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IRON WORKING IN AEGEAN THRACE DURING ANTIQUITY: NEW EVIDENCE FOR SMELTING ACTIVITY OF THE 4TH CENTURY BC AT THE CITY ON THE MOLYVOTI PENINSULA

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ABSTRACT

Iron working in Aegean Thrace during Classical and Roman times was based on different choices of raw materials from a variety of available ores, possibly determined by cultural criteria. The precursors to selective ore procurement can be seen in earlier evidence from Thasos in the form of a few iron smelting waste remains found at the cemeteries of Kastri dating to the Early Iron Age. More substantial evidence for smelting and smithing activities has been noted in the Archaic city of Thasos, but their interdisciplinary investigation is pending. So far, the only comprehensive study on smelting and smithing slag and iron objects that has provided crucial information on the differential techniques employed in iron production of the 5th century BC across this region has focused on finds from Abdera and Zone. More recently, iron slag has been collected from the northern enclosure of Abdera in the framework of an ongoing survey project (APAX) as well as during excavation at the Thasian colony of Pistyros, yet study is ongoing and only information on spatial distributions is currently available. This paper aims to briefly review the existing research data and to present new results from a recent instrumental analysis on iron working slag recovered in the framework of the Molyvoti, Thrace, Archaeological Project (MTAP). The finds derive from contexts of the 4th century BC, excavated between 2013 and 2019, and their analysis with optical microscopy and SEM/EDS offers valuable data on the smelting and smithing practices prevalent on site that display similarities with some of the other colonies of Aegean Thrace. Based on the current results limonite and/or hematite were the most commonly used ores and a Ti-rich iron source of lesser significance as suggested by the chemical composition of a single sample. The bloomery process could be characterized as efficient with minor losses of metal into the slag. The use of fluxes to lower the melting point of iron during smelting has been also confirmed. Such findings are important as they complement previous data on the technology of smelting local ores to supply the iron industries in Aegean Thrace.

KEYWORDS: iron, bloomery, smelting, smithing, slag, colonies, Thrace, Molyvoti, wüstite, fayalite, glass(y)

1. INTRODUCTION

The study of iron working in the Greek lands from the Late Bronze Age onwards, from small trinket type items to functional objects with an efficient cutting edge, is still nebulously outlined across Greece. Early iron artefacts co-existing with bronze objects start to appear in burial contexts after around 1200 BC (Morris 1989). Bronze objects still remain predominant in the investigated contexts, suggesting an enduring metallurgical tradition with continuing access to the raw materials for this industry, i.e. copper and tin (Kayafa 2006; Ben-Yosef et al. 2010). Iron becomes more common in burial contexts from the 12th to the 10th century BC (Snodgrass 1980; Morris 1989). These are prestige items in the form of rings, small plaques, pendants from the mainland, nails, rings, meteorite fragments from Crete, tanged knives and iron fragments from the Cyclades (Muhly 1980; Snodgrass 1980; Waldbaum 1980; Photos 1987).

A compilation of early iron finds from the Late Bronze Age to the 10th century BC was carried out by Waldbaum (1978) to include Athens, Euboea, the Peloponnese, Cyclades and Crete, but is now largely out-of-date. This corpus is vastly enriched now through preliminary excavation reports, but as of yet there is no concise compilation of the extant evidence. In her recent thesis, Palermo (2018) produced an updated review of published early iron artefact from the Aegean, Anatolia and Cyprus. Concerning early iron production contexts, these are scarcer since there are only two excavated examples of blacksmiths' workshops on the Aegean coast of Asia Minor. The earliest was found at Phokaia and dates to the 11th century BC (Yalçin and Özyiğit 2013) and a later one was investigated at Klazomenai and dates to the Archaic period (Cevizoğlu and Yalçin 2012). More recent interdisciplinary research on early iron working evidence has shown that this region displays elements of innovation in adopting and transforming metalworking technologies already from the LBA and EIA (Mokrišová and Verčík 2022).

Interdisciplinary studies on the technology of iron-working in Aegean Thrace have shown that distinctive technological traditions developed from Classical to Roman times based on different choices of raw materials from a variety of available ores. Such choices were partly determined by the local geology but more importantly by cultural criteria, which defined resource perception, since these are embedded in human action and affect acquisition strategies. Previous studies have mainly focused on slag analysis and some iron artefacts from several sites in the region (Photos 1987; Kostoglou 2008). This paper attempts to briefly review the existing research data and to present new results from a recent instrumental analysis of iron working slag recovered in the framework of the Molyvoti, Thrace, Archaeological Project (MTAP), which explores a site often identified as ancient Stryme.

2. EARLY IRON WORKING IN AEGEAN THRACE

The early steps of iron working in the North Aegean can be detected on the island of Thasos (Fig. 1) in the form of a few metallurgical residues excavated at the cemeteries of Kastri and dated tentatively to the Early Iron Age (Koukouli-Chrysanthaki 1992; Photos 1987; 1992). The settlement at Kastri emerges as the dominant Thracian site on the island during the Late Bronze and Early Iron Age (1200-700 BC), with access to trade networks, as can be manifested by imports including precious items in amber, blue glass and metals that were deposited in burial contexts. Four extended cemeteries surrounding the settlement were investigated in the 1970s and 1980s (Koukouli-Chrysanthaki 1992). Some pieces of metallurgical slag found in several tombs from two of these cemeteries confirmed that local copper and iron working were practiced in tandem by members of this upland community. It is unlikely that these slags were deposited with the deceased as grave goods, but their existence in layers of the Early Iron Age, between 1050 and 800 BC (phase IIB, Koukouli-Chrysanthaki 1992, 662-663), is undoubted proof for early metallurgical operations in the vicinity.

Figure 1. Map of Aegean Thrace showing the sites mentioned in the text (yellow: Early Iron Age, red: Classical/Hellenistic periods) (image credits: Google Earth)

Ten pieces of slag were sampled for analysis out of which seven were characterized as copper slag and three as iron slag (Photos1987; 1992). Two of the iron slag were found at the cemetery of Tsiganadika (tomb T21: sample no. 399 and tomb T23: sample number 383) and one at the cemetery of Larnaki (Tomb Λ2Γ) dated to phases IIB2-IIB3 of the Early Iron Age between 1050 and 800 BC (Koukouli-Chrysanthaki 1992, 662-663; 680-681). Based on the analytical results, the iron slags contain all the commonly occurring phases such as wüstite, fayalite and a glassy matrix typical for iron smithing residues. The sample from Larnaki, apart from the three major phases, also contains metallic iron prills free of slag inclusions (Photos 1992, 798). Arsenic has been detected in the matrix suggesting that the ore source may have been at Kokoti, which is the only known location where arsenic in low contents is present in the iron mineralization (Photos 1992, 798). One slag piece deriving from Tsiganadika contains relatively higher titanium contents in the wüstite and the matrix compared to that from Larnaki but no other mineralogical phases are evident to support an alternative source of the iron ore (Photos 1992, 798). It should be mentioned that it was difficult to draw conclusions on the basis of three samples only, but it has been established that the ore used was of the hematite/limonite variety (Photos 1987). Although it was not easy to control what metal would be produced each time from a polymetallic charge in the furnace, the early Thasian metallurgists reached a point to produce iron, albeit in small quantities, a fact that is also corroborated by the 'trinket' quantities of early iron finds, mostly knives.

Although being geographically far from the core regions of emergence and early adoption of iron technology, i.e. Anatolia, the Levant and Cyprus, Thasos appears well integrated in far-flung trade networks during the Early Iron Age (Ilieva 2019). Considering the typological affinities of the bronze and bimetallic knives found at the cemeteries of Kastri as well as the possible provenance of the copper from Cyprus (Stos-Gale and Gale 1992), it has been suggested that the technology of iron production was introduced along the same networks that brought these metal objects to Thasos. If the hypothesis that Phoenician and Cypriot traders who were active at Lefkandi and via the Euboean gulf reached the Thermaic gulf and Chalkidiki holds true (Sherratt 2019; Ilieva 2019), then this network could have potentially integrated Thasos. The likelihood that in the late 12th or early 11th c. BC Cypriot ships were acquainted with the Northern Aegean and that their sea-routes were later followed by the Phoenicians sounds very attractive. Yet the available archaeological evidence that could support it is still limited to a few bronze and bimetallic knives suggesting a possible early link with Cyprus (Ilieva 2019, 73; Stos-Gale and Gale 1992). It should be noted though that iron objects were in fact produced in Mycenaean centres already during the Late Bronze Age, a tradition that continued well up to the end of the palatial period in the Peloponnese. As far as the knives from Thasos are concerned, these seem to follow a locallyrooted Aegean tradition of object types. Eventually whether these links with the Mycenaean centres also brought the very concept of iron technology that was adopted by the Thracian population on Thasos is an issue open to question.

Over the course of the 8th century the population orientation moved from the transitional zones of the southwestern side of the island to the northern harbor of modern day Limenas, where Parian colonists established the city of Thasos in the first third of the 7th century BC (Muller 2010). The Parian colony was founded at the site of a pre-existing Thracian settlement. Tangible evidence for iron-working activities has been noted in the city of Thasos, close to the sanctuary of Artemision and further north at Kokkinos plot during excavations of the French School at Athens (Muller 2000). Slag, charcoal and hammer-scale from the latter location became the focus of a contextual study, which clarified their accurate dating to the first quarter of the 7th century BC (Kohl et al. 2004). Primary or secondary deposits containing slag from iron production have been also found near the Archaic agora, northwest of the Gate of Silenus and from late Archaic levels near the Gate of Herakles and Dionysos, but their interdisciplinary investigation is still pending (Fig. 2). Preliminary analysis of three such slag pieces revealed three major phases, namely wüstite, fayalite with considerable calcium contents and a silicate matrix (Photos 1987). The high total iron content of these slags together with their silica contents and their mineralogical phases suggest that they are smithing slags.

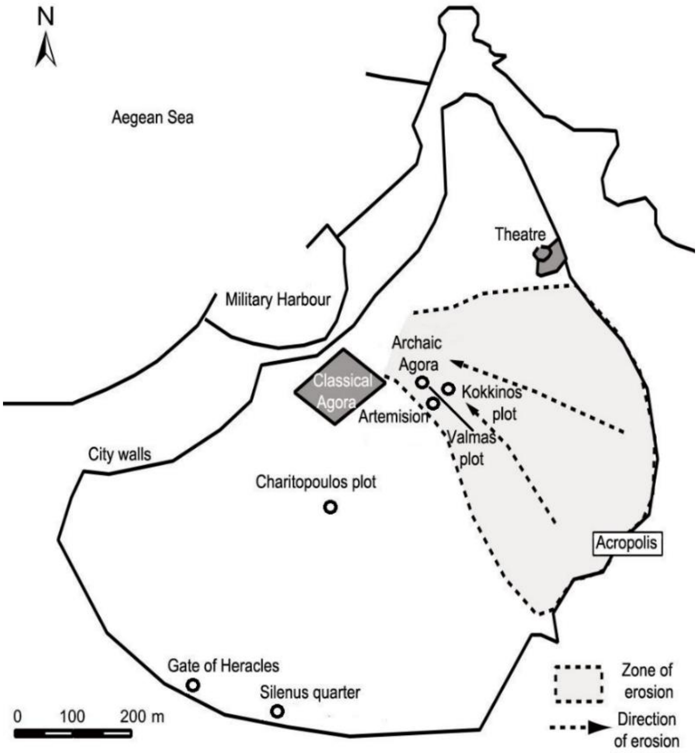

Figure 2. Plan of the city of Thasos with spots of metallurgical activities (circles) and zone of erosion of the acropolis hill (adapted from Lespez 2007).

So far, the single comprehensive study on smelting and smithing slag and iron objects that provided crucial information on the differential techniques employed in iron production across this region concerns the late 6th and 5th century BC and was conducted by Maria Kostoglou on finds from Abdera and Zone (Kostoglou 2008). Abdera, a colony of Klazomenians and Teians flourished from Archaic to Roman times as an important cultural and economic centre of Aegean Thrace (Fig. 1). So far, a few iron objects of the Classical period (5th century) have been analysed while the smelting and smithing slag studied all date to the Roman period (Kostoglou 2013, 318). The production of wrought iron with surface carburization was common with the possible use of chalcopyrite/pyrite ores from Kimmeria, as suggested by the high copper composition of an iron object. Access to iron ores, exchange of semi-finished blooms, or ingots were probably negotiated with the indigenous Thracian tribes that had control of the mineral rich zone of the Rhodope extending some 25 km north of Abdera.

More recently iron slag has been collected from the northern enclosure of Abdera in the framework of the ongoing Archaeological Program of Abdera and Xanthi carried out as a collaboration between the National and Kapodistrian University of Athens and the Ephorate of Antiquities of Xanthi (Kallintzi et al. 2020). Some concentrations of iron slag close to the northern stretch of the northern wall of the Archaic city might reflect the possible presence of workshops there, but before the ongoing analysis of sampled material is completed, it is premature to arrive at any safe conclusions. Likewise, some concentrations of smithing residues have been noted during excavation at the Thasian colony of Pistyros situated west of Abdera by the foothills of the Lekani mountain range. This study is also ongoing and only preliminary information on spatial distributions is currently available (Nerantzis et al. 2022; Nerantzis et al. in press).

Investigation on 6th-5th century BC iron metallurgy from Zone, a colony of Samothrace, confirmed that smelting of Mn-rich iron ores from the nearby site of Komaros was common (Kostoglou 2003, 65). Interestingly, smelting of Cu-rich pyrites, possibly from Kirke, has also been noted albeit infrequently. The analysed smelting slags contain three main phases: fayalite, wüstite and a glassy matrix. Smithing slags contain mainly iron oxides (wüstite) and rare iron inclusions. The resulting iron was ferritic and low-carbon steel used for various classes of objects. Evidence for welding and surface carburization has been noted, with an example of high-carbon steel (Kostoglou 2010, 183). Six spits were found in the temple of Apollo, possibly deposited as votive offerings. Examination revealed steel microstructures. They were manufactured by welding and then twisting low carbon steel to high carbon steel (Kostoglou 2008, 37), which is evidence that the smiths at Zone applied sophisticated forging techniques.

3. EVIDENCE FOR IRON PRODUCTION AT MOLYVOTI PENINSULA

The Molyvoti, Thrace, Archaeological Project is a cooperation between the Ephorate of Antiquities of Rhodope and the American School of Classical Studies at Athens (ASCSA), represented by Princeton University. It involves the study of an Archaic-Classical trading port (emporion) and polis, often identified as ancient Stryme, through excavation and pedestrian surface survey (Arrington et al. 2016). It also seeks to explore the formation and evolution of the city in its changing economic, political, and cultural contexts, taking into consideration regional dynamics and constraints as well as individual agency.

Figure 3. A. crossroads, B. House of Hermes, C. House of the Gorgon (excavation of 2015) (image credits: Greek Ministry of Culture and Sports-Ephorate of Antiquities of Rhodope)

Excavation between 2013 and 2015 (Fig. 3) revealed a crossroads between two insulas of houses as well as a complete Classical house, with multiple 4th cen. BC and 4th-6th cen. AD architectural phases, named the House of the Gorgon (Arrington et al. 2016). A second house was revealed in the first campaign and fully excavated in 2019, known as the House of Hermes, dating to the 4th cen. BC (Fig. 4). Human activity on site appears to have started in the 6th cen. BC while by the early 4th cen. BC (*ca*. 375 BC) a new town plan is evidenced following the Hippodamian system. The new grid plan of insulae consists of eight structures, four on the long side and by two, measuring 17.6 by 17.6 m each, while roads are ca. 6m. wide. The city was at least 63 ha. in size. The finds testify to some destruction in the middle of the century, possibly related to Philip II's conquest, which however did not lead to complete abandonment. Habitation at the House of the Gorgon is attested around 325 BC, when there are some changes in house planning (Arrington et al. 2016). What is noteworthy is that there is no final, second destruction horizon, but instead a strong indication that the city was slowly abandoned at the beginning of the 3rd cen. BC, during a time of insecurity and instability for the region of Aegean Thrace, when economic networks were disrupted. At the same time, life went on in the *chora*, with some limited 3rd and 2nd-cen. BC activity.

Figure 4. House of Hermes (B) and House of the Gorgon (C) (excavation of 2019)
(image credits: Greek Ministry of Culture and Sports-Ephorate of Antiquities of Rhodope)

Figure 5. House of the Gorgon (spaces with Greek letters)
(image credits: Greek Ministry of Culture and Sports-Ephorate of Antiquities of Rhodope)

During excavation, 110 pieces of slag were collected from various contexts (Fig. 6), with 18 pieces coming from the crossroads (Fig. 7) and 11 from space ι in the House of the Gorgon (Figs. 5 and 8); the space is located to the side of the courtyard, space β, and may have served as a prostas in the second 4th-cen. BC phase of the house. Smaller concentrations of slag between 1 and 8 pieces derive from other contexts of the 4th cen. BC indicated by their numbering on the excavation grid (Fig. 6).

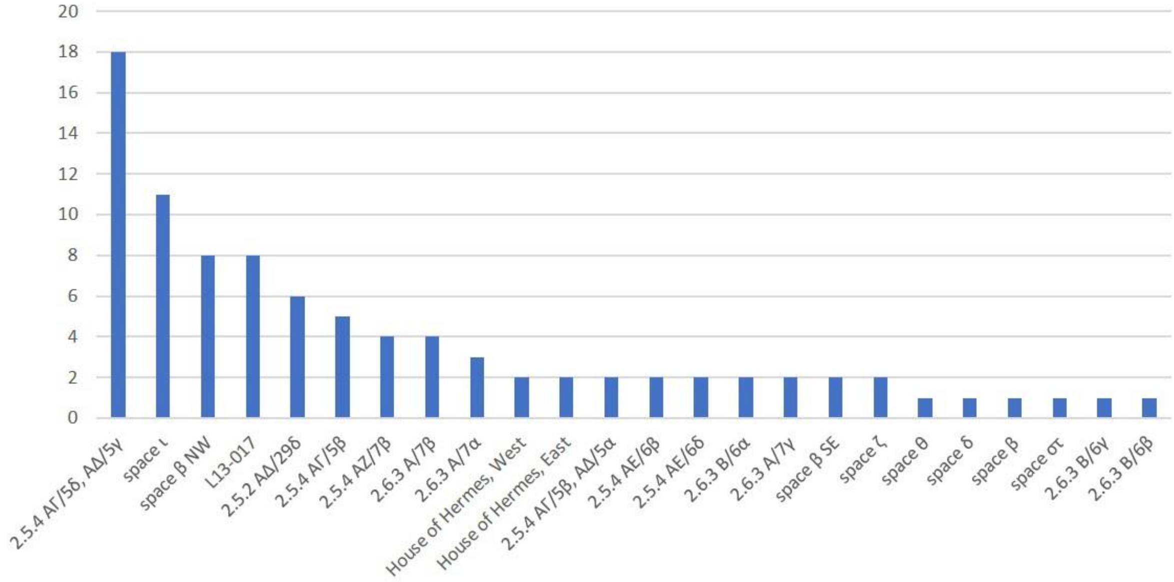

Figure 6. Slag distribution across the excavated contexts

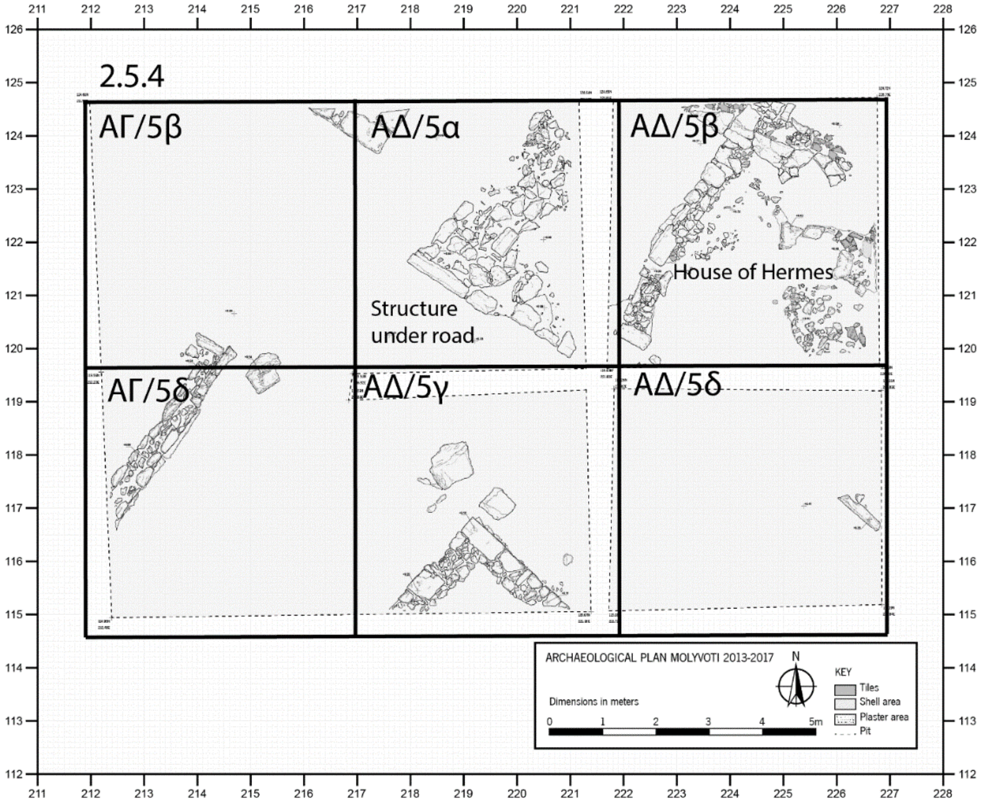

Figure 7. Plan of the crossroads
(image credits: Greek Ministry of Culture and Sports-Ephorate of Antiquities of Rhodope)

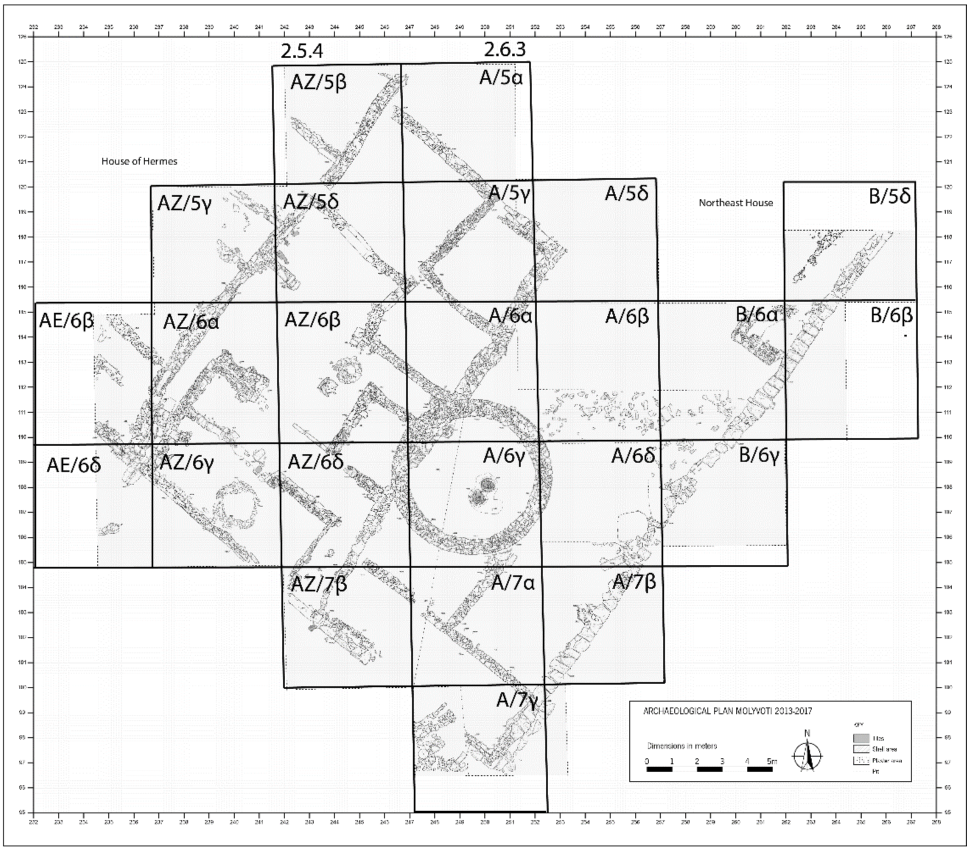

Figure 8. Plan of the House of the Gorgon
(image credits: Greek Ministry of Culture and Sports-Ephorate of Antiquities of Rhodope)

For an investigation of the metallurgical activity on site, 8 slag samples were taken for analysis at N.C.S.R. 'Demokritos' using optical microscopy and SEM/EDS. Most of the contexts whence slags were sampled from the House of the Gorgon consist of fill rather than in situ deposits. Geographically, the samples selected for analysis represent the Crossroads, the House of the Gorgon, the House of Hermes, and the exterior of the House of the Gorgon. Chronologically, samples IL 408, IL 383, and IL 314 represent the pre-Hippodamian phase, while IL 378 belongs to a post-4th cen. BC destruction phase. These are fills laid down after Philip II's destructions. The remaining samples (IL 208, IL 459, IL 465, IL 526) derive from post-classical contexts from different topsoil loci (Table 1).

Table 1. Analysed samples' contexts description

Sample No.	Locus	Description
IL 408, IL 383	L15-033	House of the Gorgon, space ι Fill for floor of ca. 375 BC
IL 314	Crossroads	Fill for road pre-375 BC
IL 378	L15-020	Outside of the House of the Gorgon, fill against walls, ca. 325 BC
IL 208	L14-061	House of Hermes, Eastern Portion - Late Roman fill
IL 459, IL 465, IL 526	Various loci	Topsoil

4. INSTRUMENTAL ANALYSIS OF THE FINDS

Optical microscopy and SEM/EDS analysis were performed at N.C.S.R. 'Demokritos'. The instrument used is a FEISEM (Quanta Inspec model) with a super ultra-thin window EDS detector. The analytical data were corrected from elements generated by the ZAF software. The bulk chemical composition of each sample and several distinct microstructural phases are reported in Table 2 (at the end). For the majority of samples, FeO contents range between 50 and 80% and SiO_2 range between 10-14%, which are typical for bloomery slag. In two cases, the lowest FeO contents (47.9% and 50.2%) coincide with higher SiO_2 (27-32%) and Al_2O_3 (5-7%) contents. Overall, phosphorus is present in the glassy phase in most samples between

1 and 4% while MnO is detected mainly in the fayalitic phase at low contents about 1.5%. The low lime (CaO) contents in all samples, around 1.5%, suggests that fluxes might have been used occasionally during smelting but not at high proportions. As the oxides of manganese and phosphorous change proportionately, this might indicate that the ore for the majority of samples consisted of a hematite/limonite variety.

The optical photomicrographs show a typical microstructure dominated by fayalite (Fe_2SiO_4) and wüstite (FeO) and lower amounts of a glassy phase. Massive laths and skeletal crystals of fayalite coexist, while the wüstite, which is embedded and intergrown within the fayalites, displays a dendritic morphology (Fig. 9a and 9b). Occasional iron prills appear as bright spots in the microstructure as a result of wüstite reduction to metallic iron (Fig. 10a and 10b).

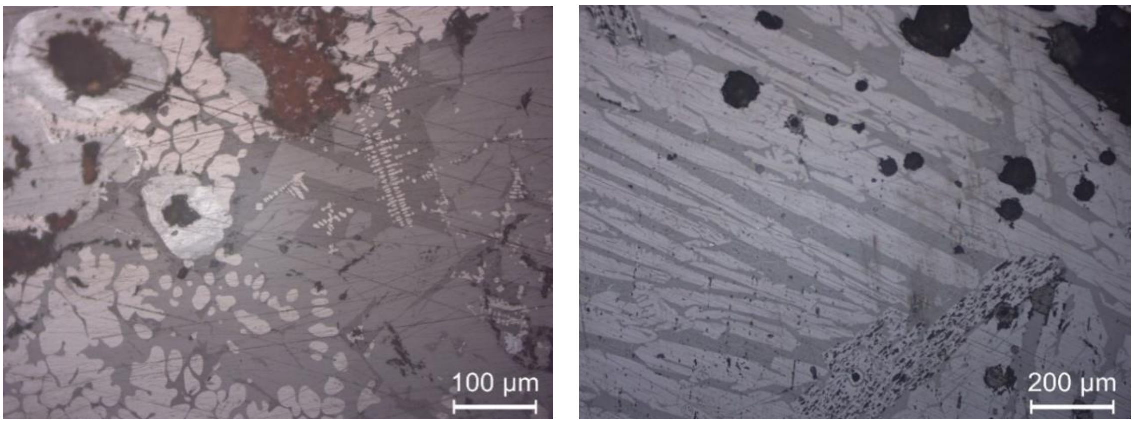

Figure 9. Optical photomicrographs (a) Sample 4 (IL 408) massive fayalite (mid grey), wüstite dendrites/two sizes (light grey), glassy phase (dark grey), (b) Sample 6 (IL 459) skeletal fayalite (light grey), glassy phase (dark grey).

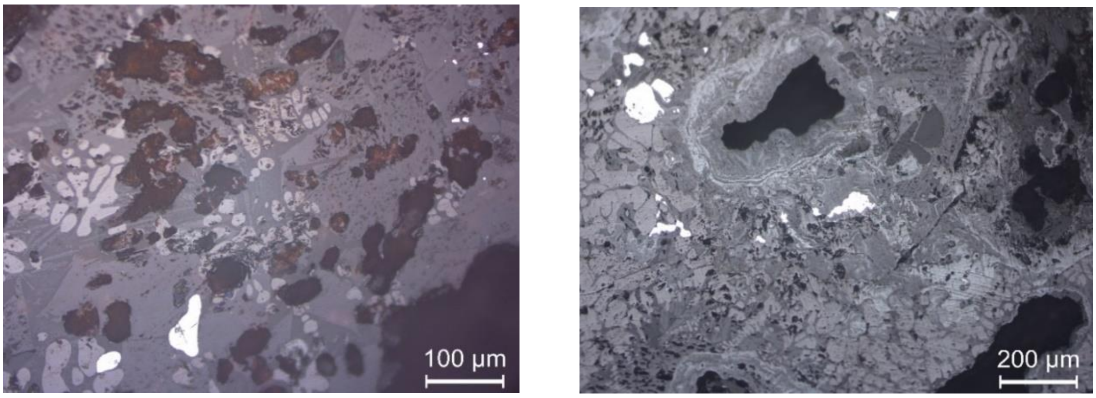

Figure 10. Optical photomicrographs (a) Sample 3 (IL 378) fayalite (mid grey), wüstite dendrites (light grey), glassy phase (dark grey), iron prills (bright white), (b) Sample 2 (IL 314) fayalite (mid grey), wüstite dendrites (light grey), glassy phase (dark grey), iron prills (bright white).

Examination under the SEM/EDS allowed for a more detailed characterisation of the mineral and metallic phases initially observed under the optical microscope. Sample 1 (IL 208) shows an inhomogeneous microstructure with typical phases of a bloomery slag, mainly wüstite dendrites, elongated laths of fayalite and interstitial glass. Regions consisting of angular inclusions of unreacted ore were trapped in the slag, possibly due to inefficient smelting conditions. An intermediate zone was noted separating the region of typical slag microstructure with that of the unreacted ore minerals. The composition of the intermediate zone shows similarities to the unreacted ore with some traces of Cu below 1% but higher Fe contents. Such features could indicate a smelting rather than a smithing slag.

Sample 2 (IL 314) reveals a similar microstructure with more extensive areas covered by skeletal laths of fayalite, wüstite dendrites and interstitial glass and some islands of unmelted ore. Low contents of phosphorus in the glassy phase and Mn in the bulk composition were detected. Notably iron prills are present concentrated in two areas, with the larger ones reaching 50-70 μm in size (Fig. 11a). A few crystals of barium sulphide were also noted owing to the presence of such minerals in association to the iron ores that were used as raw materials (Fig. 11b).

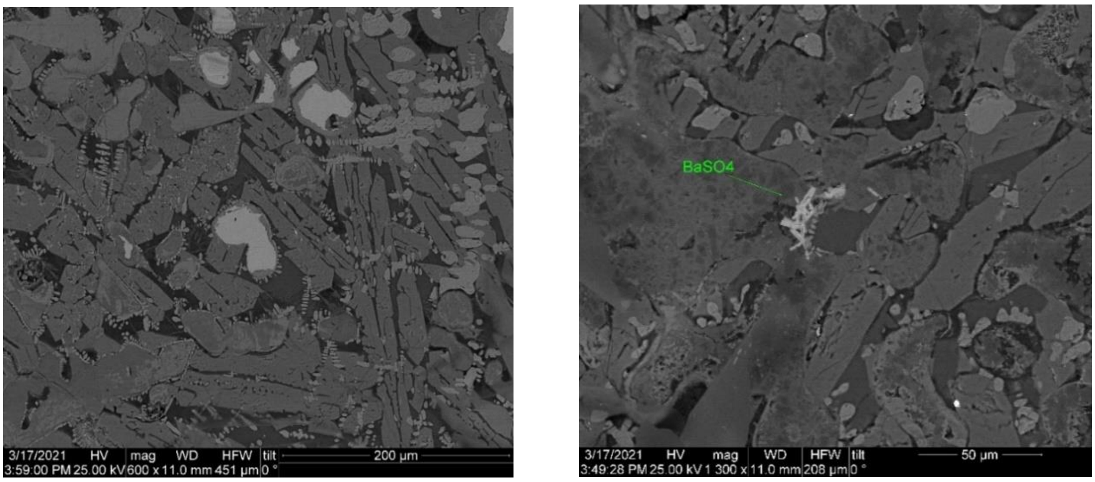

Figure 11. SEM photomicrograph, Sample 2 (IL 314) (a) Skeletal laths of fayalite (mid grey), wüstite dendrites (light grey), glassy phase (dark grey), iron prills (white), (b) fayalite (mid grey), wüstite (light grey), glassy phase (dark grey), barium sulphide crystals (white).

Sample 3 (IL 378) displays areas of typical slag microstructure dominated by well-developed dendrites of wüstite and three sizes of fayalite, from massive laths of about 150µm width and medium sized of 80µm width, to smaller ones of approximately 30µm width (Fig. 12a). A large area of vitrified ceramic material was noted, most probably part of the hearth's lining material (Fig. 12b). Such inhomogeneity is also reflected in the sample's chemical composition. Overall, the average FeO contents, around 50%, are somewhat lower than the other analysed samples. Yet in some areas conditions were reducing enough and temperatures sufficient for ore reduction to take place as revealed by the presence of iron prills.

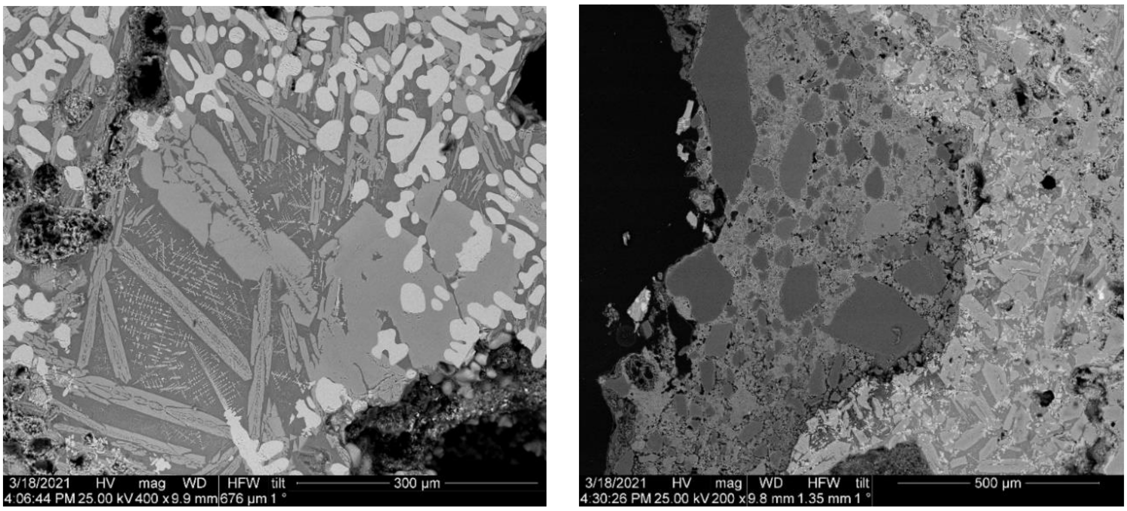

Figure 12. SEM photomicrograph, Sample 3 (IL 378) (a) Fayalite laths in three sizes (mid grey), wüstite dendrites (light grey), glassy phase (dark grey). (b) Ceramic material, part of lining (left side), slag (right side).

Sample 4 (IL 383) is a typical bloomery slag, most probably related to smelting. Its microstructure is dominated by wüstite dendrites, coexisting with fayalite laths and an interstitial glassy phase (Fig. 13a). Areas with unreacted ore pieces were also noted. Slightly increased phosphorus contents were detected in comparison to the other analysed samples. An inclusion of Pb-Ba composition was noted growing out at the edges of a pore (Fig. 13b) and some minute Pb prills at the boundaries of wüstite dendrites. The abundance of wüstite dominating the microstructure are indicative of the reducing conditions prevalent during the smelting process. Samples 7 (IL 465) and 8 (IL 526) show similar microstructural features and an overtly comparable chemical composition to that of sample 4 (IL 383).

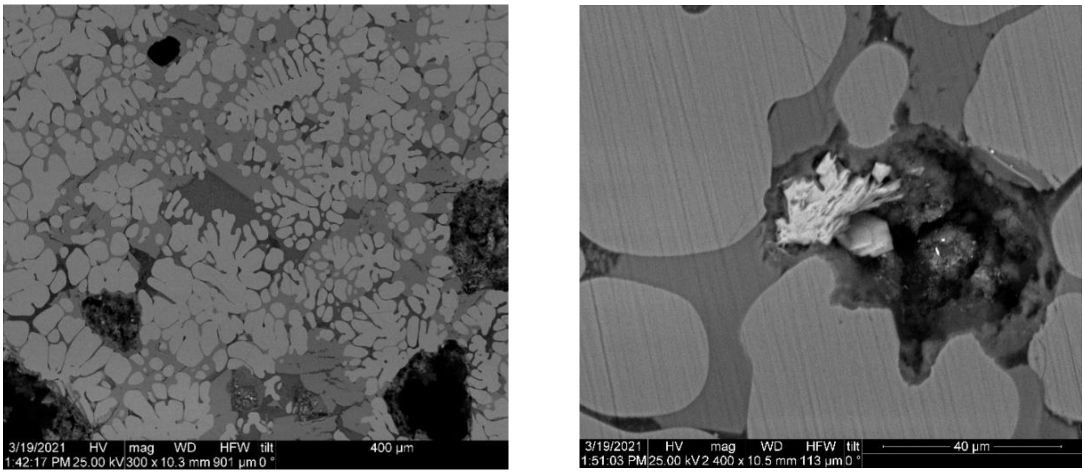

Figure 13. SEM photomicrograph, Sample 4 (IL 383) (a) fayalite (mid grey), wüstite (light grey), glassy matrix (dark grey), (b) fayalite (mid grey), wüstite (light grey), crystals of Pb-Ba composition (white).

Sample 5 (IL 408) displays some differences in both chemical composition and microstructure since apart from the typical wüstite and fayalite phases, magnetite and rhomboid spinel crystals are present (Fig. 14a). Spot analysis has determined that the latter contain TiO_2 around 2% in average. In one case a spinel measuring about 50μm across is composed of 88% TiO_2 and 5.3% FeO (Fig. 14b). Such microstructural features along with the bulk chemical composition featuring 44-50% SiO_2, 20-25% Al_2O_3 and 13-17% FeO hint to a titanium rich source for this residue. It should be noted in this context that titanium-rich iron sands have been exploited as a source of iron on southern Thasos and the northern Serres region around Vrontou, but it is generally accepted that such a mineral resource was used in iron industries of the late Byzantine and Ottoman periods (Photos et al. 1986; Nerantzis 2016, 630).

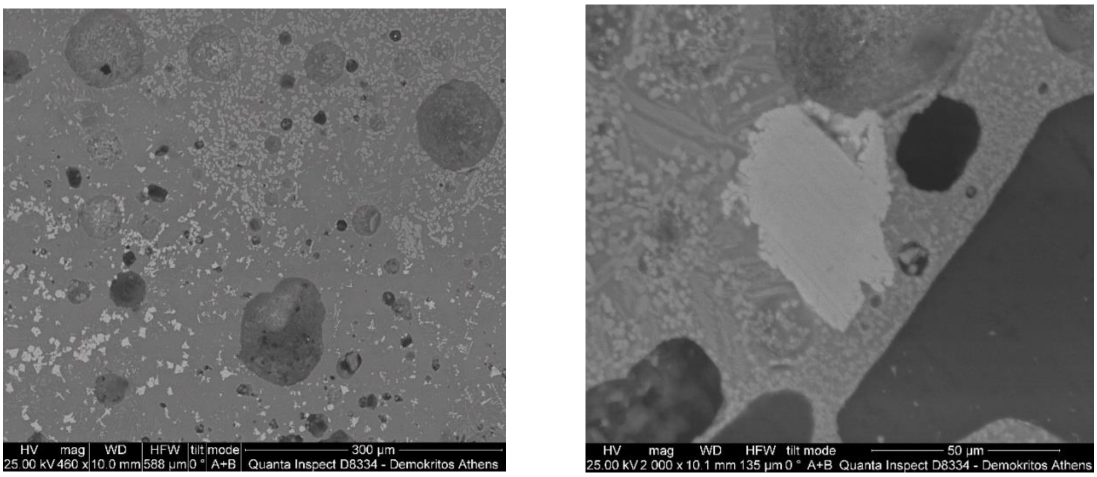

Figure 14. SEM photomicrograph, Sample 5 (IL 408) (a) magnetite crystals (mid grey - upper right part), TiO_2-rich spinel crystals (light grey - lower left part), glassy matrix (dark grey), (b) fayalite laths (mid grey), spinel crystal exceptionally rich in TiO_2 (light grey), glassy matrix (dark grey).

Sample 6 (IL 459) displays slightly different microstructural features compared to those discussed so far. It is characterised by massive and skeletal fayalite laths dominating the microstructure and a network of fine wüstite dendrites dispersed across a glassy matrix that is quite extensive in some parts (Fig. 15a and 15b). Alumina is detected in high contents reaching up to 9% in the bulk composition and up to 20% in the glassy phase. Euhedral crystals of magnetite are also present albeit more infrequently suggesting partially oxidising conditions during which air trapped in the porous system led to an oxidation of wüstite to magnetite. Interestingly, an iron-chromium spinel was noted (Fig. 16) and spot analysis revealed that it contains 1.8% MgO, 12.5% Al_2O_3, 40.2% FeO, 37.8% Cr_2O_3 and traces (0.3%) of TiO_2, which corresponds well to the composition of chromite. Such a finding might have broader implications concerning ore procurement strategies since the closest chromite ores to Molyvoti are found within metamorphosed ultramafic rocks of the Soufli ophiolites (Magganas and Economou 1988), in Evros prefecture, some 140 km away.

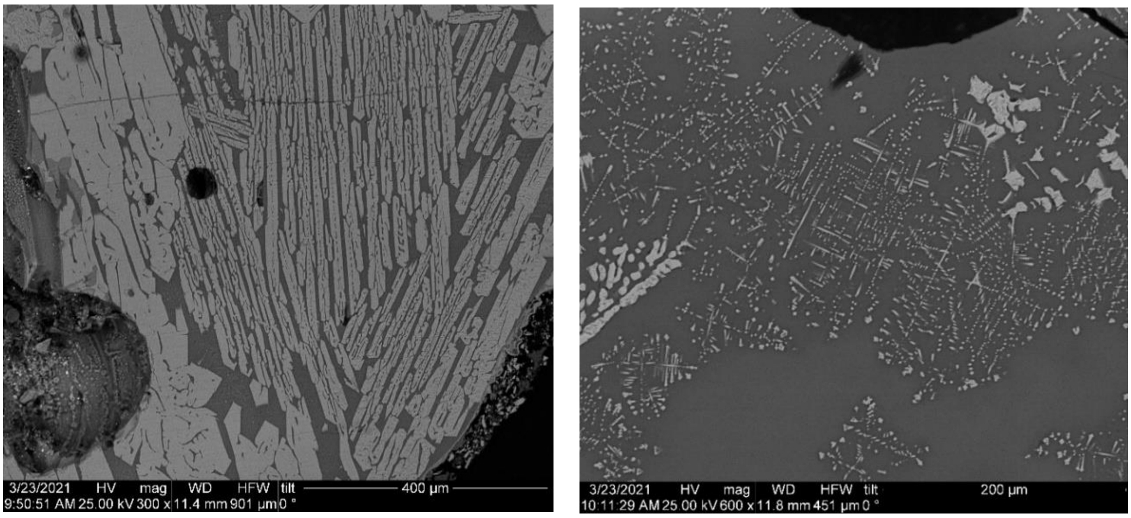

Figure 15. SEM photomicrographs, Sample 6 (IL 459) (a) fayalite laths (light grey), glassy phase (dark grey), (b) fine wüstite dendrites (white), magnetite crystals (white rhomboid crystals), glassy matrix (dark grey).

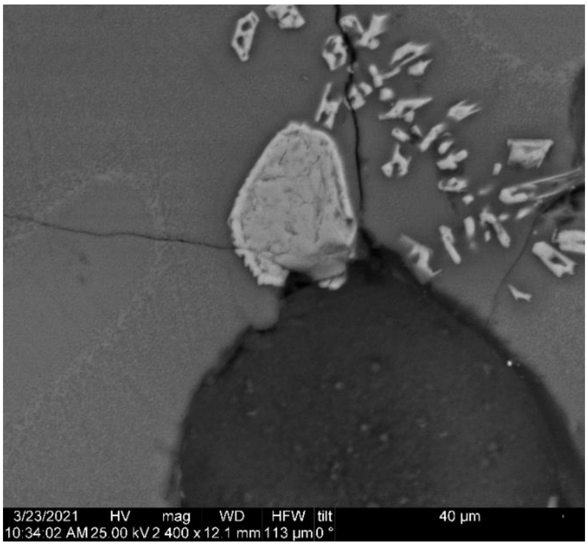

Figure 16. SEM photomicrograph, Sample 6 (IL 459) 'chromite' spinel (light grey rhombus), skeletal magnetite (light grey crystals), glassy phase (dark grey).

5. DISCUSSION

The analytical results on the Molyvoti slag corroborate with an efficient bloomery practice by which iron ores of the hematite/limonite variety were reduced to metallic iron. Slag microstructure consists of skeletal laths of fayalite, networks of wüstite dendrites, some metallic iron prills, while magnetite is rare, observed only in two occasions (sample 5-IL 408, sample 6-IL 459). Concerning the fayalitic phase, the fine skeletal laths are formed when their solidification is speeded up by exposure to cool air and this fast cooling could take place due to various choices taken during the process (Rehren et al. 2007). For the studied slags it is assumed that they could have formed either from being tapped out of the furnace or dripped down into a slag pit. The assemblage of fayalites and dendritic wüstite in smelting slags suggest furnace temperatures lower than 1200°C (Serneels and Perret 2003). The addition of fluxes such as quartz sand should be expected since this allows the iron melting temperature to be decreased to 1000-1100°C (Rehren et al. 2007; Charlton et al. 2010). In some instances, unreacted ore pieces within the slag reveal certain inefficiencies in terms of furnace operation, but in general the majority of analysed samples reflect a viable iron producing process.

An evaluation of the metallurgical evidence from Molyvoti should be attempted in relation to its geological settings while considering distances from potential sources of raw materials or other parameters affecting a sustainable iron industry. As the example from Abdera has demonstrated, such sources might lie at longer distances than the immediate vicinity of the cities. Rich mineral deposits could be found in the Rhodope Mountain range extending north of the plain of Xanthi at a distance of 25 km from Abdera. An extensive skarn formation outcrops 2-3 km NE of Kimmeria village at the contact of the Xanthi granodiorite with the marbles, consisting mainly of hematite, among other minerals (Melfos and Voudouris 2012). Both the hematite and magnetite-pyrite are good quality iron ores that could have supplied Abdera through an exchange network with the indigenous Thracian population that was inhabiting the whole region to the north, beyond the *chora* of Abdera.

In the case of Molyvoti, a similar situation could be envisaged, considering that the closest iron ore deposits could be found about 15 km to the northeast in the region of Xylagani where a gold-bearing Fe-Cu-(Zn-Pb) stratabound deposit is situated (Melfos and Voudouris2012). Further east at Marmaritsa, about 20 km east of Molyvoti, wide Fe-oxide veins cross-cut the marbles close to the sea side, and underground mining galleries are located at Ktismata (Papastamataki et al. 2001). Since these deposits lie closer to the city of Maroneia and could have potentially been incorporated into its territory, it is not clear whether the inhabitants of Molyvoti had direct access to mining rights at this location. Although it is premature to address the question of which city had access to certain mineral resources at any particular location, we could suggest that in the event that Molyvoti acquired no mining rights, the demand for iron would have been covered by importing ores, semi-finished products or blooms for further smithing and fabrication of iron objects. The importing of ores could be corroborated by the analytical results according to which several samples could be characterised as smelting residues.

Apart from potential sources of iron located within a radius of about 25 km from the examined sites, there are more numerous deposits of hematite, limonite and pyrite further north that could have reached the cities of the littoral through trade with the Thracians of the hinterland. Interestingly, the finding of chromite in one slag sample might indicate far reaching networks for ore procurement, as far as Soufli in Evros, some 140 km away from Molyvoti. Also, the presence of the titanium-rich phase (spinel) in one sample might indicate the use of titanium-rich sands for iron production earlier than is generally accepted, a hypothesis that could be substantiated with future analyses on more, securely dated finds. Evidently the bulk demand for iron ores on site would have been covered by less distant hematite/limonite deposits, as suggested by the chemical composition of the majority of analysed samples.

It is during the Classical and Hellenistic periods, between the 5th and 3rd centuries, that one could refer to proper bloomery, as a more systematic activity aiming at larger output and exploiting the local mineral resources across larger parts of Aegean Thrace. Marble quarrying and mining, large scale building projects, infrastructure for ports and ship building, and extensive trade of goods from the Balkan hinterland to the Aegean intensifies during this time and the expansion of the iron industry is undoubtedly entangled with such significant developments in the economic sphere (Archibald 2013; Tsiafaki 2021). Sustaining such iron industries requires uninterrupted access to mineral ores and timber for fuel in abundant quantities. Recent studies have shown that Thasos was thickly wooded in prehistory while erosion of the acropolis hill was severe in Classical times, caused by deforestation due to increased demand for fuel in metallurgy (Fig. 2), in addition to other applications (Sintes 2003; Sintes and Brunet 2003; Lespez 2007). Both Thasos and littoral Thrace are still rich in extensive iron deposits at numerous locations. Thus, local timber and iron ores could have supplied the workshops during the developed phase of standardized bloomery production in Classical/Hellenistic times.

6. CONCLUSIONS

The results from the current study have confirmed that iron production was practiced at the city on the Molyvoti peninsula. All the sampled residues derive from domestic contexts while an actual workshop has not been located so far. Yet the current findings are important indicators to account for the technological level acquired by the local iron workers. The data derived from the SEM/EDS analysis show that limonite and/or hematite were the most commonly used minerals for smelting. Some rare inclusions of titanium and chromium might suggest alternative sources of iron ores. For instance, the presence of increased titanium levels in one sample might suggest the use of Ti-rich iron sands but this hypothesis should be explored further with future analysis of more samples. Additionally, the lack of any chromium-bearing ores in the vicinity of Molyvoti could suggest importing of raw materials from further afield. Analysis of additional samples, which is ongoing will provide a clearer picture on such issues. Overall, the analysed slags show that the bloomery process was efficient and similar to that witnessed on other sites in the region, mainly Abdera and Zone (Kostoglou 2008). High temperatures around 1100°C were attained and kept stable during smelting while fluxes, were used as suggested by the presence of increased CaO contents, particularly in the glassy phase. Our current results complement previous studies and confirm that iron was effectively produced from local deposits across Aegean Thrace in more sites than have been previously examined. It is intended to expand this research with analysis on iron objects from Molyvoti in order to assess the quality of produced iron and evaluate their fabrication histories including an evaluation of the carburization techniques that had been applied.

To briefly summarize the available information, we could suggest that although a well-established ironworking tradition had gradually developed in this region, it was only available to some cities, while others seem to have lagged behind in the application of advanced carburization techniques (Kostoglou 2008). Whether this is a matter of differential access to raw materials, namely direct versus negotiated access, or longer experimentation with forging techniques, or indeed a matter of choice dictated by cultural parameters, it is not easy to address for the time being. In any case producing iron and steel of good quality would offer advances in sectors of technological expansion, economy and trade. The sites with less advanced technological means could reflect cases of preferential appropriation or even denial of certain techniques and are therefore useful examples to illustrate alternatives in socio-technical practices that are necessary for more nuanced interpretations of ancient technologies.

Table 2. Compositional analysis of Molyvoti slag determined by SEM/EDS, values in wt% (n.d.: not detected)

		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	PbO	SO_3	BaO	Cl_2O	K_2O	CaO	TiO_2	MnO	FeO	Cr_2O_3
Sample 1 IL 208	bulk	n.d.	0.62	2.11	9.86	0.84	n.d.	n.d.	n.d.	0.21	0.25	0.96	n.d.	0.47	76.19	n.d.
	bulk	n.d.	0.47	0.89	4.51	0.57	n.d.	n.d.	n.d.	0.25	0.2	0.5	n.d.	0.32	83.04	n.d.
	fayalite	n.d.	1.73	1.17	25.83	n.d.	n.d.	n.d.	n.d.	n.d.	0.32	1.88	n.d.	1.39	60.9	n.d.
	fayalite	0.23	1.52	1.78	22.72	n.d.	n.d.	n.d.	n.d.	n.d.	0.43	1.71	n.d.	1.38	63.19	n.d.
	wüstite	n.d.	0.42	1.69	2.33	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	0.29	0.56	85.1	n.d.
	wüstite	n.d.	n.d.	1.62	2.75	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	0.53	0.47	0.58	84.38	n.d.
	glassy phase	2.13	0.06	12.81	37.82	1.31	n.d.	0.13	n.d.	n.d.	4.27	11.93	n.d.	0.66	25.99	n.d.
	glassy phase	2.15	n.d.	12.02	35.15	1.35	n.d.	0.06	n.d.	n.d.	3.58	10.15	n.d.	0.53	31.51	n.d.
	unmelted ore	n.d.	1.3	3.02	9.75	2.05	n.d.	n.d.	n.d.	n.d.	0.31	0.9	n.d.	0.52	70.8	n.d.
	unmelted ore	n.d.	0.71	2.01	8.56	2.05	n.d.	n.d.	n.d.	0.22	0.26	0.91	n.d.	0.46	75.76	n.d.
	interm. zone	n.d.	1.07	1.4	2.46	0.65	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	n.d.	1.58	82.79	n.d.
		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	PbO	SO_3	BaO	Cl_2O	K_2O	CaO	TiO_2	MnO	FeO	Cr_2O_3
Sample 2 IL 314	bulk	n.d.	0.82	2.7	13.37	0.73	0.95	n.d.	n.d.	n.d.	n.d.	0.66	n.d.	0.65	72.1	n.d.
	bulk	n.d.	0.64	3.13	14.25	0.67	0.61	n.d.	n.d.	n.d.	0.24	0.8	0.19	0.66	70.92	n.d.
	bulk	n.d.	0.61	3.28	16.2	0.68	0.86	n.d.	n.d.	n.d.	0.49	1.06	0.27	0.78	68.18	n.d.
	fayalite	n.d.	1.62	0.64	28.64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.03	n.d.	1.57	59.84	n.d.
	wüstite	n.d.	n.d.	1.12	0.91	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	n.d.	0.3	0.6	86.81	n.d.
	glassy phase	n.d.	n.d.	5.54	20.45	2.88	n.d.	1.17	n.d.	0.24	n.d.	0.95	n.d.	0.62	61.31	n.d.
	glassy phase	2.28	0.11	11.38	37.61	1.76	n.d.	0.68	n.d.	n.d.	4.9	10.29	0.41	0.62	26.97	n.d.
	glassy phase	2.81	n.d.	13.97	36	2.05	n.d.	0.77	n.d.	n.d.	5.01	8.75	0.41	0.54	26.71	n.d.
	unmelted ore	n.d.	n.d.	n.d.	0.97	n.d.	n.d.	n.d.	n.d.	0.22	n.d.	n.d.	n.d.	n.d.	88.92	n.d.
	iron prill	n.d.	n.d.	0.73	0.96	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	0.31	0.62	0.48	87.03	n.d.
		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	PbO	SO_3	BaO	Cl_2O	K_2O	CaO	TiO_2	MnO	FeO	Cr_2O_3
Sample 3 IL 378	bulk	1.1	4.02	7.04	27.06	0.58	n.d.	n.d.	n.d.	n.d.	0.98	2.74	0.16	0.46	50.26	n.d.
	bulk	0.89	5.45	5.67	26.28	0.62	n.d.	n.d.	n.d.	n.d.	1	2.75	0.36	0.66	50.68	n.d.
	bulk	1.16	4.35	26.47	26.76	0.25	n.d.	n.d.	n.d.	n.d.	0.92	2.4	0.31	0.51	51.16	n.d.
	ceramic phase	1.75	2.02	9.44	65.65	1.7	n.d.	n.d.	n.d.	n.d.	1.72	1.35	n.d.	n.d.	15.99	n.d.
	fayalite	0.08	11.97	n.d.	39.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.79	n.d.	0.7	42.51	n.d.
	fayalite	n.d.	10.22	0.64	38.92	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.94	n.d.	0.79	43.64	n.d.
	wüstite	n.d.	n.d.	1.74	0.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.47	n.d.	87.46	n.d.
	wüstite	n.d.	1.3	2.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	0.49	86.14	n.d.
	glassy phase	3.37	0.29	21.2	41.88	1.16	n.d.	0.32	n.d.	n.d.	3.8	9.51	0.22	0.25	16.2	n.d.

	glassy phase	3.15	0.28	19.72	44.22	1.04	n.d.	0.14	n.d.	n.d.	4.09	9.87	0.23	n.d.	15.53	n.d.
	unmelted ore	n.d.	n.d.	1.29	6.36	1.32	n.d.	0.92	n.d.	n.d.	n.d.	0.79	n.d.	n.d.	80.37	n.d.
	unmelted ore	n.d.	0.23	1.62	11.43	0.69	n.d.	1.11	n.d.	0.42	n.d.	0.79	n.d.	n.d.	75.32	n.d.
		Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**PbO**	**SO_3**	**BaO**	**Cl_2O**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Cr_2O_3**
Sample 4 IL 383	bulk	0.45	0.68	1.95	9.33	0.96	n.d.	0.89	n.d.	n.d.	0.58	1.38	n.d.	0.64	74.81	n.d.
	bulk	0.87	1.14	2.83	11.51	1.16	n.d.	0.99	n.d.	n.d.	0.54	1.2	n.d.	0.64	71.18	n.d.
	bulk	0.88	1.17	2.77	12.88	1.24	n.d.	0.98	n.d.	n.d.	0.47	1.27	n.d.	0.66	69.38	n.d.
	fayalite	n.d.	0.9	28.77	n.d.	0.36	n.d.	n.d.	n.d.	n.d.	n.d.	3.84	n.d.	1.09	58.52	n.d.
	wüstite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.46	89.57	n.d.
	Pb-Ba crystal	n.d.	n.d.	n.d.	n.d.	n.d.	34.96	n.d.	59.85	n.d.	n.d.	1.42	n.d.	n.d.	3.4	n.d.
		Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**PbO**	**SO_3**	**BaO**	**Cl_2O**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Cr_2O_3**
Sample 5 IL 408	bulk	1.21	5.91	21.91	51.54	n.d.	n.d.	n.d.	n.d.	n.d.	1.23	2.15	0.75	1.26	12.63	n.d.
	bulk	1.88	5.07	24.47	48.43	n.d.	n.d.	n.d.	n.d.	n.d.	0.78	1.46	0.79	0.67	14.81	n.d.
	bulk	3.07	5.06	25.97	44.54	0.22	n.d.	0.3	n.d.	n.d.	0.26	0.36	0.47	0.71	17.15	n.d.
	spinel (50μm)	n.d.	2.52	1.66	1.41	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	88.02	n.d.	5.38	n.d.
	spinel	n.d.	3.53	8.8	3.51	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	0.7	2.11	1.63	71.63	n.d.
	inclusion	0.29	12.61	45.34	4.43	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	0.25	0.62	0.82	31.93	n.d.
	inclusion	0.72	19.12	13.63	54.61	n.d.	n.d.	n.d.	n.d.	n.d.	1.14	n.d.	n.d.	n.d.	7.95	n.d.
	glassy phase	2.49	3.07	17.59	62.16	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	3.85	1.42	0.54	7.0	n.d.
	glassy phase	0.37	0.89	30.52	46.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16.32	n.d.	0.35	4.72	n.d.
		Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**PbO**	**SO_3**	**BaO**	**Cl_2O**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Cr_2O_3**
Sample 6 IL 459	bulk	1.4	0.53	7.13	32.88	0.28	n.d.	0.28	n.d.	n.d.	1.73	1.99	n.d.	0.54	47.92	n.d.
	bulk	0.83	0.92	4.93	31.38	n.d.	n.d.	n.d.	n.d.	n.d.	1	1.33	n.d.	0.58	53.12	n.d.
	Si-rich area	1.7	0.74	9.76	68.57	n.d.	n.d.	n.d.	n.d.	n.d.	3.99	2.28	0.42	0.4	10.91	n.d.
	fayalite	0.21	2	0.58	28.51	0.28	n.d.	n.d.	n.d.	n.d.	n.d.	0.36	n.d.	0.63	60.67	n.d.
	fayalite	0.18	0.85	1.28	28.76	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	0.76	n.d.	0.56	60.67	n.d.
	fayalite	n.d.	1.01	0.35	28.84	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.44	n.d.	0.56	61.89	n.d.
	magnetite	n.d.	0.8	3.39	3.99	n.d.	n.d.	n.d.	n.d.	n.d.	0.25	n.d.	1.14	0.41	80.52	0.29
	Fe-Cr crystal	n.d.	1.81	12.57	2.26	n.d.	n.d.	n.d.	n.d.	n.d.	0.24	n.d.	0.37	n.d.	40.23	37.81
	glassy phase	3.35	0.14	20.49	50.76	0.56	n.d.	0.16	n.d.	0.03	n.d.	6.68	0.79	0.22	15.14	n.d.
	glassy phase	2.31	1.06	12.14	59.24	n.d.	n.d.	n.d.	n.d.	n.d.	4.37	3.4	0.56	0.36	14.9	n.d.
	unmelted ore	n.d.	n.d.	0.93	16.19	1.85	1.79	n.d.	n.d.	n.d.	n.d.	1.35	n.d.	0.3	69.82	n.d.

		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	PbO	SO_3	BaO	Cl_2O	K_2O	CaO	TiO_2	MnO	FeO	Cr_2O_3
Sample 7 IL 465	bulk	1.29	1.9	2.4	14.9	1.32	n.d.	n.d.	n.d.	n.d.	0.44	0.82	n.d.	0.64	68.66	n.d.
	bulk	0.48	1.09	2.84	14.41	0.67	n.d.	n.d.	n.d.	n.d.	0.2	0.69	n.d.	0.58	71.13	n.d.
	fayalite	n.d.	1.36	0.72	31.68	0.56	n.d.	0.32	n.d.	n.d.	n.d.	1.68	n.d.	1.09	56.32	n.d.
	fayalite	n.d.	2.04	1.22	28.63	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.05	n.d.	0.83	59.59	n.d.
	wüstite	0.46	0.97	0.85	0.64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	86.86	n.d.
	wüstite	n.d.	0.79	0.65	0.66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.53	87.62	n.d.
	unreacted ore	n.d.	n.d.	0.51	1.76	n.d.	n.d.	1.34	n.d.	0.3	n.d.	n.d.	n.d.	0.58	85.94	n.d.
	unreacted ore	n.d.	n.d.	4.36	15.04	n.d.	n.d.	0.63	n.d.	n.d.	n.d.	0.26	n.d.	n.d.	71.72	n.d.
	glassy phase	0.22	0.26	9.69	30.4	1.72	n.d.	n.d.	n.d.	n.d.	0.33	0.84	n.d.	0.43	50.5	n.d.
		Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**PbO**	**SO_3**	**BaO**	**Cl_2O**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Cr_2O_3**
Sample 8 IL 526	bulk	0.32	0.75	2.37	10.16	1.08	n.d.	0.82	n.d.	0.39	0.51	2.6	0.22	0.32	72.25	n.d.
	bulk	0.39	0.37	2.13	10.25	0.72	n.d.	0.5	n.d.	0.19	0.55	2.74	0.16	0.33	73.5	n.d.
	wüstite	n.d.	0.68	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	0.18	n.d.	31.12	n.d.
	glassy phase	0.41	0.34	5.09	39.95	4.87	n.d.	0.13	0.64	n.d.	2.46	11.53	n.d.	n.d.	82.48	n.d.
	unreacted ore	n.d.	n.d.	0.83	5.59	0.64	n.d.	0.44	n.d.	0.19	n.d.	0.42	n.d.	n.d.	88.72	n.d.

AUTHOR CONTRIBUTION

Conceptualization, N.N. and M.T.; methodology, N.N.; software, N.N.; validation, N.A., D.T. and M.T.; formal analysis, N.N.; investigation, N.N.; resources, M.T.; data curation, N.A.; writing—original draft preparation, N.N.; writing—review and editing, N.N., M.T. and N.A.; visualization, N.N.; supervision, M.T.; project administration, D.T. and M.T.; funding acquisition, N.N. All authors have read and agreed to the published version of the manuscript.

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