Examination of copper slags from the Early Bronze Age site of Daskaleio-Kavos on the island of Keros (Cyclades, Greece)

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Introduction

The earliest metal artefacts known at present from the Cyclades *(Figure 1)* date to the Final Neolithic (FN: c. late 5th millennium-late 4th millennium) with examples from the Zas Cave on Naxos (Zachos 1996; Zachos and Douzougli 1999), Phtelia on Mykonos (Maxwell 2002), and Strophilas on Andros (Televantou in press). From the same period come the earliest finds of slag and metallurgical ceramics associated with copper production from the settlement of Kephala on Kea (Coleman 1977). The evidence for indigenous Cycladic metallurgy during the Final Neolithic is still limited but this previously little documented period is rapidly becoming better understood through a number of recent excavations in this region. Future examination and publication of the emerging data promise a much more informed picture of Final Neolithic Cycladic metallurgy.

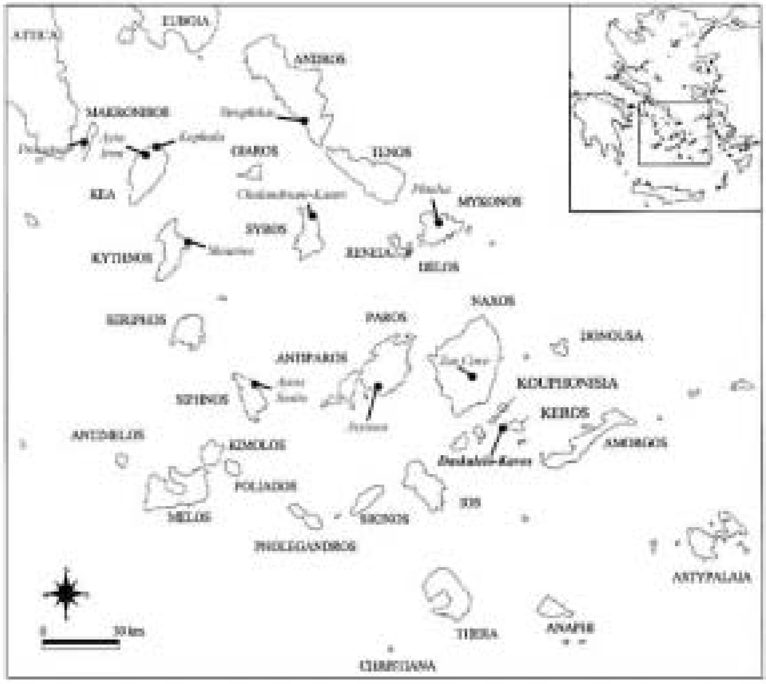

Figure 1. Map of the Cyclades showing the sites mentioned in the text (adapted with changes from Broodbank 2000b: 325)

In the ensuing Early Bronze Age (EBA) both the metal artefacts and the metallurgical remains increase substantially in the archaeological record. A remarkable boost in the visibility of metallic artefacts is attested during the EBII period (c. 2700-2200 BC), which was characteristically assigned the term *Metallschock* (Renfrew 1972: 338). Metallurgy was seen as one of the prime stimulants for the important social changes observed in the Cyclades during the EBII (Branigan 1974, 1977; Renfrew 1967, 1972), although this direct association has been challenged by Nakou (1995), who stresses the possibility of a change in depositional patterns rather than, or as well as, a sudden increase in metal production and usage, particularly as the majority of these finds have been recovered from burial contexts.

In terms of metallurgical activities on the other hand, developments in archaeometallurgical research in this region during the last two decades leave no doubt that by the Early Bronze Age copper, lead and silver were produced locally in the Cyclades. Several slag heaps or scatters have been reported for example on Kea (Caskey *et al.* 1988; Papastamataki 1998), Kythnos (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Hadjianastasiou 1998; Hadjianastasiou and MacGillivray 1988; Stos-Gale 1998; Stos-Gale *et al.* 1988), Seriphos (Gale *et al.* 1985), and Siphnos (Wagner and Weisgerber 1985) although the degree to which these have been studied varies considerably and many remain undated. Among them the most well-known examples are the lead/silver mining and smelting site of Ayios Sostis on Siphnos (Wagner *et al.* 1980; Wagner and Weisgerber 1985) and the copper smelting site of Skouries on Kythnos (Gale *et al.* 1985; Hadjianastasiou and MacGillivray 1988; Stos-Gale *et al.* 1988), which have both provided conclusive evidence for EBA metal production. The role of these islands in early metallurgy is additionally supported by the results of an extensive lead isotope analysis programme, through which a large number of Aegean metallic artefacts were analysed and compared to potential Cycladic ore sources and production remains (see for example Gale and Stos-Gale 2002; Stos-Gale 2000 and references within).

The metal production sites studied so far in the Cyclades are typically relatively large slag heaps in close proximity to potential ore sources, but are all located at a distance from any known EBA settlements. Evidence for the metalworking stages that follow smelting, such as melting and casting, has not been identified in the near vicinity of these heaps, leading to suggestions that the metal was most likely transported to settlements for further processing and artefact manufacture (Barber 1987: 112; Broodbank 2000a: 293-7). Metallurgical remains have indeed been recovered from a number of EBA settlements, albeit in contrast to the western Cycladic slag heaps, their quantities are considerably smaller in these cases, usually only a few handfuls. Slag, metallurgical ceramic fragments, and/or litharge have been reported from Kastri on Syros (Bossert 1967; Stos-Gale *et al.* 1984; Tsountas 1899), Ayia Irini on Kea (Stos-Gale 1989; Wilson 1999), Provatsa on Makronissos (Lambert 1973; Spitaels 1982) and close to the EBA cemetery of Avyssos on Paros (Tsountas 1898). With the exception of a small number of lead isotope analyses no further analytical examination of such material had been undertaken to date. As the slag and ceramic specimens may in principle be associated with either smelting or melting, the absence of appropriate studies inhibits a clear distinction between the two possibilities.

A collaborative fieldwork project between the Universities of Athens, Ioannina and Cambridge and the Ephorate of Prehistoric and Classical Antiquities of the Cyclades (*Annual*

Report 1986-7; Whitelaw 2003), carried out on the EBA site of Daskaleio-Kavos on the island of Keros in 1987, brought to light among numerous other finds, a small collection of metallurgical remains. Within the context outlined above, this material presented an excellent opportunity for a comprehensive technological investigation that would not only clarify the types of activities undertaken on the site but also contribute to the overall assessment of the organisation of metallurgy in EBA Cyclades. The collection included small fragments of slag, metallurgical ceramics, copper and lead metal, iron minerals and a single litharge specimen. The finds were all small, while the total weight of slag recovered did not exceed 300 g. Samples from all the different types of material were selected for analysis. Laboratory examination has been completed and a comprehensive presentation of the results is currently under preparation by the present author for publication in the forthcoming volume on the 1987 project on Daskaleio-Kavos (editors Renfrew *et al.*). This paper will present a shorter overview of the results only from the slag analyses, which represent the main type of material examined.

The site

Kavos lies at the western edge of Keros island, facing Daskaleio islet a few metres off the coast *(Figure 2)*. A recent geoarchaeological study concluded that the EBA shoreline of this area was 2.5-5 m below modern sea-level, suggesting that Daskaleio was at that time possibly connected to Kavos by a low thin stretch of land (Bassiakos and Doumas 1998).

Archaeological interest was drawn to Daskaleio-Kavos following extensive looting in the 1950's and 1960's. The looting activities concentrated mainly on a 'special deposit' at the northern end of Kavos and resulted in severe destruction of its structural features and unrecoverable loss of priceless material. Subsequent sanctioned excavations recovered hundreds of fragments of broken marble anthropomorphic figurines and vessels, which appeared to have been deliberately broken in antiquity, as well as other lithics, pottery and metal finds establishing the 'special deposit' as the richest accumulation of prestige material known from an EBA Cycladic context (Doumas 1964; Renfrew 1972: 531-2; Hadji-Vallianou 1975; Zapheiropoulou 1967, 1968, 1975). The nature of the 'special deposit' has given rise to intense controversy among Aegean prehistorians. The wealth and intriguing nature of the finds, in combination with the catastrophic damage to its structural features caused by looting, have left behind a puzzling image, with suggestions divided between a funerary or ritual character (Bassiakos and Doumas 1998; Broodbank 2000b; Doumas 1964, 1990; Renfrew 1984, 1991).

In the south-central part of Kavos, habitation is testified both by the excavation of a house (Doumas 1964) and the abundance of domestic pottery (Broodbank 2000b). Settlement remains have also been noted on the islet of Daskaleio (Doumas 1972). Unfortunately the preoccupation with the role of the 'special deposit' has undermined research into the remaining areas of the site and fieldwork has been limited. On the basis of the pottery the site is dated to the Early Bronze Age II period (EBII: c. 2700-2200 BC), with very little evidence for earlier or later use (Broodbank 2000b; Doumas 1964, 1972). The variability in the pottery shapes and fabrics (Broodbank 2000b) together with the wealth of other apparently imported material, portray a widely connected site. In his recent treatise of the EBA Cyclades, Broodbank (2000a) attributes the high influx of materials on Daskaleio-Kavos to the nodal position of the site within a wider inter-island maritime communication and trade network.

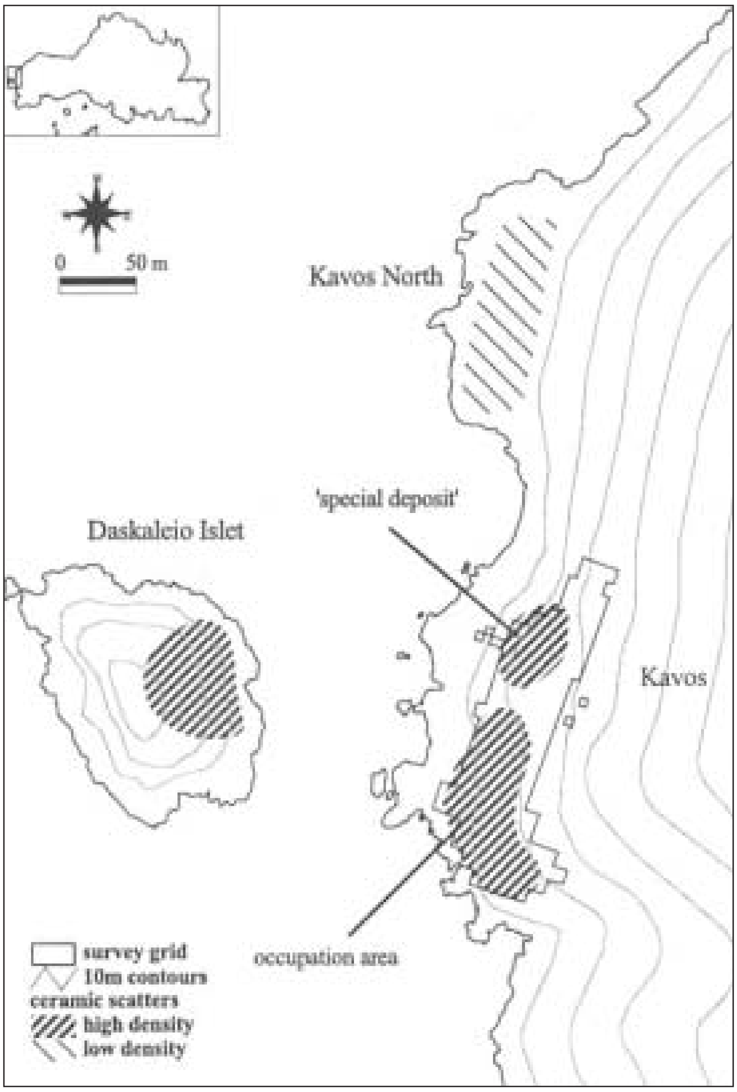

Figure 2. Plan of the site and the surveyed area (Broodbank 2000a: 224). Reprinted with permission from C. Broodbank and T. Whitelaw.

The 1987 fieldwork project involved systematic gridded surface collection over the entire Kavos area and excavation in the special deposit. Surface collection was additionally carried out on a low exposed promontory slightly to the north of Kavos, known as Kavos North *(Figure 2)*. The project did not expand to the islet of Daskaleio. The finds presented in this paper were all collected during the surface survey from south-central Kavos (samples labelled KK) and Kavos North (samples labelled KKN).

Analytical methodology

Samples were cut from each specimen and mounted in resin to prepare polished sections. Initial examination under the optical microscope was supplemented by analysis of individual phases and inclusions using the attached Energy Dispersive X-ray facilities on a Scanning Electron Microscope (SEM: JEOL JSM-35CF). Bulk composition measurements of the slag and metallurgical ceramic fragments were carried out on the electron microprobe with an attached wavelength dispersive X-ray spectrometer (WDS-EPMA: JEOL Superprobe JXA-8600). Ten to fifteen areas (c. 0.02 mm^2 each) were analysed in each case. The results presented here are averages of the measurements for each sample, normalised to 100 % to compensate for porosity. The following elements were analysed for[1]: Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, As, Sn, Sb, Pb, Bi, expressed as oxides, and Cl. Metal prills in the slags were analysed using point measurements on the electron microprobe searching for S, Cl, Fe, Co, Ni, Cu, Zn, As, Ag, Sn, Sb, Au, Pb, Bi.

Results of the analytical examination of slag samples

Fourteen slag samples were examined. With the exception of one (sample KKN3 discussed separately below), they were classified into two groups on the basis of both macroscopic and analytical differences.

Group 1

Macroscopic characteristics

A total of nine slag samples were attributed to this group. Their size is small, reaching a maximum of 5 cm in their largest dimension *(Figure 3)*. They are all grey-black in colour with little or no external green staining. A ropey-flow texture is visible on the upper surface of some of the specimens. With the exception of a couple of samples that showed a little magnetism, the majority did not respond to a hand-held magnet.

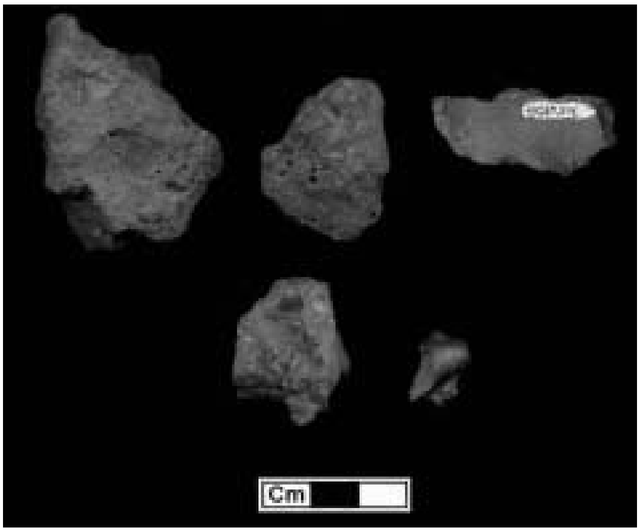

Figure 3. Examples of Group 1 samples.

Bulk and phase composition

Bulk composition measurements given in *Table 1* showed that silica (36-46 %) and iron oxide (33-42 %) are the main constituents, followed by calcium oxide (10-19 %) and smaller amounts of other gangue elements. Copper contents are relatively low ranging between 0.4-0.8 % (estimated as CuO). The low copper and high iron content of these slags immediately suggests a smelting rather than melting origin.

Additional evidence for an association with smelting stems from the microstructure of these specimens. Overall, despite variations in the size and distribution of the different phases both within and between sections, a common pattern is observed with reference to the nature of phases present and

Table 1. EPMA results (weight %) of bulk analyses on all the slag samples. Top: Group 1, Middle: Group 2
Results have been normalised to 100% to compensate for porosity, while the measured totals are given in the last column labelled MT.
Note: Elements consistently measuring below the detection limits of the method (c.0.05%) have not been included in these tables.

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	As_2O_3	SnO_2	Sb_2O_3	PbO	MT
KKN1	0.5	4.1	2.7	39.7	0.1	0.1	0.2	14.9	0.1	0.2	37.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	93.1
KKN4	0.4	4.3	2.6	40.8	0.5	0.0	0.2	12.0	0.1	0.2	38.6	0.0	0.0	0.4	0.0	0.0	0.0	0.0	93.5
KKN5	0.3	4.5	1.9	40.0	0.1	0.0	0.1	13.9	0.1	0.2	38.5	0.0	0.0	0.4	0.0	0.0	0.0	0.0	95.3
KKN8	0.2	3.7	2.1	41.4	0.7	0.1	0.0	11.3	0.1	0.2	39.5	0.0	0.0	0.5	0.0	0.0	0.0	0.0	95.1
KKN9	1.0	4.5	3.1	46.0	1.3	0.1	0.8	10.0	0.1	0.2	32.5	0.0	0.0	0.4	0.0	0.0	0.0	0.0	95.8
KKN10	0.4	5.3	2.1	45.5	0.2	0.0	0.1	11.9	0.1	0.2	33.6	0.0	0.0	0.5	0.0	0.0	0.0	0.0	94.3
KK1	0.7	3.6	3.3	35.8	0.5	0.1	0.3	18.6	0.1	0.2	36.1	0.0	0.0	0.8	0.0	0.0	0.0	0.0	96.5
KK10	0.3	4.0	1.8	39.4	0.5	0.1	0.0	11.2	0.1	0.2	41.9	0.0	0.0	0.6	0.0	0.0	0.0	0.0	95.5
KK11	0.6	3.6	2.9	38.9	0.4	0.1	0.2	13.3	0.1	0.2	39.1	0.0	0.0	0.6	0.0	0.0	0.0	0.0	97.7
KKN2	1.3	2.7	7.9	30.1	0.0	0.5	0.9	5.6	0.3	0.4	39.7	0.1	0.2	2.6	0.1	0.0	0.0	7.5	93.8
KKN7	0.8	0.9	4.9	23.4	0.0	0.0	0.3	4.2	0.2	0.0	48.4	0.0	0.5	9.6	2.2	0.0	0.0	4.5	98.7
KK3	0.7	0.8	3.3	18.8	0.1	1.9	0.1	1.4	0.1	0.4	43.8	0.0	0.2	10.1	7.4	0.4	0.1	10.2	90.4
KK12	0.6	0.8	8.0	25.3	0.5	0.1	0.7	3.6	0.4	0.0	53.9	0.0	0.0	2.8	2.5	0.0	0.0	0.8	87.8
KKN3	0.0	0.3	0.0	5.6	0.0	2.5	0.0	0.2	0.0	0.0	59.9	0.0	0.0	31.4	0.0	0.0	0.0	0.0	86.4

their relative abundance. In most samples the dominant phase is fayalite (Fe_2SiO_4), surrounded by a glassy matrix, while fine and dispersed magnetite (Fe_3O_4) crystals are also present in most cases *(Figure 4)*. Fayalite crystals (*Table 2*) in these samples usually accommodate significant amounts of magnesia (8-9 %) and lower quantities of calcium (2-5 %) and manganese (0.2-0.3 %) oxides. In sample KK1 the iron silicate crystals are much richer in calcium with an atomic ratio of approximately 1:1 between iron oxide, silica, and calcium oxide. The composition is more consistent with the mineral kirschsteinite ($CaFeSiO_4$), while small amounts of magnesium oxide were also noted. The crystallisation of these calcium-rich phases in this sample are not surprising given the comparatively high calcium contents detected in the bulk analysis of KK1.

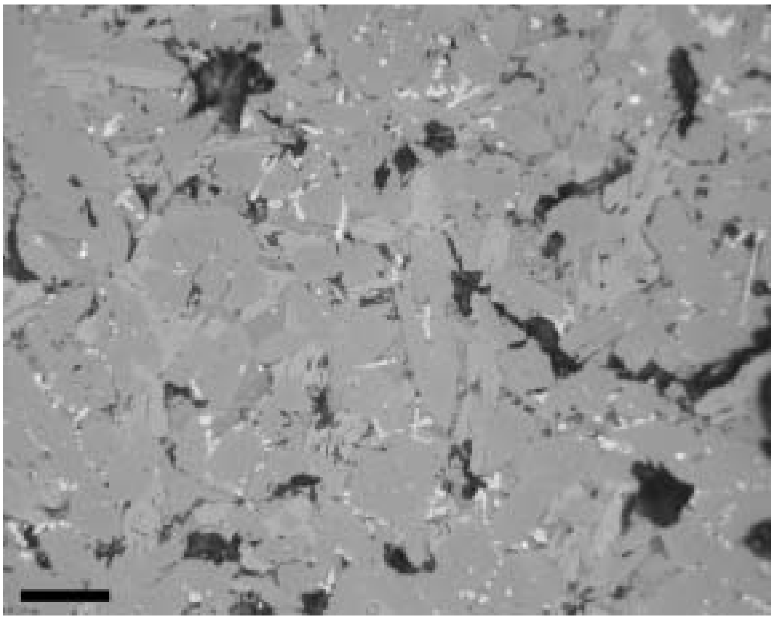

Figure 4. Reflected light photograph of the microstructure of sample KKN8, showing fayalite (medium grey), magnetite (light grey), glass (dark grey), and porosity (black) (scale: 50 µm).

The slags are virtually free of any unreacted or partially reacted primary materials, as are typically observed in early (usually pre-EBA) copper production slags (see for example Hauptmann 1989, 2003). The predominance of fayalite indicates reducing conditions, with oxygen pressures below 10^{-8} atm (Moesta and Schlick 1989), while the overall microstructure of these specimens suggests that the primary materials fully reacted to form a relatively homogeneous melt. Low copper losses are attested from the bulk composition measurements.

Entrapped prills in the Group 1 slags are mostly mixed copper and iron sulphides (matte). In the larger ones, different phases of the Cu-Fe-S system can be discerned within individual prills (*Figure 5*). Analyses of several matte prills from each sample were carried out on the electron microprobe but no other elements apart from copper, iron, and sulphur were detected. In addition to the matte, minute prills that resembled copper metal were also identified in the optical microscope, but these were too small and could not be analysed further.

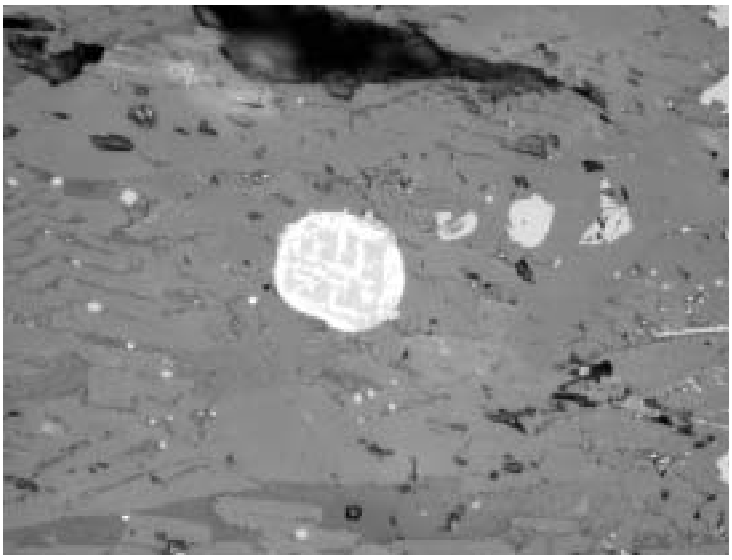

Figure 5. Reflected light photograph of the microstructure of sample KK1, showing kirschsteinite (medium grey), magnetite (light grey), glass (dark grey), and a large matte prill in the centre with a lamellar texture (scale: 10 µm).

Table 2. SEM analyses (weight %) of individual phases in Group 1 slags, normalised to 100% (Fe-Si: iron silicates; magn.: magnetites; MT: measured total).

Fe-Si	**MgO**	**SiO_2**	**CaO**	**MnO**	**FeO**	**MT**
KK1	5.3	31	22	0.3	42	88
KKN1	9.5	31	3.5	0.2	56	89
KKN4	7.9	31	2.3	0.3	59	87
KKN5	8.3	31	4.5	0.3	55	88

MAGN.	**MgO**	**Al_2O_3**	**SiO_2**	**CaO**	**TiO_2**	**Fe_3O_4**	**MT**
KK1	0.9	1.9	0.4	0.6	0.5	93	95
KKN1	0.3	1.4	1.0	0.4	0.4	93	95
KKN4	b.d.l.	1.4	2.4	0.8	0.5	92	96

GLASS	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**Fe_2O_3**	**CuO**	**MT**
KK1	0.7	2.4	4.9	40	0.3	0.5	20	0.2	29	b.d.l.	90
KKN1	b.d.l.	4.0	1.8	45	0.1	b.d.l.	23	b.d.l.	24	b.d.l.	92
KKN4	b.d.l.	2.1	2.3	42	b.d.l.	b.d.l.	20	b.d.l.	30	b.d.l.	90
KKN5	b.d.l.	2.4	1.8	42	0.2	b.d.l.	20	b.d.l.	30	0.2	91

The presence of matte testifies to the addition of sulphidic minerals in the furnace charge. Several independent studies using different methodologies have concluded that from the early stages of metallurgy sulphidic copper ores could be smelted in processes that did not require particularly strongly reducing conditions or elaborate treatment as was the case for the matte smelting process carried out in later periods (Hauptmann *et al.* 2003; Moesta and Schlick 1989; Rostoker *et al.* 1989; Zwicker *et al.* 1985).

In these case studies the sulphidic minerals entered the charge either as minor accessory components to a mainly oxidic ore (co-smelting), or formed the bulk of ore used. The resulting microstructure of the slags is frequently very similar, showing the same broad characteristics as the Group 1 slags from Kavos (cf Moesta and Schlick 1989; Zwicker *et al.* 1985). In the absence of remains of undecomposed ore in the slags, or discarded fragments on the site, it is difficult to decide with certainty the exact nature of the raw materials with reference to use of primary or secondary minerals.

Group 2

Macroscopic characteristics

Three out of the four slags attributed to this group show very similar external characteristics (*Figure 6*). They are grey-black in colour, with iron oxide and green copper oxide staining on their outer surface, the latter being particularly intense in and around the pores observed upon sectioning. They are very small, their largest dimension reaching a maximum of 1.5 cm, and magnetic. A very characteristic feature of these samples is the appearance of several tiny (c. 0.1 cm) green prills, which protrude on the outer surface.

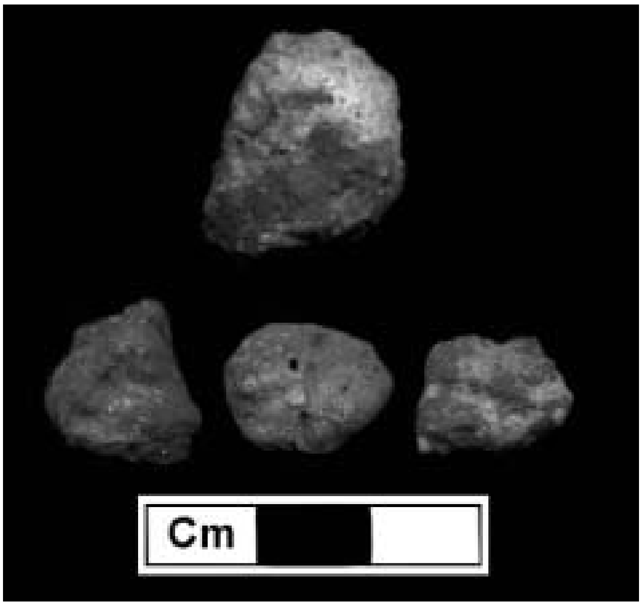

Figure 6. Group 2 samples (top: sample KK12).

Sample KK12 is somewhat different macroscopially, but was included in this group mainly because of analytical similarities. This black slag reaches nearly 3 cm in length, is largely covered externally by a thin (~0.1 cm) solid green corrosion layer and also shows red-brown iron oxide staining on one side. External green prills were not visible and the sectioned surface did not show the intense green staining observed in the other samples.

Bulk and phase composition

The bulk analyses of Group 2 samples (*Table 1*) differ significantly between samples, due to the internal heterogeneity within each sample in terms of frequency, size, and distribution of phases (see below). Compared to Group 1, these samples show higher iron oxide contents (40-54 %), which predominates over silica (19-30 %), higher alumina (3-8 %) and lower calcium oxide (1-6 %). The copper contents are also much higher (CuO: 3-10 %), while particularly characteristic is the presence of other base metals, the most common being lead (PbO: 0.8-10 %), arsenic (As_2O_3: 0.1-7.4 %)[1], and to a lesser extent nickel (NiO: 0-0.5 %).

The microstructure of these slags is generally very heterogeneous and also differs between the four samples. The frequency, size and distribution of the different phase components varies between each section. All the samples are rich in magnetite embedded in a glass matrix (see *Table 3* for analyses of these phases). Sample KK3 shows a particularly high concentration of magnetite, with little glass, which is in agreement with the lower percentages of silica and other gangue elements measured in the bulk analyses of this section (*Table 1*). Fayalite crystals are only present in two samples (KKN2, KK12) (*Figure 7*). Analyses showed that these also incorporate small amounts of magnesia and calcium oxide (*Table 3*). A concentration of iron oxides in the shape of wüstite (FeO) was observed in sample KKN2, although the presence of this phase is limited to one area of the sample, the remaining being dominated by magnetite.

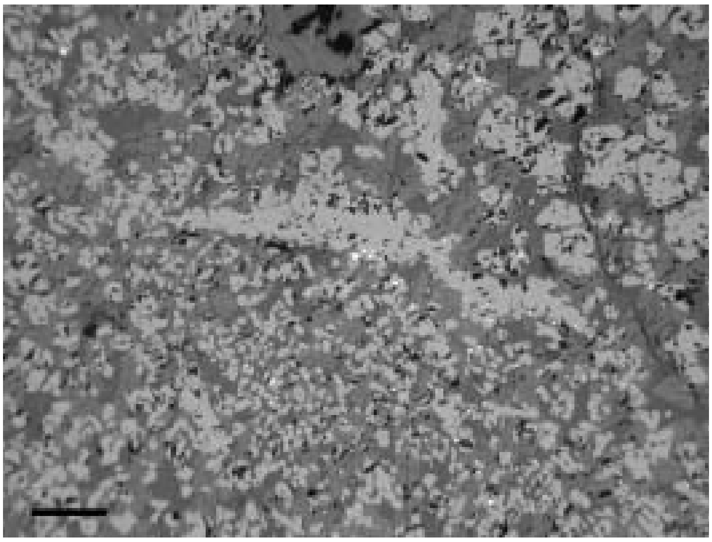

Figure 7. Reflected light photograph of the microstructure of sample KK12, showing magnetite crystals and large magnetite aggregate (light grey), fayalite (medium grey), and glass (dark grey) (scale: 100 μm)

Inclusions of unreacted or partially reacted raw materials are also common. Magnetite is often observed in large and irregularly shaped aggregates, which usually include within them distinct copper prills (*Figure 7*). These formations are interpreted as the remains of the partially reacted limonitic part of mixed copper and iron ores (Hauptmann *et al.* 2003). A few quartz fragments were also discerned. Analysis of these on the SEM showed that they usually contain small amounts of iron, copper, lead, and/ or nickel, possibly indicating a geological association between the quartz and the iron and base metal-bearing minerals.

The Group 2 samples are all very rich in copper prills, which vary significantly in size, the largest being visible macroscopically in the cut sections. Electron microprobe point analyses showed that these are arsenical copper prills, usually incorporating distinct lead metal inclusions (*Table 4*)[2]. The distribution of arsenic in these prills is uneven with arsenic enriched zones appearing within a matrix of lower or even negligible arsenic contents, as is typically encoun-

Table 3. SEM analyses (weight %) of individual phases in Group 2 slags, normalised to 100% (Fe-Si: iron silicates; magn.: magnetites; MT: measured total).

Fe-Si	MgO	SiO_2	CaO	MnO	FeO	Total
KKN2	7.8	30	2.1	1.0	59	83
KK12	2.8	28	2.6	0.0	66	92

MAGN.	MgO	Al_2O_3	TiO_2	MnO	Fe_3O_4	NiO	MT
KK3	1.9	1.4	b.d.l.	0.7	96	0.8	96
KK12	0.2	4.4	0.3	0.0	95	b.d.l.	98
KKN2	2.1	3.1	0.3	0.5	94	0.6	92

GLASS	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	As_2O_3	PbO	MT
KK3	1.8	0.4	5.4	53	0.0	0.7	2.9	0.0	0.3	20	4.5	3.2	7.8	73
KK12	1.6	0.0	10.9	43	0.1	3.3	13	0.0	0.0	28	0.1	0.0	0.0	89
KKN2	2.5	0.4	9.1	36	0.0	2.0	13	0.1	0.4	29	0.2	0.0	7.0	89
KKN7	0.8	1.6	6.9	41	0.0	1.5	10	0.2	0.0	26	2.2	0.9	8.5	88

tered even in low arsenic copper alloys (Budd and Ottaway 1991; Northover 1989). The separation of lead in copper is not surprising given the almost complete immiscibility of the two metals in the solid state (Hansen and Anderko 1958: 610). Tiny lead prills were also identified, either distinct or attached to copper prills. Lower levels of several other elements were detected during electron microprobe analysis, the main being iron, nickel, and antimony.

In addition to copper prills, sample KK12 also bears separate matte prills. As can be seen from the analyses in Table 4, these generally show lower arsenic contents than the copper prills from the same sample. The observation agrees with the results of Yazawa (1980), who proposed that during copper smelting, arsenic impurities tend to concentrate in the metal phase rather than the slag or the matte.

The chemical composition and microstructure of the Group 2 slags indicate that these are the by-products of arsenical copper production. The identification of partially decomposed starting materials, the presence of fayalite in two samples, and the relatively significant concentrations of silica and other gangue elements in the bulk all point to a smelting origin for these specimens. The predominance of magnetite indicates only slightly reducing conditions (Moesta and Schlick 1989), while the presence of fayalite and possibly also wüstite in some samples together with their overall heterogeneity show that the operating conditions are likely to have fluctuated considerably during the process. Despite the observed inclusions of partially decomposed materials, the formation of fayalite suggests that at least part of the mixture reacted forming a melt. Relatively high copper losses are attested in the bulk analyses.

Production of arsenical copper alloys can be achieved via several pathways depending on the nature of the starting materials (see for example Budd *et al.* 1992; Lechtman 1991, 1996; Lechtman and Klein 1999; Pollard *et al.* 1991; Rostoker and Dvorak 1991). Although arsenical copper alloys are common among EBA Cycladic metal artefacts, little is known about their production. To date only a few of the slags from the large smelting site of Skouries on Kythnos were found to contain appreciable amounts of arsenic in the entrapped copper prills (Gale *et al.* 1985), while the majority of material analysed so far does not agree with production of alloyed copper (Bassiakos and Philaniotou in press). The commonly held view that in the broader Aegean the alloy was produced 'accidentally' by smelting arsenical-copper ores (Gale and Stos-Gale 1989), has been challenged by recent finds from the sites of Chrysokamino (Catapotis *et al.* 2004) and Poros (Doonan *et al.* 2004) on the island of Crete. Mixing of arsenic and copper ores is suggested for Chrysokamino, while addition of arsenical minerals to copper metal is proposed for Poros.

Table 4. EPMA point analysis of copper and matte prills in Group 2 samples (weight %). Analyses KKN7I and KKN7J were carried out on the same prill analysing arsenic poor and arsenic rich zones respectively, although their small size does not allow complete separation of the two. Low totals, where observed are due to the small size of the prills, while totals above 100% usually result from the unavoidable simultaneous measurement of two adjacent phases.

	S	Fe	Ni	Cu	As	Ag	Sn	Sb	Pb	Bi	Total
KKN2A	0.0	3.1	3.7	88.0	0.1	0.0	0.0	1.8	0.1	n.a.	96.8
KKN2B	0.0	1.0	2.0	90.0	0.5	0.0	0.0	2.2	0.1	n.a.	95.9
KKN2D	0.0	0.0	0.9	89.6	2.3	0.0	0.0	0.4	2.6	n.a.	95.8
KKN2G	0.0	2.0	3.7	89.1	1.5	0.0	0.0	0.5	0.1	n.a.	97.0
KKN2H	0.0	0.4	2.3	95.8	0.0	0.0	0.0	0.3	0.6	n.a.	99.6
KKN7A	0.1	2.4	1.3	77.3	14.4	0.0	0.2	0.3	4.3	n.a.	100.2
KKN7C	0.0	2.1	0.1	90.8	5.6	0.0	0.0	0.1	0.0	n.a.	98.7
KKN7I	0.0	0.0	0.0	93.5	4.3	0.1	0.0	0.0	0.0	n.a.	97.9
KKN7J	0.1	0.0	0.0	71.7	28.0	0.1	0.0	0.4	0.0	n.a.	100.3
KKN7O	0.0	0.2	0.4	92.1	6.7	0.0	0.1	0.1	0.1	0.0	99.7
KK3D	0.0	2.2	0.5	75.7	16.3	0.0	0.0	0.7	1.7	0.0	97.2
KK12A	0.0	2.8	1.4	94.0	1.8	0.1	0.0	0.0	0.0	0.1	100.2
KK12B	21.1	7.3	0.0	67.6	0.1	0.0	0.0	0.0	0.0	0.0	96.1
KK12D	0.0	2.1	1.3	90.4	6.6	0.1	0.0	0.0	0.0	0.0	100.3
KK12E	0.4	6.7	0.5	70.5	21.1	0.0	0.0	0.1	0.2	0.1	99.5
KK12F	18.8	11.0	0.5	65.4	1.4	0.0	0.0	0.0	0.0	0.0	97.1
KK12G	0.0	3.6	1.6	91.3	4.7	0.0	0.0	0.0	0.0	0.0	101.3

The absence of associated ore fragments in the Kavos collection does not allow a clear conclusion to be drawn regarding the route followed for the production of arsenical copper on this site. The identification of quartz crystals with traces of copper found within the slags suggests that copper most likely entered the charge as a mineral rather than in its metallic form. The presence of other base metals in the slag in addition to arsenic such as lead, antimony, and nickel suggest the use of polymetallic ores, but whether these elements co-existed in the ore or whether different minerals were deliberately mixed in the furnace charge remains at present uncertain.

A remark should also be made concerning the surprisingly high levels of lead in some of the bulk analyses of the Group 2 samples, which in sample KKN2 in particular, appear to be higher than the copper contents. It should, however, be noted that during bulk analyses, areas exceptionally rich in copper prills were avoided. This practise would result in a lower copper to lead ratio in the measurements than may be true in reality, as the former mainly appears as distinct prills, while the latter is also present in significant quantities in the glass. Still, the overall lead composition in these samples is usually notably high. Although low levels of lead in copper smelting slags are not uncommon in the Old World (see for example Hauptmann 1989), these do not usually exceed 1 %. Examples of copper smelting slags with lead contents comparable to the Group 2 samples have not been found in the literature examined so far.

Sample KKN3

Macroscopic characteristics

The external appearance of sample KKN3 is very similar to the Group 2 slags. The sample is small (<2 cm in length), very magnetic, black with limited green staining and tiny green prills on its outer surface. Despite this resemblance KKN3 showed markedly different compositional and microscopic features, which necessitated a separate classification.

Bulk and phase composition

Bulk analysis of KKN3 showed that the sample mainly consists of iron (FeO: 60 %) and copper oxides (CuO: 31 %). Silica and the other gangue oxides are surprisingly low (Table 1), while other base metals, as identified in the Group 2 slags, are not present above the detection limits of the analytical method used.

The bulk composition is clearly reflected in the microstructure of this sample. Magnetite crystals predominate, often surrounded by a thin band of delafossite ($CuFeO_2$), while separate thin elongated delafossite crystals are also present in parts of the section (*Figure 8*). The glass phase is very limited. Circular copper chlorides are frequent in this section, possibly formed from the re-deposition of leached salts. Copper prills are commonly seen within the magnetite crystals. Analyses of these prills only detected copper and iron. Arsenic, lead and other base metals noted in the Group 2 slags are all below detection limits in these prills.

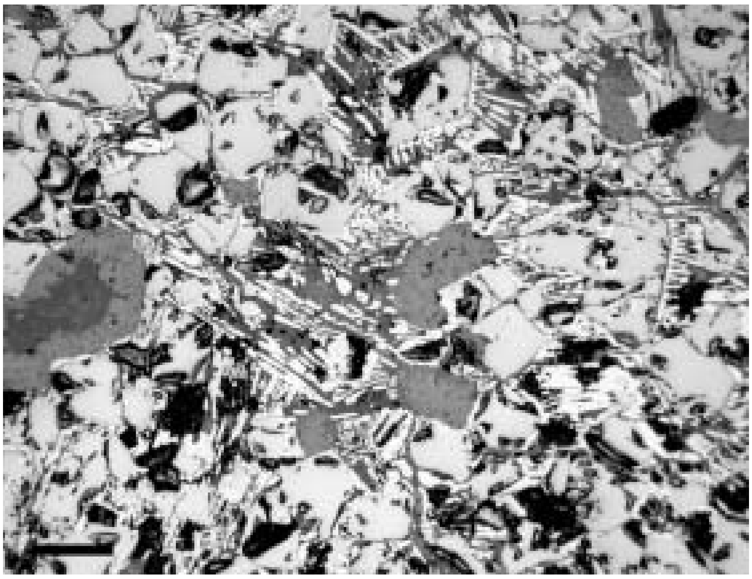

Figure 8. Reflected light photograph of the microstructure of sample KKN3, showing magnetite (light grey) and delafossite (white, elongated). Dark grey inclusions are copper chlorides (scale: 50 µm).

Sample KKN3 shows unique characteristics different than the other samples analysed from the collection. The absence of other base metals, characteristic in Group 2 slags, makes an association with these specimens unlikely, despite the similarities in external characteristics. The phase composition of sample KKN3, mainly composed of magnetite and delafossite, indicates relatively oxidising conditions and probably short reaction times (Bachmann 1982; Hauptmann 2000: 556; Moesta and Schlick 1989). It is likely that the material represents partially reacted dross, spilled from the reacting mixture at the early stages of smelting.

An alternative proposal may be envisaged based on the results of Moesta and Schlick (1989) on the Bronze Age copper smelting furnaces of Mitterberg. The authors suggested a two-step smelting sequence of copper from sulphidic ores, which involved initial formation of matte and subsequent oxidation to copper metal in the same furnace. The microstructure of the relevant slags is similar to the Group 1 slags from Daskaleio-Kavos for the first step, while a slag rich in magnetite and delafossite was formed from the oxidising process. Needless to say such an association cannot be deduced at this stage but the possibility should be considered if further similar material is recovered. As at this stage the sample is unique in the collection it has to be considered as an accidental by-product.

Discussion

The results of the analytical examination of the slags from Daskaleio-Kavos challenge to some extent the previously held model, which proposed a spatial separation of metallurgical activities in the EBA Cyclades, with smelting carried out on the western Cycladic slag heap sites and further metalworking in the settlements (Barber 1987: 112; Broodbank 2000a: 293-7). Admittedly, the scale of production appears to be much smaller in this case.

Particularly interesting are the indications for variability in the metallurgical processes on Daskaleio-Kavos. Evidence for processing of at least two different types of copper was brought forward, while a single litharge specimen identified in the collection (see Georgakopoulou in prep.) raises the possibility that lead-silver metallurgy was also practised on the site. Specimens conclusively associated with metalworking have not been identified, but as the material was all produced from surface investigations and excavation has not been carried out, absence of evidence should not be regarded as evidence for absence.

Several interesting questions now arise. The first is the provenance of the ores used on Daskaleio-Kavos. Was the material local or was it brought to the island from elsewhere? To date systematic search for potential prehistoric ore sources has not been carried out on Keros. Bassiakos and Doumas (1998) report a weak iron-copper mineralization on the island, but this is very limited and it is not clear whether it could have been a source even for small-scale production. On the other hand, the use of at least two different types of ore and the accepted high influx of other imported materials on Daskaleio-Kavos appear to favour the suggestion of an external source. Final interpretation will, however, need to await further study, using appropriate methodology targeted specifically at addressing the question of provenance.

Another issue that needs to be considered is whether the two processes are strictly contemporaneous or whether they reflect a shift in the use of different materials in the period when the site was inhabited. The implications are interesting in terms of assessing the organisation of metallurgy on the site, proposing reasons for the selection of different sources, and comparing the technological details of each process. The Group 2 slags, for example, appear to be associated with a less sophisticated process, with higher metal losses and incomplete reaction of the primary materials, although the small number of samples available for analysis at this stage inhibits a direct comparison. Do the observed differences mirror technological advancements or are they associated with intentional or unintentional adaptation of the operating conditions to the use of different materials? Excavation of stratified material will be necessary in order to examine whether further refinement of the chronological association between the two processes can be made.

In closing, it should be stressed that the nature of metallurgical processes carried out on Daskaleio-Kavos should not necessarily be expected to be similar to those practised on other contemporaneous Cycladic settlement sites. On the contrary it is the identification of potential similarities or differences (whether in working only specific metals, carrying out only some steps of the production sequence, or using different sources) that is necessary in order to obtain a more complete picture of the organisation of metallurgy in EBA Cyclades.

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Notes

1 In order to discriminate between the lead and arsenic contents of the sample on the WDS spectrometer, lead was measured on the Mα line and arsenic on the Lβ line.

2 Analyses presented in Table 4 are point measurements and, given the heterogeneity of the arsenical copper prills, should not be taken as representative of the metal's composition.

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