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ABSTRACT
The paper examines diachronically the technological knowledge and the level of copper metallurgy at Kastro Palaia, Volos, in Magnesia, examining various objects with dates from the Early Bronze Age through to the Early Christian era. Of the 70 objects that have been examined so far using pXRF, a small sample was selected for further metallographic and chemical analyses. In this way, the manufacturing processes for the production of each object were identified, as well as the alloy used. Combining the results of these two methods with the typology of the objects provided safe conclusions concerning the technological knowledge and the specialisation of metal production at Kastro Palaia from the Bronze Age to the Early Christian era. In the end, the potential provenance of the copper was also examined.

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Iolkos; copper metallurgy; copper ores; XRF; SEM-EDS; lead isotopes

1. Introduction

Kastro Palaia, the historical nucleus of the city of Volos in North Central Greece, is an artificial hill, formed by continuous habitation since prehistoric times. It commands the most important exit from the fertile Thessalian plain, the breadbasket of Greece. The site, identified with ancient Iolkos, is famous as the starting point of Jason's metallurgical reconnaissance to the Black Sea and further on to Georgia, in search of the Golden Fleece (Decourt, Nielsen, and Helly 2004: 719, no. 449) (Figure 1).

Over the past century excavations have revealed evidence for several Bronze Age elite settlements in and around the bay of Volos, with sophisticated architectural remains, such as tholos tombs and high-status material finds (Skafida, Karnava, and Olivier 2012; Skafida et al. 2015). The excavations of Dimitris and Maria Theocharis at Kastro Palaia in the 1950s unearthed buildings belonging to the urban nucleus of the settlement, including metal workshops, while more recent investigations by the Ephorate of Antiquities of Magnesia[1] revealed an organised settlement of the Bronze Age (3000–1100 BC) (Theocharis 1957, 1958a, 1958b, 1961, 1962; Theocharis and Theochari 1970).

During the Early Iron Age and Iron Age (10th–8th centuries BC) the settlement continued to flourish. Although not extensively excavated, the cemetery to the north and northwest of the Palaia hill reveals that habitation continued on the site until the Early Christian period; notable among the architectural finds are buildings such as a workshop for glass production (Smirniou et al. 2017), bath installations, an aqueduct, and the remains of a monumental Doric temple that has been attributed to Artemis Iolkia (Skafida 2012).

A five-year inter-disciplinary project was initiated in 2009, aiming at the study, re-evaluation and publication of the archaeological evidence from the excavations of D. R. Theocharis in 1956–1961 (Stamatopoulou 2011). It has become apparent that during the Late Bronze Age Kastro Palaia constituted the northernmost administrative and commercial centre of the Mycenaean world, with an archive of Linear B clay tablets and palatial-type architecture with plastered walls and floors, and timber frame walls (Skafida et al. 2015). The study of the ceramic material shows far-reaching connections of the site with other sites in the southern Greek Mainland, such as the Argolid, Euboea, Aegina, Crete, as well as the Syro-Palestinian coast.

In order to understand the methods of the production and distribution of metal artefacts, and any changes that may have occurred over time, it is necessary to study the physical and chemical properties of these artefacts through metallurgical methods. This paper aims to initiate this discussion by examining metal object manufacture at Kastro Palaia. The results gained from the selected samples can then be used to

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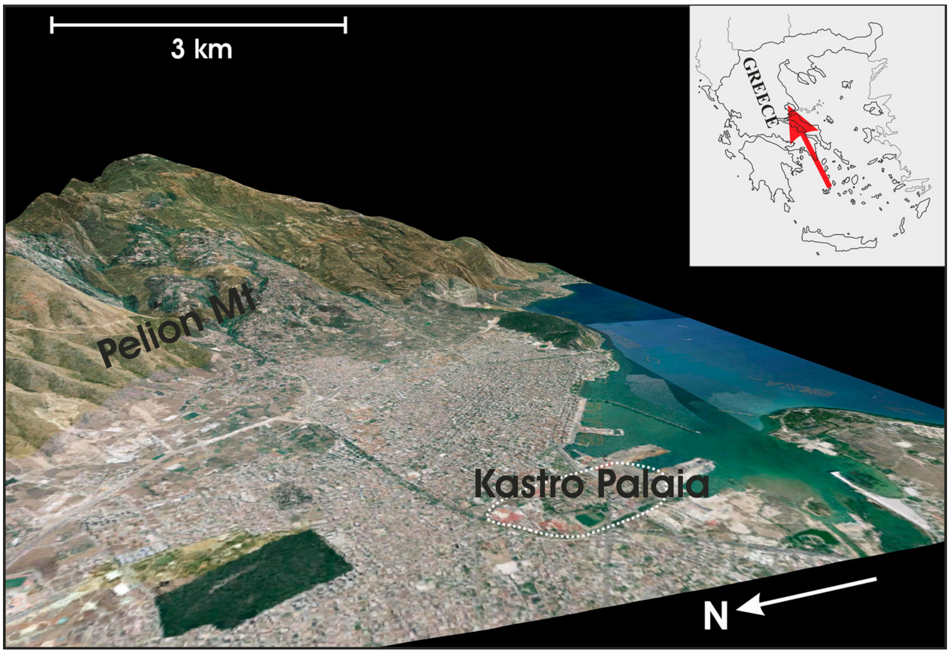

Figure 1. Geographic map of Kastro Palaia/ancient Iolkos in the modern city of Volos, Greece.

address the question whether the metallurgical activities on the hillock of Kastro Palaia were a specialised industry or not (Rehren et al. 2013).

In general, there are two main factors involved in craft specialisation: the number of persons involved in the production and the manufacturing skills which are gained from the repetition of the procedures (Tselios 2006).

Normally, two kinds of evidence are used to identify craft specialisation (Schiffer 1991), direct evidence related to the place where production takes place and indirect indications concerning the organisation of production, which can be detected in the final objects. In archaeology, direct evidence is almost completely absent, and information is predominantly obtained from the final metal objects. However, in our case, we have some information of direct evidence and this helped us to better understand the craft specialisation.

2. Main aspects of the study

The main aspect of this study is the technological examination of the metal artefacts found in the excavation of D. Theocharis, where a metallurgical workshop was found, as well as from the nearby sites within the hillock of Kastro Palaia; they cover a chronological period from the Early Bronze Age to the Early Christian period. This examination includes the determination of the alloy recipes and the metalworking practices performed for the manufacture of the objects, a discussion of the potential provenance of the raw metal used, and finally the identification of other objects related to metallurgical activities. Overall, the study contributes to the interpretation of the economics of a specific chronological period and to the technological knowledge of production and the availability of resources.

3. The material

The studied material consists primarily of metal artefacts, but also includes a piece of casting debris found at Kastro Palaia, a metallurgical slag sampled from Pelasgia, an ancient metallurgical area in Mt. Othrys, and copper ores from Mt. Pelion and Mt. Chalcodonion. This study is a follow-up to the previous one which included the crucibles and slags that were found in the metallurgical workshop (Rehren et al. 2013). Several crucible fragments (Figure 2) from this specific site are linked to the Palace workshop and its predecessor building and are dated both to the EBA and the LBA period; chemical analyses of metallurgical remains from within the crucibles indicate the range of alloy compositions for which they were used, including arsenical copper and tin bronze.

3.1. Copper and copper alloy objects

The objects selected are representative of the total amount of the objects found at Kastro Palaia. As this study is not based on a typological approach, the intention is not to study all objects from all sites on and around the hillock of Kastro Palaia, but to take samples from as many types of objects as possible, since our intention is to obtain information about all the artefacts by studying only a part of them (Drennan 1996; Orton 2000). Of course, we were not able to select as many objects as we wished due to their bad preservation state and the fact that a very small sample had to be cut from the object for the analyses. Thus, the

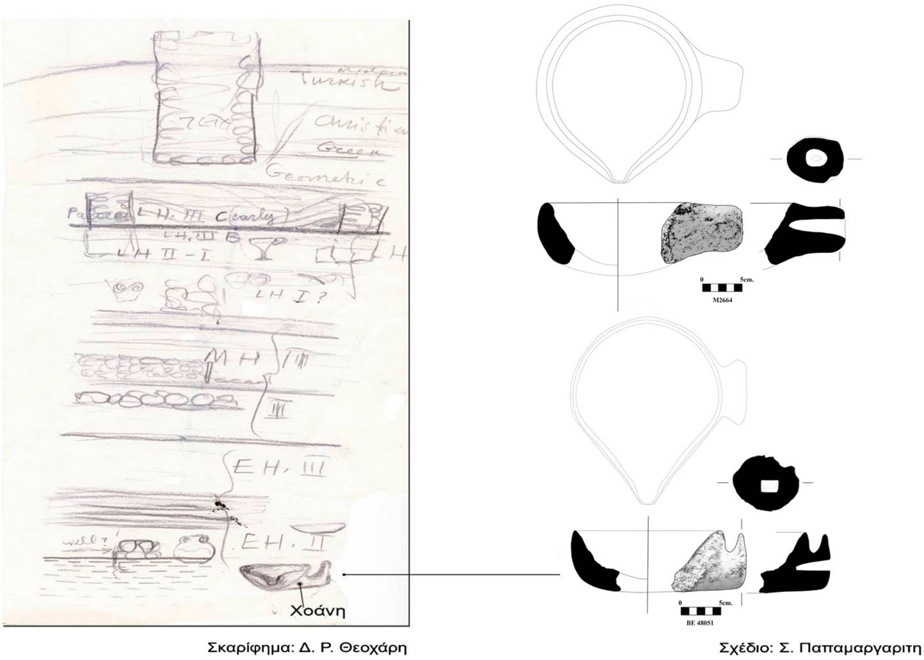

Figure 2. Fragments of crucibles dated to EBA and LBA (after Rehren et al. 2013).

best solution was to begin with non-invasive analysis in situ using the pXRF of the local Ephorate of Antiquities and then select objects to be sampled on the basis of the results obtained.

The 70 objects selected for this study from Kastro Palaia (Table 1) have been found during excavations of the Bronze Age metallurgical workshops and settlement, the Early Iron Age tombs, the Iron Age settlement and finally from the settlement dated to Hellenistic, late Roman and early Christian periods. The intensive building activity during the Early Christian years resulted in considerable disruptions to the underlying layers. Thus, the Archaic period is not presented here due to the poor dating of the objects.

The assemblage consists mainly of daggers, fibulae, buckles, pins, bracelets (Figure 3), rings, earrings, an arrow head, a piece of copper slag and some other objects which cannot be identified due to their bad preservation state.

3.2. Copper ore sources in the area

In our attempt to detect and record ancient local sources of copper, detailed mapping of ores was conducted and three main areas with copper minerals were found. The ores are located in Mt. Othrys, Mt. Pelion and Mt. Chalcodonion, respectively, where copper minerals such as malachite and azurite were sampled.

In Mt. Othrys area copper minerals are found among scattered doleritic veins (Koutsovitis 2009). Sulfides such as pyrite have been deposited from hydrothermal fluids (Sovatzoglou-Skounaki 1983). Native copper has been found in a number of altered hydrothermal veins. Ancient metallurgical activity is located in southern Mt. Othrys, including a number of ancient mines and several slag heaps (Tizzoni et al. 2008). Sherds among the slags date to Hellenistic times. A metallurgical slag from the area of Pelasgia (S. Othrys) was sampled during the present study.

In Mt. Pelion, ore containing malachite and goethite was sampled from an ancient mine near Ksourichti village. Several deposits of galena, pyrite, chalcopyrite and sphalerite are located in the area from Zagora to Ksourichti village in northeastern Pelion. Sherds found within the mines imply a Roman exploitation phase in the area.

In Mt. Chalcodonion, at an open pit near Kokkina village copper carbonate hydroxides such as malachite and azurite in veins among the ophiolitic series were sampled. Mt. Chalcodonion hosts several copper deposits and probably the mountain is named after its copper deposits (Chalcodonion = gives copper). Modern exploitation probably destroyed any ancient mining evidence.

4. Methods

4.1. Analysis in situ in the laboratory – portable X-ray fluorescence

Initially, non-invasive analysis with pXRF was used *in situ* to study most of the objects at the Ephorate's Conservation Laboratories. The pXRF used is a portable, though not handheld, ED-XRF spectrometer developed at the Institute of Nuclear Physics, NCSR Demokritos. According to Karydas et al. (2009, 813–814),

> the XRF spectrometer consists of an Rh-anode side-window, low power X-ray tube (50 W, 40 kV, 125 μm Be window), a PIN X-ray detector and a

Table 1. List of the 70 objects selected for the analysis.

Date	Object	Object ID	Items
Late Bronze Age	Pins	M 2681,002	5
		M 2681,008 (h)	
		ID 17717	
		ID 17159	
		ID 17760	
	Daggers	M 2681,005	3
		M 2219	
		ID 17760	
	Nail heads	M 2681,002	1
	Ring/hoop:	M 2684,001	1
	Unidentified object	ID 17142	1
1400 BC	Arrow head	AE 04	1
1400 BC	Casting debris	AE 03	1
Early Iron Age	Fibulae	M 2191,001	12
	Foot of fibula	M 2191,001a	
		M 2191,002	
		M 2191,002a	
		M 2192	
		M 2195	
		M 2196	
		M 2678,001	
		M 2678,006,001	
		M 2678,006,002	
		M 2678,003	
		M 2678,005	
	Pins	ID 17719	1
	Rings	M 2601	5
		M 2194	
		M 2218	
		M 2681,009	
		ID 17188	
	Bracelets	M 2193	2
		M 5562	
	Wire	M 2601	1
	Awls	M 2681,004	2
		M 2604	
	Dagger	ID 17711	1
	Needle	ID 17707	1
	Nail head	M 2681,001	1
Iron Age	Pins	BE 1011	4
		BE 1010,001	
		BE 1010,002	
		ID 17049 (BE 2860,001)	
	Sheet	ID 17721	1
Hellenistic/Roman	Earrings	M 2603,003 (c)	4
		M 2603,003 (e)	
		M 2603,004 (d)	
		M 2603,004 (f)	
	Ring	M 2603,004 (a)	1
Late Roman/Early Christian 4th–7th AD	Ring	BE 556	1
	Bracelet	BE 548	1
	Sheets	ID 17746	2
		BE 549	
	Nail	BE 553,001	1
	Buckles	BE 553,002	2
		BE 558,002	
	Pins	ID 17714	2
		BE 557	
	Unidentified object	ID 17176	1
	Wires	BE 558,001	3
		BE 561,001	
		BE 561,002	
	Foot of statuette	ID 17187	1
Not safely dated	Tool	ID 17195 (M5683.4)	1
	Rod	ID 17189	1
	Ring	BE 620	1
	Sheets	ID 17191	2
		ID 17192 (M5683.7)	
	Pins	ID 17190 (M5683.6a)	2
		ID 17194b (M5683.9)	

Figure 3. Bracelet M5562 (found in child burial) dated to EIA period.

multichannel analyzer (MCA) card. The analytical range of this portable XRF spectrometer extends from Z = 14 (silicon) up to Z = 92 (uranium). The device can operate under two distinct conditions: one unfiltered mode with the voltage set at 15 kV and a filtered one with the voltage set at 40 kV. Two laser pointers are mounted in the spectrometer head in such a way that the intersection point of their beams coincides with the crosspoint of the incident X-ray beam axis and the detector axis. The beam spot at the sample position has a diameter of less than 2 mm.

The spectrometer head is attached to a movable mount that allows easy movement in the *X* and *Y* directions. The sample is mounted on a stage that can be moved in the *Z* direction.

4.1.1. Optical microscopy (OM)

Samples were taken from selected objects for metallographic analysis (Scott 1991; Tselios 2006). This analysis involved mounting of the samples in resin blocks and polishing in order to provide a clean cross or longitudinal section for analysis. Examination by optical microscopy allowed the determination of the manufacturing procedures used in the creation of the objects (Scott 2010) as well as any alteration occurring due to corrosion products (Tylecote 1976; Scott 1991) and whether any microstructure, such as grain deformation due to hammering, typical casting structures etc was obvious (Buchwald and Leisner 1990; Scott 1991). The samples were etched for 5 seconds in alcoholic ferric chloride solution ($FeCl_3$) (Scott 1991, 2002). In some cases, a sound metal core was preserved, allowing the performance of reliable chemical analysis, while in most of them only a little or no metal was left, with the layers of corrosion predominating; however, the corrosion pattern as well as the metallographic structure preserved in the corrosion allowed, in most cases, to identify the original surfaces of the objects.

The Optical Microscopy was performed at the Archaeological Materials Science (AMS) Laboratories of UCL Qatar.

4.2. Scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS)

After the metallographic examination, selected samples were subjected to chemical analyses using an JEOL JSM-6610LV Scanning Electron Microscope equipped with an Oxford Instruments X-Max^N Energy Dispersive Spectrometer, at the AMS Laboratories of UCL Qatar, in order to gain a more detailed understanding of the chemical composition of the artefacts and, in general, of the alloys used. On each sample surface, multiple area measurements (6–12) were taken, in order to ensure that the analytical results of each sample were representative of the object.

4.2.2. Lead isotopic analysis (LIA)

As an initial exploration to discuss the potential provenance of the metal, the abundance ratios of the lead isotopes of five samples of selected objects from Kastro Palaia, two samples of copper ores, from Kokkina near Mt. Chalcodonion and Mt. Pelion, respectively, and one slag from the area of Pelasgia were determined in order to gain useful information about the raw material. The analyses were carried out by Dr Sabine Klein at Goethe University in Frankfurt am Main, Germany.

The choice of the metal samples was made based on their trace element contents and archaeological context. The Pb concentration in one of the five artefact samples was too low for secure determination of its lead isotope ratios, so it was excluded from the final results.

5. Results and discussion

5.1. The use of alloys by period

5.1.1. Early Bronze Age

Apart from an Early Bronze Age crucible that was found at Kastro Palaia and has revealed the use of both arsenical copper and tin bronze (Rehren et al. 2013) no other objects of this date were found at the hillock. However, there are some metal objects from nearby Late Neolithic and Early Bronze Age sites, i.e. Sesklo, Dimini, Petromagoula (Tsountas 1908; McGeehan-Liritzis and Gale 1988), Pefkakia (Theocharis 1973) and the Late Neolithic settlement in Mikrothives (the material is still under study), where both arsenical copper and tin bronze were used for the manufacture of objects in this early period.

5.1.2. Late Bronze Age

The Late Bronze Age samples found both in the metallurgical workshops and the settlement show that unalloyed copper, low and medium tin bronze as well as arsenical bronze were used. In the cases where arsenic is present in the range of c. 0.5–0.8 wt%, this could be attributed to the possible use of arsenical copper scrap in the tin bronze melt, however, the use of ores with moderate As content cannot be excluded (McGeehan-Liritzis and Gale 1988; Radivojević et al. 2013) (Table 2). In addition to the evidence for working from the crucibles and moulds, there is a newly-analysed piece of casting debris which shows a fully corroded as-cast dendritic structure of the alloy (Figure 4) with relict delta phase in the original metal area, and the formation of tin oxide crystals in the outer parts (Figure 5). The shape and composition of these crystals are typical for the "hot oxidation" or partial burning of bronze during casting, and therefore further evidence for the activity at the workshop in Kastro Palaia.

Weapons are mainly manufactured with Cu–Sn alloy. In one case we found c 1 wt% Pb by pXRF analysis (dagger M 2219); this could be attributed possibly to recycling since lead is unusual to have been alloyed intentionally for weapons, unless they were to be used only for funerary purposes. Unusually, the object shows only c 5 wt% Sn, only half of what one would expect for a Mycenaean dagger. However, the results may have been affected by corrosion, suppressing the tin and enhancing the lead reading during surface

Table 2. Quantitative XRF and SEM-EDS results of the LBA samples.

LBA settlement	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	As	Pb	Sn	Sb
	ID 17760	Dagger	SEM-EDS	Metal	0.3	nd	89	0.3	nd	10	nd
	M 2681,005	Dagger	XRF	Corroded	0.5	0.2	92	0.4	0.3	6	0.2
	ID 17760	pin	SEM-EDS		0.4	nd	83	2	6	8	nd
	ID 17159	Pin	SEM-EDS	Metal	nd	nd	99	nd	nd	nd	nd
	ID 17717	pin	SEM-EDS	Corroded	nd	nd	89	nd	1	0.2	nd
	M 2681,002	pin	XRF	Metal	0.2	0.2	96	0.3	0.2	2	0.1
	ID 17142	Unidentified object	SEM-EDS		nd	nd	98	2	nd	nd	nd
LBA workshop	M 2219	Dagger[2]	XRF	Corroded	1	0.3	91	0.4	1	5	0.8
	M 2681,002	Nail head[3]	XRF	Corroded	0.2	0.2	96	0.2	nd	2	0.7
	M 2681,008	Pin	XRF	Corroded	1	0.4	88	0.6	1	8	0.5
	M 2684,001	Ring/hoop	XRF		1	0.3	92	0.5	nd	4	0.3
	AE 3	Arrow head	XRF	Corroded (surface)	10	0.2	85	0.5	nd	1	1
			SEM-EDS	Corroded (core)	0.4	nd	61	0.5	3	14	nd
	AE 4	Casting debris	SEM-EDS[4]		1.4	nd	37	1	nd	4	nd

Note: All values in wt%.

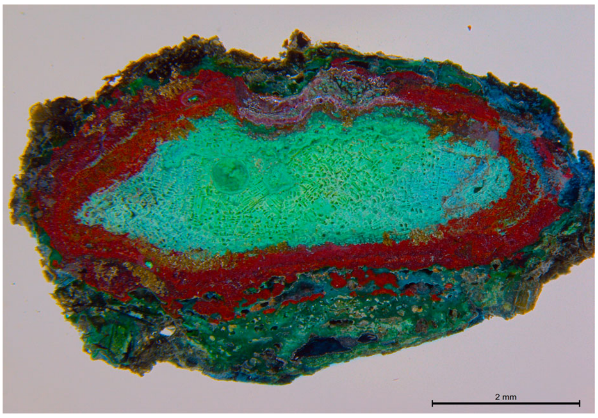

Figure 4. Casting debris AE04 dated to LBA. Fully corroded, shows the as-cast dendritic structure of the alloy. Optical microscopy image (see image for magnification).

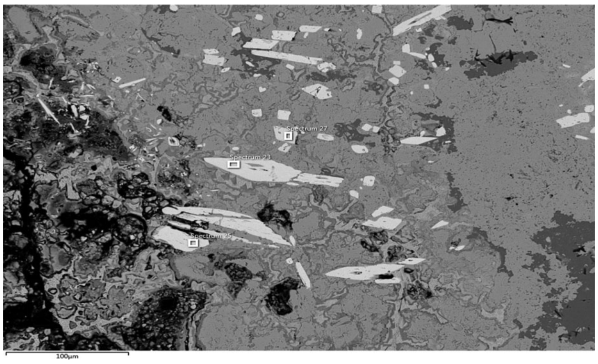

Figure 5. Casting debris AE04 dated to LBA. SEM image showing tin oxide crystals in the outer parts.

analysis. Another dagger, whose metal core was analysed by SEM-EDS (ID 17760), yielded 10 wt% Sn and no detectable lead (Table 2). The jewellery, i.e. pins and rings, is manufactured either of copper or tin bronze. The nail head is made of Cu–Sn alloy and the unidentified object is made of arsenical copper (Cu–As). One object, an arrow head with a square stem (Figure 6a, b), was analysed both by pXRF and by SEM-EDS; there is a remarkable discrepancy in the results, with the SEM-EDS data of the inner part of the stem giving high tin readings demonstrating that this used to be a good-quality bronze, while the external pXRF analysis only shows minimal tin content. This difference is most likely due to the different solubility of copper and tin corrosion products, with the copper salts migrating out from the corroding bronze and being deposited at the outer surface of the object, while the tin (hydr)oxide remains fixed in the original position of the metal, seemingly enriched due to the loss of copper. Thus, the SEM-EDS tin concentration is certainly too high, while the pXRF data is certainly too low. The original composition would have been somewhere in between the two, but the complete corrosion of the object makes it impossible to determine the original tin content of the alloy.

5.1.3. Early Iron Age

The Early Iron Age samples include a variety of objects mostly consisting of jewellery and excavated both from the settlement and the tombs found in the site, including a fibula analysed for its lead isotope ratios (see below). In their majority the objects are made of tin bronze, while in few cases arsenic is present in an amount of 1%. This could be again attributed either to recycling or to the use of ores with moderate arsenic content (Table 3). The outlier is a dagger with ID number 17711 which is made of almost pure copper and includes 0.2% Se.

5.1.4. Iron Age

Only five samples of the assemblage belong to this period, mainly pins. All varieties of copper alloys are present here, i.e. unalloyed copper, arsenical copper, tin bronze and arsenical bronze (Table 4). The particular observation here is that arsenical copper is still in use even in this late period.

5.1.5. Archaic period

No samples from the archaic period were selected as they were few and very badly corroded.

(a) (b)

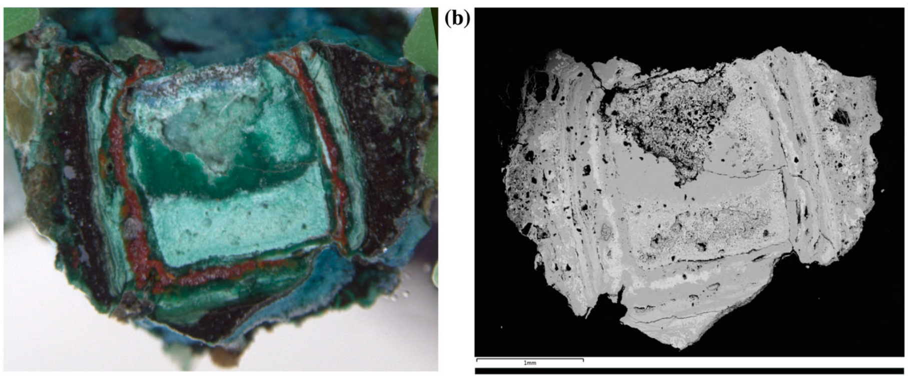

Figure 6. (a) Arrow head AE03 dated to LBA. Optical microscopy image; see Figure 6(b) for scale. (b) Arrow head AE03, showing the original square cross section and various corrosion layers (different grey shades). SEM image X30.

Table 3. Quantitative XRF and SEM-EDS results of the EIA samples.

EIA tombs	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	As	Pb	Sn	Sb
	M 2191,001	Fibula	XRF	Corroded	0.2	0.1	97	0.2	0.2	0.5	0.1
	M 2191,001 a	Fibula	XRF	Corroded	0.6	0.1	81	0.4	2	16	0.1
			SEM-EDS		1	nd	68	0.2	1	13	nd
	M 2191,002	Fibula	SEM-EDS[5]	Corroded	0.1	nd	88	0.1	0.3	7	nd
	M 2192	Fibula	XRF	Corroded	2	0.2	95	0.4	nd	1	0.6
			SEM-EDS		0.1	nd	86	0.5	0.5	12	bdl
	M 2195	Fibula	XRF	Corroded	0.8	0.3	82	0.4	1	15	0.7
	M 2678,001	Fibula	XRF	Corroded	2	0.3	96	0.3	nd	1	0.4
			SEM-EDS		0.8	nd	92	nd	nd	4	nd
	M 2678,006,001	Fibula	XRF	Corroded	0.2	0.2	98	0.5	nd	0.4	0.5
			SEM-EDS		0.3	bdl	91	bdl	nd	8	nd
	M 2678,006,002	Fibula	XRF	Corroded	2	0.3	91	0.6	nd	4	0.4
			SEM-EDS[6]		0.2	nd	46	1	0.5	20	nd
	M 2196	Fibula	XRF[7]	Metal	1	0.2	92	0.5	1	4	0.5
			SEM-EDS		nd	0.1	92	0.3	0.4	6	0.1
	M 2193	Bracelet	XRF	Corroded	3	0.3	95	0.5	nd	0.3	0.6
	M 5562	Bracelet	XRF	Metal	0.7	0.2	95	nd	nd	4	0.1
	M 2194	Ring	XRF	Corroded	4	0.2	91	0.5	nd	4	0.3
	M 2601	Ring	XRF	Corroded	1	0.2	88	0.3	0.5	10	nd
			SEM-EDS[8]		nd	nd	84	0.2	1	13	nd
	M 2601	Wire	SEM-EDS[9]		nd	nd	64	0.2	1	14	nd
	M 2681,001	Nail head	XRF	Corroded	0.4	0.1	97	0.2	nd	1	0.2
	M 2681,009	Ring	XRF	Corroded	8	0.1	76	1	nd	13	0.7
	ID 17711	Dagger	SEM-EDS[10]	Corroded	0.4	nd	98	0.1	0.3	0.2	nd
	ID 17707	Needle	SEM-EDS[11]	Corroded	0.3	nd	69	0.1	1	12	nd
	ID 17719	Pin	SEM-EDS[12]	Corroded	0.1	nd	89	0.5	3	6	Nd
	ID 17188 (M 5683)	Ring	XRF	Corroded	1	0.3	71	1	nd	26	0.3
			SEM-EDS[13]	Metal	0.3	nd	86	1	0.8	9	nd
	M 2678,005	Foot of fibula	XRF		1	0.1	95	0.6	nd	1	0.7
			SEM-EDS		0.2	nd	86	0.5	0.4	13	nd
	M 2678,003	Fibula	XRF	Corroded	0.3	0.4	92	1	nd	2	0.8
	M 2218	Ring	XRF	Corroded	5	0.2	87	0.5	nd	5	0.8
	M 2681,004	Awl	XRF	Corroded	2	0.2	91	0.4	nd	6	0.3
	M 2604	Awl	XRF	Not very clean metal	3	0.2	85	1	7	3	0.1

Note: All values in wt%.

5.1.6. Hellenistic-Roman period

Five samples belong to this period, mostly earrings and one ring and they have been manufactured with gun metal (Table 5). Two of them have been analysed by both pXRF and SEM-EDS; in both cases the pXRF analyses report very high lead concentrations which are not at all found in the SEM-EDS analyses of the sound metal cores. Most likely, this is due to the known enrichment of lead corrosion products on the surface of the metal (Orfanou and Rehren 2015), even from very low initial concentrations. In contrast, the zinc values are much lower in the pXRF analyses, only about half of the values found in the metal core. Zinc typically is removed preferentially from the near-surface part of corroding brass, due to the good solubility of its corrosion compounds under burial conditions; the SEM-EDS data of around 13 wt% Zn in the alloy are consistent with the date of the objects, and

Table 4. Quantitative XRF and SEM-EDS results of the Iron Age samples.

Iron Age	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	As	Pb	Sn	Sb
	BE 1010,001	Pin	XRF	Corroded	0.7	0.2	88	0.5	nd	10	0.1
			SEM-EDS[14]		0.4	nd	90	0.5	nd	6	nd
	BE 1010,002	Pin	XRF	Corroded	0.2	6	90	0.3	2	0.2	0.2
	BE 1011	Pin	XRF	Corroded	4	0.2	93	2	nd	0.1	0.3
			SEM-EDS[15]	Metal	nd	nd	98	2	nd	nd	nd
	ID 17049 (M 2860,001)	Pin	SEM-EDS[16]	Corroded	0.1	nd	68	6	1	5	nd
	ID 17721	Sheet	SEM-EDS[17]	Corroded	0.2	nd	76	nd	nd	nd	nd

Note: All values in wt%.

Table 5. Quantitative XRF and SEM-EDS results of the late Hellenistic/Roman samples.

Hellenistic-Roman	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	Zn	As	Pb	Sn	Sb
	M 2603,003c	Earring	XRF	Metal	0.5	0.2	75	7	0.3	13	4	0.5
			SEM-EDS[18]	Metal	0.2	-	83	13	0.1	nd	3	0.1
	M 2603,003e	Earring	XRF	Metal	0.6	0.1	78	11	0.4	6	4	0.3
	M 2603,004d	Earring	XRF	Metal	1	0.1	67	6	0.2	23	2.5	0.2
			SEM-EDS	Metal	0.1	nd	83	13	nd	nd	3	0.1
	M 2603,004f	Earring	XRF	Metal	0.8	0.2	80	13	0.4	3	2	0.6
	M 2603,004 a	Ring	XRF	Metal	1	0.1	81	7	0.2	7	3	0.4

Note: All values in wt%.

early cementation brass. The presence of a few percent of tin in all objects is remarkable, and confirmed by both pXRF and SEM-EDS analyses. Since at this time clean brass was already widely available it is possible that this was a conscious addition in order to improve the colour of the alloy, making it more golden.

5.1.7. Late Roman-Early Christian era (4th–7th cent AD)

Fourteen objects belong to this late period from Kastro Palaia, mainly jewellery. We observe four types of metal used, i.e. unalloyed copper, bronze, brass and gun metal (Cu–Zn–Sn) (Table 6). The brass ring shows the same separation in lower zinc values according to the pXRF analyses compared to the SEM-EDS data as the ear rings from the previous period, but neither lead nor tin. A few wire fragments show relatively low zinc values. Most of the bronze objects are heavily corroded, making it impossible to judge their original alloy composition; the unrealistic high lead content which is present in some samples could be attributed to the enrichment of the surface due to corrosion processes (Orfanou and Rehren 2015). The same may be true for the lead content of the two wire fragments, made probably from brass originally, and still showing around 5 wt% zinc.

Finally, seven samples which cannot be dated with certainty have been examined as well (Table 7); two or three of them were bronze, the others are all more or less pure copper. The absence of any lead is remarkable, and the zinc concentrations are below 1 wt% in all analyses. The samples consist of various objects and from their chemical composition and their typological observation one can potentially attribute them to specific eras. However, this is still a work in progress and will not be discussed here further.

Comparing the chemical composition of the artefacts diachronically (Table 8) we observe that pins are made of relatively pure copper and bronze in all periods whereas rings are manufactured of bronze in the earlier times and of brass in later periods; earrings in particular have been manufactured with brass in later periods. Fibulae are made of bronze in the early periods while buckles are made of brass in later periods with the same pattern to occur also for bracelets. Weapons are made either of pure copper or bronze in all periods. Nail heads are made of bronze in early periods while a later dated nail found to be made of pure copper. Needles and awls are made of bronze in early periods and wires are made of brass in later eras.

5.1.8. Metallurgy and specialisation at Kastro Palaia

It has been suggested that there is often a close relation between the chemical composition and the manufacturing techniques used to create a specific type of artefact since each component of an alloy gives to the final object different properties (Papadimitriou 1990). This suggestion leads to the conclusion that ancient metallurgists knew the effects that composition had on the properties of casting and formation of copper alloys and thus they chose consciously the manufacturing

Table 6. Quantitative XRF and SEM-EDS results of the samples dated to Late Roman-early Christian era.

Late Roman-Early Christian	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	Zn	As	Pb	Sn	Sb
	BE 556	Ring	XRF	Metal	2	nd	93	4	0.2	nd	0.1	0.1
			SEM-EDS	Metal	nd	nd	85	14	nd	nd	nd	nd
	BE 548	Bracelet	XRF	Not very clean metal	0.6	0.1	68	2	0.1	22	7	0.2
	BE 553,001	Nail	XRF	Metal	nd	0.1	98	0.4	0.2	0.5	nd	nd
	BE 553,002	Buckle	XRF	Corroded	0.6	0.1	63	0.1	0.2	35	0.2	0.1
	BE 557	Pin	XRF	Metal	1	1	95	0.2	0.3	2	0.2	0.3
	BE 558,001	Wire	XRF	Metal	1	0.2	98	0.2	0.2	nd	nd	nd
	BE 558,002	buckle	XRF	Corroded	2	0.1	77	0.5	0.2	18	2	nd
	BE 549	Sheet thick	XRF	Metal	0.6	0.2	85	0.2	0.2	2	11	nd
	BE 561,001	Wire	XRF	Not very clean metal	0.3	nd	74	4	nd	20	1	nd
	BE 561,002	Wire	XRF	Not very clean metal	0.1	0.2	82	6	nd	11	1	nd
	ID 17176	Object	SEM-EDS	Corroded	0.2	nd	50	2	1	39	0.5	nd
	ID 17187	Foot	XRF	Corroded	4	nd	79	0.3	0.2	nd	16	nd
	ID 17746	Sheet	SEM-EDS[19]	Corroded	0.3	nd	46	nd	0.1	30	10	nd
	ID 17714	Pin	SEM-EDS[20]	Corroded	0.1	nd	66	nd	nd	nd	17	nd

Note: All values in wt%.

Table 7. Quantitative XRF results of samples which cannot be dated with safety.

Not safely dated	ID	Object	Method	Corrosion or metal core	Fe	Ni	Cu	Zn	As	Pb	Sn	Sb
	BE 620	Ring	XRF	Metal	0.2	0.1	99	0.4	nd	nd	nd	nd
	ID 17189	Rod	XRF	Corroded	2	0.3	93	0.3	0.5	nd	4	0.4
	ID 17190	Pin	XRF	Metal	3	0.3	95	0.4	0.4	nd	0.5	0.3
	ID 17194b (M5683.9)	Pin	XRF	Metal	nd	0.3	99	0.4	0.2	nd	0.1	0.4
	ID 17191	Sheet	XRF	Corroded	1	0.2	97	0.6	0.5	nd	0.7	0.4
	ID 17192 (M5683.7)	Sheet folded	XRF	Corroded	5	0.1	81	0.3	0.5	nd	12	nd
	ID 17195 (M5683.4)	Tool	XRF	Corroded	4	0.4	93	04	0.3	nd	2	0.3

Note: All values in wt%.

Table 8. Type of metal used for certain artefacts diachronically.

Type of metal	LBA	EIA	Iron Age	H/R	4th–6th AD
Cu	Pins	Dagger	Pins Sheet		Pins Wires Nails
CuAs			Pins		
CuSn	Pins Rings Daggers Arrow head Nail heads	Pins Rings Fibulae Bracelets Needles Awls Wires Nail heads	Pins		Pins Fibulae Wires Sheets Statuette (foot)
CuAsSn	Pins		Pins		
CuZn					Rings
CuZnSn				Rings Earrings	Bracelets

techniques and alloy composition that were required for a given type of artefact. Early excavations at Kastro Palaia had revealed several metallurgical tools such as crucibles and moulds. The moulds were stone-carved and the crucibles well-made from specifically prepared clay, and were carefully curated for multiple use (Rehren et al. 2013). This, and the almost unchanged position of the metallurgical workshop over a period of many centuries demonstrate the high level of craftsmanship at Kastro Palaia during the Bronze Age. In the more recent periods we see a similar up-to-date mastery of metallurgy, with the then-new alloy brass being routinely applied for jewellery, and both lead-free and leaded bronze being available for casting.

The correlation of specific working techniques, i.e. casting and hammering as appropriate for specific alloy types, and the selection of particular alloys for their colour and other properties at the metallurgical workshops at Kastro Palaia, diachronically, reveals the good knowledge of the craftsmen in metallurgy with high technological level, and that they were not just occasional metalworkers. On the other hand, the workshops appear to have been versatile and producing a range of artefacts from a wide range of alloys and copper sources (see below), indicating that these were serving the wider community and not narrowly specialised on a particular product only.

5.2. Manufacturing techniques

The metallographic examination allowed observation of corrosion layers and the extent of that corrosion into the metallic structure. The presence of sulfide inclusions in some samples could be an indication that the metal used was derived from a sulfidic copper ore and used without having undergone much recycling (Figure 7a, b). Where present, the surviving metal core revealed characteristic traces of the working techniques used. Both as-cast and hammered and annealed objects (Figure 8) have been identified among the samples. The practice of a range of metalworking techniques is demonstrated during the production of the objects revealing the ways the metallurgists used to form certain types of objects.

For example, pins from LBA to Iron Age were as cast with a light hammering except from one case (pin ID 17719 dated to the EIA) which seems to be heavily hammered. One pin, dated to the later period has no metal core preserved to allow us understand if the same technique of manufacture was used.

The fibulae that have been examined all belong to the EIA and the parts of the fibulae that were hammered had undertaken hard working.

Rings seem to have been worked in the same way both in the EIA and in the 4th–6th century AD period. They were as cast with a light hammering. Unfortunately, the weapons were very corroded and either it was decided not to examine them metallographically or the results obtained from some of them are too poor to be presented in more detail.

A summary of the metallographic examination of 31 objects, mostly pins and fibulae, is presented in Table 9.

5.3. Provenance of raw material

The Lead Isotope Analyses reported previously from selected copper slag found in the crucibles showed

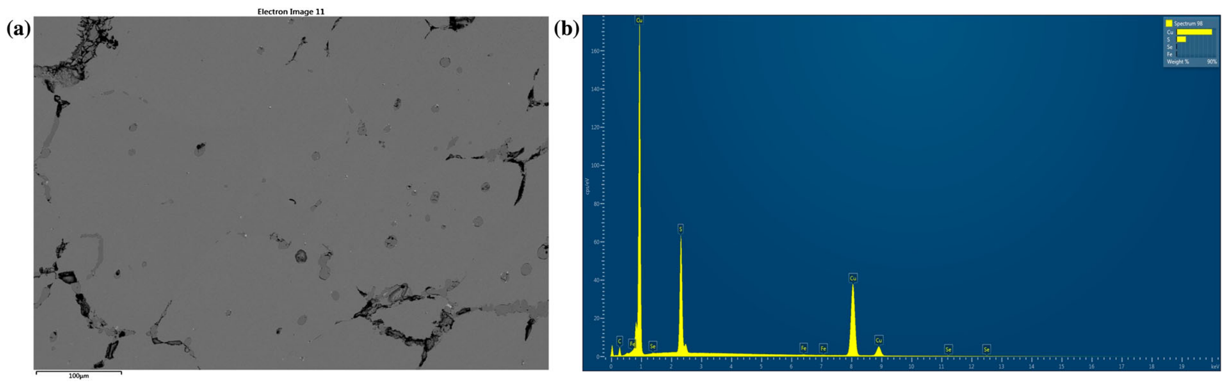

Figure 7. (a, b) Dagger ID 17711 dated to the EIA period. Sulfide inclusions (dark grey) are present in the metal core. Corrosion and shrinkage porosity outline some of the grain boundaries. SEM image and EDS spectrum.

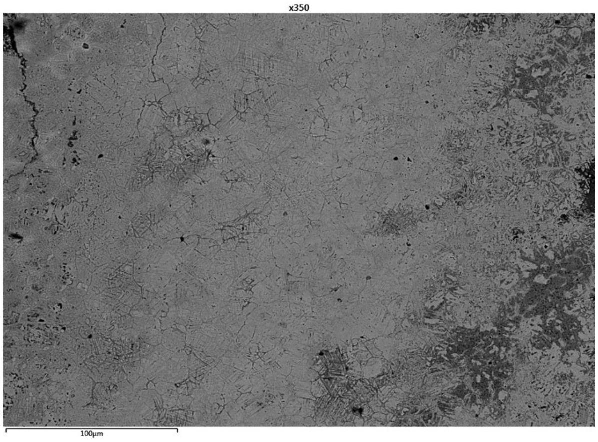

Figure 8. Pin ID 17719 dated to the EIA period. Hammered and annealed texture. SEM image, magnification 350X.

that some of their copper came potentially from Cyprus, and some probably from Laurion and possibly Bulgaria (Rehren et al. 2013: 118–119). However, since there are local copper sources found around Kastro Palaia, the supply of the metal could have been easily done straight from an adjacent mining area in the mountains Othrys, Pelion and Chalcodonion. The surrounding areas provides the geological conditions for copper extraction, and several deposits with copper minerals and indications of ancient exploitation have been recorded (Figure 9). Lead isotope analysis of several objects was therefore undertaken to gain some insights into the possible local exploitation of copper sources, and the wider supply network of copper at the site, while bearing in mind the limitations of the techniques regarding the distorting effects of recycling, and the general inability to allocate positive provenances (Table 10).

The present lead isotopic analysis reveals new data about the raw material provenance (Figure 10). For comparison, we used the published data for Mt. Pelion ores (Stos-Gale and Gale 2009) and new samples from Mt. Chalcodonion, while the North Greek isotopic data are from Pangaeon, Chalkidiki and Kilkis mining area (Stos-Gale and Gale 2009), several hundred kilometres northeast of Volos. For a wider comparison we also used published data for copper ores from Lavrion, Bulgaria, Cyprus (Larnaca and Solea axis) and Feinan/Timna in the Wadi Arabah.

The ore sampled from the mountain Chalcodonion in the area of Kokkina has almost the same isotopic signature as the Mt Pelion ore sample, although both fall outside of the bibliographical samples' plots and are nearer to the North Greek ores (Figure 10). A slag sample from the Pelasgia metallurgical area, some 50 km southwest of Kastro Palaia, is in good agreement with the range of plotted bibliographical data from Pelasgia ores (OXALID data base, Stos-Gale and Gale 2009). However, the Pelasgia ores scatter rather widely and overlap in the $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ plot closely with Cypriot ores of the Larnaca axis. On the other hand, the projection of the $^{204}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ ratios separates both the Mt. Pelion and the Pelasgia ores clearly from the Cypriot ones (Figure 11). An overlapping isotopic signature is also depicted in Figure 10 between the ores of Northern Greece, the extended range of Mt. Pelion including Mt. Chalcodonion, and some of the copper ores from Lavrion. This overlap persists even in the second projection including the $^{204}Pb/^{206}Pb$ isotope ratio.

The isotopic signatures of the four analysed copper artefacts show potentially four different geological origins. The artefact M2678,003, a pin dated to the EIA period, plots in the range of Pelasgia ore isotopic signatures and is the potentially most local artefact from the assemblage; an origin from Cypriot ores can be excluded based on the $^{204}Pb/^{206}Pb$ ratio, and a Bulgarian origin appears unlikely since the match is only marginal. The artefact M2681,002, a nail head dated to the LBA, matches closely the Bulgarian ores isotopic signature, particularly in the $^{208}Pb/^{206}Pb$ plot, and points at the legendary Black Sea connections of Iolkos during this period. The artefact M2219, a dagger dated to the LBA, falls close to the most controversial isotopic region where the Northern Greek and Lavrion ores overlap in both projections; in the $^{204}Pb/^{206}Pb$ projection it falls closer to the North Greek ore field than to the Lavrion field. The fourth artefact, M2191,001, a fibula dated to the EIA (Kilian 1975, 18, pl. I-4; Theocharis 1960, pl.38b), differs fundamentally from the other analysed objects, with a much higher $^{207}Pb/^{206}Pb$ ratio; its nearest parallel has been found in the Timna/Feinan ores (Figure 12). While this appears rather far away from Kastro Palaia, it is consistent with the documented Syro-Palestinian pottery found elsewhere at the site, and further attests to the wide-ranging connections of this important settlement.

The new LIA data enable us to re-assess the possible origin of the metal in the crucibles from our earlier study (Rehren et al. 2013). There, we had reluctantly assigned the metal in the EBA crucible BE 48051 to a potential Cypriot origin, but already pointed at the mismatch in alloy composition between the sample with its high levels of minor elements, and the typically relatively pure Cypriot copper. The new data now rules out a Cypriot origin (Figure 11), and instead opens up the possibility that the metal from this early crucible could originate from the Pelasgia region (Figures 10 and 11). The LBA crucible M2664 had been assigned a marginal possible Cypriot origin, overlapping with Bulgarian ore data. We can now all but rule out the Cypriot origin, and instead have stronger consistency with a potential Bulgarian origin of the metal in this crucible (Figure 11). For the undated small crucible fragment BE 49640 we had proposed a potential origin from the Lavrion region; this possibility still stands, but

Table 9. Optical microscopy results of selected objects.

ID	Object	Date	Metallographic structure	Other observations
AE 03	Arrow head	LBA	No metal core is preserved	Cuprite; copper chlorides
ID 17142	Unidentified object	LBA III B	No metal core is preserved; dendritic structure (?)	Heavily corroded; cuprite; copper chlorides
ID 17760	Dagger	LBA III B	Dendritic structure; interdendritic porosity	Heavily corroded; cuprite; copper chlorides
ID 17711	Dagger	EIA	Both dendrites and grains; intergranular and intragranular corrosion; round copper sulfide inclusions	Heavily corroded; cuprite; copper chlorides
ID 17159	Pin	LBA III B	No metal core is preserved	Heavily corroded; cuprite; copper chlorides
ID 17760	Pin	LBA III B	Dendrites and some grains	Very corroded
ID 17717	Pin	LBA III Γ	Dendrites	Heavily corroded
ID 17719	Pin	EIA	Cold worked after annealing; distorted twin lines; strain lines in the grains	
BE 1011	Pin	Iron Age	No metal core is preserved	Cuprite; dark green corrosion products
ID 17049 (BE 2860,001)	Pin	Iron Age	Dendrites and some grains	Very corroded
BE 1010,001	Pin	Iron Age	Cast with some cold working	Heavily corroded
ID 17714	Pin	4th–6th AD	No metal core is preserved; diameter of the original surface: 2.4 mm;	Heavily corroded; cuprite; copper chlorides
M 2678,005	Foot of fibula	EIA	Cast with some cold working; both dendrites and grains present; coring present	
M 2191,002	Fibula	EIA	Both dendrites and grains present	Heavily corroded
M 2191,001 a	Fibula	EIA	Original surface visible ; intensively worked; small grains;	Heavily corroded
M 2191,002 a	Fibula	EIA	Cast with some cold working	Heavily corroded
M 2678,006,002	Fibula	EIA	Cast with some cold working	Heavily corroded
M 2678,006,001	Fibula	EIA	Original surface visible; hammered and annealed; cold worked after annealing showing distorted twin lines and strain lines in the grains; variable grain size; porosity as dark holes; intracrystalline cracks; intergranular corrosion; redeposition of copper	Heavily corroded; cuprite
M 2196	Fibula	EIA	Original surface visible; cold worked after annealing showing distorted twin lines and strain lines in the grains; variable grain size; porosity as dark holes; intracrystalline cracks; intergranular corrosion; some coring present	Heavily corroded; cuprite
M 2192	Fibula	EIA		Heavily corroded
M 2191,001	Fibula	EIA	Original surface preserved in corrosion products; some metal core is preserved; dendrites and grains visible	Heavily corroded; cuprite; copper chlorides
ID 17188	Ring	EIA	Dendritic structure preserved	Heavily corroded; cuprite; copper chlorides
M 2601	Ring	EIA	Cast with some cold working	
BE 556	Ring	4th–6th AD	Original surface present in corrosion products; both dendrites and grains present	Heavily corroded
ID 17707	Needle	EIA	Hammered and annealed	Heavily corroded
M 2601	Wire	EIA	No metal core is preserved; original surface obvious within the corrosion products; width: 0.5 mm; grains	Heavily corroded; cuprite; copper chlorides
ID 17721	Sheet	End of Iron Age	Dendrites and grains	Heavily corroded
ID 17746	Sheet	4th–6th AD	Original surface preserved in corrosion products; dendrites and grains	Very corroded
M 2603,003c	Earring	H/R	Hammered and annealed; intergranular corrosion	Cuprite present
M 2603,004	Earring	H/R	Hammered and annealed; intergranular corrosion	
ID 17176	Unidentified object	4th–6th AD	No metal core is preserved	Heavily corroded; cuprite; copper chlorides

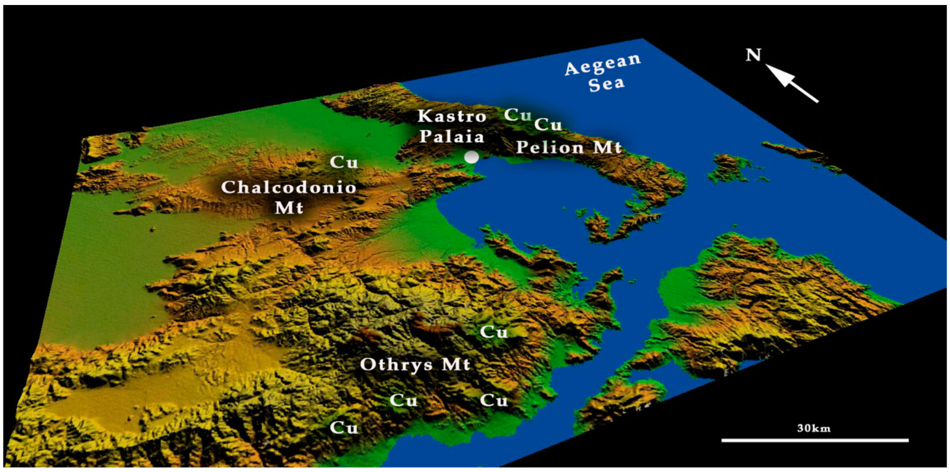

Figure 9. Map showing regions with copper ores in the wider vicinity of Kastro Palaia.

Table 10. Lead isotope ratios from ores, slags and artefacts from Kastro Palaia, Volos, Greece.

Sample no	Sample	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
M2678,003	Fibula	2.07885	0.84201	18.61016	15.67027	38.68829
M2219	Dagger	2.06673	0.83533	18.77682	15.68480	38.80704
M2681,002	Nail head	2.06804	0.83747	18.64942	15.61873	38.56778
PVORE-1	Slag (Pelasgia)	2.07786	0.84080	18.63082	15.66434	38.71136
PVORE-2	Ore (Chalkodonion-Kokkina)	2.06848	0.83273	18.85477	15.70095	39.00081
PVORE-3	Ore (Pelion)	2.06840	0.83238	18.86698	15.70443	39.02521

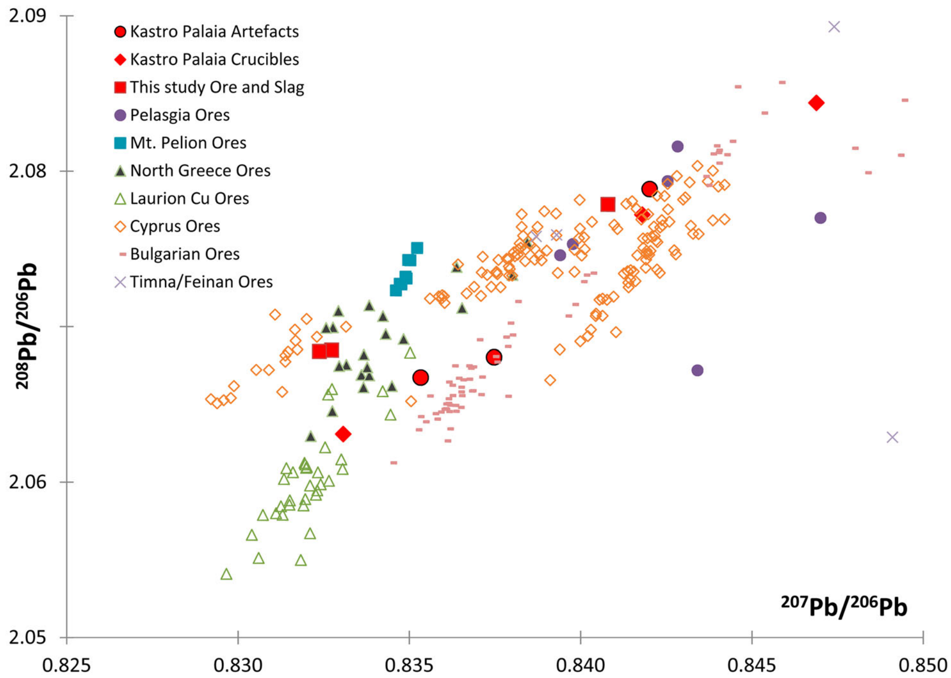

Figure 10. Plot of the $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ isotope ratios for samples analysed for this project (red solid symbols) compared to LIA data from the literature (various symbols) focussing on the wider region around Volos. See text for discussion.

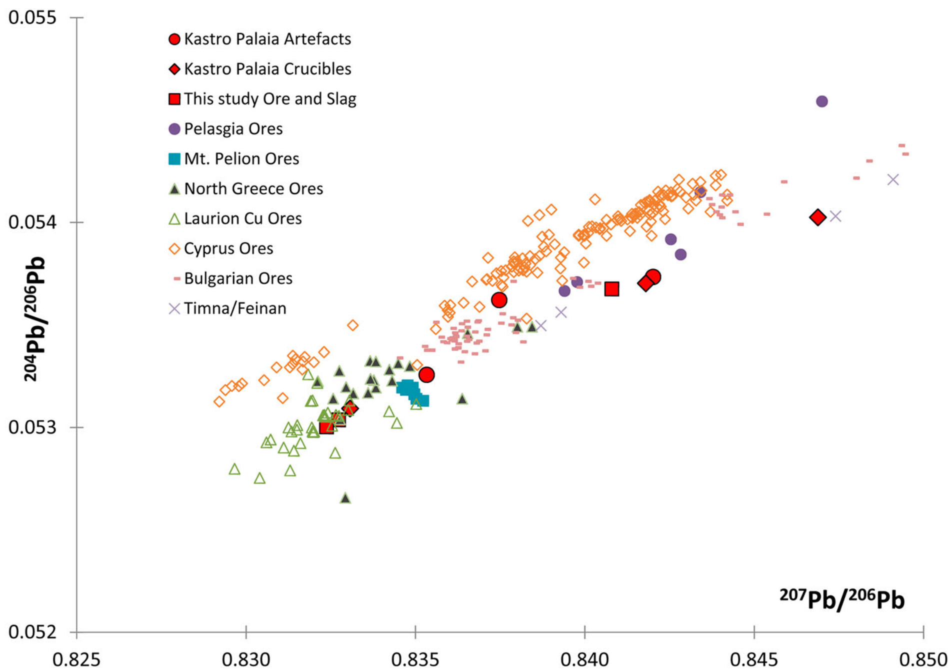

Figure 11. Plot of the $^{204}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ isotope ratios for samples analysed for this project (red solid symbols) compared to LIA data from the literature (various symbols) focussing on the wider region around Volos. See text for discussion.

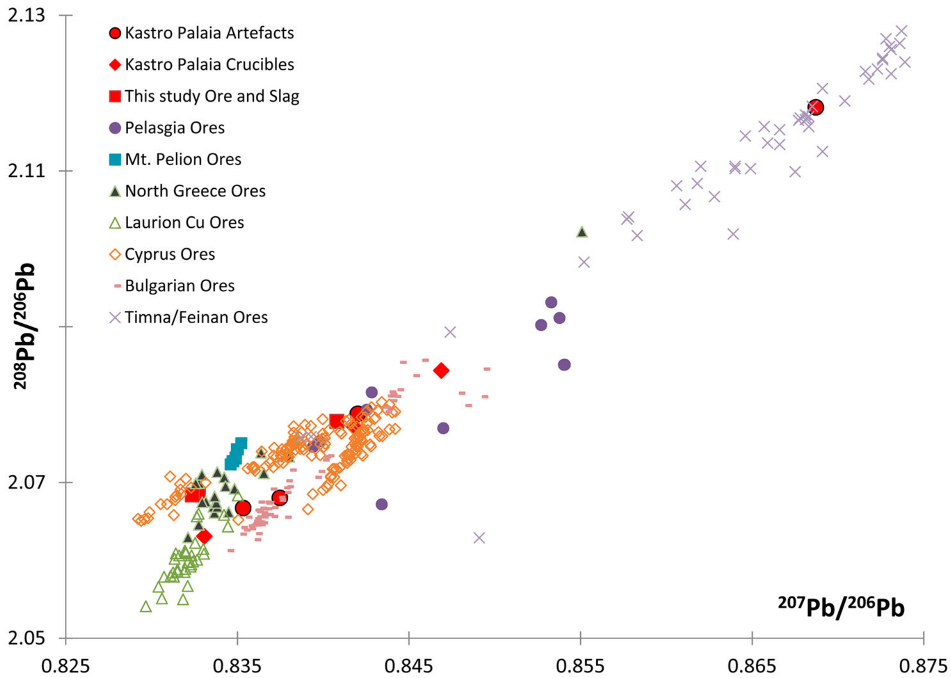

Figure 12. Plot of the $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ isotope ratios for samples analysed for this project (red solid symbols) compared to LIA data from the literature (various symbols) including data for Feinan and Timna. See text for discussion.

an equal probability exists that the metal originates from the North Greek ore region.

6. Conclusion

After an extended study of Theocharis' archives it has been concluded that metallurgical activities at the site continued diachronically from the Early Bronze Age to the Early Iron Age (Skafida et al. 2015), even though the continuous inhabitation of the settlement has destroyed a lot of evidence from the workshops themselves and hence the archaeological investigation was limited.

Among the analysed material, it is observed that jewellery is predominant over weapons or utilitarian objects. Artefacts from the Early Bronze Age to the Geometric period were made mainly of pure copper, arsenical copper, bronze and arsenical bronze, while later in the Late Roman and Early Christian period objects were made, as expected, of pure copper, bronze and brass.

The metallography revealed that a range of metalworking techniques were used for the production of the artefacts. Casting has been identified by the dendritic microstructure. Slightly worked (combination of as-cast and mild metal working), worked and intensively worked structures have been observed, as well.

Elements such as antimony (Sb), nickel (Ni), selenium (Se) are present in many samples and are attributed to the trace elements in the ore used (Craddock 1988). The appearance of Sb and Ni in the alloy could suggest the possible use of copper sulfide or Fahlerz ores, both of them commonly used during the Bronze Age (Craddock 1988). Other elements detected such as phosphorus (P), silica (Si), calcium (Ca), aluminium (Al), titanium (Ti), sulfur (S) and chlorine (Cl) are attributed to the burial environment and the corrosion factors, and therefore were not considered in the interpretation.

A high amount of tin has been detected in the casting debris that has been found in the LBA workshop area during excavations in 2010. The same high amount of tin (more than 30 wt%) has been found in metal prills from two crucibles from the LBA workshop. As argued earlier (Rehren et al. 2013), metallic tin and fresh copper were alloyed to produce bronze, showing that the LBA workshop had access to metallic tin, supporting the theory that the LBA workshop was part of a palatial establishment with access to high-value commodities and included in the long-range trading network of the time.

The pilot study on lead isotope ratios of ores, slag and artefacts of the present study matches and expands the previous crucibles' study (Rehren et al. 2013). The data confirms that the workshops had access to a range of metal sources, including probably some of the major copper sources of the Bronze Age in Jordan/Israel, Bulgaria and either Lavrion or Northern Greece. Significantly, the metal workers in Kastro Palaia, also most likely drew copper from regional sources, such as the Pelasgia area. The earlier postulated possible Cypriot origin of the copper melted in the crucibles (Rehren et al. 2013) can now be excluded based on the fuller picture; the current evidence points at origins of the metal melted in the crucibles from Bulgaria, Pelasgia, and either Northern Greece or Lavrion, and are therefore fully consistent with the observations made for the artefacts from Kastro Palaia. An exploitation of the local ores from Mt. Pelion and Mt. Chalcodonion, however, is yet to be shown.

Notes

1. The former 13th Ephorate of Prehistoric and Classical Antiquities.
2. Found with crucible 48050, see Rehren et al. (2013).
3. Found with crucible 48054, see Rehren et al (2013).
4. Mean values. Also found: O: 20 wt%, Al: 0.1 wt%, Si: 1 wt%, P: 0.2 wt%, S: 0.8 wt%, Cl: 2 wt%.
5. Also other elements like Cl, P and Ag: 0.5 wt% are present.
6. P: 0.2 wt%, S: 0.1 wt%, Co: 0.1 wt% present.
7. Most XRF results are not 100% because I do not count Zn which is monotonous present in most samples in a percentage of 0.4 wt% and Co in a percentage of 0.2–0.3 wt%.
8. Cl present.
9. P: 0.8 wt%, S: 0.1 wt% present.
10. S: 1 wt%, Se: 0.2 wt% present.
11. P: 0.2 wt%, S: 0.3 wt%.
12. S: 0.6 wt%.
13. Also: P: 0.2 wt%, S: 0.1 wt%, and a lot of Cl.
14. Also: P: 0.5 wt%, S: 2.5 wt%.
15. Also Ag: 0.2 wt%.
16. P: 0.3 wt%, S: 0.2 wt% and too much oxygen.
17. Also: O, S: 1.5 wt%, Cl.
18. Nickel was not measured with SEM-EDS.
19. Also, P: 3 wt%, Cl, Ca and O are present.
20. P: 0.1 wt%, S: 0.1 wt%.

Acknowledgements

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Notes on contributors

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