

# SERIPHOS SURFACES: A STUDY OF COPPER SLAG HEAPS AND COPPER SOURCES IN THE CONTEXT OF EARLY BRONZE AGE AEGEAN METAL PRODUCTION\*

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*Kephala and Phournoi, on the island of Seriphos, add to a growing number of EBA metal production sites identified in the south-central Aegean. Analytical examination of samples from the two sites addressed the technological parameters of the copper smelting process, indicating the use of mixed oxidic and sulphidic copper–iron ores to produce unalloyed copper with minute copper sulphide inclusions. A preliminary geological reconnaissance of the island identified several small copper mineralizations, one of them close to the site of Kephala. Nevertheless, the ore sources used remain unclear. Comparisons are made with other contemporaneous neighbouring smelting sites.*

**KEYWORDS:** SERIPHOS, CYCLADES, AEGEAN, EARLY BRONZE AGE, SLAG, COPPER, METAL PRODUCTION, SMELTING

## INTRODUCTION

Research into Early Bronze Age (EBA) Aegean metallurgy has undergone a notable shift in emphasis in the past decade. During the 1980s and 1990s, interest was focused primarily on metal provenance and circulation, sparked by the innovative and promising results of a large-scale lead isotope analysis programme (see, e.g., Gale and Stos-Gale 2002; Stos-Gale and Gale 2003 and references within). Given the geographically broad area covered in this programme, the approach taken was extensive and the results unavoidably of low resolution (Georgakopoulou in press). Several 'ancient' metal production sites were sampled for lead isotope analysis, but the majority remained otherwise undated and practically unstudied. The few exceptions, where further work had been undertaken, include the copper slag heaps of Skouries (Gale *et al.* 1985; Hadjianastasiou and MacGillivray 1988) and Chrysokamino (Betancourt 2006) on the islands of Kythnos and Crete respectively, and the lead/silver mining and smelting site of Ayios Sostis on Siphnos (Wagner and Weisgerber 1985), all securely dated to the EBA. In recent years, a significant number of archaeometallurgical projects of much smaller geographical scope have been undertaken mainly in the south-central Aegean, targeting specific sites (see, e.g., Betancourt 2006; Doonan *et al.* 2007; Georgakopoulou 2007) or small regions (see, e.g., Bassiakos and Philaniotou

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2007; Douni *et al.* in press; Papadopoulou and Chrysovergi in press) and expanding beyond metal circulation to a direct study of the metallurgical activities. Aspects of their technology and spatial distribution are addressed, thus contributing to a holistic understanding of metal production in itself, its organization and role within the corresponding communities (Costin 1991). Analytical studies of the relevant remains, as presented in this paper, lie at the core of these efforts.

The island of Seriphos (Fig. 1) is situated in the western Cyclades, an area attributed an important role in EBA Aegean copper, lead and silver supply (Broodbank 2000, 293–7). Although two undated copper slag heaps were long known at Kephala and Avessalos (Gale *et al.* 1985), Seriphos remained almost a blank both in terms of archaeological and archaeometallurgical research (Philaniotou *et al.* in press). This sparked the initiation of a collaborative field investigation on Seriphos that aimed to shed more light into the island's metallurgical past. Through this project, the slag heap of Kephala was dated to the EBA, together with a newly identified smaller slag scatter on Phournoi at the north of the island (Zacharias *et al.* 2006; Philaniotou *et al.* in press). A few prehistoric sherds recovered from the impressive slag heap of Avessalos raise the possibility that at least part of this much larger deposit may also be contemporary. A detailed description of these sites has been given elsewhere (Philaniotou *et al.* in press). This paper presents the results of the analytical investigation of a substantial suite of slag samples from Kephala and Phournoi, which addressed the technological parameters of the metallurgical processes on the two sites, as well as the outcome of the brief geological prospection undertaken on the island in search of potential copper sources.

#### SAMPLING AND ANALYTICAL METHODOLOGY

The sites of Kephala and Phournoi host large concentrations of slags and other metallurgical remains, estimated to a few thousand tons (Philaniotou *et al.* in press). In order to examine the homogeneity of these heaps, an appropriate sampling strategy needed to be devised, governed by both spatial and morphological criteria. Sampling at Kephala and Phournoi was restricted to surface collection, as excavation has not been possible so far, and was largely based on the inherent division of the material into separate deposits in each case (for a description, see Philaniotou *et al.* in press). This enabled a simple selection of sampling units, which takes advantage of the layout of each site, and can be easily reproduced in the future if necessary. Additionally, it allowed a comparison between parts of the site that might correspond to different working areas, as they are spatially separated. The sampling units are listed in Table 1 and include, apart from the main deposits defined on each site (Kephala 1, 2, 3 and Phournoi 1, 2), a single sample detached from the rock-carved furnace found at Kephala, and material from the slope below the Phournoi 1 and 2 units and from the promontory above them (Philaniotou *et al.* in press). The last group at Phournoi (Path) corresponds to a few stray slag pieces, found at the start of the path that leads to the site (distance ~1500 m south-east of Phournoi). These were included in this study in order to examine whether differences could be noted that would justify attributing them to a separate site than Phournoi. Samples were collected at random from different areas within each of the larger sub-units.

Beyond the spatial distribution of the material, sampling also took into account morphological characteristics, in order to represent potentially different types of slag. The macroscopic features used as guidelines were the size and porosity of the slags and the presence or absence of flow texture, visible inclusions and green staining on their outer surface. In addition to the majority of the slag samples, which, despite differences in these specific characteristics, are generally typical of the heaps, a few intriguing and 'exceptional' specimens were identified and analysed.

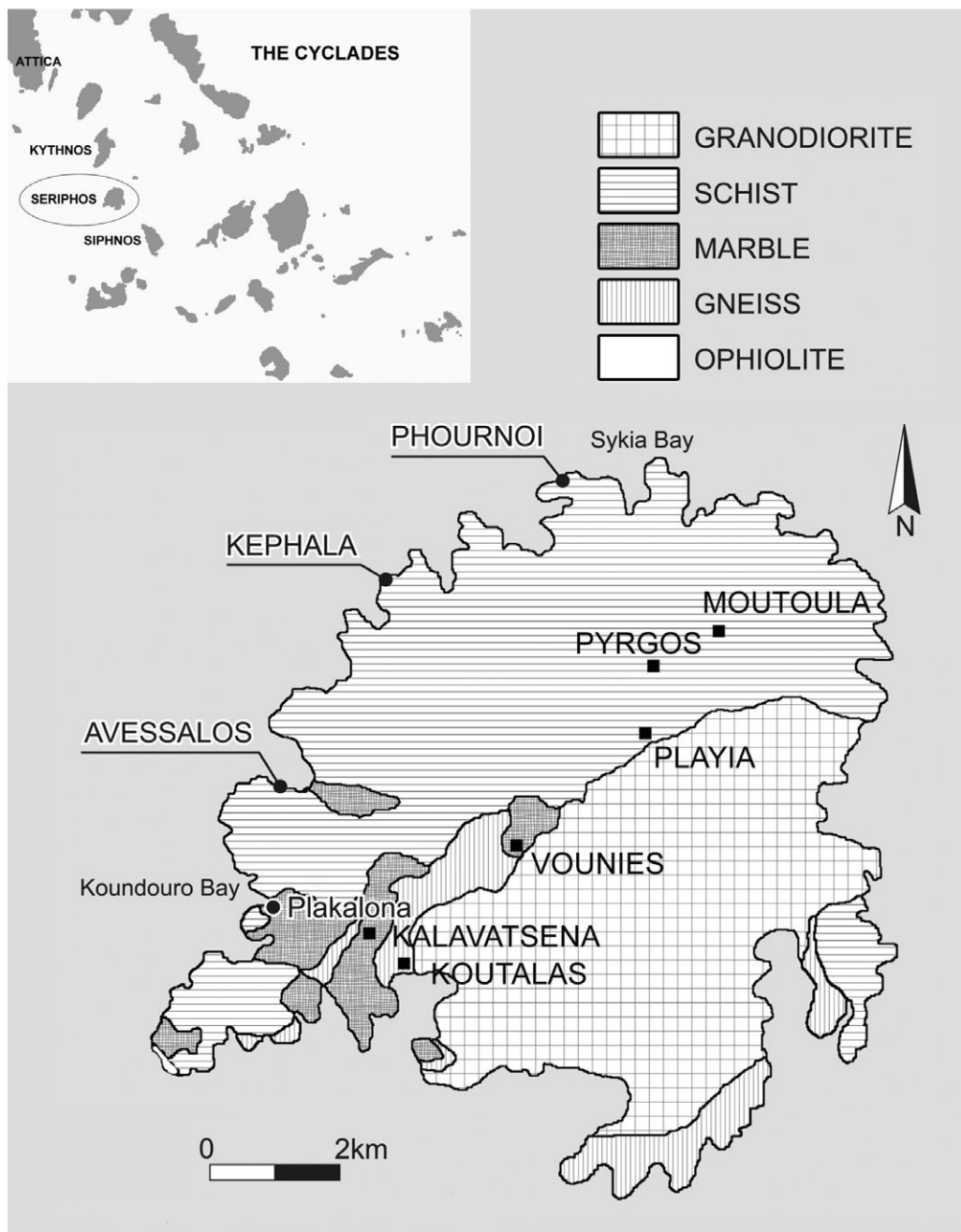


Figure 1 A simplified geological map of Seriphos (based on Salemink 1980, 345), showing archaeological (dots) and geological (squares) sites mentioned in the text.

Table 1 Definition of sampling units at Kephala and Phournoi

<i>Sampling unit</i>	<i>Description</i>
Kephala 1	Eastern large deposit at north-facing slope
Kephala 2	Western large deposit at north-facing slope
Kephala 3	Small scatter at south-facing slope
Furnace (F)	A single sample (KEF25) was detached from the slag attached to the furnace identified at Kephala
Phournoi 1	Eastern concentration of north-facing slope
Phournoi 2	Western concentration of north-facing slope
Phournoi 3	Top of the promontory
Phournoi 4	Material rolled down the slope between Phournoi 1 and 2
Path (P)	Beginning of the path that leads to the site

Bulk chemical analyses were carried out with a polarizing energy-dispersive X-ray fluorescence spectrometer ((P)ED-XRF: Spectro X-Lab Pro2000) using a calibration method developed specifically for iron-rich materials (Veldhuijzen 2003). For these measurements, a sample was cut from each specimen and, after its external surface had been removed, was pulverized, dried and prepared into a pressed pellet. Each sample was analysed three times and the normalized averages of these are given in the tables included here. The performance of the instrument was monitored at regular intervals by including in each run three out of the four following reference materials: BCR-2, ECRM681-1, FER-2 and the Swedish Slag reference sample W-25:R (Kresten and Hjärthner-Holdar 2001), prepared into pressed pellets similar to the samples.

Microstructural examination was carried out using reflected light optical microscopy of polished mounted sections. An electron microprobe with an attached wavelength-dispersive spectrometer (EPMA: JEOL SuperProbe JXA-8600) was additionally used for a selected subsample to support the optical identification and provide data on the chemical composition of individual phases and embedded metal prills. Analyses of mineral phases were carried out at 15 kV, using the ZAF correction procedure and searching for Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe and Cu, expressed as oxides. In the case of metallic prills, measurements were made at 25 kV for S, Cl, Fe, Co, Ni, Cu, Zn, As, Ag, Sn, Sb, Pb, Au and Bi. A scanning electron microscope with an attached energy-dispersive spectrometer (EDS–SEM: JEOL JSM-35CF) was also used, where necessary, for semi-quantitative measurements of specific phases.

## RESULTS

### *Bulk composition*

A total of 54 slag samples from both Kephala (labelled KEF) and Phournoi (labelled FOU) were analysed with (P)ED-XRF. The results are given in Table 2, while the main components are depicted in the anorthite–FeO–SiO<sub>2</sub> ternary diagram shown in Figure 2, following the methodology outlined by Bachmann (1980). The samples from each site show significant variability between them in the content of their major and minor oxides, as is clear from the high relative standard deviation values in Table 2. The majority, however, plot within the fayalite region of the diagram (Fig. 2). The samples from Phournoi tend to show higher silicon contents, some falling in the tridymite region. Samples KEF4 and KEF10, which bear the highest

Table 2 Averages of three analyses of slag samples from Kephala (labelled KEF) and Phourmoi (labelled FOU) on the (PED)-XRF, normalized to 100% (MT: measured total). Unit numbers (1, 2, 3, 4, F, P) correspond to sampling units Kephala 1–3, Phourmoi 1–4, Furnace and Path (see Table 1). Elements consistently measuring close to or below the detection limits of the instrument have not been included here. Averages and relative standard deviations are calculated for the major and minor oxides for each site

Unit	Na <sub>2</sub> O (%)	MgO (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	S (%)	K <sub>2</sub> O (%)	CaO (%)	TiO <sub>2</sub> (%)	MnO (%)	FeO (%)	CuO (%)	NiO (ppm)	ZnO (ppm)	As <sub>2</sub> O <sub>3</sub> (ppm)	Ba (ppm)	MT (%)
KEF1	1	0.5	4.2	2.5	40	0.0	0.3	4.1	0.1	0.5	4.4	120	104	<100	648	88
KEF3	1	0.6	3.3	2.1	36	0.0	0.2	8.2	0.0	0.2	0.8	<100	116	<100	<100	93
KEF4	1	0.5	2.4	5.3	45	0.2	1.0	18	0.1	0.5	24	<100	461	272	228	94
KEF23	1	0.9	2.5	5.5	33	0.2	0.5	3.8	0.2	0.3	52	<100	505	<100	355	92
KEF24	1	0.6	4.6	2.4	43	0.0	0.3	8.7	0.1	0.3	38	<100	1141	<100	112	95
KEF31	1	0.7	3.6	2.3	37	0.1	0.2	8.9	0.0	0.2	46	<100	<100	<100	<100	93
KEF32	1	1.0	0.9	4.6	22	0.2	0.8	1.7	0.1	0.1	58	715	804	129	<100	95
KEF33	1	0.5	2.9	0.7	31	0.0	0.1	6.2	0.0	0.2	57	<100	<100	<100	<100	95
KEF34	1	0.6	4.7	2.2	42	0.0	0.2	8.7	0.1	0.3	38	266	1140	<100	112	94
KEF35	1	0.7	2.7	4.7	38	0.0	0.6	7.0	0.1	0.3	45	145	302	353	239	92
KEF36	1	0.6	4.6	1.8	40	0.0	0.3	9.2	0.0	0.2	43	<100	146	<100	149	94
KEF5	2	0.8	2.3	5.7	28	0.2	0.8	2.4	0.2	0.2	56	197	516	174	275	93
KEF6	2	0.8	2.0	6.6	31	0.2	0.7	3.3	0.2	0.2	54	<100	495	<100	323	97
KEF7	2	0.6	8.1	4.2	33	0.0	0.3	8.6	0.1	0.2	43	<100	245	<100	178	94
KEF8	2	1.0	1.1	6.8	32	0.3	0.8	2.0	0.3	0.2	55	<100	714	<100	400	96
KEF9	2	0.5	1.5	6.2	33	0.0	0.5	3.9	0.2	0.4	51	<100	559	<100	<100	96
KEF10	2	0.5	8.2	4.8	40	0.0	0.2	17	0.1	0.2	27	<100	314	<100	<100	98
KEF13	2	0.6	2.8	5.0	32	0.8	0.5	7.2	0.2	0.4	49	<100	481	<100	963	90
KEF14	2	0.6	2.9	5.5	36	0.0	0.8	10	0.2	0.5	42	<100	740	151	538	93
KEF26	2	0.7	2.3	4.2	36	0.0	0.7	3.7	0.1	0.3	50	<100	337	196	<100	93
KEF38	2	0.8	2.7	4.6	38	0.0	0.6	7.0	0.1	0.3	45	127	299	355	233	92
KEF39	2	0.6	8.1	5.0	34	0.0	0.3	11	0.1	0.3	37	115	355	<100	112	94
KEF11	3	0.6	1.2	4.7	30	0.1	0.6	1.5	0.2	0.2	60	<100	510	<100	<100	93
KEF15	3	0.9	2.6	5.6	35	0.0	0.9	9.6	0.2	0.6	43	<100	379	<100	1311	92
KEF16	3	0.6	0.5	3.2	31	0.1	0.6	4.6	0.1	0.3	57	<100	526	197	582	94
KEF40	3	0.4	0.8	2.3	26	0.0	0.1	0.2	0.9	0.4	64	<100	1006	145	1750	95
KEF25	F	0.7	3.1	2.4	36	0.0	0.4	8.2	0.1	0.4	44	148	614	<100	471	87
KEFmean		0.7	3.2	4.1	34.7	0.1	0.5	6.9	0.1	0.3	47.1					
KEFRSD		22.0	65.7	40.2	15.0	157.0	50.9	63.0	61.3	39.4	20.0					

Table 2 (Continued)

	Unit	Na <sub>2</sub> O (%)	MgO (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	S (%)	K <sub>2</sub> O (%)	CaO (%)	TiO <sub>2</sub> (%)	MnO (%)	FeO (%)	CuO (%)	NiO (ppm)	ZnO (ppm)	As <sub>2</sub> O <sub>3</sub> (ppm)	Ba (ppm)	MT (%)
FOU1	P	0.5	0.6	4.5	35	0.0	0.4	1.8	0.1	0.9	53	2.8	<100	549	<100	2004	95
FOU2	P	0.7	1.4	4.2	33	0.0	0.5	2.4	0.2	0.3	56	1.2	<100	447	147	927	99
FOU3	P	1.2	2.0	8.7	28	0.4	1.3	2.8	0.3	0.6	52	2.8	<100	302	<100	330	104
FOU4	P	0.8	1.8	5.0	34	0.0	0.7	3.2	0.2	0.4	51	2.8	269	341	<100	576	101
FOU9	1	1.5	3.5	8.8	50	0.1	1.3	7.9	0.3	0.3	26	0.7	119	109	<100	314	97
FOU10	1	0.7	4.5	3.7	38	0.4	0.4	4.5	0.1	0.3	46	1.0	<100	114	<100	272	93
FOU11	1	0.7	3.1	5.1	25	0.1	0.5	3.4	0.2	1.8	57	2.8	<100	363	<100	1799	101
FOU12	1	0.6	1.3	5.6	34	0.1	0.5	2.7	0.1	0.4	53	1.9	<100	557	275	731	96
FOU24	1	1.1	3.2	4.4	41	0.3	0.6	8.0	0.2	0.7	40	0.5	<100	382	130	2687	98
FOU27	1	0.6	2.4	4.0	32	0.1	0.3	5.6	0.2	0.4	52	1.0	<100	173	<100	2259	98
FOU28	1	1.0	2.9	6.1	32	0.1	0.8	5.5	0.2	0.3	49	1.2	<100	148	<100	283	99
FOU13	2	0.5	11.2	7.2	43	0.0	0.8	7.6	0.2	0.3	27	1.4	<100	264	<100	108	93
FOU14	2	1.1	4.7	9.1	51	0.0	1.9	4.8	0.3	0.3	21	5.8	375	154	<100	196	97
FOU15	2	0.9	3.0	5.8	38	0.1	0.8	2.7	0.2	1.0	45	3.1	175	400	<100	1523	101
FOU16	2	0.6	1.7	3.9	34	0.1	0.4	4.1	0.1	2.1	51	2.1	<100	992	<100	1133	98
FOU21	2	0.6	1.6	4.0	35	0.0	0.4	4.3	0.1	2.1	50	2.0	<100	1030	<100	1185	97
FOU22	2	1.0	2.6	5.9	39	0.1	0.8	5.0	0.3	1.4	43	1.6	<100	702	118	2333	97
FOU29	2	1.3	2.4	8.8	37	0.1	1.3	4.0	0.3	0.4	43	1.5	<100	413	109	1102	100
FOU30	2	0.8	6.1	5.0	49	0.1	0.6	5.7	0.2	0.4	31	0.9	<100	409	118	1074	98
FOU5	3	1.0	1.3	7.1	39	0.3	0.7	2.7	0.3	0.4	46	1.1	<100	269	128	2550	102
FOU6	3	0.6	2.5	8.6	51	0.2	1.3	6.2	0.3	0.2	29	0.4	<100	167	<100	311	99
FOU19	3	0.9	3.3	7.8	47	0.0	1.2	15	0.3	0.5	21	1.8	<100	135	147	228	89
FOU26	3	0.9	2.3	7.9	48	0.3	1.3	5.5	0.3	0.3	32	0.9	<100	203	<100	344	97
FOU7	4	0.3	5.7	4.2	44	0.2	0.7	10	0.2	0.3	34	0.6	<100	186	<100	254	98
FOU8	4	1.2	2.9	6.1	29	0.2	1.0	4.2	0.3	0.3	52	2.1	<100	145	<100	525	99
FOU17	4	0.9	4.4	3.5	43	0.2	0.4	7.3	0.1	0.3	38	1.7	<100	129	<100	133	97
FOU18	4	1.2	2.3	7.8	38	0.1	0.9	2.3	0.2	0.3	46	1.4	<100	351	142	321	99
FOUmean		0.9	3.1	6.0	38.7	0.1	0.8	5.2	0.2	0.6	42.3	1.8					
FOURSD		32.6	66.6	30.7	18.7	76.2	48.9	56.4	35.6	89.5	25.9	62.3					

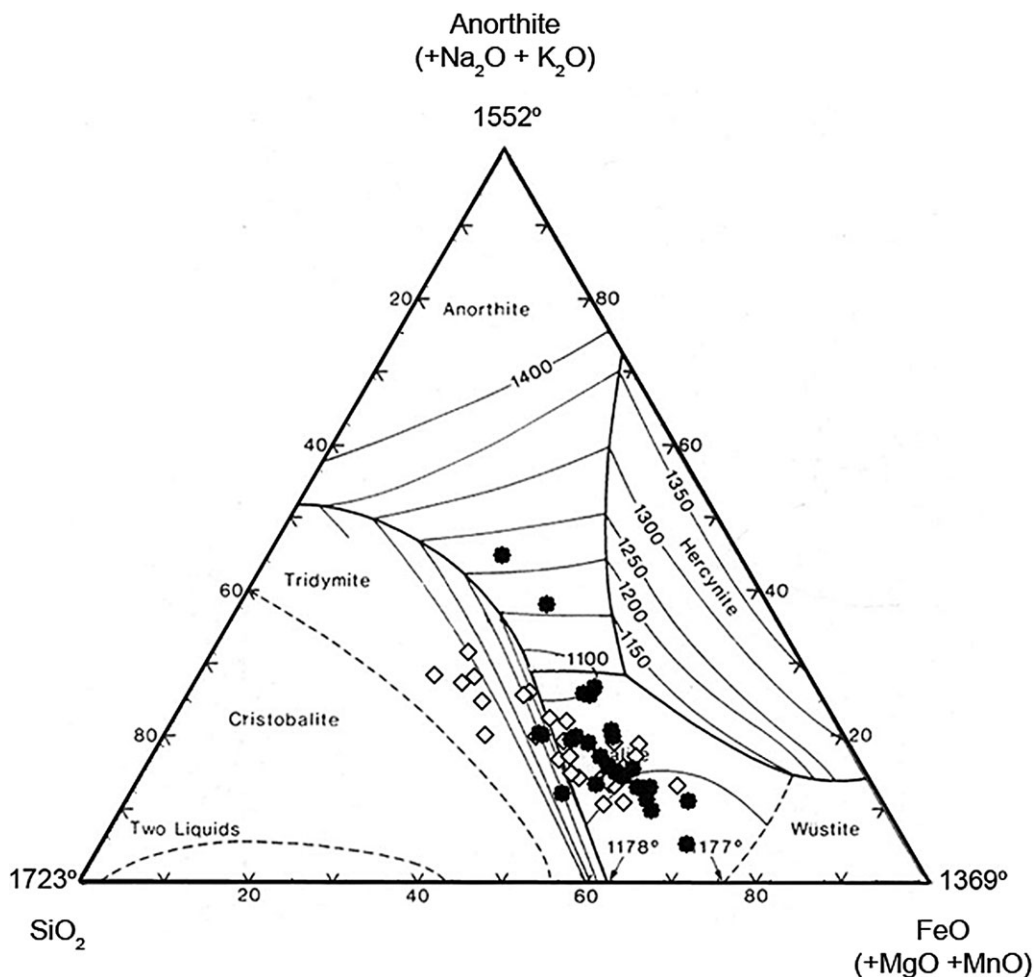


Figure 2 Kephala (black dots) and Phournoi (open rhombus) slags represented on the anorthite– $\text{SiO}_2$ – $\text{FeO}$  ternary phase diagram.

calcium contents, naturally plot towards the anorthite region, while a few more iron-rich samples (e.g., KEF32, KEF40 and FOU11) approach the iron oxide edge. Microstructural examination showed that copper is present both as individual metallic phases and as an oxide within the slag matrix. Given that it is impossible to estimate the relative ratios of the metallic to the oxide form of the element with the analytical methods used, the total copper content is presented in Table 2 as an oxide ( $\text{CuO}$ ). The copper oxide contents average 2% across all the samples, although significant variability is noted here as well. The sulphur contents do not exceed 0.4% with the exception of sample KEF13, which is discussed in more detail below. Other base metals commonly found as alloying components in copper, such as arsenic, zinc, nickel and lead, are only present in trace quantities. Among the trace elements, notable barium contents were found both within the Phournoi (300–2500 ppm) and the Kephala (<50–1500 ppm) slags.

### *Microstructure and phase composition*

The bulk composition is reflected in the microstructure of these samples. In the majority, the dominant phases are iron silicates of the olivine group ( $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ ) embedded in a glassy matrix in which minute, recrystallized iron silicate crystals can often be discerned. The composition of the silicates ranges between that of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and forsterite ( $\text{Mg}_2\text{SiO}_4$ ), with low contents of calcium and manganese, typical minor constituents of these phases (Bachmann 1982, 14). Crystals consistent with the pyroxene group ( $(\text{Fe}_x\text{Mg}_{1-x})\text{CaSi}_2\text{O}_6$ ) were identified among some of the calcium-rich samples (KEF4 and KEF10). Iron oxides, primarily magnetite, were also identified in almost all the samples in variable distribution and relative abundance both within and certainly between samples. Analyses showed that these phases usually accommodate small amounts of alumina and titanium oxide. Magnetite bands were noted in some samples either extending across the upper external surface on fragments with flow textures, or within the slags. In the latter case the microstructure of the section between the two sides of the magnetite band was often different, in terms of size and distribution of phases (Fig. 3), while the mineral phases were usually very small near the bands, indicating rapid cooling in contact with air (Hauptmann *et al.* 2003, 205).

Inclusions of unreacted or partially reacted materials in the slags from Seriphos are rare but, nevertheless, very informative where present. Two types were observed. The first are large, irregularly shaped magnetite aggregates, partly dissolving in the slag matrix and usually incorporating copper prills, typical intermediate phases of partially reacted secondary copper-rich iron ores (Hauptmann *et al.* 2003). They usually appear in samples that are overall richer in iron oxide crystals. Undissolved inclusions of quartz fragments were encountered mainly in the Phournoi samples plotting within the silica-rich part of the diagram in Figure 2. These are also usually thermally altered.

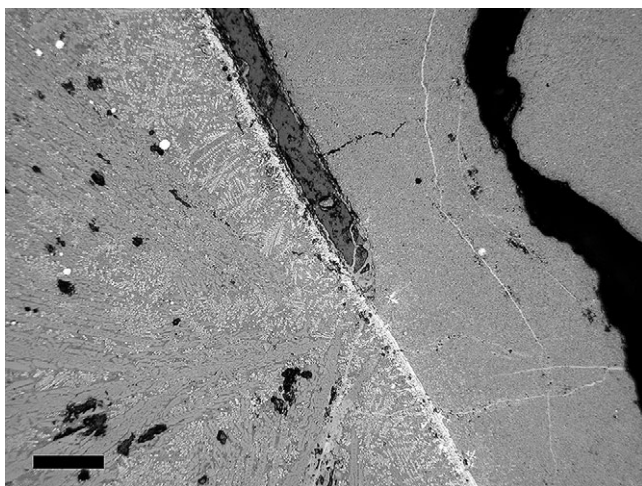


Figure 3 A reflected light microphotograph of sample KEF26 (scale 50  $\mu\text{m}$ ), showing a magnetite band (light grey) running across the sample. The slag is composed of minute crystals of fayalite (medium grey) and magnetite (light grey) with matte prills (circular, white) in a glassy matrix (dark grey), while the size of these phases differs between the two divided parts.

Fragments of ceramic or vitrified ceramic were trapped in a few samples, typically at or near their external surface. In all cases, the ceramic appears to be closely bound to the slag, without a clear separating line between the two phases. These fragments are probably parts of the furnace walls, which have been detached and incorporated in the slag, as they appear similar, at least macroscopically, to the ceramic furnace fragments found at the sites. Given that the clay has survived instead of dissolving in the slag, it is most reasonable to suggest that this happened at the end of the metallurgical process, whether deliberately (i.e., by breaking the furnace) or accidentally due to the friable nature of the walls.

Particularly interesting observations were made on sample KEF13. Similarly to most samples, fayalite predominates here, with a little dispersed magnetite surrounded by a glassy matrix. Large inclusions are visible even macroscopically in this section. Examination under the optical microscope revealed that these correspond to remnants of partially reacted copper–iron sulphidic minerals (Fig. 4), explaining the comparatively high sulphur contents detected in the bulk analysis of this sample (Table 2). These sulphides are heterogeneous and show various different phases of the Cu–Fe–S system (e.g., pyrite, chalcopyrite, bornite, covellite and chalcocite), which can be distinguished on the basis of their optical properties. Their shape is often delineated by the surrounding fayalite crystals. In some areas lamellar textures, frequent in mixed copper–iron sulphides (Ramdohr 1980, 453–7), are observed. Several observations lead to the suggestion that these represent partially reacted primary materials, rather than phases recrystallized from sulphidic melts such as the rounded matte prills (cf., Schreiner *et al.* 2003, 490) commonly observed in the majority of slags from Kephala (see below). First is the recognition of minute eutectoid structures in the inclusions (cf., Bachmann 1982, 25 and plate XI f). Secondly, iron oxide crystals have started to form around these sulphides, while the presence of large holes around them is consistent with the evaporation of sulphur dioxide. These observations are indicative of the progressive oxidation of iron sulphide to oxide and the corresponding enrichment of the sulphide in copper. The process appears to have been terminated before the reaction was completed, leaving behind a specimen that allows a unique insight into the smelting

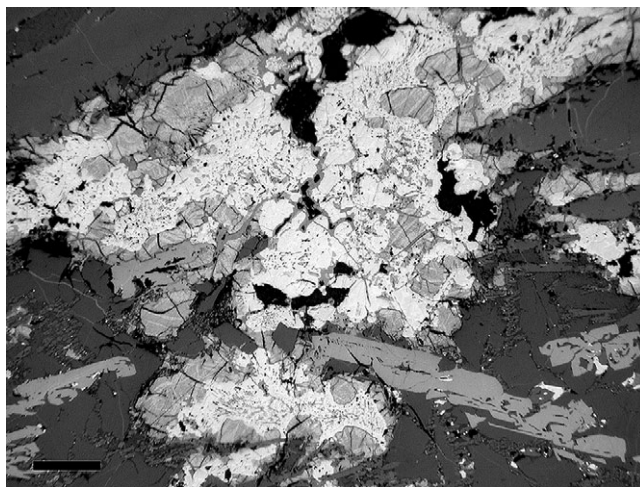


Figure 4 A reflected light microphotograph of sample KEF13 (scale 100  $\mu\text{m}$ ), showing one of the large sulphidic inclusions, a mixture of bornite, chalcocite (different shades of grey) and chalcopyrite (white) with eutectic texture. Iron oxide laths (elongated, light grey) are forming around the inclusion.

mechanism. Isolated fragments of partially reacted copper–iron sulphidic minerals were also observed in two samples from Phournoi (FOU9 and FOU15), but here the reaction does not appear to have progressed significantly.

### Composition of prills

The slags from Kephala and Phournoi invariably bear embedded prills of copper metal and/or more frequently copper–iron sulphide (matte). Several samples have both types of prills, in many cases a matte rim surrounding the copper metal (see similar in Hauptmann *et al.* 2003, 205, fig. 7). Prills from 19 slag samples from Kephala and 17 from Phournoi were analysed using point measurements on the EPMA. A minimum of three prills (copper metal and/or matte) were analysed from each sample. In addition, one isolated copper prill from Kephala (KEF41) and one from Phournoi (FOU31) were recovered and analysed in the same way. The full results of these analyses are given in Georgakopoulou (2005) and a summary is presented in Table 3.

Table 3 Averages of point analyses on copper prills in individual slag samples and the averages of all matte prills from Kephala and Phournoi slags, respectively (wt%). The numbers in parentheses show the number of prills analysed, from which the averages were calculated. Elements consistently detected below 0.1% are not included (bdl, below detection limit, c. <0.05%)

	S	Fe	Ni	Cu	As	Bi
<i>Copper</i>						
KEF1 (7)	0.1	4.8	bdl	95.2	0.1	bdl
KEF7 (5)	0.1	3.9	bdl	94.7	0.1	bdl
KEF9 (2)	bdl	2.8	bdl	97.6	0.4	0.1
KEF10 (3)	0.1	1.6	bdl	98.1	0.2	0.1
KEF14 (1)	0.8	5.0	bdl	92.1	1.8	bdl
KEF24 (3)	0.1	3.9	bdl	93.6	0.2	0.1
KEF25 (4)	0.1	2.8	bdl	96.6	0.2	bdl
KEF32 (6)	0.1	3.2	bdl	98.2	bdl	bdl
KEF35 (3)	bdl	3.3	bdl	93.6	1.2	0.6
KEF40 (1)	bdl	bdl	0.4	98.6	0.1	bdl
KEF41	bdl	bdl	0.1	98.0	0.3	bdl
FOU4 (5)	0.1	2.0	0.1	98.4	0.2	bdl
FOU14 (5)	bdl	1.4	bdl	97.6	0.4	0.1
FOU15 (2)	bdl	3.8	bdl	97.2	bdl	bdl
FOU26 (2)	bdl	4.7	bdl	96.3	bdl	bdl
FOU39 (2)	0.1	3.8	bdl	95.4	0.3	bdl
FOU31	bdl	bdl	0.1	98.9	bdl	bdl
<i>Matte</i>						
KEFav (60)	22.2	6.9	bdl	68.5	0.1	bdl
FOUav (72)	22.9	5.7	bdl	69.8	bdl	bdl

#### Notes

1. The analysis of copper prill KEF40 is the average of three point measurements on the one large prill found protruding on the surface of the slag.
2. Analyses KEF41 and FOU31 are averages of multiple analyses on the isolated copper prills recovered.

Aside from copper, the other main element identified within the copper metal prills is iron. With the exception of sample KEF40 discussed below, the iron content in the remaining enclosed metal prills is usually elevated, covering a wide range between 0.1% and 5.5%, and averaging around 3.5%. The copper prills in these slags are, however, generally very small and enclosed within an iron-rich matrix. It is therefore possible that the high iron contents measured are due to simultaneous measurement of the surrounding phases and should in this case be disregarded. This is further supported by the analysis of a single large prill (diameter ~1 cm) enveloped within a copper sulphide rim protruding on the upper surface of sample KEF40. The iron content of the uncorroded copper metal core is below the detection limit of the analytical method used (~0.05%). Iron contents below 0.1% were also measured in the two isolated copper prills, KEF41 and FOU31. Small copper sulphide inclusions could be distinguished within the copper metal in all three prills.

The copper prills have negligible contents of other base metals, the main one being arsenic, which still, however, usually measured below 0.5%. Arsenic contents above 1% were only found in copper prills in samples KEF14 (1.8% As measured in one prill) and KEF35 (1.8, 1.5 and 0.5% As in three separate prills). These should not be disregarded, but at this stage they constitute an exception. A similar phenomenon with a few slag samples bearing arsenic-rich prills (albeit higher arsenic contents than for the two Kephala slags) in a majority of non-arsenical copper slags was encountered at the site of Skouries on Kythnos (Gale and Stos-Gale 1989; Bassiakos and Philaniotou 2007). This observation had formed the basis for the proposal that arsenical copper production in the EBA Aegean was a result of 'accidental' smelting of arsenic-rich copper ores (Gale and Stos-Gale 1989), a suggestion that has since been repeatedly challenged (see, e.g., Bassiakos and Philaniotou 2007; Catapotis and Bassiakos 2007; Georgakopoulou in press). The number of samples that bear arsenic-rich copper prills on Kephala is low and their arsenic content is additionally relatively low. It would therefore be premature to argue for the use of different types of ore (arsenical and non-arsenical) at this stage (cf., Georgakopoulou 2007 for such an example), or for the production of arsenical copper in any large extent on these two sites.

### *Other materials*

The samples discussed below were collected from the field as specimens showing 'exceptional' external characteristics, different from the majority of slags. They are usually small in size, with a length of only a few centimetres and covered entirely or largely by a layer of secondary green copper salts. The examination of these samples using optical microscopy and scanning electron microscopy concluded that these can be distinguished into three types:

(a) *Unreacted minerals*. Specimen KEF29 is composed primarily of secondary iron and copper minerals, while traces of chalcopyrite are preserved within quartz inclusions. Specimens FOU39 and FOU40 are schist fragments with traces of green copper minerals between the schist layers, often associated with small quartz veinlets, parallel to the schistosity. On one edge of FOU39 an almost circular slag droplet, similar in phase and chemical composition to the other Phournoi examples, is attached to the schist fragment. The two are in close contact but do not appear to be reacting (Fig. 5), suggesting that the slag fell on the schist fragment outside the furnace. These three samples probably correspond to fragments of ore that were either deliberately discarded for being too poor in copper or accidentally dropped during processing. Their identification provides important information regarding the nature of the raw materials used for smelting.

(b) *Fragments of partially reacted furnace charge*. The central part of samples FOU20 and FOU38 consists of quartz and schist fragments mixed with secondary and primary copper-iron

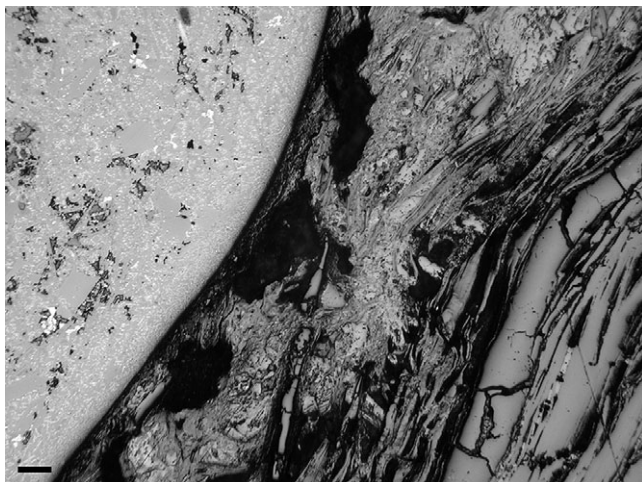


Figure 5 A reflected light microphotograph of sample FOU39 (scale 100  $\mu\text{m}$ ), showing the point of attachment of a slag droplet and a copper-enriched schist fragment.

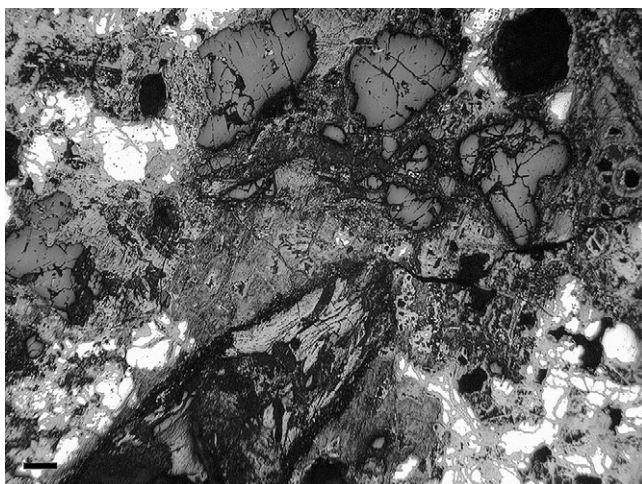


Figure 6 A reflected light microphotograph of sample FOU20 (scale 100  $\mu\text{m}$ ), showing quartz and schist fragments and residual sulphides (bright white) surrounded by a weathered copper-iron rich matrix.

minerals (Fig. 6). In their outer parts, both show evidence that they had started to react, such as eutectic textures in sulphides, indicating partial oxidation in the molten stage. Slag ‘proper’, of a typical olivine composition, has formed on their edges. The specimens clearly constitute part of the original furnace charge, only partially reacted, mainly towards the outer surfaces.

(c) *Isolated matte*. The core of samples KEF12 and KEF27 is composed of secondary copper and iron minerals, with iron hydroxide delineating the grain boundaries of the original sulphides. The latter are partially preserved in the centre of the grains, the larger showing a transition from a copper–iron sulphide in their centre to an external chalcocite or covellite ( $\text{Cu}_2\text{S}$  or  $\text{CuS}$ , respec-

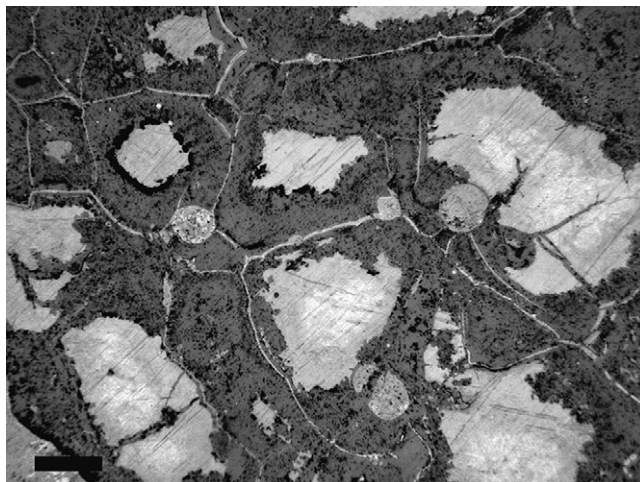


Figure 7 A reflected light microphotograph of sample KEF12 (scale 50  $\mu\text{m}$ ), showing copper–iron (brighter parts inside the larger ones) to copper sulphides in a completely weathered matrix. Note the slightly curved grain boundaries and the circular eutectics formed at the triple junctions.

tively) exterior zone, while in the smaller only the blue copper sulphides can be seen (Fig. 7). The grain boundaries are slightly curved with eutectic formations at their triple junctions, while elongated lines of a second eutectic phase can be distinguished in the weathered matrix under cross-polarized light. This microstructure conforms to that of a sulphidic melt freezing from a high temperature, and these specimens were therefore identified as matte formed during smelting and probably discarded at the end of the process as they could not be processed further.

Sample KEF28 is layered, consisting of an outer surface of green post-depositional copper salts followed by a dense sulphidic band, which analyses showed corresponds mainly to copper sulphide with minor amounts of iron. The atomic ratio of copper and sulphur is consistent with the mineral chalcocite,  $\text{Cu}_2\text{S}$ . The sulphide shows progressive weathering towards the inner parts of the sample, and is attached on the other side to a porous conglomerate with fragments of quartz and schist mixed with soil. The specimen was therefore recognized as matte (mainly copper sulphide), which came out of the reaction vessel or furnace while molten, possibly as an accidental spill, and came into contact with soil mixed with rock fragments.

#### POTENTIAL COPPER SOURCES ON SERIPHOS

The geological setting of Seriphos is mainly determined by the intrusion of granodioritic magma within a system of previously metamorphosed rocks (Marinos 1951; Salemink 1985). The granodiorite extends over more than one third of the surface of Seriphos, specifically the central and southeastern parts, while units of gneiss, schist and marble are exposed in the remaining parts of the island, as shown in Figure 1.

Seriphos is well known for its iron ore deposits, which were subjected to intense modern mining until the mid-20th century, while fragmentary pieces of evidence suggest exploitation of these resources in earlier historical periods (Davies 1935; Galanos 1962). Two types of iron mineralization can be distinguished: magnetite deposits found nearly all along the northern and

southern contact zone of the granodiorite mass and the metamorphic rocks, and hematite–limonite deposits formed mainly within the marble units of the western and southwestern part of Seriphos (Marinos 1951). In addition, mixed sulphidic deposits, primarily galena, are known in north-east Seriphos in the areas of Moutoula and Pyrgos. The Moutoula deposits were exploited in the 19th century for galena (Kordellas 1902), while a possibly earlier undated gallery has also been noted (Marinos 1951; Gale and Stos-Gale 1981).

Copper minerals are frequently reported in the geological literature as minor accompanying constituents to the iron ore deposits of Seriphos, but, as these are of no modern economic significance, their location and nature are not described in any detail (Marinos 1951; Salemink 1985). We undertook a brief geological reconnaissance on the island, aiming to identify and characterize copper mineralizations that could have served as ore sources in antiquity. Our search was not exhaustive, but was mainly based on a thorough examination of the geological literature and subsequent field investigation of some potentially interesting areas. Previous archaeometallurgical investigations on the island had already reported two such occurrences (Gale *et al.* 1985; Gale and Stos-Gale 2002).

Copper mineralizations were sampled at four different locations: Koutalas, Kalavatsena, Playia and Vounies. All four areas have been subjected to modern iron mining, primarily for hematite–limonite at Koutalas and Kalavatsena and for magnetite at Playia and Vounies, and relics of these activities abound. Galanos (1962) reports that at the end of the 19th century a permit for the extraction of sulphidic copper ores from the wider area of Kalavatsena was granted to a private citizen, but it is unclear whether such exploitation did in fact take place (Kordellas 1902, 17). Overall, it appears that copper minerals are more frequent in the southern part of the island in association with the hematite–limonite deposits. Samples were collected either from spoil heaps found outside modern mining galleries or from exposed road sections, while modern mine galleries were not entered at this stage. The samples were analysed with (P)ED-XRF as for the slags (Table 4). Further examination with X-ray diffraction (XRD) and EDS–SEM was undertaken where necessary. Most of the samples collected are secondary green copper minerals, while sulphidic minerals were only found at Playia and Kalavatsena. The samples from Vounies were identified as chrysocolla ( $\text{CuSiO}_3$ ), which is reported in the area (Salemink 1980, 352). Elements known in early copper alloys (e.g., arsenic, lead, nickel and antimony) are only present in trace quantities in these minerals, with the exception of some of the samples from Koutalas. Arsenic-rich green secondary copper minerals were found here, identified as conichalcite ( $\text{CaCuAsO}_4(\text{OH})$ ) on the basis of the XRD spectrum. This mineral appears to coexist with non-arsenical copper minerals at Koutalas.

Besides this broader geological reconnaissance on the island, the areas around the slag heaps were searched for copper. A very limited mixed secondary copper and iron mineralization was identified approximately 750 m south-east of the Kephala slag heap, close to the Hellenistic tower of Kephala. It appears to be associated with a volcanic outcrop that intersects the schist unit in this area. Although not noted on the published geological map, this occurrence is in agreement with Salemink (1980), who notes the presence of numerous igneous dykes within the metamorphic units, often bearing small quantities of copper and other minerals in their joints. Examination under the microscope revealed minute residual sulphides frequently preserved within the principally secondary mineralization (Fig. 8). Other base metals are only present in trace quantities. Indications for ancient exploitation were not noted, but the area merits substantial further exploration. Copper minerals have not been identified so far in the vicinity of Phournoi.

Table 4 The location, description and results of (P)ED-XRF analyses (major and minor elements in wt%) of geological samples from Seriphos (highlighted samples are primarily sulphides and results are given as elements rather than oxides)

Location	Description	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CuO	As <sub>2</sub> O <sub>3</sub>
RK1	Kephala tower	0.5	7.9	2.7	29	0.1	0.1	<0.1	0.5	0.1	0.1	21	24	0.2
RK2	Kephala tower	0.3	7.7	2.6	28	0.1	0.1	<0.1	0.5	0.1	0.1	21	24	0.2
KOU1	Road section at Koutalas	0.4	15	2.0	14	0.5	<0.1	0.2	12.0	0.1	0.5	1.2	22	19
KOU2	Outside mine gallery at Koutalas	0.3	9.8	0.9	12	0.2	<0.1	<0.1	21.0	<0.1	0.4	0.5	21	11
KOU3	Outside mine gallery at Koutalas	0.4	0.9	4.3	12	<0.1	1.5	0.1	3.2	0.2	<0.1	30	24	0.1
KOU4	Outside mine gallery at Koutalas	0.5	18	2.8	6.2	0.3	<0.1	0.1	17.0	0.1	0.3	1.6	28	29
KOU5	Outside mine gallery at Koutalas	0.3	16.0	1.5	1.0	0.6	<0.1	0.1	17.0	<0.1	0.9	1.0	27	29
KAL1	Kalavatsena spoil heaps	0.5	1.1	2.5	27	<0.1	3.9	0.1	1.4	<0.1	0.5	5.8	35	<0.1
KAL2	Kalavatsena spoil heaps	1.0	<0.1	0.1	3.8	<0.1	6.2	0.2	0.1	<0.1	<0.1	55	<0.1	<0.1
KAL3	Road section at Kalavatsena	0.5	1.8	10	56	<0.1	0.3	0.1	2.5	<0.1	0.3	8.1	5.0	<0.1
KAL4	Road section at Kalavatsena	0.8	0.9	0.6	26	<0.1	1.2	0.2	1.7	<0.1	0.1	23	30	<0.1
KAL5	Kalavatsena spoil heaps	1.2	<0.1	<0.1	5.6	<0.1	34.0	0.1	<0.1	<0.1	<0.1	37	<0.1	<0.1
PL1	Road section at Playia	0.3	2.0	1.8	29	<0.1	<0.1	0.6	4.5	0.1	0.2	31	8.4	<0.1
PL2	Playia spoil heaps	0.7	<0.1	<0.1	<0.1	<0.1	28.0	<0.1	<0.1	<0.1	<0.1	51	0.3	<0.1
PL3	Playia spoil heaps	<0.1	1.3	<0.1	9.9	<0.1	22.0	<0.1	17.0	<0.1	0.2	22	14	<0.1
VOU1	Vounites, outside a mine gallery	0.4	3.8	4.1	23	<0.1	0.1	<0.1	1.8	<0.1	1.5	0.8	39	<0.1
VOU2	Vounites, wall of mine gallery	0.1	0.2	0.7	3.0	<0.1	0.7	0.1	0.1	<0.1	0.3	73	0.2	<0.1
VOU3	Vounites, outside a mine gallery	0.3	23.0	1.1	60	<0.1	<0.1	<0.1	2.4	<0.1	0.3	2.3	1.5	<0.1

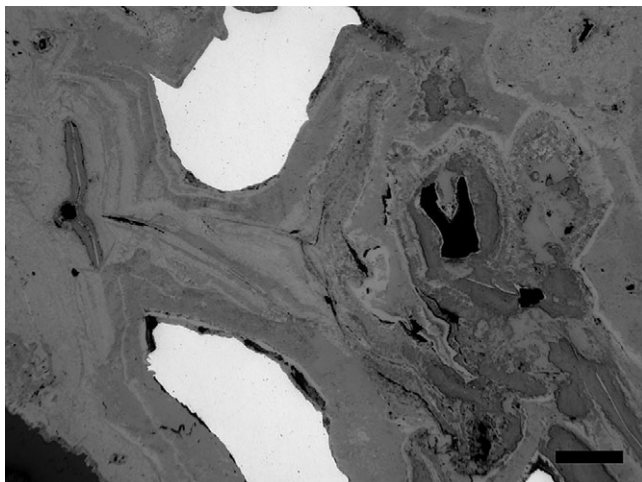


Figure 8 A reflected light microphotograph of a mineral sample from the Kephala tower (scale 100  $\mu\text{m}$ ), showing pyrite inclusions (white) in a secondary copper–iron mineral matrix.

#### THE TECHNOLOGICAL PARAMETERS OF COPPER PRODUCTION AT KEPHALA AND PHOURNOI

This study is the first comprehensive analytical examination of material from Kephala and Phournoi, with the exception of a few analyses of Kephala slags published in the past (Gale *et al.* 1985; Dimou and Economou 1997). The deposits of metallurgical remains are substantial on both sites and neither has been excavated to date. An effort was made to develop an appropriate sampling strategy that would ensure that spatially distinct parts of the sites were examined and that potentially different types of material were included but, admittedly, temporal variability cannot be assessed at this stage. The analyses carried out so far have not detected any consistent compositional differences among the different sampling units of Kephala and Phournoi that would suggest internal spatial division of activities. The slags are also broadly similar between the two sites, and for this reason Kephala and Phournoi will be considered together in the following discussion.

#### *The nature and source of the ores used*

The ores smelted on both Kephala and Phournoi appear to have been a mixture of secondary oxidic and primary sulphidic minerals. Evidence for the latter is far more prevalent in this study than in other broadly contemporaneous Aegean sites, where only minute matte prills within the slags suggest the incorporation of sulphides in the furnace charge (see, e.g., Bassiakos and Philaniotou 2007; Catapotis and Bassiakos 2007). In addition to these, on Seriphos trapped primary minerals were recognized in some slags (KEF13, FOU9 and FOU15), along with sulphide-rich partially reacted furnace charge fragments (FOU28 and FOU38), and small isolated matte fragments (KEF12, KEF27 and KEF28). This is the first time that such materials have been identified at EBA Aegean smelting sites (cf., Catapotis and Bassiakos 2007, 79). The majority of such evidence resulted from the study of specimens originally included as macroscopically ‘exceptional’ samples in addition to a larger sample of ‘representative’ material. It is presently

impossible to conclude whether this suggests a more extensive use of sulphidic minerals on Seriphos compared to neighbouring sites, or whether it is the result of the application of a more diverse sampling strategy.

Despite these finds, it is not advocated that smelting of solely sulphidic ores was taking place on Kephala and Phournoi. The sulphur levels in the slags are generally low. Furthermore, the few unreacted or partially reacted mineral fragments collected from the two sites (KEF29, FOU20 and FOU38) are mixtures of both secondary and primary minerals. The iron oxide aggregates associated with copper prills found in some of the slags are also indicative of the incorporation of secondary minerals. Matte and copper prills coexist in many slags. All of the above observations lead to the suggestion that co-smelting of oxidic and sulphidic minerals was taking place in a one-step process. The ratio of the two components is impossible to deduce on the basis of present evidence and is unlikely to have been stable. It should be noted that compared to the few thousand tons of slag estimated for the two sites (Philaniotou *et al.* in press), the few grams of matte presently identified form only a very minor component. Further excavated material is necessary for more substantiated quantification. It is, however, likely that the sulphidic component relates largely to residual material in a primarily oxidized ore. The presence of minute sulphidic remains in the secondary copper mineralization identified close to the Kephala tower, as well as the broader geology of the region, support this suggestion. In any case, the results from Seriphos add to a growing number of studies that show that, from the early stages of metallurgy, sulphidic copper ores were smelted, whether solely (see, e.g., Zwicker *et al.* 1985; Moesta and Schlick 1989; Bartelheim *et al.* 2003; Bourgarit *et al.* 2003), or together with oxidic ores (see, e.g., Rostoker *et al.* 1989; Rostoker and Dvorak 1991; Hauptmann *et al.* 2003; Schreiner *et al.* 2003), without the need for strongly reducing conditions or elaborate treatment.

The study of partially reacted inclusions within the slags as well as the discarded mineral fragments suggests that the copper minerals were naturally accompanied by secondary iron minerals, quartz, as well as schist. The close association of silica and iron-bearing components would have made the ores largely self-fluxing, although it is possible that the smelters deliberately manipulated the composition of the charge to balance the two components and achieve a better slag composition. This is, however, impossible to prove or disprove archaeologically in this case. The role of schist as a host rock to the copper mineralization was shown, at least in the case of Phournoi, by the examination of samples FOU39 and FOU40. This observation may be of some importance in the case of Seriphos in terms of locating the ore sources. The island's geological setting consists of different rock units, with an extensive schist unit found at the northern part, where both slag heaps are located. Minor copper mineralizations are known to exist within this unit, such as the one identified in the near vicinity of Kephala. The recovery of copper-bearing schist fragments from the Phournoi slag heap does not, however, provide conclusive evidence for the exploitation of a local source. Schist is common on many Cycladic islands, while copper-bearing schist is known on the neighbouring island of Kythnos (Bassiakos and Philaniotou 2007). A notable paradox on Seriphos is that the richest ore deposits, primarily iron with minor copper, are known in the southwestern part of the island. The slag heaps, however, are found further north, in an area (the schist unit) that is poor in ores, except from the mixed sulphidic deposits of Moutoula. The possibility is raised that additional slag heaps existed further south that have been destroyed, covered by modern workings or simply not been identified yet.

The provenance of the ores used on these smelting sites has not been fully addressed so far. The brief geological survey confirmed the presence of copper mineralizations on Seriphos, while similar occurrences are known to exist on neighbouring islands and in nearby regions (see, e.g.,

Gale and Stos-Gale 2002; Bassiakos and Philaniotou 2007). It is possible that these sites relied not only on local sources, but additionally or solely on ores transported from neighbouring regions, as has been suggested for the site of Skouries on Kythnos (Stos-Gale 2000; although see discussion in Georgakopoulou *in press*). Substantially more fieldwork within and beyond Seriphos, as well as a relevant analytical programme combining lead isotope and trace element analyses, would be necessary in order to examine whether distinctions can be made on the microscale of the Cycladic islands and surrounding areas (Georgakopoulou *in press*). Lastly, it is important to stress that the copper mineralizations of Seriphos and the neighbouring islands are always of very small scale and would certainly not be considered as copper ores in modern terms. Whether richer deposits existed on the island and were largely exploited in antiquity or even during modern iron mining is at this stage impossible to say.

A final remark concerns the content of the ores in other base metals commonly appearing as alloying elements in early copper artefacts, particularly arsenic. Earlier work on Kythnos had suggested that mixed-arsenical copper minerals are found on the island (Gale *et al.* 1985), leading to the broader perception that such minerals are frequent in the western Cyclades. The samples included in that study were, however, iron ores with low copper and arsenic contents (see discussion in Georgakopoulou *in press*), while further work on Kythnos has challenged the availability of arsenical copper ores on the island (Bassiakos and Philaniotou 2007). The unreacted or partially reacted ore fragments collected from the two slag heaps on Seriphos show only trace quantities of arsenic or other base metals. In addition, most of the mineralizations identified on the island are of pure copper mixed with iron ores. An important exception is Koutalas, where, for the first time, truly mixed secondary arsenical copper minerals are recognized in the region of the western Cyclades. The low arsenic content of the slags and of the discarded ore fragments on Kephala and Phournoi, however, imply that this source is not associated with the two slag heaps studied here.

### *Temperatures and redox conditions*

The chemical composition and microstructure of the slags allow insight into other operating parameters of the smelting process, such as the temperature, redox conditions, and the efficiency of separation between slag and metal, the latter being largely dependent on the viscosity of the slag. Although the chemical and microstructural characteristics of the slags from Kephala and Phournoi are broadly similar, substantial diversity is observed—evident, for example, in the range of chemical compositions attested and the different abundance of crystalline phases present among the samples. This heterogeneity is not surprising given the absence of strictly controlled conditions in early copper production furnaces, which unavoidably results in variability, even within the slags from the same smelting operation.

The rarity of unfused raw materials in the slags from Kephala and Phournoi and their overall microstructure indicate that in most cases conditions were appropriate for the furnace charge to fully react. Estimation of temperatures reached during smelting can be carried out with the use of ternary phase diagrams (see, e.g., Bachmann 1980), although the approach is restricted by several limitations that unavoidably only allow rough approximations (see, e.g., Kresten 1986; Hauptmann *et al.* 1988, 39; Kongoli and Yazawa 2001). On the basis of Figure 2, the liquidus temperatures for the majority of these slags are around 1100–1200°C, suggesting smelting temperatures in this range, with some parts of the furnace probably being hotter; a picture common in contemporaneous copper-producing industries in different parts of the Old World. The appearance of some of the Phournoi slags in the silica-rich part of the diagram is related to

the presence of partially reacted quartz fragments within them, as discussed above, and therefore temperature estimations for these should be disregarded. On the other hand, iron-rich samples such as KEF32 and KEF40 are close to the wüstite region. The absence of wüstite and the high concentrations of magnetite observed in these samples highlight the inability of these diagrams to deal accurately with systems under intermediate oxygen partial pressures (Kongoli and Yazawa 2001).

In terms of redox atmosphere within the furnace, a consideration of the phase composition of the slags in relation to the appropriate diagram showing phase transitions as a function of oxygen fugacity and temperature (for the buffer curves for the Fe–Si–O system and for copper reduction (Cu<sub>2</sub>–Cu), which are relevant for the study of these slags, see Craddock 1995, 18; Schreiner *et al.* 2003) gives a wide range of oxygen pressures between 10<sup>-6</sup> and 10<sup>-10</sup>. A more accurate estimation would not be presently appropriate, as the variable abundance of olivine and magnetite noted in these slags indicates variable conditions between but also possibly within smelts (cf., Hauptmann *et al.* 1988, 40). The abundance of magnetite in most samples and the oxidizing nature of the reaction in sample KEF13, however, argue against a strongly reducing atmosphere.

Separation of metal from slag is an important parameter for the success of a smelt and depends largely on the viscosity of the slag. A low viscosity ensures better separation from the metal by allowing it to drain through (Bachmann 1982). Additionally, liquid slag could be tapped outside the furnace and would further facilitate the separation from the metal. The use of quantitative calculations for viscosity estimations (see, e.g., Bachmann 1980) is considered inappropriate in the case of ancient slags (Kresten 1986). Following the example of Schreiner *et al.* (2003), however, some conclusions on the viscosity of the slags from Seriphos can be drawn using certain macroscopic observations. First, because undissolved inclusions are rare, it is clear that in most cases the raw materials had fully reacted. Evidence that the slags were molten at the operating temperatures also stems from the observation of flow patterns on the upper surface of many of the fragments. Large copper prills are rare and the majority have diameters below 10 µm, showing that the metal could drain through the liquid slag. The presence of a flow texture on the outer surface of the slags does not necessarily imply that the slags were tapped outside the furnace, as it could also result from molten slags crystallizing within the furnace. However, both the observation of magnetite bands associated with minute crystal phases and the identification on the sites of larger masses of slag with a flow texture that appeared to have cooled *in situ* on the schist bedrock suggest that at least some of the slag was tapped outside the furnace.

### *Composition of the final product*

On the basis of the analyses of numerous copper prills from both Kephala and Phournoi, it is suggested that the final product was unalloyed copper metal. It is possible that some arsenical copper was also produced, but arsenic-rich copper prills were extremely rare and, furthermore, the arsenic contents within them were still comparatively low. This is an important observation in the context of EBA Aegean copper production, where arsenical copper is a commonly attested alloy. The production of arsenical copper has long been considered to be the result of ‘accidental’ smelting of mixed-arsenical copper ores, based on the analyses of a few samples from the slag heap of Skouries on Kythnos (Gale and Stos-Gale 1989). The widespread production of arsenical copper on the western Cyclades, a region where the majority of EBA Aegean smelting sites are known, has been challenged by further work on Kythnos (Bassiakos and Philaniotou 2007) and now also by the results of the work undertaken on Seriphos. Similarly, proposals for the widespread availability of mixed-arsenical copper ores are contested, as discussed above. These

results, together with other evidence now being brought forward from other sites (see, e.g., Catapotis and Bassiakos 2007; Doonan *et al.* 2007), call for a reconsideration of the pathways followed in the production of this alloy in the EBA Aegean (Georgakopoulou *in press*).

Turning to the iron content of the copper produced, this ranged substantially (0.1–5.5%) in the prills trapped in the slag, but was notably below 0.05% in the large copper prill in sample KEF40 and in the two isolated prills KEF41 and FOU31. It was proposed above that the elevated iron contents in the prills could be partly due to an analytical error, given their small size and the iron-rich surrounding matrix, and that the actual iron content of the copper produced may have been much lower. It is noteworthy that most contemporaneous copper artefacts from this region have very low iron contents, usually below 0.1% (see, e.g., Craddock and Meeks 1987; Mangou and Ioannou 1997; Sherratt 2000, 72–95). Copper artefacts with an iron content around 0.05% have in the past been interpreted as products of early slagless copper smelting of very pure copper ores (Craddock and Meeks 1987; Craddock 1995, 137–44), a suggestion that clearly does not hold for the EBA Aegean, where slag deposits abound. The observation of copper with iron below 0.05% among the samples studied here raise the possibility that such low-iron copper could in fact be produced during smelting even in properly slagging processes, possibly because of less reducing atmospheres in the furnaces than those attained in later periods. Admittedly, the number of samples with securely analysed iron contents is presently very small and a much more systematic study will be necessary in order to address this possibility. Furthermore, the effect of temperatures and redox conditions on the iron content of the copper produced remains to be investigated. The direct expectation of iron-enriched copper from ‘slagging’ smelting processes (Craddock and Meeks 1987), however, may need to be reconsidered, particularly in intermediate redox conditions, as appears to be the case here (*cf.*, Hauptmann 2007, 204–11).

#### FURTHER DISCUSSION

This paper has focused on the analytical results of the archaeometallurgical study on Seriphos, but there are additional important aspects to be considered. Although these cannot be treated here at length, a brief mention will be made in closing.

Similarly to other slag heaps known in the south-central Aegean, Kephala and Phournoi appear to be isolated from any contemporaneous settlements. The organization of metallurgical activities on these sites is therefore difficult to address at this stage, as it is not clear whether they were associated with a single specific settlement or, alternatively, constituted long-term seasonally visited places specifically for metal production; whether by the same or different groups of people, from within the island or beyond (Catapotis 2007). The study of the small collection of metallurgical remains recently recovered from the contemporaneous settlement of Plakalona in the southwestern part of the island (Pantou *in press*), may shed some light on the relationship of local communities with the metallurgical activities undertaken on Seriphos.

The setting of these sites is characteristic and common to other copper production sites known in the south-central Aegean (*cf.*, Betancourt 2006; Bassiakos and Philaniotou 2007). The main concentrations of material on both slag heaps extend from just below the crest of the promontories and down the north-facing slope to the direction of the prevailing winds, suggesting that exploitation of natural draught for furnace operation may have played an important role (*cf.*, Hauptmann and Weisgerber 1992, 63–4; Juleff 1996; Pryce *et al.* 2007, 554).

Finally, few furnace fragments with perforations were identified at Kephala and Avessalos (Philaniotou *et al.* *in press*). Perforated furnaces appear in several Aegean sites and have formed the subject of interesting studies and discussion (see, e.g., Betancourt 2006; Bassiakos and

Philaniotou 2007; Pryce *et al.* 2007; Catapotis *et al.* 2008). The examples from Seriphos present important differences, as they constitute only a minority of the total furnace fragments on each site, while specimens with more than one hole are rare (Philaniotou *et al.* in press). Perforated furnace fragments were not found on Phournoi.

Kephala and Phournoi add to a growing number of copper production sites identified on the western Cycladic islands that highlight the importance of this region in Aegean EBA copper supply. The present study has provided a significant insight into the technological parameters of the copper smelting activities represented and has provided interesting data that can be compared with those from other neighbouring contemporaneous sites, working towards a regional assessment of Aegean EBA copper production.

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#### REFERENCES

- Bachmann, H.-G., 1980, Early copper smelting techniques in Sinai and Negev as deduced from slag investigations, in *Scientific studies in early mining and extractive metallurgy* (ed. P. T. Craddock), 103–34, British Museum Occasional Paper No. 48, The British Museum, London.
- Bachmann, H.-G., 1982, *The identification of slags from archaeological sites*, Occasional Publication No. 6, Institute of Archaeology, London.
- Bartelheim, M., Eckstein, K., Huijsmans, M., Krauß, R., and Pernicka, E., 2003, Chalcolithic metal extraction in Brixlegg, Austria, in *Archaeometallurgy in Europe*, vol. 1, 441–7, Associazione Italiana di Metallurgia, Milan.
- Bassiakos, Y., and Philaniotou, O., 2007, Early copper production on Kythnos: archaeological evidence and analytical approaches to the reconstruction of the metallurgical process, in *Metallurgy in the Early Bronze Age Aegean* (eds. P. M. Day and R. C. P. Doonan), 19–56, Sheffield Studies in Aegean Archaeology 7, Oxbow Books, Oxford.
- Betancourt, P. P. (ed.), 2006, *The Chrysokamino metallurgy workshop and its territory, Hesperia* Supplement 36, ASCSA Publications, Princeton, NJ.
- Bourgarit, D., Mille, B., Prange, M., Ambert, P., and Hauptmann, A., 2003, Chalcolithic fahlore smelting at Cabrières: reconstruction of smelting processes by archaeometallurgical finds, in *Archaeometallurgy in Europe*, vol. 1, 431–40, Associazione Italiana di Metallurgia, Milan.
- Broodbank, C., 2000, *An island archaeology of the early Cyclades*, Cambridge University Press, Cambridge.
- Catapotis, M., 2007, On the spatial organisation of copper smelting activities in the southern Aegean during the Early Bronze Age, in *Metallurgy in the Early Bronze Age Aegean* (eds. P. M. Day and R. C. P. Doonan), 207–23, Sheffield Studies in Aegean Archaeology 7, Oxbow Books, Oxford.
- Catapotis, M., and Bassiakos, Y., 2007, Copper smelting at the Early Minoan site of Chrysokamino, in *Metallurgy in the Early Bronze Age Aegean* (eds. P. M. Day and R. C. P. Doonan), 68–83, Sheffield Studies in Aegean Archaeology 7, Oxbow Books, Oxford.
- Catapotis, M., Pryce, O., and Bassiakos, Y., 2008, Experimental study of copper-smelting shaft furnaces, in *Aegean metallurgy in the Bronze Age* (ed. I. Tzachili), 113–21, Ta Pragmata Publications, Athens.
- Costin, C. L., 1991, Craft specialisation: issues in defining, documenting, and explaining the organisation of production, in *Archaeological methods and theory 3* (ed. M. Schiffer), 1–56, University of Arizona Press, Tucson, AZ.
- Craddock, P. T., 1995, *Early metal mining and production*, Edinburgh University Press, Edinburgh.
- Craddock, P. T., and Meeks, N. D., 1987, Iron in ancient copper, *Archaeometry*, **29**, 187–204.

- Davies, O., 1935, *Roman mines in Europe*, Clarendon Press, Oxford.
- Dimou, E., and Economou, G., 1997, Mineral chemistry and mineralogical composition of ancient slags all over Greece, in *Ancient Greek technology*, 313–23, Society of Macedonian Studies, Thessaloniki.
- Doonan, R. C. P., Day, P. M., and Dimopoulou-Rethemiotaki, N., 2007, Lame excuses for emerging complexity in Early Bronze Age Crete: the metallurgical finds from Poros Katsambas and their context, in *Metallurgy in the Early Bronze Age Aegean* (eds. P. M. Day and R. C. P. Doonan), 98–122, Sheffield Studies in Aegean Archaeology 7, Oxbow Books, Oxford.
- Douni, K., Georgakopoulou, M., Andrikou, E., and Kakavoyianni, O., in press, A regional approach to Early Helladic silver production in southeastern Attica, in *Prehistoric metal production in the Aegean: material evidence and analysis* (ed. Y. Bassiakos), Springer-Verlag, Heidelberg.
- Galanos, F., 1962, *Seriphos, part 1*, Athens.
- Gale, N. H., and Stos-Gale, Z. A., 1981, Cycladic lead and silver metallurgy, *The Annual of the British School at Athens*, **76**, 169–224.
- Gale, N. H., and Stos-Gale, Z. A., 1989, Some aspects of early Cycladic copper metallurgy, in *Mineria y metallurgia en las antiguas civilizaciones Mediterraneas y Europeas* (ed. C. Domergue), 21–37, Madrid.
- Gale, N. H., and Stos-Gale, Z. A., 2002, Archaeometallurgical research in the Aegean, in *The beginnings of metallurgy in the Old World* (eds. M. Bartelheim, E. Pernicka and R. Krause), 277–302, Leidorf, Rahden/Westf.
- Gale, N. H., Papastamataki, A., Stos-Gale, Z. A., and Leonis, K., 1985, Copper sources and copper metallurgy in the Aegean Bronze Age, in *Furnaces and smelting technology in antiquity* (eds. P. T. Craddock and M. J. Hughes), 81–101, British Museum Occasional Paper 48, The British Museum, London.
- Georgakopoulou, M., 2005, *Technology and organisation of early Cycladic metallurgy: copper on Seriphos and Keros, Greece*, unpublished Ph.D. thesis, University of London.
- Georgakopoulou, M., 2007, The metallurgical remains, in *Keros, Dhaskalio Kavos: the investigations of 1987–88* (eds. A. C. Renfrew, C. Doumas, L. Marangou and G. Gavalas), 380–401, McDonald Institute Monographs, McDonald Institute for Archaeological Research, Cambridge.
- Georgakopoulou, M., in press, Lead isotope analysis and metal production models for the Bronze Age Aegean, in *Prehistoric metal production in the Aegean: material evidence and analysis* (ed. Y. Bassiakos), Springer-Verlag, Heidelberg.
- Hadjianastasiou, O., and MacGillivray, S., 1988, An Early Bronze Age smelting site on the Aegean island of Kythnos; part two: the archaeological evidence, in *Aspects of ancient mining and metallurgy* (ed. J. E. Jones), 31–4, The Classical Association, Bangor and North Wales Branch, Bangor, Wales.
- Hauptmann, A., 2007, *The archaeometallurgy of copper: evidence from Faynan, Jordan*, Springer-Verlag, Heidelberg.
- Hauptmann, A., and Weisgerber, G., 1992, Periods of ore exploitation and metal production in the area of Feinan, Wadi ‘Arabah, Jordan, *Studies in the History and Archaeology of Jordan*, **4**, 61–6.
- Hauptmann, A., Rehren, Th., and Schmitt-Strecker, S., 2003, Early Bronze Age copper metallurgy at Shahr-i Sokhta (Iran), reconsidered, in *Man and mining* (eds. Th. Stöllner, G. Körlin, G. Steffens and J. Cierny), 197–213, Der Anschnitt, Beiheft 16, Deutsches Bergbau-Museum, Bochum.
- Hauptmann, A., Weisgerber, G., and Bachmann, H.-G., 1988, Early copper metallurgy, in Oman, in *The beginning of the use of metals and alloys* (ed. R. Maddin), 34–51, The MIT Press, Cambridge, MA.
- Juleff, G., 1996, An ancient wind-powered iron smelting technology in Sri Lanka, *Nature*, **379**, 60–3.
- Kongoli, F., and Yazawa, A., 2001, Liquidus surface of FeO–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaO slag containing Al<sub>2</sub>O<sub>3</sub>, MgO, and Cu<sub>2</sub>O at intermediate oxygen partial pressures, *Metallurgical and Material Transactions*, **32B**, 583–92.
- Kordellas, A., 1902, *The mineral wealth and salt pans of Greece from a geological, statistical, and historical perspective*, Sakellariou, Athens.
- Kresten, P. 1986, Melting point and viscosities of ancient slags: a discussion, *Journal of the Historical Metallurgy Society*, **20**, 43–5.
- Kresten, P., and Hjörthner-Holdar, E., 2001, Analyses of the Swedish ancient iron reference slag W-25:R, *Historical Metallurgy*, **35**, 48–51.
- Mangou, H., and Ioannou, P. V., 1997, On the chemical composition of prehistoric Greek copper-based artefacts from the Aegean region, *The Annual of the British School at Athens*, **92**, 60–72.
- Marinos, G., 1951, Geology and metallogenesis of Seriphos island, *The Mineral Wealth of Greece*, **1**, 95–127.
- Moesta, H., and Schlick, G., 1989, The furnace of Mitterberg: an oxidising Bronze Age copper process, *Bulletin of the Metals Museum*, **14**, 5–16.
- Pantou, P., in press, Evidence of prehistoric habitation and metallurgical activities on Seriphos: the site of Plakalona, in *Prehistoric metal production in the Aegean: material evidence and analysis* (ed. Y. Bassiakos), Springer-Verlag, Heidelberg.

- Papadopoulou, Z., and Chrysovergi, M., in press, Akrotiraki revisited: metallurgical evidence from the southern part of Siphnos, in *Prehistoric metal production in the Aegean: material evidence and analysis* (ed. Y. Bassiakos), Springer-Verlag, Heidelberg.
- Philaniotou, O., Bassiakos, Y., and Georgakopoulou, M., in press, Early Bronze Age copper production on Seriphos (Cyclades, Greece), in *Metallurgy: understanding how, learning why. Studies in honour of James D. Muhly* (eds. P. P. Betancourt and S. C. Ferrence), INSTAP Academic Press, Philadelphia, PA.
- Pryce, O., Bassiakos, Y., Catapotis, M., and Doonan, R. C., 2007, 'De Caerimoniae' technological choices in copper-smelting furnace design at Early Bronze Age Chrysokamino, Crete, *Archaeometry*, **49**, 543–57.
- Ramdohr, R., 1980, *The ore minerals and their intergrowths*, Pergamon Press, Oxford.
- Rostoker, W., and Dvorak, J. R., 1991, Some experiments with co-smelting to copper alloys, *Archaeomaterials*, **5**, 5–20.
- Rostoker, W., Pigott, V. C., and Dvorak, J. R., 1989, Direct reduction to copper metal by oxide–sulfide mineral interaction, *Archaeomaterials*, **3**, 69–87.
- Salemink, J., 1980, On the geology and petrology of Seriphos island (Cyclades, Greece), *Annales Géologiques des Pays Helléniques*, **30**, 342–65.
- Salemink, J., 1985, *Skarn and ore formation at Seriphos, Greece as a consequence of granodiorite intrusion*, Offset-drukkerij Kanters B.V., Alblasserdam.
- Schreiner, M., Heimann, R. B., and Pernicka, E., 2003, Mineralogical and geochemical investigations into prehistoric smelting slags from Tepe Sialk/central Iran, in *Archaeometallurgy in Europe*, vol. 1, 487–96, Associazione Italiana di Metallurgia, Milan.
- Sherratt, S., 2000, *Catalogue of Cycladic antiquities in the Ashmolean Museum, the captive spirit*, vol. 1, Text, Oxford University Press, Oxford.
- Stos-Gale, Z. A., 2000, An overview of lead isotope data for provenance studies and the trade in metals in the Bronze Age Mediterranean, in *Metals make the world go round: the supply and circulation of metals in Bronze Age Europe* (ed. C. F. E. Pare), 56–69, Oxbow Books, Oxford.
- Stos-Gale, Z. A., and Gale, N. H., 2003, Lead isotopic and other isotopic research in the Aegean, in *Metron: measuring the Aegean Bronze Age* (eds. K. P. Foster and R. Laffineur), 83–101, Aegaeum 24, Université de Liège, Liège/University of Texas at Austin, Austin, TX.
- Veldhuijzen, H. A., 2003, 'Slag\_Fun'—a new tool for archaeometallurgy: development of an analytical (P)ED-XRF method for iron-rich materials, *Papers from the Institute of Archaeology*, **14**, 102–18.
- Wagner, G. A., and Weisgerber, G., 1985, *Silber, Blei und Gold auf Sifnos*, Der Anschnitt, Beiheft 3, Deutsches Bergbau-Museum, Bochum.
- Zacharias, N., Michael, C. T., Georgakopoulou, M., Kilikoglou, V., and Bassiakos, Y., 2006, Quartz TL dating on selected layers from archaeometallurgical kiln fragments: a proposed procedure to overcome age dispersion, *Geochronometria*, **25**, 29–35.
- Zwicker, U., Greiner, H., Hofmann, K.-H., and Reithinger, M., 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* (eds. P. T. Craddock and M. J. Hughes), 103–15, British Museum Occasional Paper No. 48, The British Museum, London.