# Third Contact ore mineralogy at Laurium, Greece

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*ABSTRACT: 19th-century descriptions of Third Contact ores and the accompanying geological cross sections of unmined ore bodies in the same area, and at the same elevation as the ancient galleries, are useful in evaluating the nature of the ancient ores mined at Laurium. When these are supplemented by recent information on the geology and mineralogy at Laurium, and on the chemistry and mineralogy of the slag and tailings, a better understanding of ancient furnace charges emerges. The ore charged to the smelting furnaces appears to have consisted predominantly of argentiferous galena supplemented by oxide ore, including cerussite. Only the dark-coloured cerussite with sulphide/sulphosalt inclusions was argentiferous and a source of silver. Cerussite had several functions in the smelting operations including: as a source of lead oxide to reduce slag viscosity and to oxidise galena, as a source of silver, and as a contributor of lead necessary to scavenge silver. Closure of the mines at the end of the 1st century BC may have resulted from much of the pure galena ore being mined out leaving lower grade oxide ore and the more complex sulphide ore, not amenable to ancient beneficiation processes. The decline of Athens as an international power and the scarcity of wood for the furnaces contributed to the end of mining at Laurium.*

## Introduction

Over the last few decades, there has been discussion on the nature of the ore mined, the ore processing and the smelting technology practised by the Greeks during the Classical and Hellenistic Periods (5th–1st centuries BC) at Laurium (*eg* Conophagos 1980, Bachmann 1982, Fragiskos 2000). This paper focuses on the contributions that writings by 19th-century French engineers and archaeologists made to the resolution of the question of ore mineralogy, particularly for the deeper Third Contact (see below). 20th-century papers on the geology and mineralogy at Laurium (Fig 1) and on the slag and tailings mineralogy and chemistry expand our understanding of the ore and gangue minerals. The identification of the ores at the Third Contact is important because it is the starting point for subsequent debates on ore processing and smelting.

According to Conophagos (1980, 92 and 94) Greek miners discovered the Third Contact ores in the early 5th century BC. The Third Contact was richer than the higher zones because:

- it was more continuous, since it was largely protected by the overlying rock sequence from erosional losses;
- it was thicker, particularly if the lead ores in the immediately overlying schist are included; and
- it had a slightly higher silver content, probably related to the preservation of more sulphide ore.

Figure 2 is a schematic illustrating the salient points of the Laurium ore deposits; it is a composite of information from a number of sources (Huet 1885, Conophagos 1980 and Freiburg 1999, 20–21). The schematic is not to scale, but the ancient shafts reached the Third Contact at an average depth of 70m (Wendel and Holzen 1999, 12) and a maximum of 110m. The sequence of mineralized marbles and schists is folded into a broad, north-trending anticlinal structure. Abundant cross-fracturing in the upper portions of the fold contributed to the concentration of mineralizing fluids in an area extending from the Agrileza-Souresa area on the south through Camaresa to Plaka on the north. The ores occur as hydrothermal replacement deposits (Petrascheck 1976, 25) developed in Mesozoic dolomitic marbles at the contacts within adjacent schists. They are blanket-like deposits or *manto* ores that run parallel to the schist/marble contacts. The deepest and richest ore zone occurred along the Third Contact between the Lower Schist and the top of the underlying Lower Marble. Stockwork zones of miner-

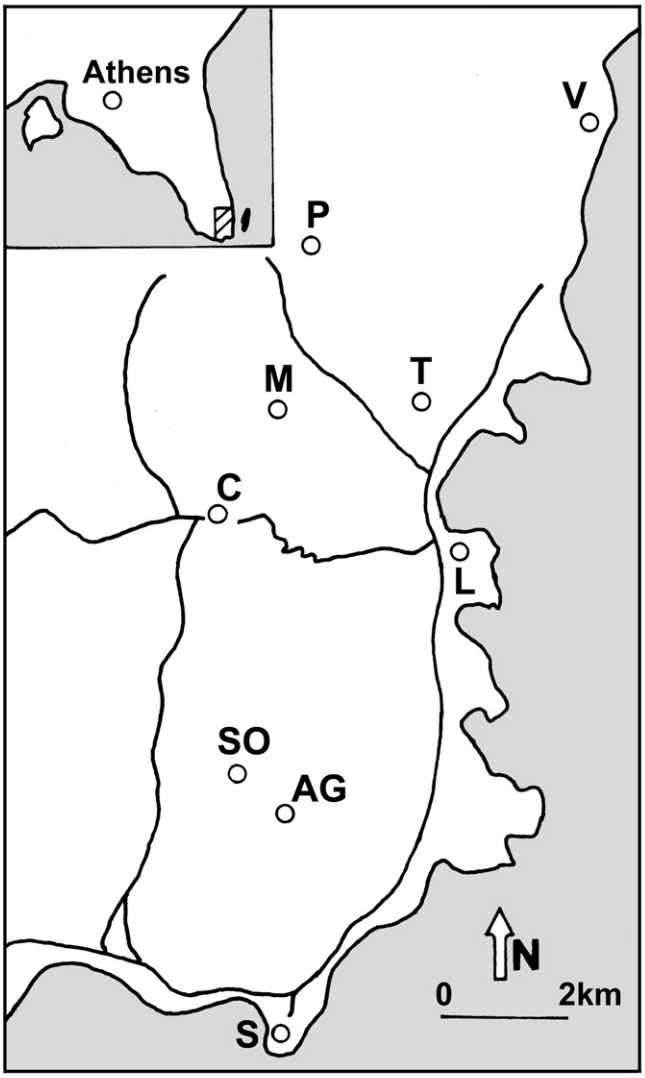


*Figure 1: Laurium is about 60km southeast of Athens. On the local map are Laurium or modern Lavrio (L), Cape Sounion (S), Agrileza (AG), Camaresa (C), Merkati (M), Plaka (P),Thorikos (T), Souresa (SO) and Vromopoussi (V). Most of the mined area at Laurium lies east of the north-south road through Camaresa.*

alized fractures (Fig 2, C3c) occur beneath the *mantos* (Fig 2, C3b). Potier (1880, 11) reported large masses of rich galena ore developed in the *manto* above areas of major intersections among fractures. These galena ores extend down into the underlying fractures where they formed a core of lead ore embedded in more extensive masses of smithsonite (calamine). In the case of the Third Contact, a zone of mineralized veins, lenses and disseminations of sulphides are present within the Lower Schist for several metres above this contact (Fig 2, C3a and Fig 3). The enclosing low-permeability schist protected these sulphides from oxidation. Huet (1878, 16) called this largely sulphide ore in the Lower Schist the 'Subordinate Third Contact'. The *manto* and stockwork ore bodies carry primary sulphides oxidized in varying amounts to a host of secondary minerals.

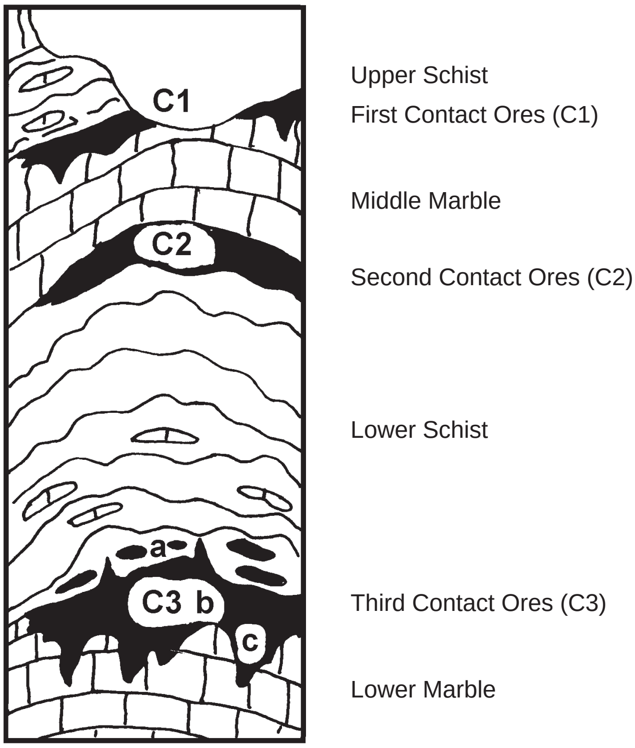


*Figure 2: Schematic stratigraphic section illustrating the Mesozoic sequence of marbles and schists and the main ore bodies at Laurium. C3a represents the lenses and veins of ore in the lowest few metres of the Lower Schist, C3b is the main* manto, *and C3c the stockwork ores.*

## 19th-century studies of the ore bodies at Laurium

Normally the question of what was mined in ancient times, before records of geology and production were kept, is either left in a speculative state or at best based on a few ore fragments found on long-abandoned mine dumps or as inclusions in slag. As noted by Willies (1991), open cast and underground workings more often than not are destroyed by subsequent mining. But Laurium is different because there is no evidence of significant mining efforts after the 1st century BC until the French resumed large-scale underground mining there in the 19th century. In the 1860s (Conophagos, 1980, 48–50) mining focused on the surface deposits of ancient slag assigned to the Société Grecque and to the ancient waste rock processed by the Société Roux-Serpieri. These companies (merged into the Société Usines in 1873) recovered a considerable tonnage of argentiferous lead, but the amount of lead and silver derived from each of these two surface sources is unknown. Serpieri organised the Compagnie Français des Mines du Laurium (CFML) in 1875 for the sole purpose of exploiting argentiferous lead ores underground. These underground operations initially explored the ancient shafts and galleries, but were considerably expanded when CFML recognized the largely untapped zinc ore

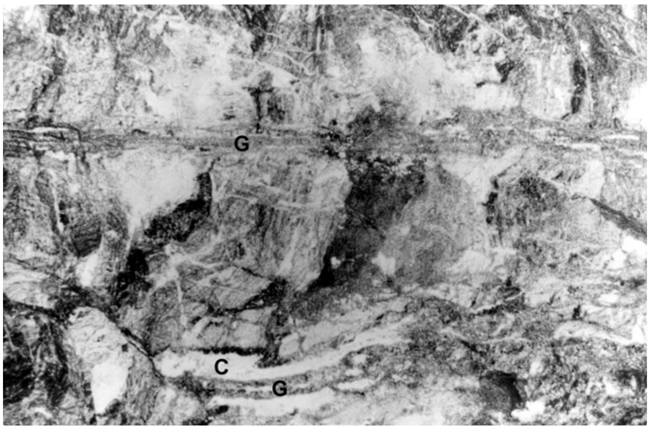


*Figure 3: Roof of a 19th-century-AD gallery developed along the Third Contact showing vertical veins of galena, pyrite, and sphalerite (G) several centimetres thick cutting brecciated Lower Schist. White areas are coarsely crystalline calcite (C). Camaresa, Jean-Baptiste Shaft area.*

bodies. Processing and smelting operations for Société Usines and for CFML were independent operations. Potier (1880, 1–4) indicated that CFML began underground mining, principally at the Third Contact, in the central part of the Laurium District around Camaresa. CFML recovered zinc from the enormous reserves of calamine (an obsolete term for smithsonite or $ZnCO_3$ (Bayliss 2000, 34)) and sphalerite (ZnS) largely left intact by the Greek miners. Significant amounts of lead-silver ore were mined by CFML from the ancient galleries and from newly developed Third Contact ore bodies in the same area and at depths identical to those obtained in ancient times. A map showing the extent of the ancient galleries (some 300km in total) was published in 1890 and is reproduced by Conophagos (1980) and by Wendel and Holzen (1999, 12).

Most of the 19th-century reports were written by French engineers who were consultants for CFML (*ie* Huet and Potier) or who were at least conversant with economic geology (*ie* Fuchs and de Launay). The exception is Edouard Ardaillon who trained in archaeology and geography and from 1892 to 1898 was affiliated with the French School in Athens (Kounas 1972, 13). His consuming interest was in the mines at Laurium and he referenced the CFML engineers he consulted while writing *Les Mines du Laurion dans l'Antiquité* (Ardaillon 1987). Huet (1878, 270) and Potier (1880, 4) stressed the

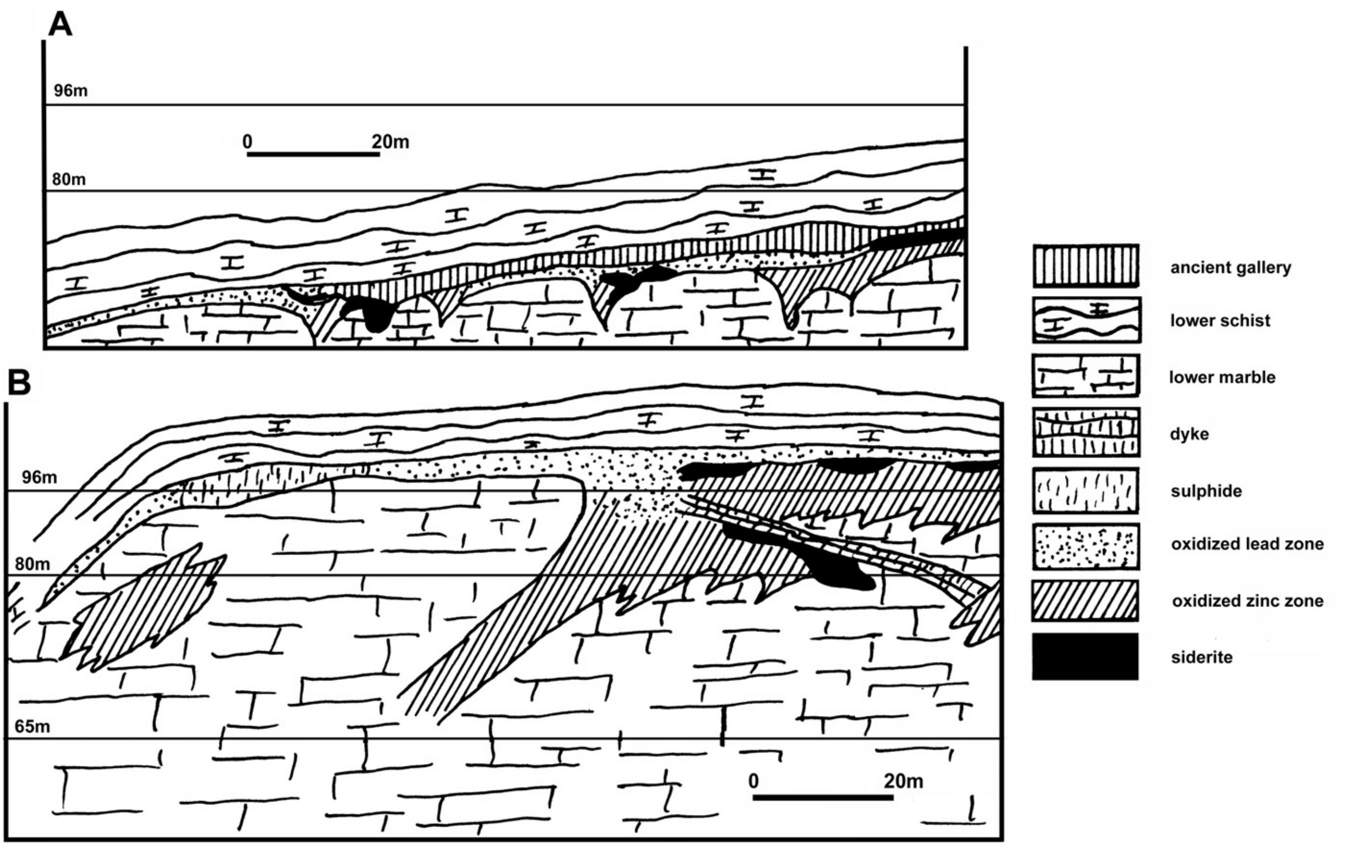


*Figure 4: A: Southern half of the north-south cross-section of the Third Contact drawn through Camaresa (modified from Huet 1885, Grand Cross Section). The ancient galleries (labelled voids on his drawing) followed the cerussite-rich upper* manto. *B: The geology and mineralogy of unmined Third Contact* manto *and stockwork ores in the area of the Jean-Baptiste shaft at Camaresa (modified from Huet 1885, Cross Section No 3). The oxidized lead zone of the upper* manto *and the underlying smithsonite or zinc-rich zone are clearly shown. Although the oxidized components are sharply separated into the two zones, the primary sulphides occur throughout the* manto. *Galena is also present in the stockworks.*

importance of their observations of the mineralogy of the intact ore pillars and of the waste rock in and around the ancient galleries to CFML's exploration programme. However, a more compelling reason for relying on these 19th-century reports for a description of the ancient ores lies in Huet's scaled cross sections of the Third Contact ore bodies (Huet 1885, appendix). These cross sections, drawn for the central part of the Laurium District around Camaresa, demonstrate the zoning of the *manto* ores and clearly show that the ancient galleries were excavated in the upper oxidized lead zone (Fig 4A). More importantly, a number of his cross sections illustrate Third Contact oxidized lead ores (Fig 4B) that were mined in the 19th century by CFML. Elevations relative to sea level are on all of the sections. Surface elevations for the mining area around Camaresa range from 130 to 180 metres and, when combined with maximum depth for the ancient shafts of 110 metres (Conophagos 1980, 198), it is very apparent that these new ore bodies mined by CFML are largely at the same level as the 5th-century BC ores. The proximity of the 19th-century underground operations and the ancient galleries strongly suggests CFML miners exploited similar kinds of ore bodies to those mined earlier by the 5th-century BC Greeks.

It is clear from the location of the ancient galleries, as described by both Huet and Potier, that the ancient miners tended to preferentially follow the galena. The *manto* ores with galena and cerussite were their primary source since wherever they encountered these ores they completely mined them out. Huet (1879, 16) and Potier (1880, 20) state that the ancient galleries were also developed in the Lower Schist ('Subordinate Third Contact') where galena was typically not oxidized. In some of Huet's cross sections he shows small galleries in the stockwork veins, but there is no evidence that these were heavily mined. The reason may be that it was not profitable to go after these narrow veins of galena engulfed in masses of smithsonite. Potier (1880, 12) states that they (CFML) had not found a rich area of lead ore that did not show a trace of the ancient exploitation.

## Results of the 19th-century studies of the ore bodies

Huet (1878, 15 and 21) described the Third Contact *mantos* as carrying 'considerable' cerussite ($PbCO_3$) with veins and masses of the galena (PbS), sphalerite, and pyrite ($FeS_2$). He particularly noted that sulphides were very abundant in the central part of the district around Camaresa (1885, 543–4). Huet commented (1885, 564) that the Third Contact oxide ores were less rich in silver than the sulphide ores. In a more detailed description of an ancient gallery near Mercati (northeast of Camaresa) at the contact with the Lower Schist, Huet showed galena hosted in iron oxide grading down into galena-rich siderite ($FeCO_3$). The floor of the gallery is siderite with minor galena and below this is a basal zone of smithsonite. He reported that in the central part of the Laurium District siderite was a very important gangue mineral while farther south, the primary gangue minerals are quartz and fluorite. Potier (1880, 11) in his schematic cross section and description of the Third Contact ore showed a *manto* of cerussite with veins and masses of galena and sphalerite, in a matrix of oxide minerals and quartz. Smithsonite is the dominant mineral at the base of the *manto* and in the underlying stockwork. Galena occupies the central part of the stockwork veins. He noted (*ibid*, 10) that the rich Third Contact ore consisted of 'considerable' cerussite with veins of galena and sphalerite with a tenor of 2.0kg of silver per ton of lead. Fuchs and De Launay (1893, 381) said that Third Contact ore is galena, sphalerite, and pyrite disseminated in a siderite matrix with cerussite and smithsonite around the sulphide masses. Ardaillon (1897, 16) describes the Third Contact ore as sulphide hosted in quartz and fluorite and makes the interesting observation that cerussite is rare at Laurium. The minerals listed as part of the ores at Laurium by Ardaillon (1897, 59) are galena, sphalerite, pyrite, cerussite, calamine, siderite, calcite, quartz, fluorite, and halloysite (one of the kaolinite group of clay minerals).

## 19th-century CFML ore processing, smelting and production

The annual report by CFML for 1879 is very illuminating in regard to the nature of the lead ores mined in 1878, fairly early in the history of the operation. The oxidized lead ore referenced in this report (called ferruginous-oxide lead ore in later reports) is cerussite and some galena in a gangue of iron oxide and various carbonates. Galena enriched by washing came from the initial breaking and hand sorting underground followed by the crushing of mixtures of galena, sphalerite and pyrite. It appears that hand-sorting underground of lead ores (Huet 1887, 36–7) was limited to separation of oxide material from sulphides; of zinc ores (calamine and sphalerite), where possible, from oxide or sulphide; and simple sulphide mixtures. In the latter case the breaking of sulphide ore resulted in three categories, galena with pyrite, galena with sphalerite, and galena with pyrite and sphalerite. Some of the smelting furnaces produced a copper-nickel matte (*ibid*, 36) indicating that copper and nickel sulphide/arsenide ores (*eg* chalcopyrite ($CuFeS_2$), bornite ($Cu_5FeS_4$), millerite (NiS), gersdorffite (NiAsS),

*Table 1: CFML lead ore production in 1878*

| Beneficiated ore type | Beneficiated ore (tons) | Benficiated ore as % of total lead mined | Ore type as % of beneficiated ores |
|---|---|---|---|
| galena from washeries | 879.0 | 7.1 | 34.9 |
| hand-sorted galena | 44.5 | 0.4 | 1.8 |
| oxidized lead ore | 1591.5 | 12.9 | 63.3 |
| Total (tons): | 2515.0 | | |

and rammelsbergite (NiAs), all present in the modern sulphide ores (Wendel *et al* 1999a)), were also retained in the product taken to the smelter. The total amount of lead ore mined in 1878 was 12,348.8 tons. Table 1 shows the different categories of lead ore after beneficiation. There was a very small amount (0.4%) of galena in the ore bodies amenable to breaking and hand-sorting. Most of the galena came from the crushing and washing of mixed sulphide ore. CFML also smelted 40.4 tons of pig lead derived from earlier operations. The oxidized lead ore was clearly a major source of the lead and silver produced in the 19th century, making up 63.3% of the beneficiated material. As noted below, this oxidized ore was crushed and smelted and no additional grinding and washing was done. The successful breaking and hand-sorting of galena was likely of prime importance to the ancient miners. In the case of mixed sulphide ores, if the sulphides are coarse enough breaking with a hammer and hand sorting is effective. Potier (1880, 21) illustrated this with a description of a small contemporary operation in the Vromopoussi Concession (NE Laurium). Here, veins and lenses of galena associated with sphalerite and pyrite were mined and processed from the basal part of the Lower Schist. 27% of this galena was hand picked and the remainder was crushed and then separated in an undescribed washing structure.

Huet goes into some detail in describing the crushing, grinding, sieving and washing of the mixed sulphide ore (1878, 37–8). Except for crushing, no further mechanical processing was performed on the ferruginous-oxide lead ore. Instead it was introduced directly to the smelting furnaces where it served several functions; it was a slag/matte forming material and the PbO lowered its viscosity. It was also a source of Pb for scavenging the silver and a source of silver. There is support for the direct smelting of low-grade silver-lead ore without grinding and washing in CFML (1879, 5–6). This report states that 'for those ores of argentiferous lead which from their composition we can not enrich mechanically and can not export because of the low tenor, we have constructed smelting furnaces' and 'considering the price of lead during 1878 our ferruginous-oxide lead ores are of minimum value and can not be economically exported to Marseille' (translation by the author). Further, CFML (1893, 6) and Fuchs and DeLaunay (1893, 384) mention the Lead Works at Laurium, consisted of 4 roasting furnaces and 9 smelters, where the 'poor ore' was smelted 'on the spot'. As noted above, the oxide ores were the lower grade ore. How much lower is indicated by Papadimitriou (2000b), who stated that cerussite ore typically carried 0.5–1.0kg silver per ton of lead ore which is in agreement with Huet's figure of 1.0kg or less of silver per ton of lead ore when comparing the oxide ore of the First Contact with the Third Contact ore (1885, 533 and 540). Third Contact ores were greater than 2.0kg silver per ton of lead ore (Huet 1878, 14) which probably reflects the increasing importance of the sulphide ores at the deeper level.

By the late 19th century the silver and lead appear to have been entirely derived from sulphide ore. CFML (1893, 10) lists their production for that year as calamine, galena, mixed sulphurous ore (blende, pyrite, galena) and manganiferous pyrite. Ardaillon (1897, 16) commented that cerussite (perhaps used just as a term for oxidized lead ore) was rare. The *mantos* dip eastward placing them at increasingly-deeper levels where less oxidation may have occurred and more sulphide ore was therefore preserved. Galleries excavated along the more strongly oxidized up-dip, nearer to the surface portions of the Third Contact, would have been more readily available to the ancient miners, and to CFML in the early stages of their mining.

Support pillars of finely crystalline galena in mixed sulphide ore or galena in massive quartz were left behind by the 5th-century BC miners, because they could not find an efficient method to liberate and separate the galena without reducing it to powder. However, where the sulphide mix was simple (*eg* galena, sphalerite and/or pyrite) and coarse enough (individual grains of centimetre size) galena can be broken away with cobbing hammers. Iron cobbing hammers have one or two wedge-shaped edges on the peen and are used for the initial liberation of ore minerals (Richards 1925, 6–7). These were used by the ancient miners at Laurium (Conophagos 1980, 176–177, figs 9-8, 9-10 and 9-11). Ardaillon (1897, 60) stated that the ancient waste rock typically carried a maximum of 8–10% lead and that this was the result of the initial breaking and sorting in the mine area. This suggests that lead ores, both the galena (86% lead) and cerussite (77% lead) were systematically liberated from the mined ore. Potier (1880, 4) noted that much of the waste rock around the mines consisted of calamine and sphalerite. Interestingly, he states that waste material occasionally contained significant amounts of silver (2.0 to as much as 6.0kg of silver per ton of lead ore and less than 10% lead). This may have been the result of the ancient miners not recognizing silver-bearing mineral species (*eg* argentojarosite) included in the waste. Discrete masses of galena as veins or as coarsely crystalline material enclosed in galena, sphalerite, and pyrite mixtures, in zinc ore (both sphalerite and calamine), or in iron oxide, calcite, siderite or quartz-fluorite gangue could be profitably mined with the ancient technology. In 1878, shortly after CFML began mining, 62.3% of the furnace charge came from ferruginous-oxide lead ore, 36% from galena and 1.5% from pig lead (from previous smelting operations, not necessarily 1878 ore). Papadimitriou (2000a, 35) suggested a portion of this ferruginous-oxide lead ore may have been reclaimed from low grade waste rock abandoned by the ancient miners. However the rights to the surface waste belong to the Société Usines not to CFML. We do not know how much, if any, of the ancient ore-grade backfill and support pillars contributed to CFML's mined ore. Both galena and the oxidized lead ore were sources of silver in the 19th century and in the 5th century BC as well.

There are a number of factors that limit any comparison between the ancient mining and ore processing and those of the 19th century. Mechanical crushing of mixed sulphide ores coupled with the washing in circular buddles allowed for a much better liberation and separation of enriched galena than the ancient hand-sorting and washing operations of the 5th century BC. Nineteenth-century shaft furnaces with mechanical bellows and much better refractory linings were much more efficient and able to handle lower grade ore as well as the mixed sulphide ore. The importance of the 19th-century reports to the question of ancient furnace charge is that significant amounts of lower grade silver-bearing oxide ores were available and that this crushed oxide served a number of purposes, perhaps as applicable in the 19th century AD as in the 5th-century BC smelting operations (see above). Limited by their technology, the ancient miners targeted relatively pure masses of galena rather than complex mixtures of sulphides. Potier (1880, 9) states that the ancient miners followed the galena. However, the excavation of ancient galleries throughout the ferruginous-oxide lead ore of the upper *manto* coupled with the small amount of lead retained in the waste rock, suggests that the lower grade, silver-bearing, ferruginous-oxide lead ore was also liberated and sent to the smelting furnaces.

## 20th-century mineralogy

There seems to be general agreement that the silver-bearing ore minerals at Laurium were some combination of galena and cerussite. Silver carried by galena is derived from microscopic inclusions of silver-bearing sulphides or sulphosalts (typically Cu or Pb plus Sb, and/or As and S) exsolved during its crystallization (Gaines *et al* 1997, 65). This is well illustrated in Gale *et al* (1980, table 5) where it is clear, at least for the galena samples from Laurium, that silver is associated with inclusions of tetrahedrite (probably freibergite, $(Ag, Cu, Fe)_{12}(Sb, As)_4S_{13}$) and of arsenopyrite (FeAsS). Under high temperature and pressure conditions, and in the presence of excess bismuth and antimony (Raines 2000, 397), silver may substitute for lead in the galena crystal structure. However, on cooling and crystallization, all three of these elements will exsolve as noted above. Cerussite forms as a replacement of lead minerals during the secondary oxidation stage. Little cation substitution occurs within the cerussite crystal structure (Gaines *et al* 1997, 446) and when argentiferous cerussite is smelted the silver comes from these inclusions. Cerussite carrying these inclusions is grey to black in colour (Gaines *et al* 1997, 446) and occurs at Laurium (Ardaillon 1897, 16; Kohlberger 1976, 124 and personal observation). Dark-coloured cerussite typically forms an alteration rim around a core of galena and may completely replace it. Putzer (1948, 33) reported that crusts of 'resinous coloured', silver-bearing cerussite were scarce, but a four-metre-thick mass was observed in the Plaka area. Much of the cerussite described from Laurium is white to yellowish, sometimes red with an iron oxide coating (Katerinopoulos and Zissimopoulou 1994, 104), and may contain little or no silver.

There are at least 20 silver-bearing mineral species including galena and cerussite found at Laurium (Wendel *et al* 1999a). Most of these are silver-bearing sulphides and sulphosalts which are associated with the main primary sulphide ores (galena, sphalerite, and pyrite). Silver-rich pyrite in Third Contact ore was reported by Huet (1885, 545). There are fewer recognized secondary silver minerals from the oxide zone reported from Laurium. Argentojarosite, which may contain up to 20% silver (Palache *et al* 1951, 565), has been suggested as another source of silver at Laurium (Wendel *et al* 1999b, 45). Boyle (1968, 44–6) pointed out that wad (various manganese oxide species) and limonite (goethite) often carried significant silver values. Silver occurs as inclusions of various silver-bearing mineral species or as silver adsorbed on the edges of grains. Goethite is ubiquitous at Laurium and at least six manganese oxide minerals including the silver-bearing aurorite are present. Although the close association of the dark argentiferous cerussite and argentiferous galena was a likely observation by the ancient miners (and smelter operators), it is unlikely that other discrete silver-bearing species in both the primary and secondary ores were recognized.

## The recent debate over ore mineralogy

The arguments on the mix of silver-bearing ore minerals mostly hinge on metallurgical reasoning. Conophagos' (1980) discussion of the ancient smelting charge gave four reasons why he believed that argentiferous oxide ore was the main constituent of this charge and argentiferous galena secondary (see also Bachman 1982 for a review of Conophagos).

According to Conophagos (1980, 278 and 302) there is no evidence of prior roasting of the sulphide ore since no remains of roasting furnaces were ever found at Laurium. In his view no more than 20% of the furnace charge carried galena. Presumably the 20% provides enough flux (iron oxide, carbonate and silica) mixed with sulphide ore to keep the galena fragments (with a low melting temperature) from fusing together, reducing airflow and halting the oxidation process. However, as pointed out by Tylecote (1987, 109), separate furnaces for oxidation and reduction were not necessary. The difference between oxidizing (roasting) and reducing (metal-reducing) conditions is the mix of fuel and ore treated in a single furnace at a particular stage. Roasting may also have been done in the open with inter-layered pallets of wood and ore (see Tylecote 1987, 111), but preservation of such structures is unlikely.

Secondly, Conophagos (1980, 284) noted that the sulphur content of the slags is very low, typically less than 1% (see also Bachman, 1982, 247–8, table 1). He interpreted the low sulphur content to mean that low sulphur, oxidized lead ores were the major portion of the furnace charge. Low sulphur slag can equally be the result of a prior roasting of the galena and is not proof that lead sulphide was not the main constituent. Rehren *et al* (1999, 307) proposed to deal with the oxidation of the sulphide in the furnace charge by having the operators add back lead oxide (litharge) produced in an earlier cupellation stage. Conophagos (1980, 292, fig 11-5) plotted slag composition on a $SiO_2$, FeO, and CaO ternary diagram on which most of the analyses fell slightly closer to the CaO-$SiO_2$ edge than the FeO corner. He also enclosed a small area (closer to the FeO corner) on the ternary diagram illustrating the position of the range of slag compositions making up an ideal, low viscosity melt. Additional analyses by Tylecote (1987, 302) and several from Bachman (1982, 248–9, table 1) complement the earlier slag compositions from Conophagos. With the exception of two slags from Bachman showing elevated FeO, all slags plot well outside of the area of ideal low viscosity. Conophagos characterized these slags as highly siliceous and viscous. They were sufficiently viscous to retard the separation of some of the lead which occurs as globular particles entrained in the ancient slag. Melting point temperatures plotted by Conophagos on the ternary diagram suggest normal operating temperatures for the ancient furnaces in the range of 1200–1300°C. Most of the above slags contained 10% or better Pb and 6% or more ZnO. The latter has the effect of raising viscosity while the former, in the form of PbO, is most important in substantially reducing the viscosity of the melt and making the separation of lead and scavenging of silver more complete. Cerussite-bearing oxide ore probably had several functions in the smelting operations including:

- a source of PbO to reduce slag viscosity and to oxidize the galena
- a source of lead necessary to scavenge silver
- a source of silver.

Clearly one of the results of adding litharge to the furnace charge as postulated by Rehren *et al* (1999) is, in addition to the oxidation process, that the viscosity of the melt would be lowered and lead more easily separated. It is also possible that the ancient charge included slag to reclaim silver-lead globules entrained in it. According to Hofman (1918, 322) adding slag to the charge helps the smelting process because it easily remelts and makes the charge less dense. Interestingly, CFML included slag and litharge (the combination made up 20% of their total charge) as part of the charge to the shaft furnaces in which they produced argentiferous lead in the 1930s.

The third reason given by Conophagos (1980, 304) for favouring the oxide ore as the furnace charge was that it was impossible to separate the main sulphide minerals (galena, sphalerite, and pyrite) by gravitational means. He proposed a sluice model for the beneficiation of the mined ore at the flat-washing platforms at Laurium. He further recognized that the sluicing would not be an effective means of separation among these sulphides. Kepper (2004) argued that the flat-washing platforms were not designed for sluicing. The stand tank at the rear of the platform was not a water supply tank to feed sluices, rather it served as a large settling basin. He demonstrated, using a hindered settling model, that it would not be difficult to separate the sulphides. With regard to these mixed sulphide ores, what is far more important is the difficulty of liberating them during the breaking, crushing and grinding operations (see below).

Conophagos' fourth reason for rejecting galena as the major component of the furnace charge was based on analyses of waste rock. He (1980, 302) cited an 1870 analysis showing 0.9% galena and 17.7% Pb and further noted that in general waste rock contains less than 10% galena. He inferred from this that little galena in the ore bodies escaped oxidation and therefore cerussite-bearing oxide ore was the dominant material mined and sent to the smelting furnace. Some concern was expressed by him over the possibility that post-mining weathering of the finely crystalline galena in the waste rock might bias the sample toward oxide ore. Photos-Jones and Jones (1994, 340) reported the presence of cerussite, but no galena, in remnants of tailings at one of the flat-washing platforms. They suggested that weathering fine grains of galena might account for its absence. More recently, Rehren *et al* (2002, 32) described sections containing millimetre-sized grains of galena enclosed in a finely crystalline rind of cerussite collected from some well-preserved tailings at a washing structure near Thorikos. They concluded that the paucity of galena in these tailings results from post-mining weathering.

## Gangue mineralogy: 20th-century contributions

Much of what is called 'siderite' in the 19th century reports appears to be any one of several iron-bearing (ferroan) carbonates including ferroan calcite, ferroan dolomite, ankerite (Ca Mg Fe Mn)$CO_3$, and true siderite (Katerinopoulos and Zissimopoulos 1994, 36; Wendel *et al* 1999a). This primary carbonate gangue was particularly susceptible to alteration to iron oxide. There is an intimate mixture of iron-bearing carbonate and iron oxide gangue in many areas at both the First Contact (personal observation) and the Third Contact around Camaresa (C Slomos, personal communication). Putzer's (1948) detailed analysis of the geology and mineralogy of the ores at Laurium corroborates these 19th-century studies. The important gangue minerals (Putzer 1948, 25) are calcite, fluorite and siderite (in places ankerite) associated with clay, mica and earthy iron oxide. Fluorite is an indicator of silver-rich galena and appears to be common throughout the Laurium district, typically occurring with calcite or quartz. He noted that silver is unevenly distributed with the richest galena in the Souresa, Agrileza and Camaresa areas. Wendel *et al* (1999a) report fluorite as a gangue mineral from all but a few of the mines from Plaka in the north to Sounion in the south.

Tailings mineralogy described by Photos-Jones and Jones (1994, 340) consisted of fluorite (dominant component), calcite, quartz, cerussite, barium muscovite, and kaolinite. Rehren *et al* (2002, 33) listed siderite, goethite, calcite, fluorite, sphalerite, cerussite, and galena (including galena cores with cerussite rims) in tailings recovered from several sites. Tailings results corroborate the geological descriptions of the gangue minerals. The slag chemistry and phase mineralogy (Bachmann 1982, 248) seems to support calcite (and probably some combination of iron-bearing carbonate minerals) as a major component of the furnace charge. The abundance of calcium carbonate along with quartz and/or clay is perhaps reflected in hedenbergite (Ca Fe silicate) rather than fayalite (Fe silicate) being the main silicate phase. Mg from dolomite and Al from the clays (in the charge and from clay furnace linings) would explain the spinel (Mg $Al_2O_4$) phase. If clay and carbonate collected from the tailings at the washing platforms was used as a binder (Conophagos 1980, 302; Kepper 2004) to make briquettes of the ore prior to smelting, than the binder contributes to the slag chemistry. The common occurrence of fluorite in the slag attests to the fact that fluorite was a common guide to galena and further supports the importance of galena to these ancient ore charges.

The physical properties of gangue minerals are important to the successful liberation of ore. Calcite, dolomite, ankerite, fluorite, and sphalerite (as gangue for galena) typically are coarsely crystalline here and possess excellent cleavage. Breakage with hammers followed by grinding and crushing should have resulted in a pre-washing concentrate suitable for further beneficiation at the washing workshops.

## Discussion

19th-century French operations at Laurium, in the same area and at the same levels as the 5th–1st century BC miners, explored ancient galleries, studied the waste rock, and excavated new galleries for the purpose of mining both zinc and lead-silver ores. Their work is a useful addition to more recent studies of mineralogy. Although their initial liberation of ore by breakage with hammers probably differed little from the ancient practice, mechanical crushing and the use of circular buddles allowed them to process a different ore. Shaft furnaces with mechanical bellows and high refractory lining probably allowed them to profitably smelt more complex sulphide mixtures along with lower grade oxide ores. Nonetheless, their ore charge included a significant component of lower grade silver-lead bearing oxide ore in addition to the sulphide (Table 1). It is likely that cerussite was the major source of the lead and silver in this oxide ore, although other minerals (*eg*, argentojarosite) may have contributed.

The ore body geology and mineralogy for the Third Contact is summarized below:

- The Third Contact *manto* is a zoned ore body. Oxidized lead ore occurs at the top of the *manto* and oxidized zinc ore in the basal part and in the underlying stockworks.
- The location of the ancient galleries clearly shows that the ancient Greeks followed the galena. Silver-bearing galena associated with the oxidized lead (chiefly cerussite) ore was mined from the upper zone of the *mantos* and from veins in the stockworks in the underlying oxidized zinc zone. Beds and veins of galena in the basal part of the overlying Lower Schist were also important. The preservation of sulphides above the oxidized *manto* resulted from the impervious character of the Lower Schist to oxidizing waters.
- The small amount of lead retained in the ancient waste rock coupled with the numerous galleries excavated by ancient miners in the upper, oxidized *manto* ore supports the contention that oxidized lead ore was part of their furnace charge.
- More oxidized ores, richer in cerussite, probably occurred in the up-dip, higher elevations of the *manto*. These ores were more accessible to the ancient miners and to CFML, early in their operations at Laurium.
- Sulphides were much more abundant along the Third Contact *manto* than at higher stratigraphic levels.
- The major sulphides include various mixtures of galena, sphalerite, and pyrite.
- Numerous other sulphides and sulphosalts, some silver-bearing, also occurred within the sulphide ore. However, the difficulty in breaking and sorting such complex sulphide mixtures generally precluded their addition to the ancient furnace charge. Such complex sulphide ores were left as pillars in the ancient galleries.
- Sulphide ore carried higher silver values than the oxide ore.
- Primary gangue mineralogy changed along the strike of the *manto* from calcite and various iron-bearing carbonate minerals and fluorite in the Camaresa-Mercati area, to more fluorite and quartz to the south.
- Iron oxide, particularly immediately below the Lower Schist roof, along with associated secondary silver-bearing oxide minerals such as cerussite, argentojarosite etc. was common throughout the Third Contact *manto*. Iron and manganese oxides, if they were incorporated as part of the smelting flux, may have made further contribution to the silver production. However, the low FeO content of the slags may indicate that much of the iron came from associated iron-bearing carbonates rather than iron oxides such as goethite.
- Grey and black cerussite contained the silver-bearing inclusions so only part of the total cerussite in the oxide zone was a source of silver.

## Conclusions

19th-century exploration of the 5th–1st-century BC mined area near Laurium by CFML combined with more recent studies point to galena as the major ore mineral smelted in the ancient furnaces. The reported abundance of cerussite, most likely in the more oxidized higher levels of the Third Contact accessible to the ancient miners, suggests it too was a significant component of the furnace charge. Although only the darker, inclusion-rich cerussite was a source of silver, the mineral cerussite (a component of the silver-bearing ferruginous-oxide lead ore) had several functions in the smelting operations. These include: a source of PbO to reduce slag viscosity and to oxidize the sulphide ore, a source of silver and a contributor of lead necessary to scavenge silver. Oxidized ores, such as those carrying cerussite, probably reduced the roasting time and fuel consumption in the ancient furnaces. Cerussite may have played a role similar to that for litharge as proposed by Rehren *et al* (1999); possibly as availability of cerussite declined litharge was substituted. There is precedent for the use of cerussite as an ore of both lead and silver in ancient times. Cerussite and galena ores were mined from several stratigraphic levels in a sequence of dolomitic marbles on the island of Thasos in the northern Aegean prior to and contemporaneously with Laurium (Higgins and Higgins 1996, 120; Pernicka and Wagner 1982, 421 and 423; Vavelidis and Amstutz 1983, 362 and 364).

Closure of the mines after the end of the 1st century BC may have resulted from much of the pure galena ore being mined out leaving lower grade oxide ore and the more complex sulphide ore, not amenable to the ancient beneficiation processes. The decline of Athens as an international power and the scarcity of wood for smelting probably played a role as well. Athens no longer controlled the sea, and shipments of wood from external sources could no longer be counted on to supply the smelters. Economic power had already shifted to Macedonia, rich in gold and silver resources (Seltman 1965, 200 and 206). Macedonia had both abundant water and wood, making the cost of mining considerably less than at Laurium. Combine resources with control of those resources and Macedonia had the clear advantage over the Athenians.

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