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# What did the ancient Greeks mine at Laurion and when did they mine it?

**ABSTRACT:** *The Laurion district was one of the most extensive and influential silver mining areas in the ancient world. Evidence from archaeology and lead isotopes indicate that it was exploited for silver from the 4<sup>th</sup> millennium BC, probably accompanied by production of lead and copper, with exploitation of iron considered very likely in the 1<sup>st</sup> millennium BC. This paper integrates new and existing information to reassess the character of the mineralization mined by the ancient Greeks. It then applies these results to assess when the differing styles of mineralization may have been mined. The outcomes have significant implications for archaeology at Laurion. Foremost is the contrasting character of mineralization at the first and third contacts. Their significant differences are considered in several contexts: stratigraphy and structure; distribution of the mineralization; what the ancients mined; the impacts of weathering and oxidation; and their differing silver content. As a result, we believe that production from the exposed and shallow first contact mineralization was largely based on widely dispersed, thin, irregular, oxidised and lower grade deposits. These would favour numerous small independent operations with variable production that began in the 4<sup>th</sup> millennium BC and continued until the 1<sup>st</sup> millennium BC. In contrast, production from the third contact was based on substantial, thick, continuous and higher grade deposits, focussed around the central area of Kamariza. These deposits would support several larger scale, continuous and systematic mining and processing operations capable of providing a surge in silver output that could be maintained at a much higher level. This contrast in the character and grade of mineralization at the first and third contacts is sufficiently strong to link discovery of third contact mineralization with the windfall surplus received by Athens, according to Herodotus (VII.144), and dated at 483/2 BC by Aristotle (Ath. Pol. 22.7).*

**KEYWORDS:** SILVER, COPPER, ATHENS, IRON, OXIDATION

## Introduction

Mineralization at Laurion occurred over an area of more than 100 km<sup>2</sup> (Fig. 1). It was one of the most extensive and important silver mining districts in the ancient world and appears to have been exploited almost continuously from the 4<sup>th</sup> millennium BC until the early Christian era. For much of that period it likely to have also been a source of copper and lead, with the probable addition of iron in the 1<sup>st</sup> millennium BC. Discovery of the concealed, thick, continuous and higher-grade deposits of the deeper third contact, most likely early in the 5<sup>th</sup> century BC, enabled a substantial and sustained increase in silver production that transformed the Laurion district and underpinned the rising wealth of Athens.

Assessing ancient mining districts is difficult, because subsequent phases of mining usually destroyed most, or all, preceding evidence; Laurion is no exception. Our reassessment leans heavily on extensive observations made by scholars and mining professionals in the 19<sup>th</sup> century when much of the evidence of ancient mining and processing was still preserved. Their observations

are augmented by substantial recent geological and archaeological research at Laurion and adjacent areas.

To answer the question posed by the title we have addressed five key topics: the stratigraphy and structure of the district; the distribution of mineralization and its stratigraphic and structural contexts; insights into what the ancients mined; the differing impacts of weathering and oxidation; and the differing silver content of the first and third contacts, before considering the archaeological implications.

The key outcome of this work is the contrasting character of the mineralization at the first and third contacts. They share essentially the same primary mineralogy, but differ significantly in their distribution, form and silver grade. Within each of these contacts there also appear to be spatial variations in grade, which may be linked to structural factors, and proximity to the Plaka granodiorite. Another notable difference is the impacts of surface and near-surface weathering at the first contact, and sub-surface oxidation of third contact mineralization. The resulting supergene alteration of primary sulfides had economic consequences, which stemmed from the mobility of silver,

copper, iron and zinc, and the stability of lead. Not only did this supergene alteration influence mining during the first three thousand years, but it led to revival of the district in the 19<sup>th</sup> century to mine secondary zinc carbonates.

## Laurion stratigraphy and structure

At the district scale the geology of the Laurion mining district is deceptively simple with layer cake stratigraphy characterised by gentle folds and dips and dominated by marbles and schists. Nevertheless, young topography with relief in excess of 300 m, and faulting within the upper units, complicates the geological picture (Fig. 2). Southern Attica lies at the northern extremity of the Western Cycladic detachment (Grasemann, et al., 2012) and this fundamental structure, locally referred to as the South Attic Detachment (SAD), together with its subsidiary structural elements, introduces additional complexity. The presence of the SAD challenged accurate interpretations of the stratigraphy at Laurion until the work of Lekkas, et al. (2011). Importantly, the SAD has also strongly influenced the location and character of a significant proportion of the mineralization at Laurion.

Fig. 3 shows a summary of the conclusions of Lekkas, et al. (2011; 2020) about the stratigraphy, structure and age estimates at Laurion. It also shows where mineralization

is located within the stratigraphic column. At the base is the principal host of mineralization, the metamorphosed, 200–230 Ma Kamariza series of three rock units: the Lower Kamariza marble; the Kamariza schist; and the Upper Kamariza marble. This series is capped by the SAD, which is overlain by the Laurion series that includes: a discontinuous basal Pounta marble, the overlying Laurion schists, and the capping Mavrovouni marbles. A second detachment separates the upper, unmetamorphosed Pelagonian unit, with an estimated age of 140–70 Ma (Katsiavrias, Solakius and Salaj, 1991; Photiades and Carras, 2001).

Stratigraphic boundaries within the Kamariza and Laurion series clearly indicate differential movement between units and even within them (Lekkas, et al., 2020). These zones of movement are consistent with the considerable movement of the SAD, interpreted as top to south-southwest and attributed to extension of the Western Cycladic Detachment caused by slab roll-back and trench retreat (Iglseider, et al., 2011; Lekkas, et al., 2011; Grasemann, et al., 2012; Scheffer, et al., 2016; Coleman, et al., 2019). Discontinuity of the Pounta marble is interpreted to result from normal faults rooted within SAD, and probably associated with its movement. Descriptions of all stratigraphic units and their internal structure are published by Lekkas, et al. (2020). These include the SAD, which ranges from a few centimetres to tens of metres of laminated Upper Kamariza marble,

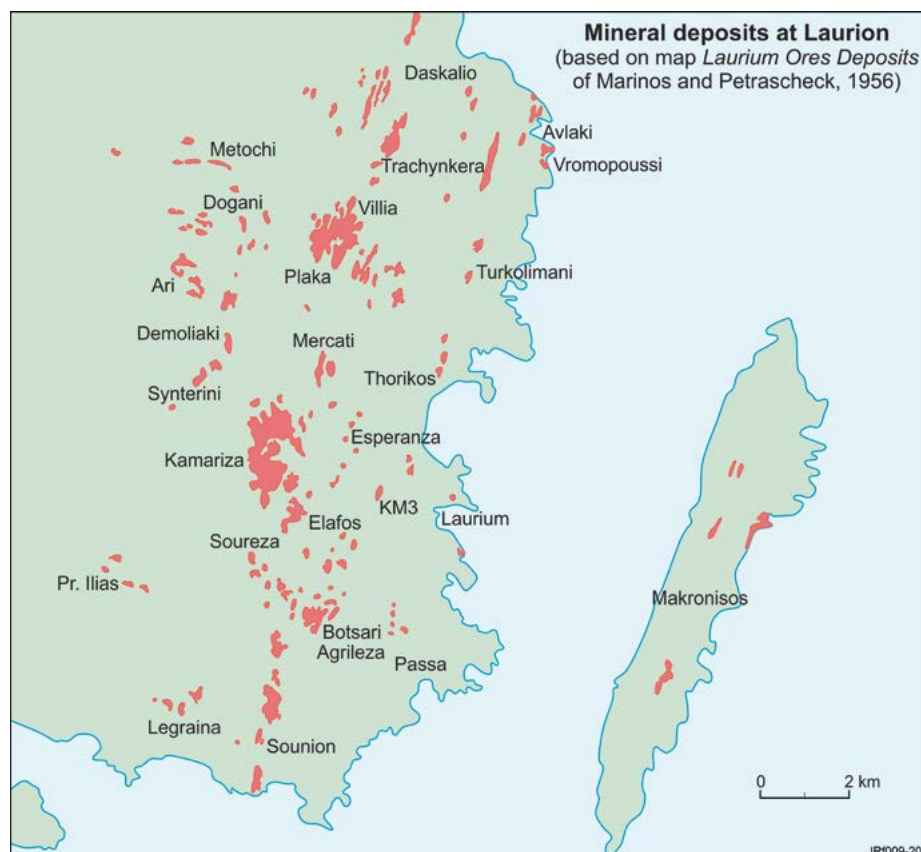
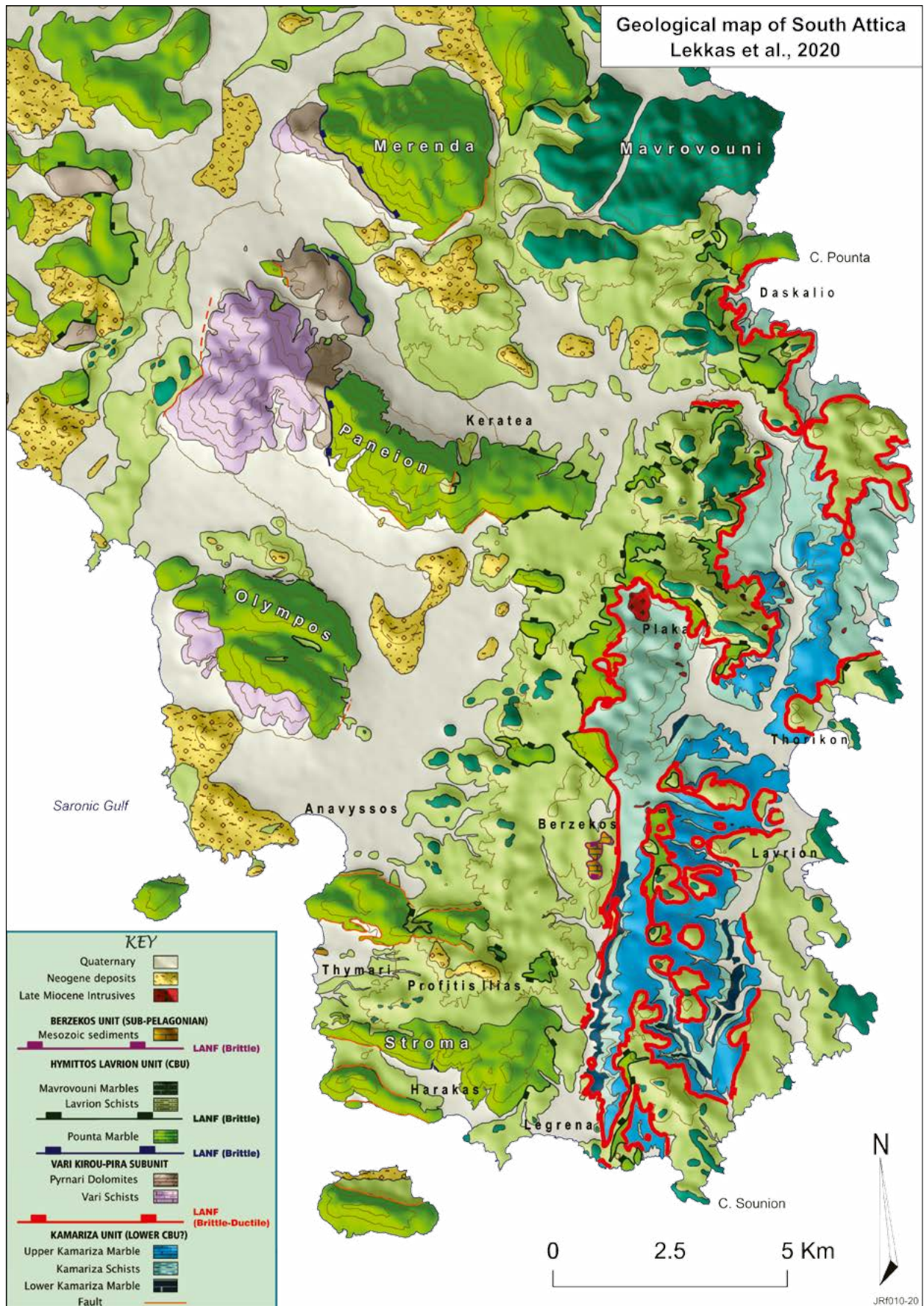


Fig. 1: Location map showing areas of mineralization on first, third and Pounta contacts (undifferentiated) within the Laurion district in plan projection, and deposits referred to in this paper. Based on the map "Laurium Ores Deposits" in Marinou and Petrascheck (1956) (preparation: by J. Ross).



together with overlying cataclastic melange, which can exceed 4 m in thickness, and is composed of angular and  
 Fig. 2: Geological map of the Laurion district, modified from Lekkas, et al. (2020) (preparation: by J. Ross).

rounded blocks, dominantly from the Laurion series, in a finer grained matrix.

The strongly deformed (ultramylonitic) Upper Kamariza marble represents a ductile component of the crustal scale detachment structure. This ductile deformation was followed by a brittle stage, which included both the marble and Kamariza schists. Deformation above the SAD was limited to the brittle stage with both the Pounta marble and Laurion schist being affected.

Fig. 3 also includes the younger granodiorite and granitoid intrusions, which appear to predate the bulk of the mineralization, with exceptions in the Plaka area (Voudouris, et al., 2008a; Skarpelis, Tsikouras and Pe-Piper, 2008; Liati, Skarpelis and Pe-Piper, 2009; Berger, 2013). These intrusions also appear to postdate most movement on the SAD. The prominent Plaka granodiorite has a surface area of about 0.5 km<sup>2</sup> and an extensive thermal aureole of hornfels within adjacent Kamariza schists. The fission track age of apatite, potassium-argon ages on biotite, feldspar and whole rock, and uranium-lead and uranium-thorium/helium ages on zircon yielded an age of 9.4 to 7.1 Ma for the igneous and hydrothermal activity of the Plaka granodiorite (Marinos, 1971; Altherr, et al., 1982; Skarpelis, Tsikouras and Pe-Piper, 2008). In addition, more than 50 narrow granodiorite and granitoid dykes occur throughout the district (Marinos and Petrascheck, 1956) and usually strike east-west and dip north.

The location of mineralization shown in Fig. 3 varies widely, but the most important concentrations exploited

by the ancient miners were at, or close to, the contact between the Lower Kamariza marble and overlying Kamariza schist, commonly known as the “third contact” (Fig. 3). Second in importance, but first to be exploited, was the “first contact” located at or close to the contact between the Upper Kamariza marble and the SAD. In this paper, reference to the first contact has been extended to include mineralization that immediately overlies the SAD, within both Laurion schists and Pounta marble. Mineralization also occurs as lenses within the Lower Kamariza marble (Fig. 3), and within the Kamariza schist in association with thin lenses of marble. Mineralized lenses occasionally occur within the Upper Kamariza marble and at its lower contact with Kamariza schist, where it is known as the “second contact” (Fig. 3). Significant veins of mineralization can occur within Kamariza schist but are rare, with known mining restricted to the Filoni 80 vein at Plaka (Conophagos, 1980; Voudouris, et al., 2008a) and Vromopoussi (Potier, 1880). Substantial mineralization has also been exploited some stratigraphic distance above the SAD, at deposits such as Ari and Demoliaki, which appear to be focussed around the contact between the Pounta marble and overlying Laurion schist (Fig. 3). These occurrences are referred to as “Pounta contact”.

Although primary sulfide mineralization at Laurion occurs in diverse stratigraphic and structural settings, it is clear from numerous detailed studies (e.g. Voudouris and Economou-Eliopoulos, 2003; Voudouris, 2005; Skarpelis, 2007; Voudouris, et al., 2008a; 2008b; Bonsall, et al.,

LAURION STRATIGRAPHY, STRUCTURE AND MINERALISATION					
		AGE (Ma)	LITHOLOGY	STRUCTURE	Pb-Zn-Ag-Cu MINERALISATION
	Pb-Zn-Cu-Ag mineralisation	≤7.1			Primary galena, sphalerite, pyrite and chalcopyrite
	Granitoid dyke	7.1-9.4	Porphyritic granodiorite	1-2m thick, ~E-W strike, altered	Relatively minor, includes some brecciation
	Plaka granodiorite	7.1-9.4	Medium grained and porphyritic hornblende granodiorite	Joints, faults, qtz veining; 0.5 km <sup>2</sup>	Cu and Mo
	Berzekos unit (Pelagonian)	~70-140	Shales, cherts, limestone	Unmetamorphosed	-
	Mavrovouni marbles	N.A.	Dark calcitic marble		-
	Lavriion schists	N.A.	Chlorite-mica schists, + basic igneous lenses	<b>Coarse grained foliation; ENE-WSW stretching lineation</b>	Some basal sections
	Pounta marble	N.A.	Calcitic marble		Upper contact and some basal sections
	South Attic detachment	5cm to >10m	Angular, lensoid, rounded clasts; mylonitic marble	<b>Top to SSW: cataclasite, mylonitic marble</b>	<b>Patchy and irregular; strongly oxidised</b>
	Upper Kamariza marble	~200	Calcitic marble		At, near upper contact; can extend to footwall
	Kamariza schists	~200	Calcite-mica schists	<b>Ultramylonite to mylonite foliation; NNE-SSW stretching lineation</b>	Fresh sulphides, in veinlets; rare veins
	Lower Kamariza marble	~200	Calcitic marble		Upper contact and within marble; supergene alteration up to >50m below

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Fig. 3: Summary of Laurion stratigraphy, structure and mineralization based on Lekkas, et al. (2020). Note that the SAD (South Attic Detachment) also includes ultramylonitic Upper Kamariza marble, which represents the ductile component of this ductile/brittle crustal scale structure (preparation: by J. Ross).

2011; Scheffer, et al., 2019) that its primary mineralogy appears to be relatively consistent throughout the stratigraphic column and across the district. Pyrite, galena, sphalerite, chalcopyrite and arsenopyrite are usually the major constituents, with significant pyrrhotite present in the Plaka area (Voudouris, et al., 2008a). Furthermore, almost all Laurion mineralization conforms to one or both of two main criteria. Firstly, most mineralization associated with the first, second, third and Pounta contacts is located at or close to the interface between mechanically stronger marble and weaker schist, a location with rheological contrast. This is a typical location for dilatant openings in dynamic tectonic settings, and a well-recognised locus for hydrothermal mineralization (Ridley, 1993; Chauvet, 2019). Secondly, many of these settings also have less permeable schist overlying marble made selectively permeable by brittle fracturing, thus providing a potential trap seal (Megaw, Ruiz and Tetley, 1988).

The concept of a trap seal for mineralizing fluids at Laurion is strengthened by the exceptional concentration of third contact mineralization in the Kamariza area. This approximately north-south trending zone is the most substantial mineralized area in the district, extending over a length of almost 3 km, and widths from 300 to 900 m. It coincides with the crest of a doubly plunging, north-south trending fold (Marinos and Petrascheck, 1956), forming an elongate domal shape.

There are extensive exposures of the SAD and first contact mineralization along the 20 km from Sounion to Daskalio (Figs. 1 and 2), resulting from interaction of topography and stratigraphy. In contrast, the third contact is rarely visible at the surface and, when exposed, mineralization is absent or just of low grade. Consequently, extensive mining of first contact mineralization is almost certain to have preceded that of the largely concealed third contact. Surface exploitation of the Pounta contact is known (Morin and Delpech, this vol.), but mapping of the main deposits, such as Ari and Demoliaki, indicate that they have been essentially exploited following shaft sinking to access steeply dipping contacts between Pounta marble and overlying Laurion schist, as shown in the map by Ardaillon (1897).

## Distribution of mineralization

The book "Laurium", published in 1956 by Marinos and Petrascheck, is an underutilised resource on Laurion. Their surface geological map was a significant advance and identified some of the key structural component we now know as the SAD. They also published other maps, including their 1 : 50,000 Mining Map of the Area of Laurium (Mining Map) which shows structural contours for two stratigraphic markers: the third and first contacts, and their elevation above sea level. The Mining Map identified the domal Kamariza fold closure, described above, but their

mistaken inclusion of Pounta marble as part of the upper Kamariza marble detracted from the utility of this map.

Nevertheless, this valuable map does show the location of individual deposits of mineralization on the first and third contacts, and their elevation above sea level. These data indicate that the authors had access to surface and underground maps produced by the French mining companies during the 19<sup>th</sup> and 20<sup>th</sup> centuries. Our inspection of some of these French maps revealed that they show both the extent of ancient exploitation, and any extensions of mining areas during the modern phase. Therefore, we assumed that the outlines of the third and first contact mineralization on the Mining Map provide the limits of the deposit, as defined by any exploitation activities, i.e. the development of ancient mining, and the extensions of modern mining. These outlines are shown in plan projection in Fig. 4.

Fig. 4A shows the widespread distribution of first contact mineralization throughout the district, including that associated with the upper contact of the Pounta marble (Pounta contact). Also shown is the surface outcrop of the Plaka granodiorite and its associated hornfels, historically referred to as "Plakite". In addition, the map shows outcrops of thin granitoid and granodiorite dykes, and the limits of a deeper intrusion, some 15 km<sup>2</sup> in area, as interpreted from 20<sup>th</sup> century aeromagnetic data by Tsokas, et al. (1998).

The spatial distribution of third contact mineralization is shown in Fig. 4B which highlights the dominance of the central Kamariza area. This mineralization is much more focussed than that at the first contact, with all known deposits occurring within a radius of about 5 km from the central Serpieri shaft at Kamariza. The core Kamariza area is located within a north-south trending domal fold closure, but north-northwest and northeast fractures within the lower Kamariza marble may also have influenced the location and trend of the mineralized lenses at the third contact (see below). Nevertheless, we do not have a detailed understanding of the main structural controls on third contact mineralization, or the distribution of the mineralized structures that acted as feeder fractures and pipes for primary mineralization.

The other third contact deposits, away from the central Kamariza area, appear to be thinner and lower grade, but information is very limited. Comparison of Figs. 4A and B suggests limited overlap of mineralized areas at the two contacts, but this difference may simply result from erosion of the SAD and first contact above the Kamariza domal crest.

## What did the ancients mine at Laurion?

It appears that interest in the ancient silver mines of Laurion increased in the 19<sup>th</sup> century, when at least two authors published comprehensive studies (Cordella, 1869;

Ardailon, 1897). They were able to enter well-preserved workings, largely untouched by any mining activity for more than a millennium, and their observations ranged from geology and mineralization through to mining methods, mineral processing, water storage and final smelting. Their preliminary observations about the form and character of the mineralization the ancients mined have been complemented by more detailed studies and mapping by French mining engineers and geologists in the 1870's and 1880's. Most of this detailed work is believed to result from due diligence assessments of operations on behalf of French banks.

Examples include Huet (1879; 1887), Potier (1880), and Cambrésy (1889). Their work was in turn complemented by the observations of Marinos and Petrascheck (1956). When combined, these records tell us much about the distribution and thickness of mineralization, and the variable alteration of primary sulfides by surface and sub-surface oxidation. They also provide information

about oxidation and the resulting downwards redistribution of zinc, iron and copper, especially within marble beneath the third contact. An important factor was the horizontal development of underground mining levels at the 96, 80, 65 and 50 m RL's. These levels were largely in Lower Kamariza marble, beneath the third contact in the core Kamariza area, and were used to determine the potential of secondary zinc mineralization and explore for deeper primary mineralization. Their locations enabled a three-dimensional view of the distribution of primary and secondary mineralization. They also provided insights into the processes that formed them and that appear to have modified the grade and distribution of silver at the third contact.

Fig. 5 provides several examples of first contact mineralization. A generalised version by the geologist Potier (1880) is shown in Fig. 5A. Unfortunately, it lacks scale, but numerous observations indicate that first contact mineralization is rarely >1 m thick. This version shows

#### Laurion mineralisation on first (A), third (B) and Pounta contacts

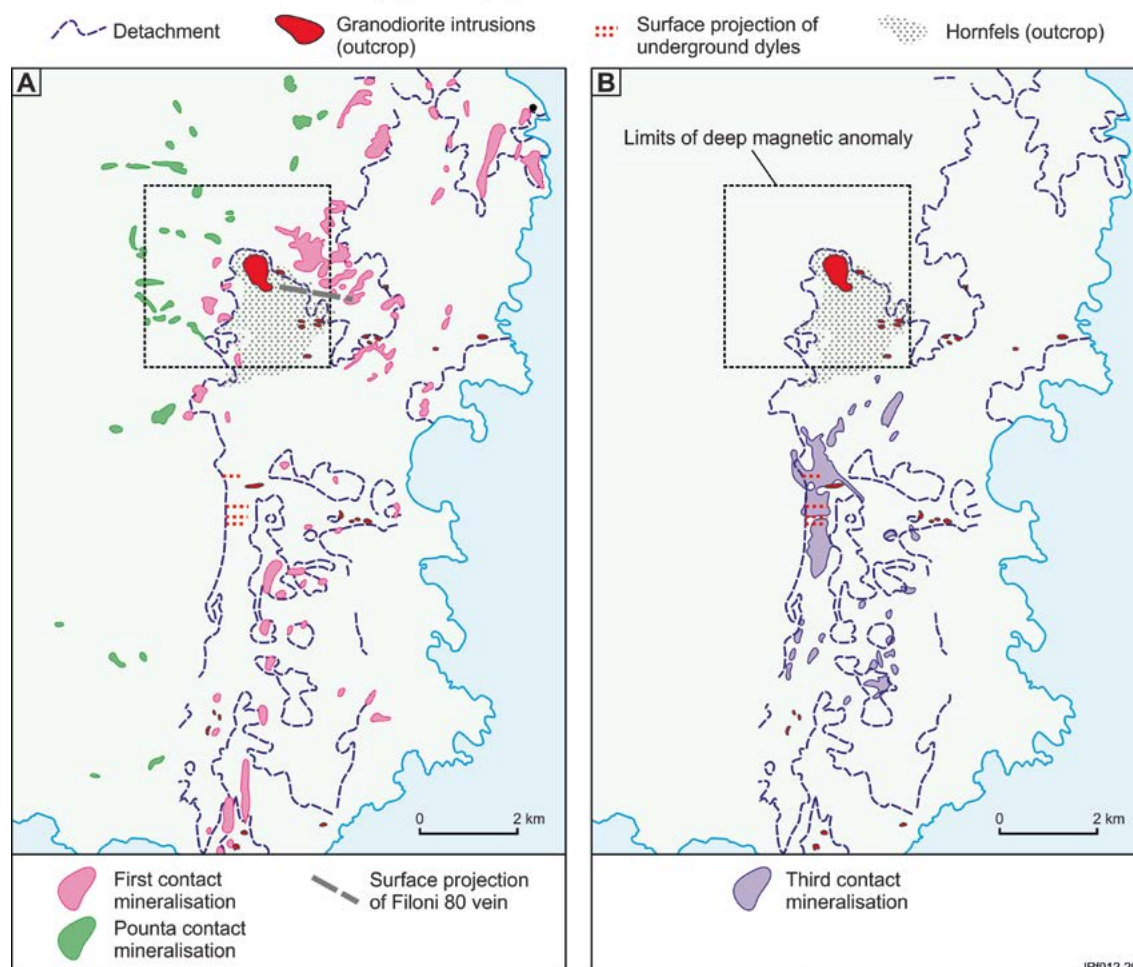


Fig. 4: Plans of Laurion district showing the surface expression of the SAD and extent of mineralization on the first and Pounta contacts (A) and third contact (B) in plan projection, derived from the 1 : 50,000 scale Mining Map of the Area of Laurium, published by Marinos and Petrascheck (1956). In addition, these plans include the surface expression of the Plaka granodiorite and narrow granitoid dykes, the hornfelsed Kamariza schist at Plaka, the plan projection of the Filoni 80 vein (Voudouris, et al., 2008a), and the approximate location of the deep magnetic anomaly identified by Tsokas, et al. (1998) (preparation: by J. Ross).

the common features of strong oxidation of first contact sulfides and downwards redistribution of secondary zinc minerals into fractures within the Upper Kamariza marble. Here it has accumulated as calamine, a mixture of the secondary zinc carbonates, smithsonite and hydrozincite, and zinc silicate, hemimorphite (Katerinopoulos, Solomos and Voudouris, 2005). A representative version of the first contact mineralization entirely within Upper Kamariza marble (Fig. 5B) was provided by Cordella (1869), with iron oxides sandwiched between secondary iron carbonates, and both containing irregular masses of residual galena. Figs. 5C and 5D from Marinus and Petrascheck (1956), provide other typical examples of the patchy and irregular first contact mineralization. Although the scale is absent, the ancient mine opening at Trachynkera in Fig. 5C is unlikely to exceed 0.9 m in height (Ardaillon, 1897). These images confirm that first contact mineralization occurs dominantly within the Upper Kamariza marble, but also within, and immediately above, the SAD. They also show mineralization at the second contact between Upper Kamariza marble and Kamariza schist. Ardaillon (1897), observed that most mineralization outside of Kamariza varied from a few centimetres to 2–3 m in thickness and was highly irregular.

Examples of third contact mineralization from the Kamariza area are shown in Figs. 6 and 7, and come from Huet (1879; 1887), Potier (1880) and Ardaillon (1897).

Fig. 6A is a north-south section through the northeast trending Jean Baptiste lens at Kamariza, which shows a 400 m extent of ancient mining with thicknesses of 8–12 m for most of that strike length. The “mine waste” within the void created by ancient mining, indicates substantial underground sorting. The north-south section in Fig. 6B shows where a shorter lens, about 15 m thick, has been mined from the central Kamariza area. This substantial thickness may have been increased by roof collapse. Old mine plans and cross sections indicate that these elongate thick lenses of Kamariza mineralization at the third contact can have widths up to 50 m.

An interesting feature of these sections is the layer of low grade oxidised “ore”, left intact by the ancients, presumably uneconomic at that time. It forms a thin base to the originally thick mineralization and extends north and south beyond the limits of ancient mining. A second feature is the near-vertical, irregular, downward-thinning lenses of calamine, often with abundant iron oxides, that extend up to 40 m below the contact in Lower Kamariza marble and can have a galena-rich core (Huet, 1879). These correspond to the term of griffons of the French miners and their dominant trend is reported as northeast (Huet, 1887), but with some northwest branches.

The formation of griffons through redistribution of zinc and iron from contact mineralization into underlying marble appears strongly influenced by steeply dipping

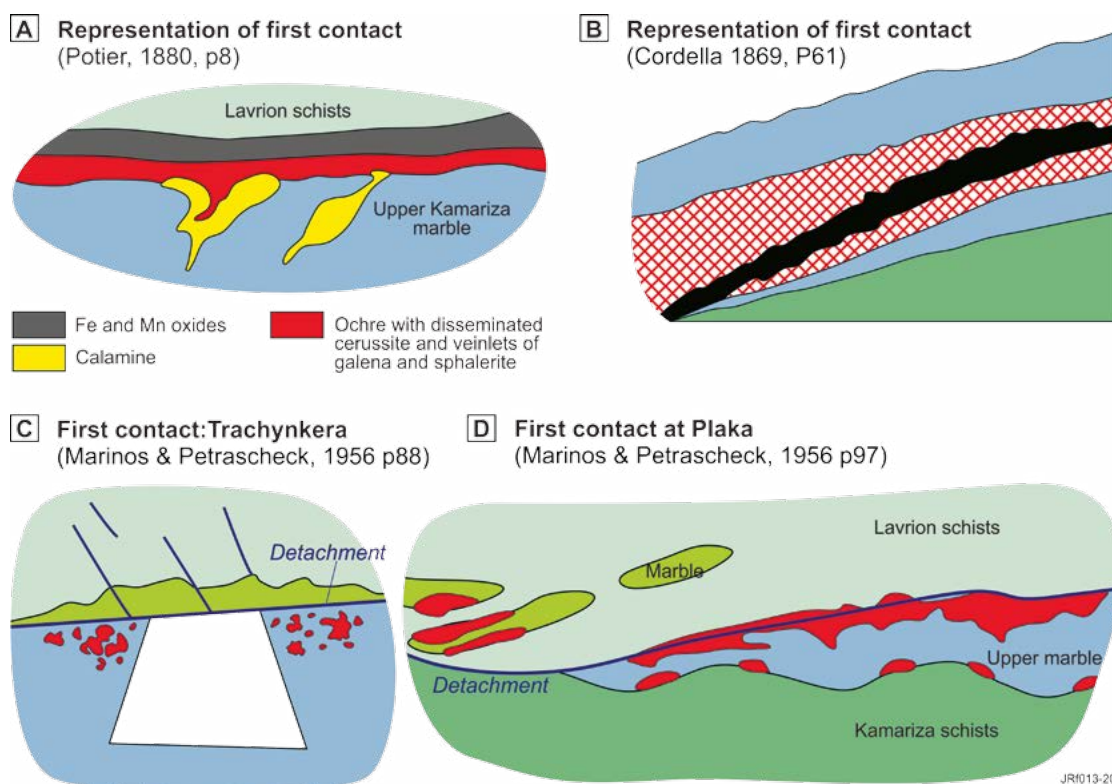


Fig. 5: First contact mineralization at Laurion: – A. Composite representation derived from Potier (1880); – B. composite representation from Cordella (1869); – C. At Trachynkera; – D. At Plaka, both derived from Marinus and Petrascheck (1956). The ancient opening in C is believed to be no more than 0.9 m high (Ardaillon, 1897), and provides scale (preparation: by J. Ross).

pre-existing fractures that mostly trend northeast. However, as shown in Fig. 6C (from Huet, 1887), it shows a horizontal concentration of calamine, about 80 m long and 5 m thick, located about 10 to 15 m below the contact. It contained a 2,000 kg pod of secondary copper minerals with about 10% native copper, indicating that

copper could also migrate downwards from the oxidising third contact mineralization. The abundance and vertical length of griffons in Fig. 6A appears to correlate with the proximity to thick contact mineralization. However, extensive griffons at the underside of the thin granodiorite dyke in Fig. 6B also indicates lateral migration of acidic

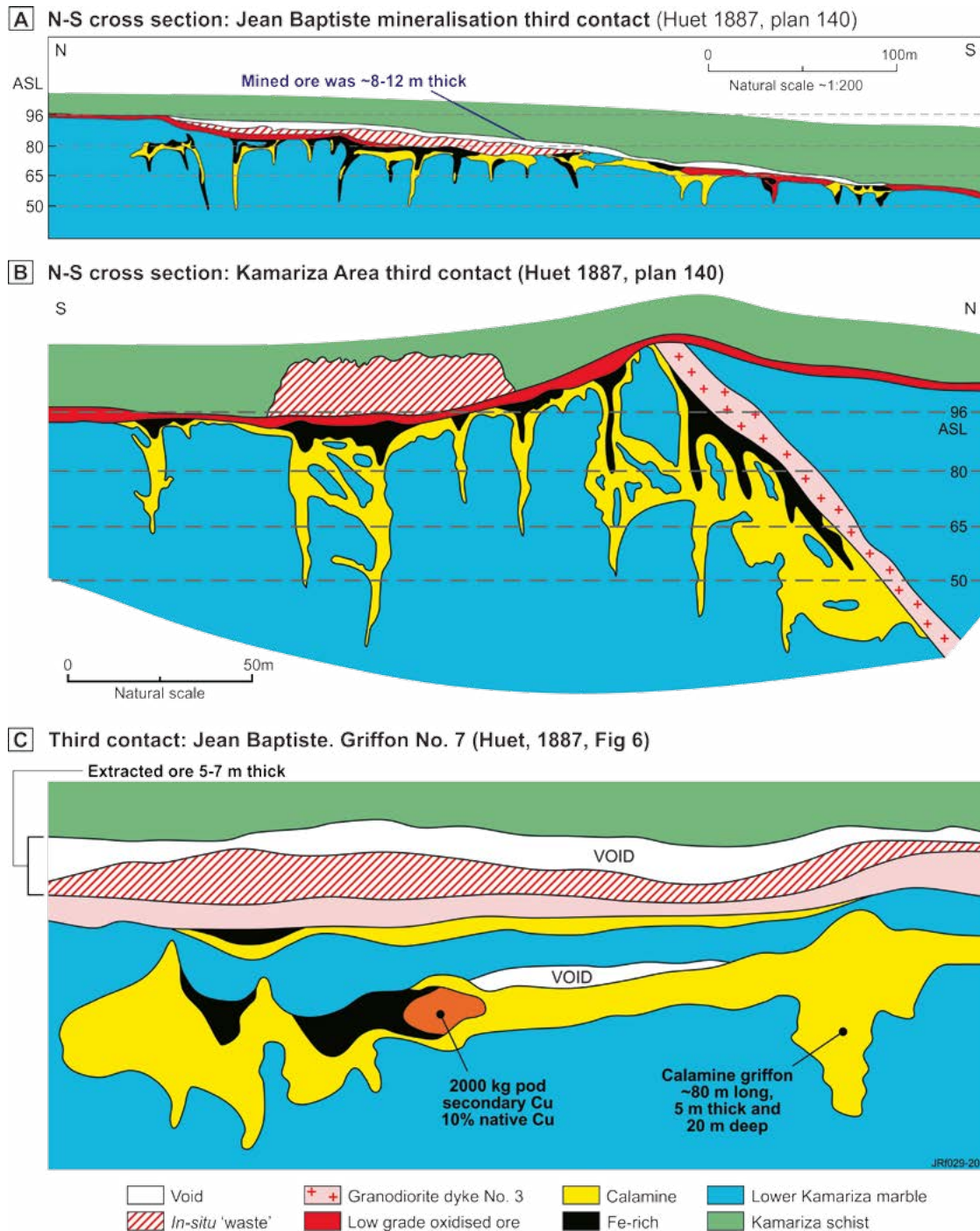


Fig. 6: North-south cross sections at natural scale of third contact mineralization at Kamariza, derived from Huet (1887, plan 140, fig. 6). – A. Section of the Jean Baptiste lens from plan 140. – B. Southerly continuation of the Jean Baptiste section (A) through the central Kamariza area. – C. Partial section through the Jean Baptiste lens showing contact mineralization and griffon no. 7 within the Lower Kamariza marble, derived from Huet (1887, fig. 6) (preparation: by J. Ross).



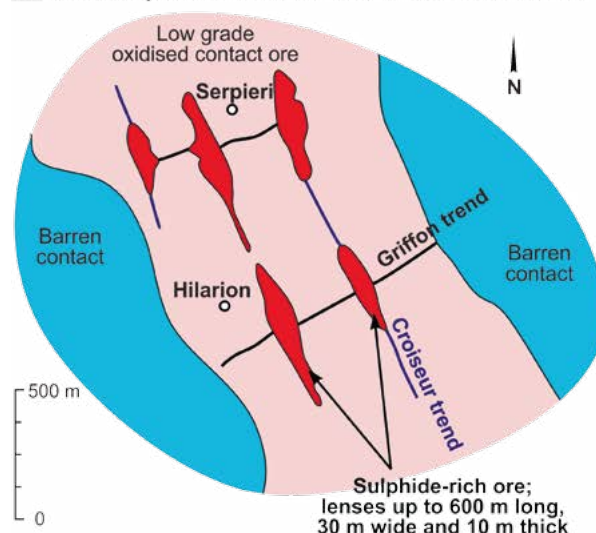
groundwater carrying zinc and iron. Huet (1887) noted that these griffons associated with undersides of dykes were devoid of lead minerals, but contained variable amounts of copper. These characteristics indicate a secondary origin for their zinc, iron, and copper contents, and that oxidation may not have caused any significant migration of lead away from the third contact.

At the south end of the main section in Fig. 6A there is a single lens of oxidised primary mineralization, which extends about 15 m below the contact. It is an example of the steeply dipping mineralized fractures within the Lower Kamariza marble, which the French termed *croiseurs*. Marinós and Petrascheck (1956), noted that such wedge-shaped veins usually trended 20–50° west of north, contained primary and oxidised sulfide mineralization, and generally extended no more than 15 m below the third contact. They attain their maximum width, or diameter, at the intersection with the third contact and probably represent channel ways for primary mineralizing fluids. Marinós and Petrascheck (1956), also noted that the northeast trending griffons are dominantly, but not exclusively, zinc-rich and can have some lead minerals in the core, whilst the northwest trending *croiseurs* consist mainly of primary and oxidised sulfides.

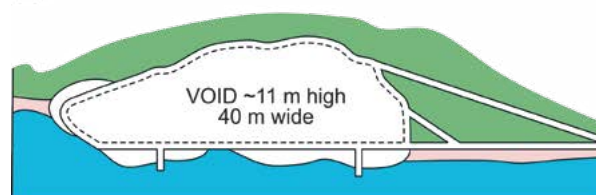
The *croiseur* trend is a central feature of Fig. 7, with Fig. 7A being a plan representation of the southern half of the Kamariza mineralization by Potier (1880). It shows elongate lenses of mineralization at the third contact up to 600 m long, 30 m wide and 10 m thick, set in a surround of low-grade oxidised mineralization and barren contact. These lenses also appear to be associated with the intersection of the griffon and *croiseur* trends. This sketch does not extend to the other lenses of mineralization in the northern half of the Kamariza area, north of the Serpieri shaft. Fig. 7B shows an unnamed cross section of a mineralized lens by Ardaillon (1897), with its dimensions scaled to the ancient underground drives, no more than 0.9 m high. The width and thickness are consistent with observations by other authors. There is very limited information about other third contact deposits away from Kamariza, but sections of the Mercati deposits by Huet (1879), show significant oxidation and limited griffon development, a combination consistent with thin mineralization. This observation is supported by the observations of Vaxevanopoulos, et al. (this volume).

So, what did the ancient Greeks mine? Until they reached the concealed, thick lenses of mineralization on the third contact in the Kamariza area, the available records indicate they were essentially mining the relatively thin, discontinuous, irregular, and often strongly oxidised shallow mineralization associated with the first contact. Oxidation equated with lower grades, according to empirical evidence from the French mining engineers and geologists. Furthermore, one published analysis suggests the possibility that primary galena in the first contact may have contained less silver than that in the third contact (see below). An exception is the higher grade, sulfide rich mineralization at Plaka in the first and second contacts,

### A Sketch plan of third contact, Kamariza area



### B Cross section of Croiseur: Kamariza



### C Third contact: Jean Baptiste, likely Croiseur

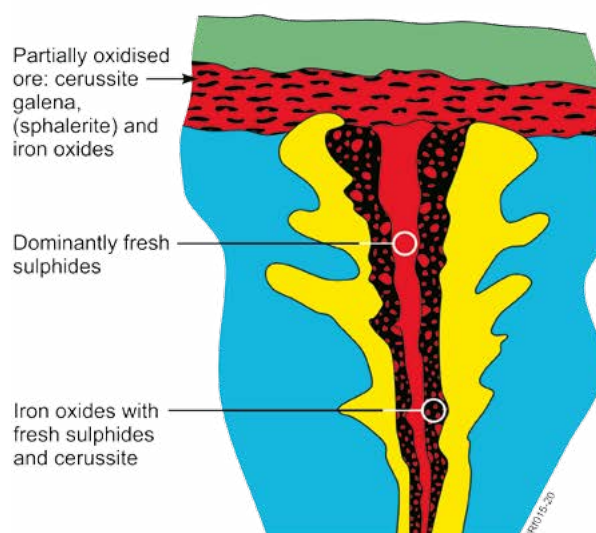


Fig. 7: *Croiseurs* and third contact mineralization at Kamariza. – A. Sketch plan of lenses of thick contact mineralization south of Serpieri shaft aligned on the *croiseur* trend and surrounded by thin, unmined, low grade oxidised mineralization; derived from Potier (1880). Note that scale bar only applies to north-south direction. – B. Cross section of a thick lens by Ardaillon (1897), showing interpretation of initial mine development by ancient miners; scale based on ancient workings being no more than 90 cm high. – C. Partially oxidised *croiseur* with primary mineralization at core and calamine margin, located beneath the third contact at the Jean Baptiste lens. Redrawn from Huet (1879), without scale, however its vertical extent is unlikely to exceed 15 m according to Marinós and Petrascheck (1956) (preparation: by J. Ross).

which was mined by the French at depths of more than 50–100 m below surface. However, there is no evidence that the ancient near surface workings at Plaka extended sufficiently beyond the strongly oxidised, low grade mineralization described below. By comparison, sinking a shaft in Kamariza schist to depths of <30 m at Kamariza would have either intersected a thick lens of mineralization or, more likely, reached low grade oxidised mineralization on the third contact. Once there, lateral development would eventually lead to the bonanza discovery.

## Supergene alteration

Surface exposure of Laurion stratigraphy is believed to have occurred about 5 Ma ago, following tectonic uplift (Krohe, et al., 2010), and would be followed by supergene alteration of any near surface mineralization. This alteration would result from the combined influence of oxidation, meteoric water and chemical weathering. Optimum conditions for oxidation of sulfides occur in hot, arid to semi-arid climates, with a preservation of the resulting non-sulfide minerals enhanced by switches of paleoclimate to hyper-arid (Reichert and Borg, 2008; Borg, 2015). These conditions resulted in iron-rich gossans and ochres at surface with varying proportions of secondary oxides, carbonates and sulfates derived from original sulfides. Such assemblages characterise near-surface first contact mineralization at Laurion, which often includes relict primary sulfides. Variations in paleoclimate, which favoured oxidation and preservation, are believed to have occurred several times at Laurion in the last 5 Ma (Biltekin, 2010). Furthermore, during the last million years oxidation processes have been amplified by several fluctuations of up to 120 m in sea level, which lowered the water table and deepened oxidation to far below current levels.

Initial oxidation of pyrite ( $\text{FeS}_2$ ) and accompanying iron-arsenic sulfides can generate acidic, metal-rich solutions which then leach other sulfides and their marble host rocks and promote mobilization of metals into the groundwater (Reichert and Borg, 2008; Skarpelis and Argyraki, 2009). Low  $pH$ -values (3–6) favour the formation of goethite ( $\text{FeO}(\text{OH})$ ), that then dehydrates to hematite ( $\text{Fe}_2\text{O}_3$ ) which forms residual gossans, and sometimes siderite ( $\text{FeCO}_3$ ), as shown in Figs. 5A and 5B. Galena ( $\text{PbS}$ ) is partially or completely replaced by cerussite ( $\text{PbCO}_3$ ) and anglesite ( $\text{PbSO}_4$ ), whilst alteration of sphalerite ( $\text{ZnS}$ ) eventually leads to precipitation at secondary sites of smithsonite ( $\text{ZnCO}_3$ ), hydrozincite ( $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ ), and hemimorphite ( $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2\text{H}_2\text{O}$ ), i.e. calamine (see Fig. 6). Chalcopyrite alters to a range of secondary copper minerals, including malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ), azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ), cuprite ( $\text{Cu}_2\text{O}$ ) and native copper. Pre and post mining oxidation has also generated a remarkable array of other secondary minerals which have been thoroughly documented (Katerinopoulos and Zissimopoulou, 1994; Rieck and Rieck, 1999;

Baumgartl and Burow, 2002; Ottens and Voudouris, 2018; Voudouris, et al., 2021).

Oxidation of primary sulfides by ingress of meteoric waters along fractures, faults and lithologic boundaries can extend to considerable depths at Laurion (Fig. 8), including below current sea level (Skarpelis and Argyraki, 2009). Initial access and movement of groundwater would have depended on factors such as thickness of mineralization, structural setting, and effective porosity and permeability of host rocks. The strongest oxidation of the third contact mineralization occurs at the base of thick lenses, or when the mineralization is relatively thin (Figs. 6, 7), suggesting influence from lateral groundwater movement along the contact between the Lower Kamariza marble and overlying Kamariza schist. In addition, the distribution of associated griffons highlights the role of vertical and horizontal fractures in the Lower Kamariza marble, and at the margins of granitic dykes, in channelling both downward and lateral movement of acidic groundwaters transporting zinc, iron, copper and silver (Fig. 6).

The impacts of weathering and oxidation on primary mineralization at Laurion is consistent with observations at similar deposits elsewhere in the world (Borg, 2015), and with well-understood chemical processes. They are also consistent with gradual neutralisation of acidic, metal-bearing solutions as they react with, and dissolve, adjacent marble (Sangameshwar and Barnes, 1983). Under such conditions lead is relatively stable, therefore cerussite and anglesite will often be intimately associated with primary galena. Anglesite is favoured at lower  $pH$ , then cerussite as  $pH$  increases from reaction with marble. In some samples these secondary minerals appear to armour the remaining galena from complete oxidation (Skarpelis and Argyraki, 2009; Fig. 9). In contrast, zinc, iron and copper are much more mobile and require an increase in  $pH$  to almost neutral before precipitation of their secondary minerals. Consequently, when primary mineralization is thick and has substantial capacity to generate acid from oxidation, their secondary minerals are likely to be some distance from the source. Comparison of Figs. 5A and 6 demonstrates the link between thickness of primary mineralization, oxidation, and movement of iron and zinc.

Silver is soluble in acid solutions and the apparent loss with oxidation, indicated in Fig. 6, is consistent with solution chemistry. However, it is not obvious where the resulting secondary silver is precipitated, a question first raised by Huet (1887). Secondary silver at Laurion occurs as the low temperature sulfide, acanthite ( $\text{Ag}_2\text{S}$ ), the chloride, chlorargyrite ( $\text{AgCl}$ ), and as native silver (Rieck and Rieck, 1999; Skarpelis and Argyraki, 2008; Ottens and Voudouris, 2018; Scheffer, et al., 2019), and their stability fields are determined by the oxidation potential and activity of Cl (Keim, et al., 2016). The presence of Cl is consistent with Laurion's proximity to the sea and its relatively dry climate, conditions that favour significant chloride contents in pre-mining groundwaters and precipitation of chlorargyrite.

Primary silver in galena occurs as inclusions of acanthite, and/or sulfosalts (e.g. matildite,  $\text{AgBiS}_2$ ; and

miargyrite,  $\text{AgSbS}_2$ ), and in solid solution (George, et al., 2015). However, with alteration of galena to cerussite and anglesite there is no place for silver in the lattice of these minerals (Keim, et al., 2016). The location of silver, which has been mobilised by oxidation of primary galena and silver-bearing sulfosalts (Voudouris, et al., 2008b), is a vexed question at Laurion, and one with significant archaeological implications.

Chalcopyrite is a significant component of the Laurion sulfide mineralization, and its mobility under oxidising conditions can result in concentrations of secondary copper minerals. Poitier (1880), noted that substantial quantities of copper were found in the form of malachite, azurite and native copper (Fig. 6C). Marinou and Petrascheck (1956), also emphasised the significance of copper at Laurion, as did Broomehead (1948). Unfortunately, analytical results are rare, but Skarpelis and Argyraki (2009) reported averages of 0.4% copper for twelve samples of gossan and 1.0% copper for nine samples of supergene mineralization. Their gossan samples appear to be a mix of first and third contact samples, whilst the supergene samples appear to all come from the third contact in

the Kamariza area and indicate some concentration of copper during oxidation.

If these results are representative, then Laurion contained sufficient copper to ensure obvious signs of green and blue secondary oxides in outcrops of oxidised first contact mineralization. Oxidation of the thinner and more irregular first contact mineralization would have also resulted in concentrations of secondary copper close to residual sulfides, which would have caught the attention of ancient miners.

### Silver contents of mineralization at the first and third contacts

Assessing the abundance and distribution of silver at Laurion is fundamental to understanding the archaeology of this region, and its consequences for ancient Athens. There is widespread agreement that mineralization at the first contact is lower grade than the third contact, but what does that mean, because there are also evi-

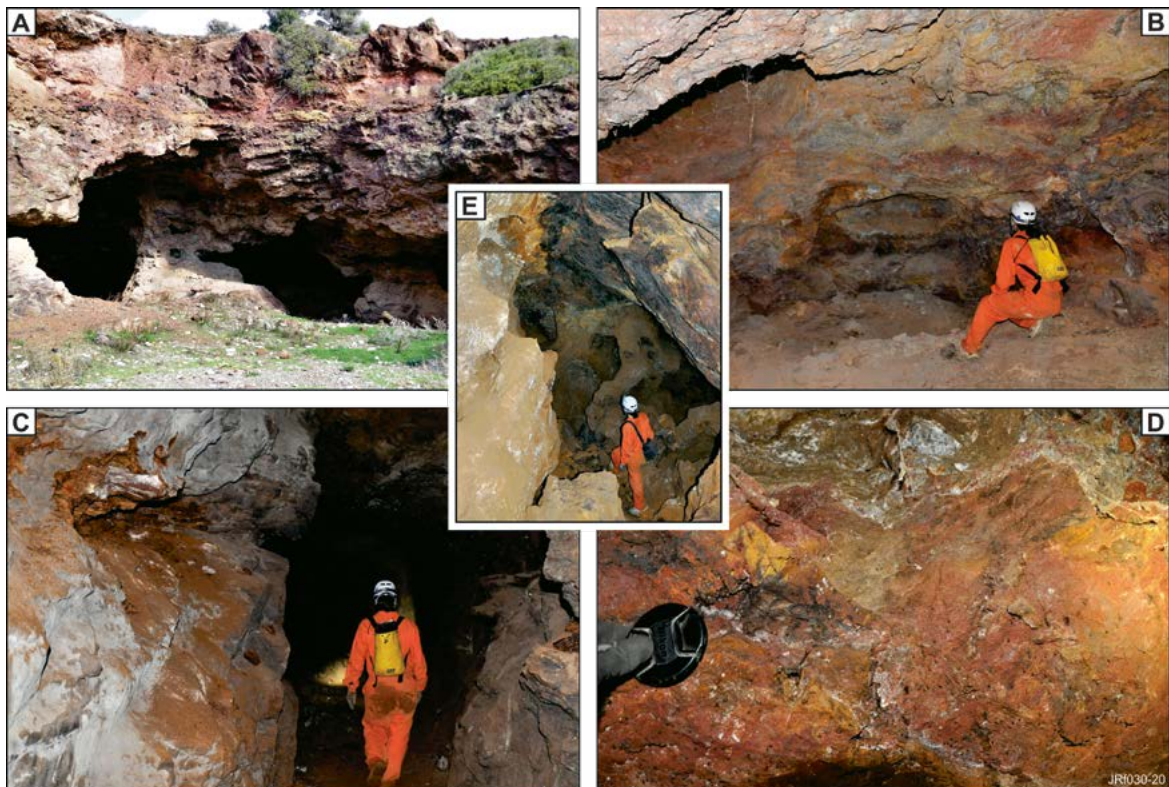


Fig. 8: Five examples of oxidised mineralization from the first and third contacts. workings – A. Exposures of first contact at Kilometre 3 with opening at right hand side about 2 m high; base of vegetation at top right is contact between the top of the detachment zone and the overlying Laurion schist (photo by James Ross). – B. Oxidised, near surface, first contact mineralization at the Elafos ELA-01 mine (photo by M. Vaxevanopoulos). – C. Jean Baptiste mine at the 80 m level in the Kamariza area; thin, oxidised third contact mineralization visible at left hand side in foreground and large void in background (photo by M. Vaxevanopoulos). – D. Thin, oxidised mineralization within Lower Kamariza marble at Mercati, at a depth of 88 m and 6 m below the third contact; camera lens cover central left hand side is 7 cm in diameter (photo by M. Vaxevanopoulos). – E. Steeply dipping oxidised contact between Pounta marble and overlying Laurion schists at Demoliaki; ancient workings clearly visible in central area of image and indicate the irregular nature of mineralization at this location. (photo by M. Vaxevanopoulos).

dence of variations in grade at both contacts? Ardaillon (1897), noted very little silver at Plaka, important levels at Kamariza, and high levels at Soureza. Other authors provided analytical results for samples of mineralization from various locations, with widely varying results (e.g. Cordella, 1869; Potier, 1880; Marinos and Petrascheck, 1956; Gale, et al., 1980; Skarpelis, 2007).

The grade of silver at Laurion has been commonly expressed as ppm silver/tonne of lead (ppm Ag/t Pb)<sup>1</sup>, a calculation that exaggerates the grade if samples with low levels of lead also contain separate sulphosalt minerals rich in silver (Voudouris, 2008b). Therefore, we believe that selection of samples that may represent what the ancient miners selected should be restricted to those containing at least 5% lead to ensure adequate dilution of any accessory silver rich sulfosalts. Furthermore, if samples from the third contact are to provide an indication of what was mined, they should contain at least 10% lead to approximate the cut-off grade thought to be used by the ancient miners (Ardaillon, 1897).

Conophagos (1980), noted that the lead content of mineralization varied across the district, and also within single ore bodies, ranging from <10% up to 40–50% lead, but with an average of about 15%. He also believed that the silver content was directly related to the lead content and that in the ancient mines it varied from 1,000 to 4,000 ppm Ag/t Pb. After considering the various processing steps at Laurion that were applied in the Classical period, Conophagos (1980), concluded that the average silver content of mined and processed ore was about 2,000 ppm/t Pb. This figure was based on the silver content of the *ecvolades*, i.e. the discarded lower grade waste

from washeries and mining. It has been widely adopted in historical studies of Laurion.

A total of 29 eligible analyses have been compiled in Table 1. Thirteen are from the first contact, eleven from the third contact and five from the Filoni 80 vein, near Plaka. They are plotted in Fig. 10 as ppm Ag/t Pb against wt.% Pb. The 13 first contact samples include three from Plaka, that were collected by Gale, et al. (1980), from modern workings in primary mineralization. They average 2,114 ppm Ag/t Pb and 46.0% lead and may include some mineralization from the second contact. But the more important issue is that: did mining of the deeper, primary mineralization at Plaka occur in ancient times? Ardaillon (1897), refers to very little silver at Plaka and there appears to be no evidence for ancient working of the deeper sulfides. Huet (1879), provides evidence of grades of about 1,000 ppm Ag/t Pb in strongly oxidised mineralization with about 8% lead at the first and second contacts at Plaka, which he refers to as “leaded iron, manganese iron and dry iron” and suggests it may have value as flux. To avoid doubt, we have deleted these three Plaka samples from our estimation of the grade of first contact mineralization exploited by ancient miners.

The remaining ten samples represent six first contact deposits with grades ranging from 509 to 4,000 ppm Ag/t Pb with an average of 1,120 ppm Ag/t Pb and 31.8% lead. References to Table 1 and Fig. 10 shows that nine of these samples range from 509 to 1,500 ppm Ag/t Pb, and average 800 ppm Ag/t Pb, with only Trachynkera, at 4,000 ppm Ag/t Pb, as the outlier. Although the sample size is small and the data imperfect, they do show some coherence. They also support the widely held belief that

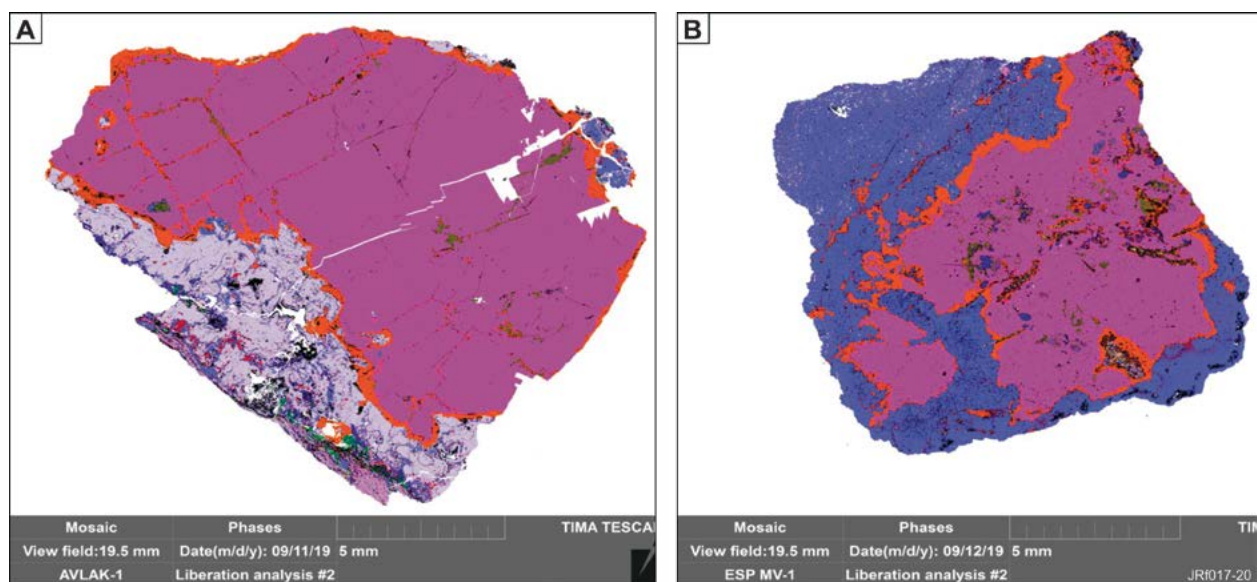


Fig. 9: TIMA TESCAN X-ray images of galena (magenta) “armoured” by cerussite (orange) during oxidation of first contact mineralization; scale bar is 5 mm. – A. From Avlaki deposit (sample 19–1) galena with incipient internal alteration to cerussite and anglesite (green), rimmed by up to 1 mm of cerussite and bordered by iron-manganese-lead oxides (mauve). – B. From Esperanza deposit (sample ESP MV 19–1), galena enclosed within hematite (blue) with more advanced internal alteration to cerussite and anglesite and a narrow rim of cerussite up to 0.5 mm wide. (Images from John de Laeter Centre, Curtin University).

first contact mineralization was lower grade than the third contact. Oxidation may explain the difference, but a sample from Sounion, analysed by Gale, et al. (1980), contains 86.3% Pb and is essentially pure galena, yet only contains 579 ppm Ag/t Pb. A result which suggests that the grade of primary mineralization at the first contact, at least at that location, may have been lower than at the third contact.

Results for eleven samples of third contact mineralization containing at least 10% lead are also shown in Fig. 10. Ten of these samples are from the Kamariza area and average 2,917 ppm Ag/t Pb and 71.2% lead. They include seven samples of almost pure galena concentrate from Skarpelis (2007), which average 2,864 ppm Ag/t Pb and 82.2% lead. The eleventh sample is from Agrileza and contains 2,500 ppm Ag/t Pb and 10% lead. The ten

samples from Kamariza average almost 3,000 ppm Ag/t Pb, much higher than first contact mineralization, and significantly higher than the estimate of Conophagos (1980). Whilst this small population should not be considered a reliable guide to the grades of silver exploited by the ancient miners at Kamariza, the higher values of silver are consistent across the range from 10% lead to almost 83% lead in individual samples. Furthermore, these results are broadly consistent with results of early sampling of mineralized support pillars in the Kamariza workings, which often included lower grade sections of mineralization. According to Cordella (1869), this sampling gave results ranging from 35–60% lead and 1,200–3,500 ppm Ag/t Pb.

The narrow, shallow dipping and high grade Filoni 80 vein at Plaka was not discovered by the ancient

Sample	Location / deposit	Contact	Source	Pb (%)	Ag (ppm)	ppm Ag / t Pb
–	Daskalio-Dardeza	First	Marinos and Petrascheck (1956)	5 <sup>1</sup>	–	1500 <sup>1</sup>
–	Vromopoussi	First	Potier (1880)	22.5	–	750
–	Vromopoussi	First	Marinos and Petrascheck (1956)	8 <sup>2</sup>	–	605 <sup>2</sup>
–	Turkolimani	First	Potier (1880)	15	–	1200
–	Trachynkera	First	Potier (1880)	9	–	4000
–	Villia	First	Potier (1880)	12.7	–	900
A4	Plaka-North	First	Gale, et al. (1980)	68.7	350	509
A5	Plaka-North	First	Gale, et al. (1980)	31.4	200	637
A6	Plaka-North	First	Gale, et al. (1980)	59.5	310	521
S12	Sounion	First	Gale, et al. (1980)	86.3	500	579
B2	Plaka	First	Gale, et al. (1980)	38.0	1240	3263
B4	Plaka	First	Gale, et al. (1980)	43.0	720	1674
B5	Plaka	First	Gale, et al. (1980)	57.0	800	1404
PLK1/1	Filoni vein		Skarpelis (2007)	84.8	5537	6529
PLK1/2	Filoni vein		Skarpelis (2007)	82.6	4932	5971
PLK1/3	Filoni vein		Skarpelis (2007)	83.1	5754	6924
E7	Filoni vein		Gale, et al. (1980)	84.6	4400	5201
W110	Filoni vein		Gale, et al. (1980)	80.4	4760	5920
–	Kamariza	Third	Cordella (1869)	32 <sup>3</sup>	–	3250 <sup>3</sup>
–	Agrileza	Third	Marinos and Petrascheck (1956)	10	–	2500
D1	Kamariza	Third	Gale, et al. (1980)	22.1	790	3575
TG60A–1	Kamariza	Third	Gale, et al. (1980)	82.5	1900	2303
SUB1	Kamariza	Third	Skarpelis (2007)	82.1	2440	2972
SUB2	Kamariza	Third	Skarpelis (2007)	82.3	2606	3166
ILA3/1	Kamariza	Third	Skarpelis (2007)	81.6	2234	2738
Serp3/4	Kamariza	Third	Skarpelis (2007)	81.7	2375	2907
ILA4	Kamariza	Third	Skarpelis (2007)	82.1	2157	2627
SUB2	Kamariza	Third	Skarpelis (2007)	82.8	2453	2962
Serp3/3	Kamariza	Third	Skarpelis (2007)	82.3	2200	2673

Tab. 1: Silver contents of Laurion mineralization. 1) Midpoint of range: 4–6% Pb; 1,000–2,000 ppm Ag/t Pb; 2) Midpoint of range: 7–9% Pb; 550–660 ppm Ag/t Pb; 3) Midpoint of range: 20–44% Pb; 3,000–3,500 ppm Ag/t Pb.

Greek miners. It is up to 2 m in thickness (Voudouris, et al., 2008a) and hosted mainly in the Kamariza schist hornfels, therefore it is neither first nor third contact. Five samples of almost pure galena from Gale, et al. (1980), and Skarpelis (2007), average 6061 ppm Ag/t Pb and 83.1% lead. According to Voudouris, et al. (2008a), galena from the Filoni 80 vein is rich in silver and contains small inclusions of silver sulphosalts, such as argentian tetrahedrite and miargyrite.

These small populations of available analyses for the first and third contacts are insufficient to draw firm conclusions. Nevertheless, they do indicate that third contact mineralization is much higher grade and provide a hint that this difference may originate in the primary mineralization, rather than result solely from stronger oxidation at the first contact. A curious feature of the available analytical results are the higher grades at Plaka and Filoni 80 vein. Both deposits are close to the Plaka granodiorite and the possibility that this intrusion may have influenced mineralization at the first contact is supported by the data of Fig. 11. It shows the distribution of anomalous concentrations of accessory non-sulfide minerals in first contact mineralization as recorded in the Mining Map of Marinos and Petrascheck (1956). Notable concentrations of fluorite, iron-manganese and iron ores occur near the extremities of the district, implying a more centralised source for the first contact mineralization. The anomalous concentrations of barite may appear closer in plan view, but they occur at significantly higher stratigraphic levels, in association with Pounta marble above the SAD.

## The archaeological implications

The archaeological implications of the geological and geochemical data presented above, are best considered in the context of current archaeological knowledge about early mining at Laurion. Firstly, the oldest direct evidence is that from Mine 3 at Thorikos (Fig. 1), where pottery sherds were recovered from a thin, undisturbed clay covering of stone tool marks at the base of an exploited vein of mineralization, a few metres within the modern opening. These have been dated as late Early Helladic II (2200–2150 BC; Manning, 1995) by Spitaels (1984). The extensive investigations at Thorikos by the Belgian Archaeological School at Athens also recovered a few sherds of Neolithic and Early Bronze Age pottery associated with tool marks of stone hammers both outside the modern mine entrance and within the ancient underground gallery (Spitaels, 1984; Nazou, 2014; this vol.). Whilst these older sherds lacked precise stratigraphic context, they do indicate that mining may have commenced in the 4<sup>th</sup> millennium BC on oxidised mineralization exposed at the surface, before following the veins several meters into the hillside.

Secondly, there are three examples of indirect evidence for early mining at Laurion that support these early dates. The first are finds of litharges on the Mesogeia plain just to the north of the Laurion district which have been dated to the Early Helladic period (c. 3100–2650 BC) at Lambrika, and those dated to the middle of the 4<sup>th</sup> millennium BC at Merenda (Kakavogianni, et al., this vol.). It is not surprising that these metallurgical finds may be the only evidence of

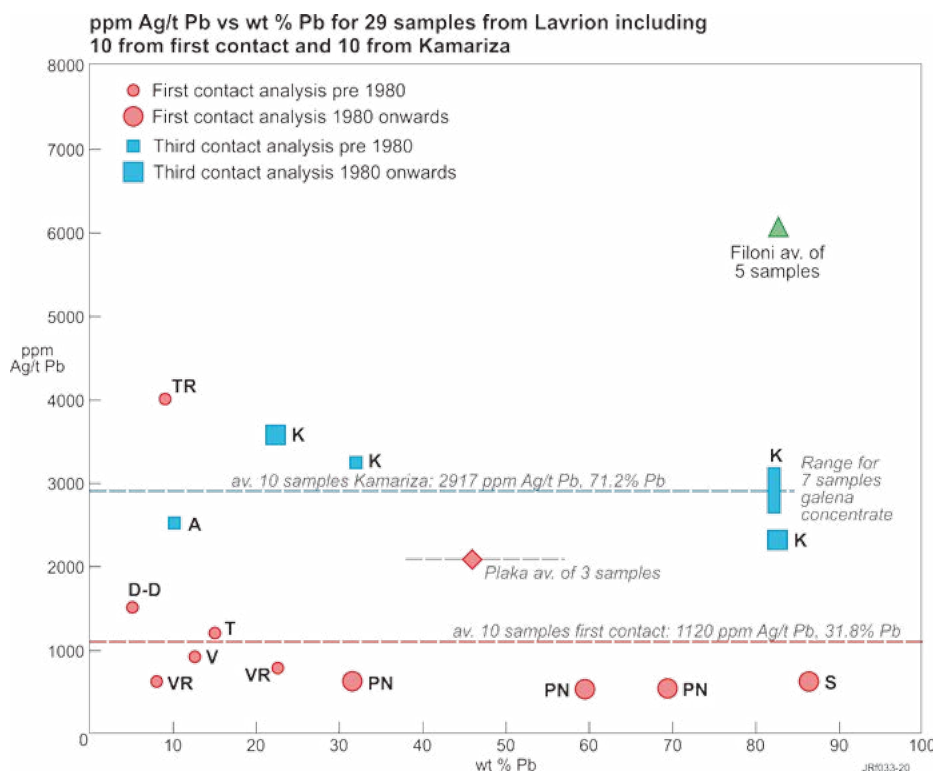


Fig. 10: Plot of wt.% Pb versus ppm Ag/t Pb for 29 published analyses from the first and third contact mineralization, and the Filoni 80 vein, at Laurion. Data includes analyses derived from 19<sup>th</sup> century publications and Marinos and Petrascheck (1956), in addition to “modern” analyses published from 1980 onwards (preparation: by J. Ross).

very early mining activities, because the reworkings of the Laurion landscape and metallurgical residues that occurred from the Classical period onwards, including the modern period, are likely to have swept up and reprocessed any older residues containing silver and lead.

The second indirect evidence are copper slags from the Early Helladic II (c. 2650–2200 BC) found at the coastal site of Raphina, located about 20 km north of the Laurion district. They have a lead isotope signature consistent with a Laurion source (Gale, et al., 2009). The third example are lead isotope data of silver, lead and copper artefacts found on mainland Greece and the Aegean islands. These results extend from the Final Neolithic silver and copper artefacts discovered in the Alepotrypa cave (Gale and Stos-Gale, 2008) through the silver, copper and lead artefacts of the Bronze Age (Gale and Stos-Gale, 2008; Kayafa, 2020; Ross and Kayafa, forthcoming). They are far too numerous to ignore in any assessment of the mining history of the Laurion district.

Laurion also had significant resources of iron ore within hematitic gossans, which were exported to Europe

during the modern mining era. According to Marinos and Petrascheck (1956), about 1.5 million tons of iron ore were exported between 1864 and 1950 (sourced from Argyropoulos, 1955). With such resources available within an established mining district it seems unlikely that some iron was not sourced from readily available surface deposits to provide tools for mining, agriculture, and weapons during the first millennium. However, besides ample evidence for iron smithing (Photos-Jones and Jones, 1994, p.355) so far no evidence for iron smelting in the Classical or Hellenistic period was ever recorded from Laurion, but only from Late Antiquity (Varoufakis, 2014).

In a series of papers Conophagos and Papadimitriou (1981) concluded that iron and steel clamps used at the Erechtheion were sourced from Laurion iron. They also suggested that a local iron industry at Laurion would have produced the essential iron tools, used by the ancient miners in the Classical period. Iron hammers and high purity, tempered chisels and picks (Ardailon, 1897) must have been a key factor in the sinking of numerous shafts to access and ventilate mining of the third contact. Varoufakis

Areas of first contact mineralisation with prominent concentrations of non-sulphide accessory minerals, (based on Mining Map of Marinos and Petrascheck, 1956)

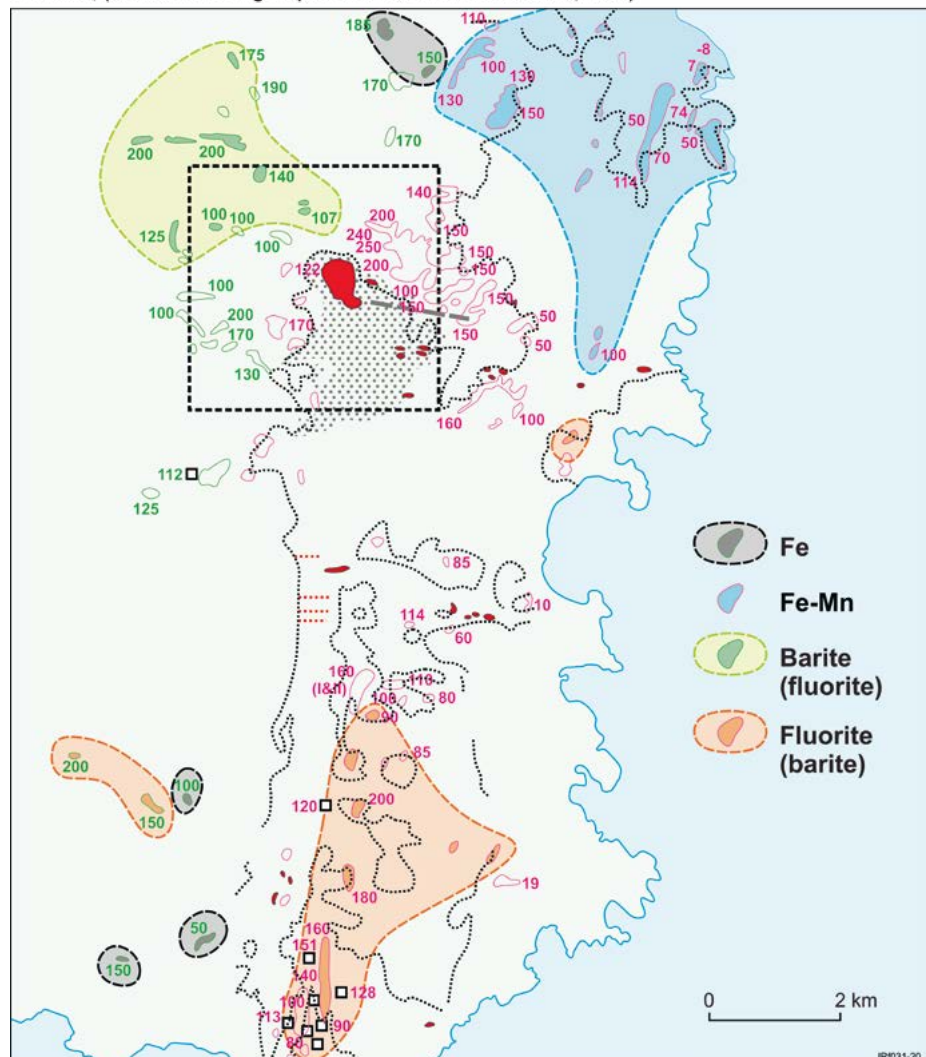


Fig. 11: Plan of first contact mineralization within the Laurion district highlighting those occurrences with anomalous concentrations of accessory minerals of iron, iron and manganese, fluorite, and barite. Base map is from Fig. 4A and information was compiled from annotations on the Mining Map of Marinos and Petrascheck (1956) (preparation: by J. Ross).

(2014), provided compelling evidence that smelted iron ore had been sourced from Laurion, based on analyses associated with a Late Roman furnace at Thorikos.

The gradually mounting archaeological evidence associated with the Laurion district encourages the conclusion that surface mining and processing commenced no later than the 4<sup>th</sup> millennium BC and continued, albeit intermittently at times, until the Christian era. Early mining was most likely focussed on silver and copper, with lead as a by-product from either reduction of argentiferous litharge, or as a commodity when the silver content was insufficient to justify cupellation (Stos-Gale and Gale, 1982). Secondary lead minerals would have been common within oxidised first contact mineralization and, when they had insufficient silver to justify cupellation, it was an opportunity to produce lead and generate additional income. This possibility is supported by the lead isotope data which indicates that Laurion was the principal source for Aegean lead artefacts during much of the Bronze age (Gale and Stos-Gale, 2008; Kayafa, in prep.; Ross and Kayafa, forthcoming).

The geology and geochemistry of the Laurion mineralization has significant potential to advance our understanding of the archaeology of the district and its mining history. Of most significance is the contrasting character of the mineralization at the first and the third contact. Whilst they share essentially the same primary mineralogy, the former is more widespread, thinner, less continuous, and lower grade, at least in most areas mined by the ancient Greeks. Stronger oxidation of the outcropping and shallow first contact mineralization amplified its difference from the third contact and contributed to its lower grade. Systematic exploitation of first contact mineralization would have often been difficult because of variable oxidation (Fig. 5A, B) and its irregularity. Therefore, it is likely that much of the mining was focussed on seeking out patches of residual galena (see Fig. 9), and cerussite and anglesite, with mineable concentrations of copper oxides being a welcome bonus.

This interpretation of the first contact mineralization at Laurion is in sharp contrast to the character and form of that at the third contact, which comes to us from 19<sup>th</sup> century records and maps of the main Kamariza area. They describe thick lenses of mineralization up to 1,500 m long, 11 m thick and ranging from 30–50 m wide. These continuous lenses of less oxidised mineralization enabled systematic mining at much higher production rates and they must have been bonanzas for the ancient Greek miners. Their discovery would have left an indelible mark on the mining history of Laurion, particularly when placed in the context of a long preceding period of mining less profitable first contact deposits.

Initial exploitation of the Kamariza deposits, and the resultant surge in silver production, would have been an exceptional event in the history of Laurion and ancient Athens. Undoubtedly, there is a strong case for linking their discovery and initial development to the account by Herodotus (7.144) of a windfall surplus to Athens from the mines at Laurion, and the dating of this event to 483/2, by Aristotle (*Ath. Pol.* 22.7). Systematic exploitation of

these thick, rich Kamariza lenses after 480 BC would have provided an almost continuous flow of wealth to the city and its residents for much of the 5<sup>th</sup> century BC and underpinned the dominance of the Athenian owl in Aegean commerce and trade.

## Conclusions

This reassessment of the mining history of the extensive lead-zinc-copper-silver deposits of the Laurion district integrates the observations of scholars and mining professionals in the 19<sup>th</sup> century, when much of the evidence of ancient mining and processing was still preserved, with the substantial body of more recent geological and archaeological research at Laurion and adjacent areas. The most significant outcome is the contrasting character of mineralization at the first and third contacts.

The first contact mineralization is more widespread, thinner, less continuous, and lower grade, at least in the areas mined by the ancient Greeks. Oxidation of the outcropping and shallow first contact mineralization amplified its difference from the third contact and contributed to its lower silver grade. It is likely that oxidation also favoured mining of secondary copper and led to significant production of copper at Laurion during the first 3,000 years, as noted by Gale, et al. (2009) and shown by Ross and Kayafa (forthcoming).

Third contact mineralization at Laurion, as represented by the core area of Kamariza, was higher grade, thicker and more continuous. These lenses of less oxidised mineralization were bonanza zones, when compared with the first contact, and their discovery would have left an indelible mark on the mining history of Laurion. The contrast between first and third contact mineralization is sufficiently strong to closely link discovery of the latter with the windfall surplus received by Athens, according to Herodotus, and dated to 483/2 BC by Aristotle.

Before that momentous discovery, mining must have been focussed on the numerous, small, discontinuous and lower grade deposits in the district. During that period the economics of mining were probably assisted by opportunistic extraction of secondary copper and production of lead. It is likely that iron became another by-product at Laurion in the first millennium, a development that provided the essential tools for shaft sinking and may have enabled the discovery of the Kamariza deposits.

The different character of first and third contact mineralization determined their different capacities to produce silver. At the first contact the numerous small deposits spread throughout the district favoured small scale, individual mining operations. Aggregate silver production may have been significant, but it is likely to have fluctuated. In contrast, the much larger third contact deposits at Kamariza were concentrated in a relatively small area and their character favoured relatively large scale, systematic, and continuous mining and processing



operations. These operations would have been capable of providing a substantial and continuous output of the silver that first transformed the mining history of Laurion and then, inevitably, assisted the transformation of Athens.

## Notes

- 1 When the recovery of silver depends on prior concentration of a particular host mineral (in this case galena) then the silver value of any area of mineralization is determined by both its Pb content (with galena the dominant source of Pb and silver at Lavrion), and the silver content of that Pb (which can vary considerably). Silver-rich galena in an area of mineralization with relatively low galena content may be equally valuable to mine and concentrate as another area of higher galena content but lower silver. For this reason, the 19<sup>th</sup> and 20<sup>th</sup> century authors who studied the Laurion mines used grade (g Ag/t Pb) rather than ppm when discussing the operations and treatment processes. We also prefer to adopt this convention because it tells us something about the ancient economics of mining at Lavrion and the relative values of the shallower and deeper ores, which are fundamental aims of our work. Nevertheless, the ppm Ag data is included in Table 1 for comparison.

## Acknowledgements

The authors wish to express their appreciation to the organisers of the Ari-Laurion conference in Bochum in November 2019 and the subsequent opportunity to publish our work. This paper has benefited from the constructive comments of Gil Davis, valuable assistance from Angelo Vartesi with the images, and help from Maria Kayafa and Steffen Hagemann with literature sources. Marco Fiorentini provided invaluable assistance with translations. We also acknowledge the support of the John de Laeter Centre at Curtin University, and its Director, Brent McInnes.

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