenistic building, VI: building of western sector, VII: storage building, VIII: temple in the sanctuary area, IX: second building attached to the fortification wall, to the north of the SE gate. Also shown is the location of the three squares where the samples derive from.

In short there are a number of intriguing questions that await the outcome of further excavations. In the absence of structural remains of metallurgical nature attention has been turned to the detailed examination of three samples of metallurgical waste, each representing a type-piece (Figures 4a-c):

- SL9.2, an Fe-Pb oxide/silicate-rich slag, constituting the majority of finds.
- SP2, an iron arsenide-rich slag, of the type often referred to as 'speiss' (only 9 such samples have been recovered); L3.
- L3, a PbO-rich material often referred to as 'litharge' (only 23 such samples have been found).

The three samples presented here are well dated by association to coinage and to the period between the middle 4<sup>th</sup> c. and the end of the 3<sup>rd</sup> c. BCE [4].

Dates and context for each sample are given as:

- sample SL9.2 (oxides/silicates) found in square EH, derives from the south of building V, in the vicinity of a circular stone-built feature, labelled K1 (Figure 3, V); the structure had a clay backing externally and internally it was filled with slag; two coins date the context to the 3<sup>rd</sup> c. BCE;
- sample SP2 (iron arsenide) comes from square ΓΩ, the sanctuary area (Figure 3, VIII), from a context that yielded a coin of Antigonus Gonatas, dating to 277-239 BCE [4].
- sample L3 (PbO-rich) was found in square ΒΨ, from a street deposit filled with slag (Figure 3, IV). Two coins, one of Alexander III, 336-323 BCE and a second of Abdera, 311-281 BCE provide the chronological framework for this sample [4].



Fig. 4a Slag - SL9.2



Fig. 4b 'Speiss' - SP2



Fig. 4c 'Litharge' - L3

## Materials and Method

Electron Probe Micro Analysis (EPMA) took place at the University of Strathclyde's Department of Physics. The instrument is a JEOL JXA-8530F field-emission electron probe micro analyser. Energy Dispersive X-ray analysis was used for all elements with the exception of four which used the following wavelength Dispersive X-ray diffracting crystals: TAPH (Fe  $L\alpha$ ), TAP (Au  $M\alpha$ ), PETH (Ag  $L\alpha$ ). For the elemental maps, a 20 kV accelerating voltage and a 40 nA beam current was used. A total of 28 elements were sought. Their concentrations are listed as normalised by weight % (Tables 1-3). The LOD for each element (in ppm) is also given to highlight the distribution of possibly indicative (for future studies) trace elements, apart from Au and Ag and in particular Ta, Pt, Hg, Sb, Bi, As; also, Pd (always below LOD).

All elements are presented in normalised weight %. Key/precious elements are highlighted. Average Limit of Detection for each element is shown at the bottom of the table. It follows that Table entries reported as zero are  $\leq$ LOD. Conversion parameter: 1%= 10000ppm.

## Results and Discussion

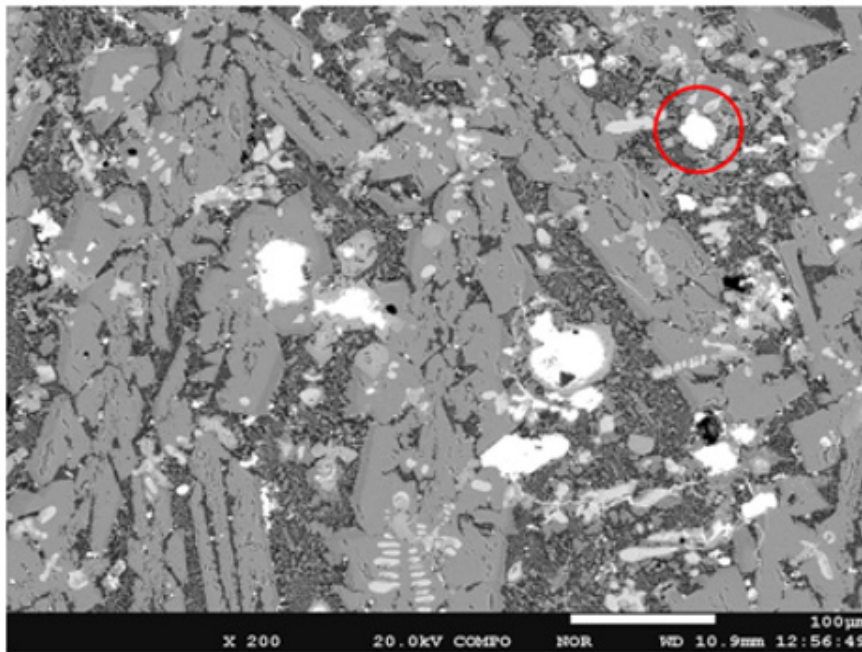
### EPMA analysis of sample SL9.2, silicate-rich

Figure 5a shows sample's SL9.2 distinct micro-crystallinity consisting of largely both oxide/silicate with small metallic

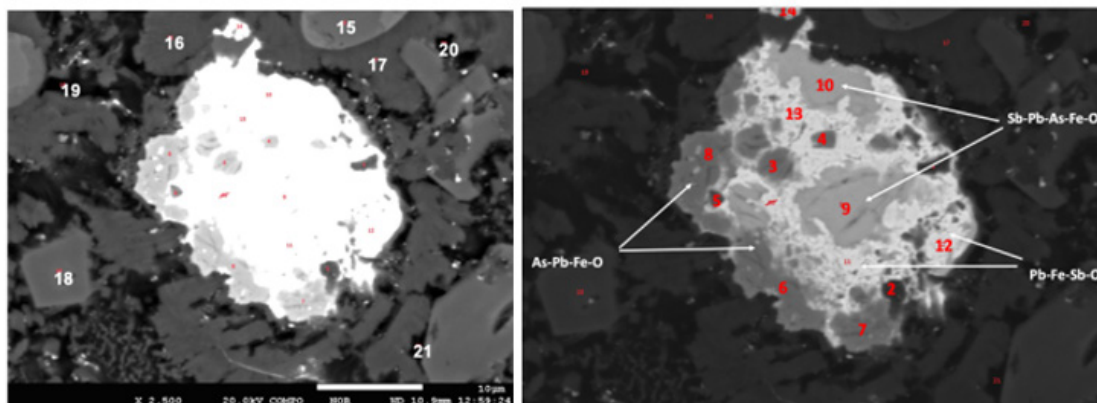
inclusions (prills) dispersed throughout the matrix. Regarding the former, there are globular dendrites of FeO (light grey), long lathes of Ca-Fe-Si-O (dull grey) and an interstitial non-crystalline/glassy phase (dark grey); all three are common phases encountered in ancient slags and the crystalline ones are referred to as wüstite and kirschsteinite, after the minerals that match their composition. We focus on the area circled within Figure 5a.

In examining Table 1, the first observation is that this is a Pb-rich slag; Pb partitions preferentially not in the Ca-Fe oxide/silicate phases (Table 1, spot analyses 15-21) but rather within the small metallic inclusions of Pb-Sb-Fe-As in different relative concentrations to each other. The silicate phase consists of average of c.29%Pb/23%Fe/13%Sb and with no As (average values taken from Table 1). Mn is not particularly prevalent. Au and Ta correlate well and are to be found within these phases, while Hg concentrates in the metallic ones -see below.

The metallic constituent is a mixture of metals of roughly 40%Pb/25%Sb/15%Fe/15%As composition (average values taken from Table 1) as can be surmised from the analysis of the metallic inclusion in Figure 5c & Table 1. What is of interest is that contrary to what one might have expected, these Pb/Sb-rich metallic prills are Au/Ag 'poor'. As already mentioned, the reverse seems to be true for the Pb-poor silicate phases, both crystalline and glassy: i.e., they are richer in Au/Ag and in Ta in particular (Table 1).



**Figure 5a:** EPMA image of an area within sample SL9.2. There are numerous metallic (light) inclusions which, although appearing homogeneous, actually are not, varying in the composition of their constituent metals (see Fig. 5c below).



**Figure 5b:** (left) and Figure 5c (right) are identical images, under different exposure, aimed at highlighting the different phases (silicate/oxide-based (dark) surrounding the metallic (light) inclusion within sample SL9.2 as seen in Fig. 5a. The metallic inclusion is made up of different phases consisting of four elements (As/Pb/Sb/Fe) in different proportions to each other. All 21 spot analyses are shown in Table 1, in weight % and with the LODs per element displayed at the bottom in ppms.

The presence and distribution of the above many elements suggest that: a. a polymetallic ore(s) was charged into the furnace; b. a relatively fast cooling rate (i.e., the slag cooled/ran out soon after forming) took place on account of the small size of each crystalline phase and the multitude of small metallic inclusions which had little time to coalesce into larger ones. This fast cooling may argue against the idea of a conventional tall, shafted furnace where the ore is allowed to sit over long(er) periods of time, and more towards a low shaft, hearth-like arrangement. However, again at this stage, this can only be a working hypothesis.

Assuming this is a typical Pistryros smelting slag, we can argue that two types of metals could in principle come out of this furnace:

one consisting primarily of antimonial lead (Pb-Sb) and another of iron arsenides (Fe-As). There is no physical evidence, so far, for the former, only for the latter (see section below).

Pb-Sb alloys have a melting point of 252°-360°C. Had the Pistryros furnace produced that type of 'alloy', then antimonial lead would run out of the furnace first i.e., at that low temperature range. On the other hand, iron arsenides (Fe-As) have a much higher melting point (c. 1000°C). Different combinations of Pb-Sb-Fe-As would have a melting point of somewhere in between.

#### EPMA analysis of sample SP2- rich in iron arsenides

As mentioned, there are no fragments of antimonial lead;

instead, we have examples of iron arsenides with Pb-Sb inclusions. Fe-arsenides are usually referred in the literature by their 19<sup>th</sup> century German name i.e., speiss. Although this term is also used in archaeometallurgy, and even in a prehistoric context, we shall

nevertheless endeavor to avoid using it here and will simply refer to it as a metallic mixture of Fe-As (with Pb-Sb) and with a small oxygen component, as the data in Table 2 suggest.

**Table 1:** EPMA analyses of oxide/ silicate (pink) and metallic (yellow) phases within SL9.2

spot analysis number	O	Mg	Al	Si	As	Ta	P	S	Ca	Ti	V	Cr	Mn	Pt	Au	Hg	Fe	Ni	Cu	Zn	Ag	Cd	Sn	Sb	Ba	Pb	Bi	Pd	Total
1	16.3	0	4.28	6.72	0.56	0	0.01	0	2.29	0	0	0	0.78	0	0	0.02	24.8	0	0.04	0.39	0	0	0	10	0.01	33.7	0.1	0	100
2	15.7	0	1.41	7.64	0.95	0	0	2.6	1.87	0	0	0	0.9	0	0	0	30.4	0.01	1.25	0.18	0	0	0	2.49	0.02	34.4	0.14	0	100
3	1.29	0	0.01	0	1.02	0	0	0	0	0	0	0	0.01	0	0	0.03	1.17	0	0.04	0.02	0	0	0.04	2.42	0.03	93.7	0.27	0	100
4	1.61	0	0.03	0	0.79	0	0	0	0	0	0	0.01	0.01	0	0	0	0.97	0	0.04	0.04	0	0.02	0.11	18.2	0	78	0.22	0	100
5	13	0	0.02	4.22	1.27	0	0	0	1.37	0	0	0	0.57	0	0	0.01	13.6	0	0.04	0.12	0	0	0	11.6	0	54	0.16	0	100
6	1.48	0	0.01	0	33.4	0	0	0	0.03	0	0	0	0.06	0	0	0.02	17.2	0.07	0.07	0.02	0	0.01	0.02	1.06	0.03	46.4	0.14	0	100
7	1.33	0.02	0.17	0.37	52.4	0	0	1.05	0.12	0	0	0	0.03	0.03	0	0	35.6	0.14	0.97	0.01	0.01	0.01	0.02	1.85	0.02	5.81	0.02	0	100
8	0.93	0	0.01	0	38.5	0	0.01	0	0.05	0	0	0	0.03	0	0	0.03	21.5	0.09	0.19	0.02	0	0.01	0.01	1.12	0.03	37.4	0.11	0	100
9	0.57	0	0	0.01	2.64	0	0	0	0	0	0	0	0.03	0.09	0.01	0.01	0.46	0.01	0.04	0	0.01	0.02	0.44	90.8	0	4.88	0.02	0	100
10	0.68	0	0.05	0.23	4.06	0	0	0	0	0	0	0	0.07	0.05	0	0.03	1.85	0.01	0.03	0.03	0.01	0.02	0.4	86.2	0	6.21	0.03	0	100
11	5.81	0	0.07	1.18	1.49	0	0	0	0.18	0	0	0	0.16	0	0	0.02	6.47	0.01	0.04	0.04	0	0	0	2.2	0.02	82.1	0.24	0	100
12	5.1	0	0.69	2.16	1.78	0	0	0	0	0.01	0	0	0.24	0.03	0	0.01	5.48	0.02	0.05	0.05	0	0.01	0	46.5	0	37.8	0.09	0	100
13	1.34	0	0.01	0	0.74	0	0	0	0	0	0	0	0.05	0	0	0.02	1.55	0.01	0.04	0.02	0	0	0.06	6.78	0	89.1	0.24	0	100
14	20.1	0.2	0.14	14	0.23	0.2	0.01	0	13	0.04	0.01	0.01	3.03	0	0	0	42.1	0.01	0.02	0.2	0	0.01	0	0.17	0.04	6.54	0.02	0	100
15	21.9	0.03	4.74	0.21	0	0	0	0	0.26	1.24	0.45	0.24	0.7	0	0.05	0	69.5	0.01	0.02	0.37	0.01	0.01	0	0.06	0.12	0.06	0.01	0	100
16	25.4	0.23	0.06	15.4	0.01	0.24	0.01	0.01	11.8	0.01	0	0	3.05	0	0.03	0	43.3	0.02	0.02	0.21	0.01	0.01	0	0.04	0.03	0.09	0.01	0	100
17	26	0.16	3.47	12.4	0	0.22	0.02	0.03	10.7	0.15	0.04	0.03	2.4	0	0.05	0	43.7	0.01	0.02	0.35	0.01	0	0	0.06	0.04	0.12	0	0	100
18	22	0.03	5.81	0.36	0.01	0	0	0.05	0.26	0.99	0.24	0.11	0.53	0	0.02	0	68.9	0.02	0.03	0.36	0	0.01	0	0.03	0.09	0.24	0.01	0	100
19	32.7	0	15.7	26.2	0.01	0.36	0.04	1.11	6.58	0.03	0	0.01	0.39	0	0.08	0	14.8	0.01	0.05	0.08	0	0	0	0.22	0.51	1.13	0.01	0	100
20	29.1	0.16	3.13	16.6	0.01	0.25	0.01	0.06	11.3	0.05	0	0	2.17	0	0.03	0	36.3	0.01	0.02	0.21	0.01	0	0	0.25	0.09	0.26	0.01	0	100
21	35.2	0.04	9.56	19.3	0	0.31	0.05	0.08	8.97	0.15	0.03	0	0.77	0	0.21	0	24.2	0.01	0.03	0.16	0.01	0	0	0.18	0.4	0.46	0	0	100
average LOD in ppm	612	21	12	30	47	56	42	113	50	42	53	64	90	183	122	145	41	46	53	59	36	37	65	41	62	88	66	38	

**Table 2:** EPMA analyses of different iron arsenide phases within SP2.

all elements in %	O	Mg	Al	Si	As	Ta	P	S	Ca	Ti	V	Cr	Mn	Pt	Au	Hg	Fe	Ni	Cu	Zn	Ag	Cd	Sn	Sb	Ba	Pb	Bi	Pd	Total
0.22	0.00	0.00	0.00	13.30	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.02	85.43	0.02	0.14	0.00	0.00	0.01	0.03	0.87	0.01	0.04	0.01	0.00	100.00	
0.19	0.00	0.00	0.01	13.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	85.63	0.02	0.13	0.00	0.01	0.00	0.03	0.87	0.02	0.05	0.01	0.00	100.00
0.18	0.00	0.00	0.01	13.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.03	0.00	85.08	0.02	0.14	0.00	0.01	0.00	0.04	0.86	0.02	0.05	0.01	0.00	100.00
0.19	0.00	0.00	0.00	13.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.03	0.00	85.41	0.02	0.13	0.00	0.01	0.01	0.04	0.87	0.03	0.01	0.01	0.00	100.00
0.88	0.01	0.03	0.01	0.88	0.00	0.00	30.13	0.04	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	67.37	0.02	0.05	0.00	0.01	0.01	0.02	0.29	0.03	0.15	0.04	0.00	100.00
3.92	0.00	0.00	0.00	1.07	0.00	0.00	26.73	0.00	0.00	0.00	0.00	0.00	1.77	0.00	0.00	0.00	28.86	0.01	0.03	37.34	0.02	0.01	0.01	0.18	0.02	0.02	0.03	0.00	100.00
1.82	0.01	0.00	0.00	17.40	0.00	0.00	16.93	0.00	0.00	0.00	0.00	1.09	0.00	0.00	0.00	0.00	43.15	0.02	0.32	15.78	0.01	0.01	0.03	3.37	0.00	0.04	0.02	0.00	100.00
0.20	0.00	0.00	0.01	0.27	0.00	0.00	34.53	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	64.58	0.02	0.07	0.00	0.01	0.01	0.02	0.18	0.03	0.00	0.04	0.00	100.00
0.36	0.01	0.00	0.02	14.26	0.01	0.00	0.68	0.00	0.00	0.00	0.01	0.00	0.04	0.02	0.00	0.00	80.64	0.02	0.20	0.00	0.00	0.00	0.07	3.10	0.00	0.56	0.02	0.00	100.00
0.36	0.00	0.00	0.01	1.01	0.01	0.00	31.84	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	63.55	0.02	0.10	0.00	0.01	0.01	0.06	2.60	0.01	0.37	0.04	0.00	100.00
0.24	0.00	0.00	0.00	5.44	0.00	0.00	25.59	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	64.91	0.02	0.12	0.00	0.01	0.00	0.03	1.52	0.01	2.05	0.03	0.00	100.00
0.16	0.00	0.00	0.00	27.57	0.00	0.00	4.92	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	49.29	0.02	0.93	0.00	2.35	0.04	0.32	13.36	0.00	1.00	0.01	0.00	100.00
0.14	0.01	0.00	0.01	39.74	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	53.88	0.02	0.79	0.00	0.01	0.01	0.05	5.06	0.00	0.04	0.01	0.00	100.00
0.12	0.01	0.00	0.00	39.53	0.00	0.00	0.21	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.00	0.00	53.96	0.02	0.84	0.00	0.01	0.00	0.05	5.16	0.00	0.04	0.01	0.00	100.00
0.14	0.01	0.00	0.00	39.42	0.02	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	54.13	0.02	0.78	0.00	0.01	0.00	0.05	5.11	0.00	0.04	0.02	0.00	100.00
0.13	0.02	0.00	0.01	39.14	0.00	0.00	0.23	0.00	0.01	0.00	0.00	0.00	0.00	0.05	0.00	0.00	54.08	0.02	0.78	0.00	0.02	0.00	0.05	5.42	0.00	0.04	0.01	0.00	100.00
0.16	0.00	0.00	0.00	12.67	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	85.56	0.02	0.14	0.00	0.01	0.00	0.06	1.32	0.02	0.03	0.00	0.00	100.00
0.23	0.00	0.00	0.00	12.75	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.00	85.30	0.02	0.14	0.00	0.02	0.00	0.07	1.35	0.01	0.02	0.02	0.00	100.00
0.14	0.02	0.00	0.00	36.97	0.00	0.00	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02	0.00	53.81	0.03	0.80	0.00	0.01	0.02	0.07	7.80	0.00	0.05	0.01	0.00	100.00
0.26	0.00	0.00	0.00	11.84	0.00	0.00	0.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	37.55	0.04	0.97	0.01	0.01	0.00	1.04	46.42	0.00	0.87	0.01	0.00	100.00
0.70	0.00	0.00	0.01	20.22	0.00	0.00	20.34	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	54.32	0.01	0.26	0.00	0.01	0.01	0.04	3.56	0.00	0.45	0.03	0.00	100.00
0.19	0.00	0.00	0.00	10.50	0.00	0.00	0.18	0.00	0.00	0.00	0.01	0.00	0.04	0.00	0.00	0.00	45.24	0.03	0.56	0.01	0.01	0.01	0.89	42.08	0.00	0.25	0.01	0.00	100.00
average LOD per element in ppm	547	18	11	27	44	47	40	39	43	41	51	61	86	167	106	133	39	37	43	4									

**Table 3:** EPMA analyses of different Pb-rich phases within L3.

Point	O	Mg	Al	Si	As	P	S	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Sn	Sb	Ba	Pb	Bi	Ag	Pt	Au	Hg	Pd	Ta	
1	4.52	0.00	26.13	0.60	0.02	0.08	0.08	64.79	0.00	0.14	0.04	0.04	0.37	0.00	0.00	0.00	0.00	0.00	0.03	3.04	0.05	900	0	0	0	0	0	100	
2	18.30	0.04	22.10	21.69	0.04	0.01	0.00	1.76	0.00	0.00	0.01	0.06	1.05	0.00	0.07	0.00	0.00	0.00	0.26	0.07	34.29	0.10	0	10	0	330	0	1320	100
3	34.48	3.61	0.07	14.99	0.86	0.01	0.00	19.31	0.00	0.00	0.00	0.02	0.07	0.00	0.16	0.00	0.00	0.00	0.04	0.05	26.18	0.08	0	0	0	0	0	850	100
4	31.41	6.03	0.16	13.74	0.75	0.02	0.00	27.86	0.00	0.00	0.00	0.03	0.17	0.00	0.01	0.00	0.00	0.00	0.02	0.05	19.59	0.05	0	0	40	0	0	1060	100
5	31.65	4.74	0.04	12.63	1.00	0.02	0.00	21.01	0.00	0.00	0.00	0.02	0.01	0.01	0.02	0.00	0.01	0.00	0.02	0.04	28.64	0.10	0	0	0	0	0	460	100
6	26.55	0.20	4.17	7.71	1.98	0.01	0.00	12.11	0.00	0.00	0.00	0.00	0.37	0.01	0.22	0.00	0.00	0.00	0.03	0.03	46.49	0.14	0	0	0	0	0	0	100
7	6.16	0.00	1.08	38.34	0.22	0.00	0.00	3.07	0.00	0.00	0.00	0.01	0.65	0.00	0.03	0.01	0.01	0.00	0.40	0.02	49.36	0.13	0	520	0	0	0	4660	100
8	28.93	5.21	0.14	13.81	0.69	0.01	0.00	24.61	0.01	0.00	0.00	0.01	0.14	0.01	0.01	0.00	0.00	0.00	0.25	0.05	26.01	0.08	0	0	0	0	0	400	100
9	12.37	0.04	0.03	2.13	0.10	0.03	0.00	10.55	0.00	0.00	0.00	0.10	0.01	0.00	0.20	0.00	0.00	0.00	0.07	0.03	74.08	0.23	0	200	0	50	0	0	100
10	1.91	0.00	0.11	3.48	0.46	0.03	0.00	8.40	0.00	0.00	0.00	0.00	0.05	0.02	0.45	0.00	0.00	0.00	0.00	0.06	84.73	0.29	0	0	0	2200	0	0	100
11	14.52	0.00	0.25	4.70	0.62	0.06	0.00	19.34	0.00	0.02	0.02	0.00	0.09	0.00	0.35	0.00	0.01	0.00	0.00	0.04	59.76	0.18	360	0	0	70	0	0	100
12	16.54	0.00	0.18	3.02	0.48	0.06	0.00	13.64	0.04	0.00	0.02	0.00	0.05	0.00	0.28	0.01	0.01	0.00	0.10	0.01	65.36	0.18	240	0	0	0	0	0	100
13	13.86	0.00	0.27	5.32	1.66	0.01	0.00	10.12	0.00	0.00	0.00	0.04	0.03	0.00	0.12	0.00	0.01	0.00	0.05	0.03	68.29	0.19	0	0	0	0	0	0	100
14	3.88	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.00	0.00	0.03	0.00	0.05	95.67	0.23	0	0	0	670	0	0	100
15	4.06	0.00	0.03	0.00	0.03	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.09	0.00	0.02	0.01	0.01	0.00	0.01	0.03	95.39	0.22	0	0	0	70	0	0	100
16	3.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.00	0.03	0.00	0.01	0.04	0.00	0.06	95.58	0.25	0	0	0	300	0	0	100
17	4.32	0.00	0.05	0.00	0.01	0.00	0.00	0.24	0.01	0.00	0.01	0.00	0.08	0.00	0.03	0.00	0.00	0.00	0.05	0.04	94.87	0.25	0	0	0	330	0	0	100
18	6.05	0.00	0.01	0.00	0.68	0.00	0.00	0.04	0.00	0.00	0.00	0.01	0.37	0.00	0.01	0.00	0.01	0.02	0.05	0.02	92.49	0.23	0	0	0	270	0	0	100
19	10.24	0.00	0.16	1.89	0.38	0.28	0.00	17.67	0.02	0.00	0.00	0.00	0.16	0.00	0.85	0.02	0.00	0.00	0.00	0.02	68.09	0.22	0	0	0	0	0	0	100
	518	21	11	28	42	39	160	31	39	49	60	85	40	48	55	61	30	88	34	52	91	70	29	161	115	136	31	55	

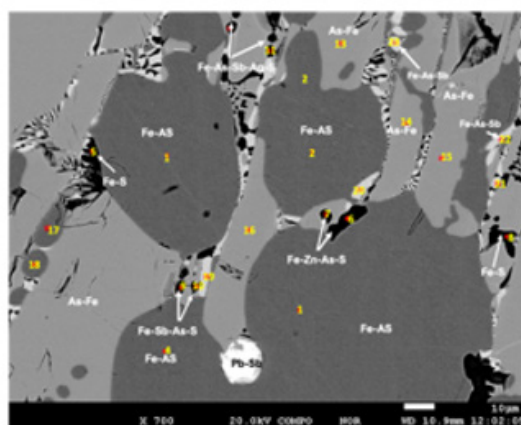
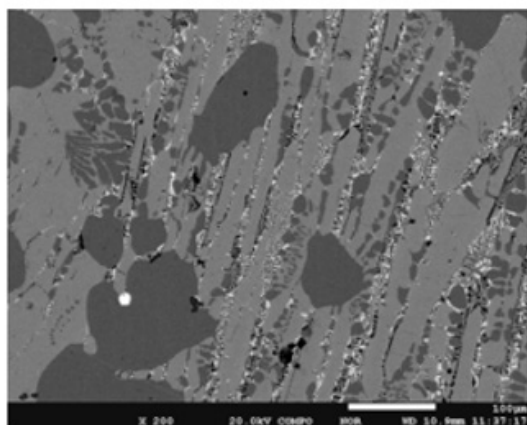
Table 2 shows spot analyses labelled from 1-22 as illustrated in Figure 6b. There is a variety (at least two) of iron arsenide phases: one, rather globular, Fe-As (dark grey) and a second, As-Fe, (long lathes), the difference between the two being in the ratio of the two elements As/Fe (Figure 6a & 6b). Thoroughly dispersed within these two iron-arsenide phases are a fine, very light grey, Sb-rich phase: also a fine, very dark grey/black Fe-Zn-Sb-S rich phase. Ag/Au are thoroughly dispersed throughout the different Fe-As phases which overall all lack any substantial quantities of Pb.

At the bottom of the picture in Figure 6b there is a metallic prill labelled Pb-Sb. We have no elemental composition for this prill; only X-ray element distribution maps (Figure 6c). From the latter it is clear that Pb and Sb are not miscible, Sb lying in the periphery of Pb. Au is finely dispersed within Pb. Ag is also to be found within Pb but concentrated in particular 'spots'. Sn is dispersed within Sb rather than Pb. Fe surrounds Pb but is absent within; finally, Cu and Zn are only finely dispersed within Pb. This is a one-pic analysis of a single

metallic prill and hardly representative but helps to illustrate the fact that precious metals may indeed concentrate within the iron arsenide phase of the slag.

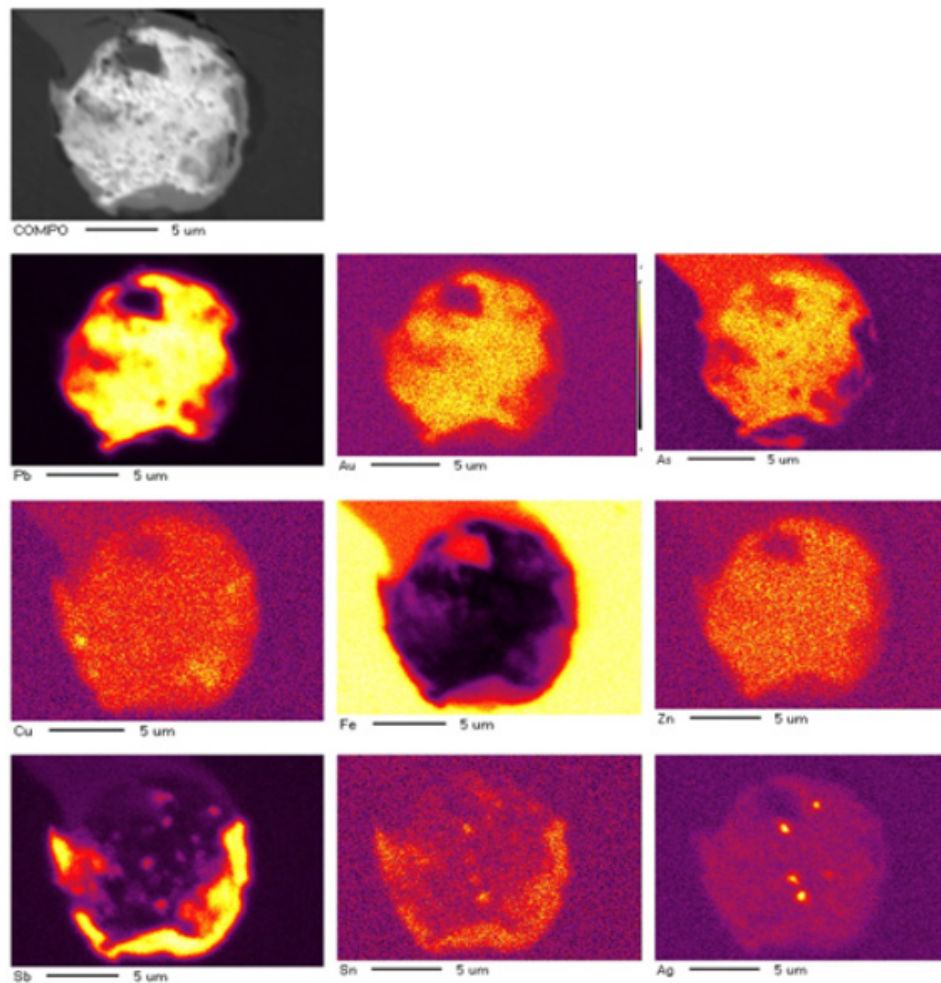
### EPMA of sample L3, lead oxide-rich

The third sample presented here consists of largely PbO. This type of materials are referred to in the archaeometallurgical literature as litharge. However, this is not the mineral litharge (i.e., pure PbO). Rather Pb is a constituent of three distinct phases. More specifically there are: a. Pb-Ca-Al-Si-O (black) and b. Pb-Ca-Si-O (dark grey) and c. a lighter phase which is near pure PbO (Figure 7). Bi is present within the litharge while Au/Ag are, as expected, low/absent (Table 3). Of interest is the presence of Ta associated with the Pb-Ca-Si (dark grey/black) phases. The trace elements Ta, Hg, Pt reported in the analyses here and their association with Au/Ag form currently the topic of an ongoing investigation into these complex materials (Photos-Jones et al, forthcoming) [18].

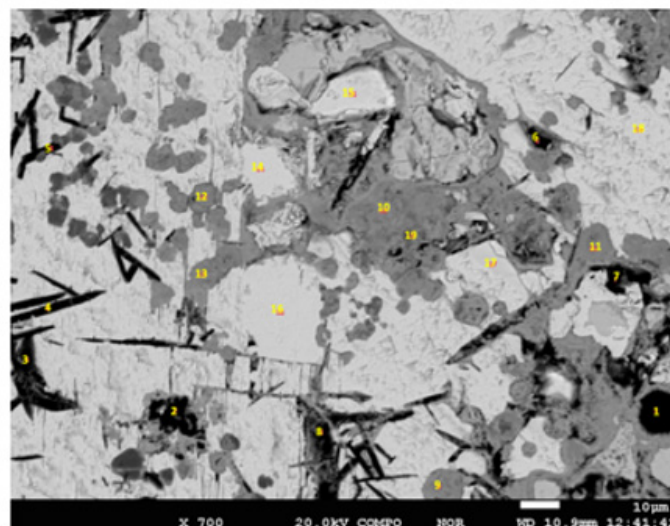


**Figure 6a:** Area within sample SP2 consisting of Fe-As-O with one metallic Pb-Sb prill, at the bottom-left of the photograph; Figure 6b Close-up of area in Fig 6a, bottom left. For X-ray distribution map of elemental composition of the Pb-Sb prill in Fig. 6b (bottom center) see Fig. 6c below.





**Figure 6c:** X-ray element distribution maps for 9 elements present within the Pb-Sb metallic prill, shown in Fig. 6b (bottom of photograph).

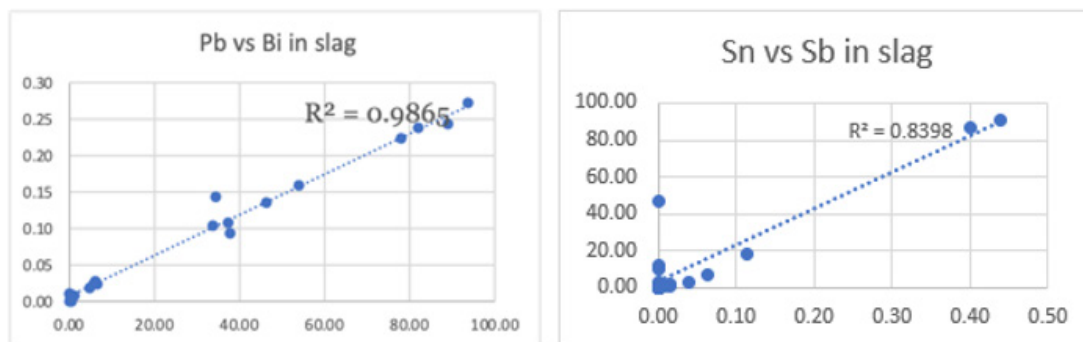


**Figure 7:** Sample L3 microstructure consisting of three non-crystalline phases: a. Pb-Ca-Al-Si-O (black); b. Pb-Ca-Si-O (dark grey) and c. PbO (light grey).

### Relationship between SL9.2/SP2/L3

This section attempts to establish whether there exists some relationship between the three samples by looking closely at some binary ratios between key elements, from the data obtained with the EPMA. There is good correlation between samples SL9.2 and L3 with regards to Pb vs Bi (Figure 8a); there is a good correlation between samples SL9.2 and SP2 with regards to Sb vs Sn (Figures 8b & 9); finally, there is a good correlation in L3 between Fe vs

Sb (Figures 10a & 10b). The first correlation (Pb vs Bi) suggests that the Pb (with Sb) metal emerging out of the smelting furnace that produced sample SL9.2, is the same (compositionally similar) to that which underwent oxidation resulting in the production of L3. The second correlation (Sb vs Sn) suggests that SP2 was either formed within the furnace together with SL9.2 or independently of it following a subsequent treatment/melting. These correlations are suggestive rather than conclusive since the paucity of analyzed finds does not allow for overriding conclusions.



Figures 8a, 8b: Binary correlations between Pb vs Bi and Sb vs Sn in SL9.2.

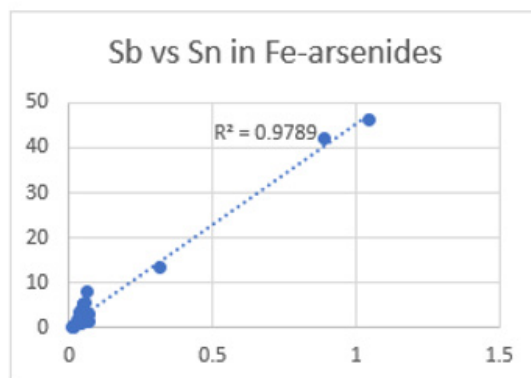
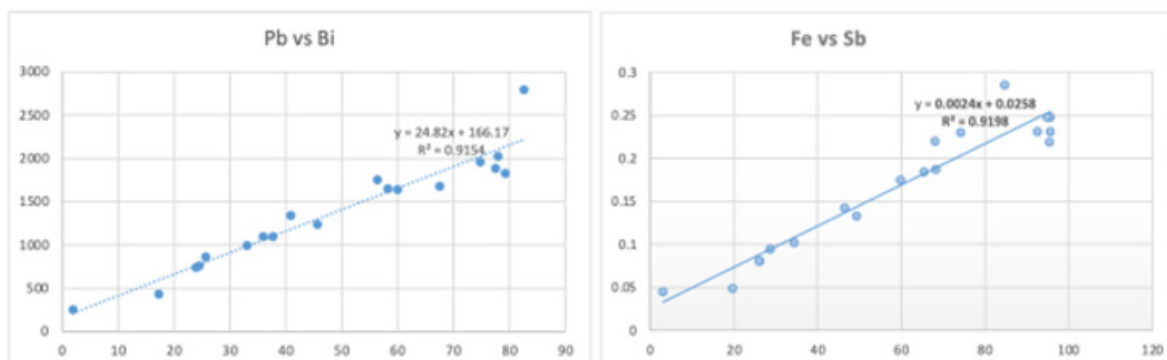


Figure 9: Binary correlations between Sb vs Sn in SP2, iron arsenides.



Figures 10a,10b: Binary correlations between Pb vs Bi and Fe vs Sb in L3.

## Short Discussion and Conclusion

The period between the 4<sup>th</sup> and the 3<sup>rd</sup> c BCE is one known from historical accounts to be fraught with (both, friendly and hostile) interactions between the many diverse ethnic groups inhabiting the area i.e., Thracians, Thasians, Athenians, Spartans and other Greek colonists and Macedonians. They continuously formed, upturned and reformed alliances with and against each other [5]. It is certain that the economically viable mineral wealth of the region in the vicinity of Pistryros (Au, Ag, Pb, Cu or Fe) was well known to all and access to the underground resource and the ability to 'exploit it' for their own benefit must have weighed heavily in their mind.

What type of 'ore' did Pistryros slag derive from? The good correlation between samples SL9.2 (silicates) and SP2 (iron arsenides) and with respect to Pb and Bi (Figure 8a), as is the presence of Au and Ag within, point to Pistryros having access to Palaia Kavala ores and of the variety highlighted by previous investigators. The source(s) of Ta, Pt, Hg, all above the EPMA's LOD, needs to be investigated further and may point further afield. The recent publication of 18 lead ingots found in a shipwreck near Comacchio Italy [14] dating to the 3<sup>rd</sup>/2<sup>nd</sup> decade BCE revealed presence of trace elements like Bi/Ag/Sb/Cu 'reminiscent' of the Pistryros furnace metallic 'load'. In this case, Sb is present in trace amounts rather than as a major/minor constituent.

What type of metal would this 'ore' generate? The slags both in their silicate/oxide and in some of their metallic phases are first and foremost Pb-rich. Metallic Pb is formed in association with Sb as shown in Figures 6b and 6c; whether antimonial Pb was indeed tapped out of the furnace, in large quantities, or not, remains a point of conjecture. The slags also produced a second metallic phase, i.e., iron arsenides, rich in Au/Ag. How were these metallic compounds further processed, and for what purpose (extraction of precious metals?) we cannot, presently, be sure.

Regarding the one sample of PbO (L3), this is devoid of Sb. Has antimonial lead been de-antimoniated i.e., heated (at low temperatures and on a hearth basis) whereupon Sb was concentrated in the (melting) slag that was formed? Again, there is a need for further investigation. Why make PbO? PbO, referred as litharge, when encountered in archaeometallurgical sites, is almost always assumed to be the waste product of desilverisation of Pb for the production of silver bullion. However, PbO, the lithargyros of the texts (Dioscorides De Materia Medica, V, 88) does not equate with that waste product at all [15]. Instead, it was clearly manufactured on its own right for its own purposes and as a medicinal mineral.

The proximity of the Pistryros metal waste to the 'winery' also raises issues regarding possible psimythion (PbCO<sub>3</sub>) making on site. Recently we had the opportunity to reevaluate the Theophrastus (On Stones, 57) method for psimythion preparation requiring large supplies of 'oxos' (poor wine) and lead metal [16]. There are no known workshops dedicated to psimythion making for that period, the only facilities required (at least in a Classical/Hellenistic setting) being considerable supplies of both (oxos and metal) and large pithoi where the reaction took place [17]. Again, Pistryros' possible involvement in psimythion manufacture has to

remain a hypothesis.

So, there are presently many scenarios regarding the metallurgical activities of the Pistryrians' in the well-dated Hellenistic contexts:

- I. They may have been smelting within their city walls, from polymetallic ores recovered from the immediate vicinity.
- II. They may have been manually processing (hand breaking) the slag physically transported from the vicinity of the mines for the recovery of metallic inclusions within, be it antimonial lead or iron arsenides or both with and without precious metals.
- III. They could be making metallic Pb, both as ingots and as raw material to synthesize minerals like psimythion (lead carbonates) via ambient temperature reactions. In that case the Pb would have likely required the removal of antimony.
- IV. They could be making lithargyros, as per the ancient mineral medicine, as well.
- V. In short there is a possibility that Pistryros indulged in a complex network of metallurgical activities requiring both high-temperatures (c. 1000°C) and low-temperatures (300-600°C) and yet more activities requiring simply ambient temperatures.

To conclude, with its intensive, potentially multi-varied, Pb-based metals activities taking place in parallel with others (agricultural-based) and in the confines of a fortified settlement, with private and public buildings, Pistryros is in a unique position to shine light on the multi-faceted life of Hellenistic Macedonia [17, 18]. It uniquely presents us with the opportunity to examine potentially interdependent metallurgical and other processes, that are the hallmark of urban sites, vis a vis the more 'one-dimensional' smelting-at-the-mine paradigm which has been the guiding model for Classical/Hellenistic Northern Greece metals exploration and exploitation, so far.

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## Conflict of Interest

The authors declare no competing interests.

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