An Archaic metallurgical workshop in Thasos (Greece): The case of Charitopoulos plot

Nerantzis Nerantzis, Giorgos Sanidas, Benjamin Jagou, Tony Kozelj, Konstantina Panoussi

STAR: Science & Technology of Archaeological Research

ISSN: (Print) 2054-8923 (Online) Journal homepage: http://www.tandfonline.com/loi/ysta20

An Archaic metallurgical workshop in Thasos (Greece): the case of Charitopoulos plot

Nerantzis Nerantzis, Giorgos Sanidas, Benjamin Jagou, Tony Kozelj & Konstantina Panoussi

STAR: SCIENCE & TECHNOLOGY OF ARCHAEOLOGICAL RESEARCH, 2018
https://doi.org/10.1080/20548923.2017.1419659

Routledge
Taylor & Francis Group

An Archaic metallurgical workshop in Thasos (Greece): the case of Charitopoulos plot

Nerantzis Nerantzis [a], Giorgos Sanidas[a], Benjamin Jagou[b], Tony Kozelj[c] and Konstantina Panoussi[d]

[a]Université de Lille 3, Halma (Histoire, Archéologie et Littérature des Mondes Anciens) UMR-8164, Pont de Bois, 59653 Villeneuve D'Ascq, France; [b]Institut national de recherches archéologiques préventives, Hauts de France, Centre de recherche archéologique d'Achicourt, 7 rue Pascal, 62217 Achicourt, France; [c]French School at Athens, Thasos, 64004, Greece; [d]Ephorate of Antiquities of Kavala-Thasos, Kyprou 14, Kavala, 65110, Greece

ABSTRACT
An important archaeometallurgical context dating to the Archaic period (700-480 BC) has been excavated at Thasos (Greece). In particular a pear-shaped metallurgical furnace was revealed while its fill and surrounding area was characterized by the abundant presence of slag, fragments of crucibles and furnace lining. Based on macroscopic examination and instrumental analysis it was shown that the slags and other waste products correspond to the melting and recycling of bronze. The significance of this finding is highlighted by the fact that the workshop is located within the urban core of Thasos. Based on the analytical results it could be suggested that bronze, containing lead was melted and recycled in crucibles at this workshop. Such ternary alloys were mostly used in bronze castings during this period. The results presented here contribute to a better understanding of certain metallurgical practices which were incorporated to the long technological tradition of Thasos.

ARTICLE HISTORY
Received 15 May 2017
Accepted 14 December 2017

KEYWORDS
Metallurgy; melting furnace; copper; slag; crucible; Thasos

Introduction

Excavation carried out during two seasons in 2008 and 2009 by the Ephorate of Antiquities of Kavala-Thasos at Thasos (Limenas) brought to light a significant metallurgical workshop dating to the late Archaic period (700–480 BC). The site is located at the plot of D. Charitopoulos (Figure 1), on the northwestern flanks of the acropolis hilltop, and lies to the southeast of the Roman Odeon. The plot covers an area of 651.31 m^2 extending along a NE–SW axis and is of rectangular shape (Figure 2). An initial, small-scale investigation that was carried out in 1981 and 1985 was restricted to the opening of trial trenches (Sanidas et al. in press). The more recent excavation revealed a considerable part of two architectural sectors, complex I to the NW and complex II to the SW, belonging to different occupational clusters.[1] These represent both spatially and temporally distinct areas, as complex II was in use during the Archaic period while complex I dates exclusively to the Roman period. Therefore, although being in close proximity each complex dates to a different chronological phase. Our current investigation focuses on the furnace (K4-8) and associated metallurgical remains that came to light in complex II dating to the late Archaic period. The study of metal production was conducted within the framework of Research Project HeMEN of the University of Lille, HALMA-UMR 8164, supported by the French School at Athens. Metallurgical installations and related residues were also found in complex I, which date to the Roman period. In particular, a stone-built furnace (K14) that preserves part of a domed superstructure has been revealed on the level of a late Roman courtyard which will become the focus of investigation in the near future.

Furnace K4-8 and the workshop context

The Archaic furnace (K4-8) to which our investigation was focused is located on the easternmost part of complex II and it was dated based on stratigraphic associations and more precisely by the pottery contained in the undisturbed fill of this feature. It is pear-shaped with an opening at the frontal, southern side while its posterior, northern side disturbed an earlier wall (T16) of Archaic date (Figure 3). Part of this reused wall was modified to facilitate attachment of the furnace. About 1 m to the north there is a parallel wall, which is contemporary to a western and southern wall, all three delimiting a rectangular space around the furnace. It appears that this working space was possibly indoors or at least partly roofed as the evidence for the building's superstructure is inconclusive. The well, which is attached to the southern wall, is an important feature in this workshop context as direct access to water was crucial for metallurgical practices.

CONTACT Nerantzis Nerantzis nerantzis.nerantzis@gmail.com

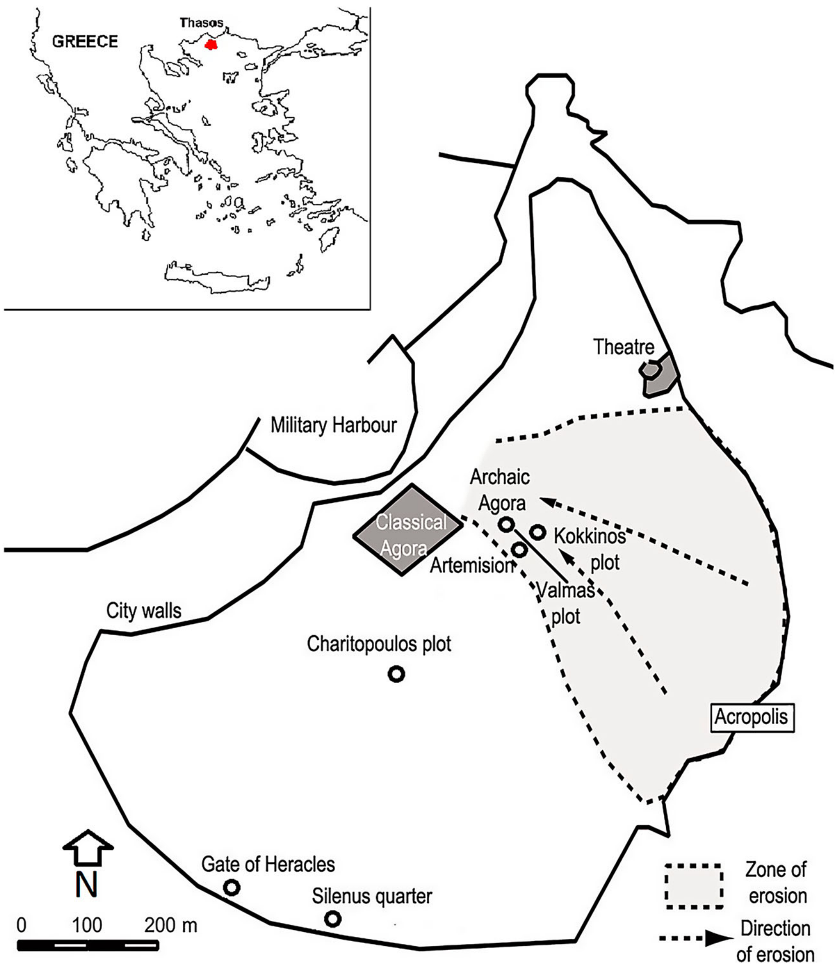

Figure 1. Map of Greece indicating Thasos and ancient city plan. Slags derive from the localities noted in circles (Drawing: Tony Kozelj and Manuela Wurch-Kozelj)

Regarding the dimensions of the furnace, its length is 1.60 m, its width 0.55–0.90 m with an opening of 0.13 m on the frontal side, while its height survives at 0.50 m (Sanidas et al. 2016, 286). On the northern side, it bears a small circular opening used for attaching a clay tuyère that was connected to the bellows. It was built of stones, lined with refractory clay on the internal surface, which was exposed to high temperatures (Figure 4). Unfortunately, the area around the furnace has been severely disturbed by later interventions, mainly due to the opening of a wartime trench by the Bulgarian army extending across the frontal side of the furnace. Therefore the data from which we can extract safe conclusions is the furnace itself, the fill inside and immediately around it and the contained material. This assemblage is contemporary and homogeneous. It contained ash, fragments of clay lining some bearing slag staining, crucible fragments and pieces of slag while the more recent pottery sherds found, all belong to the late Archaic period from the end of the sixth to the beginning of the fifth century BC at the latest (Sanidas et al. in press). This is the timeframe during which the furnace was in operation.

Metallurgical residues description and methods of analysis

An initial macroscopic examination has shown that the metallurgical material consists of two main groups of remains corresponding to different metallurgical processes. The first comprises a group four iron smithing slags (THB07aA, THB07aC, THB08, THB15) deriving from a context near the furnace. A second group of slags (THB07aB, THB07aD, THB07aE, THB07aF, THB11c-f), which were recovered from the furnace fill, have been characterized as remains related to copper production due to the presence of surface oxidation with characteristic green and reddish staining. Apart from the slag pieces, two partially slagged vitrified clay fragments, most probably belonging to the lining of the furnace walls (THB11b, THB11g) and four crucible fragments (THB09A, THB09D) have been recorded. Based on the macroscopic observations 10 samples were selected for instrumental analysis with an aim to determine the stages of bronze production and to a lesser extent those of iron working. In particular, six slags related to bronze production (THB07aB, THB07aE, THB11a, THB11c, THB11e, THB11f), one slagged, vitrified clay

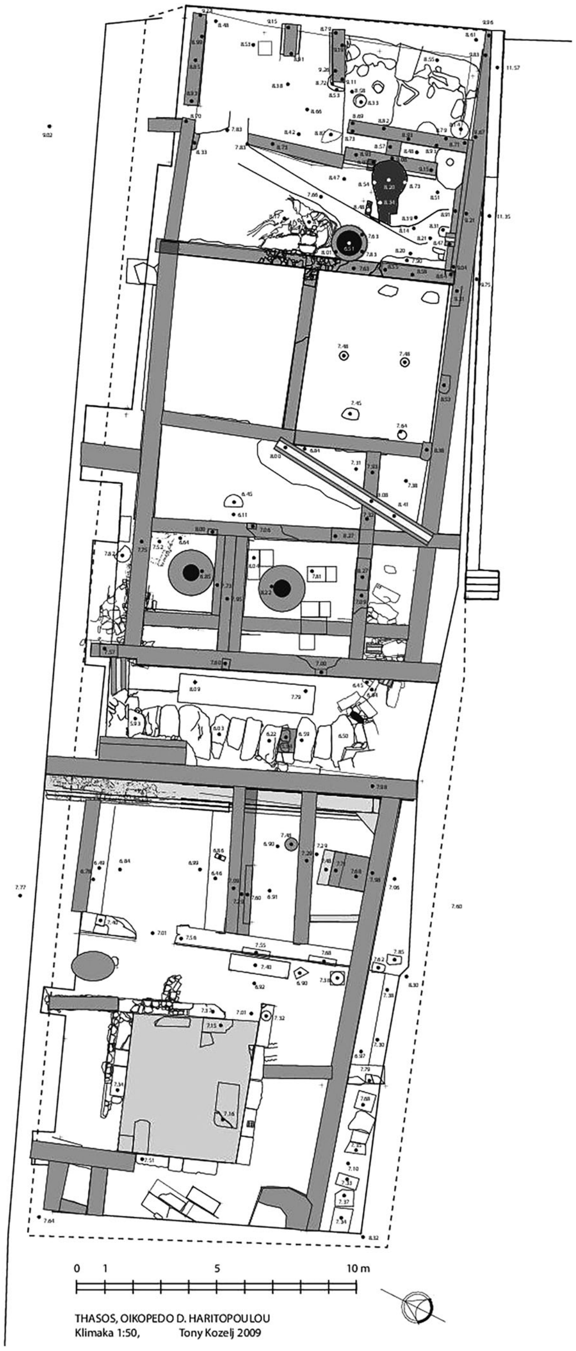

Figure 2. Plan of the excavated plot (Drawing: Tony Kozelj)

lining fragment (THB11g), two crucible fragments (THB09A, THB09D), an amorphous lump of a copper alloy (THB14) and one iron slag (THB07aA) were selected for analysis.

An instrumental analysis was conducted at the Laboratory of Archaeometry N.C.S.R. "Demokritos", Athens. The techniques used were optical microscopy, bulk compositional analysis and further examination of the distinct microstructural phases. The samples were mounted in epoxy resin and prepared with grinding and polishing papers of various grit sizes (600–2300) with a final polishing stage using diamond paste down to 1 µm. For the bulk analysis and particular micro-phases, such as metallic prills and characteristic crystals or other inclusions the SEM/EDS technique was applied. For each bulk analysis, three areas about 3×3 mm^2 in size were measured and the results presented in the tables reflect the mean value from each set of three measurements. Particular inclusions such as ore residues that might influence the analysis were avoided as were also large pores. Individual phases such as metallic prills and various crystals were analysed by the same method. All measurements were acquired using the following instrumental parameters: accelerating voltage 20 kV, working distance 10 mm, specimen tilt 0°. The data were corrected by using the ZAF programme with total analytical error of <10% for the major elements. Contents less than 0.1% are given only as indications and the data have been normalized to 100%. The results will be compared and contrasted with similar data from other localities on Thasos and the opposite Thracian mainland. For instance, comparable metallurgical residues from the Archaic agora and Artemision are still under investigation and it is planned to select samples for instrumental analysis in order to provide data comparable with those presented here.

Iron slag

Concerning the iron slag (THB07aA), its shape is flat/convex, its morphology is dense and compact with a few pores and surface oxidation suggesting that it derives from a smithing stage after the bloom had been consolidated (Sanidas et al. 2016, 287). Its microstructure consists of fayalitic laths, wüstite dendrites and a glassy matrix, which is typical for secondary smithing slags (Figure 5). A few inclusions of metallic iron were noted, which vary in size between 15 and 30 µm. Several inclusions of heterogeneous morphology, ranging between 100 and 200 µm in size were also observed. Their composition that was determined by the SEM/EDS points to un-reacted fragments of iron ore containing around 70% Fe_2O_3 and 1.0–3.5% P_2O_5 (Table 1). Fewer, minute inclusions of barite ($BaSO_4$) composition appearing as clusters in pores and cracks have been also noted. This low concentration in Ba does not contribute to the bulk composition of the sample. Yet it should be mentioned that it represents a characteristic element accompanying the iron mineralization on Thasos (Vavelidis et al. 1988). On the contrary, the presence of manganese contributes to the bulk composition with a concentration around 1.0% (presented as MnO in Table 1). The admittedly low concentrations of Mn need further investigation as this element is related to the local Fe/Mn mineralization that was targeted for iron extraction in antiquity.

Previous analyses of the Fe/Mn ores of Thasos deriving from Mavrolakkas, Tzines, Koupanada, Kallirachi, Oxia and Rachoni have determined significant concentrations of Mn, while Ba is also present in lower

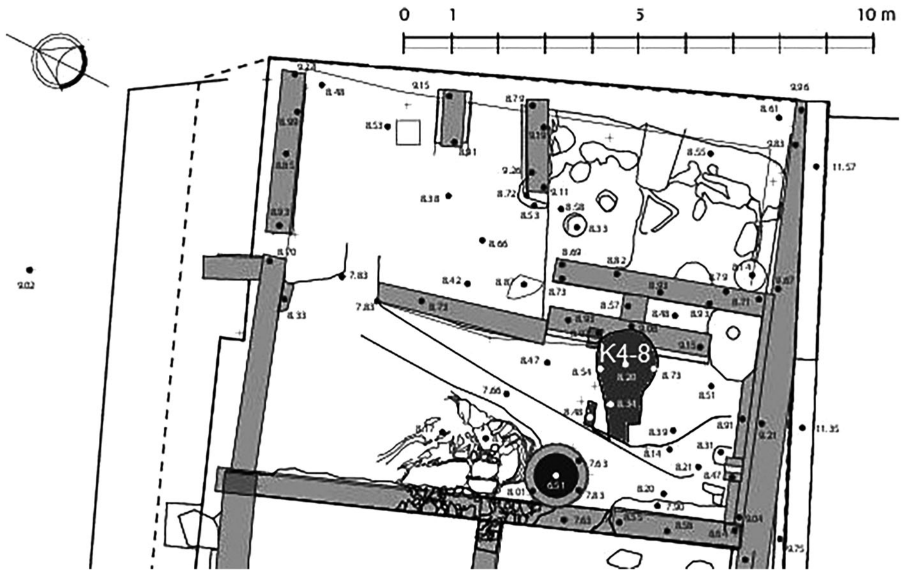

Figure 3. The workshop area with main features: furnace K4-8, surrounding walls and the well (Drawing: Tony Kozelj).

amounts (Vavelidis et al. 1988, 55). The issue of provenance of the iron ores used in Thasian metalworking sites is still under investigation by applying trace elements analysis in order to contribute crucial new data on the possible correlation of raw ores with certain mining locations on Thasos.

Residues related to bronze melting: slag, crucible fragments and furnace lining

The six slags with copper-bearing minerals on their surface have been characterized as being related to crucible activity (Figure 6). Based on their microstructural and compositional analysis it has been confirmed that at least two distinct processes were practiced at the workshop. Firstly there is evidence for the melting of bronze containing appreciable lead contents and possibly also the re-melting or recycling of such alloys. Tin-bronzes containing lead belong to a type of alloys that were commonly used during the Classical and Hellenistic periods especially for the casting of various utilitarian artefacts, statuettes or more sizeable statues and other objects (Craddock 1976, 1977; Haynes 1992).

Figure 4. The furnace K4-8.

Bulk analysis by SEM/EDS (average of three analysed areas) has shown that all crucible slags consist of silica (SiO_2) ranging between 28.8% and 61.6%, alumina (Al_2O_3) between 6.4% and 12.8% and magnetite (Fe_2O_3) between 3.6% and 10.9% (Table 2). Lower concentrations of K_2O, MgO and CaO were also detected. Copper oxide (CuO) contents are variable between 2.0% and 9.3% with one sample (THB07aE) reaching 27.1%. Tin oxide (SnO_2) contents are present in all slags in concentrations between 3.6% and 10.5% while lead oxide (PbO) contents are relatively high, ranging between 6.1% and 21.5%. The presence of zinc oxide (ZnO) that was detected in four samples in concentrations between 0.5% and 2.7%, and traces of silver found in one sample do not relate to the production of copper alloys but are due to the polymetallic nature of the deposits (Pb/Zn, argentiferous galena) present on Thasos and more broadly the whole of north Aegean.

Samples THB11a, THB11c, THB11e and THB11f contain low CuO (2–6.2%) and SnO_2 (3.6–6.0%), and slightly increased PbO (6.1–11.8%) and Fe_2O_3 (3.6–8.1%) suggesting their formation possibly during recycling of old bronze. It should be noted though that the variability of bulk tin and lead oxide content is insufficient to distinguish between alloying and recycling practices. The content of tin in metallic prills contained

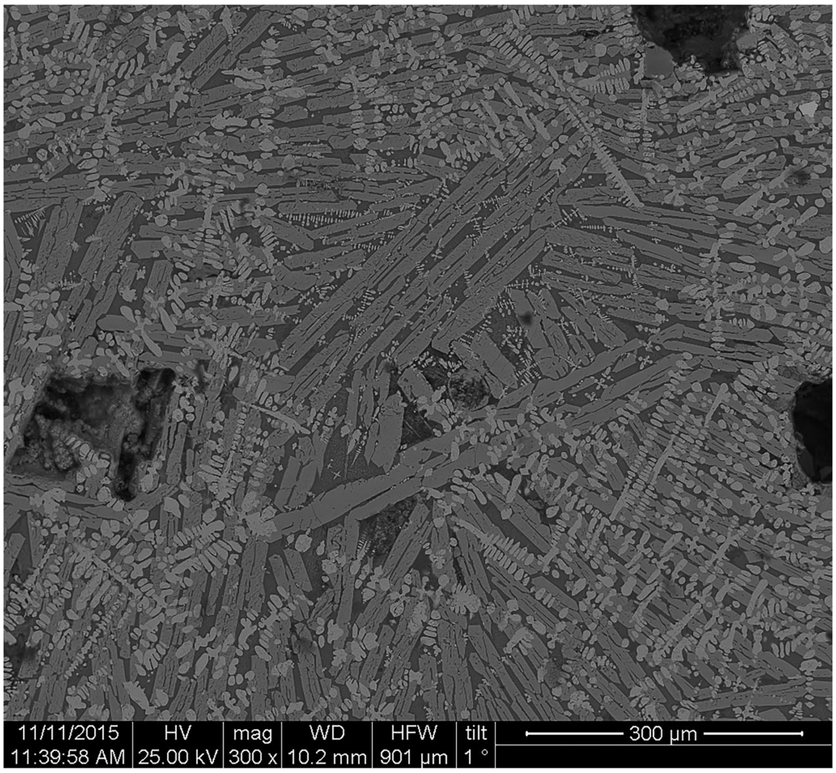

Figure 5. SEM/EDS photomicrograph of iron slag (TBH07aA). The microstructure consists of fayalitic laths (mid grey), wüstite dendrites (light grey) and a glassy matrix (dark grey).

in the slag is more indicative to a possible distinction between the two processes. As demonstrated in previous studies high-tin prills provide direct evidence for alloying copper with fresh tin (or cassiterite). Re-melting of existing bronze results in prills with a tin content equal to or below that of the recycled bronze (Rademakers, Rehren, and Voigt 2017), while high-tin prills offer far better evidence for alloying practices (Crew and Rehren 2002; Rademakers, Rehren, and Pusch 2013, 2017; Rehren 2001). Attempting to investigate the nature of the prevalent process in the Thasian workshop, that is, alloying versus re-melting, a microstructural examination and analysis of metallic inclusions in these slags was conducted.

Examination under the optical microscope and the SEM/EDS has revealed that the samples' microstructure consists of heterogeneous phases where siliceous compounds are frequent along with dendritic phases of Cu–Sn–Pb composition, elongated lamellae of tin oxide and a glassy matrix (Figures 7 and 8). The tin oxide crystals appear to be newly formed as a result of oxidation of tin from a liquid melt (Dungworth 2000; Farci, Martinón-Torres, and González Álvarez 2017; Figueiredo et al. 2010; Rademakers, Rehren, and Pusch 2013, 2017; Renzi and Rovira 2016). Their blocky and euhedral to skeletal and acicular shapes differentiates them from cassiterite crystals which are present in residues deriving from alloying (Merideth 1998). The presence of tin oxide crystals has been noted in slag from various sites in the Balkans (Glumac and Todd 1991), from Kition in Cyprus (Zwicker et al. 1985) and in crucible slags from Nichoria and Isthmia in the Peloponnese (Cooke and Nielson 1978; Rostoker, McNallan, and Gebhard 1983). Some researchers suggested that such tin oxides derived from the oxidation in the molten bronze (Klein and Hauptmann 1999), while others pointed out that they could indicate the use of cassiterite to alloy with copper (Rostoker, McNallan, and Gebhard 1983; Rostoker and Dvorak 1991; Papadimitriou, Tsaimou, and Vardavoulias 1992; Rovira, Montero-Ruiz, and Renzi 2009). Experimental work particularly focused on distinguishing these newly formed crystals from residual cassiterite minerals (Rovira 2011–2012; Rovira, Montero-Ruiz, and Renzi 2009). It was thus noted in this context that during bronze casting tin oxide inclusions had

Table 1. Iron slag sample THB07aA, bulk composition and distinct mineralogical phases (SEM/EDS analysis by oxides).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O	K_2O	CaO	SnO_2	MnO	TiO_2	Fe_2O_3	CuO	ZnO	PbO
THB07aA (bulk)	0.8	1.4	6.1	23.5	0.8	0.7	0.2	1.3	1.6	n.d.	0.6	n.d.	62.7	n.d.	n.d.	n.d.
THB07aA (fayalite)	n.d.	2.4	0.2	31.8	n.d.	1.3	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	63.3	n.d.	n.d.	n.d.
THB07aA (wüstite)	n.d.	n.d.	1.4	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	97.1	n.d.	n.d.	n.d.
THB07aA (ore inclusion)	n.d.	0.7	8.1	14.5	3.5	n.d.	0.2	n.d.	2.0	n.d.	n.d.	n.d.	70.6	n.d.	n.d.	n.d.
THB07aA (ore inclusion)	n.d.	n.d.	9.6	15.3	0.8	1.6	0.7	n.d.	0.4	n.d.	n.d.	n.d.	71.3	n.d.	n.d.	n.d.

Figure 6. Three pieces of crucible slag recovered from the furnace context.

formed even though no cassiterite was added. These highly euhedral inclusions were noted as rhomboids or as needles in the cast bronze samples. In general, if molten copper contains a high proportion of oxygen or if only small amounts of tin are used to form the bronze, then the oxygen present might react with all of the tin to form tin oxide and no tin would remain in solid solution (Dungworth 2000, 3). Interestingly, the presence of copper-based nodules within many of the tin oxide inclusions may be taken as diagnostic of the formation of tin oxide from the melt as has been shown by such experiments (Rademakers 2015, 175). Considering the Thasian slag under investigation, Figures 8 and 9 show clear examples of tin oxide forming from a liquid melt. Therefore, there is no convincing evidence for the alloying of copper with either cassiterite or metallic tin in this case. To further support this argument the metallic prills contained in these slags were examined.

Numerous copper prills were noted in all the samples, a number of which were analysed and the results are presented in Table 3. From a total of 10 analysed prills, 4 contain tin, ranging between 2.9% and 11.1%, while in the remaining 6 prills no tin was detected. Lead is present in seven prills, ranging between 1.9% and 4.3% and smaller amounts of iron, nickel and arsenic were also detected. Microstructural examination revealed that some of the prills often display a peripheral zone that bears tin crystals, distinct lead-rich phases and more rarely traces of silver. Based on these findings it could be suggested that all prills are either copper or low tin bronze further supporting the hypothesis that no clear evidence for alloying is attested. This compositional pattern is a good indicator for the loss of tin under oxidizing conditions, which causes the formation of the tin oxide crystals discussed above, rather than an alloying process. This is again verified by the presence of tin crystals in the "peripheral zone" of some prills, which is indicative of oxidation at the prill edge. To suggest an alloying process one would need either to find bronze prills with high tin contents, or residual mineral cassiterite fragments. As none are presented here, there is no way to distinguish between alloying and recycling processes. Both may have taken place, but this cannot be firmly established. For the moment, only melting ingots and/or re-melting, that is, recycling scrap can be firmly established.

The first crucible fragment (THB09D) that was examined, displays a heterogeneous texture of a vitrified clay-silicate body that bears secondary copper minerals on the surface (Figure 10). It belongs to the base and part of the body of the crucible with a diameter of 8.7–9.3 cm and surviving height of 3 cm. As described in previous detailed studies of similar material (Rademakers, Rehren, and Pusch 2013, 2017) three main parts are typically present in a section through a crucible wall: (a) an exterior, fired ceramic zone, (b) an intermediate, porous and bloated zone which marks a transition to a slagged zone and (c) a slag zone of vitrified ceramic with varying quantities of fuel ash and metal oxide. Occasionally an additional interior layer exists mainly consisting of copper and/or bronze and their oxides and corrosion products, which is usually referred to as "dross" (Rademakers, Rehren, and Voigt 2017). These three distinct zones have been microscopically identified in the studied crucibles (Figure 11). The interior slagged zone is composed of a variety of oxides as shown by different shades of grey, which at places host metallic inclusions or prills of brighter appearance. Analysis of three such inclusions has revealed an average composition of 91.1% CuO, 4.8% SnO_2 and 1.2% PbO (Table 4). This composition might be explained as the result of some metal adherence on the crucible surface during pouring, albeit in very small quantities as suggested by the prills size (10–15 µm). The bloated interface zone is clay-silicate in composition, it is tin-free while containing around 21.0% CuO and 8.1% PbO the latter being the highest contents of lead oxide detected in any of the three zones. The external zone is rich in silica but also contains up to 10.1% CuO, 0.2%

Table 2. Bulk chemical composition of crucible melting slag (SEM/EDS analysis by oxides).

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	SnO_2	MnO	Fe_2O_3	CuO	ZnO	PbO
THB07aB (bulk)	n.d.	0.6	6.7	33.5	n.d.	1.2	2.7	10.4	n.d.	10.9	9.3	2.7	21.5
THB07aE (bulk)	n.d	0.3	6.4	28.8	n.d.	n.d.	1.0	10.5	n.d.	5.3	27.1	0.5	19.7
THB11a (bulk)	1.4	1.0	10.6	43.7	2.9	2.6	15.3	4.9	n.d.	7.7	2.0	1.1	6.1
THB11c (bulk)	n.d.	2.1	7.6	50.0	n.d.	1.8	8.8	6.0	0.63	8.1	1.6	0.8	11.8
THB11e (bulk)	2.2	0.3	12.8	61.4	n.d.	5.7	2.6	n.d.	n.d.	3.6	4.2	n.d.	6.4
THB11f (bulk)	n.d.	1.0	8.4	61.6	n.d.	1.9	3.1	3.6	0.6	4.0	6.2	0.4	8.7

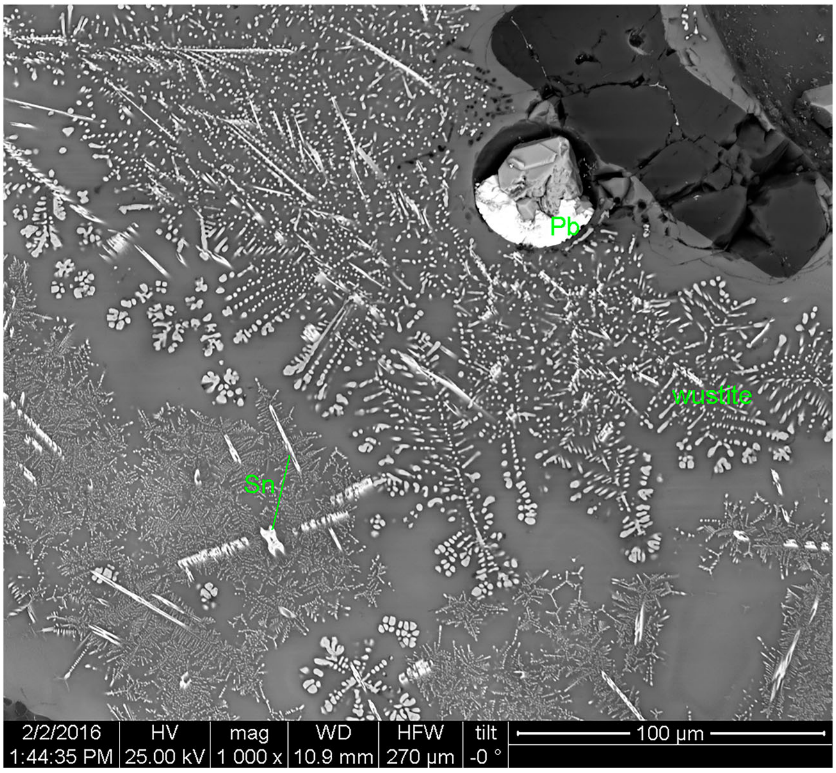

Figure 7. SEM/EDS photomicrograph of crucible slag (THB11 g) showing dendritic phases of Cu–Sn–Pb composition (white), elongated lamellae of tin oxide, a Pb-rich inclusion and glassy matrix.

SnO_2 and 3.6% PbO. For both the interface and external zone the average of three analysed spots is presented here. Such data are indicative of a bronze melting operation within the crucible under mildly oxidizing conditions as suggested by the enriched in metal oxides clay body and slagged zone. The current

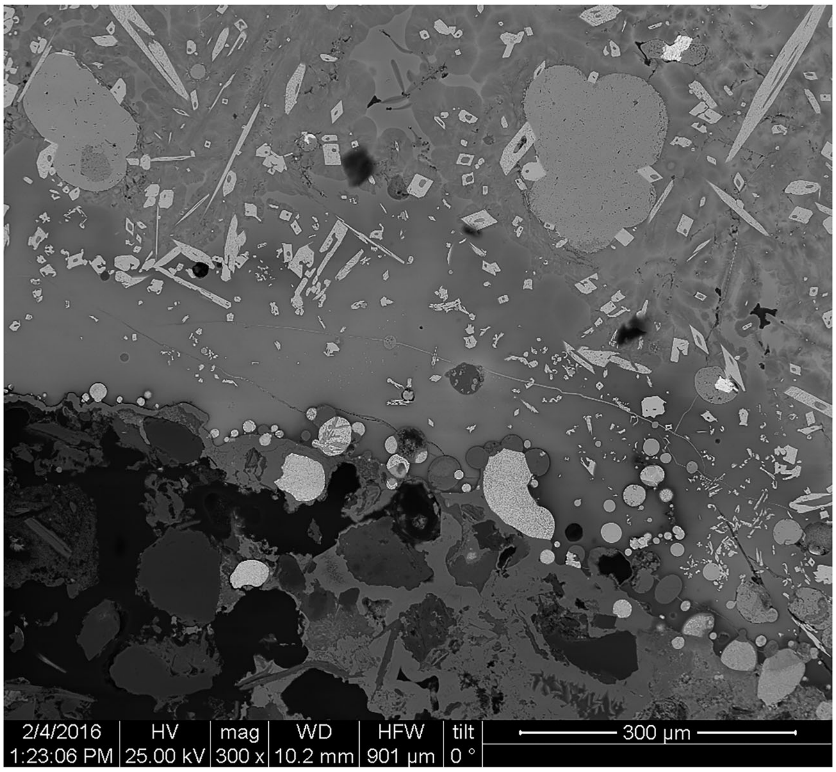

Figure 8. SEM/EDS photomicrograph of crucible slag (THB07aE). Globular and spheroid Cu–Sn–Pb inclusions, bronze kidney-shaped inclusion, elongated lamellae and rhomboid crystals of tin oxide with filled crystals cores, typical evidence for newly formed tin oxide, and glassy matrix (dark grey).

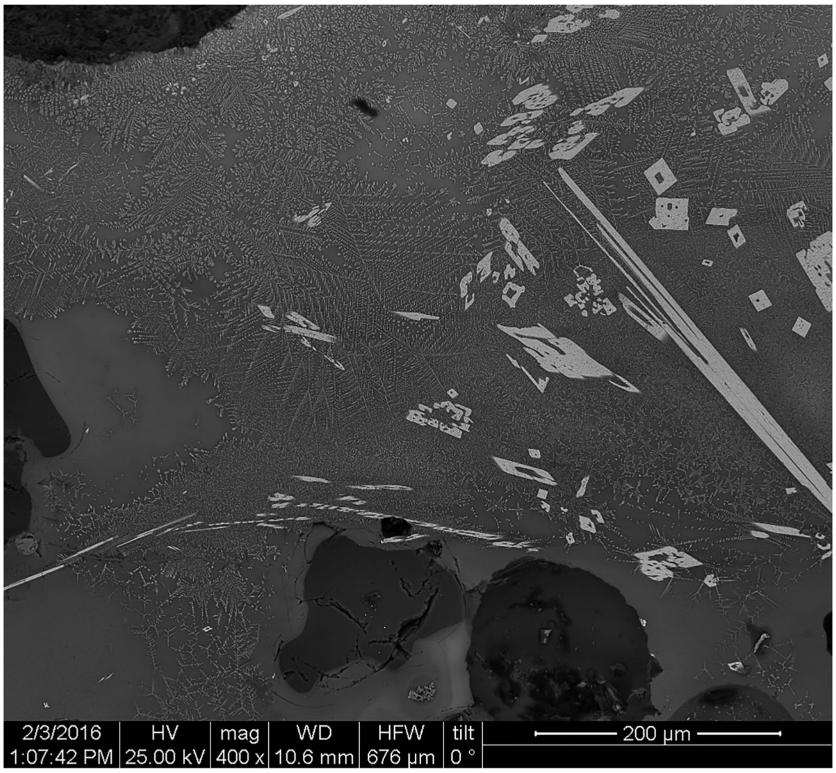

Figure 9. SEM/EDS photomicrograph of crucible slag (THB11 g). Lamellar and rhomboid, newly formed tin oxide crystals with filled cores (light grey), glassy matrix (dark grey).

results are in accordance to the findings from previous analysis on crucibles from Gordion which confirmed that body and bottom fragments are generally more enriched in metal (oxides) than rim fragments (Rademakers and Rehren 2016, 590).

The second crucible fragment (THB09A) is part of the shallow flat base, rounded in shape, which bears green, copper corrosion products on its internal surface. Examination of a section under the microscope revealed the typical three major zones: a slagged, copper-rich internal zone, a bloated interface, 2.5 mm in thickness with numerous metallic prills, and a siliceous, highly porous external zone (Figure 12). The slagged zone displays the same phases as the pieces of analysed slag: prills of Cu–Sn composition, elongated lamellae of tin oxide and a glassy matrix. The bulk chemical composition consists of considerably high PbO contents in the order of 33% and substantial SnO_2 contents reaching 10% (Table 4). It also contains 31% SiO_2, 8.8% Al_2O_3 and 2.9% Fe_2O_3 which are expected contents of metallurgical ceramics.

The fragment of slagged "lining" (THB11g) contains lower silica and alumina contents compared to the crucibles while the CuO, SnO_2 and PbO contents are substantially higher (Table 4). As this fragment is macroscopically different from the crucibles it was interpreted as a piece of clay lining from the furnace interior that at some stage came into contact with the molten bronze. Its chemical composition reflects a process by which oxidizing conditions were prevalent in the furnace resulting in the enrichment in metal oxides reacting with the ceramic matrix.

Seen in conjunction, the results from crucibles and lining suggest the loss of lead into the ceramic fabric. Lead loss through oxidation can easily lead to high PbO contents in the crucible slag since it works as a

Table 3. Composition of copper prills contained in slag and bulk composition of bronze lump (TBH14) (SEM/EDS analysis by elements).

	O	Al	Si	S	Cl	Ca	Sn	Ni	Fe	As	Cu	Pb	Ag
THB07aB prill (1)	n.d.	0.2	0.4	n.d.	n.d.	n.d.	n.d.	0.4	0.9	n.d.	95.5	2.4	n.d.
THB07aB prill (2)	n.d.	0.3	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	n.d.	95.1	2.8	n.d.
THB07aB prill (3)	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	5.3	n.d.	n.d.	n.d.	92.5	1.9	n.d.
THB11a prill (1)	n.d.	n.d.	0.2	n.d.	n.d.	0.3	11.1	n.d.	0.2	n.d.	84.4	3.6	n.d.
THB11a prill (2)	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	2.9	0.3	0.4	n.d.	91.4	4.3	n.d.
THB11g prill (1)	16.8	0.3	0.2	n.d.	19.8	n.d.	n.d.	n.d.	0.4	n.d.	59.6	2.6	n.d.
THB11g prill (2)	15.4	0.3	0.2	1.1	19.0	n.d.	n.d.	n.d.	0.2	1.0	62.4	n.d.	n.d.
THB11g prill (3)	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	98.6	n.d.	0.5
THB11g prill (4)	5.7	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	n.d.	93.7	n.d.	n.d.
THB11e prill (1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.7	n.d.	n.d.	n.d.	93.4	2.7	n.d.
TBH14 bronze lump	1.4	n.d.	0.5	n.d.	n.d.	n.d.	7.5	n.d.	0.3	n.d.	82.8	7.3	n.d.

Figure 10. Crucible fragments THB09A (top) internal surface and THB09D (bottom) base and lower body, exterior surface.

flux, forming a glassy phase with the silicate matrix of the ceramic. Oxygen is a sufficiently good "catalyst" to explain the results presented here, as lead oxidizes preferentially to copper under mild or lightly oxidizing crucible conditions. These conditions were necessary and proved efficient for the melting or recycling of bronze which appear to have been the main operations that can be firmly established based on the current findings.

Bronze alloy lump

The analysed amorphous lump of bronze (THB14) displays a ternary alloy composition with 82.8% Cu, 7.5% Sn and 7.3% Pb (Table 3). This composition is in general accordance with that determined for some of the bronze prills entrapped in the slag. It also contains traces of iron (0.3%) and in the microstructure minute inclusions of Zn were observed hinting again to the Pb/Zn mineralization of Thasos. The uses of copper alloys in the Archaic period were numerous, such as for tools, weapons, vessels, votive offerings and also for statues, of small or large proportions (Mattusch 1988, 14). For fabricating cast objects leaded bronze was more common due to the property of this alloy to better fill any intricate mould designs. Although the lead content of the analysed lump is typical for this time period, and indeed related to improved casting characteristics, it does not in itself prove any particular type of casting. Unfortunately, there are no analyses of Thasian bronze castings dating to this period to be used as comparative material. Some contemporary bronzes analysed elsewhere have an average lead content ranging between 1.5% and 6%. Although the statue of Apollo from Piraeus or the statues from Riace contain no lead, other Archaic or late Archaic works of bronze statuary were cast using ternary alloys, as for instance Zeus of Ugento: 3.58%, the Piot collection bronze: 5.68% and the Porticello philosopher: 1.5% (Haynes 1992, 87).

The question remains open concerning the raw materials for the Thasian bronze industry. Obviously,

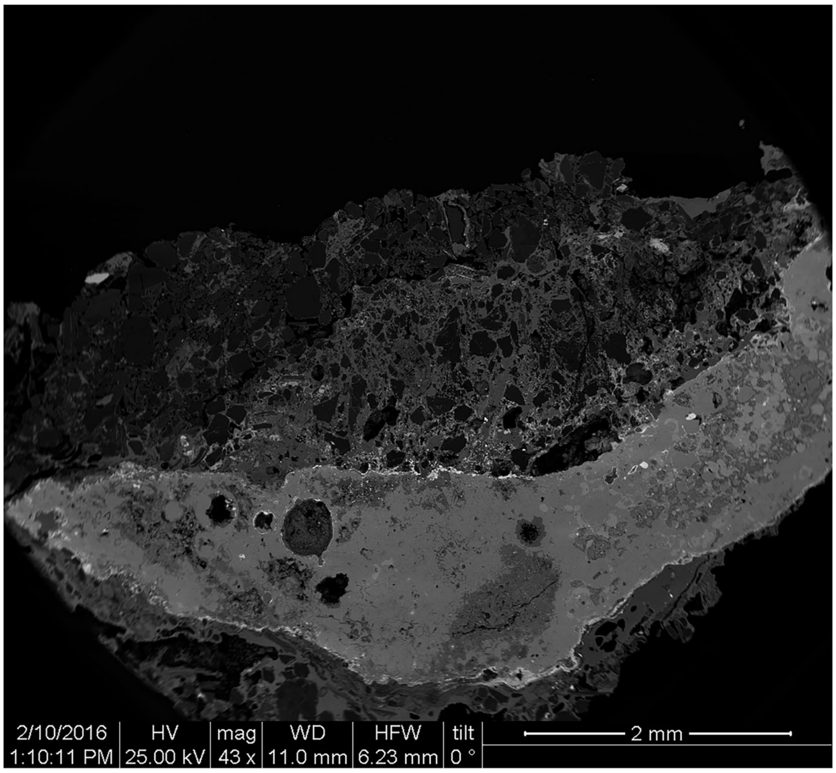

Figure 11. SEM/EDS photomicrograph of crucible THB09D. Three zones: peripheral ceramic (dark grey-upper part), porous interface (mid grey), slag zone (light grey-lower part).

Table 4. Chemical composition of crucibles (THB09D, THB09A) and slagged clay lining (THB11g) (SEM/EDS analysis by oxides).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O	K_2O	CaO	SnO_2	MnO	TiO_2	Fe_2O_3	CuO	ZnO	PbO
Crucible-THB09D (external zone bulk)	n.d.	2.3	13.3	60.0	3.3	n.d.	n.d.	2.9	n.d.	0.2	n.d.	0.4	3.3	10.1	n.d.	3.6
Crucible-THB09D (interface zone bulk)	n.d.	2.8	20.6	37.0	0.8	n.d.	n.d.	1.7	0.8	n.d.	n.d.	1.5	5.3	21.0	n.d.	8.1
Crucible-THB09D (interior zone-prills)	n.d.	n.d.	n.d.	1.4	0.8	n.d.	0.4	n.d.	n.d.	4.8	n.d.	n.d.	n.d.	91.1	n.d.	1.2
Crucible-THB09A (external zone--ceramic)	6.0	n.d.	24.5	61.6	n.d.	n.d.	n.d.	0.5	7.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Crucible-THB09A (interior zone-slag spot 1)	1.3	1.8	10.8	40.0	0.3	n.d.	n.d.	2.7	1.9	n.d.	0.7	0.5	4.1	3.4	n.d.	31.9
Crucible-THB09A (interior zone-slag spot 2)	1.1	1.3	8.8	31.1	n.d.	n.d.	n.d.	1.5	1.1	10.6	0.4	n.d.	2.9	7.3	n.d.	33.2
Slagged lining-THB11g (external zone bulk)	n.d.	n.d.	3.0	14.7	n.d.	n.d.	n.d.	n.d.	n.d.	18.9	n.d.	n.d.	1.1	17.2	1.05	43.7
Slagged lining-THB11g (interface zone bulk)	n.d.	n.d.	3.9	16.8	n.d.	10.2	n.d.	n.d.	n.d.	7.9	n.d.	n.d.	0.8	39.0	2.38	19.9
Slagged lining-THB11g (dendritic phase)	n.d.	n.d.	0.7	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	91.4	n.d.	4.9

artefacts made of copper alloys were often recycled and during this process lead quantities could have increased by repeated melting episodes. In Thasos as well as in the Lekani and Pangaeon region the exploitation of argentiferous lead ores produced large quantities of litharge which, at least in part, could have been used as a source of lead for ternary copper alloys.

Discussion and prospects

At its current stage, the study presented here substantiates what has been initially presumed concerning the production of bronze and iron in the workshop at Charitopoulos plot. At the same time, it offers secure data on the use of the metallurgical furnace that dates to the late Archaic period. Concerning iron production the macroscopic examination and limited analysis point to smithing activity. No finds that represent bloomery iron smelting or primary consolidation of the blooms have been recovered. Moreover the furnace could not have functioned as a smithing hearth; on the one hand its pear-shaped outline and the narrow opening could not have facilitated such working conditions. In general, there are not enough data concerning the actual space of iron working in form of hammerscale that point to the location of an anvil or other residues, thus the answer to this question may lie in the unexplored area of the workshop.

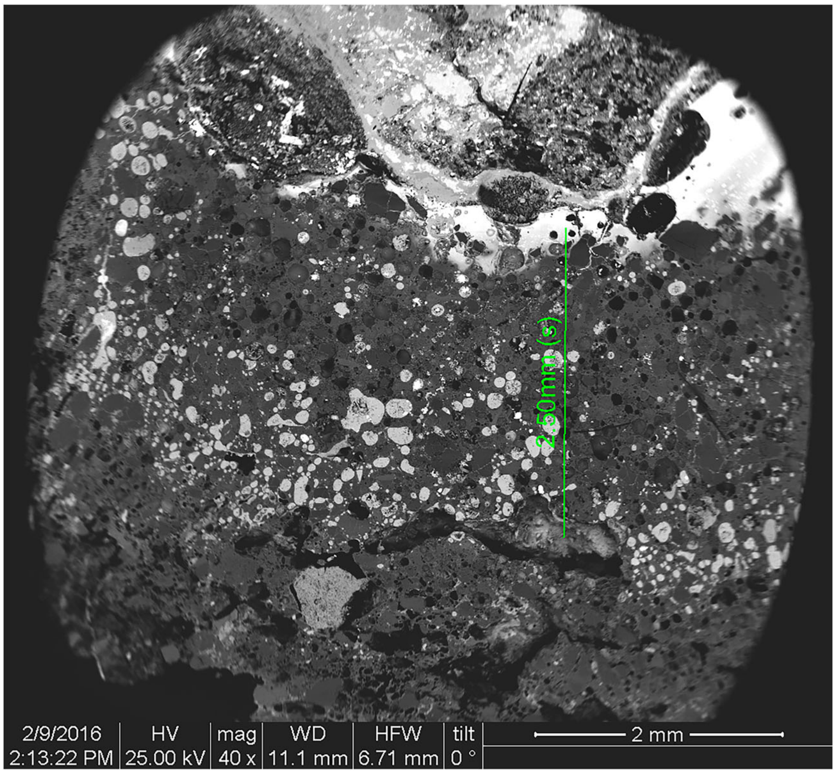

Figure 12. SEM/EDS photomicrograph of crucible THB09A. Zone of interface (2.50 mm width) between slag and ceramic material displaying a bloated surface and prills of copper.

Based on its characteristics and the associated finds it could be suggested that feature K4-8 is a crucible-furnace used for the melting of bronze. The combustion chamber with its flat bottom could facilitate the heating of crucibles placed about 15–20 cm below the tuyère level. The pear-shaped design with the opening on the frontal side could better facilitate natural draught that was necessary for more efficient operation. Its shape is rather unusual compared to the few circular excavated examples that have been published (Mattusch 1988, 228; Haynes 1992, 77). A crucible-furnace dating to the second century BC that was excavated at Kassope in Epirus had a circular combustion chamber holding two crucibles on its tiled floor and a wedge-shaped stoking area (Zimmer 1982, Figure 7). A smaller, fifth century BC circular crucible-furnace with no stoking area but also associated with casting-pits was excavated at Nemea (Miller 1977, 19). The pear-shaped Thasian example has no exact parallels and due to disturbance directly in front of its narrow opening it could not be estimated whether a stoking area or any casting-pits were associated with its use.

The crucible melting slag, clay lining and the actual crucible fragments are indicative of melting practices, which most likely involved the recycling of scrap metal or the melting of "fresh" ingots. Alloying may have taken place as well, but no direct evidence is available from the analysed remains. The leaded bronze that was used in the workshop was more frequently used for cast objects rather than those fabricated by hammering due to embrittlement caused by increased levels of lead (Staniaszek and Northover 1982, 264; Nerantzis 2015, 330). Small amounts of lead greatly reduce the viscosity of the melt and make it easier to pour. Although the addition of lead enhances significantly castability the disadvantage is that it remains insoluble in copper and bronze and appears as discrete inclusions which can propagate cracks during hammering (Northover and Evely 1995, 96).

Based on the existing results so far there is no indication that copper smelting or alloying was conducted at this workshop. Therefore it is not clear if copper was produced locally or if it was imported to the site in form of ingots. It should be noted though that the excavated area points to a quite large workshop, which has not been fully explored archaeologically and that some of its productive activities might remain elusive. Moreover, the coexistence of bronze melting and iron working remains appears as a good indication of the relatedness of these different metallurgical techniques, as they were practiced in the same workshop. Both activities were conducted in an internal area of the settlement as was the case with other metallurgical and metalworking practices in the city of Thasos witnessed for instance at Artemision and the Silenus quarter (Grandjean 1999). Eventually the issue of raw materials procurement will be investigated in relation to mining and smelting locations on the island (Sanidas et al. 2016). For the moment this study is not complete concerning the identification and provenance of the raw materials that were processed in the workshop.

Regarding the provenance of iron, as we have mentioned above, the presence of Ba is indicative being a diagnostic element of the local iron-bearing ores. The possibility of iron-bearing minerals deriving from the nearby Acropolis mine is under investigation as are the deposits of the SW part of the island (Vavelidis et al. 1988; Koželj and Muller 1988). Regarding copper, the detection of minute quantities of zinc and traces of silver in the slag might indicate the possible use of local deposits that exist at various sites on Thasos. At the same time the use of copper imported from the Thasian colonies on the Thracian mainland or elsewhere could not be excluded as equally possible alternatives. Thus three potential scenarios for the provenance of copper are under investigation: the acropolis mine and other mines on Thasos; the Thasian continent across the sea to the north or other sources at some distance from the north Aegean.

The current results are useful for approaching the *chaine opératoire* of Archaic bronze production and the organization of working space in a region of intensive metallurgical activity (Pichot 2010; Nerantzis and Papadopoulos 2013; Nerantzis, Bassiakos, and Papadopoulos 2016). This becomes even more significant for the crucial period of Greek colonial expansion in the north Aegean that has yielded limited, securely dated archaeometallurgical evidence. It also contributes new data to the existing body of metallurgical evidence from the city of Thasos that has been retrieved from Artemision, the Archaic Agora, the Silenus quarter and Heracles Gate (Grandjean 1999; Muller et al. 2004). Continuation of our investigation aims at a more precise reconstruction of the various stages of metal production and its correlation with the new data that are lately becoming available from a number of metal producing sites in Thasos and the Thracian mainland. A synthesis of the results is expected to elucidate issues of metals technology and organization of production before, during and after the period of Greek colonization in the north Aegean.

Note

1. *ADelt* 2009, (B) Chronicles.

Acknowledgements

The authors would like to thank Y. Bassiakos and E. Filippaki at N.C.S.R. "Demokritos" for the conduct of instrumental analysis of all the material presented and Anne Tichit for identifying and dating the ceramic sherds associated with the furnace context.

Notes on contributors

Nerantzis Nerantzis is an archaeologist with a PhD in Archaeological Science from the University of Sheffield, UK. He has worked for the Archaeological Service in northern Greece (Ephorates of Antiquites of Kavala-Thasos, Xanthi and Rhodope). Recently he was employed as a research associate at the University of Lille 3, HALMA, France. He has published two books on archaeometallurgy of northeastern Greece and several articles on prehistoric Eastern Macedonia and Thrace, mining and metal production in prehistory and the Byzantine period and experimental bronze working.

Giorgos Sanidas studied Archaeology at the University of Lille 3 and received his PhD in Greek Archaeology from the same university. In 2006 he became a Maître de Conférences at the School of Humanities and Social Sciences (SHS), University of Lille 3. He is responsible of the Research Project HeMEN (Habitat et Métallurgie en Grèce du Nord) in the framework of collaboration between the French School at Athens and the Greek Ministry of Culture.

Benjamin Jagou is an archaeologist specializing in iron metallurgy employed at INRAP. He is currently conducting PhD research at the Université de Paris 1, Panthéon-Sorbonne and is a collaborator of Project HeMEN.

Tony Kozelj is an architect and archaeologist employed at the French School at Athens. He is active in Thasos where he has undertaken numerous architectural/archaeological studies since the 1980s.

Konstantina Panoussi is an archaeologist and permanent member of the Archaeological Service active in Thasos where she undertook several excavations among which the excavated plot presented in the current article.

ORCID

Nerantzis Nerantzis http://orcid.org/0000-0001-6573-2518

References

Cooke, S. R. B., and B. V. Nielson. 1978. "Slags and Other Metallurgical Products." In *Excavations at Nichoria in Southwest Greece. Volume 1. Site, Environs, and Techniques*, edited by G. Rapp, and S. E. Arschenbrenner, 182–224. Minneapolis: University of Minnesota Press.

Craddock, P. T. 1976. "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman Civilisations. 1. The Greeks before the Archaic Period." *Journal of Archaeological Science* 3: 93–113.

Craddock, P. T. 1977. "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman Civilisations. 2. The Archaic, Classical and Hellenistic Greeks." *Journal of Archaeological Science* 4: 103–123.

Crew, P., and Th. Rehren. 2002. "High-temperature Workshop Residues from Tara – Iron, Bronze and Glass." *Discovery Programme Report* 6: 83–103.

Dungworth, D. 2000. "Serendipity in the Foundry? Tin Oxide Inclusions in Copper and Copper Alloys as an Indicator of Production Processes." *Bulletin of the Metals Museum* 32: 1–5.

Farci, C., M. Martinón-Torres, and D. González Álvarez. 2017. "Bronze Production in the Iron Age of the Iberian Peninsula: The Case of El Castru, Vigaña (Asturias, NW Spain)." *Journal of Archaeological Science: Reports* 11: 338–351.

Figueiredo, E., R. J. C. Silva, J. C. Senna-Martinez, M. F. Araújo, F. M. Braz Fernandes, and J. L. Inêz Vaz. 2010. "Smelting and Recycling Evidences from the Late Bronze Age Habitat Site of Baiões (Viseu, Portugal)." *Journal of Archaeological Science* 37: 1623–1634.

Glumac, P. D., and J. A. Todd. 1991. "Eneolithic Copper Smelting Slags from the Middle Danube Basin." In *Archaeometry '90*, edited by E. Pernicka and G. A. Wagner, 155–167. Heidelberg: Birkhauser Verlag.

Grandjean, Y. 1999. "Installations artisanales dans le Quartier de la porte du Silène à Thasos." In *Πρώτες Ύλες και Τεχνολογία από τους Προϊστορικούς Χρόνους ως Σήμερα*, Πρακτικά Διεθνούς Συνεδρίου, Λιμενάρια Θάσου, ΥΠΠΟ-ΙΗ' ΕΠΚΑ, edited by Ch. Koukouli-Chrysanthaki, A. Muller, and S. Papadopoulos, 161–169.

Haynes, D. 1992. *The Technique of Greek Bronze Statuary*. Mainz: Philipp von Zabern.

Klein, S., and A. Hauptmann. 1999. "Iron Age Leaded Tin Bronzes from Khirbet Edh-Dharih, Jordan." *Journal of Archaeological Science* 26: 1075–1082.

Koželj, T., and A. Muller. 1988. "La mine d'or de l'acropole de Thasos." In *Antike Edel und Buntmetallgewinnung auf Thasos, Der Anschnitt*, Beiheft 6, edited by G. A. Wagner and G. Weisgerber, 180–197. Bochum: Bergbau-Museum.

Mattusch, C. C. 1988. *Greek Bronze Statuary from the Beginnings Through the Fifth Century BC*. London: Cornell University Press.

Merideth, C. 1998. *An Archaeometallurgical Survey for Ancient Tin Mines and Smelting Sites in Spain and Portugal*. Oxford: Archaeopress.

Miller, S. 1977. "Excavations at Nemea, 1976." *Hesperia* 46: 19–20.

Muller, A., G. Sanidas, M. Sgourou, and M. Kohl. 2004. "O αποικισμός της Θάσου: Η επανεξέταση των αρχαιολογικών δεδομένων." *AErgoMak* 16 (2002): 57–71.

Nerantzis, N. 2015. "Experimental Simulation Study of Prehistoric Bronze Working: Testing the Effects of Work-hardening on Replicated Alloys." In *Archaeometallurgy in Europe III, Der Anschnitt*, edited by A. Hauptmann, and D. Modarressi-Tehrani, 329–335. Museum Bochum: Veröffentlichungen aus dem Deutschen Bergbau. Beiheft 26.

Nerantzis, N., Y. Bassiakos, and S. Papadopoulos. 2016. "Copper metallurgy of the Early Bronze Age in Thassos, North Aegean." *Journal of Archaeological Science Reports* 7: 574–580.

Nerantzis, N., and S. Papadopoulos. 2013. "Reassessment and New Data on the Diachronic Relationship of Thassos Island with Its Indigenous Metal Resources: A Review." *Journal of Archaeological and Anthropological Sciences* 5: 183–196.

Northover, J. P., and D. Evely. 1995. "Towards an Appreciation of Minoan Metallurgical Techniques." *Annual of the BSA* 90: 83–105.

Papadimitriou, G., C. Tsaimou, and M. Vardavoulias. 1992. "Bronze Production During the Hellenistic Period in the Rhodes Island." In *Archaeometallurgia Ricerche e Prospettive*, edited by E. Antonacci-Sanpaolo, 227–237. Bologna: Editrice Bologna.

Pichot, V. 2010. "Rapports 2009. Thasos, prospection minière." *BCH* 134: 519–522.

Rademakers, F. W. 2015. "Into the Crucible. Methodological Approaches to Reconstructing Crucible Metallurgy from

New Kingdom Egypt to Late Roman Thrace." Unpublished PhD thesis, University College London.
Rademakers, F. W., and Th. Rehren. 2016. "Seeing the Forest for the Trees: Assessing Technological Variability in Ancient Metallurgical Crucible Assemblages." *Journal of Archaeological Science Reports* 7: 588–596.
Rademakers, F. W., Th. Rehren, and E. B. Pusch. 2013. "Bronze Production in Pi-Ramesse: Alloying Technology and Material Use." In *Mining for Copper: Essays in Honor of Professor Beno Rothenberg*, edited by E. Ben-Yosef and Y. Goren. Tel Aviv: Institute of Archaeology of Tel Aviv, in press.
Rademakers, F. W., Th. Rehren, and M. M. Voigt. 2017. "Bronze Metallurgy in the Late Phrygian Settlement of Gordion, Turkey." *Archaeological and Anthropological Sciences*, doi:10.1007/s12520-017-0475-8.
Rehren, Th. 2001. "Die Schmelzgefässe aus Cham-Oberwil." In *Cham-Oberwil, Hof (Kanton Zug). Befunde und Funde aus der Glockenbecherkultur und der Bronzezeit*, edited by U. Gnepf Horisberger, and S. Hämmerle, 118–131. Basel: Taschenbuch–13.
Renzi, M., and S. Rovira. 2016. "Metallurgical vessels from the Phoenician site of La Fonteta (Alicante, Spain): A Typological and Analytical Study." In *From Bright Ores to Shiny Metals. Festschrift for Andreas Hauptmann on the Occasion of 40 Years Research in Archaeometallurgy and Archaeometry*, edited by G. Körlin, M. Prange, T. Stöllner, and Ü. Yalçin, 143–166. Bochum: VML Vlg Marie Leidorf.
Rostoker, W., and J. R. Dvorak. 1991. "Some Experiments with Co-smelting to Copper Alloys." *Archaeomaterials* 5: 5–20.
Rostoker, W., M. McNallan, and E. Gebhard. 1983. "Melting/smelting of Bronze at Isthmia in Greece." *Journal of the Historical Metallurgy Society* 17: 23–27.
Rovira, S. (2011–2012) *Arqueometalurgia experimental en el departamento de Prehistoria y Arqueología de la U.A.M.*, Cuadernos de Prehistoria y Arqueología Universidad Autónoma de Madrid 37–38, 105–120.
Rovira, S., I. Montero-Ruiz, and M. Renzi. 2009. "Experimental Co-smelting to Copper-tin Alloys." In *Metals and Societies, Studies in honour of Barbara S. Ottaway*, Universitätsforschungen zur prähistorischen Archäologie, edited by T. K. Kienlin and B. W. Roberts, 407–414. Bonn: Habelt.
Sanidas, G., Y. Bassiakos, M. Georgakopoulou, E. Filippaki, B. Jagou, and N. Nerantzis. 2016. "*Polykmetos sideros*: le fer en Grèce antique à partir de quelques recherches récentes." *Revue Archéologique* 2016/2: 279–301.
Sanidas G., B. Jagou, T. Kozelj, N. Nerantzis, and K. Panoussi. in press. "Υστεροαρχαϊκό εργαστήριο μεταλλουργίας στη Θάσο (Λιμένας, οικ. Δ. Χαριτόπουλου): Έρευνες κατά το 2013-2015." *AErgoMak* 29.
Staniaszek, B. E. P., and J. P. Northover. 1982. "The Properties of Leaded Bronze Alloys." In *Proceedings of the 22nd Symposium on Archaeometry*, edited by A. Aspinal and S. E. Warren, 262–272. University of Bradford.
Vavelidis, M., G. Gialoglou, E. Pernicka, and G. A. Wagner. 1988. "Die Buntmetall und Eisen- Mangan-Lagerstatten von Thasos." In *Antike Edel und Buntmetallgewinnung auf Thasos, Der Anschnitt*, Beiheft 6, edited by G. A. Wagner and G. Weisgerber, 40–58. Bochum: Bergbau-Museum.
Zimmer, G. 1982. *Antike Werkstattbilder*. Berlin: Gebrüder Mann Verlag.
Zwicker, U., H. Greiner, K.-H. Hofmann, and M. Reithingerm. 1985. "Smelting, Refining and Alloying of Copper and Copper Alloys in Crucible Furnaces During Prehistoric up to Roman Times." In *Furnaces and Smelting Technology in Antiquity*, edited by P. T. Craddock and M. J. Hughes, 103–116. London: British Museum.