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The Marble Finds from Kavos and the Archaeology of Ritual

Edited by Colin Renfrew, Olga Philaniotou, Neil Brodie, Giorgos Gavalas & Michael J. Boyd

> The sanctuary on Keros and the origins of Aegean ritual practice VOLUME III





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Edited by Colin Renfrew, Olga Philaniotou, Neil Brodie, Giorgos Gavalas & Michael J. Boyd

with contributions from

Myrto Georgakopoulou, Anno Hein, Jill Hilditch, Vassilis Kilikoglou, Daphne Lalayiannis, Yannis Maniatis, Peggy Sotirakopoulou & Dimitris Tambakopoulos

The sanctuary on Keros and the origins of Aegean ritual practice: the excavations of 2006–2008 VOLUME III





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Cover image: *The Special Deposit South from the southeast (foreground) with Dhaskalio in the background.* Inset: *(front) Head* **351***, from Trench D2, layer 1; (back) Torso* **25055** *from Trench RA, layer 14.*

Frontispiece image: Torso, waist, pelvis and upper legs of folded-arm figurine of Spedos variety (**30028** from Area P on Kavos).

Edited for the Institute by James Barrett (Series Editor) and Anne Chippindale.

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Abbreviations

centimetre diameter
gram height kilometre
length
metre
millimetre
plain polarized light
Scanning Electron Microscopy with Energy Dispersive Spectroscopy
Scanning Electron Microscopy with Back Scattered Electron imaging
special find
thickness
width
weight
cross polarized light

Unless otherwise stated, the scale for finds is in centimetres.

Preface

Colin Renfrew & Michael J. Boyd

The status of Kavos on Keros as the earliest maritime sanctuary in the world is documented by the present volume, which includes (in Part A) the full publication of the marble finds from the Special Deposit South at Keros. These constitute the largest assemblage of Early Cycladic sculptures and vessels ever recovered in a controlled excavation, although they were all found in fragmentary condition. They add significantly to the already substantial corpus of finds from welldocumented contexts in the Cycladic islands. They open new possibilities for the study of the production and the use of the rich repertoire of Cycladic artefacts of marble and thus to the understanding of ritual practice in Early Cycladic societies. The marble sculptures from the looted Special Deposit North at Kavos that have been recovered in systematic excavations will be discussed in Volume VII.

Also included here (in Part B) are chapters offering our concluding assessment of the roles of the settlement on Dhaskalio and of the two Special Deposits at Kavos. The publication The Settlement at Dhaskalio constitutes Volume I of the present series, while Kavos and the Special Deposits forms Volume II. The Pottery from Dhaskalio and The Pottery from Kavos, Volumes IV and V respectively, both by Peggy Sotirakopoulou, will complete the publication of the 2006 to 2008 excavations of the Cambridge Keros Project.

The existing and projected volumes of the Cambridge Keros Project are as follows:

Volume I: The Settlement at Dhaskalio (2013, edited by C. Renfrew, O. Philaniotou, N. Brodie, G. Gavalas & M.J. Boyd).

Volume II: Kavos and the Special Deposits (2015, edited by C. Renfrew, O. Philaniotou, N. Brodie, G. Gavalas & M.J. Boyd).

Volume III: The Marble Finds from Kavos and the Archaeology of Ritual (2018, edited by C. Renfrew, O. Philaniotou, N. Brodie, G. Gavalas & M.J. Boyd).

Volume IV: The Pottery from Dhaskalio (2016, by P. Sotirakopoulou).

Volume V: The Pottery from Kavos (in preparation, by P. Sotirakopoulou).

Volume VI: The Keros Island Survey (in preparation, edited by C. Renfrew, M. Marthari, A. Del-

laporta, M.J. Boyd, N. Brodie, G. Gavalas, J. Hilditch & J. Wright).

Volume VII: Monumentality, Diversity and Fragmentation in Early Cycladic Sculpture: the finds from the Special Deposit North at Kavos on Keros (in preparation, by C. Renfrew, P. Sotirakopoulou & M.J. Boyd).

Here we present first the marble sculptures and vessels recovered from the Special Deposit South, which are fully described and illustrated in the chapters which follow. Their contexts are given in detail in Volume II where each is listed in the detailed tables accompanying chapter 4 of that volume. There the tables are organised by trench and then by layer number, each sculptural or vessel fragment being listed by its special find number, which is unique to the excavation. The other finds from the Special Deposit South are all dealt with in detail in that volume, with the exception of the pottery, whose publication will form Volume V. The weathering of the marble finds is discussed by Maniatis & Tambakopoulos in chapter 11 of Volume II. Various features of the contexts of the finds are analysed by Michael Boyd in chapter 12 of Volume II. The potential joins noted among the sculptures recovered from the Special Deposit South are discussed in appendix 13B of Volume II and those among the marble vessels in appendix 13A (see further Chapter 4 in this volume). The lack of joins observed between finds from the Special Deposit North and the Special Deposit South is noted there. The characterisation of the marble used to produce the sculptures and vessels from the Special Deposit South is discussed in Chapter 5 of the present volume.

The finds, among the various categories, from the settlement at Dhaskalio and from the two Special Deposits at Kavos are then compared and contrasted in Part B. This allows the differing functions of the settlement and of the Special Deposits to be brought into focus, and the intensity of their use during the different phases of activity in the early bronze age to be considered further. An attempt is then made, in Chapter 10, to set the ritual functions of the sanctuary on Keros into the wider context of early ritual practice in the Aegean and beyond.

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The project was initiated with support from the Balzan Foundation and has been consistently supported with a series of grants from INSTAP (the Institute for Aegean Prehistory). The participation of Dr Michael Boyd was made possible by a generous grant from the Stavros S. Niarchos Foundation (in memory of Mary A. Dracopoulos): the Niarchos Foundation made subsequent grants in support of publication. Further financial support has come from the British Academy, the A. G. Leventis Foundation, the Leverhulme Trust, the Society of Antiquaries of London, the Research Fund of the McDonald Institute and the British School at Athens. The participation of Dr Sotirakopoulou in the post-excavation work in 2009 was supported by the N.P. Goulandris Foundation.

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The project is grateful to Christos Doumas, Photeini Zapheiropoulou, and Lila Marangou for their warm support for the enterprise. In particular Christos Doumas and Photeini Zapheiropoulou encouraged us to examine material from their prior excavations in order to consider the possibility of joining material between the Special Deposits North and South.

The excavation personnel in the 2006 to 2008 excavation seasons were thanked by name in the acknowledgements of Volumes I and II and we are grateful for their participation. We are grateful also for the continuing support of our co-workers on Ano Kouphonisi, where we were based for the excavation seasons of 2006-2008 and the study season of 2009.

The study of the figurines and marble vessels was carried out in the Naxos Museum, as was the sampling for the marble study. We are grateful to the Museum, its director, Irini Legaki, and its staff, especially Daphne Lalayannis, Ilias Probonas and Vasiliki Chamilothori.

The drawings of finds have been contributed by Jenny Doole and Tassos Papadogonas.

Photographs of finds and many of the site photographs are by Michael Boyd, with other site photographs (and some finds) by Thomas Loughlin and by other members of the excavation team. We are grateful to Vicki Herring for undertaking final work on the figures during the production process, and to Anne Chippindale, for her work on the text, and for seeing the volume through the press, and to Jenny Doole for compiling the index.

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Chapter 8

Metal Production, Working and Consumption Across the Sites at Dhaskalio and Kavos

Myrto Georgakopoulou

Introduction

In the two previous volumes of the project, metal and metallurgical finds were discussed in relation to their types and recovery contexts. Following macroscopic and typological study, representative samples of different types among these finds were selected for analysis to address specific questions relating to the acquisition, production and use of metal on the different parts and the different chronological phases of the sites at Dhaskalio and Kavos.

An analytical examination of metallurgical materials recovered during the 1987 survey on Kavos was previously presented (Georgakopoulou 2007a). That assemblage included primarily finds from the Kavos Promontory (then referred to as Kavos North) and the broader area now named the Kavos Middle Area. Dhaskalio had not been surveyed at the time, while the Kavos Special Deposit South area, corresponding roughly to the southeast part of the survey grid, was almost devoid of any metallurgical finds (Georgakopoulou in Volume II, chapter 10), as were the squares corresponding to the Kavos Special Deposit North (Georgakopoulou 2007a, 399). Nearly all of the slag and metallurgical ceramics analysed from the survey were attributed a smelting origin. Two groups of material were identified, Group 1 and Group 2, representing the by-products of two distinct processes, leading respectively to production of unalloyed copper and arsenical copper with significant lead and minor contents of other base metals. A consideration of spatial distribution patterns suggested that the concentration of slag and other metallurgical finds at Kavos Promontory far exceeded that in any other part of Kavos surveyed, a suggestion that was confirmed in the context of recent fieldwork. Furthermore, a single litharge fragment recovered from the area of the Special Deposit North had raised the possibility that cupellation was also practised on Kavos. Finally, numerous mainly small fragments of secondary iron

minerals had been recovered from all parts of the surveyed area. Their distribution and the lack of any obvious relationship to the attested metallurgical practices led to the proposal that they were probably part of the local geology. This proposal was also confirmed during current fieldwork, when it was noted that poor iron minerals have been introduced into the marble rock of Keros (Volume I, chapter 3, 32). For this reason, similar fragments of secondary iron minerals, frequently recovered during the current excavations, were not processed further in the context of the present study, as they represent natural instead of anthropogenic material.

Metallurgical finds were recovered in all main parts of the sites during the 2006-08 excavation seasons (Volume I, chapter 32; Volume II, chapters 10, 14, 15, 17 and 19), but the main recovery contexts were the Kavos Promontory and Dhaskalio. For the present analytical study, only materials from these two parts of the site were sampled. The nature of finds from the two areas is clearly different. The Kavos Promontory hosts a small-scale copper-smelting site, located on a low-level coastal promontory, facing the prevailing northern winds, a setting common amongst many contemporaneous metal-production sites in the southern Aegean (e.g. Bassiakos & Philaniotou 2007; Betancourt 2006; Philaniotou *et al.* 2011). There are no clear habitation remains of this period in the area and the only other activity possibly attested is obsidian knapping (Volume II, chapter 19). Analytical examination of further samples from this area was undertaken to assess the validity and relative abundance of the two previously recognized groups on the Kavos Promontory. Furthermore, the earlier study had left several unanswered questions, such as the nature and source of the raw materials used, the former particularly important for the Group 2 process. Recent studies have shown different approaches to the production of arsenical copper in the early bronze age southern Aegean (Catapotis & Bassiakos 2007; Doonan et al.

2007; Georgakopoulou 2007a). At Chrysokamino on Crete, mixing of copper-rich and arsenic-rich minerals was proposed (Bassiakos & Catapotis 2006; Catapotis & Bassiakos 2007), while at Poros-Katsambas mixing of copper metal with arsenic minerals (Doonan *et al.* 2007), later proposed to be speiss (Thornton *et al.* 2009). Both of these case studies challenged previous claims that arsenical copper production in the Aegean early bronze age was always carried out through smelting of naturally mixed arsenical copper ores (Gale & Stos-Gale 1989). Although Group 2 slags are clearly related to production of arsenical copper, examination of the few previously recovered samples did not provide conclusive evidence for the pathway of production followed on Kavos (Georgakopoulou 2007a).

In contrast to the Kavos Promontory, the excavations on Dhaskalio revealed clear evidence for the existence of a settlement. The nature of the metallurgical finds was also distinctly different and in line with the associated context. Numerous metal artefacts were found, from all phases, but mainly from the better documented Phase C. These were primarily copper and lead, while the two gold artefacts from Phases B and C are noteworthy primarily for the rarity of this metal in the early bronze age Cyclades, contrary to the situation in contemporaneous northern Aegean and Cretan sites (see discussion in Volume I, chapter 32). Several of these artefacts were sampled in order to address their composition and method of manufacture, as well as the provenance of the metal used. Beyond finished artefacts, a varied assemblage of metallurgical remains was also recovered from Dhaskalio, including some slag, metallurgical ceramics and numerous metal spills, as well as solitary examples of litharge and speiss. Their macroscopic features suggested, with few exceptions, that these were associated with secondary metalworking practices instead of primary metal production. The aim of the analytical examination of the material from Dhaskalio is to understand the nature and technological parameters of the processes they resulted from.

Following the presentation of the analytical results, the finds from the different parts of the site are considered comparatively, assessing the relationship between them and the overall patterns for metal production, working and consumption at Dhaskalio and Kavos.

Analytical methodology

Sections were cut from the selected samples in order to study their microstructure and chemical composition. Metallurgical remains were sectioned using a diamond-tipped wheel saw, while minute samples were removed from the metal artefacts using a jeweller's saw. The samples were mounted in resin, ground, and polished with diamond paste to 0.25 μ m. Sample preparation was done at the Fitch Laboratory of the British School at Athens and analyses at the Archaeological Materials Science Laboratories of UCL Qatar, unless otherwise stated. The sections were studied under high magnification using a reflected light microscope (Leica DM2500P). Sections of copper artefacts were furthermore etched for metallographic study, where appropriate, using alcoholic ferric chloride (Scott 2012).

A scanning electron microscope (SEM: JEOL JSM 6610LV) with an attached energy-dispersive X-ray spectrometer (EDS: Oxford Instruments XMax-N 50) was used for chemical analysis of the bulk composition and of individual phases on the same sections. Analyses were done using the Aztec software. Measurements were run in high vacuum conditions, at an accelerated voltage of 20 kV, working distance 10 mm, process time 5, and acquisition time 60 seconds livetime. A cobalt standard was measured periodically to monitor the beam current and the spot size was adjusted around 59 to achieve 40 per cent deadtime on a cobalt metal standard. A common problem in EDS analyses is the overlap of peaks, for metals particularly those of lead (PbL α) and arsenic (AsK α). In the specific software the problem appears to be largely overcome, as arsenic is measured on the AsL α and lead on the PbM lines respectively. The latter may suffer somewhat from an overlap with the sulphur K line, where the two elements co-exist, although the Aztec software offers improved deconvolution of overlaps and thus accuracy should not be too deteriorated. The performance of the instrument was measured by analysing several Certified Reference Materials (CRMs) and a summary of the data is given in Table 8.1. The CRMs in question (36X CUAS3, 32X SN5A, 32X SN7A, 32X PB10, 32X SN6 and 33X GM29) are internationally available standards widely used for calibration purposes. Unfortunately none of the available CRMs had both lead and sulphur certified, so the effect of the aforementioned overlap could not be tested. Agreement (estimated as δ %) with certified values for major elements (>1 per cent) is generally within 10 per cent, usually within 5 per cent. One exception is the measurement of lead in 32X SN7, where lead was significantly underestimated in the SEM-EDS measurements. Lead is immiscible in copper at room temperature and appears as distinct segregated phases in copper alloys, as well as in this standard. It is likely that this difference with the certified value is due to heterogeneity of lead distribution in the metal standard. Similarly the content of tin in 36X CuAs3

was significantly overestimated. Tin oxide inclusions were clearly visible as distinct phases in the standard matrix and again the difference most likely reflects heterogeneity within the material matrix. For minor elements $\delta\%$ is within 10–15 per cent and deteriorates further as contents approach the detection limits of each element.

In order to compare data acquired from the SEM-EDS, but also to obtain some further data with better detection limits, a small number of metal artefacts were also analysed using an electron microprobe (JEOL JXA 8100) with three wavelength dispersive spectrometers at the Institute of Archaeology, UCL. The instrument was operated at 20 kV, working distance of 10 mm and rastered at a magnification of ×1000. The following elements were analysed for: O, Al, Si, S, Cl, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Te, Au, Pb, Bi. Performance was again monitored with a set of CRMs and the relevant data are given in Table 8.1. It is noteworthy that arsenic generally seems to be consistently underestimated, although none of the available CRMs had significant arsenic contents. Also, similarly to before, lead and bismuth, both immiscible with copper at room temperature, were found to be less accurate than expected. Again, this picture is probably due to heterogeneity in the standard itself, with these elements being variably distributed across the section.

Arsenic contents in copper-based metals were systematically lower in the microprobe measurements compared to the SEM-EDS (Table 8.6, below). Although further CRM analyses, containing different arsenic levels, would be necessary to conclude with certainty on the accuracy of each technique, based on those analysed here, the SEM-EDS analyses appear closer to the real value. For this reason, the discussion of the results that follows considers those data, although both are given in Table 8.6.

Bulk chemical analyses on the SEM-EDS were taken using area analyses (usually *c*. 0.2 sq. mm but also dependent on the size of the specimen and the extent of corrosion), avoiding highly corroded areas where possible. Segregation is often intense in these early alloys and distinct phases of immiscible elements are discerned (e.g. sulphides, lead, bismuth). Given the potentially heterogeneous distribution of these phases in the metal, data are reported both for the bulk composition and for areas taken of the metal matrix avoiding distinct immiscible phases.

Only a selected number of metal artefacts could be sampled for analysis. In order to extend some preliminary conclusions to a larger assemblage, particularly with regard to the nature of copper alloys used on the site, qualitative surface analyses of a larger part

of the assemblage were undertaken using a portable X-ray fluorescence spectrometer. The XRF instrument used was developed at the Institute of Nuclear Physics at Demokritos and consists of a Rh-anode sidewindow low power X-ray tube (50 W, 40 kV, 75 μ m Be window), a PIN diode X-ray detector with a 500 μ m nominal crystal thickness and 165 eV FWHM at the Mn-Ka peak (Amptek). The beam spot at the sample position has a diameter of about 3 mm. The tube high voltage was set at 40 kV and the current between 30 and 60 μ A depending on the observed rate. A filter was used to eliminate peaks below approximately 2 keV. Each object was measured for approximately 500 seconds. All artefacts that were transferred to the National Museum of Athens for conservation were examined with this method. Analyses were carried out following conservation, so surfaces had been cleaned from encrustations; however, the external layer accessible to analysis with this technique is corroded and the shape of several artefacts (e.g. pins, etc.) meant that surfaces were frequently not adequate in size for analysis. These results are only considered qualitatively, but are adequate for the broad categorization of artefacts according to their alloy type.

Lead isotope analyses were carried out at the Institute of Geography and Geology of the University of Copenhagen using a VG54 Sector IT thermal ionization mass spectrometer.

Kavos Promontory

Slag

Eight slags were selected for analysis from the Kavos Promontory. They were selected to represent different parts of the newly surveyed area, as well as the excavated trenches. An effort was also made to select slag that showed different macroscopic characteristics (e.g. magnetic properties, extent of external copper staining, size etc). Approximately 40 samples of slag were originally selected to be taken to the laboratory. At this stage no preliminary analysis had been undertaken to influence sampling on the basis of whether these slags belonged to one of the two previously recognized groups (Georgakopoulou 2007a). Six of the slags were found to be consistent with Group 1, and one with Group 2. At a later stage a pXRF was used to determine whether further Group 2 slag could be identified qualitatively in the remaining assemblage of samples brought to the laboratory so a second sampling stage could take place. Only one more sample was identified as such and included. The main characteristics of these slags are very similar to those defined before for the respective groups and the reader is referred to Georgakopoulou (2007a) for a more detailed discus-

deviations caused by fluctuations in the energy of the electron beam, although all measured totals were within 2 per cent of 100 per cent. Elements consistently present in CRMs at or below 0.01 per cent were not included in this table. The table presents the certified values (cert); the means of 5 area analyses on the SEM-Table 8.1. Analyses of Certified Reference Materials on the SEM-EDS and microprobe. SEM-EDS data were normalized to 100 per cent in order to eliminate EDS and 10 on the microprobe (mean); the relative standard deviations (rsd); and the relative differences of the mean to the certified values, given as $\delta^{0/0} = (X_{mean} - X_{cert})/X_{cert} \times 100.$

	AI	Ρ	s	IJ	Ç	Mn	Fe	Co	ï	Cu	Zn	\mathbf{As}	Ag	Cd	Sn	\mathbf{Sb}	$^{\mathrm{Pb}}$	Bi
SEM-EDS																		
36X CUAS3 cert							0.00		0.00			2.90		0.00	0.01		00.0	
36X CUAS3 mean										96.73		3.02			0.25			
rsd										0.3		4.8			100.9			
δ%												4.0			2677.8			
32X SN5A cert	0.47				0.06	0.72	1.20	0.14	0.50	78.96	0.49	0.06	0.10	0.15	16.05	0.66	0.26	0.10
32X SN5A mean	0.50				0.03	0.78	1.38	0.15	0.51	78.59	0.54				17.01	0.50		
rsd	5.8				137.3	3.1	6.1	28.4	3.5	0.5	3.9				2.0	14.1		
δ%	4.6				-41.9	8.9	15.2	10.1	1.2	-0.5	9.3				6.0	-24.1		
32X SN7A cert	0.05	0.06						0.44	0.18	80.30	1.96	1.07	0.31	0.04	12.60	0.26	2.60	0.05
32X SN7A mean		0.05						0.50	0.17	81.58	2.03	1.19	0.32		12.92		1.24	
rsd		144.4						9.8	25.1	0.9	2.6	4.6	11.7		2.8		22.0	
δ%		-3.6						13.3	-1.7	1.6	3.4	10.7	5.6		2.5		-52.2	
Microprobe																		
32X PB10 cert	<0.0005		0.02			0.00	0.01		0.06	87.77	0.04	0.01			11.93	0.01	0.05	
32X PB10 mean	0.01		0.04	0.00	0.01	0.00	0.02	0.00	0.06	86.41	0.01	0.00	0.00	0.00	11.75	0.01	0.07	0.01
rsd	125.9		32.9	144.9	75.3	122.5	49.7	175.3	6.7	0.4	118.3	300.0		240.8	2.9	137.1	31.4	158.7
δ%			100.0			344.4	112.2		4.4	-1.5	-74.6	-96.0			-1.5	2.0	30.9	
32X SN6 cert	0.03		0.02		0.00	0.00	0.10	0.66	0.20	86.39	1.17	0.76	1.16	0.09	7.31	0.32	1.56	0.16
32X SN6 mean	0.05		0.07	0.01	0.01	0.00	0.11	0.77	0.22	87.06	1.06	0.53	1.17	0.09	7.16	0.28	1.32	0.08
rsd	28.2		49.6	66.4	76.3	180.7	4.1	2.8	4.5	1.2	1.9	9.0	11.7	25.1	3.9	13.1	33.9	46.9
δ%	67.1		262.2		350.0	54.2	12.5	16.9	6.5	0.8	-9.4	-30.4	0.6	0.8	-2.0	-13.1	-15.1	-49.6
33X GM29 cert			0.00		0.00	0.00	0.01		0.03	89.36	4.23	0.00	0.00		6.12	0.00	0.05	0.00
33X GM29 mean	0.01		0.01	0.00	0.00	0.01	0.01	00.0	0.03	88.80	4.27	0.00	00.0		6.23	0.00	0.05	0.00
rsd	113.6		51.4	125.0	137.1	159.7	41.1	232.2	29.8	0.5	1.0	331.7	247.1		2.5		52.0	230.1
5%			362.1			918.2	18.1		-5.3	-0.6	0.8	-14.4	-19.6		1.8	-100.0	-0.4	153.6

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and in their context column the trench (Tr) and layer (L) are given. A summary of bulk analyses results from the slags presented in Georgakopoulou (2007a) are samples were surface finds from the systematic survey on Kavos Promontory; the number denotes the grid square. Four samples are from the excavated trenches Table 8.2. Bulk analyses for Kavos Promontory slags using SEM-EDS (averages of 5; weight %; data normalized to 100%; n.d.=not detected). Context K6P

sion and technological reconstruction. Only a brief summary is presented below.

The bulk analyses of the new Group 1 slag specimens (KN1, KN44, KN128, KN174, K7P18, K7026), measured with consecutive area analyses on the SEM-EDS (Table 8.2), are in good agreement with previous results of Group 1 slag (Georgakopoulou 2007a), despite different techniques being used in the two studies. Iron (FeO: 30–42 per cent) and silicon (SiO₂: 39–47 per cent) are the major components, in a ratio of approximately 1:1 for their corresponding oxides. Calcium contents are significant (CaO: 10–14 per cent), magnesium (3–6 per cent) and aluminium (2–3 per cent) lower, while copper contents were below 1 per cent in all cases. In some of the slags sulphur was measured, again below 1 per cent in all cases.

The microstructure of the Group 1 slag shows that these had reacted well in all cases with no remains of partially reacted or unreacted components (Fig. 8.1). The main phases are magnesium-rich fayalite crystals (MgO is usually *c*. 10 per cent, showing coring in larger crystals with higher magnesium contents in the centre than the edges of the crystals) with minor contents of calcium, surrounded by a glass matrix. All samples had few and small magnetite crystals. All analysed metallic prills were copper-iron sulphides (matte), with no other base metals detected. The matte were primarily copper-rich with low iron (from analyses of 15 matte prills: Cu 60–73 per cent; S 24–29 per cent; Fe 1–13 per cent).

Group 2 slag analysed previously showed much higher variability within the group, largely due to extensive heterogeneity within individual specimens (Georgakopoulou 2007a; note also higher rsd in Group 2 slags compared to Group 1 in Table 8.2). However, the presence of significant contents of arsenic and lead and the increased iron:silicon ratios were consistent characteristics that had led to grouping this small number of slags together. Samples KN65 and K7P32 show similar features and should therefore be identified as Group 2 slag. The iron:silicon ratio is higher than 1 for the corresponding oxides (although very close to 1 for K7P32). Aluminium is significantly higher and magnesium lower than the Group 1 slag. The copper content is higher, lead was identified in the bulk analyses, while arsenic was only identified in the bulk analyses of K7P32, but is clearly also present in individual metallic phases in KN65 (see below). The main difference compared to Group 2 examples analysed before are the higher calcium contents (CaO 10–11 per cent compared to 1.4–5.6 per cent before).

In agreement with this picture, the microstructure of KN65 consists of calcium-rich olivines, with a composition similar to the mineral kirschteinite



Figure 8.1. *Reflected light photomicrograph of sample from K7P18 showing fayalite (medium grey crystals), magnetite (small, light grey) and matte prills (white, circular) in glass (dark grey) with porosity (black).*



Figure 8.2. Reflected light photomicrograph of sample from KN65, showing large magnetite aggregate at the centre of the image in slag with elongated kirschteinite (medium grey crystals), magnetite (light grey) and numerous copper prills (bright white) in glass (dark grey) with porosity (black).

Table 8.3. SEM-EDS analyses on prills in samples KN65, K7P32, and MKN7 (wt %). Low totals (<95 per cent) are due to partial corrosion of the prills. Silicon

апа саісиит	are detected probably from the surround	aing slag	matrix	, sugges	ting the	at this m	iay also	be parti	ally resp	onsible	for the 1	топ сок	ttents.		
Sample no.	Sample	Si	S	CI	Ca	Fe	Co	Ni	Си	Zn	\mathbf{As}	Sn	\mathbf{Sb}	Pb	Total
	lead-rich part of copper prill			17.9		0.8			9.6					68.1	96.3
	large copper prill		0.6	9.2		0.2		1.6	60.7		0.9		0.4	14.1	87.7
	matte		21.1			4.2			75.6						100.9
KN65	lead phase surrounding matte			17.2		3.3		0.6	8.4		3.3			70.4	103.0
	copper prill (surrounded by lead ring)					2.2		9.8	86.4		0.5		0.4		99.3
	copper prill (surrounded by lead ring)	0.1				3.7		10.5	84.1		0.7		0.6	0.3	100.0
	matte		21.7			3.0			76.5						101.1
	copper prill					1.3			91.6		6.9				8.66
	copper prill				0.1	1.4			91.6		6.2				99.3
	copper prill		0.5			0.4			92.0		5.5				98.4
K7P32	copper prill				0.1	3.2			88.9		6.6				98.7
	copper prill		0.2			3.1			91.9		6.1				101.2
	copper prill	0.1				5.3			92.5		2.4				100.3
	copper prill					4.1			91.2		5.3				100.7
	large corroded copper prill (Fig. 8.4)	0.1				0.3			82.3						82.7
	corroded copper prill	0.2		0.1		1.9			78.1					0.5	80.8
	corroded copper prill	0.1				3.0			80.0						83.1
	copper prill	0.2	2.5			7.1	1.2	15.8	68.8	0.4	1.6	0.6	0.4	1.2	99.7
	copper prill	0.1	0.1			7.7	1.4	16.2	70.1	0.6	1.8	0.7	0.5	0.5	9.66
	copper prill	0.3	0.3		0.1	7.9	1.8	19.5	67.0	0.5	1.8	0.7	0.4		100.2

 $(CaFeSiO_{4})$. The sample is rich in free iron oxides, magnetites, and there are numerous magnetite aggregates, often incorporating circular prills (Fig. 8.2). Magnetite aggregates are considered to be partially reacted remains of mixed secondary iron-copper minerals (Georgakopoulou 2007a, 387; Hauptmann et al. 2003), showing that the original charge had not fully reacted. The composition of the copper prills varies across the sample, primarily due to differential corrosion (Table 8.3). The copper prills are characterized by variable but in some cases high nickel contents (1-10 per cent) and lower arsenic and antimony (c. 0.5–1 per cent). They are also rich in lead, which appears as separate phases within the prills or as outer rings surrounding them. High chlorine contents indicate that the lead phases are corroded. These base metals were not detected in the few matte prills analysed in the same slag (see also Georgakopoulou 2007a). Arsenic and antimony are also depleted in corroded prills, highlighting the effects of preferential corrosion in the analysed composition of copper-based alloys. One large prill (c. 2.5 mm diameter) is visible even with the naked eye. Under magnification it is clear that this is in parts highly corroded and rich in separate lead phases. Note that the iron contents in this copper prill are significantly lower than in other prills analysed from this sample, an observation that has elsewhere been attributed to the possibility that surrounding iron is measured on SEM-EDS analyses in the case of smaller copper prills in slags (Georgakopoulou et al. 2011), although the subject would merit further systematic study. The microstructure of K7P32 differs from that of KN65, as olivines are absent and magnetites in a glassy matrix predominate. Although lead was not measured in metallic phases, it is present in the glass (5–6 per cent). Large magnetite aggregates abound, as well as larger denser iron oxide phases encircling copper prills, that also look like partially reacted ore (Fig. 8.3). Area analyses in these detected, apart from iron, also copper, arsenic, antimony (mainly concentrating in the copper prills), as well as lead in the glassy areas. This may be an indication that the copper metal and the alloying base metals were all part of the same ore source. The prills in this sample are arsenical copper prills (Table 8.3). Contrary to KN65 prills, nickel and antimony are below detection limits, while lead, although present in the slag overall, is not detected in the metallic phases.

MKN7

Specimen MKN7 was recovered from Trench PO1. It is small, shapeless, and covered in green secondary copper minerals and salts. Analysis of its bulk composition (Table 8.2) showed almost double iron oxide

contents compared to silica, high copper, as well as lower contents of zinc, lead, arsenic, and nickel. In section it is very heterogeneous, very rich in iron oxides with little glass and several secondary weathered copper products. In some areas both circular iron oxides, in the shape of wüstite and angular in the shape of magnetite, were identified (Fig. 8.4). Their characterization is supported by analyses on the SEM-EDS, with higher alumina contents in the magnetite crystals (c. 7–8 per cent compared to 0.5 per cent in the wüstite). Otherwise both types of oxides had minor contents of cobalt (c. 3 per cent in wüstite and 1.5 per cent in magnetite), nickel 0.5–1 per cent, zinc c. 3–4 per cent and copper 0.3 per cent, as well as c. 1 per cent magnesium and 0.5 per cent titanium, all estimated as their respective oxides. The composition of copper prills is variable, although clearly this is in large part due to corrosion (Table 8.3). The last three analyses in Table 8.3 were all carried out in largely uncorroded, small prills, found within the iron oxides. The nickel contents are significant (c. 16 per cent), followed by cobalt and arsenic, and lower amounts of antimony, zinc, tin and lead. Their cobalt and partly nickel contents are likely measured, at least in part, from the surrounding iron oxides. In corroded prills base metals other than copper were not identified, again a reflection of differential oxidation and leaching.

The composition and microstructure of this slag is more consistent with it being from a secondary process, such as copper refining or even alloying. The presence of arsenic and lead suggests associations with the Group 2 slags, although here other base metals were also detected, particularly zinc and higher nickel contents. The identification of tin is interesting, although the actual content is very low as the metal was found as minor component in very small prills. Tin and antimony were noted in one of the slags analysed previously from the Kavos survey (sample KK3 in Georgakopoulou 2007a, 386).

Metallurgical ceramics

Three metallurgical ceramics from Kavos Promontory were sampled. Two of them (KN172, K7P14) were small and shapeless, with a distinct attached slag layer. Specimen KN190, on the other hand, formed a clear rim, and its curvature suggested it was more likely to be part of a crucible than a furnace fragment. The specimen is relatively thin with a total thickness of 15 mm. The ceramic and 'slag' layers on each specimen were analysed separately on the SEM-EDS and these are given in Table 8.4. The three specimens show significant differences between them.

Sample KN172 had a thin black 'slag' layer, which is very glassy with rare magnetites and numer-



Figure 8.3. SEM-BSE (backscatter electron) image of sample from K7P32, showing a large dense iron oxide phase, probably partially reacted iron ore.



Figure 8.4. *Reflected light photomicrograph of sample from MKN7, showing rounded and angular iron oxides (light grey), numerous small bright copper prills and secondary corroded phases.*

Context 4	Analysed layer	Na_2O	MgO	Al ₂ O ₃	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	${\rm Fe}_2{\rm O}_3$	CuO	PbO
	Ceramic	1.4	6.0	14.5	62.6			2.2	5.9	1.0		6.4		
	Slag	1.5	3.2	12.0	49.5	0.5	0.2	2.2	7.4	0.6	0.6	21.7	0.5	0.2
C 1 0	Ceramic	1.2	2.0	15.9	62.4			3.9	7.1	0.7		6.8		
	Slag	0.5	1.9	7.8	48.8			1.5	10.5	0.4		28.3	0.3	
10007	Ceramic	1.5	19.2	12.0	50.8			0.3	5.5	0.8		9.6		
N01'33D	Slag	1.5	19.4	12.6	47.7			0.5	6.5	0.8		9.6	1.2	

labelled K6P were surface finds from the systematic survey on Kavos Promontory; the following number denotes their corresponding square in the grid. One Table 8.4. SEM-EDS analyses of ceramic and slag areas in metallurgical ceramics from Kavos Promontory (averages of 5; weight %, normalized). Samples

ous copper prills. No other phases could be distinguished even in high magnification. Between this layer and the ceramic one there is a clear vitrified layer with rounded pores (Fig. 8.5). Four prills were analysed in the 'slag' layer and showed nickel c. 1.5–2 per cent and variable arsenic contents that ranged from 2 to 9 per cent. Lead was below detection limits in the metal, but was detected in the bulk analyses of the glassy slag. Comparing the bulk composition between the ceramic and 'slag' layers, iron and to a lesser extent calcium are increased in the latter, but the ratio of silicon to aluminium oxides remains very similar. Copper and lead were also detected in the 'slag' phase. These differences are more suggestive of copper-working activities and not smelting (see discussion in Georgakopoulou 2007a, 390-92). Increased iron contents are suggestive of copper refining, whether deliberate or accidental through copper metal melting, whereby iron present in the copper is oxidized and reacts with the ceramic fabric. The incorporation of fuel ash in the glass phase would be responsible for the raised calcium contents. The arsenic and lead contents suggest an association with the Group 2 slags.

Specimen K7P14 also had a very thin slag layer, separated from the ceramic body by a thicker vitrified ceramic layer with large circular pores. Distinct phases were visible in the slag layer, which SEM-EDS analyses showed are elongated pyroxenes of a composition approaching that of hedenbergite (FeO.CaO.2SiO₂) with minor magnesium, as well as few magnetites (Fig. 8.6). Large magnetite aggregates were also noted and these incorporate minute copper sulphides. As noted previously, these phases correspond to partially reacted ore. Circular prills are primarily matte, copper-iron sulphides, while few copper prills were also found. Arsenic, lead, or any other alloying components were not detected. Comparison of the ceramic and slag layers shows significant compositional differences, consistent with this ceramic being involved in copper smelting. Based on the composition of the slag layer, this is associated with the Group 1 slags.

Finally, on sample KN190, the black 'slag' phase continues around the rim of the specimen. Under high magnification the 'slag' is glassy with no clearly discernible phases and numerous copper-based prills, some quite large (Fig. 8.7). The composition of the ceramic and slag are very similar, the only major difference being the presence of copper in the 'slag' layer. Iron contents are similar in both layers and the slightly elevated calcium and potassium contents in the slag should be attributed to reaction with fuel ash. The high magnesium content of the ceramic, which is reflected in the 'slag', is quite distinctive and differentiates it from previously analysed metallurgical



Figure 8.5. SEM-BSE image of sample from KN172 (scale 500 μ m), showing vitrified porous interface of ceramic with glassy 'slag' on top.



Figure 8.6. *Reflected light photomicrograph of sample from K7P14, showing pyroxenes (medium grey) and magnetites (light grey) in glass matrix with vitrified ceramic areas (porous).*



Figure 8.7. *Reflected light photomicrograph of slag on metallurgical ceramic KN190, showing glassy matrix, numerous prills (bright, circular) and porosity (black).*



ceramics from the site. This composition suggests that the fabric of this specimen should be talc ware, although the particular sample was not included in the petrographic study. Several prills were analysed and in one part of the specimen they were found to be alloys of copper with silver, with very variable contents of the latter, again undoubtedly influenced by visible corrosion. In other parts of the 'slag' layer copper prills with arsenic and lead were identified. Given that iron is not increased in the 'slag' and no other difference is detected, this ceramic appears to have been used purely for melting metal. In this sense it is unclear whether the alloys of copper and silver are from melting this type of alloy, which is presently not known from Dhaskalio-Kavos, or from melting copper and silver at different times. The ceramic is likely to have been used repeatedly in different activities.

Copper metal

A small isolated prill (KN204) collected during survey on the Kavos Promontory from square 38b, was found to be pure copper metal. The specimen is most likely a spill from the metallurgical activities taking place in the area.

Figure 8.8. *Lead isotope analysis diagrams for Kavos Promontory finds. The error bars represent average* 2σ *for each ratio calculated from the eight measurements.*

Sample type	Sample no	²⁰⁶ Pb/ ²⁰⁴ Pb	±2s+	²⁰⁷ Pb/ ²⁰⁶ Pb	±2s+	²⁰⁸ Pb/ ²⁰⁶ Pb	±2s+
	5786	18.7337	0.0087	0.837454	0.000167	2.077294	0.000709
Dhaskalio lead artefacts	11828	18.7482	0.0226	0.836341	0.000253	2.073957	0.000707
	10191	18.7172	0.0132	0.837937	0.000177	2.078272	0.000741
Dhaskalio litharge	5828	18.8601	0.0160	0.830856	0.000211	2.059000	0.000734
Special Deposit North litharge	KK19	18.7126	0.0084	0.838288	0.000177	2.078320	0.000696
	12851	18.9086	0.0297	0.830685	0.000237	2.060829	0.000955
	10003	18.9127	0.0275	0.829409	0.000237	2.056720	0.000843
Dhadadia array an antafa ata	12734/5	18.7232	0.0123	0.838874	0.000200	2.079782	0.000761
Dhaskano copper arteracts	12741	17.9632	0.0143	0.872183	0.000249	2.125277	0.000799
	12740	18.7289	0.0132	0.837993	0.000200	2.079229	0.000852
	5059	18.7355	0.0113	0.837295	0.000188	2.078235	0.000827
Dhadadia aanaa daaa	8309	18.8200	0.0181	0.833251	0.000224	2.068022	0.000848
Dhaskano copper siags	14065	18.7605	0.0187	0.838543	0.000296	2.082846	0.000880
Dhaskalio speiss	11541	18.8658	0.0278	0.831810	0.000251	2.072554	0.000990
	KN1	18.8279	0.0191	0.832882	0.000280	2.066104	0.000987
	KN44	18.8293	0.0140	0.833572	0.000252	2.069065	0.001082
Varia Dramantana anno 1 an	KN65	18.7303	0.0126	0.837710	0.000200	2.078275	0.000781
Kavos Promontory copper slags	KN128	18.7551	0.0180	0.836093	0.000252	2.074703	0.000850
	K7P18	18.8292	0.0111	0.832811	0.000176	2.064618	0.000927
	K7P26	18.7876	0.0266	0.834127	0.000252	2.067902	0.000799
Kavos Promontory copper metal	KN204	18.8274	0.0107	0.834661	0.000187	2.074049	0.000825

Table 8.5. *Lead isotope analysis results from metals and metallurgical remains from Dhaskalio Kavos. Sample KK19 was collected during the 1987 survey (Georgakopoulou 2007a).*

Lead isotope analyses

Seven samples from the Kavos Promontory were analysed for their lead isotope ratios (Table 8.5) including five of the Group 1 slags (KN1, KN44, KN128, K7P18, K7P26), one Group 2 slag (KN65) and the isolated copper metal fragment (KN204). The samples show close correspondence in their isotopic composition, with less than 0.3 per cent relative standard deviation in all three lead isotope ratios. The spread of lead isotopes within ore deposits of uniform geological and geochemical history is reported as maximum 0.3 per cent (Gale & Stos-Gale 1992) or even 0.6 per cent (Pernicka et al. 1990, 283). In principle, therefore, these slags could all have resulted from using ore from a single ore deposit. Some distinction is, however, noted, which is in agreement with the observed chemical variability. Sample KN65, the only one presently analysed from the Group 2 examples, is somewhat differentiated from the majority of other samples from the Kavos Promontory, with higher ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios and correspondingly lower

²⁰⁶Pb/²⁰⁴Pb (Fig. 8.8). Provenance is further discussed in a following section together with the Dhaskalio analyses.

Discussion of Kavos Promontory metallurgy

The new analytical data confirm and enhance our previous understanding of metallurgical practices on the Kavos Promontory. Two types of slag were identified, showing similar features to Groups 1 and 2, recognized before (Georgakopoulou 2007a). Group 1, associated with production of unalloyed copper, is now well characterized by a sufficient number of samples and shows relatively low variability in the internal chemical and microstructural composition of the slag. The presence of matte in these samples indicates the incorporation of sulphides in the original ores, although these are most likely minor components to a largely oxidic ore. The microstructure of the slags shows that the raw materials had reacted well (for a further discussion of technological reconstruction, see Georgakopoulou 2007a).



Figure 8.9. SEM-BSE image of sample from 14051 (scale 1 mm), showing ceramic and top layer of corroded metal spill.

Group 2 slags on the contrary remain less well characterized. Only two new slags associated with this group (KN65 and K7P32) were identified. Similarly few in comparison to Group 1 examples were the slags analysed previously (Georgakopoulou 2007a), suggesting that these materials are a minority at Kavos Promontory compared to Group 1. Further, targeted sampling would be necessary in order to understand the process associated with these materials. Group 2 slags are the by-products of the production of arsenical copper with high lead contents and lower amounts of nickel. The composition of the metal was found to be quite variable, a picture that is related both to corrosion, but also probably to differential redox conditions, resulting in variable oxidation of lead and arsenic with the latter present primarily in metallic form in KN65 and only as an oxide in the glass matrix in K7P32. The slag specimens in this group are very heterogeneous, with frequent fragments of partially reacted raw materials and high iron contents primarily in the form of free magnetite. As a result, the analysed slags show significant differences in their composition, forming a very diverse group. The main question regarding the Group 2 slag is the nature of the raw materials used. Arsenical copper can be produced via at least three different pathways; smelting of naturally mixed copper and

arsenic ores, smelting of distinct copper and arsenicrich ores and mixing of copper metal with arsenical minerals (e.g. Charles 1967; Lechtman 1991; Thornton et al. 2009). Furthermore, in the case of the Group 2 slag the source of their lead content additionally needs to be sought. Was this part of the copper (or arsenicrich if separate) ore, or was it deliberately added in some other form to the mixture? Although one of the primary aims of further examination of Kavos Promontory materials was to address these questions, the present study remains inconclusive on this topic (see, however, further discussion below). The identification of large iron aggregates incorporating copper-based prills rich in arsenic and lead is an indication that the use of a mixed ore is more likely. The single Group 2 slag analysed for its lead isotope composition (KN65) was also slightly distinct, but this may be a result both of mixing or use of a different mixed source. Isolated unreacted ore fragments that might help to address this question were not found on the Kavos Promontory. This issue is discussed further below.

Metallurgical ceramics are enigmatically rare in comparison to slag on the Kavos Promontory (Volume II, chapter 19). Furnace bases were not identified during small-scale excavation at this part of the site, although this absence is not surprising, as

such structures do not preserve well and would most likely have been destroyed at the end of the process. Most of the metallurgical ceramics analysed before had been found to be associated with the Group 2 slags (Georgakopoulou 2007a). Previous analyses of metallurgical ceramics from Kavos Promontory had shown that most of these were related to production of alloyed copper, although several differences had been noted. The three ceramics analysed here show entirely different characteristics between them. K7P14 is the first analysed example to be associated with the Group 1 slags and appears to have been part of the associated smelting activities, probably part of the furnace structure. KN172 can be associated with the Group 2 slags due to the presence of lead and arsenic, but contrary to previous examples (Georgakopoulou 2007a), this fragment appears to have been associated with further secondary refining or melting of metal, rather than smelting. The surface find KN190, the only specimen from the Kavos Promontory with clear morphological features suggesting it was part of a crucible, appears to be associated with melting metals and both copper with silver and copper with arsenic and lead were noted in the prills. It can thus be concluded that ceramics were used in different processes in the Kavos Promontory activities: metal production resulting in Group 1 and 2 slags, metal refining or melting. In this context their relative scarcity should probably be attributed to their friable nature and poor preservation conditions.

Dhaskalio

A selection of artefacts and metallurgical remains from Dhaskalio was sampled for analysis. Below they are discussed according to their chronological context. Descriptions of these finds can be found in Volume I, chapter 32.

Phase A

14051 is the only ceramic recovered from Phase A that shows any association with metallurgy (Volume I, chapter 32, 667). It was sectioned perpendicular to the spot where green minerals were noted. Examination under the optical microscope showed both cuprite and green copper minerals and analysis on the SEM-EDS confirmed that the ceramic has a thin layer of completely corroded copper metal with arsenic and lead (Fig. 8.9). The specimen is therefore not a metallurgical ceramic, but rather a fragment of domestic ceramic onto which copper metal was spilled, probably accidentally. Nonetheless it provides indirect evidence for melting lead-rich arsenical copper on Dhaskalio in this phase. Only one copper artefact was found in Phase A contexts, **10694**, which is a fragment of a rectangular section. The artefact is arsenical copper with approximately 4 per cent arsenic and 0.5 per cent nickel (Table 8.6). Bismuth and antimony were also identified in segregated phases but were below detection limit in the bulk on the EDS, while on the microprobe they were measured as 0.4 per cent and 0.3 per cent respectively.

Phase B

Two slags dating to Phase B (8309, 10167) were sampled. Both were medium to large rounded fragments, whose shape, size and context of discovery suggested they were on Dhaskalio for secondary usage as tools (Volume I, chapter 32, 673). Their bulk composition shows similarities in the contents of most major and minor oxides, with iron and silicon being the major components, low-medium calcium and aluminium contents, but also some differences such as the higher manganese content in 8309 and the higher copper, arsenic, and zinc in 10167 (Table 8.7). The higher copper content of **10167** is clearly reflected in the large number of enclosed copper prills, which are often quite large. Their analysis showed that they are arsenical copper with high variable arsenic contents (6-17 per cent), and minor amounts of antimony, nickel, and sulphur (Table 8.8). Traces of bismuth were identified in some prills as distinct phases, but in total were below the detection limits of the SEM-EDS. Segregated arsenic-rich phases can be distinguished in some of the larger copper prills (Fig. 8.10). The section of 10167 is relatively homogeneous with magnesium-rich (c. 10 per cent) fayalites, magnetites, glass, and mediumhigh porosity. Sample 8309, on the other hand, had relatively few copper prills; these were also found to be of arsenical copper with much lower arsenic contents, however (c. 1–4 per cent). The microstructure of 8309 (Fig. 8.11) consists of elongated olivines with medium contents of magnesium and manganese replacing iron (c. 6 per cent each), magnetites, glass, and lower porosity than 10167.

The shapeless ceramic fragment **5373** has a thin (≤ 0.5 mm) black 'slag' layer attached to the ceramic body with a thin vitrified porous layer in between. The 'slag' is glassy with some minute prills. Its composition is similar to that of the ceramic body, with a substantially increased lead content, as well as iron, copper, and arsenic. Calcium and potassium are also increased relative to the silicon (Table 8.7), as a result of absorption of fuel ash. The prills were too small to be analysed accurately, but spot analyses on the SEM-EDS showed that these are copper prills with both arsenic and, to a lesser extent, lead contents.

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	0	Al	Si	s	Ū	Fe	Ni	Си	\mathbf{As}	Ag	Sn	\mathbf{Sb}	$^{\mathrm{Pb}}$	Bi	Total
SEM-EDS															
10694 matrix (5)							0.5	97.7	4.1						102.3
10694 bulk (5)							0.5	95.0	3.7						99.2
10166 matrix (3)							1.4	91.7	2.8						95.9
10166 bulk (3)							1.3	91.6	2.9				1.1		96.9
5059 matrix (3)							0.3	94.9	3.0	0.2					98.4
5059 bulk (3)							0.2	94.3	3.1	0.2			0.9		98.7
10634 bulk (4)				1.0				96.7					0.2		97.9
12734+12735 matrix (8)							0.4	96.4	3.4			0.1			100.3
12734+12735 bulk (5)							0.4	92.1	3.2			0.2	0.8		96.7
12740 matrix (5)							0.9	91.0	4.6			0.2			96.7
12740 bulk (5)							1.0	86.3	4.6			0.2	2.0	0.7	94.7
12741 bulk (3)					5.1	0.2		59.3	0.1		8.3		0.1		73.0
12012 bulk (5)					4.1			71.3		0.8					76.3
12851 matrix (5)						0.3	0.1	93.6	2.7			0.2			96.8
12851 bulk (8)				0.8		0.4	0.1	93.4	3.4			0.5		2.1	100.7
10002 matrix (3)						0.2	0.2	98.6	1.3						100.2
10002 bulk (7)				0.9	0.1	0.2	0.2	97.1	1.9				1.7		102.0
10003 bulk (8)				0.8	0.0	0.2	0.1	97.5	0.7						99.4
Microprobe															
10694 matrix (7)	0.02	0.01	0.05	0.00	0.01	0.00	0.41	97.04	2.13	0.02		0.02	0.00	0.01	7.66
10694 bulk (7)	0.32	0.00	0.05	0.00	0.01	0.00	0.68	94.86	2.87	0.02		0.31	0.15	0.41	7.66
10166 matrix (7)	0.00	0.01	0.05	0.01	0.00	0.00	1.27	96.80	1.82	0.03		0.03	0.04	0.00	100.1
10166 bulk (7)	0.03	0.01	0.11	0.35	0.05	0.00	1.32	91.35	2.13	0.02		0.05	3.24	0.07	98.7
5059 matrix (7)	0.00	0.01	0.05	0.00	0.00	0.00	0.12	97.55	1.91	0.17		0.09	0.01	0.00	9.99
5059 bulk (7)	0.02	0.01	0.25	0.06	0.01	0.01	0.12	94.53	1.91	0.10		0.10	1.00	0.44	98.5
12851 matrix (7)	0.00	0.01	0.06	0.00	0.00	0.25	0.12	96.22	2.45	0.06		0.45	0.01	0.01	9.66
12851 bulk (7)	0.00	0.01	0.07	0.09	0.01	0.27	0.11	94.33	2.16	00.0		0.49	0.10	2.13	9.66
10002 matrix (7)	0.00	0.01	0.05	0.01	0.00	0.14	0.20	98.13	1.26	0.03		0.07	0.01	0.01	9.99
10002 bulk (7)	0.21	0.02	0.07	0.87	0.37	0.24	0.18	94.75	1.20	0.06		0.06	1.80	0.00	99.8

PbO 80.8 24.14.4 BaO 0.8 0.3 As, O_3 0.40.1ZnO 1.20.1CuO 16.70.72.1 0.41.8FeO 38.2 38.0 36.4 10.77.0 7.8 3.6 0.1MnO 3.2 0.70.2 TiO, n.d. n.d. 0.10.50.2 0.80.4CaO 19.512.2 9.9 3.3 9.3 3.6 7.1 4.7 К,О 1.1 0.9 0.5 1.73.9 1.90.70.40.10.12.1 U 0.3 SO, 0.5 P,O_5 0.8 0.2 0.2 SiO, 40.038.9 54.6 34.5 61.941.542.9 3.8 number given in parenthesis; weight %). Al,O₃ 11.9 12.3 19.1 5.9 6.8 3.1 6.7 0.9 MgO 13.42.0 2.9 3.8 7.3 1.93.0 1.2Na,O 0.9 0.9 1.1 1.31.30.40.114058 ceramic (5) 5373 ceramic (5) No. of samples **14058** slag (5) **5373** slag (5) 5828 (10) 8309 (8) 10167 (6) 14065 (8)

Table 8.7. Bulk compositions of slags, metallurgical ceramics, and litharge from Dhaskalio measured as area analyses on the SEM-EDS (averages of

Table 8.8. Analyses (SEM-EDS) of metallic phases found in slags from Dhaskalio. Most analyses are for copper prills, with the exception of the third and fourth on 14065 on lead-rich metallic phases surrounding copper prills and the last one on a matte surrounding a copper prill. All analyses given as weight %, unnormalized. Note that Si, Ca, Mn and probably some of the iron are from the surrounding matrix, due to the small size of the prills. Oxygen was also noted, but not quantified here, thus resulting in lower totals in some of the corroded prills (particularly in 14065).

	Total	99.3	100.7	98.9	9.66	98.6	99.1	100.1	100.6	102.7	101.3	97.7	106.8	95.6	94.6
	Pb												92.7	28.7	
	Sb						0.3	0.3	0.2	0.2	1.5	0.9		2.6	
	As	1.0	2.3	3.7	1.0	1.4	6.2	8.0	17.2	15.1	7.3	1.8		10.5	0.4
	ΠZ												0.4		
0	Cu	95.4	95.0	91.8	96.0	94.5	91.0	88.6	81.9	86.5	87.4	91.2	2.1	49.8	69.69
	Ni								0.6	0.4	0.4			0.5	
	Fe	2.3	2.8	2.6	2.3	2.2	1.4	2.6	0.3	0.3	4.3	3.3	3.8	2.8	3.1
	Mn	0.2	0.3	0.2	0.2	0.2									
-	Ca	0.1	0.1	0.1	0.1	0.1						0.1	1.4	0.3	0.6
	CI										0.1	0.1	4.3	0.4	
	s	0.1		0.3	0.1			0.4	0.1		0.2	0.1			19.6
	Si	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.2	0.3	0.1	2.3		1.2
00	Sample no.	8309	8309	8309	8309	8309	10167	10167	10167	10167	14065	14065	14065	14065	14065



Figure 8.10. *Reflected light photomicrograph of sample from* **10167***, showing fayalite (long, medium grey), magnetites (light grey), glass (dark grey) and numerous copper prills; in the larger prills different phases of the Cu-As system can be distinguished.*



Figure 8.11. *Reflected light photomicrograph of sample from* **8309***, showing fayalite (long, medium grey), magnetites (light grey), glass (dark grey) and infrequent copper prills (bright, circular).*



Figure 8.12. Reflected light photomicrograph of sample from 5059 after etching.

The composition is again consistent with a ceramic used for copper working, melting possibly unrefined leaded arsenical copper as iron contents also increase in the 'slag'. The much higher lead contents compared to copper in the bulk of the 'slag' layer are not surprising as lead will have the tendency to oxidize more rapidly and react with the siliceous matrix, forming part of the glassy phases (Dungworth 2000).

One of the green shapeless fragments from Phase B, 12105, originally identified as a possible copper spill (Volume I, chapter 32, 673), was found upon sectioning to be rich in magnetite crystals surrounded by secondary weathered products of iron and copper. Lead, arsenic, and chlorine were identified on the SEM-EDS bulk analyses, suggesting the fragment is most probably weathered dross from copper melting or refining. Analyses of the copper metal spill **10166** (Table 8.6) showed that it is an arsenical copper metal with approximately 3 per cent arsenic in the bulk, 1 per cent nickel, and significant lead appearing as distinct inclusions, as well as fewer copper sulphides. The lead contents between the EDS and microprobe analyses differ, reflecting the heterogeneous distribution of the inclusions in the metal matrix (1 per cent and 3 per cent, respectively). Traces of bismuth, silver, and antimony were also detected on the microprobe.

Three copper-based artefacts were found in Phase B contexts. Only one, **5059**, a thin, elongated,

rectangular fragment with a rounded edge, was analysed. It is made of an arsenical (*c*. 3 per cent) copper alloy with *c*. 0.1–0.2 per cent nickel and frequent segregated phases primarily of lead (with arsenic and minor antimony) or, less frequently, bismuth. Approximately 1 per cent of lead was detected in the bulk, while the microprobe analyses showed lower amounts of bismuth, antimony, silver and sulphur (Table 8.6). Its microstructure, revealed after etching, consists of recrystallized and twinned grains, suggesting the artefact was shaped by working and annealing (Fig. 8.12). Another artefact, **11132**, a whole needle, was analysed with portable XRF. Apart from copper, lead, arsenic, and possibly nickel were detected (Table 8.9).

Phase C

Specimen **14065** is a small slag fragment shaped as part of a tapped slag. Its bulk composition shows several differences with the two Phase B slags from Dhaskalio, the most pronounced being the presence of lead and zinc (Table 8.7). Its microstructure (Fig. 8.13) consists of polyhedral, cored olivines of a fayalitic composition with high magnesium (MgO 14 per cent), and some calcium (CaO *c*. 1 per cent), zinc (ZnO *c*. 1 per cent), and manganese (MnO *c*. 0.3 per cent) oxides, pyroxenes of a composition approaching that of hedenbergite (FeO.CaO.2SiO₂) with iron partly

Sample no.	Phase	Туре	Elements detected				
11132	В	whole needle	Fe, As, Pb				
11855	C or earlier	strip	Fe, As, Pb				
10611	С	whole pin	Fe, As, Pb				
10697	С	shapeless copper-based fragment	Fe, Sn, As (tr), Pb (tr)				
10704	С	hook fragment	Fe, Ni, As, Pb				
10788	С	tweezers fragment	Fe, As, Ag (tr?)				
11816	С	square-sectioned fragment	Fe, As (tr?), Pb (tr?)				
11839	С	square-sectioned fragment	Fe, As(tr?), Pb (tr?), Sn (tr?)				
11844	С	tweezers fragment	Fe, As (tr?), Pb (tr?)				
11856	С	strip	Fe, As, Pb				
11857	С	square-sectioned fragment	Fe, As				
12203	С	shapeless copper-based fragment	Fe, As (?), Pb				
12328	С	knife	Fe, Ni, As, Pb				
12734/5	С	adze axe	Fe, Ni, As, Pb				
12740	С	chisel	Fe, Ni, As, Pb				
12741	С	single axe	Fe, Sn, Pb (tr?)				
10002	Surface	artefact in the shape of half an ellipse	Fe, Pb				
10003	Surface	artefact in the shape of half a crescent	Fe, As (tr), Pb (tr?)				

Table 8.9. *Qualitative data from portable XRF analyses on copper–based artefacts from Dhaskalio (tr=traces – very small peak; ?=unclear if peak is there).*

replaced by magnesium (MgO *c*. 8 per cent), and glass, the latter containing both lead (PbO *c*. 30 per cent) and zinc (ZnO *c*. 1 per cent). Many prills, both matte and metallic copper, can be seen under high magnification, but in their majority these are minute, on average <3 μ m, and so could not be analysed well separately from the slag. Lead forms distinct phases usually surrounding the copper prills (Fig. 8.14). Analyses of the prills detected arsenic, nickel, and antimony at variable levels, while lead was also identified separately (Table 8.8). The prills are partly corroded. The matte were primarily copper sulphides, with little iron. Base metals are again notably decreased in the matte.

The metallurgical ceramic **14058** is a 'baking pan' fragment with a thin (max *c*. 1 mm) black vitrified, glassy layer in its inner surface. Numerous copper prills and larger phases, now completely corroded, can be seen in this layer. Analysis of a few of these only detected copper, no other base metals, but this may also be due to corrosion. Calcium and magnesium are significantly increased in the innermost glassy 'slag' part, the increase in calcium relative to silicon being by far the highest noted amongst all studied examples (Table 8.7). The increase is due to reaction with the fuel ash. With the exception of copper increased in the 'slag' layer, appearing both as prills, but also

as disseminated cuprite in the glass, the composition of the ceramic and 'slag' layers is very similar. The ceramic was therefore used in secondary metalworking activities. In fact, these types of vessel have recently been identified as heating trays, instead of crucibles (Doumas 2011). In this case it can be envisaged that the crucible would have been placed on top, heated possibly primarily from inside, but also from outside, and the copper-rich areas detected are due to metal spillage. The copper metal spill **10634** is a pure copper metal with *c*. 1 per cent sulphur and traces of lead, both identifiable on the SEM as distinct copper sulphide and lead phases (Table 8.6).

Three more isolated metallurgical finds were found in Phase C contexts. **11830** is a black magnetic specimen. Chemical analysis showed it is primarily iron oxide, while X-ray diffraction identified it as magnetite. Poor secondary iron mineralizations are known on Keros at the opposite coast of Kavos. Several small fragments of such minerals had been recovered during the 1987 survey and their distribution had already suggested that these were probably part of the local geology (Georgakopoulou 2007a). This was confirmed upon visiting Keros and although several more such specimens were recovered during the new fieldwork seasons, these were not included in the catalogue,



Figure 8.13. *SEM-BSE image of sample from* **14065***, showing pyroxenes (darker grey crystals), olivines (medium grey crystals, and iron oxides (light grey) with lighter grey interstitial glass. Minute circular bright prills can be discerned.*



Figure 8.14. *SEM-BSE image of sample from* **14065***, showing copper prill (light grey circular), partly surrounded by lead metal (white).*

Sample 11541	S	C1	Fe	Cu	As	Ag	Sb	Pb
Bulk (10)	0.3	0.3	42.9	2.3	16.9	0.5	18.2	
Medium grey elongated phases (4)	0.1		54.8	3.1	36.6		8.6	
Bright grey circular phases (5)			39.2	3.1	12.5		48.4	
Silver antimonide prill (1)		0.3	0.6	0.4		78.7	28.4	1.5

Table 8.10. Bulk and phases analyses of speiss sample **11541** taken in SEM-EDS (averages of number given in parenthesis; weight %; not normalized). Low totals in the bulk analyses are due to extensive corrosion.

being considered natural instead of anthropogenic material. **11830** is, however, different, as magnetite is not presently known in the local geology. Copper was not detected in the chemical analysis, so there is no evidence suggesting that this is connected with the copper-bearing ores used on Keros. An alternative use in metallurgy would be as flux in smelting. There is presently no reason to suggest such a use, while if this were the case such material would be expected on Kavos Promontory, where there is smelting evidence, and not on Dhaskalio. The origin of this material, or its function on Dhaskalio, if any, cannot be presently concluded.

11541 appears to be metallic macroscopically, partly covered with rusty weathering products, and was very magnetic. Its bulk composition on the SEM-EDS showed very high contents of iron, arsenic, and antimony, with lower contents of copper and silver (Table 8.10). Oxygen is detected but not quantified, which explains the low overall totals, as the material is significantly corroded. The specimen was thus identified as speiss, an intermetallic compound consisting of transition metals, in this case primarily iron, and elements of the fifth main group in the periodic table, primarily arsenic and antimony as noted here (Thornton *et al.* 2009, 308). The section shows a complex microstructure consisting of elongated phases of a composition consistent with Fe₂(As, Sb) and circular or oval phases consistent with Fe(Sb, As), both with a little copper (Fig. 8.15). The material is substantially corroded internally showing weathered stringers or circular oxides or hydroxides of the iron arsenide or antimonide. Low amounts (<0.5 per cent usually) of sodium, potassium and chlorine were identified in some of these, probably leached into the material after deposition. Several rounded phases, brighter in backscatter mode on the SEM, were identified as silver antimonides. These are largely corroded, but analysis of part of a prill that appeared to be less corroded (Fig. 8.16) showed a composition approaching Ag₃Sb, known in nature as the mineral dyscrasite, although here clearly a by-product of a high-temperature process. A little (c. 1 per cent) lead and copper were detected in these phases.

The single litharge fragment found on Dhaskalio, **5828** (from Trench VII, layer 5), consists primarily of lead oxide or hydroxide, with approximately 10 per cent of other gangue oxides, mainly of silicon (SiO₂ c. 4 per cent) and calcium (CaO 4 per cent), but also others such as magnesium, aluminium and potassium (Table 8.7). In high magnification distinct litharge crystals are surrounded by lead-rich areas mixed with the other gangue oxides. Minute distinct phases were recognized in the latter, which analyses showed are primarily potassium aluminosilicates. As with the single litharge fragment recognised previously from the Special Deposit North at Kavos (Georgakopoulou 2007a), **5828** should be identified as a litharge-impregnated cupellation hearth fragment.

Five copper artefacts from Phase C contexts were sectioned. Three of them are the three artefacts that made up the 'hoard' found in the Hall. Two of these artefacts, the adze-axe and the chisel, were found to be arsenical copper, while the single axe is a tin bronze. The adze-axe (12734 and 12735) was sampled at the cutting edge of the adze end (Fig. 8.17). Observation under the optical microscope of the section prior to etching revealed very directional porosity across the sample, suggesting already that the edge had been significantly worked (Fig. 8.18). After etching, intense strain lines were revealed in the grains, confirming that the edge had been heavily work-hardened (Fig. 8.19), as would have been necessary for this to be a functional tool. The metal is an arsenical copper with c. 3 per cent arsenic and lower amounts of lead, antimony, and nickel (Table 8.6).

The chisel (**12740**) was sampled on its side (Fig. 8.20). Porosity before etching did not show clear directionality, but etching revealed a microstructure with recrystallized and twinned grains of small size, partial deformation of twins and strain lines visible in some grains (Fig. 8.21). The microstructure is again consistent with significant working and it is expected the edge of the tool would have been worked even further. Chemical analysis showed this is also an arsenical copper with *c*. 4.6 per cent arsenic and lower contents of nickel, antimony, lead and bismuth (Table 8.6).



Figure 8.15. SEM-BSE image of sample from **11541**, showing $Fe_2(As, Sb)$ (elongated medium grey), Fe(Sb, As) (light grey rounded), corroded areas (dark grey) and few silver antimonide prills (brighter grey or white oval shaped).



Figure 8.16. SEM-BSE image of analysed silver antimonide prill in sample from **11541**, showing uncorroded area at centre of sample. Most prills identified in this specimen were corroded.



Figure 8.17. Adze-axe 12734 and 12735 showing sampling location on the left of the image (triangular dent).



Figure 8.18. Reflected light photomicrograph of sample from 12734 showing elongated porosity.



Figure 8.19. Reflected light photomicrograph of sample from 12734 after etching.



Figure 8.20. Chisel 12740 showing sampling location and extracted sample on the top left of the image.



Figure 8.21. *Reflected light photomicrograph of sample from* **12740** *after etching.*

Finally, the single axe (**12741**) is significantly weathered and very fragile even after conservation. A small section was removed from within the shaft-hole. Unfortunately the section was fully corroded and no uncorroded metal was preserved. Chemical analysis showed this to be a tin-bronze with no other elements detected above the detection limits of the technique. Approximately 8 per cent tin was measured in the bulk (Table 8.6); however, quantification of tin relative to copper will have been altered by corrosion, so the result is merely indicative.

Two additional, smaller artefacts (**12012** and **12851**) were sampled. They are both tweezer fragments and were sampled across the width of one of their arms. In the case of **12012** the section is completely weathered. Bulk analysis gave beyond copper

and chlorine only *c*. 1 per cent silver, but again the original chemical composition of the artefact cannot be estimated due to corrosion. **12851** is of arsenical copper (*c*. 3 per cent As), with significant bismuth contents (*c*. 2 per cent), seen as separated phases, as well as lower antimony, nickel, sulphur and iron. In section these elements are seen in three types of discrete phases: bismuth, copper-iron sulphides, and speiss (copper arsenate antimonates), while most of the arsenic is found in the copper matrix.

Several more copper-based artefacts from Phase C contexts were analysed with portable XRF, while some of the sampled artefacts were also analysed with this method for comparison (Table 8.9). Results are only treated as qualitative (see Methodology section). Arsenic, lead and nickel were identified in





most of the artefacts, in agreement with the picture obtained from sampling. In the absence of quantified data it is difficult to decide whether these base metals are present in sufficient amounts to define a metal as arsenical copper or pure copper with traces of arsenic, although, based on the artefacts sampled, it is most likely that these are indeed arsenical copper artefacts. Particularly important from these analyses is the rarity of tin-bronzes in the assemblage. Apart from **12741**, only one other minute, shapeless fragment (**10697**) was identified as a tin-bronze. Possible traces of tin were also found in **11839**, although the peak here was very small and cannot be confirmed without further sampling. The importance of this picture will be discussed further on in this chapter.

Unphased

Two surface copper-based finds (10002 and 10003) were also sampled, primarily to examine the possibility that these were ingot fragments, as was suspected

from original macroscopic examination. 10002 was sectioned perpendicular to its two flat surfaces. It is a significantly weathered section, but some uncorroded metal is retained. Etching revealed re-crystallized, twin grains, consistent with the artefact having been cold-worked and annealed. This microstructure is not compatible with an as-cast ingot and the specimen must be an artefact fragment, possibly the butt of a chisel, as previously suggested (Volume I, chapter 32). The artefact is of arsenical copper with c. 2 per cent arsenic and 2 per cent lead and lower amounts of sulphur, nickel, and iron. Distinct copper sulphides and lead phases were noted in the metal due to immiscibility of these phases with copper. Analysis of 10003, avoiding corroded areas, detected approximately 0.7 per cent arsenic and 0.8 per cent sulphur, the latter concentrated in distinct copper sulphides. The microstructure shows no evidence of working and is hence consistent with an as-cast structure. Both the chemical composition and the microstructure suggest that this specimen may have been an ingot fragment, cast to be worked into an artefact later. This specimen further supports the picture that copper working was taking place on Dhaskalio islet; unfortunately a specific phase cannot be attributed, as this was a surface find.

Lead isotope analysis of Dhaskalio and Kavos Promontory finds

Six copper artefacts and two copper slags from Dhaskalio were analysed for their lead isotope ratios (Table 8.5). The single tin bronze analysed, the shaft-hole axe 12741, shows a very distinct lead isotope signature with exceptionally high ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb, clearly separating it from all other specimens from Dhaskalio Kavos. The rest of the copper-based finds from Dhaskalio and the Kavos Promontory slags show a relative standard deviation between 0.3 and 0.4 per cent in their three ratios when considered together (Fig. 8.22) and thus, as discussed earlier, could theoretically be from a single source. Some groupings can be distinguished. The surface find 10003, a low arsenical copper, possibly an ingot fragment, shows the lowest ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios. **12851**, a tweezers fragment from Phase C, was of arsenical copper with the highest bismuth content of all samples and some copper sulphides. The sample is also somewhat separated from the majority at the lower ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios. Two of the 'hoard' artefacts, the adze-axe (12734 and 12735) and the chisel (12740), as well as the Phase B fragment 5059, cluster close together in their isotopic ratios. All three artefacts were found to be arsenical copper (3–4 per cent As) with variable amounts of nickel, lead and bismuth. The artefacts

are closely associated with the single Group 2 slag included here, KN65.

The two slag samples from Dhaskalio, **8309** and **14065**, from Phase B and C contexts respectively, were found to be different in their compositions (Table 8.7). Their lead isotope compositions are also distinct, with **14065** showing higher ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios, approaching the ratios of the leaded arsenical copper artefacts discussed above, although it is somewhat differentiated from them on the basis of higher ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁴Pb. **8309**, on the other hand, is closely associated with the majority of Group 1 slags, although chemically this was distinct, as it enclosed arsenical copper prills.

Three lead artefacts were also analysed, one from a Phase B context (**10191**, a rivet) and two from Phase C (**5786** and **11828**), as well as the single litharge from the site (**5828**, from Trench VII, layer 5). A litharge fragment recovered during the 1987 survey from the Special Deposit North (sample KK19: Georgakopoulou 2007a) was also included. The three lead artefacts show similar lead isotope compositions, close to that of KK19 (Fig. 8.23). The litharge sample from Dhaskalio is, however, distinct.

A sample taken from the single speiss fragment from Dhaskalio (**11541**, from Trench XV, layer 3: Volume I, chapter 32, fig. 32.34) was also submitted for lead isotope analysis. The specimen is separated from all other finds from Dhaskalio on the basis of higher ²⁰⁸Pb/²⁰⁶Pb relative to ²⁰⁷Pb/²⁰⁶Pb.

Discussion of Dhaskalio metallurgy

The analytical examination of selected metallurgical remains from Dhaskalio confirmed that these are in most cases associated with secondary metalworking activities and there is no evidence for smelting of metals in any of the identified phases. The larger slags from Phase B, which have a composition consistent with smelting, were already recognized during initial examination as tools, instead of by-products of *in situ* metallurgical activities (see Volume I, chapter 32; also below). The majority of materials analysed from all phases are associated with working arsenical copper with lead and lower amounts of nickel. There is no evidence for melting tin bronze on the site.

The identification of a single speiss fragment (**11541**) on Dhaskalio is particularly important, given recent evidence for late fourth–early third-millennium BC production of this material in Iran, with suggestions that this was deliberately made to be mixed with copper metal in arsenical copper production (Rehren *et al.* 2012; Thornton *et al.* 2009). It should be noted that, although so far still very rarely identified, the specific



Figure 8.23. *Lead isotope analysis diagrams for Dhaskalio and Kavos Special Deposit North lead-based finds. The error bars represent average* 2σ *for each ratio.*.

example is not the only speiss fragment known from an early bronze age Aegean context. The fragment of heat-treated löllingite identified by Doonan et al. (2007) in an EMI-IIA context at Poros Katsambas, considered to be the material mixed with copper to produce arsenical copper on the site, was subsequently re-interpreted as speiss (Thornton et al. 2009, 310). Several other examples are reported from later Aegean contexts (Volume I, chapter 32, 684–5; Thornton et al. 2009, 309). Given the evidence for arsenical copper production on the Kavos Promontory, could this type of material have been used to produce arsenical copper on Keros through the process that left behind the Group 2 slags? The speiss fragment from Dhaskalio, **11541**, can be characterized as ferrous speiss, as its base metal content is <3 per cent (cf. Thornton *et al.* 2009, 309). Contrary, however, to similar materials identified from roughly contemporary contexts, this example is striking for its high antimony content, making it an iron arsenide-antimonide. The low, but still significant silver content is also noteworthy. These high antimony contents are not presently reflected in the Group 2 slags (Georgakopoulou 2007a; see discussion above). Admittedly, analysed Group 2 slags

from Kavos Promontory remain few and are heterogeneous both within and between them. It is possible that further material with high antimony content, or alternatively low antimony speiss that could account for the Group 2 slags as presently known, remain unidentified on the site. The high lead content attested in these slags is also not justified by this material. So at present there is no concrete evidence to connect this material to the arsenical copper production associated with the Group 2 slags from the Kavos Promontory. Another important parameter in interpreting the role of 11541 on the site is its context. Cremated human remains were identified from the same stratigraphic context as 11541 (Trench XV, layer 3) and although the context was somewhat disturbed, it is possible that the fragment was deliberately deposited with the burial (Volume I, chapter 22, 460). It is therefore possible that this speiss fragment was not on Dhaskalio as a raw material for metallurgical practices, but rather as a burial offering, a practice with significant connotations for the role that metallurgy was attributed by the people that inhabited and used this site.

The single litharge specimen (**5828**, from Trench VII, layer 5) again suggests possible cupellation on Dhaskalio, as with the isolated example previously recognized in the Special Deposit North at Kavos (Georgakopoulou 2007a). As discussed before, however, litharge did have other uses in antiquity and, although possible, the practice of cupellation on the site cannot be confirmed based only on single isolated fragments, such as those known so far (Georgakopoulou 2007a; Volume I, chapter 32).

The majority of copper-based artefacts from Dhaskalio are arsenical copper with variable lead and lower nickel contents, as well as other metals in minor quantities. Only two tin bronze artefacts were found in the assemblage, both from Phase C contexts. Arsenical copper is the dominant alloy in the early bronze age Aegean, although tin bronzes are encountered in the Cyclades at least from the 'Kastri phase' onwards (e.g. Mangou & Ioannou 1997; Renfrew 1967; Stos-Gale *et al.* 1984), corresponding to Dhaskalio Phase B (Renfrew *et al.* 2012). Although the majority of contexts excavated from Dhaskalio date to the phases where tin bronzes are known in the southern Aegean, albeit still in small quantities, the alloy remains a minority in the Dhaskalio Kavos assemblage.

Kavos Promontory and Dhaskalio compared

It is clear from the macroscopic examination of finds, the associated contexts and the results of the analytical examination that different types of metallurgical activities are attested at Kavos Promontory and

Dhaskalio. Dhaskalio is the main habitation area of the site complex. Secondary metal-working activities were attested there, involving primarily refining and melting arsenical copper. Additionally, the recovery of artefacts testifies to the use of metals on the site. Kavos Promontory on the other hand shows no habitation remains, and appears to have been an area used for workshop activities, specifically copper smelting and obsidian knapping. Most finds from Dhaskalio can be safely attributed a chronological phase, as they were recovered from secure stratigraphic contexts. Dating of the Kavos Promontory activities is less secure and these cannot be assigned to a specific phase of the early bronze age (see discussion in Volume II, chapter 19). The question that now needs to be addressed is the relationship between the activities on Kavos Promontory and Dhaskalio. Was the metal worked and used on Dhaskalio produced on the Kavos Promontory? Can the activities in the latter be dated more closely by looking at the material from the former? What is the evidence for the raw material sources used in each case?

The vast majority of metal artefacts on Dhaskalio, as well as many metallurgical finds, are of arsenical copper, frequently with significant lead or nickel. Evidence for working leaded arsenical copper is found on Dhaskalio from Phase A and continues through to Phase C. Furthermore, the Group 2 slags from the Kavos Promontory are by-products of the production of similar types of alloys. In terms of lead isotope compositions, the one Group 2 slag (KN65) analysed shows close agreement in its isotopic ratios with the three analysed leaded arsenical copper artefacts from Dhaskalio Phases B and C (5059, the axe-adze 12734 and 12735, and the chisel 12740). These artefacts are therefore consistent with having been made by metal produced in the process resulting in the Group 2 slags, although a positive association cannot be made with complete certainty due to potential overlaps (see also below).

Three medium to large slag fragments found in Dhaskalio Phase B are considered to have been brought to the site for secondary use as pounding tools. It was suggested previously, based on proximity, that these may have been brought over from the neighbouring Kavos Promontory (Volume I, chapter 32, 672 and fig. 32.10). Two of these were analysed, but the results did not support this suggestion. Both **8309** from Trench V, layer 2, and **10167** from Trench I, floor Q, have arsenical copper prills, but both lack the characteristic elevated lead contents of Group 2 slags. Group 2 slags are heterogeneous in their composition; thus it is difficult on the basis of so few samples to be sure that they are fully characterized. Still, on current data, **8309** is additionally distinct due to its high manganese content. Its lead isotope composition is consistent with the Group 1 slags, but chemically it is also distinct from those. It is likely that these two slags were both brought to Dhaskalio from beyond Keros to be used as tools. They cannot therefore be used as indirect evidence for a more precise chronological attribution of the Kavos Promontory activities.

Both arsenic and lead were detected in the minute copper prills of the single slag analysed from Phase C, 14065, from Trench XXIII, layer 6. The specimen is, however, distinguished from Group 2 slags, on the basis of its zinc content, not identified elsewhere, while excluding the base metals its chemical composition is more similar to Group 1 than to Group 2, with similar silicon and iron oxide contents, relatively low aluminium and magnesium and medium to high calcium. In terms of its lead isotope composition, the specimen plots in proximity to KN65 and the leaded arsenical coppers, but is separated by higher ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁶Pb ratios. The few Group 2 slags presently analysed showed intense heterogeneity within and between them in their compositions; hence it cannot be excluded that slag more similar to 14065 is present on the Kavos Promontory and has not been identified so far. However, present evidence again does not conclusively support the association of 14065 with any of the slag from the Kavos Promontory.

Absolute provenance of Dhaskalio and Kavos finds and a note on potential mixing for the Group 2 slags

In the following paragraphs aspects of absolute provenance of the analysed materials from Dhaskalio and the Kavos Promontory are considered. For this, the results of this study were compared to the currently published lead isotope database for Aegean ores and slags, primarily the analyses published by the Oxford Laboratory (http://oxalid.arch.ox.ac.uk/). This has been shown to have several limitations, particularly with the small amount of currently analysed copper ores from the Aegean and the indications for overlap (Georgakopoulou 2005). As a result, although some trends are noted with potential sub-groups, a resolution down to sources in individual Cycladic islands is probably optimistic. The picture is complicated even further if potential Anatolian sources are also considered, many of which are very similar in their lead isotope signatures to the Aegean ones (e.g. Pernicka et al. 1990; 2003). The most distinctive lead isotope composition is that of the single tin bronze analysed, 12741. The lead isotope ratios of this artefact are comparable with those of some of the earliest tin bronzes in the Aegean from

sites such as Kastri on Syros and Poliochni on Lemnos (e.g. Pernicka *et al.* 1990; 2003; Stos-Gale *et al.* 1984). The distinctive signature shows that both the copper and the tin were imported to the Aegean, most probably already alloyed. The source of this clearly different copper metal remains unidentified.

The vast majority of Group 1 slags from the Kavos Promontory, as well as 8309 from Dhaskalio, concentrate in the central part of the lead isotope diagram (Fig. 8.22). Here are also found many of the western Cycladic ores and slags, primarily from Kythnos, Seriphos, Siphnos, Thasos and, to a lesser extent, Lavrion. None of the analysed Dhaskalio artefacts was found in this part of the diagram. The possible ingot fragment from Dhaskalio, 10003 at the left part of the diagram, is not directly comparable with any of the presently reported slags and ores from the Aegean. It plots close to, but outside, the presently constructed Lavrion and Seriphos fields. The sample cannot be the result of mixing different southern Aegean sources, as it plots at the edges of the presently available data. Alternative sources need to be considered, possibly in the region of the eastern Aegean or Anatolia. The tweezers fragment **12851** is in close agreement with some of the ores from Lavrion and, to a lesser extent, Seriphos. Arsenical copper slags are not presently known on Seriphos, although an arsenical copper mineralization had been identified on the island (Georgakopoulou et al. 2011).

The other cluster of samples includes the leaded arsenical coppers from Dhaskalio and the single Group 2 slag from the Kavos Promontory. These slags are in agreement with some of the analysed slags from the site of Skouries on Kythnos, but not with any of the ore samples so far analysed. Furthermore, earlier claims for the presence of arsenical copper ores on Kythnos (Gale et al. 1985) have been refuted on the basis of further analysis (Bassiakos & Philaniotou 2007). Arsenical copper does not appear to have been produced on a large scale on Kythnos or Seriphos, the two islands currently bearing evidence for large-scale production of copper in this period. Furthermore, significant quantities of lead were never analysed in these slags. The high lead contents commonly characterizing the samples in this cluster prompted a comparison with the lead isotope data for Aegean lead ores. The samples are in very close agreement with the lead ores and slags from the island of Siphnos. Additionally it should be noted that preliminary analyses of copper slags from Akrotiraki and a nearby smelting site have suggested that arsenical copper production was taking place in the early bronze age (Bassiakos et al. 2013; Pernicka et al. 1985). Further work is necessary to explore this possibility, particularly a better characterization

of the slags from Akrotiraki. Still, agreement in lead isotope ratios does not unequivocally point to specific sources, unless all plausible overlapping fields are considered. Alternative sources in Anatolia or other neighbouring regions need to be considered for this purpose. Given the complications and significant overlaps existing in the Aegean and Anatolian database for copper-based ores, such an attempt has not been made at present. For now we conclude that some structure is evident in the data, although admittedly this is based on limited samples.

A note needs, however, to be made here with regard to mixing of materials in relation to the Group 2 slags and arsenical copper production on Dhaskalio and Kavos. High lead contents in copper are taken to be accidental impurities present in the original copper ore (Pernicka et al. 1990). However, significant lead contents have not been measured in the main Cycladic copper sources and the metal has not been found in significant contents in the associated slags (e.g. Bassiakos & Philaniotou 2007; Georgakopoulou et al. 2011). Lead and copper minerals are known to co-exist in the multimetallic deposit of Lavrion; however, the lead-rich copper samples analysed here for their lead isotope compositions are clearly inconsistent with the well-characterized Lavrion deposit. Siphnos, which also hosts lead and copper mineralizations (Wagner & Weisgerber 1985), does emerge as a plausible source for the ores used to make these slags and therefore possibly the source for the original ore used to produce the artefacts (which may have been manufactured on Keros, however). If lead has been added to copper, then its isotopic composition will completely mask that of copper. As was discussed previously, mixing of materials in the production of the leaded arsenical copper slags of Group 2 remains a possibility, but one that could not be proved by the technological study of the slags. The lead isotope data however, may be telling. The absence of any artefacts from Dhaskalio consistent with the more frequent Group 1 slags from the Kavos Promontory may be an indication that the copper produced was subsequently mixed with another material for manufacture of artefacts. In this scenario slags from Groups 1 and 2 would be by-products of consecutive stages in copper production. This possibility needs to be further explored by more in-depth consideration of chemical and isotope compositions across larger assemblages of early bronze age Aegean artefacts, as well as ore deposits in the eastern Aegean and Anatolia, which are outside the scope of this chapter. Alternatively, the absence of any artefacts consistent with the Group 1 slags may be coincidental, as a small number of artefacts was analysed for lead isotopes.

Lead isotope attribution of lead or silver artefacts to specific sources is generally more straightforward. First, the two main sources of lead and silver in the Aegean, Lavrion and Siphnos, separate well in their composition, while exploitation of both deposits has been proven by direct archaeological evidence (Bassiakos et al. 2013; Kakavogianni et al. 2008; Papadopoulou 2011; Wagner & Weisgerber 1985). Furthermore, complications with mixing of different materials for alloying are less likely to cause problems (Pernicka et al. 1990). The litharge recovered from the Special Deposit North and the two lead artefacts **10191** (Phase B, a probable rivet fragment from Trench I) and 5786 (an unidentified artefact from Trench VI, layer 23, of Phase C), plot together and are consistent with a provenance from Siphnos, as they are in close agreement with lead ores, slags and litharge from this island. On the other end, **5828**, the litharge from Trench VII, layer 5 on Dhaskalio, is in agreement with a Lavrion origin. The differences between the two litharge fragments from Dhaskalio and the Special Deposit North on Kavos are also reflected in their chemical compositions, with antimony only detected in significant quantities in the latter (see also Bassiakos *et al.* 2013). Finally, **11828** (a rectangular object from Trench XXI, layer 9) shows close correspondence with the analysed samples attributed a Siphniot origin, but is outside the limits of the analysed comparative materials from Siphnos. Its lead isotope composition is intermediate between that of lead from Siphnos and Lavrion, but closer to the former. The lead used may have been the result of mixing lead from both sources; alternatively the Siphniot field may be more extensive than previously thought.

The isotopic signature of the speiss fragment **11541** is not compatible with any of the presently analysed copper or lead ore sources in the southern Aegean, although there are no indications that the original raw material was a copper or lead ore, and was more likely an iron, arsenic, antimony mineral. Further conclusions on the provenance of this material cannot be drawn presently, due to lack of data from comparative materials.

Dhaskalio and Kavos in the context of southern Aegean EBA metallurgy

The study of the metals and metallurgical finds from Dhaskalio Kavos has documented further the range of activities undertaken on the site and the variability of materials present. A relatively small smelting site is located on the Kavos Promontory outside the main settlement area on Dhaskalio. Evidence for the production of two types of copper is attested, pure

copper and arsenical copper with lead. It is still not clear whether the latter was produced in a subsequent alloying step mixing the pure copper associated with Group 1 slags with arsenic and lead-rich minerals, or whether it was made independently from naturally or intentionally mixed minerals. It was proposed previously (Georgakopoulou 2007a) that the ores used in these activities were not local to Keros and further evidence now corroborates this statement. Copper ores were not identified during fieldwork undertaken on Dhaskalio or Kavos, nor was it found during the systematic survey of the entire island undertaken subsequently (Volume VI, chapter 13). Dixon & Kinnaird (Volume I, chapter 3, 32) propose that the presence of base metal mineralizations in the vicinity of Kavos is possible, based on the local geology. The landscape is, however, significantly eroded and submerged nowadays, so that such sources would not be visible today, but may have been available in antiquity. The possibility cannot be excluded, but still the variability of raw materials used in these processes (at least two types of minerals), as well as the identification of other remains clearly non-local (e.g. litharge, speiss), suggest that use of imported raw or semi-processed materials for metallurgy on Dhaskalio Kavos is the most likely scenario.

Metallurgical activities within the settlement of Dhaskalio are of a different nature, relating to secondary metalworking activities, such as refining, casting and probably hammering into shape. A consideration of the distribution of metallurgical finds across the excavated parts of Dhaskalio did not reveal any concentrations that would point to specialized working spaces (Volume I, chapter 32). On the basis of present evidence, metallurgy was practised across the Dhaskalio site, although the number of finds from each context was small, reflecting either the small scale of activities or regular cleaning of spaces. Although Phase C is by far the most widely represented phase in the excavated contexts and thus yielded the majority of evidence for metallurgy, some indications for metallurgical practices were noted already in Phase A.

The main type of alloy worked on Dhaskalio was a leaded arsenical copper alloy, at least part of which may have been produced on the Kavos Promontory. Arsenical copper is also by far the most extensively used alloy in the recovered assemblage, although a couple of tin bronze artefacts were recognized. No evidence for working tin bronze was, however, found. The lead isotope signature of the single tin bronze artefact analysed with this method suggests that the alloy, and possibly the object itself, was imported already alloyed.

The evidence for lead and silver production or working is scarcer. Lead is widely used on Dhaskalio, typically for mending pottery, but also for a range of other objects (Volume I, chapter 32). Silver, on the other hand, was only identified as surface finds at the two Special Deposits. Specifically, two silver artefacts, a ring and a pin, were found on the surface of the Special Deposit North (Volume II, chapter 14). An early bronze age date can be attributed to the pin, based on its typology, while this is still plausible but less certain for the ring. Another silver ring was found on topsoil in one of the Special Deposit South trenches. The dating of this ring is unclear (Volume II, chapter 10). Other evidence for lead and silver metallurgy is, however, provided by the identification of the two litharge fragments, one on Dhaskalio and one previously on the surface in the Special Deposit North area. As discussed before (Georgakopoulou 2007a), these need not be direct evidence for cupellation practised locally, as litharge may have had a number of secondary uses and the number of samples recovered is small. Still, it is significant that each fragment can be clearly sourced back to separate ore sources, consistent with the two main southern Aegean sources of Lavrion and Siphnos. This distinction in two fragments further highlights the variety of imported materials on the site, both in terms of their nature, as well as the original sources.

Metallurgical remains were also recovered in small numbers from the Middle Area (Georgakopoulou 2007a; Volume II, chapter 15). Samples from these were not analysed here, but macroscopically they are more consistent with secondary metalworking, rather than primary production processes. In contrast, despite the widespread evidence for metallurgy across the site, metal is extremely scarce in the two Special Deposits, suggesting that metal did not form part of the 'prestige' artefacts deposited. The suggestion had been made previously, at least for the Special Deposit North, that this may be due to looting for metal taking place in antiquity (Whitelaw 2007). In that case the rare silver artefacts recovered in the surface of the Special Deposits would only represent a small fraction of the metal originally deposited in these contexts. However, the lack of metal finds in the unlooted Special Deposit South makes this suggestion less likely. Moreover, were small metal artefacts part of the Special Deposit North, many would have been missed by looters and recovered during excavation.

Metalworking and metal use on Dhaskalio and Kavos are in line with what would be expected from a larger Cycladic settlement of this period (see also discussion in Georgakopoulou 2007b). The identification of primary metal production is, however, more surprising. The majority of smelting evidence known from this period in the southern Aegean is associated with large-scale smelting sites isolated from settlements within the metalliferous zone of the western Cyclades (e.g. Bassiakos & Philaniotou 2007; Broodbank 2000, 292-8; Georgakopoulou 2016; Georgakopoulou et al. 2011). Small smelting sites in the vicinity of early bronze age settlements are, however, known also from elsewhere, specifically at Raphina in Attica (Theocharis 1952) and Akrotiraki on Siphnos (Papadopoulou 2011), but again both of these are found in areas close to ore sources. At Kavos Promontory ores were transported, possibly over a long distance, to be smelted in the vicinity of the settlement. The only parallels for this practice come from Crete, the sites of Kephala-Petras (Papadatos 2007) dating to the FN/ EMI, and Chrysokamino, primarily an EMIII site (Betancourt 2006). At Kephala-Petras the evidence for smelting is scarce, while at Chrysokamino the settlement pattern is different to that of Keros, with dispersed evidence for habitation in the vicinity instead of a single large settlement. Still, although perhaps for different reasons and under different circumstances, these two cases further illustrate that ores were transported through maritime routes over longer distances in the early bronze age Aegean.

The question that unavoidably comes to mind is why was this practice undertaken here? What reasons led the local inhabitants to import or transport ores themselves, when ready-smelted metal would have been much less bulky for the same amount of final product? First, it should be pointed out that the relatively small scale of remains, compared to the much larger western Cycladic smelting sites (Georgakopoulou 2016), suggests that this was a restricted activity, practised either over a short period or in small-scale events during a longer period. The Dhaskalio site certainly did not rely exclusively on the Kavos Promontory smelting for its metal supply. Availability of fuel also does not appear as a valid reason, as, even allowing for a less barren landscape than today, it is very unlikely that fuel would have been widely available on Keros to justify this practice. Practical reasons may have included minimizing time spent at the ore sources by bringing back some of the raw

materials for smelting closer to home, using smelting activities close to the settlements as training events or opportunities for demonstration to the community, or using the ores as ballast in return voyages. The predominance of imported goods on the site, however, stands against the latter.

Could metal have been smelted to be used in the ritual deposition of materials at the Special Deposits, or as part of ritual activities? The use of water-sieving in the excavation of the Special Deposit South documented the absence of metal objects in that deposit. Indirect evidence stems, however, from another workshop activity undertaken on the Promontory, that of obsidian knapping. The associated remains conclusively showed that the activities undertaken at the Kavos Promontory did not produce the blades deposited in the two Special Deposits (Volume II, chapter 19). With regard to the second suggestion, there is no way to associate smelting at the Promontory with the ritual deposition at the Special Deposits and the two practices may not have been related. The fact that smelting was taking place outside the main settlement area may have been driven as much by secrecy or mysticism as by the practicalities of cleanliness and safety close to habitation. Irrespective of how directly involved the entire community was, however, the deliberate action of bringing ore from afar to smelt in the vicinity of a habitation site, and the 'magical' transformation of stone to metal involved, would have made smelting a socially highly charged process.

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