REFERENCE ONLY

## UNIVERSITY OF LONDON THESIS

Degree PhD Year 2005 Name of Author GEORGAKOPOULOU M

**COPYRIGHT**
This is a thesis accepted for a Higher Degree of the University of London. It is an unpublished typescript and the copyright is held by the author. All persons consulting the thesis must read and abide by the Copyright Declaration below.

**COPYRIGHT DECLARATION**
I recognise that the copyright of the above-described thesis rests with the author and that no quotation from it or information derived from it may be published without the prior written consent of the author.

**LOANS**
Theses may not be lent to individuals, but the Senate House Library may lend a copy to approved libraries within the United Kingdom, for consultation solely on the premises of those libraries. Application should be made to: Inter-Library Loans, Senate House Library, Senate House, Malet Street, London WC1E 7HU.

**REPRODUCTION**
University of London theses may not be reproduced without explicit written permission from the Senate House Library. Enquiries should be addressed to the Theses Section of the Library. Regulations concerning reproduction vary according to the date of acceptance of the thesis and are listed below as guidelines.

A. Before 1962. Permission granted only upon the prior written consent of the author. (The Senate House Library will provide addresses where possible).

B. 1962 - 1974. In many cases the author has agreed to permit copying upon completion of a Copyright Declaration.

C. 1975 - 1988. Most theses may be copied upon completion of a Copyright Declaration.

D. 1989 onwards. Most theses may be copied.

***This thesis comes within category D.***

☑ This copy has been deposited in the Library of UCL

☐ This copy has been deposited in the Senate House Library, Senate House, Malet Street, London WC1E 7HU.

*C:\Documents and Settings\lproctor\Local Settings\Temporary Internet Files\OLK8\Copyright - thesis (2).doc*

# TECHNOLOGY AND ORGANISATION OF EARLY CYCLADIC METALLURGY: COPPER ON SERIPHOS AND KEROS, GREECE

**By**

**Myrto Georgakopoulou**

Thesis submitted to the University of London
for the Degree of Doctor of Philosophy

INSTITUTE OF ARCHAEOLOGY
UNIVERSITY COLLEGE LONDON

MARCH 2005

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

# ABSTRACT

This thesis investigates aspects of the technology and organisation of Early Bronze Age (EBA) Cycladic copper production based primarily on an analytical examination of metallurgical remains identified in two different contexts: the slag heaps of Seriphos and the settlement of Daskaleio-Kavos on Keros. The Cyclades show intense prominence during this period and the identification of local metal production raises important archaeological questions.

A geological reconnaissance on Seriphos established the existence of copper minerals on the island. Five occurrences were identified, sampled and characterised. The slag heaps of Kephala and Phournoi on Seriphos were dated to the third millennium BC by thermoluminescence of furnace fragments. Examination of a substantial suite of slags from these sites showed that unalloyed copper was produced; estimates of several key process parameters for the smelting operations were obtained. No indications for other metallurgical activities aside from smelting were recognised. A preliminary study of material from the still undated Avessalos slag heap was also undertaken.

Analyses of the Daskaleio-Kavos finds gave evidence for two copper-producing activities, resulting in unalloyed and arsenical copper metal, respectively. Identification of a single litharge specimen raises the possibility that cupellation was additionally carried out.

The copper slag heaps identified on Seriphos conform to a pattern known also from neighbouring Kythnos, where relatively large-scale EBA copper smelting is attested, isolated from any known contemporaneous settlements and within a metal-rich area. The dispersed distribution of these slag heaps and several technological characteristics suggest a largely uncentralised production. The finds from Daskaleio-Kavos showed that some small-scale metal production was also carried out within some of the settlements; these activities show several differences compared to those associated with the western Cycladic slag heaps. The thesis highlights the importance of appropriate technological studies in understanding the role and organisation of copper metallurgy in the EBA Cyclades.

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| LN | Late Neolithic |
| FN | Final Neolithic |
| EBA (EBI, II, III) | Early Bronze Age (Early Bronze Age I, II, III) |
| MBA | Middle Bronze Age |
| LBA | Late Bronze Age |
| | |
| EC (ECI, II, III) | Early Cycladic (Early Cycladic I, II, III) |
| EM (EMI, II, III) | Early Minoan (Early Minoan I, II, III) |
| | |
| EDS | Energy-Dispersive Spectrometry |
| WDS | Wavelength-Dispersive Spectrometry |
| SEM | Scanning Electron Microscopy |
| EPMA | Electron Probe Microanalysis |
| (P)ED-XRF | Polarising Energy-Dispersive X-Ray Fluorescence |
| CRM | Certified Reference Materials |
| XRD | X-Ray Diffraction |
| Thermoluminescence | TL |
| b.d.l. | below detection limits |
| n.r. | not reported |
| n.a. | not analysed |
| M.T. | measured total |

# ACKNOWLEDGMENTS

This research was carried out at the Institute of Archaeology (UCL) under the supervision of Thilo Rehren and Cyprian Broodbank. I have greatly gained from Thilo Rehren's expertise on archaeometallurgy and more broadly archaeological sciences and particularly wish to thank him for hours of valuable tuition on optical microscopy. Cyprian Broodbank's tireless efforts to provide me with a comprehensive and analytical background on Aegean prehistory generated, if nothing else, my keen enthusiasm on the subject. I am truly grateful to both for the guidance and inspiration they offered me throughout this period and for their prompt, constructive, and stimulating comments and corrections on earlier drafts of this thesis. In addition, I deeply acknowledge their understanding, support, and patience both on an academic and personal level. Parts of this research were undertaken at the Laboratory of Archaeometry, N.C.S.R. Demokritos, under the supervision of Yiannis Bassiakos. It was his communicable passion for Aegean metallurgy that largely prompted the start of this study and inspired many of the ideas handled in this thesis. I thank him wholeheartedly for invaluable lessons and guidance in the field and in the laboratory and for enduring and counterbalancing my often pessimistic disposition.

The work on Seriphos would probably not have been initiated had it not been for Olga Philaniotou's intense research interest on aspects of early Cycladic metallurgy. I am indebted to her for inviting me to participate in the Seriphos project and giving me permission to analyse the relevant material. I thank both Olga Philaniotou and Yiannis Bassiakos for taking the time to carry out the necessary fieldwork on Seriphos within the strict chronological limitations imposed by this thesis.

The incorporation of the Daskaleio-Kavos case study in this thesis was originally suggested by Todd Whitelaw. I am truly grateful to him for indispensable help and advice on various aspects of the study of the material from Daskaleio-Kavos, for providing me with essential information on the details of the survey methodology, and for offering constructive comments and corrections on the relevant chapter. I thank the directors of the 1987 fieldwork project on Daskaleio-Kavos, Professors C. Doumas, L. Marangou, C. Renfrew, and Mrs Ph. Zapheiropoulou for permission to examine this material. The necessary sampling permit was authorised by the Greek Ministry of Culture.

This research was funded by postgraduate studentships kindly provided by the Alexander S. Onassis Public Benefit Foundation, the Arts and Humanities Research Board (AHRB), and the Institute of Archaeometallurgical Studies (IAMS). Expenses for fieldwork on Seriphos and Naxos and thermoluminescence dating of furnace wall fragments from Seriphos were covered by awards from the Institute of Archaeology (UCL) and the Graduate School (UCL).

The thermoluminescence dating of furnace wall fragments from the sites of Kephala and Phournoi on Seriphos were undertaken very efficiently by Nikos Zacharias and Christodoulos Michael of the Laboratory of Archaeometry (N.C.S.R. Demokritos).

Panayiotis Chrysoloras, former mayor of Seriphos, showed us the site of Phournoi and guided us through the strenuous path on one of our earlier visits to the island with Olga Philaniotou and Yiannis Bassiakos. I additionally thank Yiannis Palaios, Michalis and Yiannis Kouzoupis for offering information on the island's geology and rich mining history. I am grateful to Petros Prokos and Jed Stevenson for accompanying and helping me during geological reconnaissance expeditions on Seriphos.

Laboratory work was greatly facilitated by technical advice and assistance provided by Kevin Reeves, Simon Groom, and Prakash Dodia. Xander Veldhuijzen often volunteered reliable solutions to various computer–related problems. Christoph Schultes handled several translations of German texts. I am truly indebted to Yiorgos Nazlis for his laborious work on the illustrations of this thesis and to Martha Yannacopoulou and Dimitris Chryssanthakopoulos for promptly arranging the final printing.

This thesis would not have been completed without the support and encouragement of several old and new friends. I particularly wish to thank Kevan, Martha, Elissavet, Yiorgos, Marianne, Marianna, Christoph, Valia, Nikos, Thomas, and Petros, as well as my fellow students of Aegean prehistory and archaeological sciences in the Institute of Archaeology and Demokritos. I am grateful to Elissavet and Yiorgos for providing a working environment in the final stages of this thesis. I further thank Lydia, Mary, and Takis for always taking an interest in my work and keeping me informed on recent developments in Greece.

Last but not least I wish to express my deepest gratitude to my family. My sister, Aliki, shared most of the stress and joy of this research even if from a distance. My parents, Theodore and Iphigeneia, stood by me and helped me overcome any minor or major difficulties encountered. I thank them all for making sure I could always rely on them.

# CHAPTER 1.

# Introduction

This thesis investigates aspects of the technology and organisation of Early Bronze Age (EBA) Cycladic copper production. To this end an analytical examination of metallurgical remains from the islands of Seriphos and Keros has been undertaken (Figure 1.1). The specific case studies have been selected to represent two different contexts within which evidence for the practise of early metallurgical activities has been encountered. They therefore allow interesting comparative observations, which will contribute to a more comprehensive picture of metallurgy in this region.

The Cyclades comprise a dense group of islands in the south-central Aegean, between the southeast coast of Attica and the Dodecanesian islands to the southeast (Figure 1.2). The prominence of these islands in the EBA, and some of the wider material culture similarities exhibited between them, had long been recognised by one of the fathers of Aegean prehistory, Christos Tsountas, who named the broader period ‘Cycladic’ (Tsountas 1898, 1899). Over a century later and following the investment of significant archaeological fieldwork and research efforts in this part of the Aegean, a much clearer resolution of the nature and development of early Cycladic communities is possible.

Metal artefacts first appear in the Cycladic archaeological record in the Final Neolithic (FN), contemporary with the first remains of metallurgical activities (Coleman 1977: 4), while the only possible Late Neolithic (LN) example reported so far is the gold plate from the Cave of Zas on Naxos (Zachos 1999). Both types of finds, artefacts and metallurgical remains, are far more numerous in the much better documented ensuing EBA, where conclusive evidence for the indigenous production of copper, lead and silver using local ore resources has been presented. Given the central role that metal is frequently awarded in discussions of early communities, as an indicator of trade or broader interregional contact, wealth, prestige, status and specialisation, it is not surprising that the field of metallurgy has long attracted the interest of Aegean prehistorians (e.g. Branigan 1974; Renfrew 1967). Numerous studies have dealt with aspects of EBA Cycladic metals but, as will be argued in subsequent chapters, while provenancing studies progressed rapidly, investigations into the technology of the processes involved in metal production remained largely under-explored.

Dobres and Hoffman (1994) stress the importance of small scale in-depth technological investigations, in revealing the technical attributes of past processes leading to the reconstruction of the processes themselves and ultimately assessing their social implications. Costin (1991) argues for the value of studies of production activities, as opposed but complimentary to the usually more researched distribution parameter, in understanding the overall organisation of early industries with reference to specialisation. Archaeometallurgical studies of metal production sites in various parts of the Old World have successfully shown differences not only in the technology of early copper metal production (e.g. Craddock 2001) but also in the spatial distribution of activities and accordingly their overall organisation (see for example Weisgerber 2003 for an increased centralisation of copper metallurgy in Feinan through different periods).

Along these lines this thesis aims to stand back from discussions of metal circulation in the Cyclades, which have so far dominated this field, and, using a much smaller-scale, site-directed approach, address questions of technology and their potential contribution to understanding the overall organisation of early metal production in this region.

## Outline of the thesis

The following chapter (Chapter 2) presents a brief introduction to the EBA Cycladic communities followed by a detailed review and critical assessment of archaeometallurgical work carried out to date in this region. The latter is divided into three approaches, namely, the studies of metallic artifacts, mining and metallurgical sites and remains, and lead isotope analysis, with emphasis placed on the last two, which are most relevant to this research. The general characteristics and methodological limitations of each approach are discussed together with their specific conclusions and problems within the field of Cycladic metallurgy.

Developing beyond the identified limitations of previous research in this field, Chapter 3 outlines in more detail the specific research questions addressed in this thesis, their association with the material examined and the methodology used to approach them. The selection of the specific case studies is further justified within the research framework proposed. A brief description of the analytical techniques used for examination of the material is also given.

Chapters 4 and 5 present the work carried out on the island of Seriphos. The material from Seriphos has been recovered during an ongoing collaborative project between the Ephorate of Prehistoric and Classical Antiquities of the Cyclades, represented by Ms O. Philaniotou, and the Laboratory of Archaeometry N.C.S.R. Demokritos, represented by Dr Y. Bassiakos. The present author was kindly invited to participate in the fieldwork and carry out the laboratory investigation of the metallurgical finds. The project has so far conducted surface examination and sampling of three copper slag heaps on the island. The heaps of Avessalos and Kephala had been briefly mentioned before by other parties (e.g. Gale *et al.* 1985), whereas the third one, on the promontory of Phournoi, was discovered during the aforementioned team's first visit to Seriphos. Limitations imposed by the scale of PhD research would not allow a thorough analytical study of all three sites, and therefore only Kephala and Phournoi were investigated in detail. A preliminary study of a small number of samples from Avessalos was also undertaken. Additionally, the author with the collaboration of Dr Bassiakos, particularly in the sampling stages, carried out a preliminary geological reconnaissance of the island, in search of potential copper ores. A small number of these samples were also analysed. Chapter 4 presents a broad overview of the geology of Seriphos, followed by a discussion of the methodology and results of the geological reconnaissance for potential copper sources carried out on the island. Chapter 5 discusses the results from the examination of the slag heaps on Seriphos. The setting and layout of these sites are presented, together with the sampling criteria applied during material collection. The results of the laboratory examination are outlined and inferences are drawn on the technological details of the metallurgical processes.

Chapter 6 deals with the material from the EBA site of Daskaleio-Kavos on the island of Keros. The metallurgical remains from Daskaleio-Kavos were collected in 1987, during a collaborative project between the Universities of Athens, Ioannina, and Cambridge, and the Ephorate of Prehistoric and Classical Antiquities of the Cyclades, which involved both intensive surface survey and limited excavation on the site. Permission was kindly granted to the author by the project directors to sample and analyse these specimens. The site has a long history of archaeological investigations and this is presented at the beginning of Chapter 6, together with the interpretations that have been offered to date on the role of Daskaleio-Kavos within EBA Cycladic communities. Following a detailed account of the laboratory work undertaken on the metallurgical remains during this thesis, an assessment of the nature of metallurgical activities carried out on the site is drawn. Observations on the spatial distribution of the metallurgical remains across the site are also presented.

In Chapter 7 the data obtained from the two islands studied here are considered in the light of other archaeometallurgical evidence from the Cyclades. The slag heaps on Seriphos are compared with similar sites known on other islands, searching for technological and spatial distribution patterns, while the material from Daskaleio-Kavos forms the incentive for a discussion of metallurgy within Cycladic settlements. The potential effects on metallurgy from the interaction of other neighbouring Aegean areas with the Cyclades are also briefly assessed. At the end of the chapter the emerging picture regarding the organisation of metal production in the EBA Cyclades is discussed.

The overall conclusions of this thesis are presented in summary form in Chapter 8.

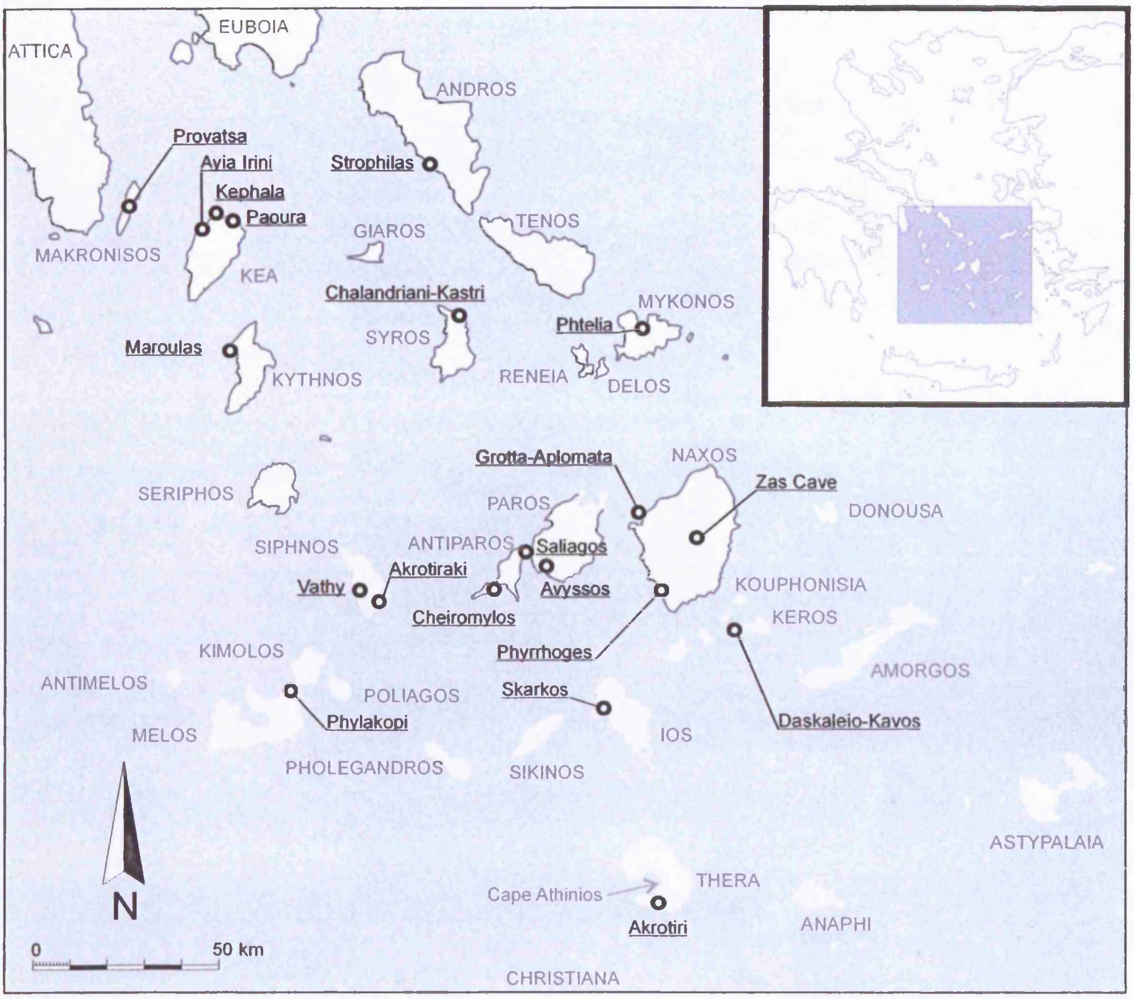


*Figure 1.1* *Map of the Cyclades, showing sites mentioned (for more detail on Kythnos, Kea, Siphnos, Seriphos, and Keros and position of slag heaps see also Figures 2.2, 2.3, 2.4, 5.1, 6.1 respectively).*

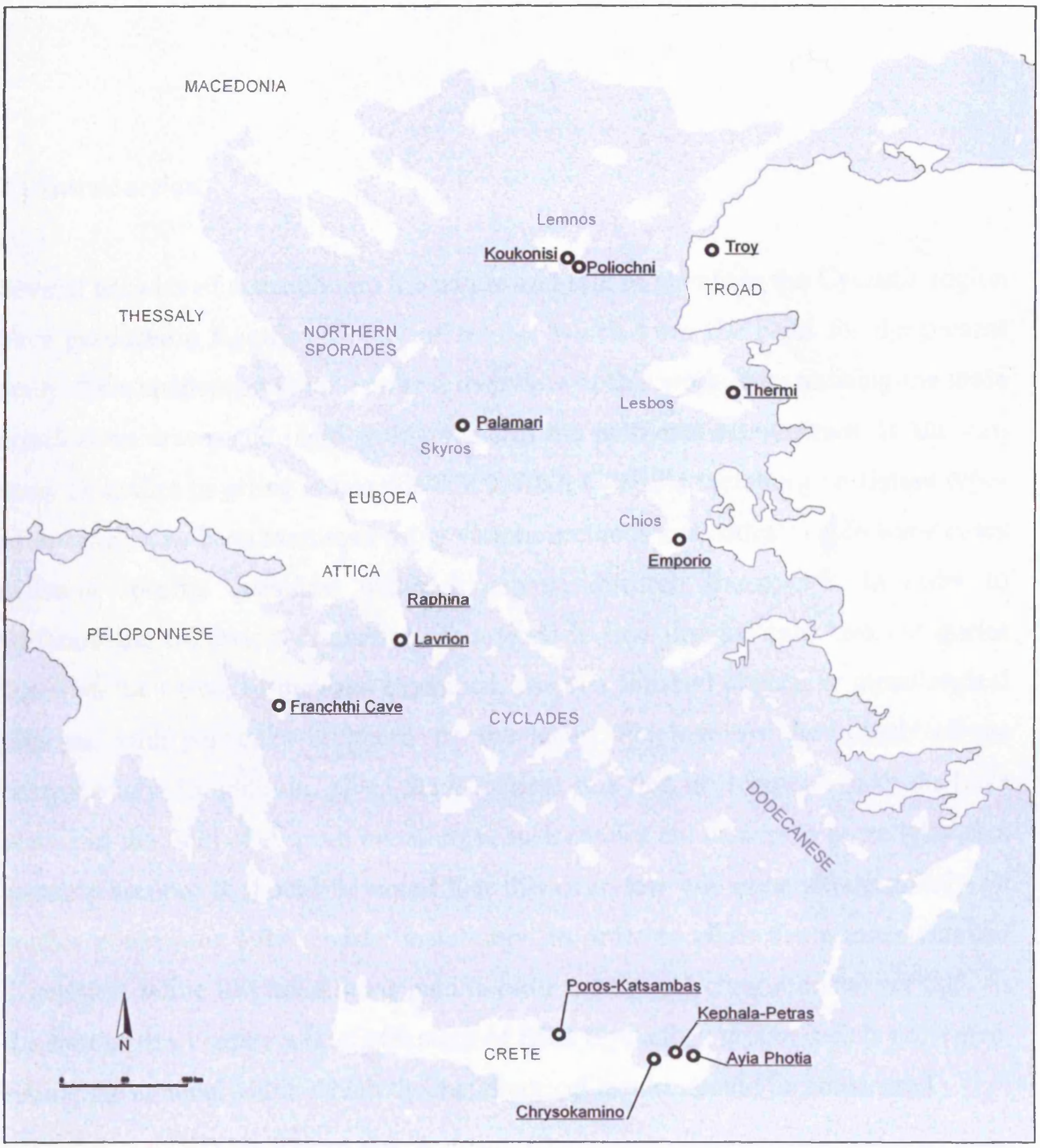


***Figure 1.2** Map of the Aegean, showing the main regions and sites mentioned (Cycladic sites given on Figure 1.1).*

# CHAPTER 2.

# Background to EBA Cycladic metallurgy

## 2.1 Introduction

Several decades of research into the nature and role of metals in the Cycladic region have produced a significant body of results, which form the basis for the present study. This chapter presents a critical overview of this work, summarising the main conclusions drawn and highlighting some of the problems encountered. In the vast array of studies targeting issues relevant to EBA Cycladic metallurgy different types of material have been examined using various methods and addressing in some cases different specific questions within a generic research framework. In order to facilitate the following discussion, this work is first divided into two categories based on the nature of material examined, whether finished objects or metallurgical remains, with particular emphasis on the latter, which forms the subject of the present study. In addition, given the important role that lead isotope analyses have played in the field of Aegean metallurgy, such studies are discussed more fully as a separate section. It should be noted that this overview will concentrate mainly on studies concerning EBA copper metallurgy, in order to allow for a more detailed discussion, while less attention is paid to other metals and chronological periods. At the start of this chapter a brief summary of EBA Cycladic communities is presented, setting the context within which the metallurgical results should be considered.

## 2.2 The islands of the Cyclades in the Early Bronze Age (EBA)

The islands of the Cyclades have attracted archaeological interest at least since the end of the nineteenth century (see for example Bent 1884; Tsountas 1898, 1899). A real surge of archaeological fieldwork, particularly after the middle of the twentieth century and continuing to the present day, involving both excavations on specific sites as well as intensive and extensive surface surveys on some islands, has brought forward an array of evidence for prehistoric communities in this part of the Aegean. To this should be added numerous studies and assessments of certain types of materials and particular features of the archaeological record to provide substantial insight into different aspects of prehistoric life in the Cyclades (for reviews of fieldwork and research concerning the prehistoric Cyclades see for example Barber 1987; Broodbank 2000a: 48-53; Davis 1992; Davis *et al.* 2001; Karantzali 1996; Renfrew 1972 and references within). Archaeological research is not, however, distributed homogeneously between or even within the different islands of the Cycladic group, as is clearly demonstrated in the schematic exploration index presented by Broodbank (2000a: 52, fig. 7). Still, the vast corpus of data provides a substantial sample, which has allowed the development of several explanatory syntheses for the Bronze Age Cyclades, such as the works of Renfrew (1972), Barber (1987), and more recently Broodbank (2000a). In the light of these comprehensive compilations and the volume and diversity of data available, the following paragraphs can be considered nothing more than the briefest sketch of those aspects of the prehistoric Cyclades that are likely to be of relevance to this study. In order to avoid an unnecessary and lengthy repetition of relevant individual publications, reference to specific sections of appropriate synthetic volumes is used, whenever possible.

The Aegean Bronze Age is traditionally divided in three periods (Early, Middle and Late-abbreviated respectively to EBA, MBA, and LBA), which are themselves further subdivided in smaller periods (Figure 2.1). Consideration of various aspects of chronology, which have at times served as battlefields for Aegean prehistorians (see for example MacGillivray and Barber 1984; Manning 1995; Warren and Hankey 1989), is outside the scope of this thesis, but a short clarification of nomenclature, for the EBA Cyclades is necessary for the following discussion. Aside from the traditional Aegean classification, which separates the EBA into a further three subdivisions (EBI, II, and III or ECI, II, III by some scholars when referring to the Cyclades), an alternative system first proposed by Renfrew (1972) involved the identification of ‘cultures’, defined according to Childe as “constantly recurring assemblages of artefacts” (Renfrew 1972: 53). Five cultures were thus defined, named after the corresponding settlements or cemeteries whose association with Aegean chronological periods is shown in Figure 2.1. A number of smaller groups (Figure 2.1) which fall either within or between these main cultures, were also proposed by Renfrew (1984a, 1972), Doumas (1977) and others (for a short summary of the development of Cycladic chronology, variations, and references see Broodbank 2000a: 53-5; Sherratt 2000: 10-4). Although the 'culture' system proves particularly useful in discussions of assemblages, particularly concerning pottery and figurines, it cannot be applied usefully to considerations of metallurgy and therefore the more traditional Aegean periods are used throughout most of this thesis, unless reference is made to a specific group of materials.

Discovery of Melian obsidian in Upper Paleolithic levels at the Franchthi Cave in the Southern Argolid (Perlès 1987, 1990), hints at the antiquity of exploitation of at least some of the Cycladic resources. Additionally, indications for somewhat more permanent occupation on the islands during the Mesolithic come from the recently radiocarbon dated site of Maroulas on Kythnos (Sampson *et al.* 2002). The expected coastal position of sites like Maroulas and subsequent sea-level rises make it unlikely that substantial traces of other such activities will have survived (Sampson *et al.* 2002).

Far more prominent is the evidence for settlements and consequently 'colonisation' (Broodbank 1999, 2000a: 107-143; Cherry 1990: 164-5, 192-203) in the Cyclades in the LN and FN. Until recently the only excavated sites for these periods were, respectively, Saliagos, situated on a small islet between Paros and Antiparos (Evans and Renfrew 1968), and Kephala on Kea (Coleman 1977), from which the corresponding cultures were christened (Figure 2.1). Since the late 1980's, a number of excavations, undertaken on other Cycladic sites, have unearthed LN strata from Phtelia on Mykonos (Sampson 2002, in press), Grotta (Hadjiianastasiou 1988) and the Cave of Zas on Naxos (Zachos 1990, 1996a, 1999), while FN occupation is attested on Zas (Zachos 1990, 1996a, 1999), Phtelia (Sampson 2002, in press), and Strophilas on Andros (Televadou in press). These are settlements, or seasonal habitation areas as proposed for Zas (Zachos 1999), while a corresponding cemetery is so far known only on FN Kephala (Coleman 1977). Other reports for Neolithic finds and potential sites identified in intensive surveys or otherwise are summarised in Renfrew (1972: 507-9), Cherry (1990: 164-5) and Broodbank (2000a: 120-5).

Although most of these excavations are still in progress and future examination and publication of the emerging data promise a much more informed glimpse of the Cycladic Neolithic, it is worth highlighting three features at this stage, stemming largely from Broodbank's (2000a: 144-174) most recent reassessment of this period. The first concerns the settlement pattern, which although admittedly based on a small sample, appears to involve relatively large and long-lived village-sized communities, widely spaced around the island landscape at least for the LN period and possibly for the ensuing FN, although some differences may be apparent particularly in terms of subsistence strategies (Broodbank 2000a: 145-50). Especially interesting in the context of the present research is the first appearance of metals during the FN or possibly even slightly earlier (Zachos 1999) on several of these sites, outlined in more detail in the next section. Finally, it should be noted that these settlements did not exist in isolation; evidence for interaction between the islands as well as with other Aegean and possibly more distant regions can be discerned in the material finds, with metal often referenced as an indicator for short or long distance contact (e.g. Broodbank 2000a: 156-65; Demoule and Perlès 1993; Nakou 1995).

The Cycladic archaeological record for the following EBA is dominated by excavations of cemeteries (Doumas 1977; Renfrew 1972: 157-66, 178-80; Sherratt 2000: 15), to a large extent fuelled by salvaging attempts in the face of continuous illicit looting, which has unfortunately in many cases resulted in irreversible loss of the associated contexts (Gill and Chippindale 1993; Marthari 2001). A number of contemporaneous settlements have also undergone excavation (Davis 1992; Davis *et al.* 2001; Renfrew 1972: 153-7, 176-8), although some, such as the ones at Kastri on Syros (Bossert 1967; Tsountas 1899) have covered only part of the settlement, while on others such as Ayia Irini on Kea (Wilson 1999) and Akrotiri on Thera (Sotirakopoulou 1986, 1990, in press(a)) subsequent phases of occupation only allow a partial glimpse of the EBA levels. Additional evidence for settlement patterns comes, however, from surface investigations and surveys carried out on many Cycladic islands but to varying degrees of intensity (summarised in Broodbank 2000a: 49-50).

On the basis of this data it appears that the settlement pattern changes in comparison to the preceding Neolithic from relatively large and dispersed village-sized settlements to much more numerous and comparatively densely spaced small and short-lived farmsteads (Broodbank 1989, 2000a: 149-56; Whitelaw 2000, 2003: 29). Also notable is the increase in the visibility of burials, with numerous known cemeteries from this period (e.g. Doumas 1977). These, like the settlements, appear to be generally small in size, while even among the nine larger known cemeteries, with fifty or more recorded burials (Broodbank 1989: 325, Table 1), a consideration of potential longevity of usage indicates that the majority are also more likely to correspond to small but longer-lived communities (Broodbank 1989: 323-5). Funerary offerings are frequent in these graves (Doumas 1977: 58-63) and while these are generally poor in the early Grotta-Pelos culture settlements, with a few marked exceptions (Broodbank 2000a: 222), they become progressively more elaborate by the EBII period (Sherratt 2000: 15-20).

The Cycladic EBA is a period of profound change, as is already hinted by its chronological subdivisions. Marked changes are noted in the EBII, with increased evidence for intensive long-range inter-regional communication and trade, which led Renfrew (1972: 451-2) to christen this period the 'international spirit' of the Aegean. Settlement density also increases in this phase and, although it is still largely characterised by small communities (Broodbank 2000a: 177), a small number of larger village-sized settlements, such as Chalandriani-Kastri on Syros (Bossert 1967; Marthari 1998; Tsountas 1899), Daskaleio-Kavos on Keros (see Chapter 6), Ayia Irini on Kea (Wilson 1999), Grotta-Aplomata on Naxos (Kontoleon 1949), and Skarkos on Ios (Marthari 1990, 1997, in press) are noteworthy. In the latest model for the EBA Cyclades, Broodbank (1993, 2000a) attributes the importance of the first four sites to their nodal position within a wider sea-trading system. A similar role has more recently been proposed for Skarkos, following an assessment of the recovered imported wares and other characteristics of the site (Marthari in press). Although some form of intra-community social stratification or prominence of certain individuals is implied from the identification of some richer graves in both the EBI and EBII Cyclades (Broodbank 2000a: 222; Doumas 1977: 58-63), there is no conclusive evidence to date to suggest a wider inter-community dominance of particular groups (Broodbank 1989).

In the later phases of the EBII (or ECIII A according to Barber 1983, 1984; Barber and MacGillivray 1980; MacGillivray 1983, 1984) a small number of Anatolian shapes are recognised among the pottery repertoire, known as the 'Kastri' group from the homonymous site on Syros, where they were first recognised (Angelopoulou 2003; Broodbank 2000a: 309-318; Renfrew 1972: 533-4; Rutter 1979; Sotirakopoulou 1993). The identification of these vessels together with the appearance of tin-bronzes on Kastri, generally also considered an import from Anatolia (Gale and Stos-Gale 1986a; Stos-Gale *et al.* 1984), and the observation of fortification walls on some of the late EBII Cycladic settlements (e.g. Angelopoulou 2003; Bossert 1967; Doumas 1964; MacGillivray 1980; Tsountas 1899), have been taken as evidence for the invasion of outsiders in the Cyclades during this period (Barber 1987: 137-9; Doumas 1988; Stos-Gale *et al.* 1984). An alternative explanation put forward recently stresses the comparatively low abundance of 'Kastri' material relative to other Cycladic forms as well as their possibly not strictly contemporaneous and certainly far wider appearance compared to the fortification evidence, suggesting an inflow of these artefacts through trade and adoption (Broodbank 2000a: 309-318; Wilson 1999: 238-9).

The last phase of the EBA and the transition to the subsequent MBA presents one of the most problematic and controversial issues of Cycladic prehistory. In terms of culture sequence the Phylakopi I group, named after the relevant levels of the Melian site, follows the Kastri group; but the exact chronological association of the two and their attribution to the Early or Middle Bronze Age periods has formed the core of the debate (Barber 1983, 1984; Broodbank 2000a: 320-349; MacGillivray 1983, 1984; Rutter 1983, 1984), whose implications "go well beyond matters of chronology" (Broodbank 2000a: 323). At the end of the third millennium an abandonment of many of the previously established settlements is noted, with signs of violent cessation of occupation in some (see for example Doumas 1988: 25-6). The majority are never re-inhabited, while on others, like Ayia Irini, occupation is again attested, following an interruption, later in the MBA. This observation, as well as the unclear association of the two aforementioned culture groups, led to the proposal for the existence of a 'gap' at the end of the EBA in the Cyclades (Rutter 1983, 1984), partly suggesting discontinuity in life on these islands. Although the opposing model for continuity largely predominates (see discussion in Broodbank

2000a: 331-5), the suggestion highlights the uncertainties that still exist to a large extent, regarding this transitional phase prior to the emergence of a few, nucleated, and later Minoan-influenced centres that prosper in the ensuing Cycladic Bronze Age periods, such as Akrotiri on Thera, Ayia Irini on Kea, and Phylakopi on Melos.

## 2.3 Studies of EBA Cycladic metal artefacts

Numerous metal objects have been uncovered from prehistoric Cycladic contexts, testifying to the use of copper and its alloys, lead, silver, and gold in this region from an early date. Metal artefacts can be studied either in terms of typology, noting features such as the type of object, details of shape and other external characteristics, or in terms of composition, following appropriate analyses. In this section, these two largely complementary approaches are viewed separately, in order to identify some of their individual contributions and problems.

### *2.3.1 Typological studies*

The earliest attempts to obtain a broader picture of EBA Cycladic metallurgy have to be attributed to the pioneering work of Renfrew (1967, 1972: 308-338) and Branigan (1974). Their studies established typological groupings for metallic finds and used comparative approaches in an attempt to investigate the origins of metallurgy in the Aegean and the social implications of its introduction. Renfrew (1967) dealt specifically with the Cycladic islands mainly during the EBA, while Branigan initially focused on Crete (Branigan 1967, 1968) and subsequently extended to the wider Aegean region covering the EBA and MBA (Branigan 1974). Several other typological studies of metal artefacts relevant to the wider Aegean region have also been presented (see for example McGeehan-Liritzis 1996; and references in McGeehan-Liritzis 1996: 317, Table 2.1.1).

Both the syntheses of Renfrew and Branigan pointed to a sudden explosion in the occurrence of metal objects during EBII, which was characteristically assigned the term *Metallschock* (Renfrew 1972: 338). Metallurgy was seen as one of the prime stimulants for cultural contact, trade, and accumulation of wealth and power, and was therefore intimately associated with the changes observed in the Cyclades during the EBII period (Branigan 1974, 1977; Renfrew 1967, 1972). Most importantly, however, these studies were among the first to suggest the existence of an indigenous Aegean metallurgy during the EBA, if not slightly earlier (Branigan 1977: 117), with influences, they proposed, from the more advanced Anatolian or Balkan industries.

Branigan (1974: 100-14, 123-7) additionally identified two primary metal industries within the Aegean, the Troadic and the Cretan, to which he attributed a prominence as early as the EBI period, and three secondary industries emerging during the EBII, the Cycladic, the mainland Greek, and the western Greek, inspired to a different extent by the two primary ones. The importance of an EBI Cretan metal industry was subsequently contested as it was argued that the majority of artefacts attributed an EBI date by Branigan, were recovered from EBI-II contexts and were most probably later, while several are considered to be Cycladic imports (Warren 1976; Watrous 1994: 703, 713-4). The characterisation of the Cycladic industry as secondary, particularly with reference to the Cretan, and the ascription of a comparatively later date are also questioned by further finds recovered since and other considerations as discussed below.

Although an assessment of the mechanisms of introduction of metallurgy in the Aegean is beyond the scope of this thesis, one important development that has emerged since these earlier typological studies should be noted. Recent excavations on several FN sites on the Cycladic islands, a period previously far less documented in this region, have challenged the idea of Cycladic metallurgy as an "innovation and an innovator" (Branigan 1974: 146) during the EBA. Numerous copper-based artefacts have been unearthed from FN contexts in the Zas Cave on Naxos (Zachos 1990, 1996a, 1996b, 1999; Zachos and Douzougli 1999), Phtelia on Mykonos (Maxwell 2002), and Strophilas on Andros (Televadou in press), while fragments of copper objects are also known from Kephala on Kea, although these are surface finds and their date is therefore not secure (Coleman 1977: 3-4). Far less frequent, but still of utmost importance, are roughly contemporaneous artefacts of gold, which include a sheet from Zas (Zachos 1990: 30, 1999: 154), a bead from Strophilas

(Televadou in press) and a pendant from Phtelia (Sampson in press). As was mentioned previously, the find from Zas is attributed to earlier LN strata (Zachos 1999). The new evidence emerging urges for a reassessment of the existence of metal awareness during the Neolithic Cyclades and the proposed associations between the adoption of metallurgy and the social transformations that appear to be taking place during the EBII period (Karantzali 1996: 163-4; McGeehan-Liritzis 1983, 1996; Nakou 1995; Zachos and Douzougli 1999). The argument is further supported by the striking rarity of excavated Neolithic cemeteries in the Cyclades and the broader Aegean, contexts which have yielded the rich metal finds in neighbouring Bulgaria, giving the Balkans a prominent position in discussions of the earliest stages of metal technology (Nakou 1995: 7; Renfrew 1978, 1986; Zachos 1999).

Two main problems significantly impede understanding of the role and extent of use of metals in different periods solely on the basis of examination of the metal artefacts. The first relates to the inherent nature of metal as a material liable to corrosion and recycling, processes that may strongly affect the presence of metal objects in the archaeological record. In contrast to pottery or stone, which will in most cases be discarded once fractured, metal can easily be re-melted and re-worked. Its recovery in the archaeological record will therefore be influenced to a certain extent by the social strategies adopted in each period regarding the deliberate deposition of artefacts, particularly with regards to finds from burials and hoards (Baboula 2000; Nakou 1995). Nakou (1995) develops these ideas in more detail for the EBA Aegean and makes a strong case relating the increase in metal finds during EBII to a change in depositional patterns rather than, or as well as, a sudden increase in metal production and usage. Attempts to compare the spread of metal usage as well as the predominance of certain types of metals, within or between different regions and periods, should include a consideration of the number and nature of excavated contexts producing these materials in each case (e.g. Nakou 1997: 635, Fig. 1).

The study of metallic artefacts in the Aegean is further complicated by problems regarding the associated records of the EBA metal finds. A substantial body of these artefacts have been unearthed in the late nineteenth and early twentieth centuries and their contextual information is often inadequate or missing (Branigan 1974: 3, 1977; Sherratt 2000: 68-109). In addition, the extensive looting of Cycladic sites resulted in the appearance of numerous metallic artefacts of dubious contexts early on in the antiquities market and in archaeological collections. The problem is most clearly demonstrated with the example of the 'Kythnos hoard', which featured prominently in the early compilations of Aegean metalwork. This group of ten copper tools, purchased by the British Museum in 1866, were attributed a Kythnian origin and an ECII date (Renfrew 1967). A re-examination of the hoard and the accompanying documentary evidence in the museum's archives concluded that eight of these objects were probably part of a larger collection of Naxian origin, while the remaining two had no firm context (Fitton 1989). Given that dating of the hoard had been based on typological association of one of the unprovenanced artefacts (Renfrew 1967), doubts were cast on the validity of their assigned date (Fitton 1989).

### *2.3.2 Compositional analyses*

A large body of compositional analyses of Bronze Age metallic artefacts from the Cycladic islands have been published over the years. These include early copper objects from Amorgos (Gale and Stos-Gale 1989a; Junghans *et al.* 1968; Renfrew 1967; Sherratt 2000: 72-95; Tsountas 1898), Naxos (Bossert 1967; Caley 1949; Gale and Stos-Gale 1989a; Mangou and Ioannou 1997; Renfrew 1967; Sherratt 2000: 72-95), the Kastri and Chalandriani site complex on Syros (Bossert 1967; Gale and Stos-Gale 1989a; Stos Gale *et al.* 1984), possibly Paros (Gale and Stos-Gale 1989a; Renfrew 1967), Thera (Mangou and Ioannou 1997; Slater and McKenzie 1980) and the 'Kythnos' hoard (Craddock 1976; Gale and Stos-Gale 1989a). It should be noted that many of these finds form part of museum collections and their contexts, as discussed earlier, are in some cases dubious.

The broad pattern that has emerged regarding the composition of early Cycladic copper artefacts suggests that copper metal and arsenical copper were the dominant materials used for EBA artefacts, with tin bronze becoming increasingly more important in the subsequent periods (see also Charles 1967; Katsa 1997). An important exception to this trend is seen in the late EBII site of Kastri on Syros, where the majority of analysed copper-based artefacts were shown to be made of tin bronze (Bossert 1967; Gale and Stos-Gale 1989a; Stos-Gale *et al.* 1984), an observation that as was discussed earlier, has been used to strengthen the suggestion that the site had strong connections with Anatolia (Gale and Stos-Gale 1986a; Stos-Gale *et al.* 1984). The majority of tin-bronzes from Kastri included smaller amounts of arsenic an observation that, Muhly (1985a: 127) proposes, may indicate an experimental stage at the transitional phase between the predominance of each alloy.

Lead and silver objects form an important part of the EBA Cycladic metal finds. In 1981 Gale and Stos-Gale (1981a) estimated that they constituted approximately 40 % of the then known metal artefacts for the EBA Cyclades. In contrast, although few examples of gold artefacts are known already from FN contexts (or even LN see Zachos 1999) in this region (Sampson in press; Televadou in press; Zachos 1990: 30, 1999: 154), only a single gold bead has been reported from EBA contexts, specifically from the cemetery of Phyrrhoges on Naxos (Papathanassopoulos 1961-2: 138). The rarity of gold appears to be restricted to the EBA Cyclades, while the metal is far more frequent in the contemporaneous Cretan and Troadic industries (Branigan 1974: 109; Gale and Stos-Gale 1981a: 181).

A number of the lead and silver artefacts have undergone chemical analyses; among them EBA lead artefacts from Amorgos (Gale and Stos-Gale 1981a; Sherratt 2000: 102-3), Antiparos (Gale and Stos-Gale 1981a), Despotikon (Gale and Stos-Gale 1981a), Kea (Gale *et al.* 1984), Naxos (Gale and Stos-Gale 1981a but see also Sherratt 100-109), and Syros (Gale and Stos-Gale 1981a; Pernicka *et al.* 1983), and LBA artefacts from Kea (Gale *et al.* 1984), Melos (Gale and Stos-Gale 1984) and Thera (Bassiakos *et al.* 1990; Gale and Stos-Gale 1981a; Pernicka *et al.* 1983) and EBA silver objects from Amorgos (Gale and Stos-Gale 1981a; Sherratt 2000: 96-99; Tsountas 1898: 187), Naxos (Pernicka *et al.* 1983), and Syros (Gale and Stos-Gale 1981a). The trace element pattern of the silver objects is consistent with the silver having been produced from smelting argentiferous lead ores followed by cupellation (Gale and Stos-Gale 1984; Pernicka *et al.* 1983). In addition, the relatively high silver content of the lead artefacts (above 0.01 %) compared with the analyses of contemporaneous litharge finds, suggests that lead was not produced by reduction of the litharge, but from smelting separate batches of silver-poor lead ores. From the analyses of the lead objects it is also concluded that the economic limit for silver production appears to have been around 0.08 % of silver in the ore for the EBA, and 0.04-0.05 % for the LBA (Gale and Stos-Gale 1981a: 215, 217; Pernicka *et al.* 1983: 293; see also Gale *et al.* 1984 for a somewhat different pattern at Ayia Irini on Kea).

In addition to the problems discussed in the previous section regarding the associated records of many Cycladic metal artefacts, another difficulty specifically concerning the analytical work should be pointed out. Craddock (1976) has highlighted some of the problems encountered in early publications of such results, where details of the sampling procedure on the artefacts as well as the analytical techniques used are often omitted. The complications are clearly demonstrated in the case of analyses of arsenical copper alloys, the dominant copper alloy of the Aegean EBA. In her recent presentation of Cycladic antiquities in the Ashmolean Museum, Sherratt (2000: 68-95) has included the analyses published for the copper artefacts in the collection. Serious discrepancies are seen in the percentages of arsenic given for some of these finds, with early analyses (see Renfrew 1967) showing in some cases no arsenic and later publications suggesting 5-6 % arsenic contents for the same objects (see Gale and Stos-Gale 1989a). Sherratt (2000) proposes that the problem may arise from differences in the sampling methodology followed in the two cases. The phenomenon of inverse segregation, typical in arsenical copper alloys, results in the solidification of an arsenic-rich phase at the surface of the metal producing a silvery outer appearance and large variation in the arsenic content between the surface and the core of an artefact (Budd and Ottaway 1991; Charles 1980). In fact, further examination of samples from the surface and the core of some of the Ashmolean objects yielded differences as high as 13 % (Sherratt 2000). As sampling details are absent, it is likely that the observed discrepancies are due to differences in the sampled area, although other factors, such as the sensitivity of the technique used, may have also contributed.

Overall, the example of the Ashmolean artefacts clearly demonstrates the difficulty in attempting to compare results from different laboratories, when necessary methodological details are absent (Craddock 1976). This problem is of particular significance in studies of Cycladic metal artefacts, where a large number of analytical programmes, using different techniques and in different chronological periods, have been carried out. While the currently available data are definitely adequate to observe broad changes in the composition of metals through time, more specific questions relating, for example, to the properties and methods of production of these artefacts will require a thorough reconsideration of previous work, including possibly additional compositional analyses, which take into account the idiosyncrasies of different metals (e.g. segregation phenomena), as well as appropriate metallographic studies, which are presently extremely rare for these objects.

## 2.4 Studies of ore sources, metallurgical remains and mining sites

Remains testifying to the practice of copper and lead-silver metallurgy have been reported from a number of Cycladic islands. These range from a mere handful of finds on some sites to the large slag heaps known on some of the western Cycladic islands. The following paragraphs summarise the relevant finds known to date together with the results of associated studies, where such exist. These are presented separately for each island, discussing both copper and lead-silver associated finds together, and focusing mostly on EBA material.

### *2.4.1 Metal sources in the Cyclades*

Prior to presenting the evidence for metallurgical activities from the Cyclades, some points regarding the distribution of ore sources on these islands should be noted. Probably the main difficulty likely to be encountered in the study of Cycladic metallurgy is the generally dispersed nature and small scale of metal ore resources on the islands. In contrast to other metal-producing centres of the Old World, such as Feinan (e.g. Hauptmann 2000), Rudna Glava (e.g. Jovanovic 1980), Timna (e.g. Rothenberg 1999a, b), or even Lavrion (e.g. Conophagos 1980), which are characterised by large, rich deposits, the Cyclades are notorious for their abundance of small restricted mineralisations, particularly with reference to the metals that are of interest to prehistoric metallurgy. The problem appears to be more pronounced for copper sources, as larger deposits for lead and possibly silver are known. An additional peculiarity is of course the fact that the Cyclades constitute an island environment. As a result, the already fragmentary picture is further complicated by the intrinsic geographical sub-division of land into smaller pieces separated by sea, creating the illusion of insular units and adding a different dimension to considerations of proximity.

Useful sources of information on ore occurrences are the reports published for some of the islands by the Greek Institute of Geological and Mining Research (IGME), as well as other similarly detailed geological accounts, and the works of earlier informed travellers to these islands such as Davies (1932, 1935) and Fiedler (1841). Given, however, the different interests of modern geologists in comparison to the aim of the archaeometallurgist these can serve only as a preliminary guide and not a substitute for in-situ fieldwork (see also Chapter 4). The presence of an ore mineralization, whether large or small, does not in itself constitute proof of exploitation in antiquity, and conclusive indications for the latter need to be carefully sought (see discussion in Rapp 1999). The following paragraphs give a very brief account of the islands for which mineralisations of the metals relevant to prehistoric metallurgy are reported. The review is based mainly on recent archaeological and archaeometallurgical literature, while earlier unsubstantiated reports are not included, as these have been assessed and discussed in detail elsewhere (see for example Pernicka 1987 for a thorough treatise and references).

Copper minerals are reported from Kea, Kythnos, Seriphos, Siphnos, Syros, Andros, Paros, Thera, Melos, and possibly Tenos (Bassiakos and Philaniotou in press; Friedrich and Doumas 1990; Gale and Stos-Gale 2002; in press; Gale *et al.* 1985; Renfrew and Wagstaff 1982: 79, 241; Tsountas 1898). Among these only the former four have been sampled for lead isotope analysis (but see discussion of sampling problems in section 2.5.2.2).

Only on Kythnos (Figure 2.2) has a more substantial field investigation of copper mineralisations been undertaken. On several of the identified copper occurrences, features pointing to possible ancient exploitation were noted (Bassiakos and Philaniotou in press; Gale *et al.* 1985). These will be described in more detail in section 2.4.4 but it should be noted that for the majority the antiquity of working has not been firmly established. Their proximity to dated EBA smelting sites on Kythnos is, however, taken as a preliminary indication for their early date. In most cases only traces of copper minerals are still visible, either as a result of suggested exhaustive ancient exploitation, as appears to be the case for the sites of Aspra Kellia and Petra (Bassiakos and Philaniotou in press), or of intense modern mining of the accompanying iron ore, as observed in Zogaki (Gale *et al.* 1985), making their identification in the field extremely difficult.

The complications that may arise as a result of such practices are clearly evident in the case of the Orkos area on Kea (Figure 2.3). The modern iron mining galleries at Orkos cut through other ancient, undated galleries. The nature of the ore exploited in antiquity is, however, uncertain. Gale (1998: 743) refutes the possibility that lead or copper were mined in this area, as ore analysed from these mines contained only traces of these metals. He does, however, point out that the ancient galleries appear to have ignored the massive iron deposits aiming for another type of ore. Additionally he reports a few pieces of copper slags in this region (Gale 1998: 743). Mendoni and Beloyiannis (1993: 94) also mention small quantities of slags in the area of Orkos, although they do not clarify their type, and 4th century sherds in the vicinity. A very limited secondary copper mineralization has been identified above the Orkos bay and this has been sampled for lead isotope analysis (Gale and Stos-Gale in press; Stos-Gale 1998). These elements challenge the direct rejection of the possibility that copper was extracted at Orkos in some time in antiquity (c.f. Gale 1998: 743). The low amounts of copper detected in the remaining ore may alternatively reflect exhaustive exploitation, but more systematic examination will be necessary in order to resolve this question in the future.

It is clear that in the absence of appropriate fieldwork and study it is impossible at this stage to assess how extensive the reported mineralisations on the other islands (aside from Kythnos and Kea) are and whether they could be regarded as an ore source, even by the comparatively limited prehistoric standards. Reference to copper mining at the end of the nineteenth century is made for the islands of Melos (Renfrew and Wagstaff 1982: 241) and Seriphos (Gale *et al.* 1985), but no further details are given regarding the source of this information (see further discussion for Seriphos in Chapter 4).

In terms of potential sources for lead and silver, galena occurrences, in some cases rich in silver, have been identified during recent archaeometallurgical fieldwork expeditions on Kea, Kythnos, Seriphos, Makronisos, Melos, Poliagos, Naxos, Antiparos, Syros, Thera, and Anaphi, while complex lead-antimony-silver ores are found on Siphnos (Bassiakos *et al.* 1990; Caskey *et al.* 1988; Davi 1998; Gale and Stos-Gale 1981a, 1981b, in press; Papastamataki 1998; Pernicka 1987; Renfrew and Wagstaff 1982: 79; Wagner and Weisgerber 1985). At least one of the occurrences present in each of the above islands has been sampled for lead isotope analysis (Gale and Stos-Gale 1981a; Stos-Gale *et al.* 1996), although the degree to which each island is represented in the relevant database is very variable (see section 2.5.2). Pernicka (1987: 665) refers to a geological report of silver minerals on Tenos, associated with mixed sulphides and traces of native metals, among them gold, silver and copper. Earlier references to lead and silver ores on Kimolos, Mykonos, Pholegandros, Donoussa, Sikinos and Kouphonisia are also found in the literature, but these need to be confirmed by further fieldwork as the validity of these reports is challenged (see discussion in Gale and Stos-Gale 1981a: 185-195; Pernicka 1987: 659-666).

Several of the identified lead-(silver) mineralisations are substantial deposits (in Cycladic terms) and have been mined in modern times (see Gale and Stos-Gale 1981a: 185-195; Pernicka 1987: 659-666). Ancient galleries apparently associated with exploitation of these metals are also reported on Seriphos and Syros but these have not been dated or studied in any detail (Gale and Stos-Gale 1981a, 1981b). Conclusive evidence for EBA mining has only been presented for Siphnos and this will be discussed further in section 2.4.3. Gold sources are known in south-eastern Siphnos (see section 2.4.3).

Other elements of prime importance in considerations of EBA Cycladic metallurgy are the accompanying constituents of the main copper alloys, arsenic and tin. Regarding the latter, no tin sources are presently known in the broader Aegean (McGeehan-Liritzis 1996; Muhly 1985b), while the long standing questions regarding the sources and provenance of tin for the Bronze Age Mediterranean in general remain largely unanswered (see for example Nowell *et al.* 2002; Pare 2000; Yener 2000 and references within). In terms of arsenic, Kythnos is so far the only island where the presence of arsenical copper ores has been postulated in the context of archaeometallurgy (Gale *et al.* 1985; Gale and Stos-Gale 1989a). The suggestion was based mainly on analyses of some of the slags from the smelting site of Skouries (see below) but also on a small number of copper minerals from potential sources on the island. Looking at the latter analyses, however, these are slightly problematic. The five minerals collected from the areas of Milyes and Zogaki are mainly iron ores, with one possibly a manganese mineral (MnO: 60.28). Copper is low (CuO: 3.68 % and 2.83 % for the Milyes samples, 0.54 %, 1.48 %, 0.57 % for the Zogaki samples) and so is arsenic ($As_2O_3$: 2.18 %, 1.53 %, 0.31 %, 0.80 %, 0.96 % respectively, data from Gale *et al.* 1985: 91, Table 4). Clearly these cannot be regarded as copper ores. This does not negate the possibility that richer copper minerals were present as both areas have been subjected to mining, mostly recent, but possibly also ancient. It is, nevertheless, impossible at this stage to judge on the basis of these data whether the arsenic is associated with the copper and would therefore be higher, had richer minerals been selected. No further analyses of copper minerals from these areas are given in the more recent work of Bassiakos and Philaniotou (in press), but a small number of analyses of copper minerals from other parts of the island showed negligible arsenic contents. Overall, the issue of the presence of arsenical copper ores on Kythnos and more widely in the Cyclades requires further clarification, particularly given the importance of arsenical copper alloys for EBA metallurgy.

Among the numerous other potential sources for EBA metallurgy in the Aegean (see Gale and Stos-Gale 2002; McGeehan-Liritzis 1996 and references within), the multimetallic deposit of Lavrion deserves a brief mention in this section, both because of its proximity to the north-western Cyclades (see also discussion in Wilson 1987, 1999: 234-9) and because it is frequently suggested as a supplier of metal to the Cycladic islands during the Bronze Age (see sections 2.5.2 and 7.5.1). Lavrion is mainly famous as a lead-silver source for Classical Athens (e.g. Conophagos 1980). Excavations at the Thorikos area in Lavrion uncovered numerous Early and Late Bronze Age fragments at the entrance and inside Mine No.

3, which strongly suggested that exploitation of these resources had started earlier (Mountjoy 1995; Mussche 1998; Spitaels 1984). The ore had been completely mined out and no indications were found as to the nature of the material sought, while the excavators assumed that it was argentiferous lead in association with the later historic activities (Spitaels 1984). The results of lead isotope analyses of numerous copper artefacts from the Aegean have raised the possibility that copper ores from Lavrion were also mined in the Bronze Age (see section 2.5.2). Copper and arsenical copper minerals are known on Lavrion (see Gale and Stos-Gale 2002: 285-6 for a brief summary of location and nature of occurrences) and it is not unlikely that these were mined in antiquity. It is, however, important to note that, with the exception of lead isotope analysis, no other direct evidence for their extraction has been presented to date. Gale and Stos-Gale (2002: 287) refer to a personal communication by Zwicker, who reports that he found copper slag in the vicinity of Mine No. 3, but no further details are given (see also section 7.5.1).

### ***2.4.2 Metallurgical remains on Kea*** (Figure 2.3)

#### *2.4.2.1 Kephala*

The earliest metallurgical debris relating to copper production in the Cyclades has been found at the FN sites of Kephala and Paoura on the north coast of Kea (Caskey 1971; Coleman 1977). The finds from Kephala consist of a few slag pieces and several fragments of metallurgical ceramics, some with slag adhering, which were identified either as parts of furnace lining or crucibles. Of particular interest for reasons discussed in section 2.4.4 is the observation of traces of perforations on the edge of some of the ceramic fragments (Coleman 1977: 4). A small number of these finds were examined by Conophagos (report in Coleman 1977: 113-4), who concluded that the slag was the result of small-scale crucible smelting of oxidised copper ores. Lavrion was suggested as a possible source for the ores, due to its proximity to Kea, but no evidence was presented to support this claim. It should be noted that no remains of ore were found. The debris from Paoura is also very limited, namely two pieces of slag and a small shapeless piece identified as either copper or copper oxide (Coleman 1977). Even though some of these finds were recovered from surface collection and doubts were cast on their antiquity (see remarks by Tylecote in Coleman 1977: 144 note B), the presence of a few fragments in stratified FN deposits at Kephala marks their significance, making them the earliest known evidence for metallurgical activities in the Cyclades.

### *2.4.2.2 Ayia Irini*

A small number of finds associated with metallurgy were unearthed from excavations of Ayia Irini Period I-III deposits (FN to end of EBII). These include four litharge specimens, copper slag, a single crucible fragment, as well as several copper and lead objects (Stos-Gale 1989; Wilson 1999: 144-147). With the exception of lead isotope analyses (discussed below), no other examination of the metallurgical remains has been presented, making it impossible to deduce the nature or technological details of the processes these correspond to. The problem is particularly evident in the case of the copper-related finds. Wilson (1999: 236) suggests that "there is no evidence for the smelting of copper ores at Ayia Irini, although imported smelted copper may have been locally melted for casting". Specimens listed as copper fragments in Wilson's catalogue (Wilson 1999: samples SF48 and SF49) are, however, reported as slag in a previous publication by Stos-Gale (1989: 287, Table 31.5), who conducted the lead isotope analyses. In the absence of appropriate analytical data it is impossible to infer the nature of these specimens and whether they correspond to smelting or secondary metalworking activities, particularly as, if they are indeed slag, they could have resulted from either type of process. The results of lead isotope analyses pointed to Lavrion, Siphnos and, to a lesser extent, a third unidentified source for the lead and litharge specimens examined (Gale *et al.* 1984; Wilson 1999), and Lavrion, Kythnos and a third source for the copper-related finds (Stos-Gale 1989; Wilson 1999). It should, however, be noted that in a more recent paper Gale and Stos-Gale (in press) state that some of the Ayia Irini Period III objects, originally attributed a Siphnian origin, are actually more consistent with ores from the lead/silver mine of Gümüsköy in Anatolia, in the light of additional data accumulated since the earlier publication (c.f. Gale *et al.* 1984; Gale and Stos-Gale in press).

Metallurgical remains from later Bronze Age periods have also been identified in several areas of the Ayia Irini site (Cummer and Schofield 1984; Georgiou 1986; Overbeck 1989), the most prominent being the finds from House A (Periods VI-VIII: LCI and LCIII). These include copper slag, crucible and mould fragments, as well as numerous litharge specimens (Cummer and Schofield 1984; Schofield 1990). Among them, only the lead and litharge specimens have been examined, using lead isotope and neutron activation analyses, the former suggesting that Lavrion becomes the dominant source for lead and silver in these periods (Gale *et al.* 1984).

### *2.4.2.3 Ayios Symeon*

A more substantial scatter of slag has been found around the church of Ayios Symeon, located on a hilltop in the south-eastern part of Kea (Caskey *et al.* 1988; Mendoni and Beloyannis 1993; Papastamataki 1998). The slags are dispersed on the surrounding slopes rather than forming a dense heap. The date of this scatter is not known. Diagnostic sherds relating to Classical, Hellenistic, and Roman times were observed, but prehistoric sherds (no further details on these are given) are also reported in the near vicinity (Caskey *et al.* 1988). On the basis of low sulphur contents in the bulk analyses of these slags the authors concluded that oxidic copper ores were smelted (Caskey *et al.* 1988; Papastamataki 1998). Microscopic observations also, however, noted the presence of copper and iron sulphides (Papastamataki 1998), which may indicate that primary sulphidic ores also entered the charge.

The provenance of the ores used at Ayios Symeon remains uncertain. The original investigators of the site suggested a local origin based on the results of the chemical analyses that showed attributes broadly consistent with the local geology (Caskey *et al.* 1988; Papastamataki 1998). It should, however, be noted that potential copper sources had not, at that stage, been identified in the near vicinity. Subsequently, a possible secondary copper mineralisation was reported close to Ayios Symeon (see comment by Photos-Jones in Papastamataki 1998: 765), but no further information is available at present. Apart from chemical analyses, lead isotope analyses of five slag samples from Ayios Symeon have been presented (Gale and Stos-Gale in press;

Stos-Gale 1998). The results were not consistent with a local origin for the ores (slags were compared with ores from the Orkos area, but see discussion of associated problems in section 2.4.1). The Ayios Symeon slags showed strong isotopic similarities to some of the slags from the Skouries heap on Kythnos (see further discussion in section 2.5.2).

#### *2.4.2.4 Evidence for metallurgy on other Keian sites*

Two crucible fragments with traces of copper are reported from the area of Troullos, approximately 500 m northwest of Ayia Irini (Caskey 1971). Sherds ranging from Early to Late Bronze Age were recovered from surface collection and limited excavation in the area.

Mendoni and Beloyannis (1993) report that scattered slag fragments are found in many locations on Kea, but note that apart from Ayios Symeon, the only other substantial concentration was observed in the area of Ellinikon. The slags are surface finds and the pottery at Ellinikon covers a wide chronological range mainly from the Late Archaic Period to the ninth century AD making it impossible at present to date more precisely the corresponding metallurgical activities.

Finally, during an intensive surface survey of northern Kea carried out in the 1980's, metallurgical remains were found at the sites of Koressia and Yialiskari, dated to Classical to Roman and Archaic to Hellenistic periods respectively, on account of the pottery (Cherry *et al.* 1991: 82, 85). No further details regarding the nature of the slags from Ellinikon, Koressia, or Yialiskari is given.

### ***2.4.3 Metallurgical remains on Siphnos*** (Figure 2.4)

The most extensive and comprehensive archaeometallurgical study in the Cyclades has been carried out on Siphnos by the Max-Planck-Institut für Kernphysik in Heidelberg in association with the Deutsches Bergbau-Museum in Bochum. The study was directed mainly at the identification of sources of gold and silver reported in the works of ancient writers to have been exploited during the Archaic and

Classical Periods (see discussion in Bent 1885; Gale 1980: 183-7; Matthäus 1985). The results of this comprehensive work, which included investigation of mining galleries and smelting sites, as well as an analytical examination of ores and metallurgical remains have been presented in detail (Wagner *et al.* 1980; Wagner and Weisgerber 1985) and only the main points are summarised here.

The investigation established the importance of Siphnos in early lead-silver metallurgy. Evidence for mining of relevant ores was found in Ayios Sostis, Ayios Silvestros, Xeroxylon, Kapsalos and Vorini. The ancient galleries had been partly destroyed in most cases by modern mining of iron ores, which took place in the nineteenth and early twentieth centuries. Among these places, the mines of Ayios Sostis were studied in more detail, particularly with reference to dating of the activities (Haustein *et al.* 2003; Wagner *et al.* 1980; Wagner and Weisgerber 1985). Using a combination of thermoluminescence and radiocarbon dating along with archaeological studies of pottery sherds it was firmly concluded that ore exploitation of this mine began as early as the first half of the third millennium BC, while the discovery of a few possibly FN sherds suggested that activities may have started even earlier (Gropengiesser 1986, 1987). Evidence for mining of lead and silver ores during the sixth and fifth centuries BC was also brought forward.

The deposits of Ayios Ioannis, Apokofto and Aspros Pyrgos in the south-eastern part of the island were found to contain significant levels of gold. Although gold was extracted from Siphnos during the Archaic and Classical periods, it is at present unclear whether exploitation of these resources also took place during the Bronze Age (Pernicka and Wagner 1985).

In terms of metallurgical remains, the authors comment on the relative scarcity of slag and other metallurgical waste in comparison with the observed extent of the mining activities (Wagner and Weisgerber 1985). They suggest that this may in part be due to recycling during later periods or because Siphnian ores were in fact transported elsewhere for smelting. At least for the EBA, however, metal production next to the mines is testified by slag and litharge finds scattered on the Ayios Sostis promontory. Small quantities of such specimens are also found at Platy Gialos and Kapsalos, but the date of the corresponding activities is not firmly established.

An interesting and usually overlooked aspect of metallurgy on Siphnos is the preliminary evidence reported so far for copper production on the island. A limited number of copper slags have been recovered from Ayios Sostis and Platy Gialos (Gale *et al.* 1980: 21; Pernicka 1987: 674; Pernicka *et al.* 1985). These were found together with a larger number of lead slags on both sites indicating possibly parallel small-scale copper production. This is not surprising given the nature of the ores on Siphnos, which in some cases contain significant quantities of copper as well as numerous other base metals (Vavelidis *et al.* 1985). Bulk analyses of the copper slags from Ayios Sostis and Platy Gialos detected variable amounts of arsenic, lead, antimony, and zinc (Pernicka *et al.* 1985: 191, 197). A small copper smelting site has also been reported recently by Philaniotou-Hadjianastasiou (2000: 209) in a location known as Petalloura. Unfortunately the site has not been studied in any more detail so far. Indirect indications for the use of Siphnian copper were additionally raised from the lead isotope analyses of some of the copper objects from the site of Thermi on Lesvos, which fell within the Siphnian lead ore field (Stos-Gale 1992: 165). The provenance of the copper used in the large northern Aegean settlements of the EBA presents a complicated issue, however, making it impossible to draw secure conclusions at present (see section 7.5.3).

With regards to habitation on Siphnos during the EBA, Tsountas (1899) partly excavated two relatively small cemeteries at Akrotiraki and Vathy. The settlement of Akrotiraki is near the cemetery but has not been excavated. More recently Philaniotou-Hadjianastasiou (2000) reports from surface survey investigations EBA habitation remains, pottery and obsidian in the broader area north of Kastro.

### *2.4.4 Metallurgical remains on Kythnos* (Figure 2.2)

In the last two decades several fieldwork and analytical archaeometallurgical investigations carried out on Kythnos have shed light on the importance of this island for early copper metallurgy (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Hadjianastasiou 1998; Hadjianastasiou and MacGillivray 1988; Philaniotou-Hadjianastasiou 2000; Stos-Gale 1989, 1998; Stos-Gale *et al.* 1988). Particularly noteworthy are the most recent collaborative investigations carried out on Kythnos between the Ephorate of Prehistoric and Classical Antiquities of the Cyclades and the Laboratory of Archaeometry N.C.S.R. Demokritos, which have brought forward substantial archaeological and archaeometallurgical evidence. Although this work is still in progress, some preliminary results have been presented (Bassiakos and Philaniotou in press). Overall, five copper slag heaps or slag scatters have been reported on Kythnos, while there are suggestions that more are present on the island, as well as several copper ore occurrences.

Among these locations the most intensively studied is the impressive Skouries copper slag heap, which extends down the slope of a coastal cliff top in eastern Kythnos (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Gale and Stos-Gale 1989a; Hadjianastasiou and MacGillivray 1988; Stos-Gale *et al.* 1988). Slag is found mixed with clay furnace lining fragments, pieces of oxidised copper ore, pottery sherds, and obsidian. One complete spherical granite hammer and a fragment of another were also recovered (Gale and Stos-Gale 1989a). The site has been dated, using AMS radiocarbon dating of fragments of charcoal found within the slag, to the third millennium BC (Stos-Gale 1989). The dates agree well with the pottery found scattered in the heap, which corresponds to the EBII period. It has actually been suggested on the basis of lack of any pottery dating later than the EBII period that this is a single period copper smelting site (Hadjianastasiou and MacGillivray 1988). It should, however, be noted that with the exception of limited excavation (discussed below), fieldwork on the site of Skouries has been confined to surface investigations.

Particularly intriguing are the round stone structures, approximately four meters in diameter, identified at Skouries (Hadjianastasiou 1998: 266, Figure 3; Hadjianastasiou and MacGillivray 1988; Stos-Gale 1989). The exact number of these structures is not known, as thick vegetation covers the area, but is estimated at about twenty. Partial excavation of one of these structures revealed a circular pit roughly forty centimetres in diameter and depth, which was lined with stones and clay. Fragments of slag and copper were found in the pit as well as in the fill of the building, while the earth around the exterior of the building was red and appeared to be burnt (Hadjianastasiou and MacGillivray 1988). It appears that the pit is the bottom of one of the furnaces but the function of the surrounding round stone structures remains a puzzle.

The uncertainties that characterise the presence of arsenical copper ores on the island, discussed previously, are also noted in the analyses of the slags. On the basis of analyses of a small number of slag samples from Skouries, Gale *et al.* (1985; Gale and Stos-Gale 1989a) concluded that accidental production of arsenical copper was carried out on the site together with the production of unalloyed copper. Their suggestion was based on electron microprobe analyses of individual copper prills found in the slag, which indicated a large spread of arsenic contents fluctuating from 0.14 % to 7.23 %. Only four out of the ten samples examined, however, gave an average arsenic content above 1 %. A recent examination of a more substantial sample from Skouries (23 samples) questioned these earlier claims, as further analyses (EDAX-SEM) of entrapped copper prills gave an average arsenic oxide content of only 0.6 %. Similar results were obtained from examination of slags from all the other copper production sites on Kythnos discussed below (Bassiakos and Philaniotou in press). Low arsenic contents are also observed in the bulk analyses of discarded ore fragments found within the heap (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Gale and Stos-Gale 1989a). Although the possibility raised by Gale and Stos-Gale (1989a) that arsenical copper was also produced on Skouries cannot be refuted (see further discussion in section 7.2.2.2), it is based on a very small sample, and further analyses to test the homogeneity of the heap, preferably from more systematic sampling, will be necessary in order to draw secure conclusions. At present there is no convincing evidence that Kythnos was a supplier of arsenical copper (see also Bassiakos and Philaniotou in press).

Three more copper slag heaps have been identified more recently on coastal promontories in north-western Kythnos: at Pounta, Sideri, and Paliopyrgos-Aspra Spitia (Bassiakos and Philaniotou in press). Although it is proposed that, based on their characteristics, all three may be related to EBA activities, this has only been confirmed for Sideri by thermoluminescence (TL) dating of furnace lining fragments (Zacharias *et al.* forthcoming), while EBA and MBA sherds have been recognised mixed within the Paliopyrgos-Aspra Spitia heap (Bassiakos and Philaniotou in press). Particularly interesting in the latter two sites was the identification of furnace lining fragments with closely spaced perforations (Bassiakos and Philaniotou in press). Similar finds are known from the EBA copper slag heap of Chrysokamino on Crete (Betancourt *et al.* 1999), possibly Raphina on Attica (Theocharis 1952: 131), and may also be related to earlier examples from Kephala on Kea (see section 2.4.2.1). It has been suggested that these represent fragments of the walls of beehive-shaped constructions, which would have formed part of the copper smelting furnaces (see further discussion in section 7.2.2.1). Outside the Aegean, parallels for these peculiar finds are known from later contexts, namely, the mid-2nd millennium BC copper production site of Non Pa Wai in Thailand (Pigott 1999; Pigott *et al.* 1997) and Bolivia (Rehren pers. comm.). The presence of these characteristic metallurgical ceramics on several Aegean copper production sites suggests technological similarities, at least in some places, during the EBA (see further discussion in section 7.2.2.1).

All of the above sites are located on windswept positions, in some cases coastal, and appear to be isolated from contemporaneous settlement sites (Bassiakos and Philaniotou in press; Hadjianastasiou 1998). A similar pattern is observed at the site of Chrysokamino on Crete (Betancourt *et al.* 1999). Additionally, several copper mineralisations, some with indications for open-air mining, have been identified in relative proximity, but not adjacent, to every slag heap on Kythnos at distances ranging roughly between 500 m and 1000 m (Bassiakos and Philaniotou in press). An open air mine dated to the EBII on the basis of identified surface pottery is known on Cape Tzoulis at some distance south of Skouries (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Hadjianastasiou 1998; Hadjianastasiou and MacGillivray 1988). It is not known whether ore from this mine was transported to Skouries for smelting as the path is difficult and steep. Hadjianastasiou (1998) suggests that the ore from Tzoulis may have been shipped elsewhere for smelting. Two other secondary copper mineralisations have been identified recently closer to the Skouries smelting site. Clear evidence for ancient exploitation was not identified but laboratory analyses showed a geochemical association with the Skouries slags. Also notable are the copper mineralisations at Aspra Kellia and Petra close to the slag heaps of Sideri and Paliopyrgos-Aspra Spitia. Traces of copper minerals are still observed on vertical quartz lenses that traverse the schist bedrock. Open-air mining is suggested by the presence of thousands of quartz fragments bearing copper minerals on the surrounding ground (Bassiakos and Philaniotou in press). Tool marks and tools were not found, which the authors suggest may be due respectively to the nature of the host rock and the lack of appropriate rock sources for the preparation of tools (see also discussion in section 7.2.2.3).

Archaeological explorations in south-eastern Kythnos have identified numerous small EBA coastal sites, possibly settlements, largely characterised by pottery and obsidian finds (Hadjianastasiou 1998). Between the modern iron mine of Zogaki, discussed previously, and the bay of Lefkes, another scatter of slag was identified. Abundant EBA pottery and obsidian fragments as well as some possibly early wall remains testify to habitation on this site, contrary to what was observed on the copper production sites of north-western Kythnos (Bassiakos and Philaniotou in press; Hadjianastasiou 1998). Regarding the metallurgical remains, several differences are also significant. The slags are generally dispersed rather than forming a dense heap and appear to have been broken to small fragments, possibly for the extraction of copper prills. The authors also note an absence of metallurgical ceramics (Bassiakos and Philaniotou in press). Similar scatters of slag and EBA pottery are known on other locations on south-eastern Kythnos but these have not been investigated in more detail.

### ***2.4.5 Metallurgical remains on Seriphos*** (Figures 4.1 and 5.1)

Seriphos has been investigated as part of this thesis and is therefore discussed in more detail in Chapters 4 and 5. At this stage it will only be noted that prior to this work, two undated copper slag heaps were known on Seriphos, at Avessalos and Kephala. Only a very limited number of bulk analyses of slags had been presented by Gale *et al.* (1985), while Dimou and Oikonomou (1997) had carried out a microstructural examination of a couple of randomly collected slag samples from each site. In terms of location, the two slag heaps on Seriphos showed many similarities with the sites identified in north-western Kythnos. A third copper slag heap at Phournoi was identified during the course of the present project, while other slag scatters on Seriphos have recently been reported by Gale and Stos-Gale (2002) and Papadimitriou and Fragiskos (2003).

### *2.4.6 Metallurgical remains on Kastri on Syros*

Excavations on the late EBII settlement site of Kastri on Syros by Tsountas (1899) and later by Bossert (1967) uncovered several specimens associated with metallurgical activities. These include slag, crucible fragments with traces of lead and copper, and two mould fragments (Bossert 1967; Stos-Gale *et al.* 1984; Tsountas 1899). Particularly interesting is the identification of a hearth, excavated by Bossert (1967) in Room 11, from where she reports copper slags and charcoal remains. A niche with several copper-based and other artefacts was also discovered near the ground in the same room. The excavator suggests, based on the concentration of metal-related material in close proximity to a hearth, that Room 11 functioned as a metallurgical workshop.

As was pointed out earlier, the copper-based artefacts from Kastri constitute an intriguing assemblage, being the only significant group of EBA tin-bronze finds known from a single context in the Cyclades. Lead isotope analyses of these artefacts have suggested an Anatolian origin for this metal (Gale and Stos-Gale 1986a; Stos-Gale *et al.* 1984). Comprehensive technological studies of the metallurgical remains from Kastri have not been undertaken and therefore the nature of the associated activities is uncertain. This is particularly clear in the opposing interpretations offered by Renfrew (1972: 315) and Muhly (1985a: 125) with regards to the activities carried out in Room 11, the former suggesting smelting and the latter melting, both lacking the necessary analytical evidence to draw any conclusions with certainty. Stos-Gale *et al.* (1984: 31) state that there is “no evidence for extractive metallurgy” on the site, noting that the single ‘slag’ fragment recovered during Tsountas’ excavations (Tsountas 1899: 124) is actually a lump of arsenical copper metal. It is not, however, clear, whether Stos-Gale *et al.* (1984) also examined the finds from the excavations of Bossert (1967), who noted that apart from the material in Room 11, dispersed slag fragments were observed around the site. At this stage it is therefore impossible to decide whether these were correctly identified in the original report (Bossert 1967) and what their nature actually is.

### *2.4.7 Metallurgical remains from other Cycladic islands*

During a trial excavation on a promontory close to the cemetery of Avyssos on Paros, Tsountas (1898) recovered five pieces of slag, mixed with pottery, subsequently attributed by Renfrew (1972: 515) to the Grotta-Pelos culture (Late FN - ECI period). The excavator reports that these were identified as copper smelting slags but unfortunately no further details are given, while based on the identification of numerous obsidian fragments in the same locality, he proposes that the area may have been used as a workshop. Renfrew (1967: 4) also reports a fragment of cast lead from the surface of the contemporaneous site of Cheiromylos on Despotikon island south of Paros, which he believes testifies to local metallurgical activities.

On Melos, crucible and mould fragments are reported from Phylakopi I (end of EBA-MBA), the former interpreted as a bronze smelting vessel, but both the metal and the activity associated are probably simply assumed (Atkinson *et al.* 1904: 191).

Specimens of slag and litharge have also been unearthed from excavations on the EBA settlement of Provatsa on Makronisos (Lambert 1973; Spitaels 1982). Further studies of these finds have not been presented.

Recent limited excavations for the construction of pillars to support the new roofing at Akrotiri on Thera have produced substantial new evidence for the previously far less documented LN to EBA phases of habitation on this site. Among the finds, particularly interesting for this study are the reported tuyère fragments, to which Sotirakopoulou (in press(a)) attributes an EBA date. This date will have to be treated with caution at this stage, as none of the finds examined so far from these early periods have come from stratified or closed contexts (Sotirakopoulou in press(a)). Metallurgical activities are also attested at LBA Akrotiri (Bassiakos *et al.* 1990; Michailidou 1995; Schofield 1990; Stos-Gale and Gale 1990).

A small collection of metallurgical material was recovered during fieldwork on the site of Daskaleio-Kavos (Broodbank 2000a: 231). These samples form part of the analytical work carried out in this study and are therefore described in more detail in Chapter 6.

Iron slags are also known on the Cyclades. A number of such finds dated to the Geometric period and recovered from both excavation and surface sampling from various sites on Andros have undergone examination by Dimou *et al.* (2001). Davies (1935: 264) also mentions iron slag from Tenos and Naxos, as well as possible lead slag from the former, but his reports have not been substantiated by more recent fieldwork and no further details are known.

## 2.5 Lead Isotope Analysis Studies in the Aegean

The application of lead isotope analysis in the study of ancient metal has had tremendous impact in the study of provenance issues. Over the last three decades a growing number of lead isotope data has emerged from the Mediterranean region and examination of a wide variety of excavated metallic artefacts has been undertaken. The method has, however, also received intense criticism and as its limitations become better understood growing confusion and debate has arisen over the validity and usefulness of the emerging results, as exemplified in the collections of papers published in the *Journal of Mediterranean Archaeology* (1995: 1-75) and *Archaeometry* (1992: 73-105 and 311-336; 1993: 241-263). Muhly (1995) has paralleled the situation in lead isotope studies with the radiocarbon dating problem faced in the 1960's whereby "initial euphoria soon gave way to feelings of profound scepticism, distrust and a sense of vindication" (Muhly 1995: 54). While radiocarbon dating overcame these difficulties to become a reliable dating method, lead isotope analysis is still challenged by some researchers (see for example Knapp 2000, 2002 and replies in Gale 2001, 2003).

The theoretical principles of the method and the analytical techniques used are well described in the literature (see for example Gale and Stos-Gale 1989b, 2000 and references within) and will not be repeated here. Lead isotope analysis has, however, contributed significantly to the field of Aegean metallurgy and, given the current state of controversy, it is worth reviewing some of the basic advantages and limitations of the method before looking at conclusions drawn from its application in the Cyclades.

### *2.5.1 Advantages and limitations of lead isotope analysis*

Lead isotope analysis offers several advantages in comparison with the more 'traditional' approach to the provenancing of metals, which involves comparison of chemical compositions. Ore sources often tend to vary greatly in minor and trace elements (Bowman *et al.* 1975; Constantinou 1982; Gale and Stos-Gale 1992a). Variations in lead isotope compositions do also occur, depending on a number of factors such as the relative proportions of uranium, thorium and lead in the original ore-forming fluids, the geological age of the deposit and the possible remobilisation of the ore after its first deposition (Gale and Stos-Gale 2000; Rohl and Needham 1998; Stos-Gale and Macdonald 1991). However, isotopic compositions within a deposit of uniform geological and geochemical history only vary within a very narrow limit, often less than ±0.3 % (Gale and Stos-Gale 1989b, 1992a, 2000). It should be noted though that even in the same deposit two veins situated side by side may have significantly different lead isotope ratios if they are the result of different geological processes. Care also needs to be taken in the evaluation of low-lead ore deposits with appreciable amounts of uranium and thorium, where continuous radioactive decay results in evolving lead isotope compositions (Gale and Stos-Gale 2000: 537-8; Pernicka 1993: 261). No deposits of this type are, however, known in the Mediterranean region (Gale and Stos-Gale 1989b). It therefore becomes clear that although in most cases lead isotope compositions will, in principle, be more confined than trace element compositions for a given ore deposit, a clear understanding of the local geological processes that led to its formation is vital to ensure that it does not represent one of the exceptional cases where this criterion is not satisfied (Gale and Stos-Gale 1989b, 2000: 511-6, 537-8).

The additional major drawback of provenance studies using chemical analyses is that the composition of the metal may vary significantly from that of the original ore (Tylecote *et al.* 1977). These differences arise from chemical processes during smelting, casting or alloying, where the addition of fuels, fluxes and other metals contribute their own minor elements in the mixture. Partitioning of elements between slag and metal depends on a number of factors, such as redox potentials, and varies for different elements, while the heat may cause some components to volatilise. In contrast, lead isotope compositions have been shown to remain unaltered during metallurgical processes (Gale and Stos-Gale 1996, 2000: 525-528). Care must however be taken when one is dealing with corroded, low-lead bronze objects because the isotopic composition may have been altered through exchange of lead from the soil or other objects in contact during burial (Gale and Stos-Gale 1989b, 2000).

Interpretation of lead isotope data in archaeology is restricted by two major problems. The first one relates to the possibility that lead from two or more discrete sources is present in a single artefact as a result of melting and re-using scrap metal, alloying or the addition of material other than the ore, such as fuels and fluxes, during smelting. The implications of such practise for provenance studies have been extensively discussed in the literature (see for example Gale and Stos-Gale 1989b, 1992a, 2000; Rohl and Needham 1998; Stos-Gale 2000) and only a brief mention of the arguments given will be presented here. The potential complications caused by lead present in the fluxes have been refuted on the ground that if such material was required during smelting of copper ores it would probably have been collected from the associated gossan and would therefore have the same isotopic composition (Gale and Stos-Gale 1982, 1989b, 2000). Similarly for charcoal, it is presumed that the trees used would have been close to the ore deposit and therefore if lead is present in the charcoal, its isotopic composition would be identical to that of the ore (Gale and Stos-Gale 2000). The change in isotopic composition from the addition of tin in the production of bronze alloys is considered negligible in view of the generally very low levels of lead associated with cassiterite ore and the relative proportions of copper and tin in bronze alloys (Begemann *et al.* 1999; Gale and Stos-Gale 1989b, 2000: 539; Pernicka *et al.* 1990: 276-7). Production of arsenical copper in the Bronze Age Aegean is assumed to be the result of smelting arsenical copper ores rather than deliberately mixing copper with high-arsenic minerals (although the issue is far from resolved see discussion in section 7.2.2.2) and therefore the isotopic composition would not be compromised by alloying (Gale and Stos-Gale 1989a, 1989b). Mixing and recycling of scrap metal remain the most complex problems in provenance studies (see for example Budd *et al.* 1995; Gale and Stos-Gale 1995). It has been proposed that there are methods through which one can detect whether an artefact has in fact resulted from mixing together metals from two or more sources based on its lead isotope composition (Gale and Stos-Gale 2000: 531-6 and references within) and that additionally the available data indicate that mixing of copper metals from very different origins is not generally common in the Bronze Age Mediterranean (Stos-Gale 2000: 58). Gale and Stos-Gale (2000: 531) acknowledge, however, that each case study needs to be viewed independently without making assumptions *a priori* and using all available archaeological and other data. In this respect it is worrying that the authors cite Renfrew (1972) in proposing that "the archaeological evidence suggests that this (recycling) may not have been a very common practise at any time in the Aegean, where it was at all times common practise to bury metal objects with the dead" (Gale and Stos-Gale 2000: 531). At least regarding the EBA Cyclades, Nakou's (1995) treatise should caution against making such broad generalisations.

The second problem associated with lead isotope analysis is the possibility that two geographically distant ore sources may have overlapping isotopic fields. In such cases definite conclusions cannot be reached based on isotope data alone. Evidence for mining during the period in question as well as the incorporation of appropriate trace element data together with the lead isotope data in multivariate statistical analysis may aid differentiation (Gale 1980; Gale and Stos-Gale 1989b; Reedy and Reedy 1991; Stos-Gale and Macdonald 1991).

It should also be stressed that sampling issues are crucial in the establishment of lead isotope signatures of ore deposits. Apart from a thorough understanding of the local geology and an accordingly suitable sampling methodology, sample sizes are another important parameter. A minimum sample size of 20 is generally considered adequate to represent accurately a lead isotope field (Gale and Stos-Gale 1992b; Reedy and Reedy 1991; Sayre *et al.* 1992a). A recent study by Baxter *et al.* (2000), however, concluded that 40 samples is a more realistic minimum and even this may in some cases be too small, while Gale and Stos-Gale (2000: 528) agree that analyses of 30 to 50 samples are ideally required.

It was initially advised by the practitioners of lead isotope analysis that the method is largely negative and that while it can definitely eliminate ore deposits as potential sources of metal for a particular object it cannot on its own indisputably pinpoint artefacts to individual deposits (Gale 1978). This is partly due to the fact that extensive fieldwork is necessary to make sure that the majority of ore deposits within a region have been considered and in addition, as was discussed above, partial overlap of fields may in some cases inhibit clear distinctions (see also Begemann *et al.* 1999: 277). Sayre *et al.* (1992b: 334-5) have questioned even the ability of the method to unequivocally exclude sources. More recently, however, Gale and Stos-Gale (2000; see also Gale 2003 and examples quoted within) have argued that the method is in a position to attribute artefacts to specific deposits following comparison with a set of ore deposits "geographically/ archaeologically reasonable to consider" and accepting that conclusions will be based "in the present state of knowledge" (Gale and Stos-Gale 2000: 523). As will be discussed further in section 2.5.2 the authors have followed the approach of attributing artefacts to specific deposits from the beginning of their research in the Cyclades (e.g. Gale and Stos-Gale 1981a).

Overall, it becomes clear that interpretation of lead isotope results is based on a number of hypotheses and is restricted by its own set of limitations. This emphasises that, like any other analytical method, lead isotope analysis does not provide a panacea for provenance studies and should be combined with suitable archaeological and archaeometallurgical evidence. Following these general remarks on the methodology, we can now turn and look more closely on how these studies have contributed to the understanding of Bronze Age Cycladic metallurgy.

### *2.5.2 Lead Isotope Analysis Studies in the Cyclades*

#### *2.5.2.1 A summary of results*

The majority of lead isotope analysis work in the Mediterranean region has been carried out by the Isotrace Laboratory of the Research Laboratory for Archaeology and History of Art of the University of Oxford. In more than two decades, the Oxford Group has produced data on a range of ore sources in the Aegean islands, mainland Greece, Cyprus, Sardinia, Bulgaria and Spain (see for example Gale and Stos-Gale 2000; Stos-Gale 2000 and references within). At the same time an impressive number of artefacts have been studied and their isotope ratios have been compared with the known fields in an attempt to trace the metal sources. Conclusions drawn from individual case studies in the Cyclades, as well as broader overviews of such work on these islands, have been presented in numerous publications (see for example Gale 1998; Gale and Stos-Gale 1981a, 1984, 1989a, 1992a, 2002, in press; Gale *et al.* 1985; Stos-Gale 1989, 1998; Stos-Gale and Gale 2003; Stos-Gale and Macdonald 1991 and more references within) and only the main points are briefly given here.

Analyses of a number of lead and silver artefacts from the Cyclades, the Greek mainland and Crete show a pattern in which Lavrion and Siphnian ores appear to be the predominant sources, with a few objects possibly relating to galenas from Chalkidiki in northern Greece and some others of unknown origin (Gale and Stos-Gale 1981a, 1981b, 2002, in press; Gale 1998; Stos-Gale and Gale 1982, 2003; Stos-Gale and Macdonald 1991). Specifically in the case of Cycladic lead and silver artefacts, a Siphnian origin is most common in the EBA, with Lavrion and the Troad also participating to a lesser extent, while Lavrion predominates in later periods of the Bronze Age. It should, however, be pointed out that more recent data have disputed the originally proposed Siphnian origin for four of the lead artefacts from Ayia Irini Periods III and IV (see section 2.4.2.2) and for the lead boats exhibited in the Ashmolean Museum (attributed an ECII date but see Sherratt 2000: 103-9 for arguments questioning their authenticity) pointing instead to the lead/silver mine of Gümüsköy in Anatolia (c.f. Gale and Stos-Gale 1981a, in press; Gale *et al.* 1984).

Lead isotope analyses of a number of EBA Aegean copper artefacts have shown strong indications of a local Cycladic origin, the majority of them actually plotting within the Kythnian field (Gale and Stos-Gale 1989a, 2002, in press; Stos-Gale and Macdonald 1991; Stos-Gale 1993, 1998), while only in the most recent publications have copper ores from Seriphos and Siphnos also been suggested as possible sources (Gale and Stos-Gale 2002, in press; Stos-Gale and Gale 2003). A smaller proportion of these objects is consistent with a Lavrion origin, while a third group form a distinct subset whose isotope ratios are not consistent with any of the known Aegean and Balkan deposits. Examples of the latter group are found among the copper-based artefacts from Kastri on Syros and Thermi on Lesbos (Gale and Stos-Gale 1986a; Stos-Gale 1992; Stos-Gale *et al.* 1984). A possibly Middle Eastern or Central

Asian origin has been suggested, but the exact source has not been identified to date. By the LBA Lavrion appears to be the predominant source of copper, followed by Cyprus, while approximately 10 % of the artefacts analysed are not consistent with any of the sources sampled so far (Stos-Gale and Macdonald 1991; Stos-Gale 2000).

In summary, the broad pattern that has emerged from the lead isotope studies indicates that the Cycladic sources were used extensively during the EBA for copper, lead and silver, but their exploitation appears to diminish in the Middle and Late Bronze Age, when the larger deposits of Lavrion and Cyprus prevail. The development of such models on the basis of lead isotope data, is, however, inherently restricted by the number, nature and associated context of the artefacts examined from each period. Despite the large number of analysed objects, a bias towards certain periods and regions is present in the Aegean database, while many of the EC artefacts analysed come from museums and are in most cases of dubious context (Gale and Stos-Gale 2002; Stos-Gale and Macdonald 1991). Clearly these suggested patterns need to be viewed with caution.

#### *2.5.2.2 Limitations and shortcomings within the Cycladic database*

As was mentioned above, over the last twenty years the Oxford Group has been involved in lead isotope measurements across the Mediterranean, covering an extensive area with varied mineralogical features. As the group must be considered among the pioneers of this work it is only reasonable that their survey could not have been exhaustive. Particularly among the Cycladic islands, where mineral occurrences are often notoriously small, it is not surprising that further fieldwork would inevitably result in the identification of more potential ore sources in the Aegean. The examples of Kea and Thera discussed below demonstrate this pragmatic limitation more clearly. In their original consideration of provenance of lead objects from Ayia Irini on Kea, Gale *et al.* (1984) had dismissed the possibility that galena deposits occurred on Kea, based on their observations during fieldwork expeditions on the island, and attributed a Lavrion provenance to these artefacts. Since then galena deposits have been reported on a number of localities on Kea (Caskey *et al.* 1988; Davi 1998; Mendoni and Beloyiannis 1993; Papastamataki 1998) and their initial claims had to be reconsidered in the light of this new evidence

(Gale 1998). Similarly, the accepted geological notion that the known galena deposits at Cape Athinios on the island of Thera were not exposed to the surface until after the volcanic eruption was challenged at the end of the 1980's (Bassiakos *et al.* 1990; Friedrich and Doumas 1990). Originally Lavrion had been suggested as the source for the litharge and lead objects found in the LBA site of Akrotiri (Stos-Gale and Gale 1990), and prior to 1990, data for only four samples of galena ores from Cape Athinios were published in the literature (Gale and Stos-Gale 1981a). As arguments for the possible exploitation of local sources on Thera were brought forward, the Cape Athinios mines had to be sampled again and the conclusions drawn thus far were re-evaluated (Gale 1998). Although Lavrion was still considered a more compatible source in both cases (although see Bassiakos *et al.* 1990 for an opposing view for Thera), even on the basis of further lead isotope data, the examples highlight the difficulty in covering exhaustively the fragmentary landscape of the Cyclades.

Turning now to potential sources that have been sampled, the Oxford Group has been widely criticised for their lack of publication of lead isotope data on ore deposits with reference to their work on oxhide ingots and the LBA Mediterranean metals trade (Budd *et al.* 1995). In the absence of this data and information on the sampling strategies employed during collection it is very difficult to assess whether the established lead isotope fingerprints presented are based on adequate and valid sample sizes. An overview of the relevant literature shows that these problems are also apparent in the Cycladic database (Gale 1978, 1980, 1998; Gale and Stos-Gale 1981a, 1982, in press; Stos-Gale 1989; Stos-Gale *et al.* 1996). Following this criticism (Budd *et al.* 1995), the Group has presented a series of publications on lead isotope data of ore deposits obtained in their laboratory.

In the relevant Aegean compilation (Stos-Gale *et al.* 1996) it is admitted that some of the early measurements presented in the 1970's and 1980's are no longer considered accurate enough and should be ignored. The list includes samples from Lavrion, Syros, Kea, Seriphos, Thera, Thasos, Kythnos, Antiparos, and Poliagos. The majority of the data presented has resulted from examination of galena ores, while copper ores are disturbingly under-represented (only some copper ores from Lavrion are given together with a single limonite-malachite sample from Pharos on

Siphnos). It is noted in the introduction to their publication that the list is not exhaustive but only presents "groups of data for occurrences for which we have numerous samples and can make repeated analyses to provide a good statistical background" (Stos-Gale *et al.* 1996: 381). On this note and in view of the discussion on minimum sample size of twenty to forty analyses in lead isotope studies, it is worrying that a mere thirteen galena samples from Kythnos and eight galena samples from Poliagos are incorporated in this collection. Given the significant role that Kythnos is attributed in EBA Cycladic copper metallurgy, it is also surprising that copper ores from Kythnos have not been included, on the basis that very few samples are available (Stos-Gale *et al.* 1996: 381). In general, with the exception of Kythnos (Stos-Gale 1989), data from Cycladic copper ore sources were virtually absent throughout the relevant literature until that time. Additionally it is noteworthy that in most publications of lead isotope fields of copper ore deposits in the Aegean, Kythnos was the only Cycladic island represented (see for example Stos-Gale and Macdonald 1991). Gale and Stos-Gale (1989b: 170) have themselves pointed out that in attempts to provenance copper, the examined objects should only be compared with fields of copper ore deposits, unless as has been proposed for Lavrion (Gale and Stos-Gale 2000: 530), it can be shown that different ores from polymetallic deposits form a homogeneous field (galena and copper minerals from Kythnos show differences in their lead isotope compositions; see Stos-Gale 1998: 723, footnote 26).

Despite the demonstrated dearth of data for copper ores from the Cyclades, conclusions were consistently drawn concerning the provenance of Cycladic and other Aegean artefacts, which pointed, with relative confidence, to Kythnos as the source (the Kythnos field being largely represented by slag analyses from the copper slag heap of Skouries, although see below), suggesting that the island played a central role in early copper production (e.g. Stos-Gale 1998 and references within). Although the role of Kythnos cannot be questioned in view of the numerous slag heaps identified on the island, it is reasonable to question whether its exclusive importance may have been exaggerated on the basis of bias in the database. It has been suggested in the past that artefacts will tend to be attributed to fields represented by more samples, as these will occupy more space in the relevant diagrams (Cherry and Knapp 1991: 100; Reedy and Reedy 1988). Similar concerns have been expressed for the predominance of Siphnos and Lavrion over other potential Aegean lead and silver sources (Reedy and Reedy 1988), although additional Cycladic islands are now more fully characterised for these metals (Stos-Gale *et al.* 1996).

In this respect it was particularly welcoming to note in the most recent publications the incorporation of copper minerals from the islands of Kea, Seriphos, and Siphnos (Gale and Stos-Gale 2002, in press; Stos-Gale and Gale 2003; a few examples in Stos-Gale 1998). Admittedly the sample sizes are still relatively small and in the most recent relevant summary of analysed specimens only four samples from Kea, seven from Siphnos, and eight each from Seriphos and Kythnos respectively are mentioned (Gale and Stos-Gale in press), although the numerical data from Seriphos, with the exception of a single specimen (Stos-Gale 1998) have not been presented. Unfortunately there is no clarification concerning the extent to which the corresponding lead isotope fields separate (even provisionally given the small number of samples) and no relevant diagram is given (except Gale and Stos-Gale 2000: 546, Figure 17.13; Stos-Gale 1998: 735, Figure 14, both with less data than currently available). Some overlap is, however, implied from the table (in Gale and Stos-Gale in press) summarising the associated sources for a number of Cycladic artefacts, where several of these are attributed a choice of sources between two or more of Kythnos, Siphnos, Seriphos and Lavrion.

Further confusion arises from the use of both ore and slag analyses in the presentation of lead isotope fields. It has been convincingly argued that slags are a potentially better comparative material with which to provenance metals than ores, as they represent a step in the metal production sequence closer to the final artefact and therefore will incorporate any possible deviation from the ore composition resulting from mixing of ores from different sources, or the addition of fuels and fluxes (Leese 1992; Pernicka 1992; Reedy and Reedy 1992). Clearly this proposal raises some concern with respect to some of the basic assumptions that underlie lead isotope comparisons of metals and ores (see section 2.5.1) and would perhaps merit further examination in the future. The situation is simple when slags found in relative proximity to mines fall within the isotopic field of the relevant ore, but complications arise when differences are observed. In the Cyclades, one area where this situation has been noted is the slag heap of Skouries on Kythnos. Although the majority of the slags from Skouries show close correspondence with the ores from Kythnos, some appear to relate to ores from Siphnos and possibly Kea and Seriphos (Gale and Stos-Gale 2000, in press; Stos-Gale 1998). This has led to the proposal that ores from different Cycladic islands were possibly brought to the Skouries site for processing, a suggestion with important implications in the consideration of the overall organisation of metallurgy in this region. Enticing as this idea may appear, the small number of copper ore lead isotope data available from the Cyclades unavoidably leads to scepticism. Could the far larger number of slags analysed from Skouries (59 according to Gale and Stos-Gale in press) be more representative of the lead isotope variation exhibited by the Kythnian ores? It should also be noted that, apart from the small sample size, only two copper mineralisations on Kythnos have been sampled for lead isotopes, while more such occurrences are now known (Bassiakos and Philaniotou in press). In that case does the overlap between slags from Skouries and Siphnian ores alternatively demonstrate partial overlap between the copper ores from these two islands?

Based on the arguments presented in this section, are we to accept the pessimistic, (but possibly more realistic?) view expressed by another group of lead isotope practitioners that "we are in the ungratifying situation that more measurements lead to more ambiguity" (Pernicka *et al.* 1990: 278; Pernicka 1992, 1993)? Will more data on copper ores from the Cyclades result in clear resolution between the islands or should we rather strive towards establishing a 'Cycladic' or even 'Aegean' field (c.f. Gale and Stos-Gale 1992b; Pernicka 1992), an important achievement nonetheless?

### *2.5.2.3 Lead isotope analysis and the Cyclades: a less controversial future?*

Studying the archaeological lead isotope literature one can broadly attribute the relevant papers to two kinds: one kind that presents purported results, with ostensibly relatively straightforward answers, although not discounting the potential problems, and another kind that discusses the numerous complexities of the method, often with elaborate details of mathematical, geological or other scientific nature. It is not surprising that the technique has created some confusion and cynicism among interested scholars. Within this context and given the criticism presented above, can there be a less controversial future for lead isotope application in the Cyclades?

It is the opinion of this author that the problem, at least for the Aegean, does not lie within lead isotope analysis as a technique, as despite its limitations it still represents the best provenancing tool for metals, but rather with the way it has been applied to address archaeological problems in this region. The Cyclades represent only a very small part of the impressive area covered by the work of the Oxford Group. Additionally these islands were among the very first regions to be investigated (see for example Gale 1978), at a time when archaeometallurgical research in the Cyclades was only beginning, with the investigations on Siphnos. In the following years lead isotope analysis efforts progressed comparatively rapidly and in most cases independently from any other archaeometallurgical work, analysing and attributing numerous objects to what, as has been demonstrated previously, appears to be a largely unbalanced database. As a result, papers related to lead isotope analysis by far outnumber any other type of archaeometallurgical work in the Aegean and we are often in a position where we know where the material in question may be coming from but not what it is!

Within this context lead isotope analysis appears to have been used as an indirect method of proving production (or mining) in one area, while excluding others, the former a task that could have been better achieved by direct technological and archaeological examination of the evidence, where present. Given the present state of the database and the particularities of the Cycladic environment, the resolution often implied by the interpretation of the results appears to be overly ambitious. Comparing artefacts with the slag heap of Skouries, for example, only leads to a statement of what has been established by the archaeological evidence, namely that the site was a copper production centre in the EBA. What would have been desirable, however, would have been to compare the different copper smelting sites and assess whether they can be distinguished using lead isotope analysis and other suitable techniques, and then progress to examine whether particular patterns can be discerned. At present and in the absence of adequate data from other similar smelting sites in the Cyclades one cannot securely claim that particular artefacts were produced specifically on Skouries. The possibility of overlap of the lead isotope field of Skouries with those from other smelting sites has not been excluded. Similarly, for the ores, a more comprehensive database might be in a position to attribute sources to production sites. If, additionally, lead isotope analysis is to be used to substitute for other evidence that may be largely absent due to subsequent activities, as is the case for prehistoric copper mining in Lavrion, one should expect a very comprehensive sampling of other potential sources in order to demonstrate a clear separation. The extent to which such resolution will be possible within such a small geographical region will have to be examined in the future (the demands being also determined by pragmatic considerations of what is achievable balancing costs and labour), and additional data types, whether archaeological and/or chemical, need to be incorporated for this purpose.

These comments are not meant to discredit the value of the work carried out so far. On the contrary it is believed that, given the laborious nature of this technique and the state of knowledge at the start of these efforts, the results produced are indeed remarkable, both in terms of fieldwork as well as number of analyses. The accumulated database provides a good basis, which will, however, need to be progressively refined appropriately, depending on the nature of questions asked.

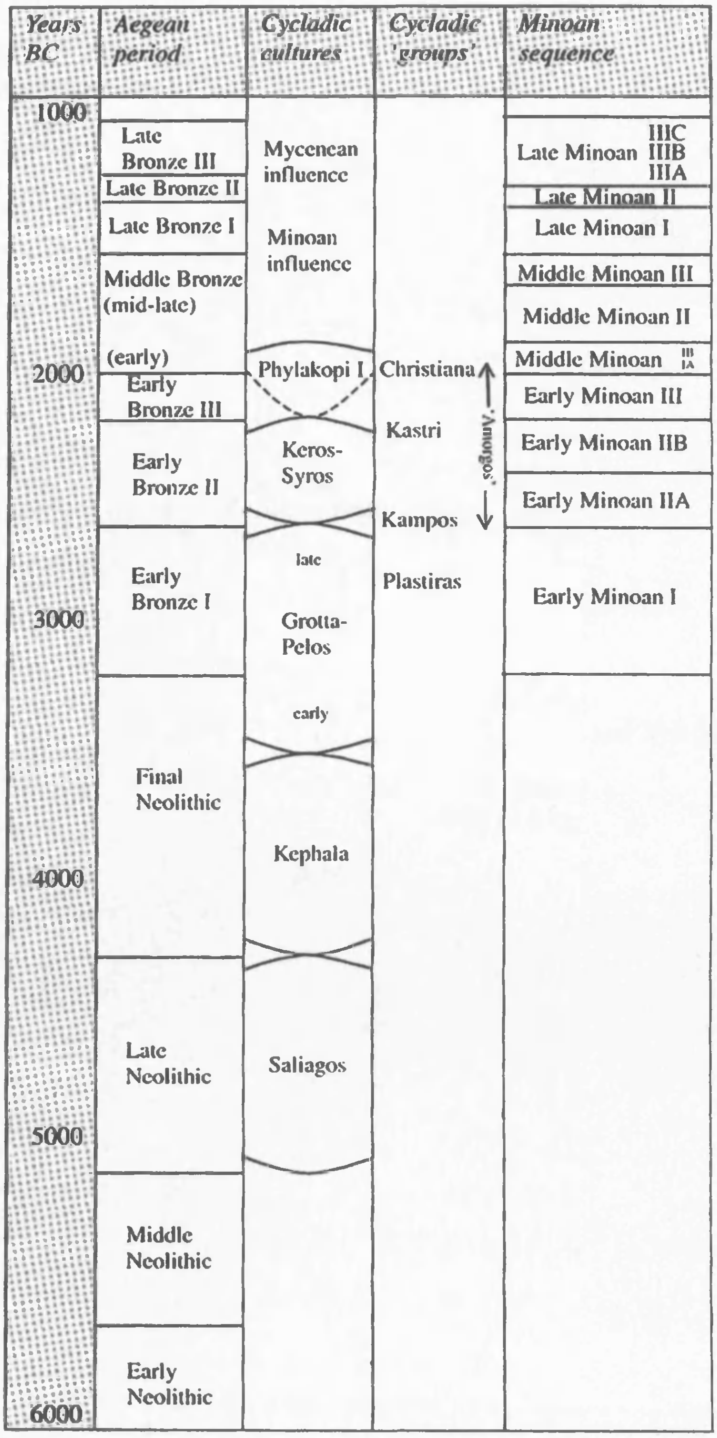


***Figure 2.1*** *Chronological chart for the Neolithic and Bronze Age Aegean (simplified Middle and Late Bronze Age) showing synchronisms between Cycladic cultures, groups, and Minoan sequence (adapted from Broodbank 2000a: Figure 1).*

***Figure 2.2*** *Map of Kythnos, showing sites mentioned (a small copper mineralisation has also been identified in the vicinity of the Skouries slag heap (see Bassiakos and Philaniotou in press) but this is not noted separately on this map).*

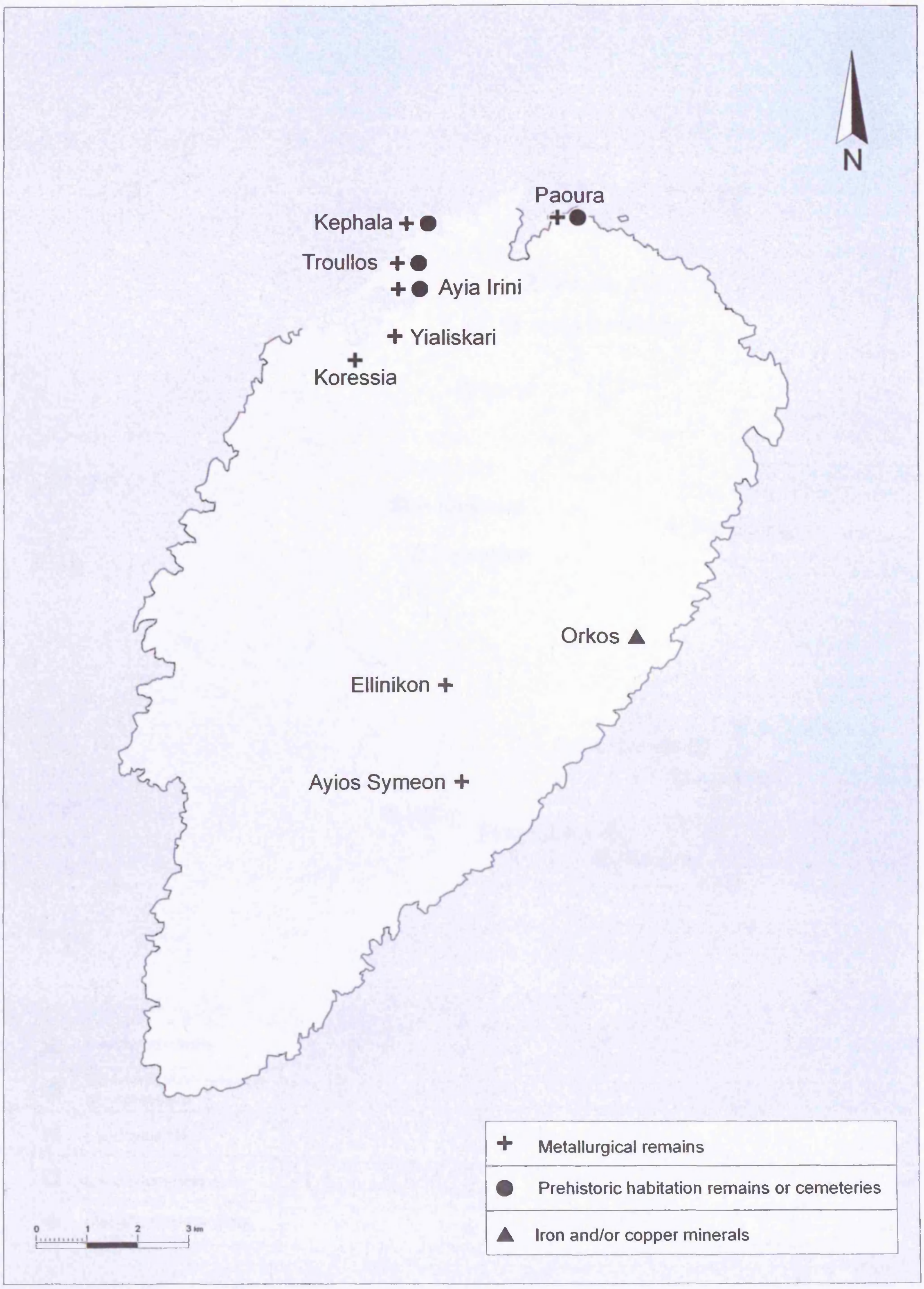


*Figure 2.3* Map of Kea, showing sites mentioned.

*Figure 2.4* *Map of Siphnos, showing sites mentioned.*

# CHAPTER 3.

# A research framework and methodology for the analytical study

## 3.1 Introduction

From the review presented in the previous chapter it becomes apparent that substantial work relevant to metallurgy has been carried out in the Cyclades, but that this research, largely dominated by provenancing studies, has tended to investigate the islands from the view of a wider geographical exchange-based framework, producing broad patterns relating mainly to the circulation of materials. Numerous finds testifying to metallurgical activities have been brought forward, but these remain largely under-explored, with the exception of the very fruitful efforts carried out on the islands of Siphnos and Kythnos (see references in sections 2.4.3 and 2.4.4). It has been shown that production of copper, lead and silver was carried out in the Cyclades during the EBA but further in-depth investigations of particular sites and groups of material will now be necessary to unravel the details of the technology and organisation of metal production in this region. Within this broad research agenda this chapter outlines the specific questions addressed in this thesis, their relation to the case studies examined, and the methodology used to approach them. Information regarding the analytical techniques used and relevant sample preparation are given at the end.

## 3.2 Metal production sites and metallurgical remains in settlements

Looking at the review of finds associated with EBA metallurgical activities in the Cyclades given in Chapter 2, one can broadly separate two contexts within which these appear, namely those associated with metal production sites and those found within settlements. Regarding the first, at least on the basis of the dated and studied sites of north-western Kythnos and Siphnos, these appear to be isolated from any known contemporaneous habitation sites, while the evidence so far presented testifies to the practice of only some of the stages of the metallurgical sequence. More specifically for copper production, using the simplified diagram presented in Figure 3.1, smelting is attested on the Kythnos sites, as well as possibly subsequent breaking of the slag into smaller pieces to extract the copper prills (Bassiakos and Philaniotou in press; Gale *et al.* 1985: 85). Mining and possibly beneficiation[3.1] appear to have been carried out relatively close to, but not necessarily adjacent to, the production sites. Shipping of the ore from other places, as was suggested from the lead isotope analyses of the Skouries slag heap (e.g. Stos-Gale 1998) cannot be excluded, but this possibility will need to be assessed more thoroughly with further data. At present there is no evidence to suggest that further metalworking activities were practiced in these areas.

Based on these findings, it has been proposed (Barber 1987: 112; Broodbank 2000a: 293-7) that in the EBA Cyclades metal production (smelting) was carried out close to the sources, with the metal then being transported to the settlements, for further processing and artefact manufacture. However, despite the numerous metallurgical remains recovered in small quantities from EBA Cycladic settlements, no comprehensive technological studies of such material have been undertaken (see section 2.4).

The case studies examined in this thesis represent examples from both contexts; with the Seriphos sites showing close correspondences to those on Kythnos, and Daskaleio-Kavos, despite its peculiarities (see section 6.2), exhibiting characteristic traits of a settlement (Broodbank 2000b). The results will therefore allow for the first time a more substantiated comparison between two different settings for metallurgical activities in the EBA Cyclades.

---

[3.1] Large quantities of quartz fragments bearing traces of copper minerals were observed at the suggested mining sites of Aspra Kellia and Petra some distance to the northeast of Sideri (Bassiakos and Philaniotou in press).

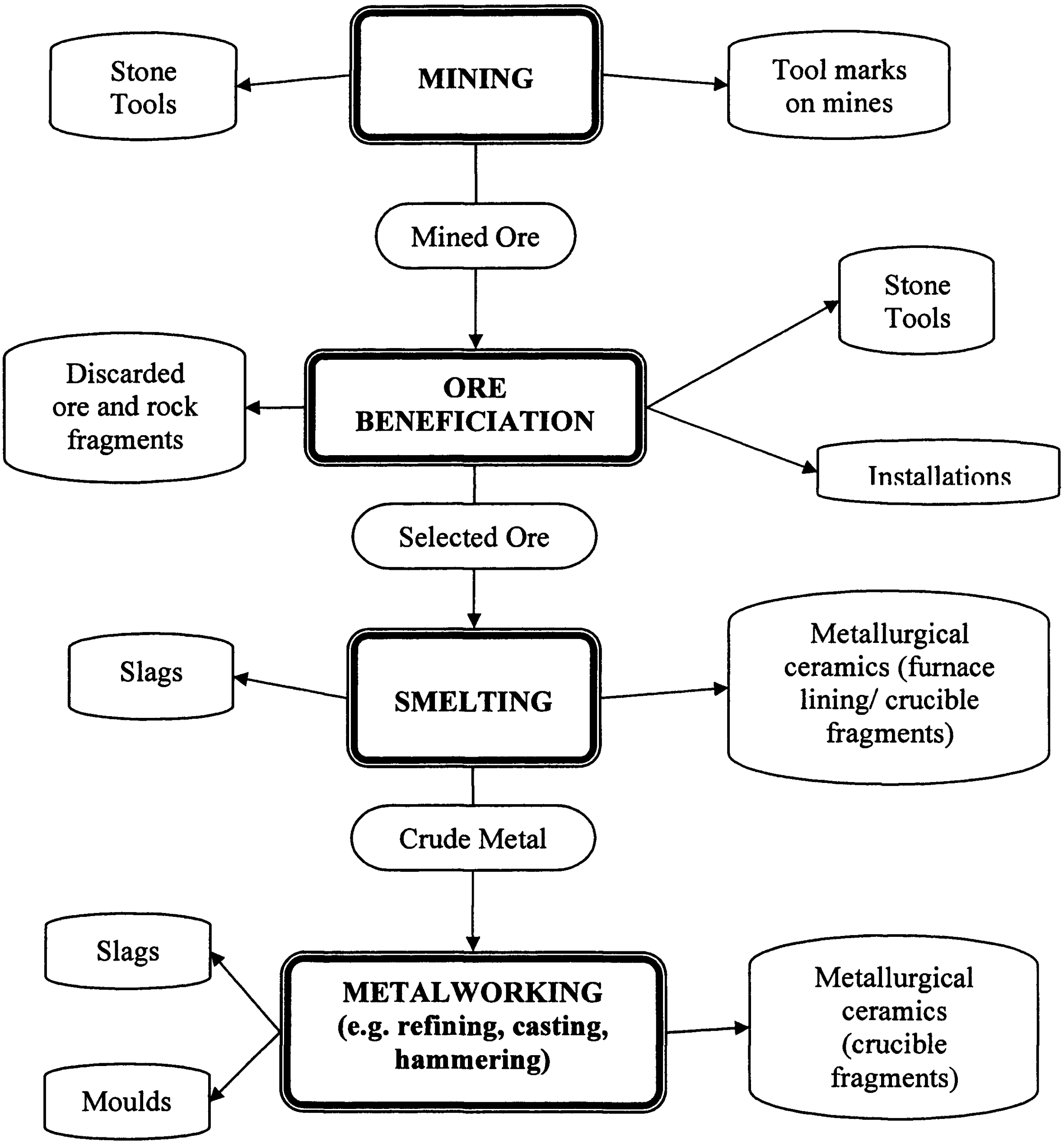


***Figure 3.1** General flow diagram showing basic steps followed in the production of copper artefacts with some of the main associated finds and other evidence, possibly recoverable in the archaeological record.*

## 3.3 Spatial distribution of activities within each site

### *3.3.1 Seriphos*

On Seriphos I had the opportunity to participate during fieldwork and was allowed to carry out my own sampling on each site, under the supervision of the representative of the Ephorate of Prehistoric and Classical Antiquities of the Cyclades, Ms O. Philaniotou. Excavation has not been possible to date so only surface samples could be collected.

The first question that needed to be addressed was whether there is evidence for the practise of other activities aside from smelting. The sites were thoroughly examined for any remaining features that could be associated with particular stages of the production sequence such as ore beneficiation or slag crushing installations. Notes and measurements were additionally made to draw some preliminary conclusions about the surface distribution of the material in each case.

Another important parameter that needed to be examined was the homogeneity of the slag heaps. As will be shown in Chapter 5, the material extends over a significant area on all sites. It was therefore essential to investigate whether the nature and composition of the slags are relatively similar throughout, or whether differences could be observed, which would need to be explained. The variability detected between the studies of Gale *et al.* (1985) and Bassiakos and Philaniotou (in press) in terms of arsenic content in the slags of Skouries (and also the lead isotope variability) raise the possibility that these heaps may not be the result of activities that necessarily exhibit altogether common characteristics. Ultimately, to address this question adequately, a much larger number of samples than could be analysed in the course of this thesis will be necessary, ideally also from excavated material. At this stage, however, some preliminary observations can be made based on an appropriate sampling methodology.

A thorough reconnaissance of the sites was carried out for this purpose before sampling. The two main slag heaps investigated, Kephala and Phournoi, were divided into appropriate sections largely determined by the observed surface distribution of material around the area. Samples were collected separately from each of these units. Certain characteristics of the slags were used as parameters to ensure that potentially different types of material were collected. The details of the sampling methodology will be discussed in more detail for each individual site in Chapter 5.

### *3.3.2 Daskaleio-Kavos*

Nearly all the metallurgical remains from Daskaleio-Kavos were collected during the gridded surface collection part of the collaborative project carried out on the site in 1987; stratified data are therefore not available. The question in this case was whether any particular patterns could be discerned from the two-dimensional distribution of the material across the site that would indicate particular working areas. The excellent records kept during collection have allowed such an assessment and the results are discussed in Chapter 6.

## 3.4 Technology of metallurgical activities

Ultimately, the goal of a scientific examination of metallurgical remains and investigation of relevant sites is to develop a detailed model for the metal production sequence from mining to artefact manufacture, which can then be used to draw socio-economic inferences concerning the organisation and role of these activities. Such a reconstruction involves both the spatial organisation of the activities and their technological details. While the discussion in the previous two sections can broadly be attributed to an investigation of the spatial distribution, this section deals with the questions regarding the technology of the metallurgical processes.

Figure 3.1 presents a general basic flow diagram for the production of copper, which includes some of the main types of waste products that may result. The use of such a general flow diagram suggests uniformity in the production of a particular metal. Indeed this picture holds only to the extent that these processes are governed by the universal laws of physics and chemistry, and that specific pathways need to be followed for the reduction of ores to metals. This does not, however, exclude the possibility for variability in individual contemporaneous local industries within each of the steps of the relevant production sequence. In addition, metallurgy has witnessed important technological changes through time, with processes showing broadly increasing sophistication, without meaning to imply a necessarily similarly linear or synchronous development in every case.

These points are clearly evident in a recent assessment of smelting technologies in the eastern Mediterranean from the Chalcolithic to the Late Bronze Age, where Craddock (2001: 158) notes that "although the principles of the furnaces and smelting technology were broadly similar from Crete to Palestine, there were significant differences between the processes at each of the sites investigated that were only partly attributable to local ore types and environment". Ottaway (2001) also demonstrates with examples the possibilities for variability in each step of the production sequence, with particular reference to recognising innovation and specialisation.

It is therefore important to understand the details of these processes in each local industry in order both to evaluate the level of sophistication and complexity involved, and to identify any similarities or differences that may point to the existence of a uniform or localised, diverse technology within a region. The waste material of these operations present the best evidence in this direction as they retain some of the characteristics that indicate the relevant details sought for this purpose.

### *3.4.1 Nature of processes*

From Figure 3.1, one can see that the most common metallurgical remains, namely slags and metallurgical ceramics, can result from both smelting and melting. Examination of the composition and microstructure of both types of material will allow a clarification of the nature of the processes represented on each site. The context of the finds also plays a crucial role. For example, the scale and location alone of the slag heaps on Seriphos clearly point to smelting, without necessarily excluding other activities as well.

### *3.4.2 Technological parameters of processes*

Technological parameters include aspects such as the nature of the ores used (e.g. oxidic vs. sulphidic) and the accompanying host rock, furnace structure, redox and temperature conditions, use of fluxes etc. Which of these can be assessed in each case will naturally depend on the evidence available and will be discussed more fully in the results sections of each case study.

At this stage it is only noted that, apart from field observations on Seriphos, and macroscopic examination of the samples, compositional and microstructural analyses of the material have been carried out for this purpose. Slags are particularly informative in this respect as they are composed of different mineralogical phases, whose presence and relevant abundance determine the properties of the slag, and reflect directly some of the central technological parameters of the processes. The success of a metallurgical operation is mainly determined by the quality of slag produced (Bachmann 1982a). As the nature and composition of slags is in turn influenced by the raw materials and furnace conditions employed, the identification of the mineralogical constituents present can be used to draw conclusions concerning these parameters (e.g. Bachmann 1980, 1982a; Moesta and Schlick 1989). Additional evidence is obtained from similar analytical examination of other material present on these sites, such as discarded ore fragments and metallurgical ceramics.

### *3.4.3 Composition of the metal*

The final product of the metallurgical operations, the raw metal in the case of smelting or the finished object in the case of metalworking, is usually absent from the sites, with the exception of a few spills or fragments. These fragments and the tiny metallic inclusions usually entrapped within the slag were routinely analysed to measure the composition of the metal worked. This information is particularly important with reference to early copper alloys. As was discussed in the previous section, many of the EBA objects are either arsenic or tin bronzes, but with the exception of a few analyses of slags from Skouries (Gale and Stos-Gale 1989a) evidence for their production or working is lacking. One of the aims of this examination was, consequently, to investigate whether the relevant activities were associated with processing 'pure' or alloyed copper.

## 3.5 Seriphos as a potential source of copper ores

The archaeometallurgical projects on Kythnos and Siphnos, where EBA metal production sites have been confirmed, have shown that appropriate ores were present on these islands, usually in relative proximity to the sites. Clearly, the existence or not of a similar pattern on Seriphos needs to be investigated.

Large copper ore deposits are not known on Seriphos. Copper minerals are, however, present, usually in small quantities and dispersed in various locations around the island. Two such mineralisations have been reported by Gale and Stos-Gale (1989a, 2002). A full-scale geological/archaeomining survey, as was carried out on Siphnos (Wagner and Weisgerber 1985), combined with a characterisation of the island's copper ore occurrences, was not possible within the time and resource limitations of this thesis. Instead, a preliminary reconnaissance of potential copper sources was undertaken. This exercise aimed at highlighting the presence of copper on Seriphos, hopefully opening the route to future more detailed research. Details of the methodology followed and results obtained are presented in Chapter 4.

## 3.6 Sample preparation and analytical techniques

The scope of the analytical investigation was to address questions regarding the technology of the processes involved. As these sites have not been studied before, a basic characterisation of the materials was necessary. Broadly, the present examination can be separated into two parts, which are routinely used in the characterisation of metallurgical remains: the bulk composition measurements and the examination of the microstructure. Use of particular techniques for each was largely dependant on availability of instruments.

This section presents a brief outline of those aspects of the laboratory methodology that were common to all the material examined. Only the specifications for the instruments used for analysis are given, together with any particular attributes specifically used in this thesis. The theory behind each method and description of relevant instruments are extensively discussed in the literature (see for example Ciliberto and Spoto 2000; Tite 1972 and references within) and are not repeated here.

### *3.6.1. Examination of the microstructure*

The microstructure of the material examined in this thesis was studied using a combination of optical and electron microscopy. Polished mounted sections were prepared for this purpose.

#### *3.6.1.1 Preparation of mounted sections*

Polished mounted sections instead of thin sections were prepared for use with optical and electron microscopy as only the former are appropriate for use with reflected light and electron microscopy and easier to prepare. A section was cut from each specimen, mounted in resin (Epoxy resin MetPrep) and allowed to set overnight. The sample was then progressively ground through a series of Si-C grinding papers to 4000 mesh and then polished using diamond paste to ¼ μm. The samples were carbon coated for use with electron microscopy to reduce the amount of surface charging.

#### *3.6.1.2 Optical microscopy*

Examination of the microstructure of the metallurgical remains was carried out first on a reflected light optical microscope. Reflected light microscopy was used instead of transmitted light as the former allows the identification of opaque phases commonly present in slags (e.g. metals, sulphides etc.). Individual phases and inclusions present in the metallurgical remains can be identified on the optical microscope based on differences in their optical properties (Craig and Vaughan 1981; Ramdohr 1980). Additionally, qualitative observations on other features relevant to microstructural study such as porosity, degree of heterogeneity, and relative abundance and size of different phases, were noted.

#### *3.6.1.3 Electron microscopy*

Electron microscopy offers the advantage of allowing visual imaging and simultaneous compositional measurements of small areas or points within a section. The method was used to support the optical identification of minerals and provide additional data on the composition of individual phases. The entrapped metal prills or small isolated metal fragments were also analysed with these techniques.

Two instruments were used for the analysis of individual phases within the examined specimens: a scanning electron microscope with an attached energy-dispersive spectrometer (EDS-SEM: JEOL JSM-35CF) and an electron microprobe with an attached wavelength-dispersive spectrometer (WDS-EPMA or EPMA: JEOL SUPERPROBE JXA-8600). The theory behind each type of instrument and spectrometer is discussed by Scott *et al.* (1995) and Watt (1997). The WDS-EPMA offers several advantages in quantitative analysis compared to the EDS-SEM (e.g. better detection limits and accuracy) but is also restricted by several limitations (see Watt 1997: 431, Table A3.4 for a comparison of the two spectrometers). Because of the nature of wavelength-dispersive spectrometers only a selection of elements can be analysed in each run, compared to the entire spectrum analysed in energy-dispersive systems. Measurements are hence generally much slower, while in the case of these two particular instruments access to the electron microprobe was much more limited. For these reasons the scanning electron microscope was used routinely for phase analyses, while the electron microprobe was only used for a small number of samples. More specifically, phase analyses on the WDS-EPMA have only been carried out on a selection of samples from the sites of Kephala and Phournoi. Points were analysed for this purpose on both instruments as the majority of phases studied are too small to allow area measurements.

Phase analyses on the EDS-SEM were carried out at 20 kV, using the Phi-Rho-Z correction procedure (ISIS analytical software by Oxford Instruments). The detector was calibrated at regular intervals against a cobalt standard. The detection limits of the instrument are approximately 0.1 % but are also largely dependant on the nature of the element analysed for and potential matrix effects. The performance of the instrument was tested by analysing a set of Certified Reference Materials (CRM) and comparing the results obtained with the certified values given in each case. The nature of CRMs used and a full list of results from these analyses are given in Appendix 1 (Tables A1.1 and A1.2). Table 3.1 below presents the averages and normalised averages[3.2] of these measurements. The obtained totals are lower than expected in all the CRMs examined. The light elements, sodium, magnesium, aluminium, and silicon are underestimated in all the samples. The deviation for each element is different between specimens, which is largely due to different matrix effects. Analyses for the elements between phosphorus and manganese show close correspondences with the certified values, at least in the relatively low amounts (with the exception of calcium) these are present in the analysed CRMs. Iron contents are much lower than the certified values in the case of the iron-rich CRMs (FER-4 and ECRM676-1), while they are in good agreement in the case of the basalt glasses (BHVO-2 and BCR-2). Results obtained with this technique have to be considered only semi-quantitatively. For the purpose of phase analyses, the EDS-SEM is, however, appropriate as identification is additionally facilitated by the optical observations.

---

[3.2] The averages obtained have been normalised to the sum of the certified analyses instead of 100 % in order to make the results more directly comparable.

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FER4(A) | b.d.l. | 1.25 | 1.59 | 42.4 | b.d.l. | 0.33 | 0.25 | 2.67 | b.d.l. | b.d.l. | 0.46 | 0.22 | 29.3 | 78.5 |
| FER4(AN) | b.d.l. | 1.52 | 1.94 | 52.0 | b.d.l. | 0.40 | 0.30 | 3.27 | b.d.l. | b.d.l. | 0.57 | 0.27 | 35.9 | 96.2 |
| **FER4** | **0.05** | **1.41** | **1.70** | **50.1** | **0.13** | **0.11** | **0.29** | **2.23** | **0.07** | **n.r.** | **n.r.** | **0.19** | **40.0** | **96.2** |
| ECRM676-1(A) | b.d.l. | 1.15 | 5.12 | 13.0 | 1.35 | 0.38 | 0.50 | 18.7 | 0.23 | 0.16 | b.d.l. | 0.89 | 45.7 | 86.0 |
| ECRM676-1(AN) | b.d.l. | 1.34 | 5.98 | 15.2 | 1.57 | 0.44 | 0.58 | 21.8 | 0.27 | 0.18 | b.d.l. | 1.04 | 53.4 | 100 |
| **ECRM676-1** | **0.13** | **1.92** | **6.42** | **13.7** | **1.35** | **0.30** | **0.52** | **17.9** | **0.32** | **0.12** | **n.r.** | **1.08** | **56.8** | **100** |
| BHVO-2(A) | 2.14 | 5.86 | 11.1 | 43.6 | b.d.l. | b.d.l. | 0.43 | 10.8 | 2.61 | b.d.l. | b.d.l. | b.d.l. | 11.6 | 88.3 |
| BHVO-2(AN) | 2.43 | 6.65 | 12.6 | 49.5 | b.d.l. | b.d.l. | 0.49 | 12.3 | 2.96 | b.d.l. | b.d.l. | b.d.l. | 13.2 | 100 |
| **BHVO-2** | **2.22** | **7.23** | **13.5** | **49.9** | **0.27** | **n.r.** | **0.52** | **11.4** | **2.73** | **0.03** | **0.03** | **0.13** | **12.3** | 100 |
| BCR-2(A) | 2.72 | 2.91 | 11.1 | 47.4 | b.d.l. | 0.42 | 1.61 | 6.72 | 2.21 | b.d.l. | b.d.l. | 0.19 | 13.1 | 88.6 |
| BCR-2(AN) | 3.07 | 3.29 | 12.6 | 53.6 | b.d.l. | 0.47 | 1.82 | 7.59 | 2.50 | b.d.l. | b.d.l. | 0.21 | 14.8 | 99.9 |
| **BCR-2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **n.r.** | **1.79** | **7.12** | **2.26** | **0.04** | **0.00** | **0.15** | **13.8** | **99.9** |

***Table 3.1*** *Averages (A) and averages normalised to the sum of the certified values (AN) of the analyses of Certified Reference Materials on the EDS-SEM: JEOL JSM-35CF (full results in Appendix 1, Table A1.2). Rows in bold correspond to the certified values given for each specimen (n.r.: not reported). Highlighted values should be read as elements instead of oxides.*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | NiO | CuO | $SnO_2$ | $Sb_2O_5$ | PbO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BIR-1(A) | 1.87 | 9.73 | 15.7 | 46.9 | 0.03 | b.d.l. | 13.6 | 0.93 | 0.17 | 11.0 | 0.01 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.9 |
| **BIR-1** | **1.82** | **9.70** | **15.5** | **48.0** | **0.02** | **0.03** | **13.3** | **0.96** | **0.18** | **11.3** | **0.02** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **101** |
| BHVO-2(A) | 2.27 | 7.15 | 14.0 | 50.5 | 0.29 | 0.44 | 11.6 | 2.75 | 0.16 | 11.4 | 0.02 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| **BHVO-2** | **2.22** | **7.23** | **13.5** | **49.9** | **0.27** | **0.52** | **11.4** | **2.73** | **0.13** | **12.3** | **0.01** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **100** |
| BCR-2(A) | 2.30 | 3.65 | 14.0 | 54.5 | 0.41 | 1.63 | 7.40 | 2.24 | 0.17 | 13.8 | 0.01 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| **BCR-2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **1.79** | **7.12** | **2.26** | **0.15** | **13.8** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **100** |
| GlassA(A) | 14.4 | 2.60 | 0.93 | 67.0 | 0.10 | 2.91 | 5.08 | 0.82 | 1.01 | 1.02 | 0.02 | 1.09 | 0.21 | 1.56 | 0.06 | 98.6 |
| **GlassA** | **14.3** | **2.66** | **1.00** | **67.0** | **0.13** | **2.87** | **5.03** | **0.79** | **1.00** | **1.09** | **0.00** | **1.17** | **0.19** | **1.75** | **0.12** | **99.9** |
| GlassB | 17.2 | 1.01 | 4.30 | 62.4 | 0.77 | 1.04 | 8.90 | 0.09 | 0.19 | 0.36 | 0.09 | 2.41 | 0.02 | 0.33 | 0.45 | 99.5 |
| **GlassB** | **17.0** | **1.03** | **4.36** | **62.3** | **0.82** | **1.00** | **8.56** | **0.09** | **0.25** | **0.34** | **0.10** | **2.66** | **0.04** | **0.46** | **0.61** | **99.8** |
| GlassC | 1.03 | 2.64 | 0.87 | 34.7 | 0.11 | 3.17 | 5.48 | 1.25 | b.d.l. | 0.23 | 0.08 | 1.12 | 0.18 | b.d.l. | 36.7 | 87.6 |
| **GlassC** | **1.07** | **2.76** | **0.87** | **36.2** | **0.14** | **2.84** | **5.07** | **0.79** | **0.00** | **0.34** | **0.00** | **1.13** | **0.19** | **0.03** | **36.7** | **88.1** |
| GlassD(A) | 1.35 | 3.85 | 5.26 | 55.1 | 4.22 | 11.8 | 15.3 | 0.41 | 0.53 | 0.51 | b.d.l. | 0.30 | 0.06 | 0.69 | 0.22 | 99.5 |
| **GlassD** | **1.20** | **3.94** | **5.30** | **55.5** | **3.93** | **11.3** | **14.8** | **0.38** | **0.55** | **0.52** | **0.00** | **0.38** | **0.10** | **0.97** | **0.48** | **99.9** |

***Table 3.2*** *Averages (A) of the analyses of Certified Reference Materials on the WDS-EPMA: JEOL SUPERPROBE JXA-8600 (full results in Appendix 1, Table A1.3). Samples Glass B and Glass C were only analysed once. Rows in bold correspond to the certified values given for each specimen (n.r.: not reported). Highlighted values should be read as elements instead of oxides.*

Analyses of oxidic phases on the WDS-EPMA were carried out at 15 kV, using the ZAF correction procedure and searching for the following elements: Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, and Cu, expressed as oxides. A number of CRMs were analysed on this instrument and the results are presented in detail in Appendix 1 (Table A1.3). Averages and certified values are given in Table 3.2. Unfortunately homogeneous sections of iron-rich materials were not available in the CRM collection and pressed powders as used in the EDS-SEM (see Appendix 1) could not be used in this case. The results obtained show very close agreement with the certified values for all the examined specimens.

The electron microprobe was additionally used for all the measurements of entrapped metal and sulphidic prills in the slags or isolated metal fragments. In this case measurements were made at 25 kV and the instrument was set up to measure with point analyses for the following elements: S, Cl, Fe, Co, Ni, Cu, Zn, As, Ag, Sn, Sb, Pb, Au, Bi. Each element was tested separately against an appropriate standard before each session. The WDS spectrometer offers an important advantage against the EDS for the measurement of copper alloys. The $K\alpha_1$ energy line of arsenic overlaps with the $L\alpha_1$ line of lead and does not allow quantitative EDS measurement of arsenic and lead separately in the case of samples where both elements are present. Both elements are important for early copper metallurgy and indeed they were found to co-exist in some of the samples from Daskaleio-Kavos (see Chapter 6). The WDS spectrometer allows one to overcome this problem by setting the detector to measure arsenic in the $L\alpha_1$ line (see also Shugar 2000: 148-9) as was done in the analyses presented in this thesis.

### *3.6.2. Bulk composition measurements*

Bulk composition measurements were carried out using a polarising energy dispersive X-ray fluorescence spectrometer ((P)ED-XRF) or the electron microprobe (WDS-EPMA). Pressed pellets were used in the first case and polished mounted sections in the second.

### *3.6.2.1 Preparation of pellets for (P)ED-XRF*

Pressed pellets were used for (P)ED-XRF measurements. Although whole objects can be analysed on the instrument, pellets were preferred as they ensure homogenisation of the material and provide a flat surface allowing for quantitative measurements. Sample removal was not a problem with the material examined in this thesis. For the preparation of the pellets, samples were cut from each specimen, ensuring that their exterior surface was not included, in order to avoid contamination from the soil. These were covered in paper and crushed with a hammer into smaller pieces. An automatic agate ball mill was used for pulverisation. Samples were run for approximately 10 minutes until a fine powder was obtained. The vessel and agate balls were cleaned thoroughly with industrial methylated spirit after each run and additionally with sand after approximately three runs, or as necessary, to avoid cross-contamination. Powders were subsequently transferred to glass tubes, covered with a medical wipe paper to avoid contamination, and dried overnight in an oven at 105 °C.

Pellets were prepared using 2.5 g of sample diluted with 0.4 g of industrial wax. The two components were mixed thoroughly until a visually homogeneous mixture was obtained. Relatively small quantities of sample were used, in order to be able to include some of the smaller specimens, while having in all cases similar-sized pellets. In the case of large finds, larger quantities of sample were pulverised and homogenised before weighing out the pellet sample to ensure a composition more representative of the whole. The samples were pressed to a 24 mm diameter pellet, with a resulting thickness of around 0.3 cm. Approximately 2 g of boric acid powder were added on top of the sample at the press to create a supporting back and to enhance the durability of the pellet.

### *3.6.2.2 Polarising Energy Dispersive X-ray Fluorescence Spectroscopy*

The (P)ED-XRF spectrometer used in this thesis is a *Spectro X-Lab Pro2000*. The specific technique was chosen among a range commonly used for bulk composition measurements (e.g. atomic absorption spectroscopy and neutron activation analysis) for several reasons. First, it was easily and freely accessible to the author. Secondly, it allows, with some limitations (e.g. overlapping peaks), quick and reliable quantitative results, if an appropriate sample preparation methodology is used (see above). The technique was therefore appropriate for the purposes of this thesis, which aimed at providing a first characterisation of a relatively large number of samples.

Measurements for slags and ores rich in iron were carried out using the calibration method developed specifically for iron-rich materials (Slag_Fun) by Veldhuijzen (2003) with some modifications. Calibration curves for each element have been constructed by measuring and comparing with a set of CRMs. However, elements such as: Cu, Ni, Zn, As, Pb, Ag, Sn, Sb, Hg, Bi, which are important to the study of copper slags, are under-represented in these CRMs. Their calibration gradients were therefore imported to the Slag_Fun method from one of the standard calibration methods of the instrument (T-quant) and the resulting method has been named Cu_Slag. Non-iron rich materials have been measured using T-quant.

With every run a glass tablet (Sq-1), which was provided with the instrument, was used to check for contaminants and instrument drift. Additionally, a set of three CRMs were included each time. These were selected out of the four following samples: BCR-2, ECRM681-1, FER-2, Slag W-25:R, and were prepared as pellets with the same quantities and procedure described above for the other samples. The analyses were used both to examine the quality of the data produced each time but also to test the overall performance of the instrument. Table 3.3 gives a summary of the averages and normalised averages of all the analyses for each CRM together with their certified composition for comparison (for a description of the four CRMs used and a full list of results of each individual run see Appendix 1: Tables A1.1, A1.4a and A1.4b). The results are in good agreement with the certified values for the major and minor elements, particularly when comparing with the normalised values (see below for necessity to normalise results). Deviations are naturally seen, but these are neither consistent (elements overestimated in some CRMs are underestimated in others probably due to different matrix effects), nor particularly high. Veldhuijzen (2003) notes that the lighter elements sodium, magnesium, and aluminium may be slightly problematic using the currently set calibrations, but the variations observed in these analyses are again not systematic between the different samples and an absolute associated error cannot be predicted.

In terms of trace elements very few results are reported among the certified data (see Table A1.4b). For elements such as barium and strontium, which are reported for more than one CRM, the comparison with the results obtained with the (P)ED-XRF spectrometer is good. Additionally, the instrument has been repeatedly tested by other users and overall the data obtained for the majority of trace elements are very satisfactory (Groom pers. comm.). Two elements have been found to be problematic (Groom pers. comm.) and have been excluded from the results presented in this thesis. These are cobalt (Co) and niobium (Nb), which are systematically overestimated in iron-rich materials, the first due to an overlap with the iron energy line and the second because of problems with the calibration curve of the element in the analytical software program used.

The overall totals of these analyses are in some cases slightly lower than expected (see Table 3.3). This is most probably due to the small size of the analysed pellets (diameter 24 mm) in comparison to the sample holder (diameter 36 mm). A smaller supportive paper base (cut as an open circle) was prepared each time and inserted in the sample holder to hold the specimen analysed. As a result, a small part of the analysed sample may have been partially obscured from the detector by the cut paper. The amount of sample hidden will be variable between different analyses as it depends on the position of the cut paper relative to the detector window in each case. Bulk analyses obtained by this method were therefore consistently normalised in order to obtain more comparable results.

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BCR2(A) | 2.83 | 2.18 | 14.9 | 51.8 | 0.24 | 0.02 | 1.82 | 6.66 | 2.17 | 0.07 | b.d.l. | 0.17 | 13.2 | 96.1 |
| BCR2(AN) | 2.94 | 2.27 | 15.5 | 53.9 | 0.25 | 0.02 | 1.89 | 6.92 | 2.25 | 0.07 | b.d.l. | 0.18 | 13.7 | 99.9 |
| **BCR2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **n.r.** | **1.79** | **7.12** | **2.26** | **0.04** | **0.00** | **0.15** | **13.8** | **99.9** |
| ECRM681-1(A) | 0.29 | 1.13 | 11.8 | 16.5 | 1.90 | 0.09 | 0.52 | 3.55 | 0.45 | 0.14 | 0.07 | 0.27 | 45.5 | 82.2 |
| ECRM681-1(AN) | 0.30 | 1.17 | 12.3 | 17.1 | 1.97 | 0.10 | 0.54 | 3.67 | 0.47 | 0.14 | 0.07 | 0.28 | 47.1 | 85.2 |
| **ECRM681-1** | **0.09** | **1.48** | **10.6** | **17.8** | **2.02** | **0.26** | **0.59** | **3.92** | **0.48** | **0.15** | **0.06** | **0.28** | **47.5** | **85.2** |
| FER2(A) | 0.40 | 2.56 | 6.04 | 51.9 | 0.29 | 0.15 | 1.57 | 2.19 | 0.18 | b.d.l. | b.d.l. | 0.13 | 36.1 | 101 |
| FER2(AN) | 0.40 | 2.53 | 5.99 | 51.4 | 0.29 | 0.15 | 1.56 | 2.17 | 0.18 | b.d.l. | b.d.l. | 0.12 | 35.8 | 101 |
| **FER2** | **0.41** | **2.10** | **5.16** | **49.2** | **0.27** | **0.17** | **1.33** | **2.17** | **0.18** | **n.r.** | **n.r.** | **0.12** | **39.4** | **101** |
| Slag W-25:R(A) | 0.93 | 0.17 | 7.12 | 22.0 | 0.14 | 0.09 | 1.03 | 1.40 | 0.33 | 0.03 | 0.01 | 2.72 | 64.5 | 101 |
| Slag W-25:R(AN) | 0.95 | 0.18 | 7.25 | 22.4 | 0.14 | 0.09 | 1.05 | 1.42 | 0.34 | 0.03 | 0.01 | 2.78 | 65.7 | 102 |
| **Slag W-25:R** | **0.61** | **0.38** | **7.14** | **24.7** | **0.26** | **0.04** | **1.02** | **1.42** | **0.32** | **0.02** | **0.00** | **3.01** | **63.5** | **102** |

***Table 3.3** Averages (A) and averages normalised to the sum of the certified values (AN) of the analyses of Certified Reference Materials (full results in Appendix 1, Table A1.4) on the (P)ED-XRF: Spectro X-Lab Pro2000 (major and minor elements in weight %). Rows in bold correspond to the certified values given for each specimen (n.r.: not reported). Highlighted values should be read as elements instead of oxides.*

### *3.6.2.3 Bulk analyses of small samples using the electron microprobe*

The majority of specimens from Daskaleio-Kavos were too small to allow for the preparation of pressed pellets for (P)ED-XRF in addition to the mounted sections. The sections prepared for microscopic examination had to be used for the bulk analyses as well. Area analyses on the electron microprobe were used for this purpose. The electron microprobe was selected instead of the (P)ED-XRF spectrometer for three reasons. First, the small size of many of these sections would result in very low overall totals if analysed on the (P)ED-XRF. Second, some of the specimens bear significant quantities of both lead and arsenic (see Chapter 6) and therefore, for the reasons discussed previously, a wavelength-dispersive spectrometer would allow better quantification. Third, this methodology allowed for separate measurement of the ceramic and slag parts of the metallurgical ceramics, which needed to be examined in the case of Daskaleio-Kavos, in order to address specific technological questions (see Chapter 6).

The WDS was set up to measure at 15 kV for the following elements: Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, As, Sn, Sb, Pb, Bi, presented as oxides, and Cl. This selection of elements was based on the results of an initial screening analysis by (P)ED-XRF and additional theoretical considerations. Ten to fifteen measurements of areas magnified at 800x (each measuring roughly 160x120 μm) were taken for each sample and the mean of these analyses was calculated. The electron microprobe was programmed to carry out the analyses at random intervals to avoid any subjective bias by the operator. As a result it was possible that some areas included exceptionally large holes. For this reason, measurements with particularly low totals were not included in the final mean. The results were subsequently normalised to 100 % to compensate for porosity.

A small number of slag samples from Daskaleio-Kavos were sufficiently large to allow for preparation of pressed pellets and mounted sections and these specimens were analysed both by (P)ED-XRF and WDS-EPMA respectively. Apart from the obvious differences, such as the measurement of only certain elements on WDS-EPMA compared to the entire spectrum on (P)ED-XRF, the two instruments show close correspondences if one accounts for the inherent heterogeneity of slags (see Chapter 6 for results and discussion).

# CHAPTER 4.

# Seriphos: geology and potential copper sources

## 4.1 Introduction

Seriphos is situated between Kythnos and Siphnos (Figure 1.1), the two islands that have to date provided the most substantial evidence for the presence of copper, lead and silver sources in the Cyclades and for the production of these metals during the EBA. The slag heaps on Seriphos, which will be discussed in Chapter 5, testify to the local practice of copper production at this island as well. But does the island bear ores that could potentially have been used for these activities? While Seriphos is well known for its extensive iron deposits, which have been subjected to intense modern mining, little is known about the existence of copper minerals on the island. References to small occurrences can be found in the relevant geological literature, but as the majority of geological research carried out on the island was directed at the identification of ore deposits of modern economic significance, these are usually merely mentioned in passing. Two occurrences are also reported by Gale *et al.* (1985) and Gale and Stos-Gale (2002). The geological reconnaissance carried out for this thesis therefore represents the first extensive study targeted specifically at an assessment of copper resources on Seriphos.

In this chapter, a brief overview of the island's geology is presented, based on the relevant literature. Subsequently, five locations with copper mineralisations, identified during the geological field investigation, are presented in more detail together with some preliminary analyses.

## 4.2 Aims and methodology of the geological investigation of Seriphos

The aim of the geological study of Seriphos was to draw attention to the presence of copper occurrences on the island and provide a basic characterisation of their nature.

The methodology followed for this purpose can be summarised as follows:

1. The literature on the geology of Seriphos was studied and references to copper minerals were noted.
2. A selection was made among the areas identified from the literature as potentially interesting for copper and these were visited and examined in the field. The search involved a general reconnaissance of the area in question, rather than a systematic survey, and was also greatly facilitated by conversations with local inhabitants. The survey was not exhaustive and the examples presented below are only some of the copper occurrences present on Seriphos. It should also be noted that the investigation was limited to surface observations. Modern mine galleries were not entered, as several of the latter on Seriphos are considered dangerous, due to the possibility of collapse, and entrance is forbidden (Papastavrou and Zographos 1979: 3).
3. Once a mineralisation was identified, the general characteristics of its geological setting were noted, including evidence for modern iron mining and its effects on the surrounding landscape. Samples were collected for analysis.
4. In addition to the above fieldwork, which covered different parts of the island selected on the basis of geological reports, attention was also directed to the areas surrounding the slag heaps, in search of possible sources that might be located in the direct vicinity. The search was of necessity again non-comprehensive so that absence of evidence cannot at this stage be considered evidence for absence.
5. The final step of this study involved a basic laboratory investigation of the collected samples using X-ray fluorescence bulk analyses of pressed tablets (see section 3.6.2). Three runs were carried out for each sample. Tables given in this chapter present averages of the three analyses in each case and only include elements consistently identified above 0.1 %. Full results are presented in Appendix 2. A very limited number of samples were examined from each mineralisation. The purpose of these preliminary analyses was to demonstrate the presence of copper in each case, determine whether the associated minerals were present in primary sulphidic and/or secondary oxidic form and identify any major elements accompanying the copper minerals, particularly with reference to those that could have played a role in

prehistoric copper alloying, such as arsenic, lead or tin. The results should not be viewed as representative of each occurrence, as systematic sampling and a much larger body of analyses would be necessary in that case.

## **4.3 The geology of Seriphos** (Figure 4.1)

The geology of Seriphos is mainly determined by the intrusion of a granodioritic magma within a system of previously metamorphosed rocks (Ktenas 1917; Marinos 1951; Perdikatsis and Papastavrou 1993; Salemink 1985). The intrusion of the granodiorite, which is dated to about 8.3-9.2 million years ago (Gournellos *et al.* 1986), resulted in metamorphic and metasomatic phenomena affecting the surrounding rock units. Salemink (1985) discusses these processes in more detail and proposes, on the basis of extensive petrological and mineralogical studies on the island, a sequence of events for the formation of the observed geological setting. The presence of pneumatolic and hydrothermal metal-bearing solutions caused the formation of the substantial ore deposits known on the island (Marinos 1951). Particularly important in the search of metal sources is the observation of skarn units in several parts along the metamorphic contact zone. These metasomatic calcium-iron-magnesium-silicon bearing rocks are often found accompanied by iron, copper, zinc, lead and other metal deposits (Einaudi *et al.* 1981; Salemink 1985). The geological setting of Seriphos is divided in three broad categories of rocks, the metamorphic rocks, the granodiorite and the sedimentary deposits (Gournellos *et al.* 1986). In the following paragraphs these are described briefly and the types of large ore deposits known on the island are discussed.

### *4.3.1 The geological setting*

#### *4.3.1.1 The granodiorite*

The granodiorite extends over more than one third of the surface of the island, specifically the central and south-eastern parts. Its composition corresponds to a biotite-hornblende granodiorite with a grain size rarely exceeding 2 mm (Marinos

1951; Salemink 1980). Its main constituents are plagioclase, orthoclase, microcline, biotite, green hornblende, and quartz, while apatite, sphene, zircon, orthite and ore minerals are often found as accessory components (Marinos 1951; Salemink 1980). In some of the flat-lying areas near the contact zone with the surrounding rocks, the granodiorite forms border facies, which are similar in chemical and mineral composition to the main magmatic body but differ in texture and structure (Salemink 1980, 1985). They are coarser grained with an average grain size of 5 mm. A large number of igneous dykes, with compositions ranging from dioritic to granitic, spread out from the granodiorite to the surrounding metamorphic units (Marinos 1951: 102-3; Salemink 1980: 349-50).

#### *4.3.1.2 The metamorphic rocks*

Two tectonic units can be distinguished within the metamorphic system, a lower and an upper unit (Gournellos *et al.* 1986: 85, Figure 1). The lower unit consists of gneisses, marbles and schists.

The gneiss unit is exposed in different areas at the south and southwest part of the island. The gneisses are mainly composed of quartz, with albite-oligoclase and muscovite present in smaller amounts. Idiomorphic biotite forms the major constituent of the dark bands of the gneisses. Minerals often identified in accessory amounts include sphene, zircon, apatite, and opaque minerals (Salemink 1980).

A relatively large marble unit is exposed at the southwest of the island, while smaller units are also seen east of the Avessalos bay and at the centre of the island in contact with the granodiorite. The lower half of the marbles are grey, dolomitic and thin-bedded, while the upper half are white and calcitic. Their principal constituents are calcite, dolomite and minor quartz in the former, and calcite and minor quartz in the latter (Salemink 1980, 1985).

The schist unit extends across the northern part of the island and in smaller areas in the southwest and southeast. Gradual changes are seen across the schist unit as a result of the metamorphic reactions caused by the granodiorite intrusion. The north part consists of albite-sericite-chlorite schists. Moving towards the intrusive contact, zones of epidote-actinolite schists, diopside-hornblende-hornfels, scapolite-diopside-hornblende, and finally scapolite-garnet-hornblende-hornfels (boundaries marked on Figure 4.1 by isograds) are seen progressively (Salemink 1980, 1985). Large masses of white marble are observed in some areas within the schist unit, while a blue marble three to four meters thick occurs at the south-western part (Gournellos *et al.* 1986).

The upper unit occupies the extreme south-western peninsula and comprises crystalline dolomites, schists and ophiolitic rocks (Gournellos *et al.* 1986). Magnetite and serpentine are the primary components of the latter, while sporadically grains of primary olivine are preserved (Salemink 1980).

#### *4.3.1.3 The sedimentary deposits*

Sedimentary deposits occupy very small areas on the island and do not contribute significantly to the general morphology. They are mainly recent river deposits and are usually located along the coasts and in the low gradient surfaces in the centre of the island (Gournellos *et al.* 1986).

### ***4.3.2 The ore deposits***

Marinos (1951) divides the ore deposits of Seriphos in three categories and the same categorisation is followed here:
a) rich iron ores (magnetite)
b) poor iron ores (limonite, hematite etc)
c) mixed sulphidic ores

#### *4.3.2.1 Magnetite deposits*

Magnetite deposits of different dimensions are found nearly all along the contact zone of the granodiorite mass and the metamorphic rocks. These are of pneumatolitic and hydrothermal origin (Ktenas 1917; Marinos 1951). Magnetite is found dispersed as small crystals within the host rocks or less frequently in large bodies. The formation of magnetite was dependant on a number of factors, including the nature of the surrounding metamorphic units, the gradient of the contact zone, and the relative depth from the apex of the granodiorite (Marinos 1951; Zachos 1951). In general, the hornfelsic schists are more susceptible to magnetite formation, while a low gradient and a vertical proximity to the granodiorite apex, as well as the presence of igneous dykes in the surrounding units, are also favourable conditions (Marinos 1951; Zachos 1951). As a result, the form and quantity of magnetite occurrences varies in different regions of the contact zone.

The northern part of the contact zone can be divided into four areas with respect to the presence of magnetite deposits. These are only briefly described below, while a detailed account of the local geological setting and its association with the development of magnetite occurrences is presented by Marinos (1951) and Zachos (1951). The eastern part from Diasela to the bays of Kentarchos and Tracheilas shows no significant concentrations of magnetite deposits although it is included in the schist metasomatic zone, which appears to be the most susceptible to magnetite formation (Marinos 1951; Zachos 1951). The second part includes the region extending between Diasela and Ayios Dimitrios further to the southwest, but still within the schist unit. Within 200 m of the contact zone massive skarn and ore deposits have developed. Magnetite is found throughout this area in small concentrations, as well as in a few larger deposits. It is often associated with smaller concentrations of pyrite and minor chalcopyrite (Salemink 1980). Deposits exploited in the early 20th century include those of Playia, Ayios Dimitrios and Ayios Vlasios (Marinos 1951; Zachos 1951). The third part extends from Ayios Dimitrios to Mykonion where the granodiorite is in contact mainly with marbles and gneiss. At Vounies metasomatic processes within the dolomitic marbles resulted in extensive skarn and iron ore formation (Marinos 1951; Salemink 1980). Contact with the granodiorite mass has in some parts affected the marble, resulting in the formation of diopside (Marinos 1951). Magnetite is the main component of the ore bodies. Associated minerals include pyrite and minor chalcopyrite. Small veins of blue-green actinolite, hematite, quartz, calcite and/or adularia cut through these bodies. A small, localised copper mineralisation in the form of the secondary copper mineral chrysocolla has also been reported (Salemink 1980: 352). Dispersed grains of magnetite, pyrite and chalcopyrite are also found in the skarn zone surrounding the marble unit above the Avessalos bay (Salemink 1980). The gneiss unit in this area is frequently intersected by bodies of andraditic garnet, hedenbergitic diopside, and iron-rich epidote, which are usually accompanied by disseminated and small to medium magnetite deposits (Marinos 1951; Salemink 1980; Zachos 1951). In the fourth part, from Mykonion down to the bay of Koutalas, granodiorite is in contact with gneiss. The local geology and geomorphology does not favour formation of large deposits and magnetite occurrences are in general smaller and more dispersed (Marinos 1951; Zachos 1951).

In the southern part of the contact zone another three potentially interesting areas for magnetite formation are seen. On the south-western promontory of Chalara, layers of marble are observed within the schist unit in contact with the granodiorite body. Magnetite was formed in large bodies but these have been extensively mined in modern times (Zachos 1951). Magnetite in this area is associated with extensive skarns of hedenbergitic diopside and andraditic garnet. Accompanying minerals in this case include scapolite, actinolite and pyrite, while late veins of epidote, quartz, calcite and hematite cross through the system (Salemink 1980). Within the gneiss unit of Psari promontory at southern Seriphos, at the contact with the granodiorite, magnetite appears in considerable quantities as small crystalline particles (Marinos 1951; Salemink 1980). These have in parts been weathered to hematite and limonite (Zachos 1951). Finally, at the south-eastern promontory of Tsilipaki, the granodiorite mass comes in contact with gneisses and schists. Magnetite is frequent in disseminated grains within these rocks and less often in larger bodies, which have undergone modern exploitation (Marinos 1951: 116).

#### *4.3.2.2 Hematite-limonite deposits*

A different type of iron mineralisation is found at the western and south-western part of Seriphos (Marinos 1951; Papastavrou and Zographos 1979). Within the marble unit extensive hematite-limonite deposits were formed, which were independent of the previously described magnetite occurrences. These are of hydrothermal origin and their concentration at this part of the island is due to the presence there of marbles, which were susceptible to replacement by iron bearing solutions (Marinos 1951). The resulting ore is distributed unevenly within the marbles, resulting in irregular masses of differing richness in iron. Both at the lower dolomitic and at the upper calcitic marbles metasomatic reactions resulted in the formation of ankeritic dolomite in parts. The hematite-limonite ore is found associated with idiomorphic calcite and quartz. In the upper calcitic marbles barite and fluorite accompany the iron ore (Salemink 1980). Within the ankeritic dolomites small concentrations of pyrite, chalcopyrite and arsenical and oxidic minerals particularly of copper occur (Marinos 1951; Salemink 1980). The hematite-limonite mineralisation continues further north below the schist unit and is exposed again within the marbles above the Avessalos bay. Part of this entity lies beneath the sea level (Marinos 1951). Smaller, much more limited occurrences of this type of iron ore are also found in southeast Seriphos at the promontory of Tsilipaki, at the schist unit of south-western Seriphos and in small veinlets within the granodiorite (Marinos 1951).

The hematite-limonite ores have been extensively mined in modern times and it is estimated that 6.5 million tons were extracted in the period 1869-1940. Mining centres include Mega Leivadi, Koundouro, Avraam, Aspros Kavos, Mavra Voladia, Mountaki, Avessalos, Almiros, and Karvounolakkos (Marinos 1951: 118; Papastavrou and Zographos 1979). Remains of these operations are clearly evident today in the south-western part of the island. The ore was exported mainly abroad for smelting, while the only such attempts that took place in Greece were carried out in Euboea and proved unsuccessful (Marinos 1951: 123).

#### *4.3.2.3 Mixed sulphidic deposits*

In the area of Moutoula, in northeast Seriphos, mixed sulphidic deposits occur within the schist unit, which is frequently intersected by marble layers. Pyrite, sphalerite, and galena occur in different ratios across the deposits and are accompanied by hematite and quartz, as well as secondary oxidic minerals (Marinos 1951; Papastavrou and Zographos 1979). The deposits are believed to be of hypothermal origin and to have formed at the contact of the schist with the marble by replacement (Marinos 1951). The sources have been exploited in the nineteenth century for galena (Kordellas 1902: 17) and it has been suggested that one of the galleries may be related to operations carried out in antiquity (Gale and Stos-Gale 1981a; see also section 4.4.6). Similar ore deposits have been reported further south, in the vicinity of Pyrgos, still within the northern schist unit (Papastavrou and Zographos 1979).

## 4.4 Copper mineralisations investigated during the geological reconnaissance

From the above discussion it becomes apparent that small copper mineralisations are reported from various geological contexts around the island, usually as accompanying elements to the much larger iron ore deposits. In the following paragraphs specific mineralisations identified in the field during the geological reconnaissance are described in some more detail.

### *4.4.1 Kephala*

The promontory of Kephala is situated to the east of Ellinikon bay in the north-western part of the island (Figure 4.1). The copper slag heap of Kephala had been reported previously (Gale *et al.* 1985) and has been examined in more detail in this study (see Chapter 5). The small copper mineralisation discussed below was identified on our final visit to the Kephala slag heap. It is located approximately 750 m to the southeast of the heap, close to the Kephala tower (Figure 4.2). Initially only a localised green colouration was spotted on the schist bedrock (Figure 4.3), but upon breaking it became clear that the green copper minerals extended inside the rock (Figure 4.4), still, however, in very small quantities. Geological reconnaissance of the area in search of copper minerals had been carried out in all four previous expeditions of the author to Kephala, but this occurrence had been missed. This highlights the difficulty in identifying such small outcrops generally in the Cyclades and urges for more careful and systematic investigations before drawing conclusions on the presence or absence of sources in the proximity of metallurgical remains.

Geologically, Kephala belongs to the schist unit of northern Seriphos, while small quartz veins, which run parallel or perpendicular to the schist direction, are also typically observed. A large outcrop of volcanic rock cuts into the schist bedrock close to the area, where the copper mineralisation was identified. This occurrence appears to correspond to one of the numerous igneous dykes, which intersect the metamorphic units as reported by Marinos (1951: 102) and Salemink (1980: 349-50). Salemink (1980: 355) notes that small veins containing the minerals epidote, actinolite, hematite, pyrite, adularia, quartz and/or calcite are frequently found along the joints of such igneous occurences, with small secondary copper mineralisations of malachite, azurite or chrysocolla appearing where such veins form concentrated networks. Such a geological association between the igneous rock formation at Kephala and the observation of copper minerals in the nearby vicinity seems very probable.

The copper is present mainly as green secondary minerals together with secondary iron minerals. Two samples of these minerals accompanied by the host rock were crushed and prepared as powders for (P)ED-XRF (Tables 4.1, 4.2; Appendix 2). The analyses confirmed the presence of substantial amounts of copper (CuO: 24 %), which could have been increased by appropriate sorting and beneficiation. Among the elements that could have played a role in prehistoric alloying only arsenic was detected above the ppm level, but still in very small amounts ($As_2O_3$: 0.2 %). The low sulphur content ($SO_3$: 0.1 %), agrees with the field and macroscopic observations that copper and iron are mainly present as secondary minerals (oxides, hydroxides, carbonates). In addition to the (P)ED-XRF pellets, a single mounted section was prepared and studied under the optical microscope. Aside from the secondary minerals, minute inclusions of pyrite were observed (Figure 4.5), which shows that small amounts of the primary sulphidic minerals are also preserved.

| **Sample No** | **Description** |
|---|---|
| **RK1, 2** | From Kephala tower, schist with secondary copper and iron (non magnetic) minerals |

***Table 4.1*** *Description of copper mineral samples analysed from the Kephala tower area.*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$P_2O_5$** | **$SO_3$** | **CaO** | **$TiO_2$** | **MnO** | **$Fe_2O_3$** | **CuO** | **$As_2O_3$** | **Sum** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **RK1** | 0.5 | 7.9 | 2.7 | 29 | 0.1 | 0.1 | 0.5 | 0.1 | 0.1 | 21 | 24 | 0.2 | 86 |
| **RK2** | 0.3 | 7.7 | 2.6 | 28 | 0.1 | 0.1 | 0.5 | 0.1 | 0.1 | 21 | 24 | 0.2 | 85 |

***Table 4.2*** *Averages of (P)ED-XRF analyses for two copper mineral samples from Kephala (weight %). (Note for all the (P)ED-XRF analyses in this chapter: low totals are probably due to the presence of carbonates and hydroxides typical in secondary ores.).*

Evidence for exploitation of this occurrence was not observed in the field. It should, however, be noted that as the mineralisation was identified at the later stages of fieldwork, a detailed investigation of the area has not been possible so far. A possible association of these minerals with the Kephala slags, beyond the fact of proximity, is suggested by the observation in the heap (mainly Kephala 3, see section 5.2.1) of fragments of a similar igneous rock to the one that cuts through the schist bedrock in the vicinity of the Kephala tower. Whether the specific dyke is the source of these fragments will need to be investigated with appropriate petrographic and chemical analyses, particularly as the igneous rock appears to be closely related to the copper mineralisation. Even if the fragments were brought from this nearby source, however, smelting of ores from this location cannot be demonstrated with certainty, because the igneous material could have been used for other purposes, such as tool-making.

The proximity of these minerals to the Kephala slag heap urges further examination in the future. This should include a full field investigation of the area, assessing the extent of the copper mineralisation and searching for possible traces of ancient exploitation, as well as further laboratory analyses of systematically collected mineral samples and comparison of these with the slags using chemical composition and lead isotope analyses.

### *4.4.2 Koutalas*

This area was investigated following the observation of green copper staining on the section of the road that leads to Koutalas bay. The staining was observed on the gneiss bedrock, which dominates in the area, together with marble units accompanied by large hematite-limonite deposits, typical of south-western Seriphos. Above the road modern iron mining galleries abound. Numerous fragments of rock bearing green copper minerals were seen outside a large gallery (Figure 4.6). In some places these were concentrated as if discarded there on purpose, possibly by mineral collectors, who frequent Seriphos, attracted by the island's renowned rich mineral wealth. The iron deposits of Koutalas have been subjected to extensive modern mining. Aside from the galleries and spoil heaps, remains of installations for the transportation of the extracted ores are visible in the wider area.

Five samples, collected both from the road section and outside the mining gallery, were analysed with (P)ED-XRF (Tables 4.3, 4.4; Appendix 2). Most of the specimens were slightly enriched in copper minerals by hand sorting prior to crushing. Copper is present in significant concentrations (CuO: 20-30 %), but particularly interesting in these samples is the abundance of arsenic ($As_2O_3$: 10-30 %) in four of them. It is clear from the analyses presented that arsenic is associated with the copper minerals. Furthermore, the negligible concentrations of sulphur confirm the macroscopic observation that these are predominantly secondary oxidic ores.

In order to examine the nature of the arsenical copper minerals, a small amount of green powder was analysed by X-ray diffraction (XRD). The powder was first mounted on an aluminium stub and analysed qualitatively on the EDS-SEM to ensure that both arsenic and copper were present. Calcium was the only other element identified. The XRD spectrum (Figure 4.7) agrees well with the pattern for the mineral conichalcite ($CaCuAsO_4(OH)$), which explains the relatively high calcium contents seen in the (P)ED-XRF analyses of most samples (see below for sample KOUT3, which forms an exception). The slight shift between the two spectra is due to the positioning of the sample in the analytical equipment.

Sample KOUT3 is mainly an iron mineral, which includes numerous veins of green copper minerals (see Figure 4.6). For (P)ED-XRF analysis parts of the sample rich in copper were selected. It is interesting to note that despite the relatively high copper contents (CuO: 24 %) in KOUT3, arsenic is very low ($As_2O_3$: 0.1 %). This observation indicates that both arsenical and non-arsenical secondary copper minerals are most likely to be present in this occurrence. The comparatively high levels of barium (c. 0.25 % for KOUT3 and c. 200 ppm for the other samples, see Appendix 2: Table A2.1b) in this sample agree with the reported frequency of barite in the hematite-limonite deposits of south-western Seriphos (Marinos 1951; Salemink 1980).

| Sample No | Description |
|---|---|
| KOUT1 | Sample from road section, green copper minerals and iron minerals crushed with host rock, but enriched in copper |
| KOUT2 | Sample from outside mine gallery, green copper minerals with host rock, enriched in copper |
| KOUT3 | Sample from outside mine galleries, iron ore (non magnetic) with veins of green copper minerals, enriched in copper |
| KOUT4 | Samples from outside mine gallery, small pieces of secondary copper and iron minerals (non magnetic), enriched in copper |
| KOUT5 | Samples from outside mine gallery, very dark green minerals and iron minerals (non magnetic), outside mine gallery |

*Table 4.3 Description of mineral samples analysed from Koutalas.*

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | CuO | $As_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KOUT1 | 0.4 | 15 | 2.0 | 14 | 0.5 | 0.0 | 0.2 | 12 | 0.1 | 0.5 | 1.2 | 22 | 19 | 86 |
| KOUT2 | 0.3 | 9.8 | 0.9 | 12 | 0.2 | 0.0 | 0.0 | 21 | 0.0 | 0.4 | 0.5 | 21 | 11 | 76 |
| KOUT3 | 0.4 | 0.9 | 4.3 | 12 | 0.0 | 1.5 | 0.1 | 3.2 | 0.2 | 0.0 | 30 | 24 | 0.1 | 77 |
| KOUT4 | 0.5 | 18 | 2.8 | 6.2 | 0.3 | 0.0 | 0.1 | 17 | 0.1 | 0.3 | 1.6 | 28 | 29 | 104 |
| KOUT5 | 0.3 | 16 | 1.5 | 1.0 | 0.6 | 0.0 | 0.1 | 17 | 0.0 | 0.9 | 1.0 | 27 | 29 | 94 |

*Table 4.4 Averages of (P)ED-XRF analyses for mineral samples from Koutalas (weight %).*

The identification of arsenical copper minerals on Seriphos is important because whilst arsenical copper is the dominant alloy in EBA Cycladic metallurgy, potential sources of the relevant minerals have not been previously reported within an archaeometallurgical context in this region (see section 2.4.1 for problems with the suggested Kythnian sources). Arsenical copper minerals are reported in the geological literature (Marinos 1951: 118) within the hematite-limonite deposits of south-western Seriphos, so it is possible that additional occurrences are exposed in this part of the island.

### *4.4.3 Playia*

The area of Playia is situated within the contact zone of the granodiorite and the schist, where favourable conditions have led to the formation of extensive skarns and magnetite deposits (section 4.3.2). Although magnetite is abundant all along this part of the contact zone, the massive deposits of Playia are considered the most extensive in this area. Four such bodies were exploited intensely at the start of World War I (Zachos 1951: 141). Galleries, spoil heaps and remains of rails for transport of the ore are still visible today. Localised green copper minerals were observed on the road section over Playia (Figure 4.8). Samples were collected from these and from the spoil heaps outside the mining galleries. Three specimens were analysed using (P)ED-XRF (Tables 4.5, 4.6; Appendix 2).

As is frequently reported in the geological literature regarding magnetite deposits (Marinos 1951: 117; Papastavrou and Zographos 1979: 12; Salemink 1980: 355), analyses showed that the magnetite in Playia is accompanied by small concentrations of pyrite and to a lesser extent chalcopyrite (see analyses PL2 and PL3). Analysis of sample PL1 confirmed that the green staining on the road section of Playia is associated with the presence of secondary copper minerals, weathered products of the minor chalcopyrite occurrences. These are present in very small quantities. Possible alloying elements are only present in trace quantities (Table A2.1b).

| Sample No | Description |
|---|---|
| PL1 | Green copper minerals and accompanying host rock from the road section over Playia |
| PL2 | Mainly pyrite, with some magnetite, collected from the spoil heap outside a mine gallery |
| PL3 | Pyrite and chalcopyrite on host rock, collected from the spoil heap outside a mine gallery |

*Table 4.5 Description of samples analysed from Playia.*

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | CuO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PL1 | 0.3 | 2.0 | 1.8 | 29 | 0.0 | 0.6 | 4.5 | 0.1 | 0.2 | 31 | 8.4 | 79 |
| PL2 | 0.7 | 0.0 | 0.0 | 0.0 | 28 | 0.0 | 0.0 | 0.0 | 0.0 | 51 | 0.3 | 80 |
| PL3 | 0.0 | 1.3 | 0.0 | 9.9 | 22 | 0.0 | 17 | 0.0 | 0.2 | 22 | 14 | 87 |

*Table 4.6 Averages of (P)ED-XRF analyses for samples from Playia (weight %). Sample PL2 (highlighted) is mainly a sulphide and results are given as elements (atom %).*

Copper at Playia is present only in minor amounts and mainly as chalcopyrite. Secondary copper minerals were only observed in the road section and are most likely the products of weathering and leaching of this exposed surface. Playia is a typical example of the presence of primary copper minerals as minor accessory components in the much larger iron ore deposits, as is frequently stated in the geological literature (see above).

### *4.4.4 Vounies*

The geology of the Vounies area was described previously (section 4.3.2). The magnetite deposits here were exploited in the nineteenth century, as is testified by numerous mining galleries in the area, and it is estimated that 37,225 tons of ore were extracted between 1890 and 1899 (Marinos 1951: 116). The area of Vounies was briefly explored in search of the secondary copper mineralisation of chrysocolla ($CuSiO_3$) reported in the area (Salemink 1980: 352). A localised concentration (covering an area of c. 1 $m^2$) of fragmented pieces of green-light blue copper minerals was found on the ground outside an iron mine gallery (Figures 4.9, 4.10). Their distribution indicates that they may have been deliberately broken, possibly by mineral collectors.

Three samples were analysed from Vounies (Tables 4.7, 4.8; Appendix 2). The first sample (VOUN1) was enriched in copper minerals and the analysis showed negligible sulphur and other base metal contents. As it is impossible to isolate completely the copper minerals from the siliceous host rock, bulk (P)ED-XRF could not determine whether the copper mineral here is chrysocolla. Additionally, as the mineral is amorphous XRD could not be used for this purpose. A section was mounted and point analyses of the copper minerals were carried out on the EDS-SEM (Table 4.9). Silicon and copper are present almost in a 1:1 ratio with a slight excess of the former, probably from the surrounding matrix (see also calcium content). These analyses are therefore consistent with the identification of the mineral as chrysocolla.

| Sample No | Description |
|---|---|
| VOUN1 | secondary green-blue copper minerals with host rock, enriched in copper minerals |
| VOUN2 | iron ore from wall of mine gallery, non magnetic, black colour, iridescent |
| VOUN3 | host rock of Cu minerals |

***Table 4.7** Description of samples analysed from Vounies.*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | MnO | $Fe_2O_3$ | CuO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VOUN1 | 0.4 | 3.8 | 4.1 | 23 | 0.1 | 0.0 | 1.8 | 1.5 | 0.8 | 39 | 74 |
| VOUN2 | 0.1 | 0.2 | 0.7 | 3.0 | 0.7 | 0.1 | 0.1 | 0.3 | 73 | 0.2 | 78 |
| VOUN3 | 0.3 | 23 | 1.1 | 60 | 0.0 | 0.0 | 2.4 | 0.3 | 2.3 | 1.5 | 91 |

***Table 4.8** Averages of (P)ED-XRF analyses for samples from Vounies (weight %).*

| | O | Si | Ca | Cu | Sum |
|---|---|---|---|---|---|
| Vounies 1 | 30 | 19 | 0.5 | 33 | 83 |
| Vounies 2 | 31 | 18 | 0.3 | 30 | 79 |

***Table 4.9** EDS-SEM point analyses on copper minerals from Vounies (atom %).*

### *4.4.5 Kalavatsena*

The geology of Kalavatsena is dominated by the presence of scarn formations, which are accompanied by iron ore deposits. Papastavrou and Zographos (1979: 13) report that hematite-limonite deposits are found together with magnetite and pyrite. The former were exploited in the last century by the company of the mining engineer Grohman, who discarded the magnetite and sulphidic minerals (Papastavrou and Zographos 1979: 13). Galleries and spoil heaps in the area testify to these activities. In his treatise of the history of Seriphos, Galanos (1962: 148) reports that at the end of the nineteenth century a permit for the extraction of sulphidic copper ores from the wider area of Kalavatsena was granted to a private citizen. It is not clear whether such exploitation did in fact take place (Kordellas 1902: 85), but a visit to Kalavatsena confirmed the presence of copper minerals in the area (see also Gale *et al.* 1985).

Green copper staining is observed in the road section above Kalavatsena, while green copper minerals are seen among the discarded iron ores in the spoil heaps. Five samples from Kalavatsena were analysed with (P)ED-XRF (Tables 4.10, 4.11; Appendix 2). The presence of copper in secondary oxidic minerals is confirmed by these analyses, while potential alloying elements are generally negligible. Two of the samples analysed included high concentrations of pyrite (KAL2 and KAL5). The copper content is low in these, although based on the report by Galanos (1962) and the identification of secondary oxidic minerals, it is probable that sulphidic copper minerals are also present in this region.

| **Sample No** | **Description** |
|---|---|
| **KAL1** | Secondary green copper minerals in host rock, collected from spoil heaps, enriched in copper |
| **KAL2** | Magnetite and iron pyrite |
| **KAL3** | Green copper minerals in host rock, from road section above Kalavatsena |
| **KAL4** | Green copper minerals in host rock, from road section above Kalavatsena, enriched in copper |
| **KAL5** | Pyrite with host rock, from spoil heaps |

***Table 4.10** Description of samples analysed from Kalavatsena.*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **Cl** | **$K_2O$** | **CaO** | **MnO** | **$Fe_2O_3$** | **CuO** | **Sum** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KAL1** | 0.5 | 1.1 | 2.5 | 27 | 3.9 | 0.5 | 0.1 | 1.4 | 0.5 | 5.8 | 35 | 78 |
| **KAL2** | 1.0 | 0.0 | 0.1 | 3.8 | 6.2 | 0.0 | 0.2 | 0.1 | 0.0 | 55 | 0.0 | 66 |
| **KAL3** | 0.5 | 1.8 | 10 | 56 | 0.3 | 0.1 | 0.1 | 2.5 | 0.3 | 8.1 | 5.0 | 85 |
| **KAL4** | 0.8 | 0.9 | 0.6 | 26 | 1.2 | 0.9 | 0.2 | 1.7 | 0.1 | 23 | 30 | 85 |
| **KAL5** | 1.2 | 0.0 | 0.0 | 5.6 | 34 | 0.0 | 0.1 | 0.0 | 0.0 | 37 | 0.0 | 78 |

***Table 4.11** Averages of (P)ED-XRF analyses for samples from Kalavatsena (weight %). Sample KAL2 and KAL5 (highlighted) are mainly sulphides and results are given as elements (atom %).*

### *4.4.6 Moutoulas*

The mixed sulphidic deposits of Moutoulas were described in section 4.3.2.3. These were intensely mined in the nineteenth century (Marinos 1961; Papastavrou and Zographos 1979) and the remains of large galleries and spoil heaps are still visible in the area (Figure 4.11). Several references to ancient mining at Moutoulas, probably for lead and silver, can be found in the literature (see for example Marinos 1951: 124; Gale and Stos-Gale 1981a: 188-90). Gale and Stos-Gale (1981a) report that lead slag and litharge were found at the entrance of a gallery that appears to correspond to ancient exploitation, but the antiquity of mining and processing of these ores has not been established. The area was visited very briefly, and the potential ancient remains could not be located. As the project was mainly directed at the identification of copper minerals on Seriphos only a small number of samples was collected from the spoil heaps for examination (Tables 4.12, 4.13; Appendix 2). Analyses showed that these correspond to sulphidic minerals of iron, lead and zinc (pyrite, galena, and sphalerite), while copper contents are negligible. The presence of copper in the area of Moutoulas cannot be excluded, however, particularly as Galanos (1962) reports that a permit for exploitation of copper and argentiferous lead in this area was granted at the end of the nineteenth century. Silver contents in the galena sample (MOUT3) are low (c. 200 ppm see Table A2.1b), but much higher silver (1000 and 3359 ppm) was found in the two galena samples from Moutoulas analysed by Gale and Stos-Gale (1981a: 187, Table 1), indicating that ores sufficiently rich in silver even for EBA standards may be present in this deposit (the suggested limit for economic recovery of silver during the EBA is 0.08 % of silver in the lead ores, see section 2.3.2). Clearly the mixed sulphidic deposits of Moutoulas merit careful examination in the future, particularly due to several references to ancient mining in this region.

| **Sample No** | **Description** |
|---|---|
| **MOUT1** | Mixed sulphidic minerals with host rock |
| **MOUT2** | Mainly pyrite |
| **MOUT3** | Mainly galena |

*Table 4.12 Description of samples analysed from Moutoulas.*

| | **Na** | **Si** | **S** | **Fe** | **Zn** | **As** | **Pb** | **Cu (ppm)** | **Sum** |
|---|---|---|---|---|---|---|---|---|---|
| **MOUT1** | 0.0 | 9.1 | 19 | 18 | 12 | 0.2 | 11 | 93 | 70 |
| **MOUT2** | 1.5 | 0.0 | 38 | 40 | 0.0 | 0.1 | 0.1 | 0 | 81 |
| **MOUT3** | 0.0 | 0.8 | 11 | 2.0 | 3.3 | 0.1 | 62 | 138 | 80 |

*Table 4.13 Averages of (P)ED-XRF analyses for samples from Moutoulas (atom %).*

## 4.5 Discussion

The preliminary geological investigation of potential copper ore sources on Seriphos proved to be very rewarding. The study demonstrated the presence of copper minerals on Seriphos at several locations and has hopefully provided a basis for a future full-scale archaeomining investigation on the island. Evidence for ancient exploitation has not been recorded so far, but the present survey can by no means be considered detailed or exhaustive. Among the five locations investigated, two are of prime importance for this study and should be highlighted. First, the copper mineralisation close to the Kephala tower merits careful examination due to its proximity to the slag heap (Chapter 5). Secondly, the presentation of arsenical copper minerals found at Koutalas forms the first substantiated report of such occurrences to be generated by an archaeometallurgical project in the Cyclades. These are potentially of considerable value given the predominance of arsenical copper alloys in EBA Cycladic metallurgy. Further research is now mandatory to establish whether south-western Seriphos was a source of arsenical copper in antiquity. At present, traces of ancient practices, testifying to mining and/or production in the area, have not been found. However, modern mining has significantly altered the landscape of the area and it is most likely that, were such remains once present, their recognition would be largely impeded by the relics of modern activities. Still, given the importance of arsenical copper in early metallurgy, it is proposed that further work, including characterisation of the minerals and lead isotope analysis, should provide a valuable database to which artefacts and metallurgical remains can be compared.

Another element that becomes apparent from the above discussion is the dispersed and generally small-scale, though potentially rich, nature of the copper mineralisations identified on Seriphos. This phenomenon, which is generally characteristic of the Cycladic islands (see Chapter 2), hinders their identification during fieldwork and makes small-scale regional in-depth archaeometallurgical surveys essential in the search of potential sources exploited in antiquity. Naturally one needs to distinguish between restricted, occasional occurrences and actual ores (see for example Ixer and Pattrick 2003: 10), the latter implying mineralisations rich enough to warrant 'profitable exploitation'. The criteria defining 'profitable exploitation' in different periods and among different societies are bound to be diverse and potential ancient metal sources cannot be simplistically excluded on the basis of modern preconceptions. A similar study on Kythnos (Bassiakos and Philaniotou in press), the only other island extensively surveyed for copper sources potentially used in antiquity, brought to light some evidence suggesting that such small mineralisations could have been the source of the local EBA slag heaps. The indications are not conclusive as tools and tool marks are scarce (see also sections 2.4.4 and 7.2.2.3).

The limiting factors suggested for Kythnos are only two of the problems likely to be encountered in future archaeomining investigations. On Seriphos, and indeed in most of the metalliferous Cycladic islands (see also references in Chapter 2), one cannot disregard the effects of extensive modern mining. The landscape is often covered by large deposits of rubble from these activities and modern mining galleries may have destroyed earlier evidence to a great extent. Fieldwork expeditions need to be complemented by other appropriate studies, such as analytical comparisons and examination of associated records and other literature sources (see also Rapp 1999).

Finally, as stated already, several references are made in the literature to ancient mining on Seriphos, but unfortunately these are in most cases unclear both as regards the metal possibly sought and the associated dating, while in some cases the statements are not supported by any relevant evidence (see for example Kordellas 1902; Marinos 1951; Papastavrou and Zographos 1979). The indications for ancient lead-silver mining and possibly production at Moutoulas were discussed before (section 4.4.6). In addition Davies (1935: 260) reports two fourth-third century B.C. black glaze lamps, one of the second or first century B.C. and a plain one from galleries close to Koundouro. He also says he was shown another 'primitive' lamp from a mine close to Mega Leivadi. Healy (1978: 118, Pl3a) illustrates a fifth century lamp but does not give details for the exact location where this was found. Galanos (1962: 146) notes that modern mining engineers on Seriphos claimed they came across 'Classical' galleries during their works. The suggested dates need to be viewed with caution but the evidence for ancient exploitation (of iron and/or copper?) in one or more periods in antiquity is strong. The island's resources were also mined in later historical periods (Davies 1935: 260-1; Galanos 1962), while the modern history of Seriphos is intimately connected with the operation of the mines until the beginning of the 1960s. The relics of these intense activities are widely attested in various parts of the island (Figure 4.12), forming an important historic industrial heritage, which is unfortunately slowly being lost as appropriate measures for their preservation have not been taken. An archaeomining investigation on Seriphos would not only enhance our understanding of local EBA metallurgy, to which the evidence presented in the next chapter testifies, but would allow a diachronic glimpse of what promises to be a rich and varied mining and metallurgical past. For the present, the focus of this analysis shifts to archaeometallurgical evidence accumulated from the study of the copper slag heaps on the island.

*Figure 4.1 Geological map of Seriphos (adapted from Salemink 1980: 345, Figure 2), showing sites mentioned and mineralisations sampled (in blue).*

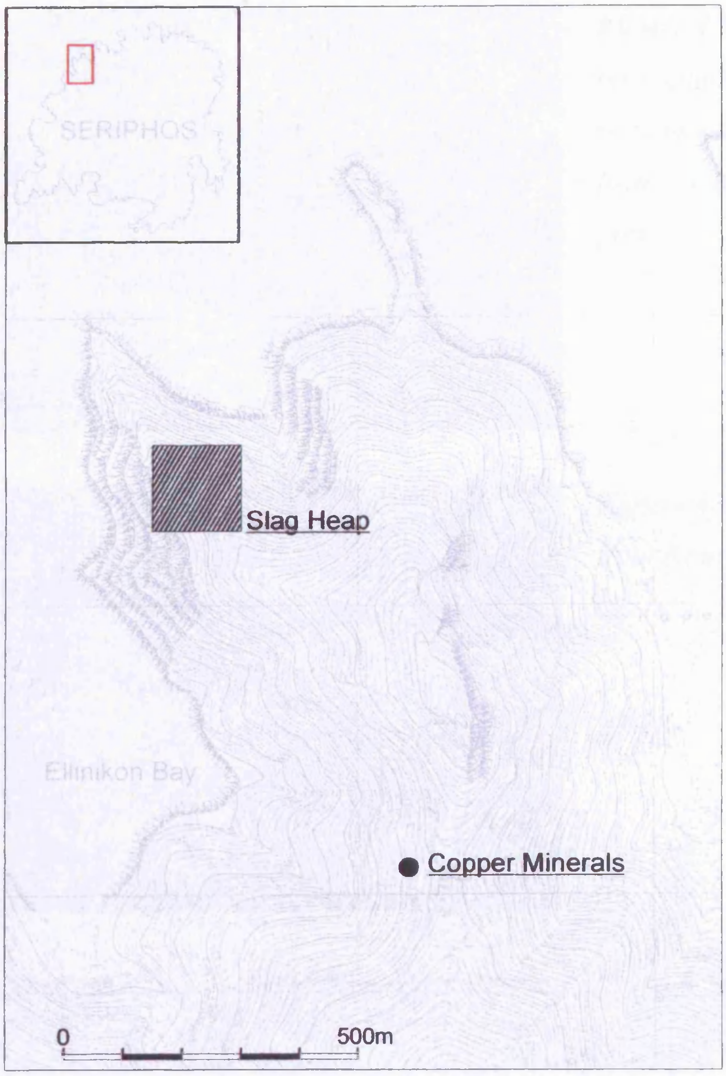


**Figure 4.2** *Map of Kephala promontory showing position of copper minerals at Kephala tower in relation to the slag heap.*

**Figure 4.3** *Green copper minerals on the surface of the schist bedrock at the Kephala tower.*

**Figure 4.4** *Green copper minerals after hammering the schist bedrock at the Kephala tower.*

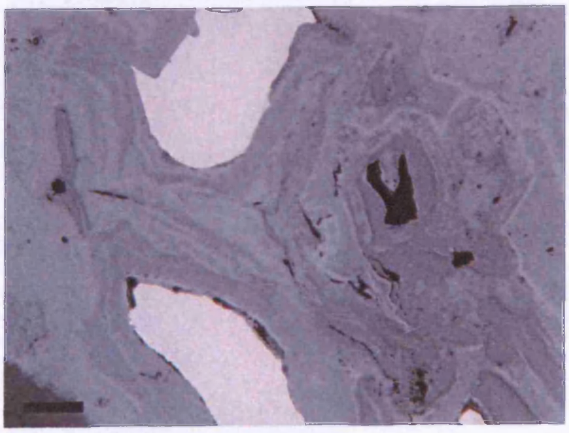


***Figure 4.5** Reflected light microphotograph of pyrite inclusions (cream white) in the mineral samples from the Kephala tower (scale 100 µm).*

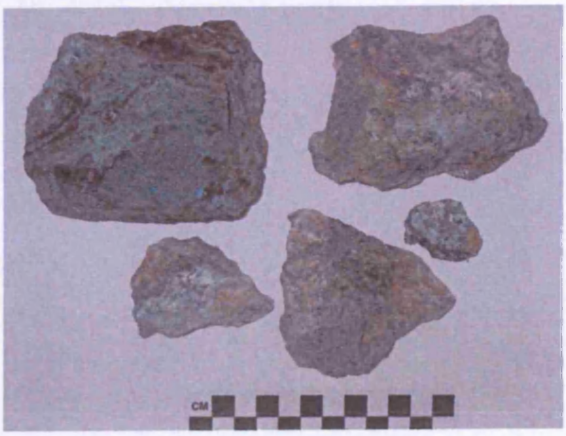


***Figure 4.6** Copper mineral samples from Koutalas (sample KOUT3 at the top left).*

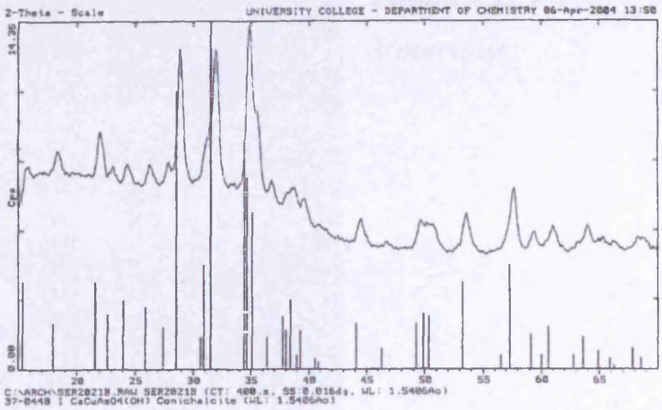


***Figure 4.7** XRD spectrum of arsenical copper mineral sample from Koutalas.*

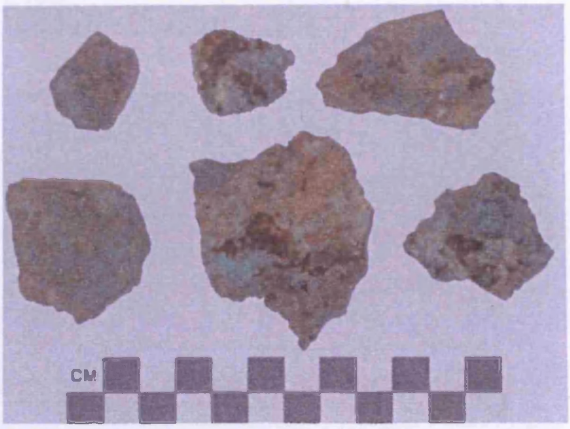


***Figure 4.8** Secondary copper minerals on host rock collected from the road section over Playia.*

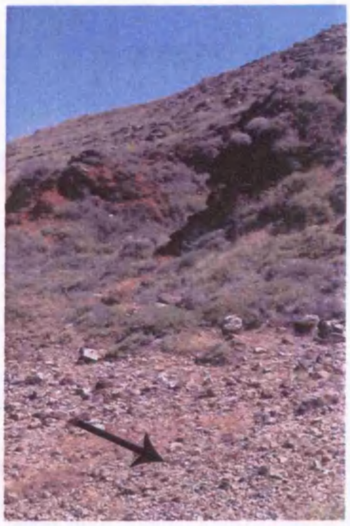


***Figure 4.9*** *Iron ore mining gallery at Vounies (the black arrow shows where the copper minerals were found).*

***Figure 4.10*** Scatter of copper minerals found at Vounies.

***Figure 4.11*** Mining galleries at Moutoulas.

***Figure 4.12*** Relics of modern iron mining at Mega Leivadi.

# CHAPTER 5.

# Seriphos: the metal production sites; description, sampling, and analyses

## 5.1 Introduction

Seriphos is frequently mentioned as a possible important EBA Cycladic metal producing island, together with the adjacent islands of Kythnos and Siphnos (see for example Barber 1987: 14; Broodbank 2000a: 292; Gale and Stos-Gale 2002; Philaniotou-Hadjianastasiou 2000; Stos-Gale and Gale 2003). These suggestions were primarily based on two long-known copper slag heaps at the sites of Avessalos and Kephala (see for example Gale *et al.* 1985). Contrary to Kythnos and Siphnos, however, where archaeometallurgical projects have been undertaken leading to important results (Chapter 2), the two copper slag heaps on Seriphos remained until recently undated and largely under-studied. In one of their latest overviews of isotopic work in the Aegean, Stos-Gale and Gale (2003: 88) stress the necessity for an archaeometallurgical investigation on this island. As outlined in Chapter 1, this situation prompted the start, in the year 2000, of an ongoing collaborative archaeometallurgical investigation on Seriphos between the Ephorate of Prehistoric and Classical Antiquities of the Cyclades and the Laboratory of Archaeometry N.C.S.R. Demokritos (Philaniotou 2004). The team had in the past carried out similar work on Kythnos with great success (Bassiakos and Philaniotou in press). The author was kindly invited to join the Seriphos project, participating in the fieldwork and carrying out the necessary laboratory analyses.

In addition to the sites of Avessalos and Kephala, several other metallurgical sites have recently been identified on Seriphos (Figure 5.1). The first, at Phournoi, was discovered at the start of the above-mentioned investigation and has not been presented in detail before (Philaniotou 2004). Other slag scatters on Seriphos have recently been reported by Gale and Stos-Gale (2002, in press) and Papadimitriou and Fragiskos (2003). For this thesis, a substantial suite of samples from the sites of Kephala and Phournoi has been examined and is discussed in more detail below. A small number of analyses were also carried out on a limited number of slags from Avessalos; but the site remains undated and the number of samples examined was small. Thus, the study of Avessalos is still at a very preliminary stage and, apart from a brief presentation of the results, is not included in the present analysis. The smaller slag scatters reported recently by Gale and Stos-Gale (2002, in press) and Papadimitriou and Fragiskos (2003) have not been studied further during this project.

Seriphos is one of the least studied Cycladic islands, not only in terms of archaeometallurgy, but generally regarding prehistoric archaeology. Renfrew (1972: 511) reports a small number of BA artefacts attributed a Seriphian origin but states that no EBA sites were known at the time. With the exception of the slag heaps (see dating of Kephala and Phournoi below), the picture does not seem to have changed substantially in more recent times. A single site dated by the surface pottery finds to the EBI period has been recognised in the course of this collaborative project in the southern part of the island on the top of the Koundouro bay in an area known as Plakalona (Philaniotou 2004). This scarcity of EBA sites on Seriphos should not be taken to indicate an actual dearth of prehistoric habitation, but more likely reflects the absence of archaeological investigations on the island.[5.1] In his initial review of the Aegean islands Davis (1992: 728) characterises Seriphos as the least known island of the western Cyclades, while in the more recent addendum to this review the authors (Davis *et al.* 2001: 88) note that "Seriphos remains almost a blank as far as its prehistory is concerned". Only the slag heaps of Avessalos and Kephala are mentioned as possibly of EBA date (Davis 1992: 728; Davis *et al.* 2001: 88). Broodbank (2000a: 52) also acknowledges the lack of archaeological research on the island by attributing a 'poor' level of archaeological exploration (the lowest) to Seriphos. The scarcity of archaeological data from Seriphos will inevitably limit the potential for discussion of aspects relevant to the organisation of metallurgy on the island and more generally in the Cyclades (see Chapter 7). On a more positive note,

---

[5.1] See Doumas (1963) for a brief archaeological investigation of the impressive cave above the Koutalas bay. The pottery is mainly of Hellenistic and Roman date with a few Classical sherds. Prehistoric pottery is not reported but it should be noted that excavation was not carried out.

however, it is hoped that the results of this project will establish the island's importance and offer a stimulus for further archaeological work.

This chapter begins with a description of the two main slag heaps examined in this thesis, Kephala and Phournoi. The next section presents the results of the thermoluminescence (TL) dating carried out on furnace wall fragments from the two sites, followed by the results of the laboratory analyses carried out by the author. At the end of the chapter a short description of the other metallurgical sites known on Seriphos is given starting with the results of the preliminary examination of the Avessalos site and material.

## 5.2 Description and sampling of the slag heaps of Kephala and Phournoi

This section presents the two sites from which substantial material has been collected and analysed as part of this thesis. For reasons discussed in section 3.3.1, the sites were divided into separate areas for sampling as set out below.

### *5.2.1 The slag heap of Kephala*

The slag heap of Kephala has been briefly reported in the past by Gale *et al.* (1985), who also presented preliminary bulk analyses of four slag fragments. Microstructural observations from two randomly collected samples from Kephala were given by Dimou and Oikonomou (1997). The site has been studied more fully during the fieldwork part of the present collaborative project and a larger number of samples (c. 40 in total) were analysed in the course of this thesis.

#### *5.2.1.1 Location and layout*

The slag heap of Kephala is situated at the north-western part of the island (Figure 5.1). Roughly 800 m to the east of the slag heap are the remains of a Hellenistic circular tower constructed from large marble slabs (Philaniotou-Hadjianastasiou

2000). The site is located within the northern schist unit. Close to the Kephala tower an igneous dyke and copper minerals were observed (see section 4.4.1).

The main concentration of metallurgical material on Kephala extends down the north-facing slope of the promontory (Figures 5.2 and 5.3). Two separate deposits are observed on this side of the site. They measure 85x30 m (Kephala 1: eastern concentration) and 110x40 m (Kephala 2: western concentration) and are located at a distance of roughly 100 m between them. The thickness of these deposits does not appear to exceed 0.5 m (see also Gale *et al.* 1985: 83 for the same estimate), but excavation would be necessary to confirm this approximation, deduced at present merely from surface observations. Based on these preliminary figures, the total volume of material present at this part of the site is estimated at a maximum of 3500 m$^3$. Slag is found mixed with fragments of clay furnace walls, which represent c. 5 % of the surface material, and other associated finds (see below).

Scatters of metallurgical remains are also observed on the south-facing slope in substantial quantities, but in a far more dispersed distribution. At this side in particular are areas covered with small, centimetre-sized slag pieces (Figure 5.4). It is possible that these represent locations where slag was deliberately broken, possibly for the extraction of prills, although at this stage, and in the absence of other associated evidence (tools, associated installations) in the immediate vicinity, this cannot be concluded with certainty. Among the slag scatters of the south-facing slope, one was more closely examined and sampled (Kephala 3). Kephala 3 is a low density slag scatter (compared to Kephala 1 and 2) close to the western edge of the promontory (Figure 5.3). The slag fragments here are dispersed mainly on the schist bedrock. Furnace wall fragments are virtually absent, while the slags are all small to medium in size. Particularly interesting was the identification in this part of the heap of angular or orthogonal fragments of igneous rocks (max. length 15 cm), macroscopically similar to the igneous rock occurrence close to the Kephala tower (see section 4.4.1). Traces of slag and green colouration were noted on one of these fragments (Figure 5.5). These igneous rock fragments from Kephala 3 have not been examined further for this thesis and their role in the metallurgical operations is still unclear. They may have been brought to the site as host rock of the copper ore or alternatively used as tools or building materials for the furnace. Further fieldwork and laboratory studies will be necessary to distinguish between the different possibilities. It is also hoped that further research on this site will incorporate a petrological and geochemical comparison between the samples found in the heap and the igneous rock occurrence of the Kephala tower to establish whether there is an association between the two.

### *5.2.1.2 Description of the material*

The Kephala slags are grey-black in colour. Although green staining is often absent in the outer surface of the fragments, it is clearly visible upon breaking, immediately indicating that these slags are associated with copper metallurgy. The size of the slag fragments varies widely from small broken pieces (<1 cm) to few large masses of consecutively tapped slag (Figure 5.6), the latter noted mainly at Kephala 1 (max. height 30 cm; cf. Avessalos in section 5.6.1).

Based only on their external characteristics, the larger slag fragments could be divided into three preliminary broad categories. The first one includes those that show a flow texture on their upper side (Figure 5.7). An indication that slag was possibly allowed to run and cool outside the furnace was observed on Kephala 2, where a thin (c. 1 cm) layer of in situ cooled slag showing flow features was identified stuck on the schist bedrock (sample KEF7 detached for analysis). At the time that this find was noted, it was already being fragmented into smaller pieces, due to natural weathering, an observation that highlights the possible contribution of erosion on the observed small size of some of these finds. The second type of slag observed is dense and very crystalline, probably corresponding to material that cooled slowly within the furnace. Large, elongated crystals were clearly visible in some of the larger fragments (Figure 5.8). The third category comprises the remainder of the slags, which do not show any of the distinctive features of the previous two classifications. Among them some specimens are significantly porous, while some bear small inclusions of rocks and burnt clay. These three categories do not represent a strict typological framework, particularly as the majority of specimens would be attributed to the last residual group. They are merely noted in order to highlight two distinctive features observed in some samples.

Ceramic furnace wall fragments represent approximately 5 % of the surface material on Kephala (Figure 5.9). The thickness of the ceramic fragments varies (c. 1.5-4 cm) and their colour ranges from orange-red on their outer surface to a grey-black vitrified layer on their inner surface. Slag, often bearing green staining, is frequently attached to the latter. Inclusions of refractory materials such as quartz and schist are seen in the ceramic matrix, while impressions of burnt-out organic materials are clearly evident in the outer side.

In the Kephala 2 deposit a concentration of furnace wall fragments that bear traces of perforations (Figure 5.10) was found, reminiscent of similar finds known from Kythnos (Bassiakos and Philaniotou in press), Crete (Betancourt *et al.* 1999), and possibly Kea (Coleman 1977: 4) and Raphina (Theocharis 1952: 131). In one specimen in particular the entire hole was preserved (diameter on the external surface 3 cm). The shape of the holes suggests that these were formed by pushing the wet clay inwards and in some cases slightly downwards. Most of these fragments only bear the imprint of a single hole, but on one specimen two were identified with a distance of 5.5 cm between them (Figure 5.11). These specimens show somewhat different characteristics to the majority of the other ceramic fragments on Kephala. They are generally thicker (3 to 5 cm) and although their inner surfaces are vitrified, in most cases they do not seem to bear attached slag. These differences raise the possibility that two types of metallurgical ceramic finds are present on the site, which could, for example, correspond to either two chronologically different processes, or serve different purposes in contemporaneous operations. It should, however, be noted that only six specimens with evidence for perforations have been identified on Kephala so far, compared to dozens without them, so it is not safe at this stage to draw conclusions on the existence of two types of metallurgical ceramics. One cannot disregard the possible effect of erosion on these ceramics, which may have significantly reduced the thickness of some of these specimens, or even eradicated the indications of holes in some cases.

It is, however, important to note that in contrast to Sideri on Kythnos (Bassiakos and Philaniotou in press) and Chrysokamino on Crete (Betancourt *et al.* 1999), where similar finds are reported in large quantities, the specimens on Kephala are far less frequent and indications for multiple holes are rare (cf. Stos-Gale 1998: 733,

Figure12). On the other hand, it is interesting to note that in his itinerary on Seriphos island, Varlas (1998) quotes information offered to him by a local, who claimed that his grandfather had seen the remains of two to three of these furnaces standing and recalled that they had "holes all around them like lanterns" (Varlas 1998: 130). Although this testimony needs to be viewed with caution, the description agrees with reconstructions offered by other scholars for the furnaces of Sideri (Bassiakos and Philaniotou in press) and Chrysokamino (Betancourt *et al.* 1999). The quotation supports the possibility that the amount of perforated ceramics in the heap may at some time have been higher than noted during our fieldwork. Additionally, the description of these furnaces lends further credit to the proposal that the rarity of fragments with multiple holes should not be taken as an indication for their absence on the original installations.

A single stone tool has so far been found on Kephala 2, possibly a hammer stone (Figure 5.12). It consists of igneous rock possibly associated with the nearby dyke. Its surfaces are rounded, it bears one shallow indentation and shows signs of wear on its front edge. Two round slag fragments were also recovered from the heap (Figure 5.13). Their intriguing shape raises the possibility that they were also used as tools.

### *5.2.1.3 Furnaces*

Just below the crest of the promontory, south of Kephala 1 and towards the south-facing slope, the remains of two furnaces were identified (for location see Figure 5.3). The furnaces are carved into the schist bedrock (Figure 5.14). One is better preserved than the other and the diameter of its bottom surface is approximately 25 cm. A clear layer of slag is seen on its side, while smaller droplets of slag are also preserved on parts of the sides on both furnaces, together with traces of green staining. Apart from this, the furnaces are almost clear of slag or other metallurgical remains, although dispersed scatters of material are seen in the surrounding area. It is interesting to note that although the largest concentration of material on Kephala is found on the north-facing slope, these two installations face towards the southeast. The vast majority of scatters of metallurgical remains identified in the Aegean are located on the north-facing slopes of windy promontories, usually stretching from just below the summit downwards, which suggests that the metallurgical activities were making use of the prevailing northern winds (see discussion in section 5.5.5). It is possible that the direction these furnaces are facing indicates operations during different wind conditions or alternatively an altogether lack of dependence on natural drafts in this case.

### *5.2.2 The slag heap of Phournoi*

#### *5.2.2.1 Location and layout*

To the western side of Sykia Bay, on the promontory of Ayios Nikolaos, at the northern part of the island, a new metallurgical site was discovered during this project (Figure 5.1).[5.2] The area is given by the locals (Chrysoloras pers. comm.) the names Phournoi (Greek for furnaces), Gaidourospilia (Greek for donkey cave), or Skala (Greek for small harbour). The first one will be used for the purposes of this thesis. The geological setting is the same as on the Kephala promontory, namely schist often bearing quartz veins, in some cases enriched in iron minerals. No traces for copper mineralisation have been detected so far in the area.

The slag heap at Phournoi is much smaller than the one at Kephala (Figures 5.15 and 5.16). Metallurgical remains extend from just below the summit down the north-facing slope, which has a steep inclination, and it appears that fragments have rolled down towards the sea. Very few pieces are seen on the other side, while some stray pieces of slag were also observed at the beginning of the path that leads to the site (c. 1500 m southeast). The heap can be divided into two sub-units, where the concentration of finds is denser and the material appears to be in situ. They measure 14x10 m (Phournoi 1: eastern concentration) and 16x13 m (Phournoi 2: western concentration) and are separated by barren schist bedrock. The latter is located approximately 3 m topographically lower than the former, while the distance between them at their southernmost edges is 28 m. The depth of these deposits varies depending on location but does not generally seem to exceed 40 cm, while

---

[5.2] I would like to express my deepest gratitude to Mr Chrysoloras, former mayor of Seriphos, who informed us of this site and kindly accompanied us along the strenuous path on our first visit.

much of the site appears to be mainly a surface scatter. These are obviously only rough estimates, deduced from surface observations. Both deposits are located just below the crest of the promontory. On the flat area at the top of the promontory (Phournoi 3) metallurgical remains are generally smaller and very dispersed. Further down the slope hundreds of fragments that appear to have rolled down the slope lie on horizontal planes of the schist bedrock. On the basis of the measurements presented for Phournoi 1 and Phournoi 2, the volume of material on these two main concentrations should not exceed 140 m$^3$. Although this figure is a very rough estimate, in the absence of secure data on the depth of these deposits, it clearly demonstrates the much smaller size of Phournoi in comparison to Kephala (estimated volume for Kephala 1 and Kephala 2 c. 3500 m$^3$).

#### *5.2.2.2 Description of the material*

The heap is composed again mainly of slag, with ceramic furnace wall fragments constituting approximately 5-10 % of the total surface material (Figure 5.17). A few isolated copper prills and a very small number of schist and quartz fragments bearing oxidised copper minerals were also recovered. Stone tools were not found on this site.

The slag fragments on Phournoi are generally smaller than on Kephala and range from less than 1 cm to about 20 cm in length; with a maximum height of 10 cm. Green staining is frequently observed on their outer surface, indicating an association with copper metallurgy. Some fragments show a flow texture on their upper surface indicating that slag had reached the fully molten state. The furnace wall fragments show similar characteristics to the ones described for Kephala and their thickness varies from 1 to 4 cm. Fragments with evidence for holes have not been identified so far.

### *5.2.3 Sampling at Kephala and Phournoi*

The decisions made during sampling at the sites of Kephala and Phournoi were governed by several factors. Firstly, one of the aims of the analytical investigation was to examine whether metallurgical heterogeneities could be observed within and between the heaps (see section 3.3.1). Secondly, sampling had to be restricted to surface collection as excavation has not been possible so far. Thirdly, the number of samples needed to be balanced between ensuring a sufficient number was analysed to enable substantiated conclusions, while not exceeding the practical limitations of this thesis in terms of resources and time. Fourthly, it should be noted that previous comprehensive analytical studies of material from these sites had not been undertaken (with the exception of limited slag samples from Kephala in Dimou and Oikonomou 1997; Gale *et al.* 1985) and criteria for distinguishing macroscopically between potentially different types had not been established.

In order to cover a larger area on both sites and ensure that potentially different contexts were represented, sampling was largely based on the inherent division of the material into separate deposits in each case. This strategy enables a simple selection of sampling units, which takes advantage of the layout of each site, and can be easily reproduced by potential future researchers working on these heaps. Additionally, it enables a comparison between parts of the site that may correspond to different working areas, as they are located at some distance from each other and appear to be somewhat spatially separated. Within each of these sub-units, which are defined below in more detail, samples were collected at random rather than following a systematic procedure such as gridding. This collection strategy was sufficient for the purposes of the present examination. A more systematic collection strategy would have produced far larger quantities of material, which would need to be further sub-sampled prior to analysis. Overall the process would be much more labour-demanding with no particular advantages for this first analytical study. It should, however, be noted that in the larger sampling units care was taken not to collect samples situated in close proximity to each other, but to ensure that different areas were represented by sampling every few metres across the diagonal of each unit.

On Kephala samples have been recovered from four contexts (see section 5.2.1.1 and Figure 5.3):

1. Kephala 1: eastern large deposit at north-facing slope
2. Kephala 2: western large deposit at north-facing slope

3. Kephala 3: small scatter at south-facing slope
4. Furnace: a single sample (KEF25) was carefully detached from the slag attached to the identified furnace.

On Phournoi samples have been recovered from five contexts (see section 5.2.2.1 and Figure 5.16):

1. Phournoi 1: eastern concentration of north-facing slope
2. Phournoi 2: western concentration of north-facing slope
3. Phournoi 3: top of the promontory
4. Phournoi 4: material that has rolled down the slope below Phournoi 1 and 2
5. Path: beginning of the path that leads to the site.

The last group (Path) corresponds to the few stray slag pieces, found at the start of the path that leads to the site (distance c. 1500 m southeast of Phournoi). These were included in this study to examine whether substantial differences could be noted that would justify attributing these to a separate site than Phournoi.

Establishing criteria to ensure that potentially different types of slag are represented during surface sampling of these heaps is a difficult task. Even at the smaller site of Phournoi, the volume of slags present is substantial. Slags are inherently materials that may vary considerably macroscopically even if they result from the same process. In some cases it is possible to establish a slag typology to guide preliminary identification but this would normally follow and be largely based on an analytical investigation (see for example Koucky and Steinberg 1982; Chapter 6 in this thesis). Prior to sampling both sites were thoroughly investigated, but macroscopically distinct types of slag could not be distinguished on either. Even the three broad categories described for the Kephala material (see section 5.2.1.2) do not represent a firm classification, as only comparatively few specimens conform strictly to one of the first two diagnostic categories. It was therefore decided that a number of basic macroscopic features would be used as guidelines during sampling of the slags. These were the size and porosity of the slags and the presence or absence of flow texture, visible inclusions and green staining on their outer surface. The description of the samples analysed is given in Appendix 4 (Appendix 4: Tables A4.1 and A4.6 for Kephala and Phournoi respectively). In addition to the majority of the slag samples, which despite differences in these specific characteristics are generally typical of the heaps, a few intriguing and 'exceptional' specimens were identified, collected, and analysed.

## 5.3 Dating of Kephala and Phournoi

The first issue that needs to be addressed in the study of these heaps is their dating. Diagnostic pottery sherds are rare on these sites. Although a few sherds have been recovered from both sites, diagnostic material was only found at Phournoi. An EBII date was recently attributed to the site based on these finds (Philaniotou 2004). Charcoal remains in the slags are notoriously rare in the Cycladic smelting sites, forbidding in most cases the application of radiocarbon dating (Bassiakos and Philaniotou in press; Gale and Stos-Gale in press). The same phenomenon was observed on both Kephala and Phournoi. Numerous slag fragments were broken in search of charcoal residues but none were found. In view of these limitations, TL dating of the furnace wall fragments, which are abundant on both sites, presented the best alternative method. This dating approach has been applied successfully to several other Aegean smelting sites (see for example Stos-Gale 1998; Wagner *et al.* 1980; Zacharias *et al.* forthcoming). Unfortunately, the method has larger error ranges than radiocarbon dating, in the range of several hundred years, but is still sufficient to attribute the sites to a broad chronological period.

A total of six samples were submitted for analysis, two from Phournoi 1, two from Kephala 1, and two from Kephala 2 (for description see catalogue in Appedix 3). A larger number of samples was considered necessary from Kephala in view of the potentially two different types of furnace wall fragments identified (perforated and non-perforated). Perforated fragments have not been observed on Kephala 1, while from Kephala 2 one of the samples submitted was from the small collection of specimens with a single hole (KEF2B). Thicker samples were selected where possible and preferably those that did not bear heavy slagging. Analyses were carried out by the TL Dating team in the Laboratory of Archaeometry, N.C.S.R. Demokritos in Athens, who have in the past carried out similar work on specimens from Sideri on Kythnos (Zacharias *et al.* forthcoming). A report was kindly prepared by Dr N. Zacharias, which includes the details of the methodology followed and a complete table of results (Appendix 3).

A total of five reliable analyses (sample KEF2B was analysed twice) were obtained from Kephala and two from Phournoi. A mean value of 4640±240 years B.P. is calculated for Kephala and 4940±360 years B.P. for Phournoi. Both sites therefore fall roughly within the first half of the third millennium BC, corresponding to the Aegean EBA, with the site of Phournoi possibly a little earlier than Kephala, although the associated errors do not allow a secure distinction. The results for Phournoi are in agreement with the pottery recovered from the site (Philaniotou 2004). Within the analyses of Kephala the three analyses from Kephala 2 consistently give a somewhat earlier date than the two analyses from Kephala 1, but the relatively small number of samples analysed and the large errors attached to individual analyses also preclude at this stage anything more than a qualitative observation. The results are particularly exciting as it is possible for the first time to attribute, with more certainty than previous suspicions, an EBA date to at least two of the metallurgical sites on Seriphos, enabling safe consideration of this island in discussions of prehistoric Aegean metallurgy.

## 5.4 Results of the analytical examination of metallurgical remains from Kephala and Phournoi

This section presents the results of the analytical investigation of material from Kephala and Phournoi. The collection of analysed samples includes several types of material, the main one being the slags. The results are presented separately for each site and are divided into three types of material, the slags, the isolated copper metal prills, and the other materials (minerals, partially reacted ores, matte). Furnace wall fragments have not been included in this investigation, but a full petrographic and chemical study of such specimens is planned for the future.

### *5.4.1 Analytical results for the samples from Kephala*

#### *5.4.1.1 Slags*

Macroscopic characteristics

A description of the slags analysed from Kephala is given in Appendix 4 (Table A4.1). The samples were selected to cover a range of macroscopic characteristics as discussed in section 5.2.3.

Among the thirty slag samples examined, five should be highlighted as they form part of larger specimens noted in the field. Samples KEF3 and KEF4 have been taken from the larger masses of slags seen in Kephala 1, which appear, macroscopically at least, to have resulted from consecutive tapping (Figure 5.6). Sample KEF7 was detached from a layer of slag found on Kephala 2, which appeared to have run and cooled on the schist bedrock (shows flow texture). Sample KEF10 is from a bowl-shaped crystalline slag, which appeared to have cooled in situ (Figure 5.18). Finally, KEF25 was taken from the layer of slag seen on the side of one of the furnaces (Figure 5.14).

Bulk compositions

A total of twenty-seven slag samples from Kephala were large enough to be analysed as pellets with (P)ED-XRF (see section 3.6.2). Each sample was analysed three times and the normalised averages for the major and minor elements are presented in Table 5.1 (full results in Appendix 4: Tables A4.2a and A4.2b).

The main components are silica ($SiO_2$: 22-45 %) and iron oxide (FeO: 24-64 %) followed by lower amounts of other gangue components, the most important in terms of quantity being calcium oxide (CaO: 1-18 %), alumina ($Al_2O_3$: 1-7 %), and magnesia (MgO: 0.5-8 %). Significant variability is seen in the contents of these elements between the different samples. As a rule, the iron contents appear to be inversely correlated with the silica and calcium oxide contents and to a lesser extent with magnesia. Samples KEF4 and KEF10, for example, are exceptionally rich in calcium oxide (18 and 17 % respectively) but have the lowest contents of iron among all the samples (24 and 27 % respectively). Samples KEF40 and KEF32, on the other hand, have among the highest iron contents (64 and 58 % respectively) with low silica (25 and 22 % respectively) and calcium oxide (0.9 and 1.7 % respectively). Sulphur is generally below 1 % with the exception of sample KEF13 ($SO_3$: 1.9 %), which will be discussed in more detail below. Copper contents[5.3] are also variable (CuO: 0.3-10 %) but generally average between all the samples at around 2 %. Other base metals commonly found as alloying components in copper, such as arsenic ($As_2O_3$: 15-355 ppm), zinc (ZnO: 80-1100 ppm), nickel (NiO: 0-700 ppm), and lead (PbO: 0-650 ppm) are only present in trace quantities (for analyses of trace elements see Appendix 4: Table A4.2b). Barium is present in almost all the samples reaching a maximum of 1300 ppm, while several other elements were consistently detected at trace quantities, usually not exceeding 100 ppm.

---

[5.3] Observations under the optical microscope and analyses of phases in all the slag samples presented in this thesis showed that copper is present both as individual metallic phases and as an oxide within the slag matrix. Given that it is impossible to estimate the relative ratios of metallic to oxide form of the element with the analytical methods used, tables of bulk analyses measurements present the total copper present as an oxide (CuO).

|  | Unit | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF1** | 1 | 0.5 | 4.2 | 2.5 | 40 | 0.1 | 0.3 | 4.1 | 0.1 | 0.5 | 44 | 4.4 | 88 |
| **KEF3** | 1 | 0.6 | 3.3 | 2.1 | 36 | 0.0 | 0.2 | 8.2 | 0.0 | 0.2 | 49 | 0.8 | 93 |
| **KEF4** | 1 | 0.5 | 2.4 | 5.3 | 45 | 0.4 | 1.0 | 18 | 0.1 | 0.5 | 24 | 3.2 | 94 |
| **KEF23** | 1 | 0.9 | 2.5 | 5.5 | 33 | 0.6 | 0.5 | 3.8 | 0.2 | 0.3 | 52 | 0.7 | 92 |
| **KEF24** | 1 | 0.6 | 4.6 | 2.4 | 43 | 0.0 | 0.3 | 8.7 | 0.1 | 0.3 | 38 | 2.0 | 95 |
| **KEF31** | 1 | 0.7 | 3.6 | 2.3 | 37 | 0.2 | 0.2 | 8.9 | 0.0 | 0.2 | 46 | 0.3 | 93 |
| **KEF32** | 1 | 1.0 | 0.9 | 4.6 | 22 | 0.4 | 0.8 | 1.7 | 0.1 | 0.1 | 58 | 10 | 95 |
| **KEF33** | 1 | 0.5 | 2.9 | 0.7 | 31 | 0.0 | 0.1 | 6.2 | 0.0 | 0.2 | 57 | 1.1 | 95 |
| **KEF34** | 1 | 0.6 | 4.7 | 2.2 | 42 | 0.0 | 0.2 | 8.7 | 0.1 | 0.3 | 38 | 2.2 | 94 |
| **KEF35** | 1 | 0.7 | 2.7 | 4.7 | 38 | 0.0 | 0.6 | 7.0 | 0.1 | 0.3 | 45 | 1.6 | 92 |
| **KEF36** | 1 | 0.6 | 4.6 | 1.8 | 39 | 0.0 | 0.3 | 9.2 | 0.0 | 0.2 | 43 | 0.9 | 94 |
| **KEF5** | 2 | 0.8 | 2.3 | 5.7 | 28 | 0.5 | 0.8 | 2.4 | 0.2 | 0.2 | 56 | 3.0 | 93 |
| **KEF6** | 2 | 0.8 | 2.0 | 6.6 | 30 | 0.6 | 0.7 | 3.3 | 0.2 | 0.2 | 54 | 0.9 | 97 |
| **KEF7** | 2 | 0.6 | 8.1 | 4.2 | 33 | 0.1 | 0.3 | 8.6 | 0.1 | 0.2 | 43 | 1.2 | 94 |
| **KEF8** | 2 | 1.0 | 1.1 | 6.8 | 32 | 0.7 | 0.8 | 2.0 | 0.3 | 0.2 | 54 | 0.8 | 96 |
| **KEF9** | 2 | 0.5 | 1.5 | 6.2 | 33 | 0.1 | 0.5 | 3.9 | 0.2 | 0.4 | 51 | 2.4 | 96 |
| **KEF10** | 2 | 0.5 | 8.2 | 4.8 | 40 | 0.0 | 0.2 | 17 | 0.1 | 0.2 | 27 | 1.0 | 98 |
| **KEF13** | 2 | 0.6 | 2.8 | 5.0 | 32 | 1.9 | 0.5 | 7.2 | 0.2 | 0.4 | 48 | 1.4 | 90 |
| **KEF14** | 2 | 0.6 | 2.9 | 5.5 | 36 | 0.0 | 0.8 | 10 | 0.2 | 0.5 | 42 | 1.2 | 93 |
| **KEF26** | 2 | 0.7 | 2.3 | 4.2 | 36 | 0.1 | 0.7 | 3.7 | 0.1 | 0.3 | 50 | 2.0 | 93 |
| **KEF38** | 2 | 0.8 | 2.7 | 4.6 | 38 | 0.0 | 0.6 | 7.0 | 0.1 | 0.3 | 45 | 1.6 | 92 |
| **KEF39** | 2 | 0.6 | 8.1 | 5.0 | 34 | 0.0 | 0.3 | 11 | 0.1 | 0.3 | 37 | 3.0 | 94 |
| **KEF11** | 3 | 0.6 | 1.2 | 4.7 | 30 | 0.3 | 0.6 | 1.5 | 0.2 | 0.2 | 60 | 1.5 | 93 |
| **KEF15** | 3 | 0.9 | 2.6 | 5.6 | 35 | 0.1 | 0.9 | 9.6 | 0.2 | 0.6 | 43 | 1.6 | 92 |
| **KEF16** | 3 | 0.6 | 0.5 | 3.2 | 31 | 0.3 | 0.6 | 4.6 | 0.1 | 0.3 | 57 | 2.0 | 94 |
| **KEF40** | 3 | 0.4 | 0.8 | 2.3 | 25 | 0.3 | 0.2 | 0.9 | 0.4 | 0.2 | 64 | 5.1 | 95 |
| **KEF25** | F | 0.7 | 3.1 | 2.4 | 36 | 0.0 | 0.4 | 8.2 | 0.1 | 0.4 | 44 | 4.5 | 87 |

***Table 5.1*** *Averages of three analyses of slag samples from Kephala on the (P)ED-XRF, normalised to 100 % (major and minor elements in weight %; MT: measured total). Unit numbers (1, 2, 3, F) correspond to sampling units Kephala 1-3 and Furnace.*

Microstructure and phase composition

The slag sections were all studied under the optical microscope and the observations made for each sample are summarised in Appendix 4 (Table A4.3). Mineral identification was supported by point analyses on the electron microprobe on a selection of samples and the results are given in Appendix 4 (Table A4.4).

In the majority of samples the dominant phases are iron silicates of the olivine group ($(Fe_xMg_{1-x})_2SiO_4$), embedded in a glassy matrix. In some samples the glass matrix appears to have re-crystallised and minute iron silicate crystals can be discerned (Figure 5.19). The composition of the larger iron silicates, which could be analysed separately (Table A4.4), shows that they correspond primarily to fayalite ($Fe_2SiO_4$) with the iron replaced to a variable degree by magnesium. In a few cases the magnesia contents are exceptionally high (see for example analyses KEF8a-c, MgO: 24-34 %; FeO: 25-33 %) and the corresponding atomic ratios between magnesia, silica, and iron oxide reflect a composition between the minerals fayalite and forsterite ($Mg_2SiO_4$). Fayalite crystals also usually accommodate low amounts of calcium and manganese, typical minor constituents of these phases (Bachmann 1982a: 14).

In the calcium-rich samples KEF4 and KEF10 (see Table 5.1) crystals with high calcium contents consistent with the pyroxene group ($(Fe_xMg_{1-x})CaSi_2O_6$) were identified. The analyses in sample KEF4 (see Table A4.4) reflect an atomic ratio between silica, magnesia, iron and calcium oxides of 4:1:1:2 in all the crystals and therefore a composition between the minerals hedenbergite ($CaFeSi_2O_6$) and diopside ($CaMgSi_2O_6$). Sample KEF10, on the other hand, appeared even macroscopically to be very crystalline (Figure 5.18). The glassy component is indeed very little in this sample, while the crystalline phases are large (Figure 5.20). A number of different crystalline phases, both fayalites and pyroxenes, were identified during analysis on the electron microprobe (see Table A4.4).

Apart from the iron silicates, iron oxides are also present in almost all the samples (Figure 5.19). Their shape indicates that these are mainly magnetite ($Fe_3O_4$), which analyses showed usually accommodate small amounts of alumina and titanium oxide. Quantification of the different phases was not attempted, but optical observations suggest that magnetite is less frequent than the silicates in most cases, although the distribution and relative abundance of phases varies both within and certainly between samples. Samples KEF32 and KEF40, which had shown high iron oxide contents in the bulk analyses, are comparatively rich in magnetite (compare Figures 5.19 and 5.21), while free iron oxides are virtually absent from the samples KEF4 and KEF10, which had the lowest iron oxide contents among all the samples (Figures 5.20 and 5.22).

In general the microstructure of these slags shows that the primary materials fully reacted in most cases and the slag re-crystallised from a relatively homogeneous melt. Inclusions of unreacted or partially reacted materials are rare but can, nevertheless, be very informative where present. In some of the samples relatively large irregularly-shaped magnetite aggregates were observed (Figure 5.23). These usually appear in those samples that are somewhat richer than the others in iron oxide crystals. The aggregates are either seen as rigid inclusions in non-reactive contact with the slag matrix, or partly decomposing and dissolving in the melt. Copper prills are frequently associated with them. Similar agglomerations were noted in the EBA slags from Shahr-i Sokhta (Hauptmann *et al.* 2003). They are interpreted as the remains of the partially reacted limonitic part of mixed copper and iron ores. The other type of undissolved inclusions of primary materials noted in these samples were quartz fragments. Examples were found within samples KEF8 and KEF31 and appear in both cases to be partially reacted (Figure 5.24).

Small inclusions of ceramic or vitrified ceramic were noted in some samples, usually at the edge of the sections (Figure 5.25). These are usually closely bound to the slag without a clear separating line between the two phases. Small isolated ceramic fragments were observed externally during the initial macroscopic examination of some slags (Figure 5.26). Examples are samples KEF2 and KEF14, where vitrified ceramic inclusions were also identified during microscopic examination. The presence of these undissolved inclusions indicates that these were incorporated to the slag at the end of the process and did not have time to react. They are probably fragments detached from the furnace wall and carried by the still partially molten slag.

Another interesting microstructural feature noted in some specimens was the presence of thin magnetite bands. Specimen KEF16, for example, showed a flow texture on its upper side (Figure 5.27). A section was cut to include this part of the sample and examination under the optical microscope showed a thin continuous magnetite band running across this external surface (Figure 5.28). Similar features were, however, also noted within rather than at the edge of sections. An example is seen in sample KEF26, where a thin magnetite band runs across the section (Figure 5.29). The sample also showed flow texture on its upper surface but this time the section was taken from the middle of the specimen. The microstructure of the section between the two sides of the magnetite band is different, one showing larger phases than the other. The difference in the size of the crystals is a reflection of differences in the cooling rate between the two parts, slower cooling allowing the formation of larger crystals. Magnetite bands are typical textures resulting from the cooling of molten slag in contact with air (Hauptmann *et al.* 2003: 205). In the case of sample KEF16, the magnetite band in combination with the flow texture seen on the upper side of the specimen indicates that the slag ran and cooled outside the furnace. Internal magnetite bands, as observed in sample KEF26, point to a temporary cooling zone, where slag tapped out of the reaction vessel starts to crystallise and partially oxidise in contact with air before the next layer of slag is deposited on top.

Particularly interesting observations were made on sample KEF13. Similarly to most samples, fayalite predominates in this sample, with little dispersed magnetite surrounded by a glassy matrix (see corresponding analyses in Table A4.4). Large inclusions are visible even macroscopically in this section. Examination under the optical microscope revealed that these correspond to remnants of partially reacted copper-iron sulphidic ores (Figure 5.30). These sulphides are heterogeneous and show various different phases of the Cu-Fe-S system (e.g. pyrite, chalcopyrite, bornite, covelline, and chalcocine), which can be distinguished on the basis of their optical properties. In some areas lamellar textures, frequent in mixed copper-iron sulphides (Ramdohr 1980: 453-7) are observed (Figure 5.31). The presence of these large sulphides explains the comparatively high sulphur contents detected in the bulk analysis of this sample (Table 5.1). The shape of these inclusions is often delineated by the surrounding fayalite crystals (Figure 5.32).

Several observations lead to the conclusion that these represent partially reacted primary materials, rather than phases recrystallised from sulphidic melts like the rounded matte prills (cf. Schreiner *et al.* 2003: 490), commonly observed in the majority of slags from Kephala (see below). First is the recognition of minute eutectoid structures (Figure 5.31) in the inclusions (cf. Bachmann 1982a: 25 and plate XIf). Secondly, magnetite crystals have started to form around these sulphides, while the presence of large holes around these inclusions is consistent with the evaporation of sulphur dioxide (Figure 5.33). These observations are indicative of the progressive oxidation of iron sulphide to magnetite and the corresponding transformation of the copper-iron sulphide to a copper-enriched product. The process was terminated before the reaction was completed leaving behind a specimen that allows a unique insight into the smelting operation, demonstrating the use of mixed copper-iron sulphidic minerals (see also below).

Analyses of the entrapped prills

The slags from Kephala invariably bear entrapped prills of copper metal or copper-iron sulphide (matte). Several samples have both types of prills (see Appendix 4: Table A4.3), in many cases copper metal prills being surrounded by a matte rim, while in other samples one or the other type appears to predominate. Their size is generally small, rarely exceeding 10 µm in diameter. As a rule the matte prills are larger than the copper metal ones; the latter are often extremely small (c. 1 µm) and therefore impossible to analyse (identification in these cases was based on their optical characteristics). Prills from nineteen slag samples were analysed on the EPMA (see section 3.6.1.3). A minimum of three prills (copper metal and/or matte) was analysed from each sample and the results are presented in Appendix 4 (Table A4.5). The purpose of these analyses was mainly to determine whether any of the common alloying components of copper, such as arsenic, tin, or antimony, are present.

Most prills have negligible contents (generally below 0.5 %) of other base metals, mainly arsenic and nickel. The only exceptions were samples KEF14 and KEF35. A single copper metal prill with 1.8 % arsenic was found in sample KEF14 (analysis KEF14E). The other prills analysed from this sample were all matte with arsenic contents below 0.5 %. In sample KEF35 three copper metal prills were analysed with corresponding arsenic contents of 0.5 %, 1.5 %, and 1.8 %. Only 0.1 % arsenic was detected in the single matte prill analysed from the same sample. The lower arsenic contents detected in the matte compared to the copper metal prills in these samples are not surprising. In his experimental study on the distribution of various elements in copper, slag and matte during copper smelting, Yazawa (1980) noted that arsenic impurities tend to concentrate in the metal phase rather than the slag or the matte, although he acknowledges that the behaviour of these impurities is complicated and largely depends on the prevailing physico-chemical conditions.

On the basis of these results it appears that production of mainly unalloyed copper was carried out on Kephala. The three analyses (two samples) with slightly higher arsenic contents should not be disregarded, but at this stage they constitute an exception. A similar phenomenon with a few slag samples bearing arsenic-rich prills in a majority of non-arsenical copper slags was encountered at the site of Skouries on Kythnos (Bassiakos and Philaniotou in press; Gale and Stos-Gale 1989a). As was argued for Skouries (see section 2.4.4), the number of samples that bear arsenic-rich copper prills on Kephala is low and it would be premature to argue for the use of different types of ore (arsenical and non-arsenical) at this stage (cf. for a different case with the material from Daskaleio-Kavos in Chapter 6). Although this possibility cannot be excluded, it is equally likely, given the inherent heterogeneities of ore deposits, that these slags were produced using batches of ore from the same source but slightly enriched in arsenic impurities. The arsenic would then concentrate in the copper metal prills (Tylecote *et al.* 1977; Yazawa 1980). Three parameters are in favour of this interpretation. Firstly, arsenic is commonly detected in the bulk analyses of the Kephala slags in trace quantities (Table A4.2b). Secondly, bulk arsenic contents in KEF14 and KEF35 are in similarly low levels as in other samples. Thirdly, arsenic is frequently found in minor quantities in the prills of the other Kephala slags. These observations indicate that arsenic is generally present as a trace component in the ores used on Kephala. The slightly higher arsenic contents in the prills of KEF14 and KEF35 do not justify suggesting a separate origin for the raw materials used in the production of these slags.

Another element of interest in early copper metal analyses is iron. Craddock and Meeks (1987) have argued that the earliest copper artefacts (EBA and earlier) are characterised by low iron contents (generally up to 0.05 %), while higher iron contents are encountered in later artefacts. The variation, they propose, results from the different physico-chemical conditions prevailing in the associated smelting operations. The earliest metal production processes are believed to have involved the use of high grade ores, with little iron present and therefore insignificant slagging, while the more reducing conditions of the later slagging smelting operations would force some of the iron minerals present in the raw materials to react with the copper metal, leading to the presence of higher quantities of iron in the produced copper (Craddock 1995: 138; Craddock and Meeks 1987). The copper metal prills entrapped in the Kephala slags are very small and enclosed within an iron-rich matrix. As a result secure quantitative measurement of their iron content is not possible as the analyses will incorporate some of the surrounding iron. The high iron contents (in some cases exceeding 5 %) measured in many prills are likely to reflect this situation. For this reason the majority of iron contents detected in these prills should be disregarded at this stage, with one exception discussed below.

A very large prill was found and analysed from sample KEF40. The prill was protruding on the upper surface of this specimen and was covered externally by a green corrosion layer (Figure 5.34). A section was cut to include both the prill and the surrounding slag. Studied under the optical microscope, it was deduced that the copper metal prill is significantly weathered but retains in its core a large part of the unweathered metal. The circular prill (corroded and uncorroded parts) is enveloped within a copper sulphide rim (Figure 5.35). Small copper sulphide inclusions can be distinguished within the uncorroded copper metal matrix. These different components were analysed using point measurements on the EPMA and the results are given in Table 5.2. The iron content of the uncorroded copper metal core is below the detection limit of the analytical method used (c. 0.05 %). Additionally, low amounts of nickel (c. 0.4 %), arsenic and silver (c. 0.1 %) were detected. It is also interesting to note that the smaller matte prills found within the slag contain higher amounts of iron (c. 5 %) than the sulphidic rim surrounding the large prill. The difference may be a result of simultaneous measurement of the surrounding iron-rich matrix, as discussed previously, particularly as the majority of matte studied optically from this specimen were of light blue colour, typical of chalcocine ($Cu_2S$).

| | S | Fe | Ni | Cu | As | Ag | Total |
|---|---|---|---|---|---|---|---|
| **KEF40(Cu)** | 0.0 | 0.0 | 0.3 | 99 | 0.1 | 0.1 | 100 |
| **KEF40(Cu)** | 0.0 | 0.0 | 0.4 | 99 | 0.0 | 0.1 | 99 |
| **KEF40(Cu)** | 0.0 | 0.0 | 0.4 | 98 | 0.1 | 0.1 | 98 |
| **KEF40(I)** | 19 | 0.0 | 0.0 | 78 | 0.0 | 0.0 | 97 |
| **KEF40(R)** | 20 | 0.0 | 0.0 | 77 | 0.1 | 0.0 | 97 |
| **KEF40(R)** | 20 | 0.0 | 0.0 | 76 | 0.0 | 0.0 | 97 |
| **KEF40G** | 19 | 4.9 | 0.0 | 75 | 0.0 | 0.0 | 100 |
| **KEF40H** | 17 | 4.5 | 0.0 | 77 | 0.0 | 0.0 | 99 |

***Table 5.2*** *EPMA point analyses on the large copper metal prill with surrounding matte in sample KEF40 and other small matte prills in the same sample (weight %). Cu: copper metal core of large copper prill, I: sulphide inclusions in the copper metal core of the large copper prill, R: sulphide rim surrounding large copper prill, KEF40G and H: analyses of other smaller matte (diameter c. 10 μm) in sample KEF40.*

### *5.4.1.2 Isolated copper metal prill*

A single isolated copper metal prill was recovered during surface collection on the Kephala slag heap (sample KEF41). Although it is very likely that many more similar specimens are present in the heap, the large volume of material present, makes it particularly difficult to recognise them in the field due to their small size.

A suitable mounted section was prepared and studied first under the optical microscope and subsequently analysed by EPMA (Table 5.3). Tiny light blue sulphidic inclusions can be distinguished within the copper metal matrix. Apart from copper, the analyses only detected nickel, arsenic, and silver above the detection limits of the instrument, but still in very low amounts (0.1-0.3 %). Iron contents are below the detection limit. Analyses of the sulphidic inclusions confirmed that these are copper sulphides (copper may be slightly overestimated from the surrounding matrix).

| | S | Fe | Ni | Cu | As | Ag | Total |
|---|---|---|---|---|---|---|---|
| **KEF41A** | 0.0 | 0.0 | 0.1 | 100 | 0.3 | 0.1 | 100 |
| **KEF41B** | 0.0 | 0.0 | 0.2 | 97 | 0.3 | 0.1 | 98 |
| **KEF41C** | 0.0 | 0.0 | 0.1 | 98 | 0.2 | 0.1 | 99 |
| **KEF41D** | 0.0 | 0.0 | 0.2 | 99 | 0.2 | 0.1 | 99 |
| **KEF41E** | 0.0 | 0.0 | 0.1 | 98 | 0.3 | 0.1 | 98 |
| **KEF41F** | 18 | 0.0 | 0.0 | 78 | 0.0 | 0.0 | 96 |
| **KEF41G** | 18 | 0.0 | 0.0 | 78 | 0.0 | 0.1 | 96 |

***Table 5.3** EPMA point analyses on KEF41 (weight %). Analyses A-E were done on the copper metal matrix, while F-G on the tiny sulphidic inclusions.*

### *5.4.1.3 Other materials*

The samples discussed below were collected from the field as specimens showing ‘exceptional’ external characteristics, different from the majority of slags (see section 5.2.3). Suitably prepared mounted sections were studied by optical microscopy. Identification has been supported by analysis by EDS-SEM or EPMA, where necessary.

KEF12

Sample KEF12 was collected from the Kephala 3 area. The specimen is very small, approximately 3 cm in length, and was almost completely covered externally by a green corrosion layer (Figure 5.36).

The mounted section showed a distribution of large irregularly shaped ‘islands’ of mixed copper and iron sulphides within a matrix of weathered secondary copper and iron minerals (Figure 5.37). The sulphidic grains often show a transition from a copper-iron sulphide (chalcopyrite and/or bornite, yellow-white and violet colour) in their centre to an external light blue or blue chalcocine or covelline ($Cu_2S$ or CuS respectively) exterior zone. In the smaller grains only the blue copper sulphides can be seen. Iron hydroxides (bright red at crossed polarised light) define the edges of the original sulphidic grains in the weathered matrix and eutectics are seen in their triple junctions. An external thin layer of magnetite has formed towards the outer edge of the sample, while a single quartz fragment was observed on one side (Figure 5.38). Copper salts, deposited from weathering, form the outermost layer of the sample, which corresponds to the green coating observed macroscopically at the exterior surface of the specimen.

A small number of EPMA point analyses were done on the sulphidic 'islands' (Table 5.4). Apart from copper, iron, and sulphur, only arsenic and silver were detected in minor quantities (c. 0.1-0.2 %). The relative ratios of copper, iron, and sulphur in these analyses should not be taken as representative of a particular sulphidic mineral as the individual phases within these mixed sulphides are too small and tightly intergrown to be analysed separately.

| | **S** | **Fe** | **Cu** | **As** | **Ag** | **Total** |
|---|---|---|---|---|---|---|
| **KEF12A** | 27 | 5.8 | 62 | 0.2 | 0.1 | 95 |
| **KEF12B** | 30 | 1.1 | 69 | 0.2 | 0.2 | 100 |
| **KEF12C** | 27 | 7.1 | 60 | 0.2 | 0.1 | 94 |
| **KEF12D** | 28 | 0.8 | 71 | 0.2 | 0.1 | 100 |

***Table 5.4*** *EPMA point analyses of the sulphidic 'islands' in sample KEF12 (weight %).*

The specimen is clearly a partly weathered copper-iron sulphide. The question that needs to be addressed is whether it corresponds to matte or whether it is a mineral sample discarded (deliberately or accidentally) prior to smelting. Conclusive evidence for heating was not observed on this sample (see others below). Its texture, however, showing curved grain boundaries and circular eutectics in the triple junctions, conforms with the microstructure expected when a sulphidic melt freezes from a high temperature (Rehren pers. comm.). It is therefore proposed that KEF12 is matte formed during smelting and probably discarded at the end of the process as it could not be processed further.

KEF27

This small roughly oval-shaped specimen was collected from the Kephala 2 area. Externally it is covered with a green layer and shows limited orange-brown staining (Figure 5.39).

The section revealed that the sample shows many similarities in its microstructure to sample KEF12. Its matrix is composed of weathered copper and iron minerals and shows intense porosity (Figure 5.40). Iron hydroxide delineates the grain boundaries of the original sulphidic minerals, which are slightly curved and show eutectic formations at their triple junctions. Contrary to KEF12, sulphidic remnants are rare and much smaller. They show a similar pattern as observed previously with a copper-iron sulphidic (yellowish/violet) core and a copper sulphide (blue) external zone. A thin skin of magnetite surrounds the exterior surface of the specimen, followed by an outermost green layer of copper salts. Studied under crossed polars in the reflected microscope, elongated lines of a second phase of eutectic formations can be distinguished in the weathered matrix (Figure 5.41).

Similarly to KEF12, this sample shows characteristics typical of a frozen copper-iron sulphidic melt and is therefore identified as corroded matte. Compared to KEF12, KEF27 is much more weathered, retaining only very small amounts of the original sulphidic components.

KEF28

This small, thin (width 0.3 cm), non-magnetic sample was collected from Kephala 1. From the side three layers can be distinguished macroscopically (Figure 5.42). The upper one is green, the middle black, and finally the bottom surface is orange-brown and was described in the original macroscopic examination as schist mixed with soil. A section was cut across to include all three layers.

The green outer surface corresponds to post-depositional copper salts. This is followed by a dense sulphidic band, which analyses (Table 5.5) showed corresponds mainly to copper sulphide (atomic ratio of copper and sulphur is consistent with the mineral chalcocine $Cu_2S$) with minor amounts of iron. The layers that follow show a progressive weathering of the sulphide from partially to completely weathered, towards the inner parts of the sample (Figure 5.43). In the completely weathered parts, remains of a eutectic texture of the sulphide with, most probably, magnetite are still clearly visible. The other edge of the sample corresponds to a porous conglomerate with fragments of quartz, schist and other rocks mixed with soil (Figure 5.44). Irregularly shaped inclusions of sulphides are also observed between the rock fragments. The sulphides are in close contact with the rock fragments but do not appear to have reacted.

| | S | Fe | Cu | Total |
|---|---|---|---|---|
| **KEF28a** | 18 | 0.5 | 80 | 98 |
| **KEF28b** | 19 | 0.5 | 81 | 100 |

***Table 5.5** EDS-SEM area analyses on mixed sulphidic band in sample KEF28 (weight %).*

On the basis of these observations it is proposed that sample KEF28 corresponds to matte (mainly copper sulphide), which came out of the reaction vessel or furnace while molten and came into contact with soil mixed with rock fragments. The specimen may correspond to an accidental spill.

### KEF29

Specimen KEF29 was collected from Kephala 1. Externally it appears to be a secondary iron and copper mineral, only a little magnetic, mainly brown-red in colour with green staining in parts (Figure 5.45).

Examination under the optical microscope confirmed that this specimen is mainly composed of secondary iron and copper minerals. The matrix of the specimen is mainly composed of secondary iron hydroxides (goethite and/or limonite), which show intense orange-red internal reflections in crossed polarised light. The primary sulphidic mineral appears to have completely weathered, but its original lamellar texture is retained in parts (Figure 5.46). Chalcopyrite inclusions are, however, observed within quartz fragments, which are enclosed in the iron hydroxide matrix (Figure 5.47). The sulphides have been preserved in this case as they are protected from weathering by the surrounding quartz. Point analyses of these phases on the EDS-SEM (Table 5.6) showed that the atomic ratio of sulphur, iron, and copper is approximately 2:1:1 confirming the optical identification of these minerals as chalcopyrite. Apart from silica, which comes from the surrounding quartz, no other elements were found above the detection limits of this method. Cuprite and green secondary copper minerals have been deposited in parts of the outer edge of the specimen.

| | **Si** | **S** | **Fe** | **Cu** | **Total** |
|---|---|---|---|---|---|
| **KEF29a** | 0.3 | 34 | 33 | 32 | 99 |
| **KEF29b** | 0.3 | 32 | 32 | 35 | 99 |

***Table 5.6** EDS-SEM point analyses on sulphidic minerals found within quartz fragments in sample KEF29 (weight %).*

The specimen shows no indications of having been heated. It more probably corresponds to a fragment of ore, which was either deliberately discarded for being too poor in copper or accidentally dropped during processing.

KEF30

Specimen KEF30 (Figure 5.45) is brown-red in colour, in parts stained green and shows little magnetism. Small fragments of attached quartz and schist can be discerned macroscopically.

Examined under the optical microscope, the sample shows intense porosity and is composed of fragments of schist and quartz, which face in different directions (Figure 5.48). Green secondary copper minerals and iron hydroxides have been deposited between these rock fragments, usually filling the pores, while tiny specks of primary sulphidic minerals can be seen within some of the rock fragments. The scarcity of internal alignment between the rock components and the high porosity do not conform to a geological origin for this sample. Instead, it seems more probable that it represents a conglomerate of rock fragments and iron and copper minerals, crushed, naturally or artificially, and loosely consolidated together over time. Such a formation is not surprising in a metallurgical working area, where rock and mineral fragments abound on the surface.

### *5.4.2 Analytical results for the samples from Phournoi*

#### *5.4.2.1 Slags*

Macroscopic characteristics

A description of the samples analysed from the slag heap of Phournoi is given in Appendix 4 (Table A4.6). A total of twenty-eight slag samples were examined from this site, collected from the five sampling areas described in section 5.2.3. As at Kephala, the slags were selected to cover a range of macroscopic characteristics (Figure 5.49).

Bulk compositions

Twenty-seven slag samples from Phournoi were large enough to be analysed as pellets with (P)ED-XRF. Each sample was analysed three times and the normalised averages for the major and minor elements are presented in Table 5.7 (full results in Appendix 4: Tables A4.7a and A4.7b).

| | Unit | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU1** | P | 0.5 | 0.6 | 4.5 | 35 | 0.0 | 0.1 | 0.4 | 1.8 | 0.1 | 0.9 | 53 | 4.4 | 88 |
| **FOU2** | P | 0.7 | 1.4 | 4.2 | 33 | 0.0 | 0.1 | 0.5 | 2.4 | 0.2 | 0.3 | 56 | 0.8 | 93 |
| **FOU3** | P | 1.2 | 2.0 | 8.7 | 28 | 0.1 | 1.0 | 1.3 | 2.8 | 0.3 | 0.6 | 51 | 3.2 | 94 |
| **FOU4** | P | 0.8 | 1.8 | 5.0 | 34 | 0.0 | 0.1 | 0.7 | 3.2 | 0.2 | 0.4 | 51 | 3.0 | 93 |
| **FOU9** | 1 | 1.5 | 3.5 | 8.8 | 50 | 0.0 | 0.2 | 1.3 | 7.9 | 0.3 | 0.3 | 26 | 1.0 | 98 |
| **FOU10** | 1 | 0.7 | 4.5 | 3.7 | 38 | 0.0 | 0.9 | 0.4 | 4.5 | 0.1 | 0.3 | 46 | 1.5 | 93 |
| **FOU11** | 1 | 0.7 | 3.1 | 5.1 | 25 | 0.0 | 0.4 | 0.5 | 3.4 | 0.2 | 1.8 | 57 | 1.4 | 90 |
| **FOU12** | 1 | 0.6 | 1.3 | 5.6 | 34 | 0.0 | 0.2 | 0.5 | 2.7 | 0.1 | 0.4 | 53 | 1.2 | 93 |
| **FOU24** | 1 | 1.1 | 3.2 | 4.4 | 41 | 0.0 | 0.7 | 0.6 | 8.0 | 0.2 | 0.7 | 40 | 1.6 | 92 |
| **FOU27** | 1 | 0.6 | 2.4 | 4.0 | 32 | 0.0 | 0.2 | 0.3 | 5.6 | 0.2 | 0.4 | 52 | 1.6 | 92 |
| **FOU28** | 1 | 1.0 | 2.9 | 6.1 | 32 | 0.0 | 0.3 | 0.8 | 5.5 | 0.2 | 0.3 | 49 | 3.0 | 94 |
| **FOU13** | 2 | 0.5 | 11.2 | 7.2 | 43 | 0.0 | 0.0 | 0.8 | 7.6 | 0.2 | 0.3 | 27 | 1.6 | 92 |
| **FOU14** | 2 | 1.1 | 4.7 | 9.1 | 51 | 0.0 | 0.0 | 1.9 | 4.8 | 0.3 | 0.3 | 21 | 2.0 | 94 |
| **FOU15** | 2 | 0.9 | 3.0 | 5.8 | 38 | 0.0 | 0.3 | 0.8 | 2.7 | 0.2 | 1.0 | 45 | 0.7 | 92 |
| **FOU16** | 2 | 0.6 | 1.7 | 3.9 | 34 | 0.0 | 0.3 | 0.4 | 4.1 | 0.1 | 2.1 | 51 | 2.0 | 95 |
| **FOU21** | 2 | 0.6 | 1.6 | 4.0 | 35 | 0.0 | 0.1 | 0.4 | 4.3 | 0.1 | 2.1 | 50 | 10 | 95 |
| **FOU22** | 2 | 1.0 | 2.6 | 5.9 | 39 | 0.0 | 0.3 | 0.8 | 5.0 | 0.3 | 1.4 | 43 | 1.1 | 95 |
| **FOU29** | 2 | 1.3 | 2.4 | 8.8 | 37 | 0.0 | 0.3 | 1.3 | 4.0 | 0.3 | 0.4 | 43 | 5.1 | 95 |
| **FOU30** | 2 | 0.8 | 6.1 | 5.0 | 49 | 0.0 | 0.3 | 0.6 | 5.7 | 0.2 | 0.4 | 31 | 0.9 | 95 |
| **FOU5** | 3 | 1.0 | 1.3 | 7.1 | 39 | 0.0 | 0.8 | 0.7 | 2.7 | 0.3 | 0.4 | 45 | 0.9 | 97 |
| **FOU6** | 3 | 0.6 | 2.5 | 8.6 | 51 | 0.0 | 0.5 | 1.3 | 6.2 | 0.3 | 0.2 | 28 | 1.2 | 94 |
| **FOU19** | 3 | 0.9 | 3.3 | 7.8 | 47 | 0.0 | 0.1 | 1.2 | 15 | 0.3 | 0.5 | 21 | 0.3 | 93 |
| **FOU26** | 3 | 0.9 | 2.3 | 7.9 | 48 | 0.0 | 0.7 | 1.3 | 5.5 | 0.3 | 0.3 | 32 | 0.9 | 94 |
| **FOU7** | 4 | 0.3 | 5.7 | 4.2 | 44 | 0.0 | 0.5 | 0.7 | 10 | 0.2 | 0.3 | 34 | 0.8 | 96 |
| **FOU8** | 4 | 1.2 | 2.9 | 6.1 | 29 | 0.0 | 0.6 | 1.0 | 4.2 | 0.3 | 0.3 | 52 | 2.4 | 96 |
| **FOU17** | 4 | 0.9 | 4.4 | 3.5 | 43 | 0.0 | 0.5 | 0.4 | 7.3 | 0.1 | 0.3 | 38 | 4.5 | 87 |
| **FOU18** | 4 | 1.2 | 2.3 | 7.8 | 38 | 0.0 | 0.3 | 0.9 | 2.3 | 0.2 | 0.3 | 46 | 2.0 | 93 |

***Table 5.7** Averages of three analyses of slag samples from Phournoi on the (P)ED-XRF, normalised to 100 % (major and minor elements in weight %; MT: measured total). Unit numbers (1, 2, 3, 4, P) correspond to sampling units Phournoi 1-4 and Path.*

The main constituents are again iron oxide (FeO: 21-57 %) and silica ($SiO_2$: 25-51 %), followed by calcium oxide (CaO: 2-15 %), alumina ($Al_2O_3$: 4-9 %), and magnesia (MgO: 1-11 %). Sulphur contents do not exceed 1 % (expressed as $SO_3$). Copper contents range from 0.5-6 % (expressed as CuO) and the average for all the analysed samples is around 2 %. Among the trace elements (Table A4.7b), barium is the most important in terms of quantity, ranging between 100-2700 ppm. Zinc (ZnO: 100-1000 ppm) and arsenic ($As_2O_3$: 10-450 ppm) were detected in all the analysed samples in low quantities, while nickel and lead were only present in some samples, reaching a maximum of 600 ppm and 200 ppm respectively.

Microstructure and phase composition

The microstructure of these specimens was studied using the optical microscope, while the composition of individual phases was analysed for a selection of samples by EPMA. A summary of the optical microscopy examination is given in Appendix 4 (Table A4.8), while the EPMA data are given in Appendix 4 (Table A4.9).

As is the case at Kephala, the slags from Phournoi are mainly composed of iron silicates and lower amounts of iron oxides surrounded by a glassy matrix (Figure 5.50). Analyses of the iron silicates (Table A4.9) confirmed that these have a fayalitic composition with variable amounts of magnesium, while calcium and manganese oxides were detected in some cases as minor impurities. The iron oxides appear to be mainly magnetite, showing angular edges, typical of this phase (Wingrove 1970). They usually accommodate low amounts of alumina and titanium oxide. In samples FOU3 and FOU25 rounded iron oxides were identified in addition to magnetite. Their shape is consistent with wüstite (FeO). They are found either as isolated crystals or as larger agglomerations enclosing matte prills (Figures 5.51 and 5.52).

Remains of partially reacted quartz and magnetite aggregates are also present in these samples, albeit rarely. Even in the sections where such remnants were observed they are usually surrounded by a fully dissolved slag matrix (Figure 5.53). Partially reacted copper-iron sulphidic minerals were observed in samples FOU9 and FOU15 (Figure 5.54).

Upon sectioning samples FOU22 and FOU24, large fragments of ceramic were found enclosed within the slag matrix, near or at the edge of the specimens (Figure 5.55). These fragments are composed of a red-orange ceramic layer with inclusions of schist and quartz and a vitrified layer with large circular vesicles at the contact with the slag. The slag appears to be closely attached to the vitrified ceramic (Figure 5.56). These ceramic fragments show macroscopic similarities to the furnace wall remains at the Phournoi slag heap, at least in terms of the nature and the size of the refractory inclusions within the ceramic. The visual and microscopic examinations suggest that these may correspond to fragments detached from the furnace, incorporated in the melt, and therefore trapped within the slag matrix. Given that the clay has survived instead of dissolving in the slag, it is most reasonable to suggest that this happened at the end of the metallurgical process, whether deliberately (i.e. by breaking the furnace) or accidentally due to the friable nature of the wall. At this stage, and given that furnace wall fragments have not been included in this study, these samples have not been analysed further. It is, however, hoped that additional insight into the nature and role of these fragments will be gained by future study, which will include analysis of the ceramic fabric (chemical and petrographic), detailed comparison with the furnace wall fragments and a thorough examination of the microstructure of these specimens and their association with the surrounding slag.

Analyses of the entrapped prills

Both matte and copper metal prills are found in the slags from Phournoi. They are usually of minute size, rarely exceeding 10 μm in diameter. In some samples both types of prills could be identified optically but copper metal prills were of extremely small size and could not be analysed. A large number of matte and/or copper prills from seventeen slag samples were analysed using point measurements by EPMA and the results are given in Appendix 4 (Table A4.10).

The analyses showed that production of unalloyed copper was carried out at Phournoi. Arsenic and nickel were the only possible alloying constituents detected in these prills but both were consistently below 1 %. Iron contents vary significantly but for the reasons discussed in section 5.4.1.1, quantitative measurement of iron in these prills is impossible using this particular technique and the relevant results should be viewed with caution.

### *5.4.2.2 Isolated copper metal prills*

Two small copper metal prills, FOU31 (diameter: 0.5 cm) and FOU32 (diameter: 0.3 cm) were recovered from Phournoi 3 and Phournoi 1 respectively. They are both covered externally by green corrosion products. The prills were sectioned and it was revealed that uncorroded metal survived only in sample FOU31, while FOU32 was completely weathered. Only the former was therefore analysed further by EPMA.

The copper metal in sample FOU31 incorporates minute sulphidic inclusions. Point analyses were carried out on the copper metal matrix and the sulphidic inclusions separately and the results are given in Table 5.8. Iron contents are below the detection limit in the copper metal matrix, while the only other element identified was nickel at 0.1 %.

| | S | Fe | Ni | Cu | Total |
|---|---|---|---|---|---|
| **FOU31A** | 0.0 | 0.0 | 0.1 | 99 | 99 |
| **FOU31B** | 0.0 | 0.0 | 0.1 | 98 | 99 |
| **FOU31C** | 0.0 | 0.0 | 0.1 | 98 | 99 |
| **FOU31D** | 0.0 | 0.0 | 0.1 | 100 | 100 |
| **FOU31E** | 19 | 0.3 | 0.0 | 78 | 97 |
| **FOU31F** | 19 | 0.2 | 0.0 | 78 | 97 |

***Table 5.8** EPMA point analyses on FOU31 (weight %). Analyses A-D were done on the copper metal matrix, while E-F on the tiny sulphidic inclusions.*

### *5.4.2.3 Other materials*

FOU20

This small specimen was recovered from the top of the Phournoi promontory (Phournoi 3). Externally it is almost entirely covered by a green layer of weathering products (Figure 5.57). A section was cut, mounted and studied using the optical microscope and the EDS-SEM.

The section is very heterogeneous, showing a number of different components. Quartz and schist fragments are found mainly in the centre of the sample together with copper-iron sulphides (Figure 5.58). They are surrounded by a matrix of weathered copper and iron minerals. The sulphides continue around the edges of the sample, where they show characteristic eutectic textures (Figure 5.59), a clear indication that they had started to oxidise in the molten stage. On one of the edges slag 'proper' has formed. The slag comprises of fayalitic crystals surrounded by a glassy matrix, which is now almost entirely corroded (Figure 5.60). Partially dissolved sulphidic minerals can still be discerned within the slag. A small number of EDS-SEM point analyses was carried out on the fayalitic crystals, which confirmed their optical identification (Table 5.9). Similarly to fayalite crystals analysed in other slags from Phournoi, they include substantial amounts of magnesium oxide and lower amounts of calcium and manganese oxides. The crystals are very small and the surrounding matrix was also probably analysed, which explains the high overall total.

The specimen clearly constitutes a partially reacted mixture. Evidence for heating is seen mostly towards the outer edges, suggesting that the sample had started to react from the outside but that the heat did not reach the inner parts.

| | MgO | $Al_2O_3$ | $SiO_2$ | CaO | MnO | FeO | CuO | Total |
|---|---|---|---|---|---|---|---|---|
| **FOU20A** | 9.3 | 0.8 | 31 | 0.4 | 0.3 | 58 | 3.3 | 103 |
| **FOU20B** | 8.1 | 0.4 | 34 | 0.4 | 0.4 | 60 | 1.7 | 105 |

***Table 5.9** EDS-SEM point analyses (weight %) on two fayalite crystals in the slag part of sample FOU20. The crystals are very small and analyses are likely to include the surrounding areas, which explains the presence of copper, the slightly overestimated silica content (silica content of pure fayalite is 30 %), the presence of alumina, and the high overall total.*

FOU38

Sample FOU38 was collected from the Phournoi 1 area. It is very small and covered externally almost entirely by a green weathered layer (Figure 5.61). Microscopic examination showed that the matrix of the sample is composed of secondary iron and, to a lesser extent, copper minerals with fragments of quartz and schist and a few inclusions of copper-iron sulphides. Similarly to FOU20, slag has formed at one of the edges of the sample (Figure 5.62). The slag consists of small fayalite crystals and several distinct matte prills surrounded by a glass matrix, which is completely weathered on part of the slag. The matte prills have been analysed by EPMA and the results are given in Appendix 4 (Table A4.10). Apart from copper, iron, and sulphur no other elements were found above the detection limits of this instrument (low totals in these analyses are due to the small size of the prills).

Partially reacted sulphides are seen further below the same side where the slag has formed (Figure 5.63). The sulphides show eutectic textures, while a long magnetite aggregate with prills has formed from the reaction and oxidation of the sulphidic minerals (Figure 5.64). The microstructure of sample FOU38 also suggests that it constitutes part of a furnace charge, which was, however, only heated partially from one side and the reaction was not completed.

## FOU39

Sample FOU39 was collected from Phournoi 1. Macroscopically it appeared to be a small schist fragment bearing a little attached slag and green copper minerals (Figure 5.65).

Examination by optical microscopy confirmed that the sample is composed of two parts, an almost circular slag droplet attached to a schist fragment (Figure 5.66). The two are in close contact but do not appear to be reacting, suggesting that the slag fell on the schist fragment outside the furnace. The slag is composed of fayalite crystals, magnetite dendrites, copper and matte prills (see analyses in Table A4.10), surrounded by a glass matrix, which shows intense red reflections from the presence of cuprite (Hauptmann *et al.* 2003). The schist fragment is traversed by small quartz veinlets, which run parallel to the schist direction, and is rich in green secondary copper minerals, which appear to have been deposited between the schist layers (Figure 5.67). These observations suggest that schist, associated with quartz, is likely to have been the host rock of the copper minerals used at Phournoi.

## FOU40

Sample FOU40 was collected from Phournoi 1. Macroscopically it appears to be a small schist fragment with traces of secondary green copper minerals (Figure 5.68). A section was studied under the optical microscope and it was confirmed that the specimen is schist with small amounts of secondary copper minerals on one edge (Figures 5.69 and 5.70). The copper minerals are located between the schist layers, often associated with small quartz veinlets, which also follow the schist direction. The specimen shows no signs of having been heated. The examination of sample FOU40 also supports an association between the schist-quartz host rock and the copper mineralisation. The particular sample is likely to have been discarded, being too poor in copper.

## 5.5 Evaluating the technological parameters of metal production on Kephala and Phournoi

The slag heaps of Kephala and Phournoi are both relatively large and potentially complex and at this stage sampling has been restricted to surface collection. This study is the first comprehensive analytical examination of material from these sites and the number of samples analysed is small in comparison to the large volume of material present. Nevertheless, an effort was made to develop an appropriate sampling strategy that would ensure that different parts of the site were covered and potentially different types of material included. The analyses carried out for this thesis allow a first evaluation of some of the technological parameters of the metallurgical activities at Kephala and Phournoi, which will be presented in this section. The results from the examination of slags and other metallurgical remains from the two sites show strong similarities. For this reason, Kephala and Phournoi will be considered together in the following discussion.

### *5.5.1 The nature of the ores used*

Conclusive evidence for the use of primary sulphidic ores for EBA copper production was found among the material examined from both sites. The slags usually bear small matte prills, typical products of smelting copper-iron sulphides, while remains of partially reacted sulphidic minerals were observed in a few of these samples (KEF13, FOU9, and FOU15). In addition to the slag, firm archaeological and scientific evidence was given for the presence of both matte and weathered or partially reacted sulphide ore fragments. Sulphides were found within the isolated unreacted and partially reacted mineral fragments (KEF29, FOU20, FOU38) from Kephala and Phournoi, even if only in small quantities, as in sample KEF29, while three samples from Kephala (KEF12, KEF27, KEF28) were identified as matte fragments, either accidentally spilled or possibly deliberately discarded at the end of the process. This is the first time matte fragments have been recognised in EBA Cycladic smelting sites. The information deduced from these samples highlights the importance of including in the analyses of metallurgical remains macroscopically ‘exceptional’ samples in addition to a larger sample of ‘representative’ material.

Several recent studies have shown 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 the matte smelting process (Craddock 1995: 149-53) carried out in later periods. These processes involved either solely or mainly the use of sulphidic ores (e.g. Bartelheim *et al.* 2003; Bourgarit *et al.* 2003; Moesta and Schlick 1989; Zwicker *et al.* 1985) or the co-smelting of secondary oxidic ores together with sulphides (e.g. Hauptmann *et al.* 2003; Rostoker *et al.* 1989; Rostoker and Dvorak 1991; Schreiner *et al.* 2003). Different routes can be followed in the smelting of sulphidic ores but the resulting slags may show strong similarities that will make exact reconstruction of the process difficult.

The problem is illustrated by comparing, for example, the results of the studies of Zwicker *et al.* (1985) and Moesta and Schlick (1989). In their smelting experiments of sulphidic copper ores in a crucible, Zwicker *et al.* (1985) showed that 75 % recovery of the metal was possible by a primary step of complete roasting at 800°C followed by heating the resulting roasted concentrate at 1100°C with charcoal. The resulting slag showed inclusions of copper iron sulphides either formed as distinct prills or as inclusions in copper metal prills surrounded by a slag composed of iron silicates and magnetite. Moesta and Schlick (1989) have proposed a different process for the Bronze Age copper furnaces at Mitterberg. Following examination of slagged furnace lining taken from different heights within the furnace they estimated the prevailing furnace conditions and concluded that the sulphidic ores were initially smelted in moderately reducing conditions with the resulting matte subsequently being oxidised after removing the slag. They suggested that the whole process could be carried out in a simple hearth structure. The microstructure of the slag from the first stage of this operation is mainly fayalitic with frequent matte inclusions, very similar to the slag produced by Zwicker *et al.* (1985) and to the majority of slags analysed from Kephala and Phournoi. A similar microstructure could also be expected from smelting a mainly oxidic ore with sulphides present as minor constituents. It is therefore clear that the phase composition of the analysed slags does not allow a clear understanding of the details of the smelting process and additional evidence is necessary to draw secure conclusions.

A few observations made during analysis of the Kephala and Phournoi slags provide further information. Firstly, the relatively large partially reacted sulphidic minerals in some of the slags (KEF13, FOU9, and FOU15) indicate that dead roasting prior to smelting is unlikely. Secondly, there is no evidence at present to support a two-step process, as suggested by Moesta and Schlick (1989), although this picture may change with future sampling and analyses. Matte and copper prills co-exist in many samples, which also suggests that both products resulted from the same process. Thirdly, the amount of matte recovered from both slag heaps is small, although it should be stressed that both the absence of excavated material and the potential effects of weathering may have partly contributed to this picture. Finally, the few unreacted or partially reacted mineral fragments collected from the two sites (KEF29, FOU20, and FOU38) are mixtures of both secondary and primary minerals. This evidence suggests that the ores probably consisted of both oxidic and sulphidic minerals that were co-smelted, as outlined by Rostoker *et al.* (1989). The sulphides could have entered the charge as minor accessory components to a mainly oxidic ore. The presence of minute sulphidic remains was also recognised in the copper mineralization identified close to the Kephala tower (section 4.4.1).

Copper was closely associated with iron in the ores used. The majority of partially reacted or unreacted sulphides identified in these samples are copper-iron sulphides, mainly chalcopyrite. Similarly, secondary copper and iron minerals are intimately intergrown. The identification of magnetite aggregates with copper prills also testifies to the use of mixed copper and iron minerals (Hauptmann *et al.* 2003), but does not allow to distinguish between the use of either primary or secondary mixed ores.

The other major component of the slags from Kephala and Phournoi is silica. A few undissolved quartz fragments were found in the slags. The question that needs to be addressed is whether these were deliberately added as fluxing agents or whether they co-existed with the mineralization. Evidence is again drawn from the few discarded mineral fragments found in the heaps. Quartz fragments were identified within the copper-iron mineral sample KEF29, while quartz veinlets were noted in the copper-bearing schist fragments in FOU39 and FOU40. This suggests that both the silica and the iron-bearing components existed in close association in the ore source making the ores largely self-fluxing. It is, however, possible that the smelters deliberately manipulated the composition of the charge to balance the two components and achieve a better slag composition. This, though, is impossible to prove or disprove archaeologically.

The role of schist as a host rock to the copper mineralization was shown, at least in the case of Phournoi, by the examination of samples FOU39 and FOU40. This observation may be of some importance in the case of Seriphos in terms of locating the ore sources. As outlined in Chapter 4, the island's geological setting consists of different rock units, with an extensive schist unit found at the northern part, where both slag heaps are found. Minor copper mineralisations are known to exist within this unit and one was identified during the geological survey carried out for this thesis close to the tower of Kephala, in the near vicinity of the homonymous slag heap (section 4.4.1). The identification of copper-bearing schist minerals at the Phournoi slag heap does not, however, provide conclusive evidence for the exploitation of a local source. Schist is common on many Cycladic islands, while copper-bearing schist is known on the neighbouring island of Kythnos (Bassiakos and Philaniotou in press). Further geological fieldwork and appropriate analytical work will be necessary to identify with certainty the copper sources for both slag heaps. The question of provenance, although not addressed as a central aim of this thesis, is of prime importance in assessing the proximity of the ore sources to the slag heaps and understanding why the particular locations were selected for smelting.

### *5.5.2 Temperatures and redox conditions*

The most commonly used method for deducing the temperature reached during smelting involves estimation of the liquidus temperature of slags by plotting the bulk analysis data on appropriate ternary phase diagrams (e.g. Bachmann 1980; Morton and Wingrove 1969). The approach is, however, restricted by several limitations that only allow a rough approximation of the temperature range (e.g. Hauptmann *et al.* 1988: 39; Kresten 1986). The phase diagrams depict systems in equilibrium, a condition not normally attained during smelting. In addition, although slags are composed of a wide range of chemical components, only some of the main ones are included in these diagrams. Another shortcoming stems from the fact that the diagrams typically used in the representation of ancient copper slags represent systems under strongly reducing atmospheres ($pO_2 \sim 10^{-11}$-$10^{-12}$ atm), where all the iron is present in its ferrous state (FeO). Ancient copper smelting typically took place at intermediate oxygen partial pressures and this difference in redox conditions will significantly affect the emerging picture (Kongoli and Yazawa 2001). It should also be stressed that this approach assumes that the materials had fully reacted, while the incorporation in the analyses of areas with partially reacted inclusions will produce higher estimated temperatures (e.g. Schreiner *et al.* 2003: 493). Despite these limitations, the use of ternary phase diagrams presents a useful graphic representation of slag compositions and allows at least an approximation of the smelting temperatures used.

The microscopic examination of slags from Kephala and Phournoi showed that the primary materials had in most cases fully reacted. Using the approach outlined by Bachmann (1980) the system $SiO_2$-Anorthite ($CaAl_2Si_2O_8$)-FeO, commonly used in archaeometallurgy, was selected as most appropriate. The bulk composition data produced by (P)ED-XRF analysis were reduced to the three components, with sodium and potassium oxides added to anorthite and magnesium and manganese oxides to iron oxide (cf. Bachmann 1980). The resulting diagrams are presented in Figures 5.71 and 5.72.

The majority of slag samples from Kephala (Figure 5.71) plot within the fayalite region of the diagram, which corresponds to the lowest liquidus temperatures for this system (T~1100-1200°C). Samples KEF4 and KEF10, which showed the highest calcium oxide contents among this group, are naturally closer to the anorthite region of the diagram, with higher liquidus temperatures in the range of T~1200-1300°C. The remaining samples form a relatively tight group. Samples KEF32 and KEF40, noted for their higher iron contents, are close to the wüstite region. The absence of wüstite and the high concentrations of magnetite observed in these samples highlight the inability of these diagrams to deal with systems under intermediate oxygen partial pressures.

The slags from Phournoi spread more widely in the relevant phase diagram, possibly indicating two different groups (Figure 5.72). The first plots within the fayalitic region and the second (samples labelled in Figure 5.72) shows higher silica contents and plots within a region of the phase diagram where temperatures rise steeply giving an estimated smelting temperature between 1200-1350°C. It should, however, be noted that during microscopic examination partially reacted quartz fragments were found in these five samples (FOU6, FOU9, FOU14, FOU26, and FOU30). Given that the samples were analysed as powders similar inclusions were probably incorporated in the prepared pellets, shifting the composition of the specimens to the silica-rich region and resulting in an overestimation of the expected smelting temperature.

Overall, the temperature range for copper smelting on both Kephala and Phournoi is close to T~1100-1200°C, with some parts of the furnace probably reaching higher temperatures. Additional methods can be used to estimate the smelting temperatures, such as the experimental differential thermoanalysis of slags and the appropriate examination of furnace fragments (Hauptmann *et al.* 1988: 39). These additional studies could be applied in the future in order to test and refine the results obtained by the use of phase diagrams.

Another furnace operating parameter that can be determined from slag analyses is the redox atmosphere held during smelting. The phase composition of the slags provides an insight into this aspect of the process because different components crystallise depending on the prevailing redox conditions (e.g. Moesta and Schlick 1989). These can be deduced from diagrams depicting the relevant phase transitions as a function of oxygen fugacity and temperature (e.g. Craddock *et al.* 1985: 206; Craddock 1995: 18; Schreiner *et al.* 2003). Figure 5.73 shows the buffer curves for the Fe-Si-O system and for copper reduction ($Cu_2$-Cu), which are relevant for the study of these slags. The main components in the slags from both Kephala and Phournoi are fayalite and magnetite, and, although the former usually predominates, some samples show increased concentrations of magnetite. Wüstite is absent in almost all the specimens. Based on these observations and the temperature range deduced from the phase diagrams, the slags from Phournoi and Kephala were produced in oxygen pressures between $10^{-6}$-$10^{-11}$; that is at intermediate oxygen pressures. Depending on the relative abundance of fayalite to magnetite in each specimen the slags may result from slightly more reducing or oxidising atmospheres within this broad range (cf. Hauptmann *et al.* 1988: 40). These differences are likely to be the result of variable redox conditions between the different parts of the furnace.

### *5.5.3 Slag-metal separation*

One of the most desired properties of slag is low viscosity, in order to ensure better separation from the metal by allowing it to drain through the slag and form a larger ingot (Bachmann 1982a). Additionally, liquid slag could be tapped outside the furnace and further facilitate the separation from the metal. The use of quantitative calculations for viscosity estimations (e.g. Bachmann 1980) is considered inappropriate in the case of ancient slags (Kresten 1986). Following the example of Schreiner *et al.* (2003), however, some conclusions on the viscosity of the slags from Seriphos can be drawn using certain macroscopic observations.

First, because undissolved inclusions are rare, it is clear that in most cases the slags had fully reacted. Evidence that the slags were molten at the operating temperatures also stems from the observation of flow patterns on the upper surface of many of the fragments. Large copper prills are rare and the majority have diameters below 10 μm, showing that the metal could drain through the liquid slag. The copper contents of the slags are generally medium to low, averaging at c. 2 % (estimated as CuO), which also indicates relatively efficient copper production. It should be noted, however, that some samples showed much higher copper contents.

The presence of a flow texture on the outer surface of the slags does not necessarily imply that the slags were tapped outside the furnace, as it could also result from molten slags crystallising within the furnace. The texture of samples KEF16 and KEF26, showing characteristic magnetite bands, is, however, consistent with a melt crystallising in contact with air and with layers of slag being superimposed from a continuous flow. Additional evidence for slag tapping at Kephala is the observation of a layer of slag with flow pattern on the schist bedrock at the Kephala slag heap and the presence of larger masses of slag with flow texture seen in Kephala 1 (Figure 5.6). Although these observations suggest that some slag tapping was carried out at least at Kephala, the issue needs to be investigated further for both sites by examination of appropriately cut sections (i.e. sections including the external 'flow surface' and areas of contact between different slag 'ropes') from samples showing a flow texture. A large number of samples on both slag heaps do not show a flow pattern but are instead very crystalline indicating that they cooled slowly, probably within the furnace (see for example sample KEF23 in Figure 5.8). The effect of different cooling conditions, rather than composition, on the macroscopic appearance of slags has been highlighted by other researchers (e.g. Craddock *et al.* 1985: 204; Hauptmann *et al.* 1988: 40).

### *5.5.4 Composition of the final product*

Analyses of the copper prills found within the slags or as isolated fragments at both Kephala and Phournoi showed that unalloyed copper was produced on the two sites. Only traces of other base metals were detected in the copper, usually arsenic or nickel, which were probably present in minor quantities in the ores and concentrated in the metal during smelting (Tylecote *et al.* 1977; Yazawa 1980).

On the basis of the two isolated copper prills (KEF41 and FOU31) and the large copper prill found in sample KEF40, iron contents in the metal produced are below 0.1 %. This is much lower than the values expected for slagging smelting processes according to Craddock and Meeks (1987). A possible explanation is that smelting on the two sites was carried out under a less reducing atmosphere than the processes discussed by Craddock and Meeks (1987). In this respect it should be noted that sample KEF40 is comparatively rich in magnetite. Admittedly, the low iron contents postulated for the metal produced on the two sites are based on a very small sample number. The iron contents for the majority of prills analysed have not been considered due to the possibility of simultaneous measurement of the surrounding matrix. The iron content of the copper produced on Kephala and Phournoi presents an interesting aspect that should be studied more systematically in the future using

an appropriate methodology, but at present is in line with accepted levels for EBA copper metal.
Another feature of the copper product, which is clear in the three prills discussed before, is the presence of minute inclusions of copper sulphides (chalcocine) within the metal matrix. Such inclusions are common in early copper metals. Although iron contents are negligible in these sulphides, the sulphidic minerals introduced in the charge on Kephala and Phournoi were shown to be copper-iron sulphides (cf. Craddock *et al.* 2003; Hauptmann *et al.* 1988). The mechanism for this reaction involves progressive oxidation of the iron with corresponding enrichment of copper in the matte as was clearly evident from the partially reacted sulphidic minerals in sample KEF13, and the eutectic structures including magnetite in a sulphidic matrix.

### *5.5.5 Site layout*

One of the aims of this study was to examine whether any differences could be observed between different parts of the two sites that would indicate the practice of different metallurgical activities. The analyses carried out so far did not detect any consistent compositional differences in the slags collected from the different sampling units of Kephala and Phournoi. The number of samples analysed is, however, admittedly small in comparison to the relatively large volume of these heaps, particularly in the case of Kephala.

One observation concerning the layout of these sites should, however, be highlighted. The main concentrations of material on both slag heaps extend from just below the crest of the promontories and down the north-facing slope, facing the direction of the prevailing winds, similarly to other smelting sites identified in the Cyclades (see for example Bassiakos and Philaniotou in press). Although furnaces have not been identified in this part of the heaps to date the distribution of the material suggests that they may have been positioned in such a way as to make use of the most intense winds (cf. Hauptmann and Weisgerber 1992: 63-4; Juleff 1996). This possibility requires further attention in order to investigate whether the furnaces were operated by natural draught and how the process would have been carried out. Given that this particular setting is typical of Cycladic smelting sites, it is important to clarify the extent to which the effects of strong winds played a role in selecting the specific locations.

## 5.6 Other metallurgical sites on Seriphos

### *5.6.1 The slag heap of Avessalos*

#### *5.6.1.1 Location and layout*

The largest slag heap known on Seriphos is situated on a slope south of the bay of Avessalos (Figure 5.1). A relatively large marble unit is exposed in this area and at the contact zone with the surrounding schist substantial concentrations of secondary iron ores (hematite and limonite) have been deposited. These were exploited heavily for iron in the last century, as is testified both by remains observed in the field (mining galleries, spoil heaps and the remains of a loading bay at the south-western edge of Avessalos bay) as well as recent geological accounts (Marinos 1951; Papastavrou and Zographos 1979). Copper minerals have not been identified so far in the immediate vicinity of the heap.

The main concentration of material extends from the crest downhill on the north-facing slope (Figure 5.74), while smaller quantities were observed at the south-facing side separated from the main deposit by flat schist bedrock and a modern dirt road. The main deposit on the north-facing slope is much thicker than at the two sites discussed previously and appears to exceed 1 m depth in some of its thickest areas, in the upper part of the slope. This estimate is strengthened by observations derived from four to five pits that have been dug into the heap. The pits are aligned at the same horizontal level, their diameter and depth are both roughly 1 m and they do not reach the underlying bedrock. Judging from their layout and particularly their horizontal alignment it is possible that these represent purposefully made test pits by modern geologists or mining engineers, either for research or perhaps to investigate the possibility of re-using the heap. Although the heap is mentioned in at least one modern geological report (Papastavrou and Zographos 1979),[5.4] reference to such recent activities has not been found.

The slag heap is cut twice by a modern road, allowing some interesting observations, particularly at the upper section. The slag layer exposed in this section extends approximately 170 m in length, while the thickness of the deposit here varies considerably from 15 cm or less at the edges to roughly 80 cm at its thicker part. Based on the observations here and at the top of the slag heap it appears that the depth of the deposit is very variable and further systematic measurements will be necessary to obtain even a preliminary approximation of the volume of the slag heap. Gale *et al.* (1985) have suggested that over 100,000 tonnes of material have been deposited, which highlights the impressive size of the heap, vastly larger than Phournoi or Kephala.

The road section also presents a unique opportunity to assess some of the internal characteristics of the heap. The slag heap sits on the schist bedrock, which rises roughly 1.5 m from the road level. In some of the thicker parts of the section some stratification is observed (Figure 5.75). Two to three tentative sub-layers, defined by differences in the size of the slags, can be discerned in places. Three types of layers were observed: small slag (1-3 cm), medium slag (6-10 cm) and larger slags, which usually sit on the top. The sequence between the first two is not consistent and although usually the lower layer consisted of small slags, occasionally a layer of small slags was sitting on top of a layer of medium ones. Initially it was thought that a layer of soil separated the observed layers in some areas, but on closer inspection it was concluded that this actually corresponded to small slags covered externally by soil. The fact that stratification is only observed in parts of the section, and the absence of a clear separating soil layer, makes it impossible to decide at this stage whether these layers correspond to distinct operations carried out possibly in different chronological periods, or whether the phenomenon is simply the result of a natural re-distribution of the material as it eroded from the hilltop.

---

[5.4] Papastavrou and Zographos (1979) refer to the site Skouries in the promontory of Agriomelissa, which locals confirmed to us corresponds to the Avessalos slag heap.

A number of very interesting features are noted at the top of the hill, just above the slag heap. These consist of small, rounded, relatively shallow pits, usually about 10 cm in diameter and up to 8 cm deep, which have been carved in the schist bedrock. These are usually seen in small clusters, while in one area a number of these small pits were found arranged around a larger one (40 cm diameter) (Figure 5.76). They appear to be installations for ore or slag crushing (see also Craddock 1995: 159). The association is further supported by the identification of several stone tools in this part of the site (see below). More peculiar was the observation of vertical grooves on a schist outcrop in the same area, which were located close to a cluster of small pits (Figure 5.77). The purpose of these cuttings is not at present clear.

#### *5.6.1.2 Description of the material*

The slag fragments in the Avessalos heap are dark grey to black in colour and often show considerable green staining on their outer surface, immediately indicating an association with copper metallurgy. They vary in size from small fragmented pieces to large slabs. In some parts at the top of the heap, thick masses of slag (see analyses of AVE3 and AVE4 in section c below) are observed, as already noted by Gale and Stos-Gale (1989a: 25). These often stand nearly 1 m from the surface of the heap, show a ropey texture and appear to be the result of continuous or periodic flowing of molten slag on top of existing cooled tapped slag resembling a cooled lava formation (Figure 5.78). Entrapped pieces of schist and ceramic are frequently observed within them. Similar inclusions of schist or ceramic fragments, often relatively large (max. length c. 7 cm), are also often seen in the main body of some of the larger broken slag fragments (Figure 5.79). Similar observations have been made in some of the slags at Sideri on Kythnos (Bassiakos and Philaniotou in press). It is not clear at present whether these fragments were deliberately added to the furnace charge or whether they were carried through by the flowing molten slag.

Ceramic furnace lining or wall fragments represent less than 5 % of the surface material. Concentrations of these are seen in some parts of the heap, often together with large schist fragments, which bear evidence of heat impact and green staining, indicating that these were probably also associated with the furnace installation. It is possible that these concentrations point to actual furnace locations but in the absence of an excavation this cannot be confirmed. The thickness of the ceramic fragments is usually 2-3 cm and their outer characteristics (colour, inclusions, attached slag) are similar to the ones described for Kephala.

Particularly interesting here, as at Kephala, was the identification of some ceramic specimens with perforations. All the specimens were broken, leaving only part of the hole intact. Fortunately, adequate circumference was present in most cases to estimate that their original diameter was roughly 2 cm. The majority of the pieces only bear the traces of a single hole, but one specimen showed two.

At least seven stone tools have been identified so far on Avessalos (Figure 5.80), while other fragments, which may correspond to broken tools, have also been noted. These were all found at the top of the hill on the schist bedrock, in close proximity to the carved holes discussed previously. Their identification solely in this part of the site is a strong indication that this may represent a working area, where crushing was carried out. Six of these were granite tools and one was gneiss. They show several indentations on their surfaces, which would have served for holding. Marks of wear are frequent on their edges, while some have been partly chipped off.

Fragments of copper minerals, possibly discarded during sorting, are frequent within the heap but these are usually very small and therefore difficult to recognise. The majority appear macroscopically to be green oxidised minerals associated with quartz and/or schist.

#### *5.6.1.3 The question of dating the Avessalos slag heap*

Although no systematic efforts have been made to date the Avessalos slag heap, the site is usually considered to be later than the EBA (e.g. Gale *et al.* 1985), due to its larger size in comparison to other known EBA Aegean smelting sites. It should, however, be noted that EBA sherds were identified among the slags during fieldwork undertaken as part of the current collaborative project (Philaniotou 2004), confirming earlier reports of prehistoric pottery at Avessalos (Weisgerber 1985: 112, note 28). In addition, several characteristics were noted, which may be used to support a prehistoric date for at least part of the material. These include the position of the site on the slope of a windy promontory, a setting typical of Cycladic EBA smelting sites and the identification of perforated ceramic furnace lining fragments, also known from other Aegean EBA slag heaps. On the other hand Davies (1935: 260) reports that he found fourth century Carthaginian coins among slags at the top of the hill of Koundouro. It is, however, at present unclear whether these slags actually correspond to the Avessalos slag heap or indeed those found recently at Koundouro (cf. Gale *et al.* 1985; Gale and Stos-Gale 2002). The possibility that Avessalos is a multi-period site cannot be disregarded, particularly as preliminary indications for possible stratification were noted on the road section (see above). The dating of the Avessalos slag heap presents an important and potentially complicated problem that will need to be addressed appropriately in the future.

### *5.6.1.4 Sampling and preliminary analytical investigation of four slags from Avessalos*

The large size of the Avessalos heap and the possible stratification observed at the road section urge a thorough and systematic sampling that takes into account the particularities of this site. At this stage, such an endeavour was not deemed achievable, due to time and resource limitations. It was, however, possible to collect a small number of samples from specific contexts within the heap and perform preliminary analyses to check whether differences can be observed.

Two samples (AVE3 and AVE 4) were taken from the large, thick masses of slag at the top of the Avessalos heap (Figure 5.78) and another two samples were collected from a layer with small slags, lying below a layer of larger specimens, at the road section (AVE1 and AVE2). The samples represent the two extreme cases of slag sizes on Avessalos (see Table 5.10 for description of the samples). On the basis of their context they are most likely to reflect chronologically different activities, should this represent a multi-period site. The purpose of this preliminary examination was to see whether analytical characteristics could be distinguished between the samples from the two contexts, which would support a differentiation.

| | Context | D (cm) | W (g) | Description |
|---|---|---|---|---|
| **AVE1** | Lower layer of road section | 3.5x3x1.5 | 11.5 | Small slag, black weathered outer surface, porous |
| **AVE2** | Lower layer of road section | 3x2x1 | 8.8 | Small slag, black weathered outer surface, porous |
| **AVE3** | Large masses of slag from top of the Avessalos heap | 5.5x6.5x6* | 250* | Black slag with iron and copper oxide staining, shows flow texture features, bears a fragment of schist (length: c. 2 cm) |
| **AVE4** | Large masses of slag from top of the Avessalos heap | 3.5x3.5x3* | 61* | Black slag with little iron oxide staining, shows flow texture features, bears small fragments of quartz |

***Table 5.10** Description of samples analysed from Avessalos (D: dimensions, W: weight). Measurements marked with * indicate samples cut from larger specimens, where dimensions given are those of the samples removed.*

Samples were cut and prepared as mounted sections, which were first examined under the optical microscope. Bulk analyses were carried out using a scanning electron microscope (EDS-SEM) and measuring five different areas (c. $2x10^{-8}$ $mm^2$ each) across the section. Point SEM analyses were done on some of the entrapped metallic and sulphidic phases.

Bulk analyses of these samples (Table 5.11) did not show consistent differences between the two groups. In all four samples silica ($SiO_2$: 44-48 %) and iron oxide (FeO: 31-40 %) are the main components, followed by calcium oxide (CaO: 6-13 %) and smaller amounts of other gangue oxides. Copper oxide contents range between 1-2 %.

| | $MgO$ | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | $CaO$ | $TiO_2$ | $MnO$ | $FeO$ | $CuO$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **AVE1** | 1.0 | 6.4 | 45 | 0.3 | 1.0 | 7.5 | 0.3 | 0.4 | 37 | 0.9 |
| **AVE2** | 0.8 | 3.5 | 44 | b.d.l. | 0.7 | 9.3 | 0.2 | 1.1 | 39 | 1.8 |
| **AVE3** | 3.1 | 4.0 | 44 | 1.1 | 0.5 | 5.9 | 0.2 | 0.0 | 40 | 0.8 |
| **AVE4** | 3.4 | 2.1 | 48 | b.d.l. | 0.2 | 13.4 | b.d.l. | 0.3 | 31 | 1.3 |

***Table 5.11*** *Normalised EDS-SEM bulk analyses (weight %) of slag samples from Avessalos (b.d.l. below detection limit <0.1 %). Analyses of the Avessalos samples have been done using a different EDS-SEM, which was not calibrated each time against a standard but automatically normalised the results to 100 %. Different areas were analysed consecutively in one analysis, instead of doing separate measurements.*

Examined under the optical microscope, all four samples are consistent with having crystallised from a fully reacted melt. Remains of unreacted starting materials were not observed. Fayalite is the dominant phase in samples AVE1, AVE2, and AVE3, accompanied by magnetite (comparatively less in sample AVE3) in a glassy matrix. Sample AVE4 appears completely glassy and distinct phases could not be discerned. Small matte prills were noted in all four samples. Copper prills were only seen in sample AVE4. Two or three of the matte and copper prills were analysed on the EDS-SEM and the results are given in Table 5.12. A potentially interesting difference is noted in the arsenic contents between the analyses of samples from the two contexts. Arsenic is present in the four matte prills analysed in AVE1 (0.5 and 0.7 %) and AVE2 (2.5 and 3.2 %), while the element was below detection limit in the other two samples. This observation is very interesting, as arsenic is the most common copper-alloying component in Cycladic metals during the EBA. This tentative preliminary distinction between the two groups of slag does not, however, set a firm basis to distinguish between two chronologically different activities, as no other analytical differences have been observed and a clear stratigraphic separation is at present not established.

| | Al | Si | S | Cl | Ca | Fe | Cu | Ni | As |
|---|---|---|---|---|---|---|---|---|---|
| **AVE1a** | b.d.l. | b.d.l. | 27 | b.d.l. | b.d.l. | 2.4 | 70 | b.d.l. | 0.7 |
| **AVE1b** | b.d.l. | b.d.l. | 26 | b.d.l. | b.d.l. | 2.9 | 70 | b.d.l. | 0.5 |
| **AVE2a** | b.d.l. | 4.1 | 14 | b.d.l. | 1.1 | 14 | 63 | 0.5 | 3.2 |
| **AVE2b** | b.d.l. | 2.3 | 13 | b.d.l. | 1.1 | 4.8 | 77 | b.d.l. | 2.5 |
| **AVE3a** | b.d.l. | b.d.l. | 39 | b.d.l. | b.d.l. | 1.0 | 60 | b.d.l. | b.d.l. |
| **AVE3b** | b.d.l. | b.d.l. | 39 | b.d.l. | b.d.l. | 30 | 31 | b.d.l. | b.d.l. |
| **AVE3c** | b.d.l. | b.d.l. | 39 | b.d.l. | b.d.l. | 28 | 33 | b.d.l. | b.d.l. |
| **AVE4a** | b.d.l. | 0.7 | 23 | 1.4 | 0.6 | 3.5 | 71 | b.d.l. | b.d.l. |
| **AVE4b** | 0.6 | 1.9 | 0.2 | 2.3 | 0.5 | 4.4 | 90 | b.d.l. | b.d.l. |
| **AVE4c** | b.d.l. | 1.8 | b.d.l. | b.d.l. | 0.8 | 5.9 | 92 | b.d.l. | b.d.l. |

***Table 5.12** Normalised SEM-EDS point analyses on matte and copper prills (AVE4b, AVE4c) in slag samples from Avessalos (weight %). Elements Al, Si, and Ca are from the surrounding slag matrix (also part of Fe in these cases) when prills were too small to be analysed separately.*

Overall, the small number of samples analysed in this study prohibits any firm conclusions to be made at this stage concerning the technology of metal production on Avessalos. The slags analysed so far show broadly similar characteristics in terms of microstructure and bulk composition to the slags from Kephala and Phournoi. The differences in the arsenic contents of the entrapped prills in the two slag groups is interesting but the extent to which this is consistent in the slag heap and furthermore reflects chronologically different metallurgical operations will need to be tested in the future by further analyses using a detailed systematic sampling methodology and a large-scale dating programme. It should, however, be noted that the arsenic content of the entrapped prills in the smaller slags is also consistent with an EBA date for part of the material, given the predominance of these alloys during this period.

The fieldwork carried out on Avessalos as part of the current collaborative project and the preliminary analyses presented above have identified several interesting features, which highlight the importance of this site. The main questions regarding the associated metallurgical activities (date, technology, provenance of raw materials) remain, however, unanswered until further more comprehensive investigations are undertaken.

### *5.6.2 The slag scatters of Koundouro and Aerata*

Additional slag scatters on Seriphos have been reported recently by two teams. Gale and Stos-Gale (2002, in press) identified copper slags and pieces of obsidian close to the village of Koundouro in south-western Seriphos, which they propose may be the slags noted in the past by Davies (1935: 260). Papadimitriou and Fragiskos (2003) found copper slags at Aerata, a hill between Koundouro and Avessalos. The exact locations of these sites are not clear at present, but their proximity (both appear to be close to Koundouro village) raises the possibility that both reports are dealing with the same site. Neither of these slag scatters has been dated, while preliminary analytical results are only presented by Papadimitriou and Fragiskos (2003).

The examination of metal production on Seriphos has established the island's importance in early copper metallurgy. Four or five slag heaps or scatters are now known on Seriphos and at least two, Kephala and Phournoi, can now be conclusively attributed an EBA date. The present study has offered significant insight into the process parameters of the activities undertaken at Kephala and Phournoi and identified several issues that merit further archaeometallurgical investigation both on these as well as on the other sites known so far.

***Figure 5.1*** *Map of Seriphos, showing sites mentioned (for further locations relevant to the geology of the island see Figure 4.1). Only one site is noted for the slag scatters of Koundouro and Aerata reported by Gale and Stos-Gale (2002) and Papadimitriou and Fragiskos (2003), showing location approximately.*

*Figure 5.2* The north-facing slope of the Kephala slag heap, showing the two main deposits of material, Kephala 1 and Kephala 2, and the position of Kephala 3.

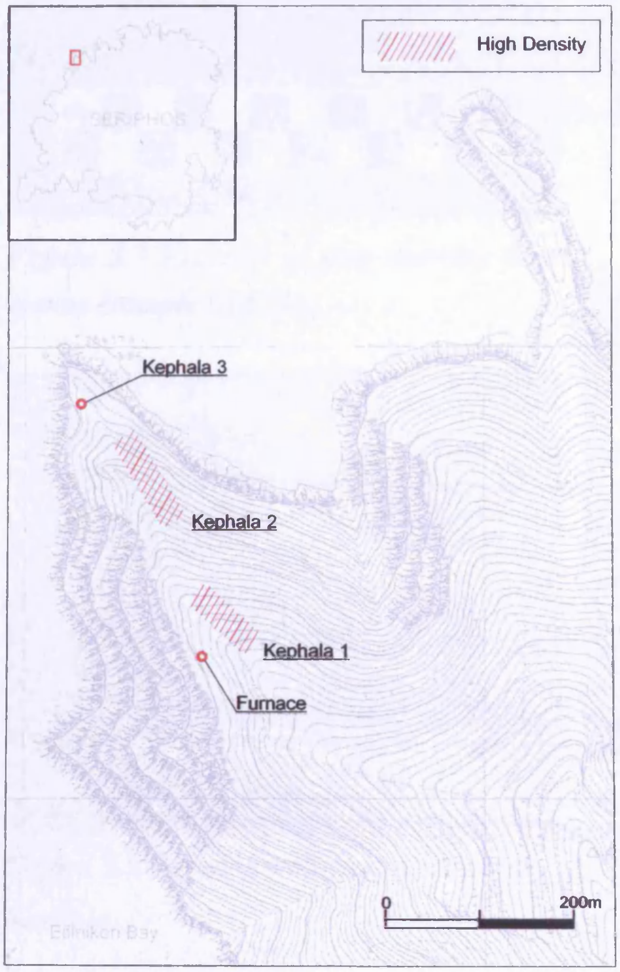


*Figure 5.3* Plan of the Kephala slag heap showing location of the sampled units.

*Figure 5.4* Area in the south-facing slope of the Kephala heap covered with broken slag fragments.

**Figure 5.5** *Igneous rock fragments from Kephala 3.*

**Figure 5.6** *Large masses of slag with flow texture at Kephala 1.*

**Figure 5.7** *Example of slag showing flow texture (sample KEF31).*

**Figure 5.8** *Example of dense crystalline slag (sample KEF23).*

**Figure 5.9** *Furnace wall fragments from Kephala.*

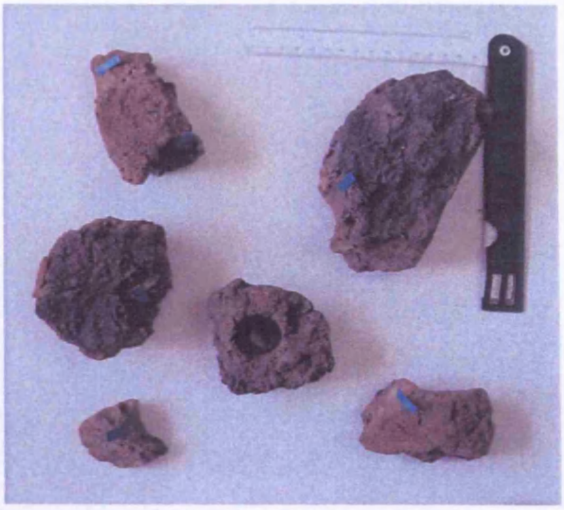


**Figure 5.10** *Furnace wall fragments from Kephala 2 with perforations (shown with blue tape).*

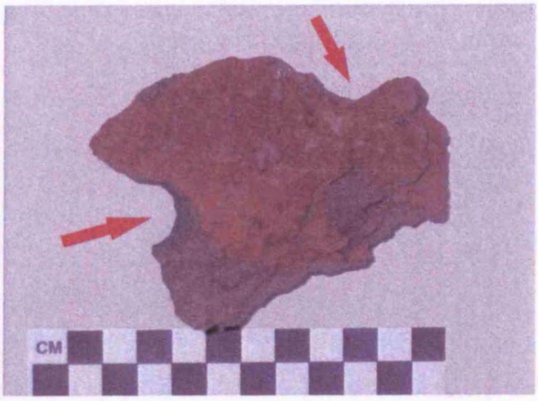


***Figure 5.11*** *Furnace wall fragment from Kephala 2 with two perforations (shown with the red arrows).*

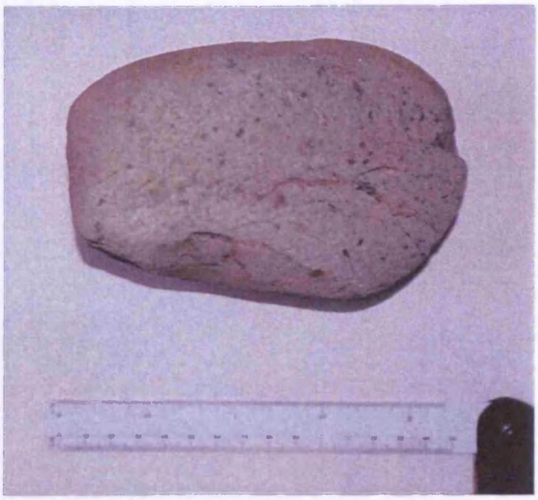


***Figure 5.12*** *Stone tool found at the Kephala slag heap.*

***Figure 5.13*** *Rounded slag from Kephala possibly used as a tool.*

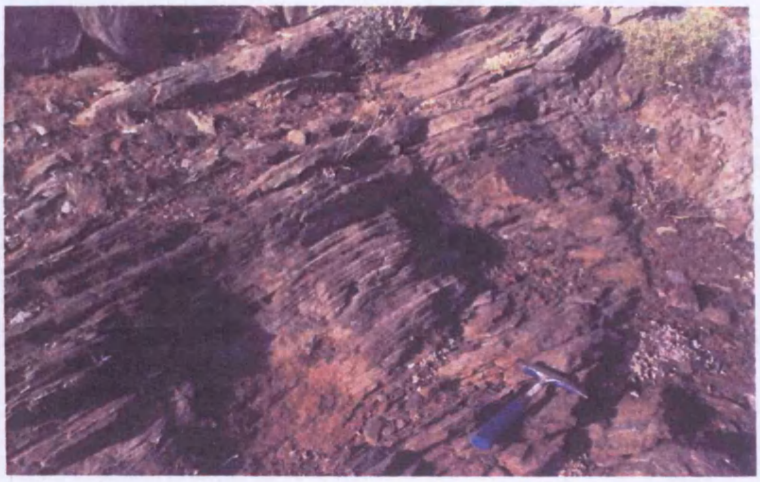


***Figure 5.14*** *The remains of two furnaces carved in the schist bedrock at Kephala. The one on the right bears a layer of slag on its right side.*

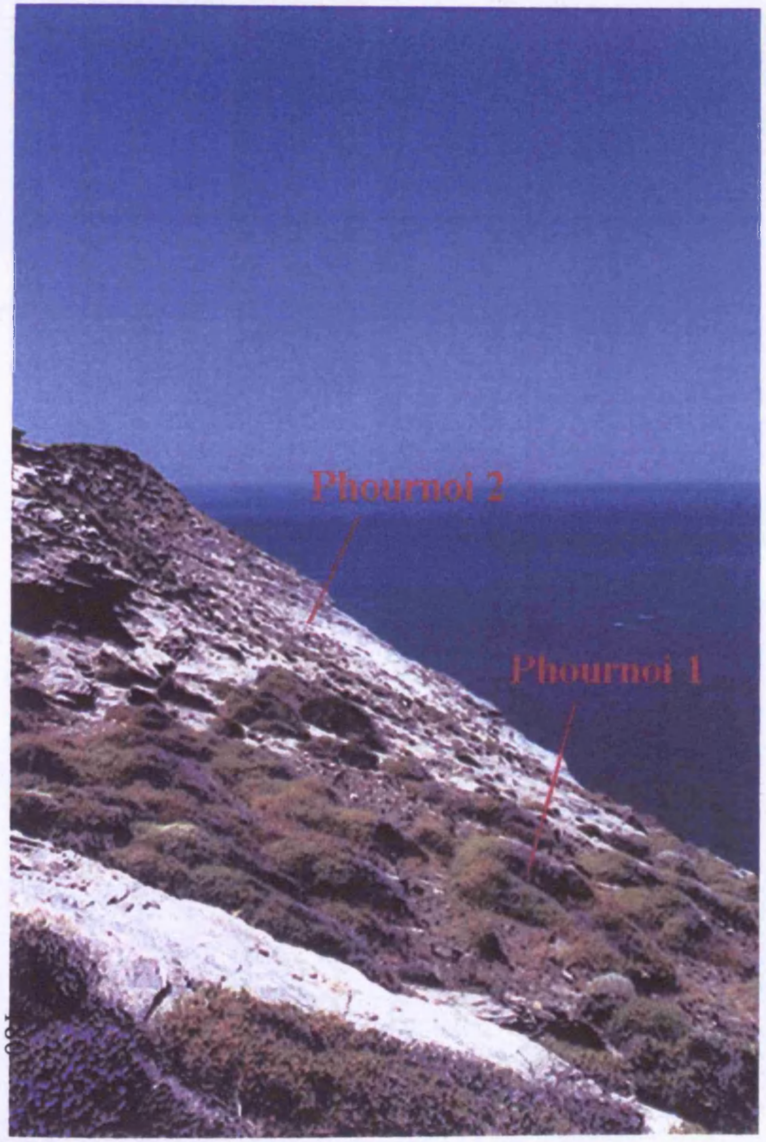


*Figure 5.15* The slag heap of Phournoi.

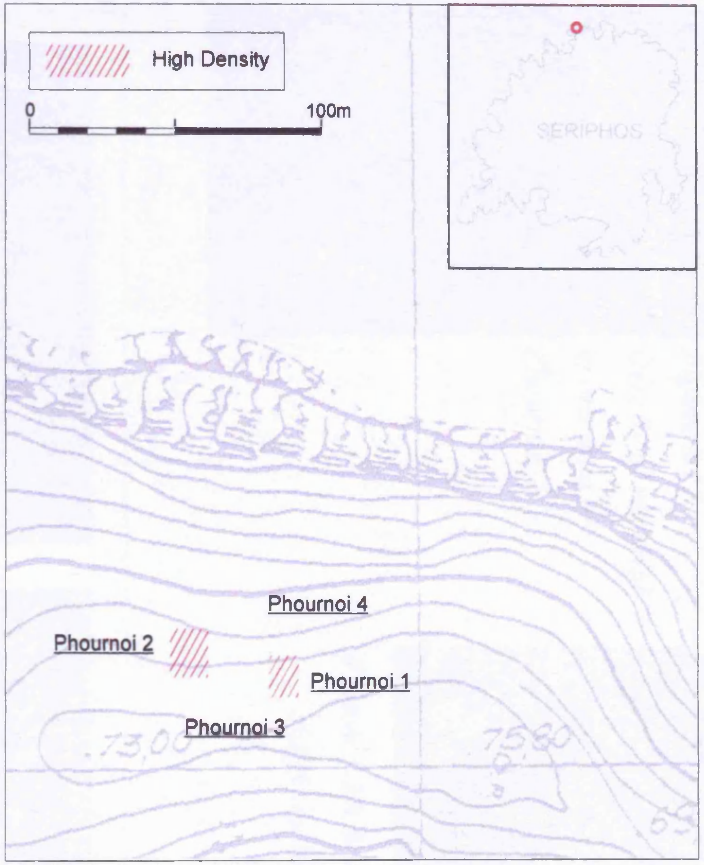


***Figure 5.16*** *Plan of the Phournoi slag heap showing location of sampled units (shaded areas are Phournoi 1 and 2).*

***Figure 5.17*** *Density of material in one area of Phournoi 1.*

***Figure 5.18*** *Bowl-shaped crystalline slag from Kephala 2 (cut sample KEF10).*

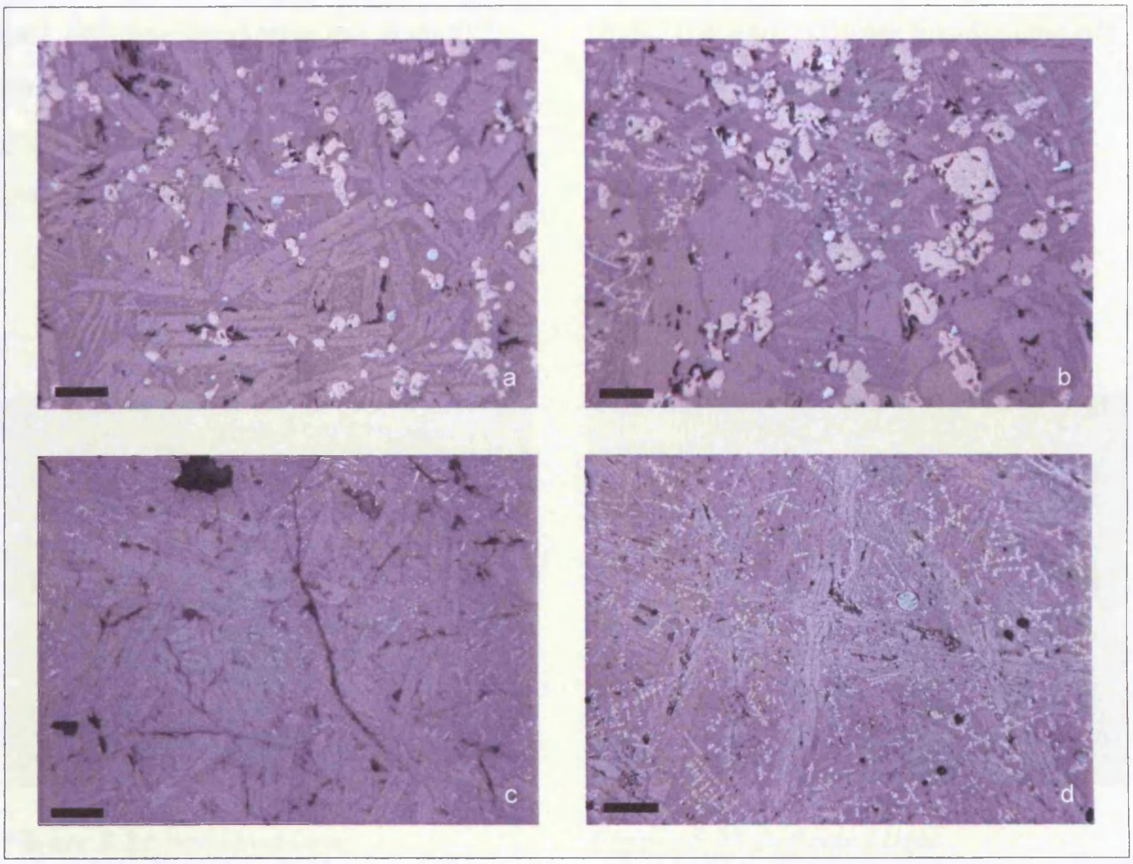


***Figure 5.19*** *Reflected light microphotographs of typical Kephala slag samples.*

*(a) From sample KEF17 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), matte (light blue) in a glassy matrix (dark grey).*

*(b) From sample KEF2 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), matte (light blue), porosity (black) in a glassy matrix (dark grey).*

*(c) From sample KEF36 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), porosity (black) in a glassy matrix (dark grey).*

*(d) From sample KEF16 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), matte (light blue), porosity (black) in a glassy matrix (dark grey).*

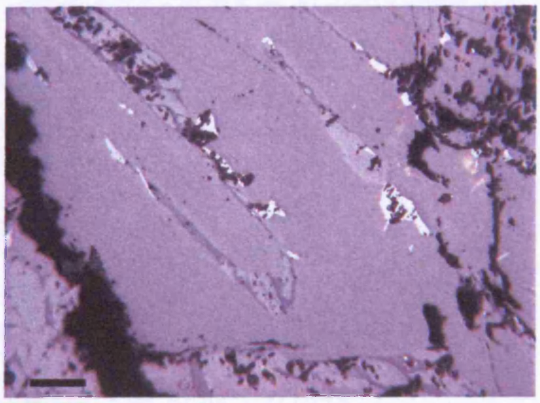


*Figure 5.20 Reflected light microphotograph of KEF10 (scale 100 μm), showing large pyroxene crystals (medium grey), fayalite (light-medium grey), magnetite (light grey-white) in a glassy matrix (dark grey).*

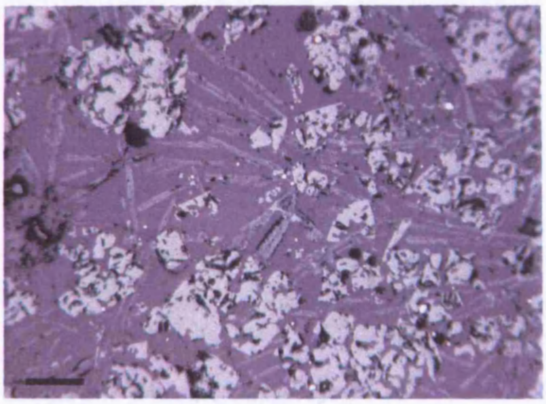


*Figure 5.21 Reflected light microphotograph of sample KEF32 (scale 100 μm), showing fayalite crystals (elongated, medium grey), magnetite (light grey), copper prills (tiny, circular, white-yellow), porosity (black) in a glassy matrix (dark grey).*

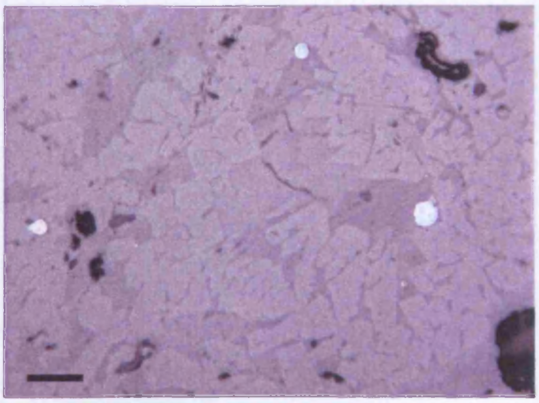


*Figure 5.22 Reflected light microphotograph of sample KEF4 (scale 100 μm), showing pyroxene crystals (medium grey), matte prills (circular, light-blue, off-white), porosity (black) in a glassy matrix (dark grey).*

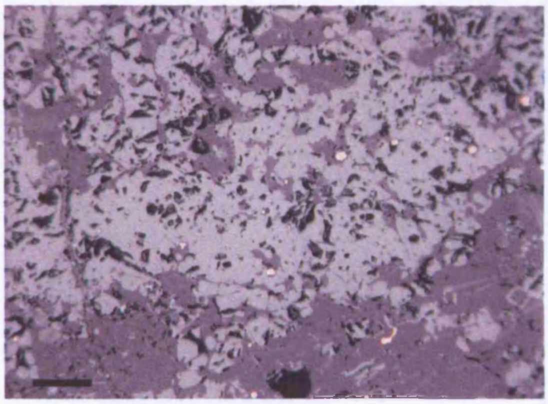


*Figure 5.23 Reflected light microphotograph of sample KEF32 (scale 100 μm), showing large magnetite aggregate (light grey), small fayalite crystals (medium grey), copper prills (circular, white-yellow), porosity (black) in a glassy matrix (dark grey).*

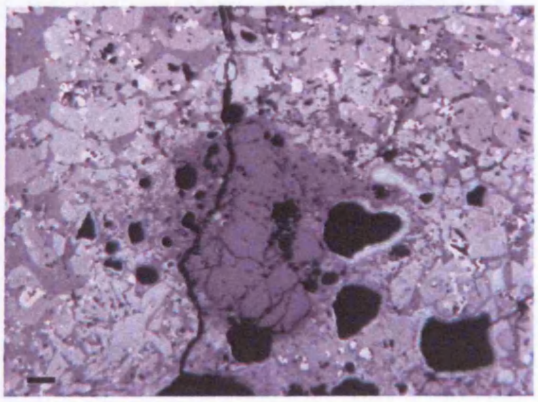


*Figure 5.24 Reflected light microphotograph of sample KEF8 (scale 100 μm), showing partially reacted quartz inclusion (centre), large pores (black), and slag matrix with fayalite (medium grey), magnetite (light grey), glass (dark grey).*

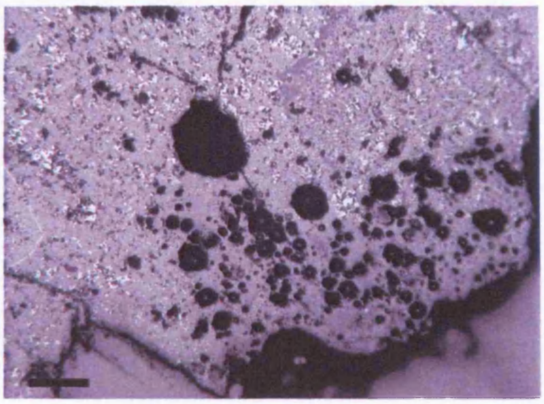


*Figure 5.25 Reflected light microphotograph from the edge of sample KEF14 (scale 100 μm), showing attachment of slag with vitrified ceramic (area with circular porosity).*

*Figure 5.26 Slag sample KEF14 bearing small ceramic fragments on its exterior.*

*Figure 5.27 Photograph of sample KEF16.*

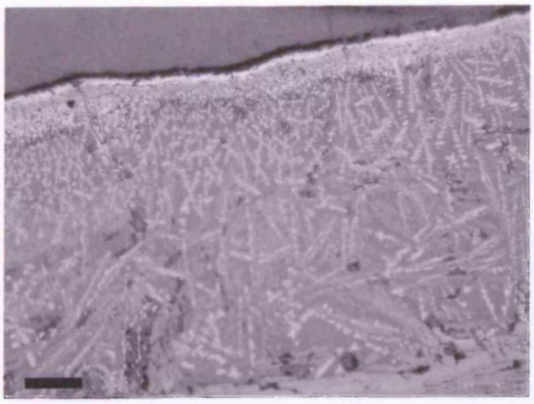


**Figure 5.28** *Reflected light microphotograph of the edge of sample KEF16 (scale 50 μm), showing continuous magnetite band (light grey) along the edge (the dark part at the top of the sample is the surrounding resin) and in the slag matrix fayalite crystals (medium grey), magnetite dendrites (light grey), in a glassy matrix (dark grey).*

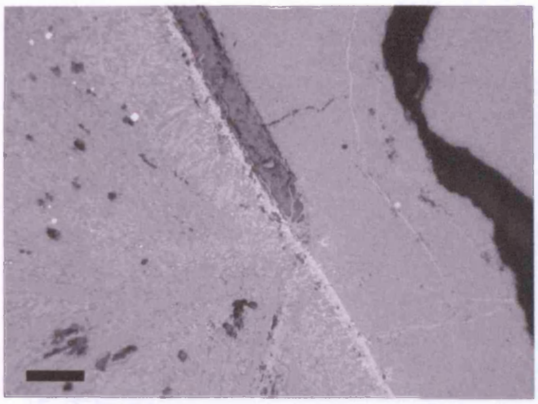


**Figure 5.29** *Reflected light microphotograph of sample KEF26 (scale 50 μm), showing magnetite band (light grey) running across the sample. The slag is composed of minute crystals of fayalite (medium grey) and magnetite (light grey) with matte prills (circular, white) in a glassy matrix (dark grey), while the size of these phases is different between the two divided parts.*

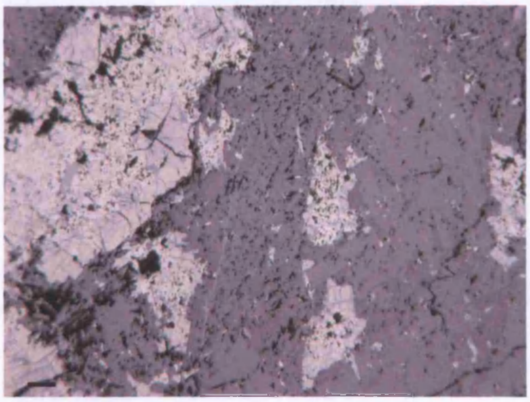


**Figure 5.30** *Reflected light microphotograph of sample KEF13 (scale 100 μm), showing large, partially reacted copper-iron sulphides remaining in the slag matrix.*

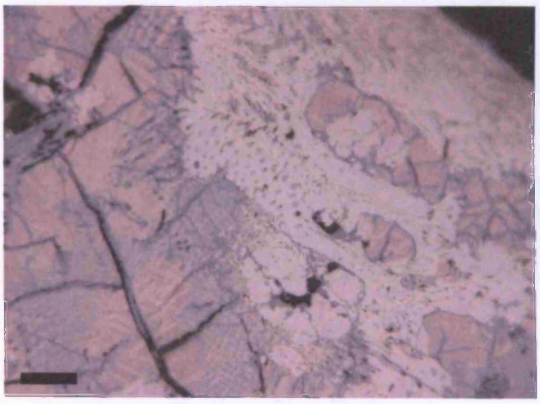


**Figure 5.31** *Reflected light microphotograph of detail of sulphidic inclusion in sample KEF13 (scale 50 μm), showing lamellar texture with bornite (light pink) and chalcocine (blue) and eutectoid texture within the chalcopyrite (cream white).*

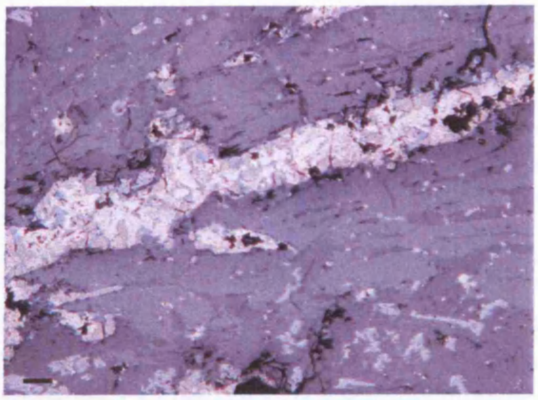


***Figure 5.32*** *Reflected light microphotograph of sample KEF13 (scale 100 µm), showing partially reacted sulphide delineated by surrounding fayalite crystals (medium grey).*

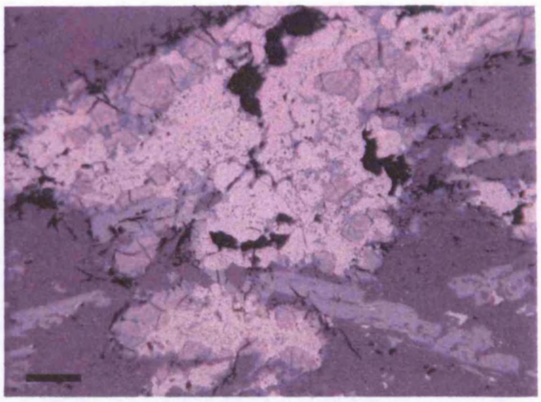


***Figure 5.33*** *Reflected light microphotograph of sample KEF13 (scale 100 µm), showing magnetite (light grey) forming around sulphidic inclusion.*

***Figure 5.34*** *Sample KEF40 bearing two external green prills.*

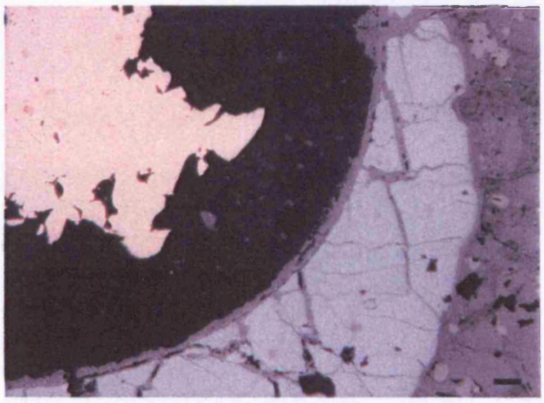


***Figure 5.35*** *Reflected light microphotograph of large prill at the edge of sample KEF40, showing copper prill (off-white) with tiny sulphidic inclusions (light blue), corroded prill (surrounding dark area), and surrounding matte (light blue).*

***Figure 5.36***
*Sample KEF12.*

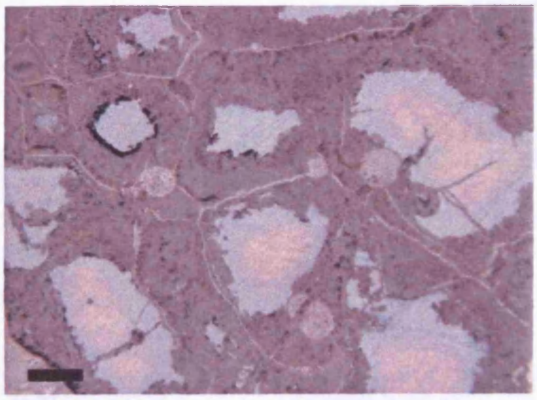


***Figure 5.37*** *Reflected light microphotograph of sample KEF12 (scale 50 µm), showing copper-iron to copper sulphides in a completely weathered matrix. Grain boundaries are slightly rounded and circular eutectics are formed at the triple junctions.*

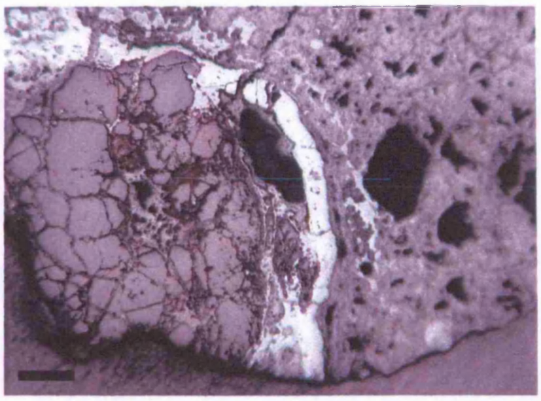


***Figure 5.38*** *Reflected light microphotograph of sample KEF12 (scale 100 µm), showing quartz fragment at the edge of the sample.*

***Figure 5.39***
*Sample KEF27.*

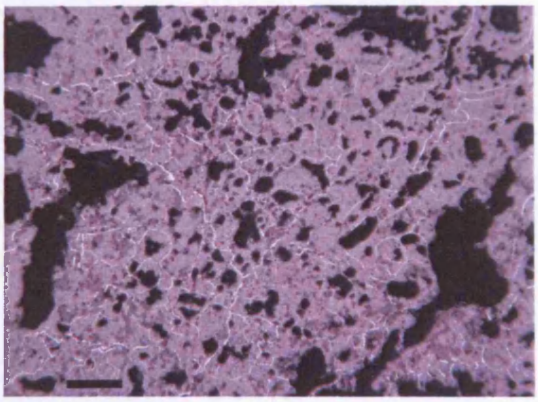


***Figure 5.40*** *Reflected light microphotograph of sample KEF27 (scale 100 µm), showing matrix of sample with weathered copper minerals, grain boundaries of original sulphidic grains (light grey-white), and porosity (black).*

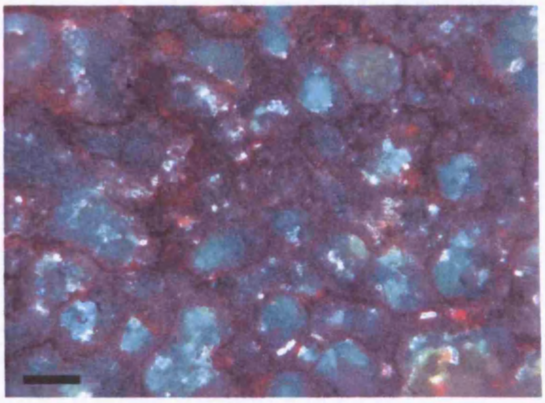


***Figure 5.41*** *Reflected light microphotograph (crossed polars) of sample KEF27 (scale 50 µm), showing the matrix of the sample with elongated eutectics within the weathered copper minerals (fine dark lines within green copper minerals).*

*Figure 5.42* Sample KEF28.

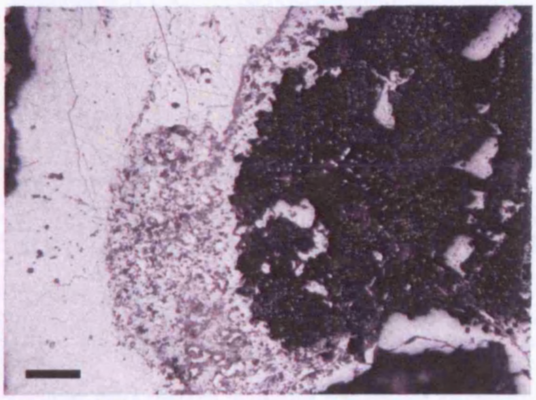


***Figure 5.43*** *Reflected light microphotograph of sample KEF28 (scale 100 μm), showing external copper sulphide band (left, off-white), partially weathered sulphide layer (middle), completely weathered sulphide with eutectics (right, dark part).*

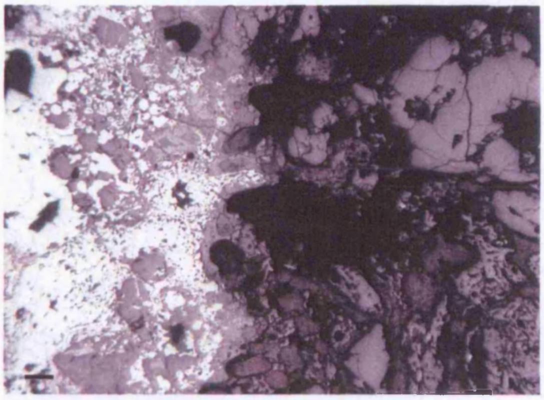


***Figure 5.44*** *Reflected light microphotograph of sample KEF28 (scale 100 μm), showing conglomerate of quartz and schist fragments at the right and poured matte (white).*

***Figure 5.45*** *Samples from Kephala 1. Left: sample KEF30; right: sample KEF29 (sample in the middle was not analysed).*

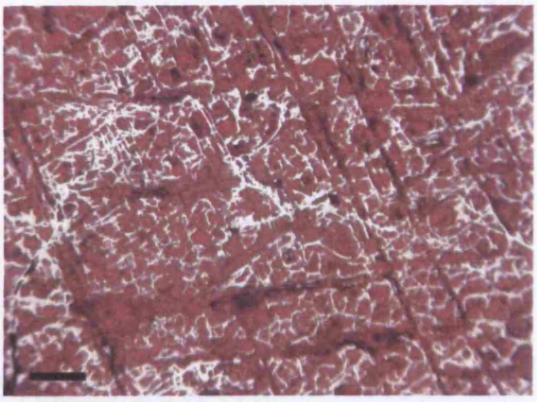


***Figure 5.46*** *Reflected light microphotograph of sample KEF29 (scale 100 μm), showing lamellar texture retained in weathered matrix of secondary iron minerals.*

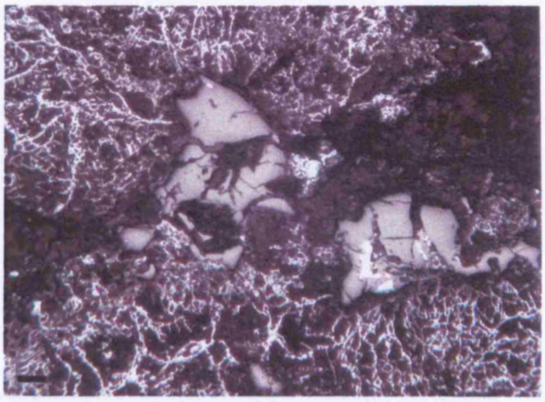


***Figure 5.47*** *Reflected light microphotograph of sample KEF29 (scale 100 μm), showing quartz inclusions bearing small sulphidic minerals in an iron hydroxide matrix.*

***Figure 5.48*** *Reflected light microphotograph of sample KEF30 (scale 100 μm), showing quartz and schist fragments mixed with soil.*

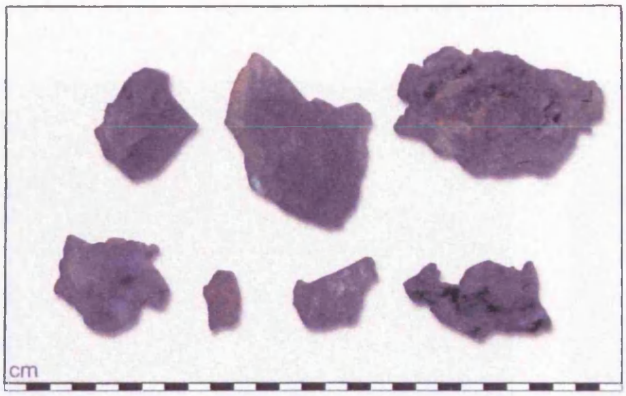


**Figure 5.49** *Examples of slags from Phournoi.*

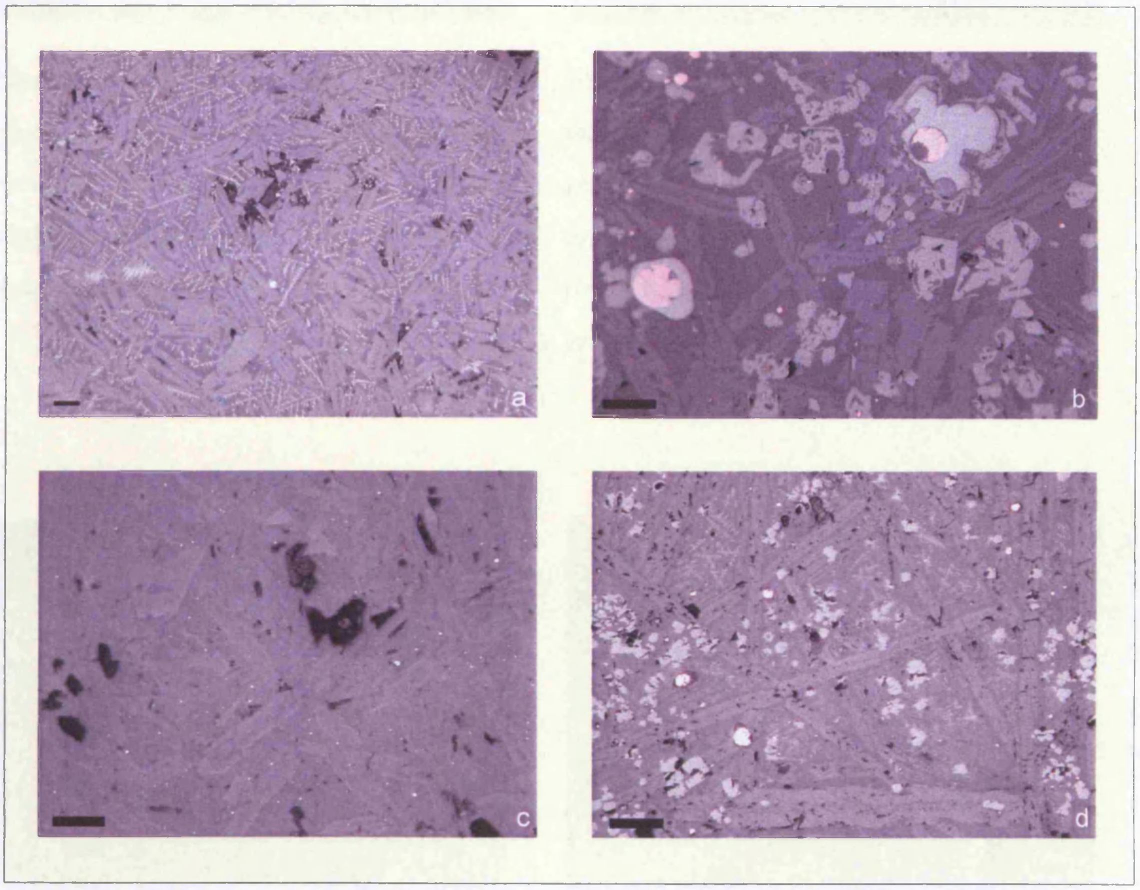


***Figure 5.50** Reflected light microphotographs of typical Phournoi slag samples.*

*(a) From sample FOU16 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), matte (circular off-white, light blue) in a glassy matrix (dark grey).*

*(b) From sample FOU4 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), copper prills (bright yellow-white) surrounded by matte (light blue) in a glassy matrix (dark grey).*

*(c) From sample FOU13 (scale 100 μm), showing fayalite (medium grey), and tiny copper and/or matte prills (circular white) in a glassy matrix (dark grey).*

*(d) From sample FOU12 (scale 100 μm), showing fayalite (medium grey), magnetite (light grey), copper prills (bright yellow-white), porosity (black) in a glassy matrix (dark grey).*

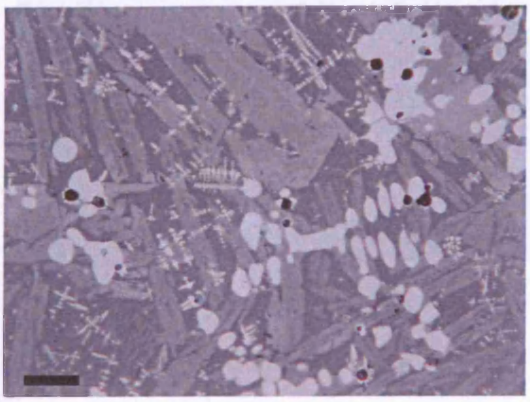


***Figure 5.51*** *Reflected light microphotograph of sample FOU25, showing fayalite (medium grey), wüstite (light grey), matte (light blue) in a glassy matrix (dark grey).*

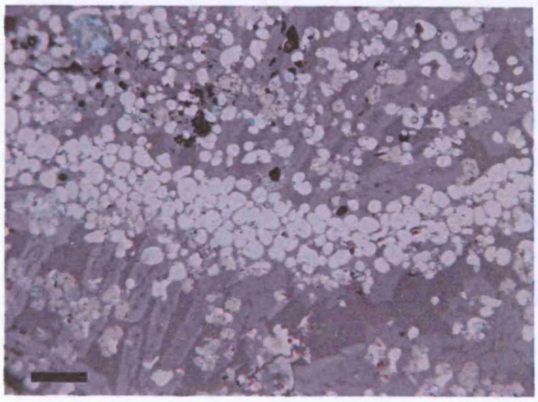


***Figure 5.52*** *Reflected light microphotograph of sample FOU3, showing fayalite (medium grey), wüstite and wüstite aggregate (light grey), matte (light blue) in a glassy matrix (dark grey).*

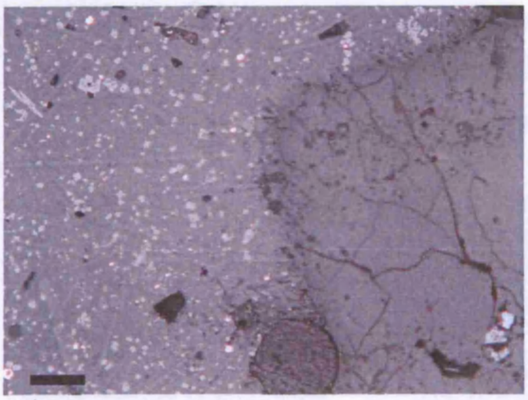


***Figure 5.53*** *Reflected light microphotograph of sample FOU14 (scale 100 μm), showing quartz inclusion (right) and slag matrix with elongated fayalite (medium grey), magnetite (light grey), and copper prills (circular bright white-orange) in a glassy matrix (dark grey).*

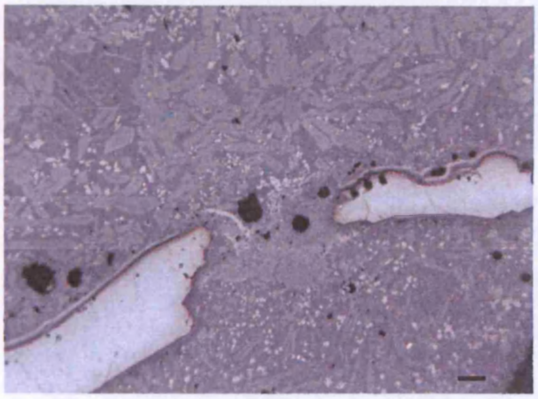


***Figure 5.54*** *Reflected light microphotograph of sample FOU15 (scale 100 μm), showing partially reacted copper-iron sulphidic minerals, with thin layer of magnetite forming around them and intense porosity. Slag matrix is composed of fayalite crystals (medium grey), magnetite (light grey), and matte (blue) in a glassy matrix (dark grey).*

***Figure 5.55*** *Sample FOU22 cut in two, showing enclosed ceramic*

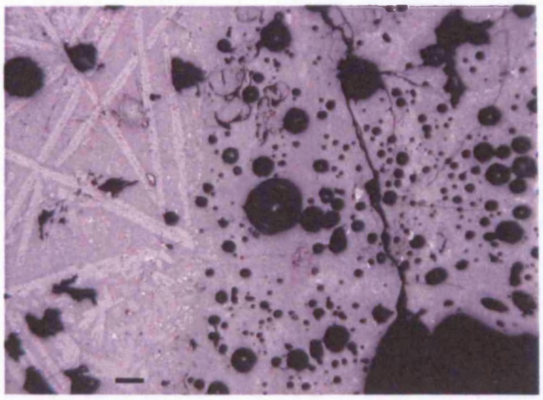


***Figure 5.56*** *Reflected light microphotograph of border of slag and ceramic in sample FOU24 (scale 100 μm).*

***Figure 5.57*** *Sample FOU20.*

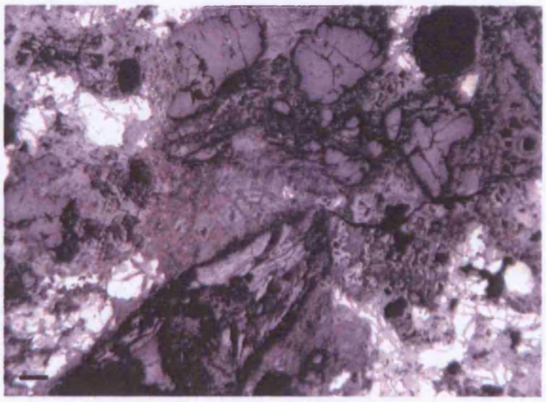


***Figure 5.58*** *Reflected light microphotograph of sample FOU20 (scale 100 μm), showing quartz and schist fragments surrounded by a weathered copper-iron matrix.*

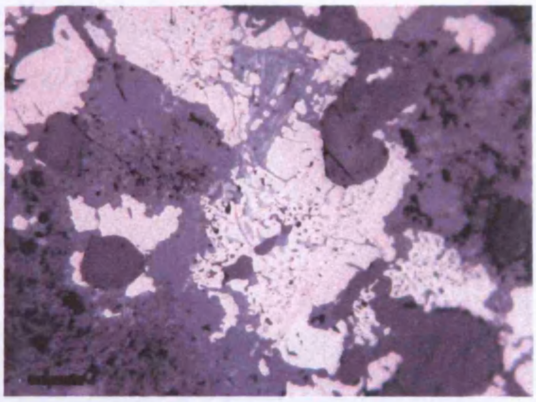


***Figure 5.59*** *Reflected light microphotograph of sample FOU20 (scale 50 μm), showing partially reacted chalcopyrite with eutectoid texture.*

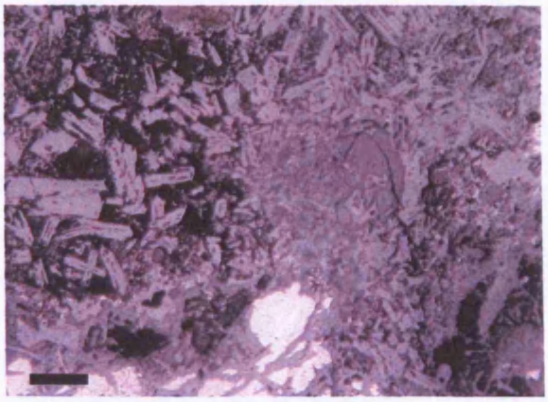


***Figure 5.60*** *Reflected light microphotograph of sample FOU20 (scale 100 μm), showing slag with fayalite (medium grey) crystals and completely weathered glass (black) and partially reacted sulphides.*

***Figure 5.61*** *Sample FOU38.*

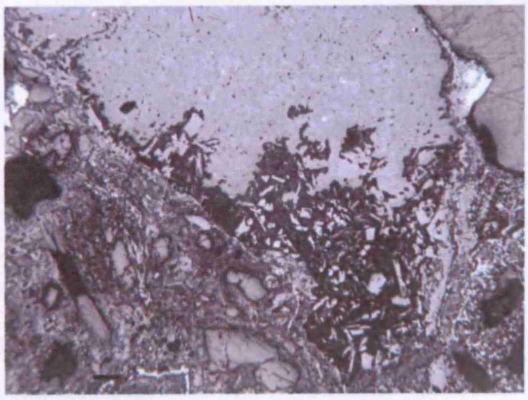


***Figure 5.62*** *Reflected light microphotograph of sample FOU38 (scale 100 μm), showing slag formed at the edge of sample, partially weathered at one side. The remaining sample bears quartz and schist fragments in a weathered copper-iron matrix.*

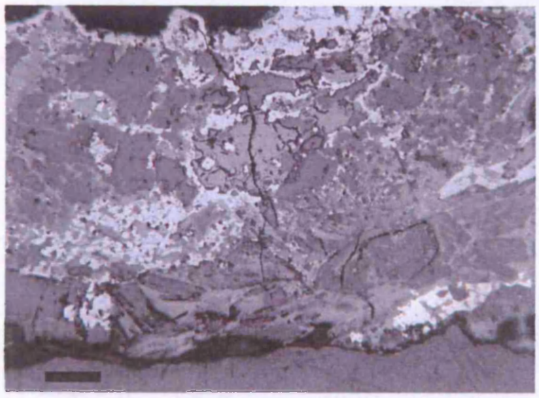


***Figure 5.63*** *Reflected light microphotograph of sample FOU38 (scale 100 μm), showing remaining partially reacted chalcopyrite (off-white) and magnetite aggregates (light grey) at the side of the sample.*

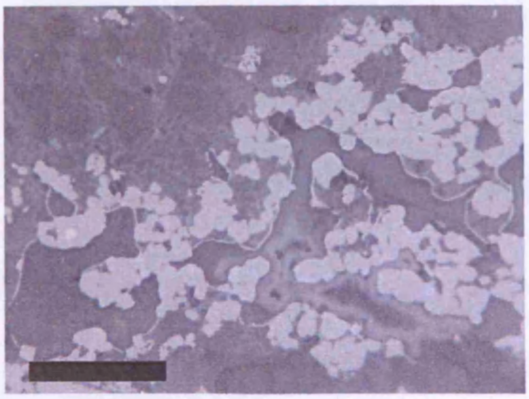


***Figure 5.64*** *Reflected light microphotograph of sample FOU38 (scale 50 μm), showing detail of magnetite aggregates (see Figure 5.63) bearing copper prills (bright cream white).*

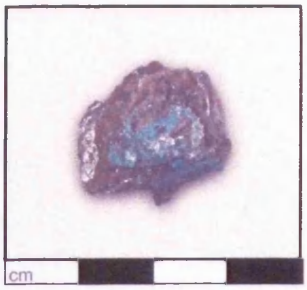


**Figure 5.65** Sample FOU39.

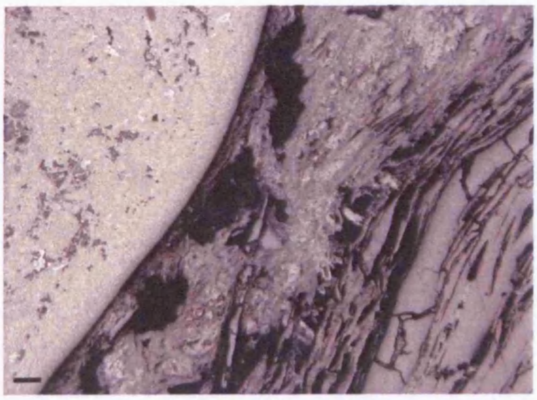


**Figure 5.66** Reflected light microphotograph of sample FOU39 (scale 100 µm), showing point of attachment of slag droplet and schist fragment.

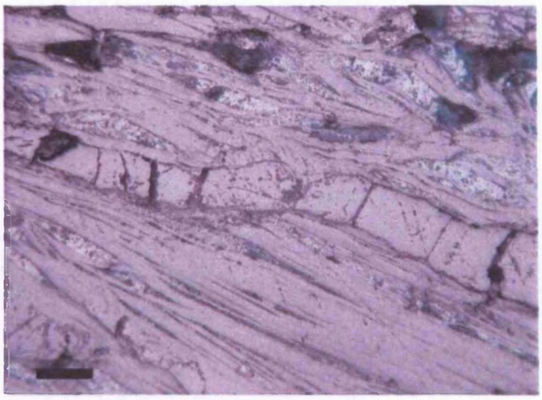


**Figure 5.67** Reflected light microphotograph of sample FOU39 (scale 100 µm), showing schist with quartz veinlets running parallel to schist direction and green copper minerals deposited between the schist layers.

**Figure 5.68** Sample FOU40

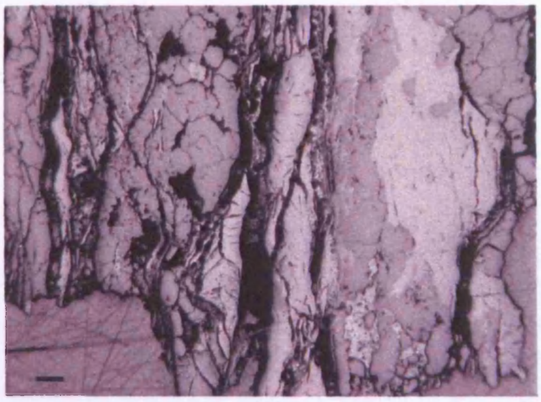


**Figure 5.69** Reflected light microphotograph of sample FOU40 (scale 100 µm), showing the edge of the sample with copper minerals.

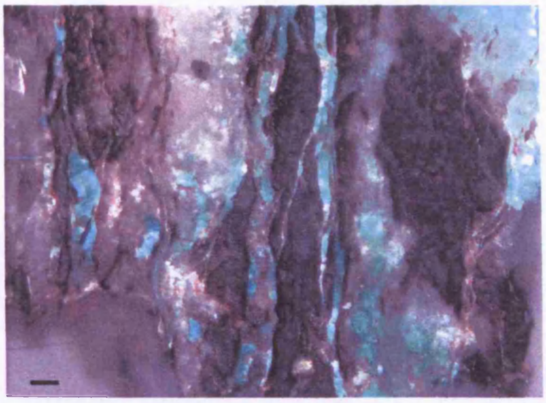


**Figure 5.70** As for Figure 5.69 (crossed polars).

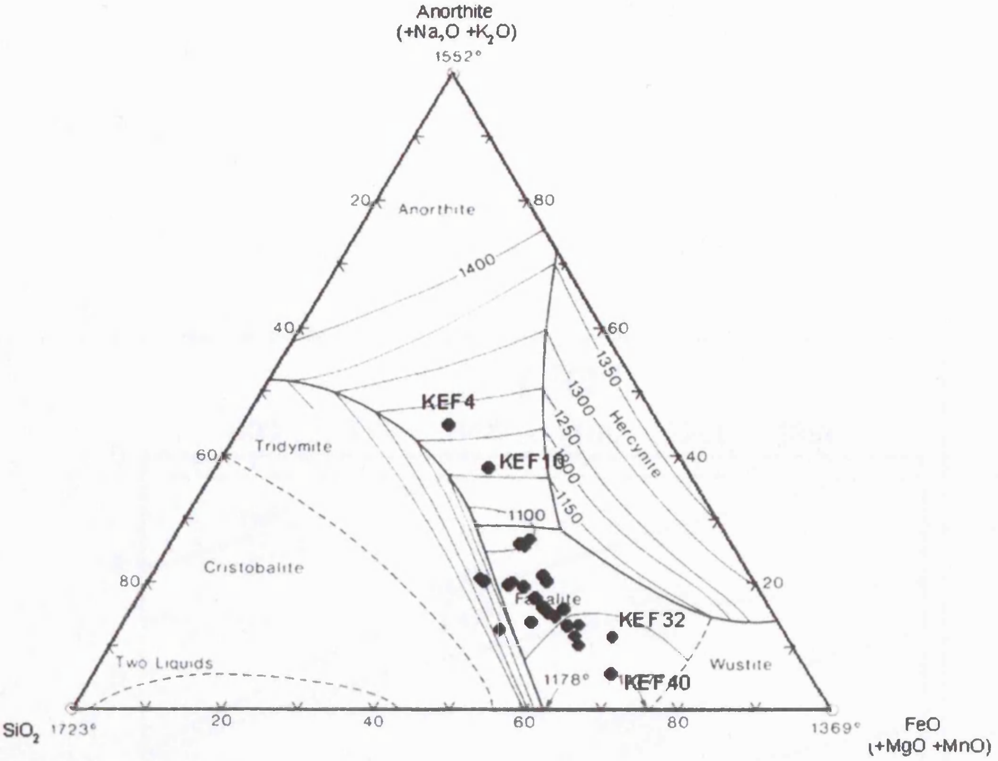


***Figure 5.71*** *The Kephala slags represented on the ternary phase diagram Anorthite-$SiO_2$-FeO.*

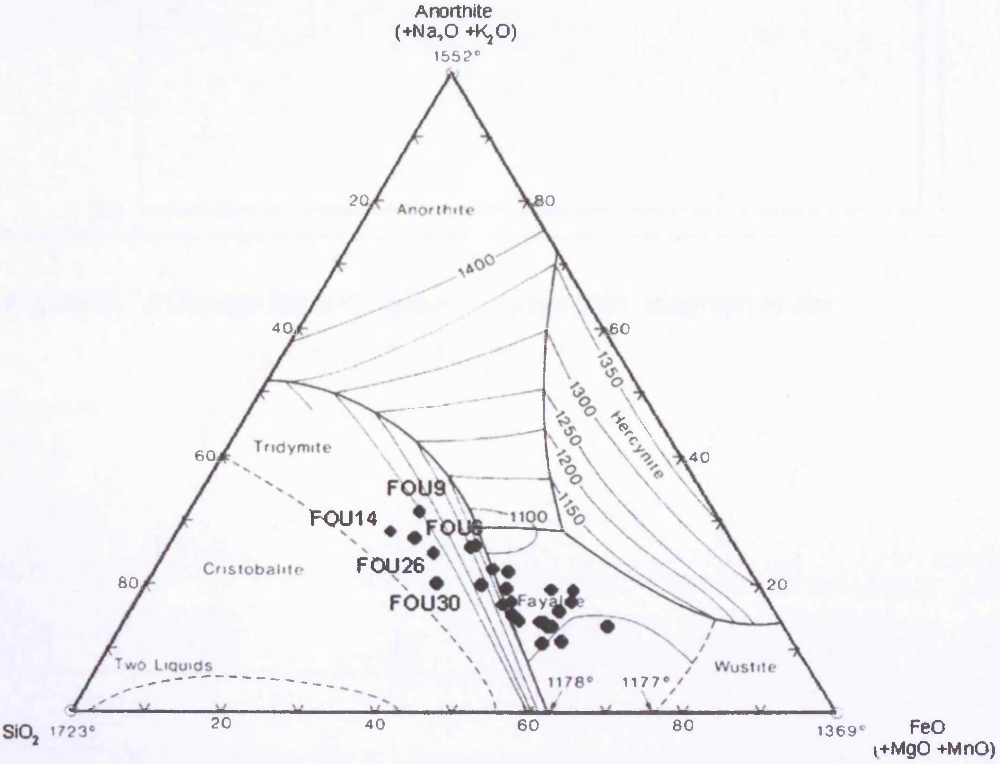


***Figure 5.72*** *The Phournoi slags represented on the ternary phase diagram Anorthite-$SiO_2$-FeO.*

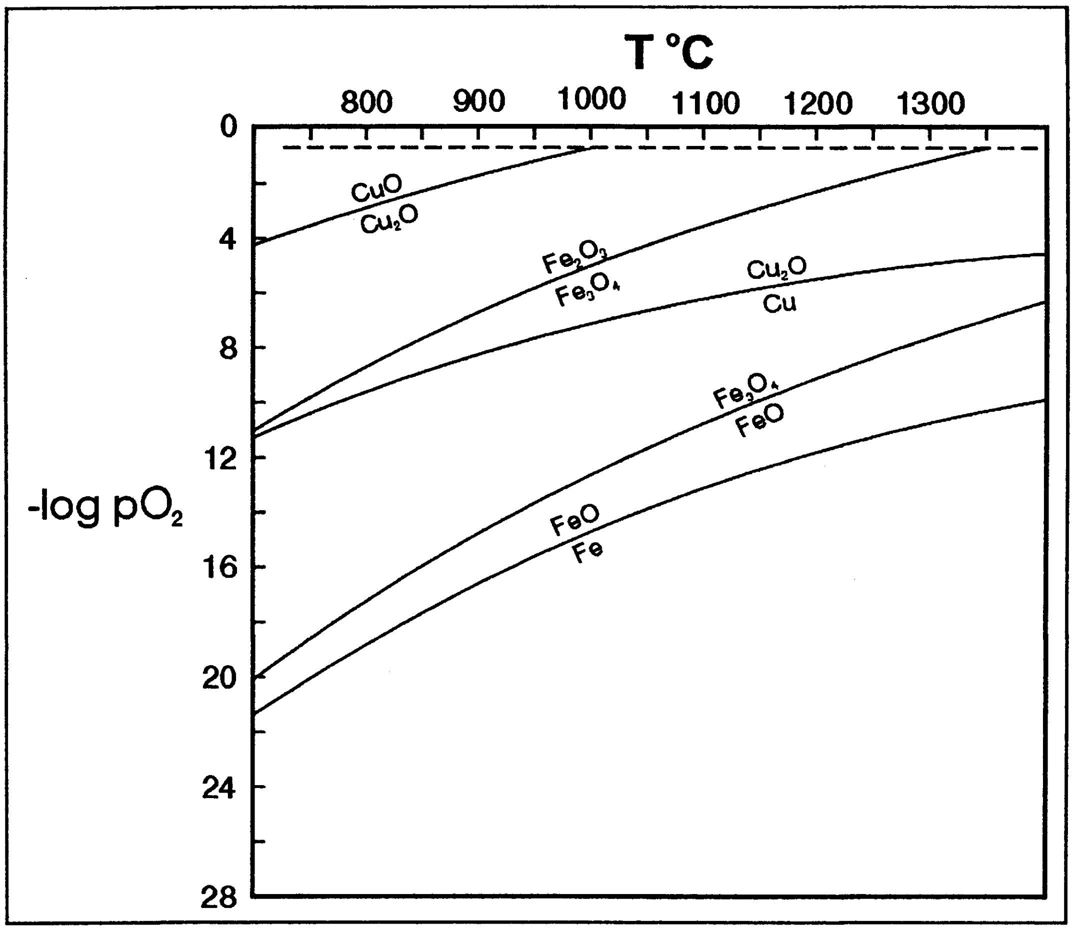


***Figure 5.73** Oxygen fugacity against temperature diagram of the system Fe-Si-O and Cu-O.*

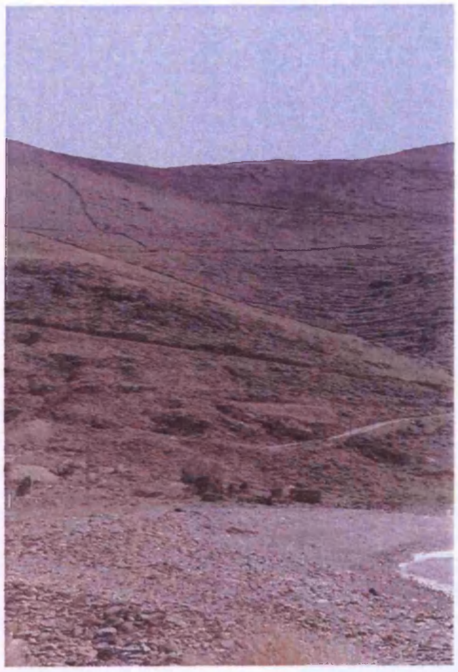


***Figure 5.74*** *View of the Avessalos heap from the Avessalos bay.*

***Figure 5.75*** *Part of the road section at the Avessalos slag heap, showing layer with small slags and larger slags above.*

***Figure 5.76*** *Large pit with small pits at its side carved on the schist bedrock on the top of the Avessalos promontory.*

***Figure 5.77*** *Small pits (left) and vertical grooves (close to the hammer) carved on the schist bedrock on the top of the Avessalos promontory.*

*Figure 5.78*

*Large masses of slag at Avessalos.*

***Figure 5.79*** *Slags from Avessalos bearing large inclusions of schist and ceramic.*

***Figure 5.80*** *Examples of stone tools found at Avessalos.*

# CHAPTER 6.

# The metallurgical remains from Daskaleio-Kavos on Keros

## 6.1 Introduction

This chapter presents the results of the analytical examination of metallurgical remains from Daskaleio-Kavos on Keros (Figure 6.1). This intriguing EBA site is probably one of the most important but also most controversial prehistoric sites in the Cyclades. As was mentioned in Chapter 1, the material presented in this chapter was recovered in 1987 together with numerous other finds, during a collaborative fieldwork project of the Universities of Athens, Ioannina, and Cambridge, and the Cycladic Ephorate (Annual Report 1986-7: 32-4; Whitelaw 2003).

Despite their small number and relatively unattractive appearance compared to some of the other finds, the metallurgical remains from Daskaleio-Kavos present a very interesting case for the understanding of EBA metallurgy in the Aegean. They represent metallurgical activities within and in the immediate vicinity of a settlement; a research area that has to date received very little attention in this region. As some of the samples in the collection bear some degree of green staining, it was immediately obvious that at least part of the finds were associated with copper metallurgy. Examination of the metallurgical remains from Daskaleio-Kavos aimed to identify the types and nature of metallurgical processes taking place and if possible the distribution of these activities within the site (see also Chapter 3). More specifically analyses were guided by the following set of broad questions: What metals were being worked? What types of processes do these remains correspond to (smelting, refining, melting etc) and how were these carried out? Were these activities confined to a certain area within the site or can evidence be drawn for the distribution of different processes across the site?

This chapter starts with a brief description of the site of Daskaleio-Kavos, the archaeological investigations carried out to date and the interpretations offered regarding its role among EBA Cycladic communities. Subsequently, the sampling methodology is discussed and the results of the analytical examination are presented, followed by a consideration of the spatial distribution of the metallurgical remains across the site.

## 6.2 The site

Kavos lies at the western edge of Keros, a small and today uninhabited island in the south-eastern Cyclades, facing Daskaleio islet a few metres off the coast (Figure 6.2). A recent geoarchaeological study on the site 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). Such a topographical setting would facilitate access from the sea, making the site an ideal harbour (Bassiakos and Doumas 1998; Doumas 1972; discussion in Fitton 1984: 33).

Archaeological interest was drawn to the site of 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 (Figure 6.2) and resulted in severe destruction of its structural features and unrecoverable loss of priceless material. A large number of marble anthropomorphic figurines, today dispersed in museums and private collections with no secure provenance, are rumoured to have originated from this particular part of the Cyclades (Broodbank 2000a: 225; Getz-Preziosi 1982; Renfrew 1991: 164). Sanctioned excavations followed and hundreds of fragments of broken marble anthropomorphic figurines and vessels, which appeared to have been deliberately broken in antiquity, lithics, pottery and metal were recovered from this deposit confirming it as the richest accumulation of prestige material known from an EBA Cycladic context (Doumas 1964; Hadji-Vallianou 1975; Renfrew 1972: 531-2; Zapheiropoulou 1967, 1968, 1975).

Apart from the special deposit, two occupation areas have been identified through surface finds and excavation of habitation remains (see Figure 6.2); one in the south-central part of Kavos and another on Daskaleio islet (Doumas 1964; Sotirakopoulou in press(b)). A building with two rooms was excavated at Kavos, while remains of houses and possibly a fortification wall were observed at the north-eastern side of Daskaleio (Doumas 1964, 1972). The excavator originally suggested that the two sites were not contemporaneous, with Kavos dating to the earlier and Daskaleio to the later EBII period (discussion in Fitton 1984: 33). Although such a transition to a potentially better fortified location such as Daskaleio in the later part of EBII is not unlikely (Broodbank 2000a: 223), two points urge against making such distinctions at this stage. On the one hand, Daskaleio has been far less intensively studied than Kavos. On the other hand in his recent detailed pottery analysis from the 1987 Kavos fieldwork, Broodbank (2000b: 331) showed that activity on Kavos continued throughout EBII and concluded that it was impossible to infer on the basis of the pottery whether the site flourished primarily during a particular part of the period. What does, however, appear to be more clear is that activity on Daskaleio-Kavos was mainly limited to the EBII period and no substantial indications of earlier or later use of the site have been found (Broodbank 2000b: 331). Other parts of Keros have provided evidence for human presence or habitation on the island in other periods, such as the earlier Pelos culture sherds from an excavation at Gerani (Renfew 1972: 521; Zapheiropoulou 1968) and the modern now abandoned settlement at Konakia (Figure 6.1).

Interpretation of Daskaleio-Kavos and its role in the EBA has proven particularly difficult. The wealth and intriguing nature of the special deposit finds, in combination with the catastrophic damage to its structural features caused by looting, have left behind a puzzling image and plenty of room for speculation. In addition, Keros is largely a barren island, particularly in the Kavos area. The only significant extent of arable land known on the island is located at Gerani about 40 minutes walk to the northeast of Kavos (Broodbank 2000a: 225). The location of such an apparently rich site on one of the smallest Cycladic islands and within an agriculturally poor environment may be considered surprising.

The main focus of the debate has been the special deposit. Initially it was suggested that the area held the remains of a large and exceptionally wealthy cemetery of a nearby settlement (Doumas 1964). In one of the initial excavation reports it is noted that traces of bones were also unearthed (Doumas 1964, 1972: 95). The peculiar features of the site later led to a very different view, which proposed that the site was a pan-Cycladic sanctuary, where ritual activities involving the breakage and deposition of prestigious objects were carried out (Renfrew 1984b, 1991). An alternative interpretation was prompted by the identification of a small cave at the uphill edge of the site and by the associations between caves and the entrance to the Underworld in later Classical mythology. It suggested that the cave may have been viewed as one such entrance and that bones periodically unearthed from other Cycladic cemeteries may have been transported to Kavos and re-deposited in the area of the special deposit together with the grave goods (Bassiakos and Doumas 1998; Doumas 1990a). Recently Broodbank (2000b) has made a strong case supporting the initial cemetery interpretation of the special deposit using a comparison between the pottery recovered during the 1987 fieldwork from the settlement and special deposit areas. The study also revealed a wide diversity in the fabrics and shapes of vessels present in both parts of the site with many identified imported types, confirming that considerable import of material was taking place at Kavos. The special deposit is therefore seen in this model as the cemetery associated with a rich settlement occupying the south-central part of the site. Contrary to the other two interpretations, which favoured the island's marginal character, Broodbank (2000a) has offered an alternative explanation for the evident prominence of the site, which lies in Kavos' perhaps not immediately recognised centrality. Within his recent treatise on the EBA Cyclades, which places significant emphasis on the role of maritime communication and trade in these communities, he proposed that the site flourished as a result of its nodal position within a wide inter-island maritime communication and trade network (Broodbank 1993, 2000a; see also Whitelaw 2003 and section 2.2).

It is not the purpose of the present thesis to investigate the role of Daskaleio-Kavos in the EBA or argue about the strengths and weaknesses of the arguments put forward so far, therefore only the main points of the ongoing controversy have been presented here. What becomes clear, however, is that the preoccupation with the role of the special deposit has undermined the research into the Kavos habitation area. With the exception of one early excavation (Doumas 1964), the 1987 surface survey is the only fieldwork study carried out in this part of the site. The situation is even worse in the case of Daskaleio islet, which remains largely unstudied. Despite the limited excavation of habitation features in the southern part of Kavos (Doumas 1964), claims supporting a total rejection of the existence of a settlement in the site have even been made (Bassiakos and Doumas 1998: 55, 62). These statements can only be viewed as weak arguments in support of the site's marginality and ritual character and are in stark contrast both with the discovery of structural features (Doumas 1964) and the dense distribution of domestic pottery at the southern part of Kavos (Broodbank 2000b). On the basis of these finds, habitation at Kavos during the EBII can be concluded with relative certainty. Therefore although the intriguing nature of the special deposit may never be resolved, partly because of the extensive damage suffered by this area despite repeated archaeological excavations that followed, research into the far less affected southern area of Kavos and Daskaleio islet could definitely be very informative. Finally, a common undeniable characteristic in all the interpretations offered to date is that the richness and variability of the finds portray a well-connected site, whether this was the result of habitation on the site of a community extensively involved in trade, or of periodic influx of peoples and material for the purpose of ritual activities.

## 6.3 Sampling and methodology

The 1987 fieldwork involved excavation in the special deposit and gridded surface collection over the entire Kavos area. Surface collection was also carried out on a low exposed promontory slightly to the north of Kavos, designated Kavos North (Figure 6.2). The project did not extend to the islet of Daskaleio. The survey at Kavos was carried out in 5x5 m squares at the northern part of Kavos, which roughly coincides with the special deposit area, and where visibility was better due to soil disturbance caused by the past looting activities (Whitelaw pers comm.). At the south-central part of the site 10x10 m squares were used.[6.1] On Kavos North, identified and surveyed only late in the project, each collection unit consisted of a circle of 2.0 m radius. The project was largely a rescue operation, as looting appears to continue on the site to the present day. As a result a complete recovery of all types of archaeological artefacts visible on the surface was considered the most appropriate sampling methodology. The collection of metallurgical remains therefore represents the total quantity of such finds identified in each unit. Figures 6.3 and 6.4 present the types of metallurgical material collected from the survey units.

A permit had been granted for the export to the UK, for study and analysis, of a sample of the material. The remainder were macroscopically measured and studied by the present author in the Museum of Naxos, where they were stored, in the spring of 2002. The collection included pieces of slag, small fragments of metallurgical ceramics often bearing attached slag, copper metal droplets, lead metal pieces, litharge, and iron minerals. The entire assemblage consists of very small pieces only a few centimetres or less in size, while the total weight of slag collected does not exceed 300 g. The details and a brief description of all the metallurgical remains recovered in the collection are given in Appendix 5 (Table A5.1). It should be noted that a small number of copper and lead objects were also uncovered (pins, wire, sheets or circular metal pieces), but these have not been included in the analytical study, which deals specifically with the metallurgical remains.

Following macroscopic examination, typical samples of the various types of material were selected for analysis. Among these finds only the slags showed notable differences in their outer appearance and were therefore divided into two preliminary groups on this basis alone. Given the relatively small overall number of slag and metallurgical ceramic fragments in the collection, an almost complete sample of these two categories in particular was chosen for analysis in order to examine how uniform these were and ensure the most reliable results. Specimens

---

[6.1] Information regarding survey methodology was kindly provided by Dr T. Whitelaw, who designed and directed the surface collection (to be published in the forthcoming volume on the 1987 project on Kavos, editors Renfew *et al.*).

that were analysed are given a sample number in Table A5.1. Samples from Kavos are labelled as KK and those from Kavos North as KKN.

Suitably prepared mounted sections were studied using the optical microscope, the EDS-SEM and the EPMA. The small size of most samples inhibited the preparation of pressed powder pellets necessary for quantitative measurements on the XRF. Bulk analyses for these samples were therefore carried out on the EPMA (see section 3.6.2.3 for details on the methodology). For the larger slags (weight >4 g), pressed tablets were additionally prepared and analysed for bulk compositions using the (P)ED-XRF. Bulk measurements of the metallurgical ceramic fragments were also carried out using the electron microprobe similarly to the slags. In this case, however, care was taken to analyse separately the different layers present in each sample (i.e. ceramic, vitrified ceramic, slag).

## 6.4 Analytical results

### *6.4.1. Slags*

A total of fourteen slag samples were examined. On the basis of their macroscopic characteristics and the analyses carried out, they were divided into two main groups and one additional unique specimen.

#### *6.4.1.1 Group 1 (KKN1, KKN4, KKN5, KKN8, KKN9, KKN10, KK1, KK10, KK11)*

Macroscopic characteristics

Nine slag samples were attributed to this group. They are all grey-black in colour with a weathered outer surface and moderate porosity (Figure 6.5). Little or no green copper staining is seen externally. With the exception of a couple of samples that showed a little magnetism, the majority of samples did not respond to a hand-held magnet. Some show a ropey/flow texture on their upper surface indicating that they reached the molten liquid state. They are all small in size reaching up to a maximum of 5 cm in their largest dimension.

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | NiO | CuO | $As_2O_3$ | $SnO_2$ | $Sb_2O_3$ | PbO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN1** | 0.5 | 4.1 | 2.7 | 40 | 0.1 | 0.1 | 0.2 | 15 | 0.1 | 0.2 | 37 | b.d.l. | 0.6 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 93 |
| **KKN4** | 0.4 | 4.3 | 2.6 | 41 | 0.5 | b.d.l. | 0.2 | 12 | 0.1 | 0.2 | 39 | b.d.l. | 0.4 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 94 |
| **KKN5** | 0.3 | 4.5 | 1.9 | 40 | 0.1 | b.d.l. | 0.1 | 14 | 0.1 | 0.2 | 39 | b.d.l. | 0.4 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KKN8** | 0.2 | 3.7 | 2.1 | 41 | 0.7 | 0.1 | b.d.l. | 11 | 0.1 | 0.2 | 40 | b.d.l. | 0.5 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KKN9** | 1.0 | 4.5 | 3.1 | 46 | 1.3 | 0.1 | 0.8 | 10 | 0.1 | 0.2 | 33 | b.d.l. | 0.4 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 96 |
| **KKN10** | 0.4 | 5.3 | 2.1 | 46 | 0.2 | b.d.l. | 0.1 | 12 | 0.1 | 0.2 | 34 | b.d.l. | 0.5 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 94 |
| **KK1** | 0.7 | 3.6 | 3.3 | 36 | 0.5 | 0.1 | 0.3 | 19 | 0.1 | 0.2 | 36 | b.d.l. | 0.8 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 97 |
| **KK10** | 0.3 | 4.0 | 1.8 | 39 | 0.5 | 0.1 | b.d.l. | 11 | 0.1 | 0.2 | 42 | b.d.l. | 0.6 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 96 |
| **KK11** | 0.6 | 3.6 | 2.9 | 39 | 0.4 | 0.1 | 0.2 | 13 | 0.1 | 0.2 | 39 | b.d.l. | 0.6 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **KKN2** | 1.3 | 2.7 | 7.9 | 30 | b.d.l. | 0.5 | 0.9 | 5.6 | 0.3 | 0.4 | 40 | 0.2 | 2.6 | 0.1 | b.d.l. | b.d.l. | 7.5 | 94 |
| **KKN7** | 0.8 | 0.9 | 4.9 | 23 | b.d.l. | b.d.l. | 0.3 | 4.2 | 0.2 | b.d.l. | 48 | 0.5 | 9.6 | 2.2 | b.d.l. | b.d.l. | 4.5 | 99 |
| **KK3** | 0.7 | 0.8 | 3.3 | 19 | 0.1 | 1.9 | 0.1 | 1.4 | 0.1 | 0.4 | 44 | 0.2 | 10 | 7.4 | 0.4 | 0.1 | 10 | 90 |
| **KK12** | 0.6 | 0.8 | 8.0 | 25 | 0.5 | 0.1 | 0.7 | 3.6 | 0.4 | b.d.l. | 54 | b.d.l. | 2.8 | 2.5 | b.d.l. | b.d.l. | 0.8 | 88 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **KKN3** | b.d.l. | 0.3 | b.d.l. | 5.6 | b.d.l. | 2.5 | b.d.l. | 0.2 | b.d.l. | b.d.l. | 60 | b.d.l. | 31 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 86 |

***Table 6.1** EPMA results (weight %) of bulk analyses on all the slag samples from Daskaleio-Kavos. 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. These appear high relative to the observed porosity in some of the Group 2 samples as a result of frequent abundance of metallic phases, which are presented as oxides. Elements consistently measuring below the detection limits of the method have not been included in these tables.*

### Bulk composition

Table 6.1 gives the EPMA bulk composition measurements for the Group 1 slags. Silica (36-46 %) and iron oxide (32-42 %) are the main constituents, with silica usually appearing slightly higher. Calcium oxide is the third highest component (10-18.5 %), while smaller amounts of other gangue elements such as the oxides of magnesium and aluminium were also detected. The overall copper content appears relatively low (CuO: 0.4-0.8 %). No other base metals often encountered in copper and copper alloys such as lead, arsenic, antimony or tin were identified above the detection limits of the analytical technique in the bulk compositions.

A few of the larger Group 1 slags were large enough to be additionally analysed as pressed pellets on the (P)ED-XRF. The normalised averages of the three runs (major and minor elements) are presented in Table 6.2 (full results in Appendix 5: Tables A5.2a and A5.2b). The results are in close agreement with those obtained by EPMA (Table 6.1). Only silica and iron oxide show some deviation with silica almost consistently measuring lower and iron oxide higher on the (P)ED-XRF. The (P)ED-XRF measurements also provide information on the trace element content of these slags (see Appendix 5: Table A5.2b). Apart from allowing a direct comparison with the EPMA analyses, the (P)ED-XRF bulk compositions of the Group 1 samples will not be considered any further as only a limited number of slags from Daskaleio-Kavos could be analysed with this method.

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN1** | 0.5 | 4.1 | 2.0 | 36 | 0.0 | 0.4 | 13 | 0.1 | 0.2 | 43 | 0.7 | 96 |
| **KKN4** | 0.5 | 4.0 | 1.9 | 37 | 0.2 | 0.4 | 11 | 0.1 | 0.2 | 45 | 0.4 | 93 |
| **KKN8** | 0.7 | 5.2 | 1.4 | 41 | 0.0 | 0.2 | 12 | 0.0 | 0.2 | 40 | 0.4 | 89 |
| **KKN9** | 1.1 | 5.2 | 2.9 | 43 | 1.1 | 0.9 | 9.3 | 0.0 | 0.2 | 37 | 0.2 | 96 |
| **KKN10** | 0.6 | 3.9 | 2.2 | 38 | 0.3 | 0.3 | 10 | 0.0 | 0.2 | 44 | 0.5 | 95 |
| **KK1** | 0.7 | 3.6 | 2.4 | 33 | 0.1 | 0.5 | 18 | 0.1 | 0.2 | 41 | 0.7 | 92 |

***Table 6.2*** *Averages of three analyses of Group 1 slag samples on the (P)ED-XRF, normalised to 100 % (major and minor elements in weight %; MT: measured total).*

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | FeO | NiO | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **KKN7a** | b.d.l. | b.d.l. | b.d.l. | 94 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.8 | 95 |
| **KKN7b** | b.d.l. | 0.3 | 1.9 | 96 | 0.6 | b.d.l. | 2.5 | b.d.l. | 1.4 | 103 |
| **KKN7c** | 0.4 | 0.3 | 1.9 | 97 | 0.5 | 0.5 | 2.2 | b.d.l. | 0.5 | 103 |
| **KKN7d** | 1.2 | 0.4 | 2.0 | 94 | 0.4 | 0.5 | 2.1 | b.d.l. | 0.5 | 101 |
| **KKN7e** | b.d.l. | 0.3 | 1.9 | 92 | 0.5 | 0.4 | 2.4 | b.d.l. | 1.3 | 99 |
| **KKN2a** | b.d.l. | b.d.l. | b.d.l. | 92 | b.d.l. | b.d.l. | 1.6 | 0.2 | 0.4 | 94 |

***Table 6.3*** *EDS-SEM point analyses (weight %) on quartz inclusions in Group 2 samples (b.d.l.: below detection limit).*

Microstructure and phase composition

Observed under the optical microscope these samples bear many cracks and usually appear more porous than was evident from their outer surface (see Appendix 5: Table A5.3 for summary of optical microscopy observations). In the majority of the samples iron silicates of the olivine group ($(Fe_xMg_{1-x})_2SiO_4$) are the dominant phases surrounded by a glassy matrix, while dispersed magnetite ($Fe_3O_4$) is also usually present (Figure 6.6). The size and distribution of the different phases within the same section varies. The identification of these phases on the optical microscope was further supported by semi-quantitative analyses of a small number of selected samples on the SEM (Appendix 5: Table A5.4). The analyses indicated that the iron silicates are basically fayalite ($Fe_2SiO_4$) with magnesium oxide partly substituting for the iron oxide, while small amounts of calcium oxide were also detected in these crystals. Aluminium oxide detected in minor percentages partly replaces the trivalent iron in magnetite, similarly calcium, magnesium and titanium oxide the divalent iron.

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 kirschteinite ($CaFeSiO_4$), with small amounts of magnesium oxide also present. The crystallisation of these calcium-rich phases in KK1 is not surprising, given the comparatively high calcium contents detected in the bulk analysis of this sample (see Table 6.1).

Internal magnetite bands were observed in several samples. These often indicate a temporary cooling zone, associated with tapping (see section 5.4.1.1). In these samples, however, magnetite bands are small, largely fragmented, and appear in different directions within the same section suggesting that they resulted from rapid and local oxidation of the melt, probably while the operation was still being carried out (Figure 6.7). They cannot therefore be taken as evidence for slag tapping.

Sample KKN9 shows a columnar growth of fayalite crystals perpendicular to one edge of the sample (Figure 6.8). This formation, termed 'spinifex texture', indicates rapid cooling of the molten solution in contact with a cold surface (Hauptmann *et al.* 2003: 205). In their study of EBA slag cakes from Shahr-i Sokhta in Iran, Hauptmann *et al.* (2003) observed a similar phenomenon, from which they concluded that at the end of smelting the molten slag was poured from the crucible and cooled outside. The spinifex texture was however identified in only one of the Kavos Group 1 samples and given that these slags are shapeless and much smaller, it would be premature to draw any similar conclusions on the basis of the current observations.

### Analyses of the entrapped prills

Metal-rich phases are frequent in these samples and they comprise mixed copper and iron sulphides (matte). It is clear from the larger matte prills that these are usually heterogeneous with different phases appearing within the same prill (Figure 6.9). Electron microprobe point analysis on these phases showed that no other base metals are present in levels above the detection limit of the analytical method used (Appendix 5: Table A5.5). The results on Table A5.5 should not be taken to represent the relative ratios of Cu/ Fe and S in each prill as these represent point analyses and several phases of different composition co-exist in the matte. Tiny prills that resembled copper metal rather than matte were identified on the optical microscope, however none have as yet been detected during electron microprobe analyses and their nature is therefore uncertain.

### Discussion of Group 1 slags

The crystallisation of fayalite from a molten slag typically requires low oxygen pressures (usually below $10^{-8}$ atm), that is reducing conditions, and its presence in slags is therefore considered a conclusive indication of smelting (Moesta and Schlick 1989). The predominance of fayalite in these slags therefore leaves no doubt that these are the by-products of smelting. Remains of undecomposed primary materials in the slag matrix, as are frequently observed in early (usually pre-EBA) copper production remains (see for example Hauptmann 1989: 123 and below), were practically absent. The only exception is the observation of one quartz fragment with iron minerals in sample KKN9, which appears to have only partially reacted around the edges (Figure 6.10). Overall the microstructure of these slags suggests that the primary materials fully reacted and decomposed during smelting, forming a relatively homogenised solution.

As was discussed in section 5.5.1 for the slags from Seriphos, the identification of matte in the slags indicates that sulphidic minerals were included in the furnace charge, either deliberately or accidentally as a minor constituent of a mainly oxidic ore. In the absence of further evidence (e.g. discarded ore fragments, partially reacted materials) it is impossible to draw any further conclusions regarding the nature of the ores used, whether mainly sulphidic or oxidic. The composition of the slags, however, points to a mainly iron and silica-rich matrix for the copper ores.

The EPMA bulk analyses results were plotted on the $SiO_2$-Anorthite-FeO phase diagram (Figure 6.11), as outlined in section 5.5.2. The samples plot within or close to the fayalite region, suggesting typical temperatures for early copper smelting in the range of 1100-1250°C. In terms of redox conditions, based on this temperature estimate and the phase composition of these specimens, which involves mainly fayalite and magnetite in a glassy matrix, the Group 1 slags fall within the broad range of oxygen pressures between $10^{-6}$-$10^{-11}$ atm (see Figure 5.73).

### *6.4.1.2 Group 2 (KKN2, KKN7, KK3, KK12)*

#### Macroscopic characteristics

Four samples were attributed to this second group (Table A5.1). Three of these show very similar external characteristics (KKN2, KKN7, KK3). They are all black, moderately porous and magnetic, often showing iron oxide and little green copper oxide staining on their outer surface (Figure 6.12). Upon sectioning intense green staining was observed particularly in and around pores. A very characteristic feature of these samples is the appearance of several tiny (usually <1 mm) green prills, which protrude on the outer surface. Nearly all the samples are very small, usually around 1-1.5 cm in their maximum dimension. The one sample that does not entirely fit the above description is KK12. This black slag reaches nearly 3 cm in length, is largely covered externally by a thin (~1 mm) solid green corrosion layer and also shows red-brown iron oxide staining on one side. External green prills were not seen and the sectioned surface did not show the intense green staining seen in the other samples. Although the macroscopic characteristics of this specimen are different from the other Group 2 samples, microscopic and analytical similarities justified its classification in this group.

The small size and oval shape of these samples, with the exception of KK12, are reminiscent of slag spilled during the metallurgical process rather than slag broken into small fragments for the extraction of copper prills, which may appear more angular. This is however only a speculation as these are surface finds and their rounded shape may be a result of erosion.

### Bulk composition

Compared to the Group 1, the bulk analyses of Group 2 slags appear much more variable, and significant differences are observed in some elements between the four samples (Table 6.1). Overall a clear predominance of iron oxide (39-54 %) over silica (19-29 %) is observed. Also notable are higher levels of alumina (3-8 %) and lower levels of calcium oxide (1.3-5.5 %) compared to the Group 1 samples. Their copper content is much higher (2.7-9.5 %). Particularly characteristic is the presence of lead and arsenic in significant concentrations (0.8-9.6 % and 0.1-7.1 % respectively) as well as nickel in smaller amounts. Antimony and tin were detected in one sample only (KK3). Most of the latter six elements were identified both in their metallic form and as oxides but are presented as oxides in Table 6.1 (see also footnote 5.3 in Chapter 5). It should be noted that parts of samples KKN2 and KKN7 in particular are enriched in exceptionally large copper prills that covered the entire area analysed. Given that with the method used for these analyses only parts of the samples could be analysed, these prills were largely avoided in the measurements in order to obtain a more comparable picture of the bulk matrix composition between all the samples. The actual content of copper therefore in the bulk of these slags and, to a lesser extent, the other base metals found in association with copper prills may in reality be higher.

### Microstructure and phase composition

The microstructure of these specimens is also variable among the different samples (Appendix 5: Table A5.3). Heterogeneities are readily observed within the same section with frequency, size and distribution of the phase components varying between different areas. Common characteristics in all the samples are the striking abundance of magnetite in a glass matrix, their high porosity, and the great quantity of copper prills frequently in relatively large sizes (Figure 6.13). Sample KK3 is particularly rich in magnetite and relatively little glass was seen (Figure 6.14). This is in agreement with the bulk analysis of this sample, which shows the lowest percentages of silica and other gangue elements in the bulk composition (Table 6.1). Analyses of the magnetite crystals showed that these accommodate variable, but generally small amounts of several other oxides, primarily alumina and magnesia, while a characteristic feature of the glass phase are the typically relatively high levels of lead (Appendix 5: Table A5.6). Elongated fayalite crystals were observed in only two samples (KKN2, KK12) (Figure 6.15). These usually accommodate varying amounts of magnesium, calcium and manganese oxides (Table A5.6). In one small area of KKN2 a concentration of iron oxides in the shape of wüstite was observed (Figure 6.16).

Dispersed inclusions that appear to correspond to primary unreacted or semi-reacted starting materials were frequently observed within the slag matrix of these samples. These can be divided in two types. One corresponds to large irregularly shaped magnetite aggregates, in some cases partially decomposed and usually including within them distinct copper prills (Figure 6.17). As was discussed in section 5.4.1.1, these are interpreted as the remains of the partially reacted limonitic part of mixed copper and iron ores (Hauptmann *et al.* 2003) and therefore strongly suggest that these slags are the products of smelting copper ores which co-existed with iron oxides and hydroxides. The second type corresponds to quartz inclusions. EDS-SEM analyses of some of these inclusions (Table 6.3) detected in some cases small amounts of iron and copper, indicating that the quartz may have been geologically associated with the copper-bearing minerals.

The effects of post depositional weathering are evident in the microstructure of most of these samples and particularly KK3, which explains the higher levels of chlorine detected in the bulk composition of this specimen. Copper chloride salts, in some cases accompanied by small amounts of oxidised iron minerals, have frequently formed in the voids and cracks of the slag (Figure 6.14).

Analyses of the entrapped prills

The samples are all rich in copper prills. Electron microprobe point analysis of these prills detected arsenic, iron, nickel, antimony, and bismuth in variable amounts

(Appendix 5: Table A5.7). Approximately 1-2 % of tin was detected in some prills in KK3. Lead and lead chloride were identified as very small prills, either distinct or attached to copper prills, and also as small inclusions within the latter. Lead and copper are almost completely immiscible in the solid state and therefore the separation of the two is not surprising (Hansen and Anderko 1958: 610). The majority of these prills can be considered arsenical copper with variable amounts of other metallic components. The distribution of arsenic in these prills is uneven with arsenic enriched zones appearing within a matrix of lower or even negligible arsenic contents. This shows both from SEM imaging on the backscattered mode and from the variability of arsenic levels in the microprobe analysis of different points within the same prills (Figure 6.18 and Table A5.7). Although at low arsenic concentrations the two metals are completely miscible, the steep liquidus and solidus lines observed in their binary phase diagram causes these micro-segregation phenomena under non-equilibrium freezing (Budd and Ottaway 1991; Northover 1989). The surprisingly high concentrations of arsenic in some cases should not therefore be taken as representative of the whole as they correspond to arsenic rich areas. Furthermore, it is not possible to estimate the total arsenic concentration in each of these prills on the basis of the present results as the analyses are point measurements. Similarly observed variations in the other metallic elements in prills in the same sample are partly due to the nature of the analytical method used (see also below).

Variations are also observed in the compositions of the prills between different samples, particularly the lower arsenic levels in prills from sample KKN2 even in the arsenic-rich phases. Rehren *et al.* (1997) have proposed that such discrepancies even within the same sample are due to a fire-refining effect, causing preferential burning of the more reactive impurities, more pronounced on smaller prills with larger surface areas relative to their volume, which would as a result show lower levels of impurities. The potential association of size with the levels of impurities in these prills was not tested during these analyses. This proposal however highlights the potential loss of certain elements during heating and supports the suggestion that despite the observed differences even in the metallic phases, these slags have resulted from the same type of process.

Two large but completely corroded prills were observed at one edge of the sections from KKN2 and KKN7 (Figure 6.19). Their corroded microstructure partly retains the original segregated dendritic structure typical of corroded as-cast copper alloys. Qualitative analysis on the SEM detected copper, iron, arsenic, lead, antimony and chlorine. These prills hence correspond to the characteristic green prills observed macroscopically at the surface of most of these samples, as well as to the uncorroded polymetallic prills found within the slags.

In sample KK12 matte prills were identified in addition to copper prills (analyses KK12B and F in Table A5.7). It is interesting to note that lower arsenic contents are seen in the matte prills in comparison to the copper prills in the same sample, in agreement with the results of Yazawa (1980) (see also section 5.4.1.1).

Discussion of Group 2 slags

Although these samples show some variation both in their chemical composition and their microstructure they exhibit several common features that prompted their classification as a single group. Most characteristic are the predominance of magnetite and the identification of other base metals aside from copper and iron, mainly arsenic and lead. 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 suggests a smelting origin for these finds as well.

Phase diagrams cannot be used for an approximation of the smelting temperature due to the heterogeneous nature of these slags and the presence of partially reacted raw materials within them. Besides, the number of Group 2 slags recovered is very small to allow detailed insight into the parameters of the corresponding process. Still, some broad qualitative comments can be made on the basis of the observations noted so far. The frequency of magnetite in glass in these samples indicates that the process from which they resulted operated at only slightly reducing conditions (Moesta and Schlick 1989), although the observation of fayalite and possibly also wüstite in some cases may indicate that more reducing conditions prevailed in parts of the reacting mixture (c.f. Figure 5.73). The heterogeneous nature of these slags and the remnants of primary materials show that in some cases the slag only partially formed a homogeneous melt. Obviously the formation of fayalite shows that at least part of the mixture had formed a reacting melt. Copper losses are much higher (2.6-10 %) than for the Group 1 slags pointing to an overall less efficient recovery of metal.

Particularly surprising are the relatively high levels of lead in some of the bulk analyses of these samples, which in sample KKN2 in particular, appear to be higher than copper contents. As was noted in the bulk analysis section, however, copper contents may be somewhat underestimated as areas with exceptionally large or concentrated copper prills were usually avoided in these measurements. 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 (note in particular analyses of KKN2 in Table A5.6). Still, the overall lead composition in these samples is usually notably high. The presence of low levels of lead, usually below 1 %, in copper smelting slags has been attested in other areas of the Old World (see for example Hauptmann 1989). Examples of copper smelting slags with lead contents comparable to the Group 2 samples have not however been found in the literature examined so far (although see for example Pernicka *et al.* 1990: 292; Stos-Gale 1992: 159-60 for EBA lead-rich copper alloy objects). This abundance of lead raises the possibility that the slags in this group are actually related to lead rather than copper metallurgy. The copper content of the slags is however high, which indicates that the starting materials contained significant amounts of this metal. Based on the value and diversity of uses of copper in antiquity, it is very unlikely that such high concentrations would have been wasted in the production of lead. In additional support of the copper smelting origin of these remains, the majority of prills, and particularly the large ones, are arsenical copper metal with lead usually present in these as minute inclusions, suggesting that this alloyed copper was the product of the metallurgical process corresponding to the Group 2 slags.

### *6.4.1.3 Comparison of Group 1 and Group 2 slags*

From the results presented in the previous two sections, it is evident that the two slag groups exhibit considerable differences between them that justify this separation.

What needs to be addressed at this stage is whether the two processes from which these remains resulted could be connected. Two options have to be considered. In the first, the process corresponding to the Group 1 material succeeds the one corresponding to the Group 2. This sequence can be excluded as none of the alloying base metals identified in Group 2 slags were seen in the analyses of Group 1 material.

The opposite sequence, Group 2 following Group 1, would involve alloying of 'clean' copper metal produced during the first step (where Group 1 slag was produced) with ores containing the observed alloying constituents. This is indeed one of three main potential mechanisms for the production of arsenical copper alloys; the other two being direct smelting of mixed copper-arsenic ores or co-smelting of copper-rich and arsenic-rich ores (Budd *et al.* 1992; Lechtman 1991, 1996; Lechtman and Klein 1999; Pollard *et al.* 1991; Rostoker and Dvorak 1991; Shimada and Merkel 1991; see also discussion in section 7.2.2.2). Ultimately, in order to distinguish between these three possibilities, evidence on the nature of the raw materials used is necessary. At present associated mineral samples have not been found among the collection of metallurgical remains from Daskaleio-Kavos. Partially reacted raw materials, whether magnetite aggregates or quartz fragments, were, however, noted in the Group 2 slags. Both showed some association with copper; copper prills have formed in the magnetite aggregates, while minor amounts of copper were detected in the quartz. This observation suggests that copper was most probably added to the mixture as a mineral rather than in metallic form, so that a relationship between the Group 1 and Group 2 slags seems unlikely.

It is at present impossible to infer whether the Group 2 process involved smelting of polymetallic ores that included all the observed base metals (for examples see Ixer and Pattrick 2003) or whether deliberate mixing of different minerals was taking place. Further research into this area by the acquisition of additional samples could be very informative as the nature of the ores used would provide insight both into the technological details of the process and potentially their provenance. Mixing of different types of ores would affect the lead isotope ratios of the resulting slag and this possibility should be borne in mind if such analyses were to be carried out in the future.

### *6.4.1.4 Sample KKN3*

Macroscopic characteristics

Macroscopically this sample shows some similarities to the Group 2 samples (Table A5.1). It is small, less than 2 cm in length, very magnetic, black with limited green staining and tiny green prills on its outer surface (Figure 6.20). Due to markedly different microscopic and analytical features, however, it is not included in that group but is dealt with separately.

Bulk composition, microstructure, and phase composition

Bulk analysis of KKN3 shows a striking predominance of iron oxide (c. 60 %), followed by a considerable copper content (CuO c. 20 %), while silica and the other gangue oxides are surprisingly low (Table 6.1). Other base metal constituents as identified in the Group 2 slags were not observed in any appreciable quantities in this sample.

Examination under the optical microscope revealed that the sample is dominated by magnetite crystals with very little glass (Table A5.3). They are 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 6.21). Analyses of the magnetite crystals showed that they contain appreciable amounts of copper (Appendix 5: Table A5.8). Copper oxide can to some extent be incorporated in magnetite at slightly reducing conditions, while delafossite forms at more oxidising conditions (Moesta and Schlick 1989). Frequent circular copper chlorides with small amounts of iron are seen. These, most likely, correspond to corroded copper prills or leached copper chlorides filling the voids. Distinct copper prills are abundant within the magnetite crystals. Electron microprobe point analysis results on these prills are given in Appendix 5 (Table A5.9). The prills are very small and it was not possible to analyse them separately. The extremely high iron percentages detected are probably due to the simultaneous measurement of part of the surrounding magnetite. The copper prills appear to be free from any other base metals with the exception of possible traces of lead. The almost complete absence of the alloying elements detected in Group 2 samples does not support an association of KKN3 with members of that group despite similarities in their external characteristics.

The microstructure of sample KKN3, with high abundance of magnetite and delafossite crystals, indicates relatively oxidising conditions. Delafossite is typically associated with melting slags (Bachmann 1982a: 16), although it is also frequently observed in early copper smelting slags and indicates too short reaction times and/or weakly reducing conditions (Hauptmann 1989, 2000: 556). It is unlikely that this slag has resulted from melting due to the low presence of silica, calcium and alkali oxides, which would be typically expected to form from the reaction of the vessel fabric with the fuel ash and the iron and copper of the melted metal (see also below). It is more probable that this sample represents semi-reacted dross, spilled from the reacting mixture at the early stages of smelting and therefore its composition is not necessarily representative of that of the charge.

It should however be noted that in their study of the copper smelting furnaces at Mitterberg, Moesta and Schlick (1989) observed a similar microstructure in the upper levels of the furnace, which they proposed resulted from oxidation of the previously formed matte. There is therefore a potential association of this sample with the Group 1 samples showing a sequence similar to the Mitterberg furnaces. This is, however, only a speculation and could only be proven by the consistent discovery of further similar samples or samples showing together a microstructure typical of Group 1 and an upper part of magnetite/delafossite composition. As this sample was unique in the collection studied, it could well represent simply an accidental by-product. At this stage no further conclusions can be drawn on this matter.

### *6.4.2. Metallurgical ceramics*

#### *6.4.2.1 Samples KK4, KK5, KK13, and KKN11*

Macroscopic characteristics

The metallurgical ceramic fragments are very small, only a few cm in length (Table A5.1), and they retain no diagnostic features that would indicate their original shape or size (Figure 6.22). It is not even possible to conclude with any certainty whether these represent parts of crucibles or furnace lining, although their small size and thickness is more reminiscent of a crucible vessel. The colour of the outer surface is orange to red, which changes to black towards the inner side of the ceramic, resulting in an inner vitrified bloated layer with circular vesicles (Figure 6.23). The vitrification on the inner side of the ceramic only, where the slag layer is attached, indicates that the corresponding vessels were heated from the inside. Small inclusions (usually less than 1 mm) of refractory materials such as quartz and schist are observed as well as impressions of burnt-out organic temper. The use of clays with inclusions stable over the temperatures attained during the metallurgical process, either inherent to the clay deposits or intentionally added, is very common in metallurgical ceramics as they would have reduced shrinkage and avoided cracking during heating (Freestone 1989; Schneider 1989). Similarly beneficial for the purposes of metallurgical activities was the addition of organic temper to the clays used, which on the one hand probably facilitated the working of the clay and additionally would have burnt out during heating forming pores and channels, thus allowing the entrapped gases and moisture to escape (Freestone 1989; Schneider 1989). Impressions of organic temper are very rare in the main pottery assemblage (Broodbank pers. comm.), indicating that the beneficial properties of these additions for ceramics used in high-temperature processes were appreciated and especially sought for the purposes of metallurgy. In most of the samples a slag layer of varying thickness is found attached to the inner surface.

The three aforementioned zones of ceramic, vitrified ceramic and slag are not preserved in all the samples. Sample KKN11, for example, only retains a black vitrified ceramic part with attached slag, while KK5 only exhibits the outer red ceramic layer with very little dark grey colouration on one side. The latter was therefore only recognised as a *metallurgical* ceramic from the macroscopic similarity of the fabric to the rest. The thickness of these fragments does not usually exceed 1 cm but the original thickness of the vessels cannot be estimated, as significant weathering is likely to have occurred due to the friable nature of the material.

Two ceramic sherd fragments with attached slag were also found in the collection (samples KK8 and KK9 in Table A5.1). One was a red schist-tempered coarse fabric sherd with a red-brown slip on one surface, and the other a medium mica quartz fabric.[6.2] Both had slag attached on one side and some vitrification was visible on the contact between the ceramic and the slag. The different fabrics of these sherds, typical of EBII pottery found at Kavos, and the fact that vitrification was restricted to the points where slag was attached and did not extend to the entire ceramic piece indicate that these are not directly related to the metallurgical process. The slag probably represents spilling during the operation, which caused some local vitrification due to the heat of the melt. The specimens were therefore not analysed any further.

### Bulk composition

Bulk analyses were carried out as area measurements on the EPMA (see section 3.6.2.3) separately for the ceramic and the slag part of each sample (Table 6.4). The areas analysed in the ceramic part were chosen so as to exclude to the degree that it was possible the quartz and other inclusions and therefore analyse only the ceramic matrix. This is largely composed of silica with about 18 % alumina. From the analysis of sample KK5, which largely only retained the plain unvitrified ceramic, it can be seen that calcium oxide, magnesia and the alkali oxides are relatively low. Similarly for the other samples, although some elements and in particular iron oxide are higher, which may in part be due to penetration of metal or slag into the ceramic layer, as is also indicated by the presence of significant quantities of copper. In sample KK4 one or two distinct copper prills were identified within the ceramic fabric, which may partly also explain the relatively high copper contents in this part of the sample.

---

[6.2] Identification of the fabrics was kindly provided by Dr C. Broodbank at the museum of Naxos during initial macroscopic study of the collection.

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CoO | NiO | CuO | $As_2O_3$ | PbO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN11VC** | 2.4 | 4.0 | 16.3 | 60.0 | 0.0 | 0.3 | 2.7 | 5.8 | 0.7 | 0.1 | 6.3 | 0.0 | 0.0 | 1.3 | 0.0 | 0.1 | 87.9 |
| **KKN11SL** | 1.8 | 1.9 | 7.8 | 35.1 | 0.0 | 0.7 | 0.9 | 11.1 | 0.3 | 0.1 | 30.0 | 0.1 | 0.1 | 4.2 | 1.6 | 4.4 | 97.0 |
| **KK4CER** | 1.0 | 2.0 | 17.8 | 53.1 | 0.1 | 0.0 | 2.6 | 5.5 | 0.9 | 0.1 | 12.1 | 0.1 | 0.4 | 3.4 | 0.0 | 1.0 | 57.4 |
| **KK4SL** | 0.6 | 1.4 | 9.3 | 35.5 | 0.0 | 0.3 | 1.0 | 11.5 | 0.4 | 0.0 | 35.1 | 0.0 | 0.1 | 1.5 | 0.0 | 3.1 | 96.6 |
| **KK13CER** | 1.1 | 2.1 | 18.6 | 57.7 | 0.1 | 0.3 | 2.6 | 1.7 | 0.9 | 0.2 | 9.7 | 0.0 | 0.0 | 4.8 | 0.1 | 0.1 | 67.6 |
| **KK13SL** | 0.8 | 1.7 | 5.1 | 18.9 | 0.2 | 1.9 | 0.4 | 7.4 | 0.2 | 1.2 | 24.4 | 0.2 | 0.6 | 28.1 | 2.8 | 6.1 | 92.1 |
| **KK5CER** | 2.2 | 1.7 | 18.5 | 67.6 | 0.1 | 0.0 | 3.6 | 1.4 | 0.7 | 0.0 | 3.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 71.2 |
| **KK6CER** | 1.6 | 1.5 | 17.6 | 67.1 | 0.0 | 0.0 | 4.0 | 3.3 | 0.5 | 0.0 | 4.2 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 72.0 |
| **KK6SL** | 3.2 | 1.8 | 13.4 | 51.8 | 0.1 | 0.0 | 3.2 | 12.2 | 0.4 | 0.0 | 3.6 | 0.0 | 0.0 | 9.1 | 0.6 | 0.5 | 90.7 |

***Table 6.4*** *Bulk EPMA analyses (weight %) of metallurgical ceramic fragments (SL: slag, VC: vitrified ceramic, CER: ceramic). Results normalised to 100%, measured totals given in column MT.*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | Cl | $K_2O$ | CaO | $Fe_2O_3$ | CuO | Sb | PbO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KK19** | 2.8 | 0.8 | 2.7 | 5.5 | 0.3 | 0.2 | 25 | 0.3 | 0.1 | 0.1 | 29 | 66 |

***Table 6.5.*** *Semi-quantitative analysis of sample KK19 on the (P)ED-XRF (weight %).*

The composition of the ceramic fabric with a silica to alumina ratio of about 3:1 indicates that the material was not particularly refractory by modern standards. Similar compositions are common in early metallurgical ceramics of the Old World (Freestone 1989; Freestone and Tite 1986; Hauptmann *et al.* 2003). Despite their comparatively poor refractoriness, refiring experiments and studies of the vitrification gradient developed during firing have shown that similar fabrics could withstand the relatively low temperatures (1000-1200°C) attained in early metallurgical operations, resulting in partial vitrification as observed in these samples as well (Maniatis and Tite 1981; Tite *et al.* 1982, 1985, 1990). The use of low refractory clays shows that a separate specialised craftsmanship for the production of refractory ceramics was not yet developed in the early stages of metallurgy, although the tempering with suitable inclusions demonstrates that at least some care was taken in this respect (Freestone and Tite 1986).

The bulk compositions of the slag layers differ markedly from those of the ceramics with the exception of sample KK6, which is discussed separately below. Iron and calcium oxide values are significantly increased, while silica and alumina levels are much lower. Similarly the content of alkalis and magnesium oxide is slightly decreased, while the content of metallic elements such as copper and lead is increased. These differences indicate that it is unlikely that the slags have resulted from pure melting or refining of copper metal, but are rather the products of smelting. Melting or refining of copper would produce a slag mainly from the vitrification of the ceramic and the reaction of the vessel fabric with the iron and possibly slag inclusions in the unrefined metal (Rothenberg 1988: 201-202). This slag would be very similar to the ceramic composition with the iron and base metal concentrations increased. In this case however apart from the iron, the silica to alumina ratio is higher in the case of the slag and so is the calcium oxide, pointing towards an addition of these elements resulting from the gangue materials probably present in the ores during smelting (Hauptmann *et al.* 2003).

Microstructure and phase composition

The slag microstructure is mainly composed of magnetite and glass, similarly to the Group 2 slags (for a summary of the optical microscopy observations on the metallurgical ceramic samples see Appendix 5: Table A5.10). Analyses of magnetite by EDS-SEM showed that, in varying degree for each sample, magnesia, and in one sample manganese and zinc oxides partly substitute for the divalent iron, and similarly aluminium for the trivalent iron (Appendix 5: Table A5.11). Significant quantities of lead and to a lesser extent copper are present in the glass. In two samples (KKN11 and KK4) another type of mineral formation was observed, less bright than magnetite and appearing in several different shapes from nearly square to partly elongated. Analysis of such crystals on the SEM showed significant quantities of calcium oxide and an iron oxide to silica ratio that partly resembled pyroxenes. The presence of considerable alumina however is surprising as the iron oxide in pyroxenes is divalent and could therefore not be substituted by alumina, which may indicate that these crystals actually correspond to melilites, a group of silicates with the general formula $(Ca/\ Na/\ K)_2(Mg/\ Fe^{2+}/\ Fe^{3+}/\ Al)(Si/\ Al)_2O_7$ (Bachmann 1982a: 15). Thin elongated crystals were in some cases observed at the border with the ceramic. Quantitative analysis on the SEM has not been possible as these are exceptionally thin but qualitative analysis did not detect copper, which therefore excludes the possibility that these are delafossites. Inclusions of undecomposed or partially decomposed starting materials (magnetite segregations and quartz) were also observed in these samples similarly to the Group 2 slags.

### Analyses of the entrapped prills

Analyses of the metallic prills found in the slag layer are given in Appendix 5 (Table A5.12). These phases show a composition very similar qualitatively to that identified in the prills of Group 2 slags. Heterogeneous arsenical copper alloys with varying amounts of iron, nickel, antimony, silver and bismuth, were observed together with lead rich phases appearing as separate prills or as inclusions within the copper metal. The quantitative differences in the alloying elements of copper observed within these analyses and between those and the Group 2 prills are probably due to point measurements in combination with the heterogeneous distribution of these elements in copper and the effects of fire-refining as discussed in section 6.4.1.2. Overall the metallurgical ceramic fragments show considerable similarities to the Group 2 slags, which strongly suggests they result from the same process. The characteristic chemical composition and phase assemblage of the slag component of these specimens and the differences in composition compared to the ceramic fabric, further support a smelting origin for the Group 2 slags.

### *6.4.2.2 Sample KK6*

Sample KK6 shows similar external characteristics to the other metallurgical ceramics discussed so far. At least two layers were identified by macroscopic examination; a red ceramic layer and a black glassy slag-like layer. The composition and nature of the former is very similar to the other specimens in this group of materials (Table 6.4). The black slag-like layer however differs markedly and hence this sample is treated separately in this section.

Observed under the optical microscope this layer appears as a uniform glassy phase, while a relatively large quartz fragment is found at the edge (Figure 6.24). No distinct mineral or metal phases were observed. The bulk analyses on this part of the sample (given as KK6SL in Table 6.4) did not show the characteristic differences discussed previously in comparison to the ceramic fabric. The silica to alumina ratio and the iron oxide and alkali contents, with the exception of soda, remain largely the same in both layers. On the contrary, calcium oxide and copper are significantly increased in the glass, while small amounts of arsenic and lead were also detected in this layer.

The difference in calcium oxide composition between the two layers in sample KK6 may be interpreted in two different ways. On the one hand it could result from smelting copper ore accompanied by the other identified base metals and embedded in a limestone/calcite host rock (Hauptmann 2003: 97). Alternatively, calcium oxide and soda may appear higher as a result of the absorption of fuel ash in the black, glassy layer. Fuel ash can give rise to significant increase in the calcium oxide and alkali compositions of slag (Evans and Tylecote 1967; Tylecote 1982: 239; Tylecote *et al.* 1977: 310). If fuel ash could be shown to be the source for these elements in this case, then the relative compositions of the two layers would be consistent with the specimen resulting from a secondary melting activity, as discussed previously. Overall, however, this sample is unique in its analytical characteristics and in the absence of additional similar or associated material it is not possible to conclude with any certainty that it corresponds to a separate metallurgical operation or what the nature of that would be.

### *6.4.3 Isolated metal prills or fragments*

The collection included several small pieces of copper metal prills or fragments whose outer surface was largely covered by a green corrosion layer (Figure 6.25). A radiograph of these finds was taken, which showed that most samples still contained an uncorroded metal core. Four samples were subsequently sectioned and mounted in resin for analysis.

Examination of these sections under the optical microscope revealed that the metal cores in these samples are not uniform but rather contain a number of small inclusions. The outer corrosion layer consists of cuprite and green secondary copper minerals. Qualitative analysis on the SEM indicated the presence of chlorine within these latter phases. The weathered surface is in some parts covered by a solid soil contamination layer.

The uncorroded cores were subsequently analysed using point analysis on the electron microprobe. The analyses showed variation between the different prills with respect to the composition of the metal matrix and the inclusions (Appendix 5: Table A5.13). Sample KKN6 shows a copper metal matrix with small amounts of nickel (c. 0.4 %) and separate small lead inclusions. In sample KK14 small amounts of iron (c. 0.5 %), nickel (c. 0.5 %), zinc (c. 0.5-1.5 %), silver (c. 0.4 %), antimony (c. 0.2 %), and arsenic (up to 0.4 %) were detected in the copper matrix. The inclusions are once again lead, which in this case is accompanied by bismuth. Sample KK17 shows an arsenical copper alloy matrix with zones enriched in arsenic due to micro-segregation (see section 6.4.1.2). The only other element detected in appreciable quantity in the matrix is silver. The inclusions in this sample are intermetallic consisting mainly of lead but also accompanied by significant quantities of arsenic, bismuth, antimony and traces of tin, nickel, and iron. Although the small size of these inclusions inhibited their isolated analysis, and copper, probably resulting from the surrounding metal matrix was also detected, the considerable increase of these impurities compared to the copper metal analyses suggests that these are largely concentrated in the lead rich phases. One almost pure bismuth inclusion was also observed. Finally the metal matrix in sample KKN12 is copper with nickel in minor amounts (c. 0.1 %), and copper sulphide inclusions. Intermetallic inclusions and copper sulphide inclusions in early copper metals are very frequent (see for example Hook *et al.* 1991) and may render bulk analyses of such artefacts partially invalid.

The qualitative similarities of three of the four analysed metal prills with those found in the Group 2 slags, particularly with reference to the lead-rich inclusions in both cases urge for a consideration of a potential association between the two. Bulk compositions of these metallic prills are not available due to the analytical method used, and internal heterogeneities have been shown to exist. However, the overall levels of impurities in the isolated metal prills, particularly with reference to arsenic, appear to be lower than those detected in the slags, which contrasts with the opposite observation by Rehren *et al.* (1997) in their comparison of crucible fabrics and isolated metal prills from Tell esh-Shuna. If the isolated prills are indeed the products of the process that formed the Group 2 slags, which seems very likely due to the qualitative similarities noted, an intermediate step causing partial burning of the more volatile impurities may be envisaged such as melting or casting. In this case the prills could represent accidental spills from the molten metal. However, in the absence of relevant finds, such as moulds or melting crucibles, the practise of such secondary metalworking activities on Daskaleio-Kavos cannot be confirmed.

Metal KKN12 is more reminiscent of Group 1 slags, particularly due to the sulphide inclusions observed and the almost complete absence of other base metal impurities. To date copper metal prills have not been identified in the Group 1 slags and therefore the structure and composition of the final product of this process cannot be concluded with certainty.

### *6.4.4. Litharge and lead metal*

One piece in the collection (sample KK19 in Table A5.1) was conclusively identified as litharge (Figure 6.26). The piece is heavy, relatively small and shapeless. Its colour is dark red-brown, in patches white, and it leaves a dark red powder behind. Litharge is a waste product of cupellation, a process used for the production or refining of silver at least since the fourth millennium BC (Hess *et al.* 1998; Pernicka *et al.* 1998). During cupellation, argentiferous lead metal, produced during a previous smelting step, is heated under oxidising conditions, forming lead oxide, while the more noble silver remains largely unreacted. Calcium-based materials are preferential to silica-rich materials for lining cupellation hearths as the latter react strongly with lead, forming a lead-silicate glass, which would result in the partial collapse of the lining. The lead oxide would then soak into the calcium-based lining leaving behind the silver metal and thus achieving separation of the two (Bayley and Eckstein 1997). Pernicka *et al.* (1998:124-125) differentiate the relevant cupellation finds in two categories: litharge, which corresponds to pure lead oxide accompanied by any base metal impurities present in the original charge, and litharge-impregnated hearth lining, which would result from the separation process described above.

Only preliminary semi-quantitative (P)ED-XRF analysis (using T-quant method) of a mounted section from this sample was carried out (Table 6.5) and showed, apart from lead oxide (c. 29 %), calcium oxide as the primary component (c. 25 %), with other gangue elements appearing much lower (percentages given correspond to 66 % measured total). Silver content was below the detection limit, while 0.1 % of copper and 0.1 % antimony was measured. The high levels of calcium and other oxides attested in this bulk analysis suggest that this find better corresponds to litharge-impregnated hearth lining according to the definition given previously. This distinction is further supported by a study of its microstructure.

The microstructure of this sample is very heterogeneous. The dominant and most clearly recognisable phases present are the relatively large, platy litharge crystals (Figure 6.27), which are partially weathered at their edges to lead (hydro-) carbonates. Other distinct, small crystals can be distinguished, usually grouped in clusters. A small number of these were analysed on the SEM and two different types of crystals were identified (Appendix 5: Table A5.14). The first are mainly sodium aluminosilicates with small amounts of potassium, calcium, iron and lead oxides. The second are composed mainly of antimony and calcium oxides with significant amounts of alumina and iron oxide and smaller concentrations of magnesia, alumina, silica, and lead oxides.

Of particular interest is the observed porosity in this sample. This consists of closed, elongated and slightly bent voids, which are partially filled in some cases with litharge crystals (Figure 6.27). In his study of litharge-impregnated hearth lining from first millennium BC contexts in south-western Spain, Keesmann (1993) noted a similar porosity, which he suggested resulted from the decomposition during heating of calcareous shells used as the raw material for calcium-rich lining. It is possible that this specimen points to a similar practise nearly two millennia earlier in the Aegean, which would present an interesting technological observation. Still, it is premature to offer such an interpretation with any certainty on the basis of a single specimen.

Three other specimens in the collection were identified as shapeless lead fragments. Polished sections were prepared from two of these samples (KK15 and KKN13) and analysed using point measurements on the electron microprobe. With the exception of 0.2 % of silver measured in a single analysis, no other base metals were identified above the detection limits of the analytical technique.

The identification of a single litharge specimen on Kavos obviously cannot be taken as concrete evidence that silver production was carried out on the site. The scarcity of litharge in the collection may be due to the obscure nature of the material and an associated difficulty in recognising it during surface survey; or alternatively reflect an actual dearth of such specimens on Kavos. It is, however, noteworthy that none of the slag samples examined appeared to be associated with lead-silver metallurgy, which also does not favour a primary production scenario at this stage. Obviously the absence of lead slag may indicate that lead was smelted elsewhere, possibly close to the ore source and the argentiferous metal brought to the settlement of Kavos for cupellation. On the other hand, litharge could result from silver recycling (Bayley and Eckstein 1997), which does appear to have been practised from very early on in antiquity (e.g. Rehren *et al.* 1996). This possibility could be explored further by comparing analyses of contemporaneous Cycladic silver objects with those of the litharge, although given the uniqueness of this sample in the collection such an investigation was considered premature at this stage.

Another point that should be borne in mind is that there are several indications in the archaeological record for the re-use of litharge. The most common is the reduction of litharge back to lead metal, as practised for example in a first millennium BC workshop in Monte Romero (Kassianidou *et al.* 1995). It should, however, be noted that reduction of litharge for lead production is not favoured for the Aegean EBA (Gale and Stos-Gale 1984; Pernicka *et al.* 1983). Other possibilities include silver refining (Rehren and Kraus 1999) and non-metallurgical functions such as the use of the material for medical purposes (Rehren *et al.* 1999), constructions (Papadimitriou and Kordatos 2001), and glass colouring (Mass *et al.* 2002 although see comments from Rehren 2003; Shortland 2003; and reply by Mass and Stone 2003). Even though all these activities are dated to much later periods and no such comparable indications are known from EBA contexts, these examples highlight the diversity in potential re-uses of litharge. The consequence is two-fold. On the one hand the argument of re-use could be used to explain the rarity of litharge samples. On the other hand, however, it raises the possibility that litharge was brought to the site from outside for further processing or use, perhaps not directly relevant to metallurgy.

In short, although the identification of this single litharge specimen raises the possibility that lead-silver metallurgy was practised on Kavos, it far from proves it or offers adequate insight into the details of the relevant processes. The identification of lead metal fragments is also intriguing although there is no firm evidence at this stage that these were produced locally. At this stage it was not considered worthwhile to pursue the study of the litharge and lead samples any further given the comparable rarity of this material. In the future, however, additional analytical work, possibly including lead isotope analyses and if possible further fieldwork would be desirable in order to address the question of presence or absence of lead-silver metallurgy on Kavos.

### *6.4.5. Iron mineral samples*

The number of iron mineral finds surpasses that of any other type of material in the collection of metallurgical remains (see Figures 6.3 and 6.4). Macroscopic examination concluded that these are non-magnetic secondary oxidic and hydroxidic ores, in some cases only partly crystalline. No external visual indications of an association with copper minerals were observed. Secondary iron minerals are very abundant in nature and are frequently observed in small occurrences in the Cyclades. Bassiakos and Doumas (1998) have reported such a small occurrence of poor secondary iron minerals associated with a little malachite around the area of Konakia further to the north-east of Kavos. A detailed geological report of the Kavos area is not, however, available at this stage. It is therefore not possible to conclude whether these finds are merely broken fragments of rock local to the site or whether they were intentionally brought there from other parts of the island or from outside.

Two samples (KK16 and KK20) were sectioned in order to examine their internal structure and also any potential association with copper minerals. The samples retain no remnants of the primary sulphidic minerals, while they exhibit the typical cellular honeycomb texture of weathered iron hydroxides. (P)ED-XRF analysis of pressed powder pellets (see Appendix 5: Tables A5.15a and b) showed that these contain small amounts of copper (1-3 %). No other base metals were detected in significant quantities.

The identification of copper in these specimens raises the possibility that these were associated with the ore used in the metallurgical processes carried out on site but were discarded as fragments overall poor in this metal. For this prospect to be explored any further a detailed geological study of the area would be necessary as it is very likely that these iron minerals have resulted from erosion of the local bedrock. If such occurrences are identified on Kavos, the possibility that an exploitable associated ore source was present in antiquity in the immediate vicinity of the site will need to be investigated through thorough geological fieldwork and appropriate sampling and analyses. Alternatively, even if local, the samples may simply represent natural fragmentation of the surrounding rocks. If a non-local character is concluded for these finds then potential uses for this material will need to be considered and an association with the local metallurgy sought through appropriate comparative analyses. At present a direct relation of these finds with the metallurgical operations carried out on Kavos cannot be established.

## 6.5 Spatial distribution and scale of metallurgical activities

Nearly all the samples related to metallurgy from the 1987 Kavos project were recovered during the surface survey. Any attempt to draw any conclusions on the scale or spatial distribution of metallurgical activities around the site on the basis of these finds is therefore restricted by several factors inherent to systematic surface collection. These problems are partly overcome, or at least the extent of their impact can be partially assessed, in the case of the Kavos survey through the consistent and detailed recording carried out during fieldwork. Unfortunately the small number of metallurgical remains identified inhibits a quantitative statistical analysis of the bias imposed by these restrictions in the emerging spatial distribution picture of these finds around the site. For this reason only preliminary qualitative comments can be made in this case. In the following paragraphs a brief overview of some of the main surface survey limitations, which apply to this project, are presented, and these are discussed in the light of the recorded data in an attempt to draw conclusions on the scale and spatial distribution of metallurgical activities on Kavos. For this analysis the surveyed area is distinguished in three parts (see Figures 6.3 and 6.4), the northern Kavos area (defined by 5x5 m units), which will be referred to as the special deposit area, the south-central part (defined largely by 10x10 m units), and Kavos North (collected using circular units).

Variable visibility between units due to vegetation can often significantly affect the quantity of material identified in each individual unit. Similarly the different ability of team members to recognise diverse types of material may also affect the resulting distribution and density of finds in the area covered. It should also be noted that the team consisted of non-specialists in the field of archaeometallurgy. In the case of Kavos the situation is further complicated by the damage inflicted to the site during looting, which may have caused significant material displacement. The low height, particularly in the case of Kavos North, means that the promontory is frequently washed by the sea potentially causing loss of material.

Pronounced differences in visibility are observed between the survey units.[6.1] Vegetation has to a large extent been cleared from the special deposit area, mainly because of illicit digging. As a result relatively high visibility characterises the majority of the relevant units and 95 % recovery of surface material larger than 1 cm in length is estimated in this case (Whitelaw pers. comm.). The south-central part of the site is frequently covered by dense vegetation resulting in variable visibility between units ranging from 5 to 90 % with a low overall average around 25 %. In the case of Kavos North visibility spans between 10 and 90 % with an overall average around 50 %. Although a quantitative analysis of the statistical bias introduced by the visibility factor is not permitted by the small total number of the metallurgical samples recovered, the potential effects it may introduce to the resulting distribution picture can be seen from one example in the case of Kavos North. Units 921 and 919 at the north-eastern part of the surveyed area (Figure 6.4), which produced the highest numbers of metallurgical remains in Kavos North, were characterised by high visibilities of 80 and 90 % respectively. These drop to 60 and 10 % in the adjacent units 917 and 915 further south, where only one sample was identified in total. Obviously the relation between visibility and recovery is not as straightforward as may appear from this example as samples have been collected from units with visibilities as low as 5 % and the reverse phenomenon is also not uncommon. However what this example highlights is that the restriction introduced by visibility alone, forbids any detailed discussion of spatial distribution at this stage. The low average visibilities in Kavos North and the south-central part of Kavos are also likely to have to a certain extent affected the number of identified remains in these areas.

In order to partly balance the general problem of potentially different abilities of individuals to recognise diverse types of materials, team members were mixed around the units during the survey and did not investigate adjacent units to the degree that this was possible. Once again the small number of samples available in this case does not allow any further assessment of any potential bias introduced by this factor. One comment that can however be made is that it appears that all the collectors involved in the survey brought in samples relevant to this study.

With reference to potential horizontal displacement of the remaining material caused by past looting, it has been suggested that, even in the areas most affected by these activities, it would most likely be very limited due to the methods applied by the illicit diggers (Whitelaw pers. comm.).

An additional point that needs to be considered is the different sampling methodology used in Kavos North compared to Kavos and the impact of this on the resulting comparative distribution. In Kavos North twenty-four circular units of 2.0 m radius were collected (Figure 6.4). Each corresponds to an area of approximately 12.6 $m^2$ resulting in a total of about 301 $m^2$ surveyed ground. The total collected area of Kavos North therefore is equivalent to approximately three of the Kavos 10x10 m units or twelve of the 5x5 m units (Figure 6.3). Moreover, with regards to the sample size in comparison to the entire area of the Kavos North promontory, if the latter is estimated at approximately 4000 $m^2$ from the outermost edges of the laid out units based on the sketch in Figure 6.4, the corresponding collected units represent only 7-8 % of that total. Considering only the slag and metallurgical ceramics collected in this survey, seventeen such finds were identified in Kavos North (Figure 6.4), which corresponds to one piece per 18 $m^2$. At this rate the number of metallurgical remains in the whole of Kavos North would be expected to surpass two hundred in total. Obviously these are only rough estimates and the actual dimensions of this scatter together with visibility variations would need to be considered before a more valid approximation of the total number of remains on the surface of Kavos North could be drawn.

One observation that is however immediately striking is the comparison in scale of such finds between this part of the surveyed area and the south-central part of Kavos. The latter corresponds to approximately 8000 $m^2$ of sampled ground, double the total estimate of the Kavos North scatter and more than twenty-six times its sampled area. Yet a total of only twelve slag and metallurgical ceramics finds were collected from this area (Figure 6.3), which corresponds to one piece per 667 $m^2$. The difference in concentration of metallurgical remains between these two sub-units appears enormous and highlights the potential effect of lower-intensity sampling in Kavos North and the danger in directly comparing the number of finds between them. The promontory of Kavos North does not appear to have been used for habitation, as was the case for Kavos, although excavation will be necessary to confirm this preliminary observation (Whitelaw pers. comm.). The apparently much larger concentration of metallurgical remains in this part of the site may therefore indicate that metallurgical activities were mostly carried out just outside the habitation area of Kavos. A similar spatial separation between the settlement and the metallurgical workshop was noted during Theocharis' (1951, 1952, 1953, 1954, 1955) excavations at the EBA site of Raphnina on Attica. This possible isolation of metallurgy from the main habitation areas may somewhat affect identification of such activities during fieldwork on settlements.

From the above discussion it is evident that the limitations inherent in the Kavos survey may be partly balanced by considering the consistent and detailed data recorded during fieldwork. The small sample size of metallurgical remains does not allow a quantitative assessment of scale and distribution of finds and therefore relevant activities within the site. Still, at least two important remarks regarding distribution can be made at this point. The first one involves a comparison of the types of material collected from the three survey sub-units. From Figures 6.3 and 6.4 it can be seen that no slag or metallurgical ceramics were collected from the special deposit, all such material originated from south-central Kavos and Kavos North. Iron minerals, copper and lead droplets and artefacts, and the single litharge specimen were the types of relevant material recovered from the survey and excavation in the special deposit area (Table A5.1 and Figure 6.3). With the exception of litharge none of the other specimens can be directly attributed to the practise of metallurgical activities in that area. Given the relatively high overall visibility in that area and the estimated low horizontal displacement caused by looting, the absence of such finds can with some certainty be taken to indicate that metallurgy was not practised at this part of the site, which is in agreement with the generally accepted view of the different nature of the special deposit compared to the rest of the site. The litharge specimen is the only find that does not appear to fit this pattern but as it is a single find, whose direct association with in-situ metallurgy cannot be conclusively proven at present, it can only be regarded as an exception at this stage. Within this part of Kavos another observation that is noteworthy is the high number of iron mineral samples collected, compared to the other areas investigated. This phenomenon may be largely attributed to the better visibility conditions at this part of the site although this is only a speculation. In addition, if these fragments have indeed resulted from the local bedrock, their abundance in this case may be the result of hammering during repeated illicit digging. The reasons for the presence of iron minerals in general at the site cannot, however, be assessed on the basis of the current finds as was discussed in section 6.4.5.

The second remark that can be drawn regarding spatial distribution involves a comparison between the types of materials identified in south-central Kavos and Kavos North with reference to the analytical results. Group 1 and 2 slags, as defined in the results section, are found in both Kavos and Kavos North and similarly copper and lead droplets and metallurgical ceramics (see Table A5.1). This observation seems to suggest that similar types of activities were being carried out in both areas and no spatial localisation can be detected. Obviously the small sample size is a limiting factor in this case as well and additional sampling would be necessary to examine this issue any further.

With regard to scale, the issues discussed at the start of this section may partly justify the small number of metallurgical remains identified in this survey despite the methodology applied, which involved a total recovery of all visible archaeological materials. The relatively low visibilities in south-central Kavos and Kavos North, which produced the majority of finds associated with metallurgy, suggest that this factor alone may have to some extent impeded the recognition of additional similar material present on the surface. Moreover, the potential effects of lower-intensity sampling on the resulting scale picture for Kavos North should not be underestimated. The preliminary comparison with south-central Kavos suggested that metallurgical activities might have been far more intensive on the former. Still, a relatively large-scale production, as envisaged for the large slag heaps of the western Cycladic islands (e.g. Gale *et al.* 1985; Hadjianastasiou and MacGillivray 1988), which appear to be isolated from a settlement context, can be excluded on Kavos, both on the grounds of the context of these finds and their infrequency in the recovered material. The metallurgical remains from this site appear to correspond to small-scale settlement-based activities.

Despite the limitations discussed in this section, the variability in the types of material collected as well as their diverse size, which is often remarkably small, indicates a thorough collection strategy. The skill of the participants and the methodology applied appear to have ensured to a large extent a diversity in the sample of metallurgical remains recovered, despite the generally obscure and specialist nature of this material. The result of such careful sampling on the conclusions drawn has been very rewarding as became evident from the analyses presented.

## 6.6 Discussion

Attempting to reconstruct and understand complex metallurgical processes from limited remains from settlement sites, and in particular surface finds as in this case, is exceptionally difficult as these are often very fragmentary and few in number. Still a lot can be deduced from suitable examination. The analytical examination of the metallurgical remains from Daskaleio-Kavos has provided strong evidence that copper smelting was taking place on Kavos during the EBA, challenging previous assumptions that production of metal was restricted to the western 'metal-rich' islands and only secondary metalworking was carried out within settlements (Broodbank 2000a: 293-7). Although more material is likely to emerge from future excavations, the small quantities identified during the thorough 1987 survey and the obvious differences between Daskaleio-Kavos and the large copper smelting sites of the western Cyclades indicate that these activities are likely to have been relatively small-scale, corresponding to household or settlement production.

The identification of two different slag groups strongly suggests that at least two distinct smelting processes were taking place on Kavos probably involving the use of different types of ores. The possibility that the two processes were part of the same sequence seems very unlikely on the basis of the present finds. An examination of the spatial distribution of these finds, to the extent that this was possible, showed that the two activities were not spatially isolated; similar types of processes were taking place at Kavos and Kavos North. Habitation at Daskaleio-Kavos appears to cover a period of up to 500 years (Broodbank 2000b: 331) and it is likely that a shift in metallurgical practices was observed during this time span changing from the use of one particular ore type to another, although the contemporaneous smelting of two different types of ore is also not unlikely. This question however can only be addressed through examination of stratigraphically recovered finds, which are at present absent.

On the basis of the present finds it is impossible to deduce whether secondary metalworking activities such as melting or casting were additionally carried out on Kavos. Two vague indications for such practise were identified during these analyses. The first relates to the metallurgical ceramic sample KK6, whose composition could correspond to a vessel used for melting, although a smelting origin cannot be conclusively excluded even in this case. Secondly, comparison of the composition of some of the isolated metal prills with those entrapped in the Group 2 slags, suggested that base metal impurities are lower in the former. A possible interpretation offered includes an intermediate melting or refining step. This is only a speculation though, and the observed differences are likely to be due to the limitations of the analytical technique used, which only measured points in combination with the inhomogeneous nature of these alloys. More firm evidence would be necessary in order to propose that secondary metalworking was indeed taking place on this site.

Adding to the apparent variability and potential complexity of metallurgical operations carried out on Kavos is the single find of litharge-impregnated hearth material and the small number of lead metal fragments, which raise the possibility that cupellation was also practised on this site. Still, recovery of further samples would be necessary to confirm this suggestion. In this case it would be interesting to carry out an additional set of analyses and examine the potential provenance association of samples associated with lead-silver metallurgy with those of the Group 2 copper slags, which showed high lead contents. Further compositional and trace element analyses would be necessary for this purpose as well as lead isotope analyses.

Overall, the issue of provenance of this metallurgical material presents an interesting field for further study. The possibly contemporaneous practise of at least two different smelting processes is not surprising in a settlement context and particularly one, which appears to be as well connected as Kavos. In agreement with other archaeological finds from the site, which appear to be imported to a large extent, it is possible that different types of ore were brought to the site for processing. In order to examine this possibility a thorough investigation of the island's geological setting would at first be necessary to determine the presence or absence of small occurrences of relevant ore, which could have been used locally. Traces of a weathered iron-copper mineralisation have been identified in northern Keros, but analytical results are not available for comparison (Bassiakos and Doumas 1998). Additionally lead isotope analysis could be used for this purpose. Despite the problems associated with this technique (section 2.5), which may at present inhibit the clear identification of the primary source, lead isotope results may help clarify whether the two different slag groups have a common origin.

Other metallurgical slags on Keros have been recovered in the past from the surface among the ruins of the modern settlement of Konakia at the northern part of the island. Pottery sherds that could help date the corresponding processes were not observed in the immediate vicinity. Bulk SEM analyses of these slags showed minor amounts of copper (0.4-0.7 %) but no metallic phases (prills or matte) were observed (Bassiakos and Doumas 1998). The microstructure of these samples also appears to differ from the ones presented in this study, as wüstite, practically absent from the Daskaleio-Kavos remains, was the primary mineral phase identified. The authors admit that in the absence of identified copper metallic phases it is difficult to conclude with certainty whether this material corresponds to copper or iron smelting. On the basis of the present results there does not seem to be an association between these finds and the ones from Daskaleio-Kavos.

The observed variability in metallurgical activities on Kavos further supports the argument that such finds from settlement contexts present a very interesting case in the study of EBA Cycladic metallurgy that merit careful examination. Given the unusual wealth and nature of this site, it is not however safe to assume that a similar range of activities was taking place on other contemporaneous Cycladic sites (see also discussion in section 7.3).

The number of finds recovered during the 1987 survey on Keros was very small and consequently did not allow a complete and secure reconstruction of the processes taking place as might have otherwise been possible. It is therefore proposed that future fieldwork and excavation at Daskaleio-Kavos may offer substantially more insight on the metallurgical activities at this site.

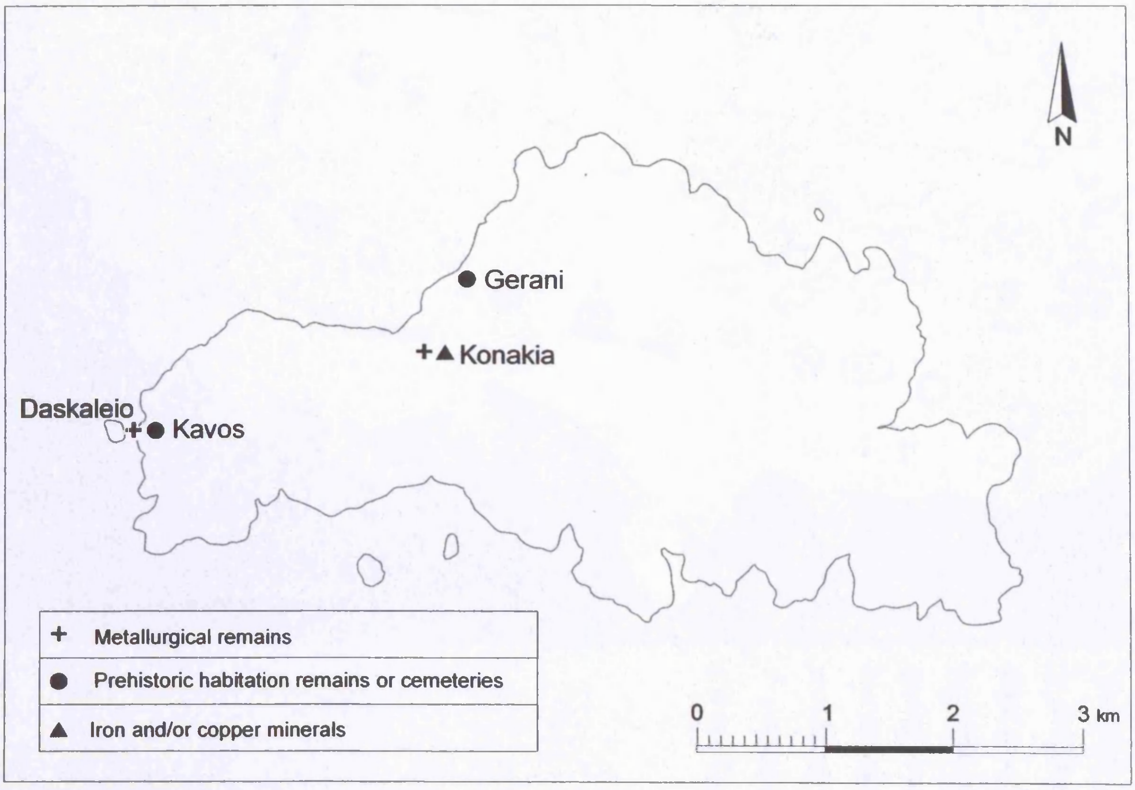


***Figure 6.1***
*Map of Keros showing sites mentioned.*

***Figure 6.2** Plan of the Daskaleio-Kavos site and the surveyed area (Broodbank 2000a: 224). Reprinted with permission from C. Broodbank and T. Whitelaw.*

***Figure 6.5*** *Examples of Group 1 slags (top from left: KKN1, KKN4, KKN5; middle: KK1; bottom from left: KKN8, KKN9, KKN10).*

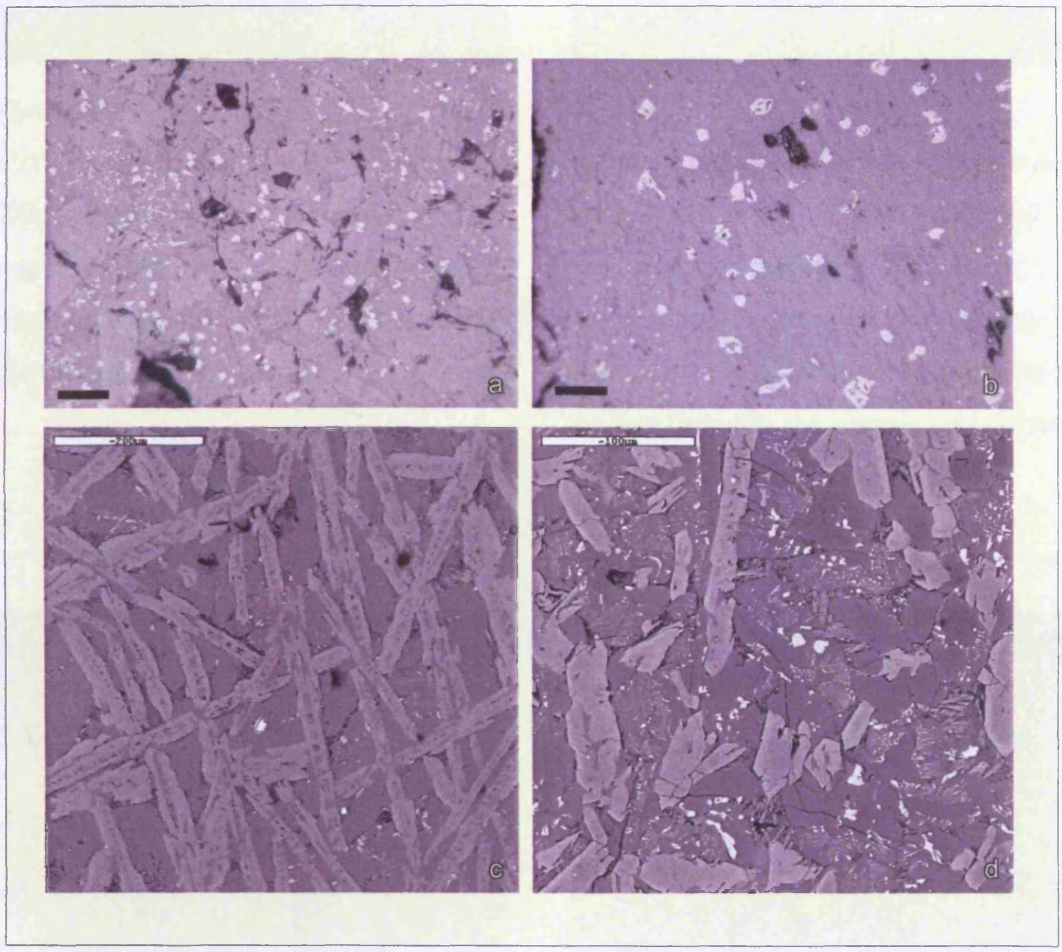


***Figure 6.6*** *Typical microphotographs of Group 1 samples*

*(a) Reflected light microphotograph of sample KKN4 (scale 50 μm), showing fayalite (medium grey) and magnetite (light grey), in a glassy matrix (dark grey).*

*(b) Reflected light microphotograph of sample KK1 (scale 50 μm), showing kirschteinite (medium grey) and magnetite (light grey) in a glassy matrix (dark grey).*

*(c) Backscatter electron image of sample KK11, showing fayalite (medium grey) and matte prills (circular white) in a glassy matrix (dark grey).*

*(d) Backscatter electron image of sample KK10, showing fayalite (medium grey) and magnetite (light grey) in a glassy matrix (dark grey).*

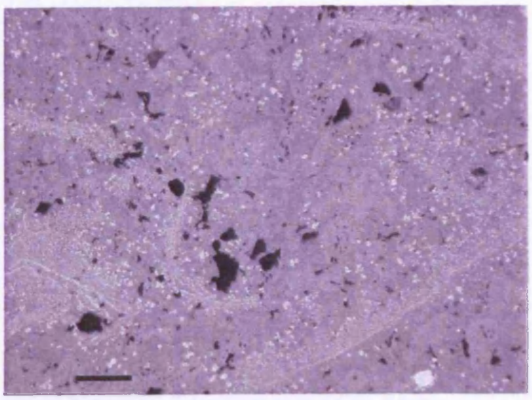


*Figure 6.7* Reflected light microphotograph of sample KKN1 (scale 100 µm), showing fayalite (medium grey), magnetite and magnetite bands (light grey), porosity (black) in a glassy matrix (dark grey).

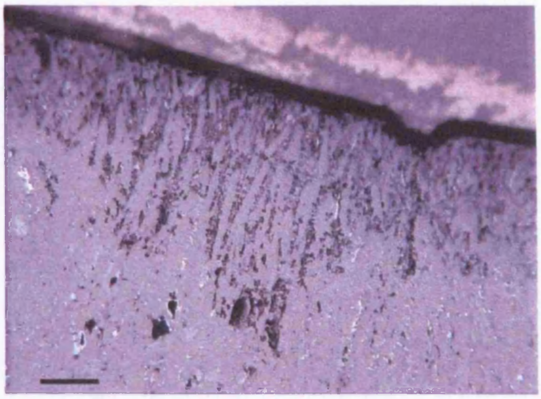


*Figure 6.8* Reflected light microphotograph of spinifex texture on one edge of sample KKN9 (scale 100 µm). Glass matrix has weathered at surface, making fayalite more clearly visible. The black line at the edge shows the gap between the sample and the resin (top of the image).

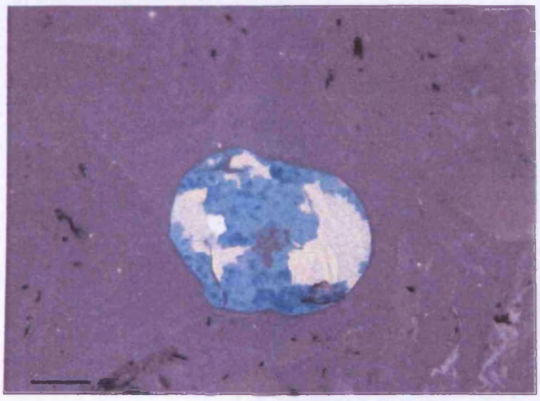


*Figure 6.9* Reflected light microphotograph of large matte prill in sample KKN10 (scale 50 µm), showing copper sulphides (light and darker blue) and copper iron sulphides (off-white and pink).

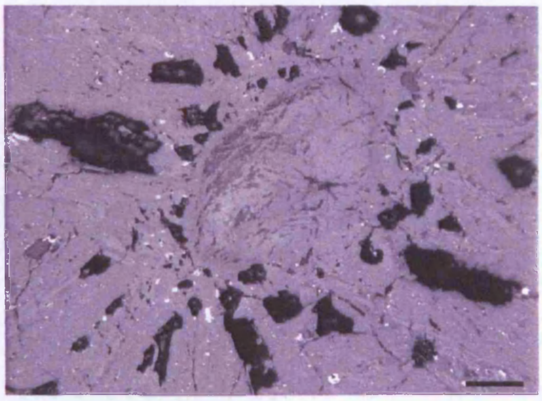


*Figure 6.10* Reflected light microphotograph of partially reacted quartz inclusion in sample KKN9 (scale 100 µm).

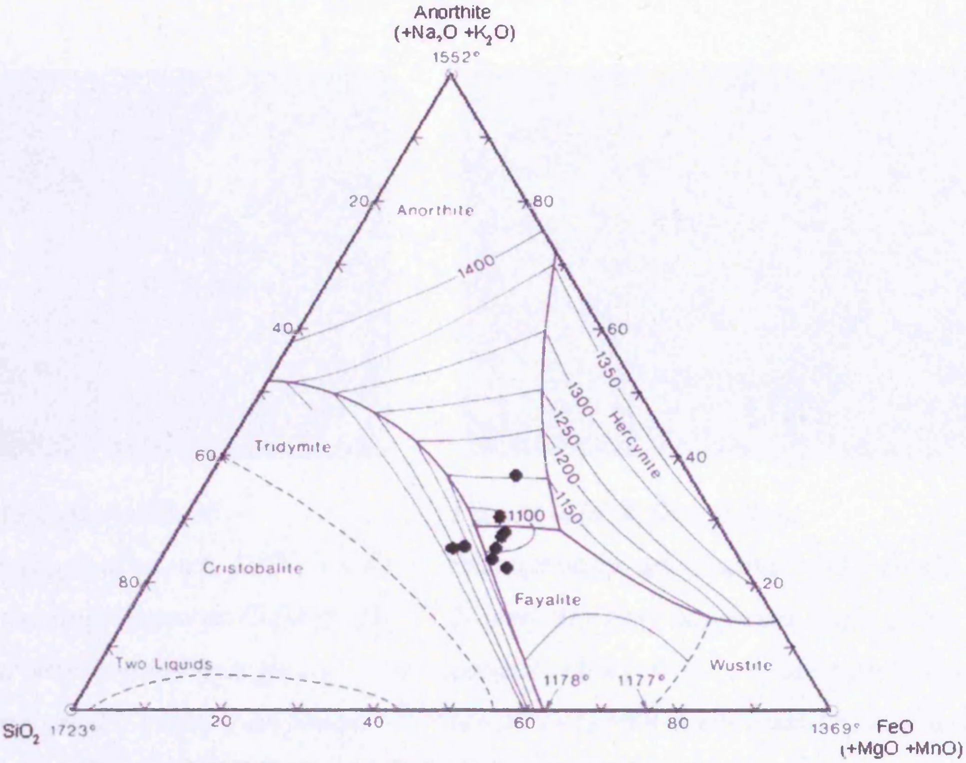


***Figure 6.11*** *The Group 1 slags represented on the ternary phase diagram Anorthite-$SiO_2$-FeO.*

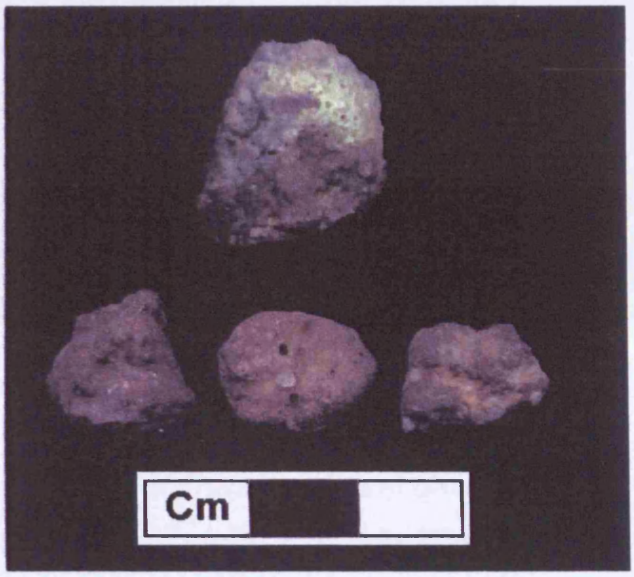


***Figure 6.12*** *Group 2 samples (top: sample KK12, bottom from left to right: KKN7, KKN2, KK3).*

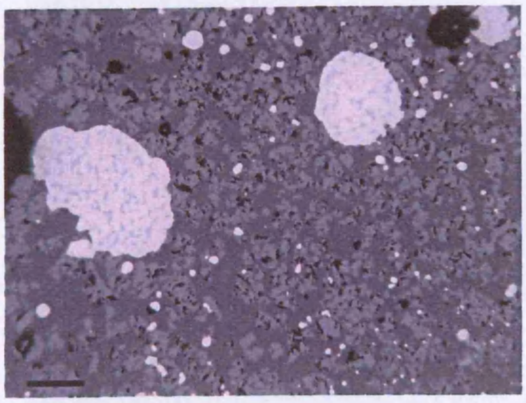


*Figure 6.13* Reflected light microphotograph of sample KKN7 (scale 100 µm), showing magnetite (light grey) and copper prills (white) in a glassy matrix (dark grey). Arsenic-rich phases (appearing light blue) can be discerned in the larger copper prills.

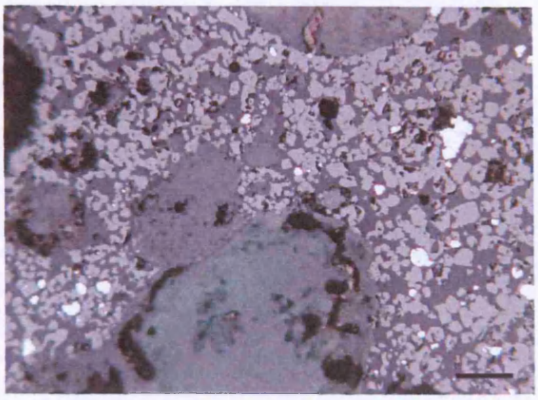


*Figure 6.14* Reflected light microphotograph of sample KK3 (scale 50 µm), showing magnetite (light grey), copper prills (white), copper salts filling the pores (green) surrounded by a glassy matrix (dark grey).

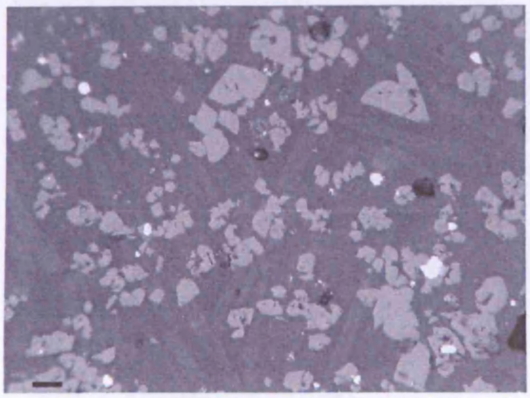


*Figure 6.15* Reflected light microphotograph of sample KKN2 (scale 10 µm), showing fayalite (medium grey), magnetite (light grey), copper prills (off-white), and glass (dark grey).

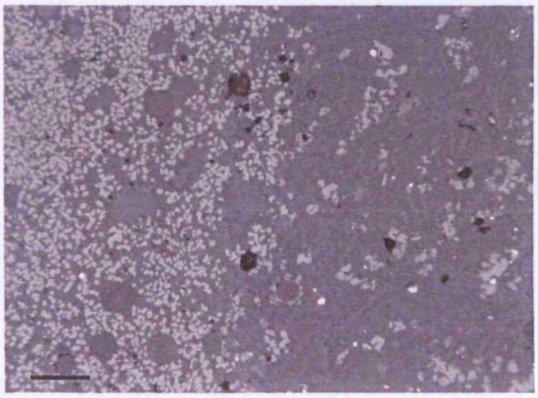


*Figure 6.16* Reflected light microphotograph of sample KKN2 (scale 50 µm) area, showing concentration of wüstite (light grey, rounded crystals, at the left part of the image), and fayalite (medium grey), copper prills (off-white), magnetite (light grey, angular crystals) and glass (dark grey).

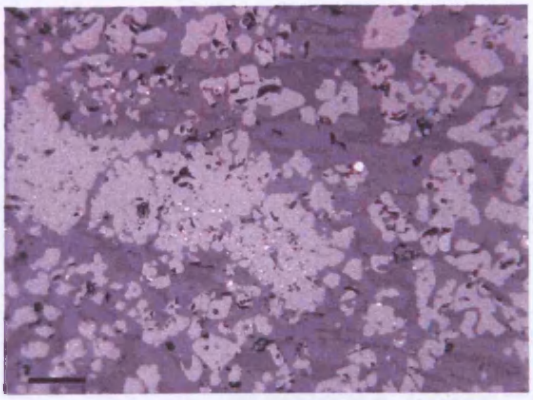
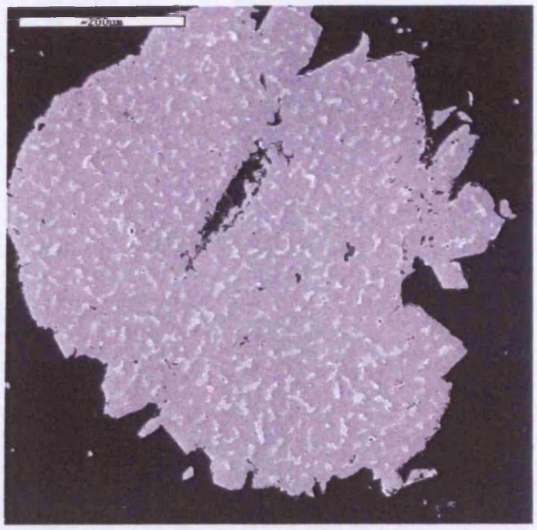


***Figure 6.17** Reflected light microphotograph of sample KK12 (scale 50 µm), showing magnetite aggregate (light grey) with copper prills (off-white) and matte (blue).*



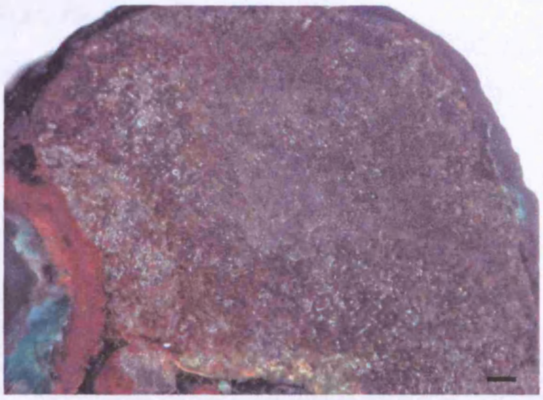


***Figure 6.18** Backscatter electron image of copper prill in sample KKN7 showing arsenic rich zones (lighter grey).*

***Figure 6.19** Reflected light microphotograph (crossed polars) of completely corroded prill at the edge of sample KKN2 (scale 100 µm), which retains original as-cast dendritic microstructure.*

***Figure 6.20** Sample KKN3.*

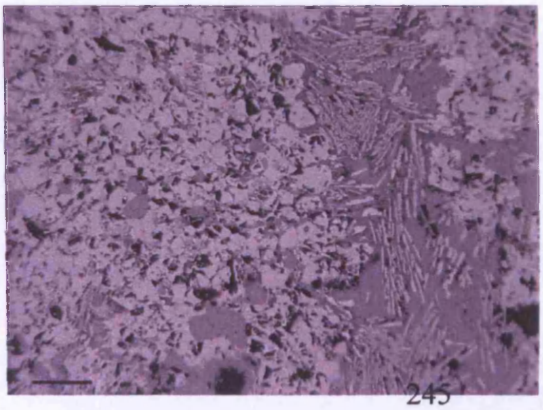


***Figure 6.21** Reflected light microphotograph of sample KKN3 (scale 100 µm), showing magnetite (light grey isometric grains), delafossite (light grey platy crystals), copper prills (bright yellow-white, circular), and copper chlorides (dark grey, circular).*

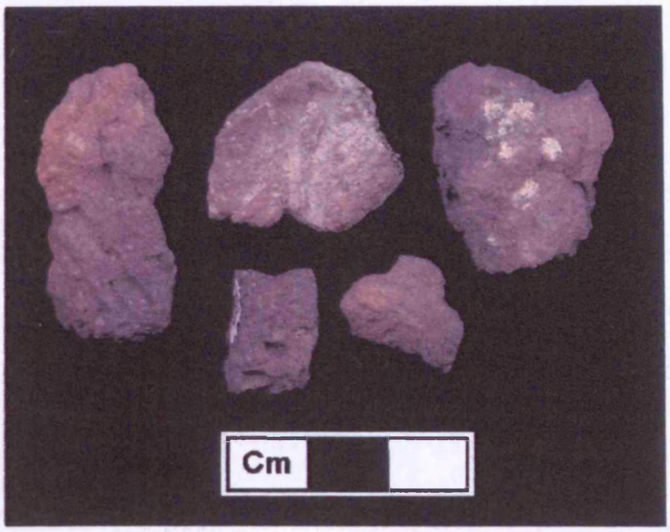


***Figure 6.22*** *Metallurgical ceramics.*

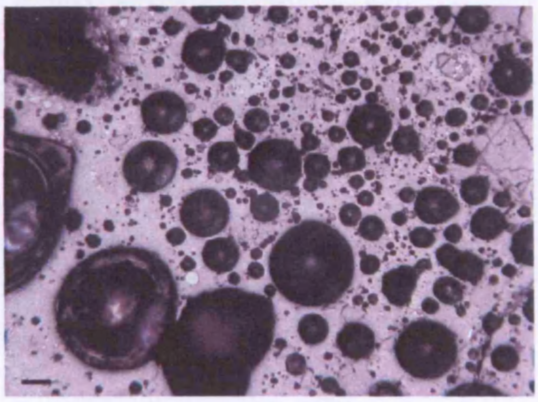


***Figure 6.23*** *Reflected light microphotograph of sample KKN11 (scale 100 μm), showing area of vitrified ceramic with circular porosity (black).*

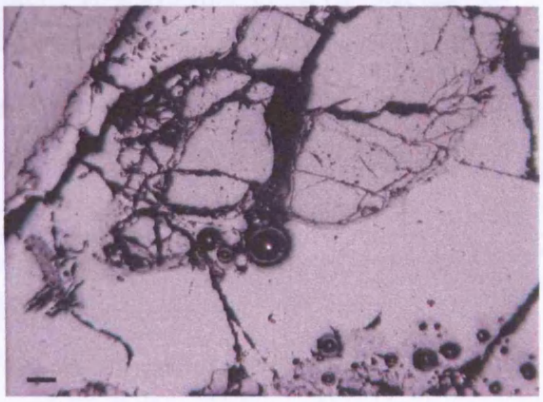


***Figure 6.24*** *Reflected light microphotograph of sample KK6 (scale 100 μm), showing contact of ceramic with glassy slag layer. Quartz inclusion is seen at the top of the image (surrounding resin at the top left).*

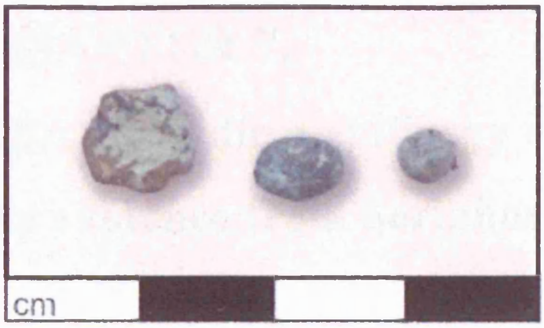


***Figure 6.25*** *Examples of isolated metal fragments.*

***Figure 6.26*** *Litharge-impregnated hearth lining fragment (sample KK19).*

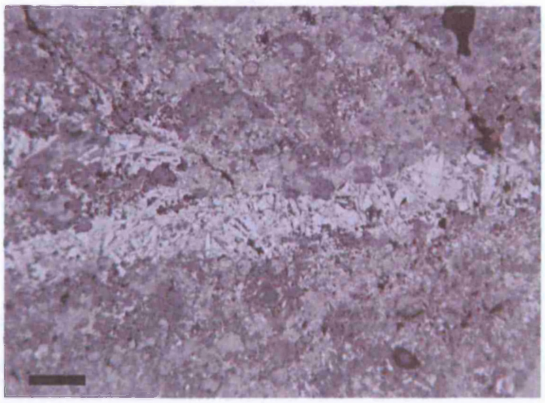


***Figure 6.27*** *Reflected light microphotograph of sample KK19 (scale 100 μm), showing litharge crystals (white, platy) filling elongated pore and other distinct crystals (circular/polygonal, light pink).*

# CHAPTER 7.

# EBA Cycladic metallurgy reconsidered in the light of the evidence from Seriphos and Daskaleio-Kavos

## 7.1 Introduction

In the early chapters (Chapters 2 and 3) of this thesis it was argued that despite a long history of research into EBA metallurgy in the Cyclades, studies have mainly focused on aspects of circulation and consumption of metals. Metal production had until now received less and more peripheral interest, with investigations limited almost entirely to the islands of Siphnos and Kythnos. The following chapters (Chapters 4-6) presented the results of archaeometallurgical work on the technology of copper production on two other islands, namely Seriphos and Keros, case studies that represent two very different contexts with evidence for metallurgical activities. The purpose of this chapter is to investigate how the emerging data compare with evidence gathered from other Cycladic sites and to consider how these may contribute to formulating a model concerning the organisation of EBA Cycladic metal production on a regional level. Given that the material of this thesis dealt almost exclusively with evidence relating to copper metallurgy (with the exception of the single litharge specimen from Daskaleio-Kavos), the emphasis is on this metal.

In the following sections some characteristics of the slag heaps on Seriphos are considered together with evidence from other similar EBA sites known from the Cyclades (mainly from Kythnos) and more generally from the Aegean. The study of the Daskaleio-Kavos material forms the basis for a discussion of the potential and importance of metallurgical remains from settlement sites. In addition, as activities associated with primary metal production were also attested on Daskaleio-Kavos, a comparison is drawn with the western Cycladic metal production sites. Subsequently, EBA Cycladic metallurgy is placed within the context of the broader

Aegean, considering briefly other neighbouring areas and the effects of their interaction on this early industry. The chapter closes with a short discussion of the picture obtained so far regarding the organisation of metallurgy in the EBA Cyclades.

## 7.2 Seriphos and the western Cycladic slag heaps

As was discussed in section 2.4.1, although small mineralisations are found dispersed across the Cyclades, the western part of the island complex is comparatively metal-rich. In this region, and more specifically on the islands of Kythnos, Seriphos, and Siphnos, extensive slag heaps associated with EBA metal production are found. The following paragraphs discuss and compare some specific attributes that have emerged from the study of these sites relating mainly to aspects of their spatial distribution and technology.

### *7.2.1 Aspects of spatial distribution*

#### *7.2.1.1 Distribution and location of the slag heaps*

An important development of archaeometallurgical work during the last few years has been the increase in the number of EBA slag heaps known on the western Cyclades. In addition to Kythnos, EBA copper production is now known to have taken place on Seriphos as well (see Chapter 5). It also emerges, both from Seriphos and from the recent study on Kythnos carried out by Bassiakos and Philaniotou (in press), that copper production is testified at more than one site on each island. On Kythnos, apart from Skouries, Sideri has been dated to the EBA using TL, while Lefkes and Paliopyrgos-Aspra Spitia were dated to the EBA (the latter also to the MBA) on the basis of surface pottery. On Seriphos the sites of Kephala and Phournoi were dated to the EBA on the basis of TL dating of ceramic furnace fragments (Appendix 3), as well as diagnostic pottery collected from the latter (Philaniotou 2004). Additionally, the identification of EBA sherds on Avessalos, (Philaniotou 2004) together with other indications (see section 5.6.1), suggest that at least part of this heap may also be associated with prehistoric metallurgy. Apart from these sites, copper slag scatters or heaps are reported from Kea and Siphnos (see section 2.4), but their date remains uncertain.

Distance between the slag heaps is variable. On Kythnos, where more sites are known to date, these are found both in different parts of the island (e.g. the northwest, the east, the southeast), but also as clusters of several clearly distinct sites, as seen at the northwest. The slag heaps identified so far on Seriphos (including the undated scatters reported by Gale and Stos-Gale (2002; in press) and Papadimitriou and Fragiskos (2003)) all occupy promontories along the western to north-western coast of the island, while it is certainly likely that further similar sites are located in other less studied areas (see also below).

Another characteristic that should be highlighted is that the slag heaps on both Seriphos and Kythnos differ markedly in terms of their size and the volume of material present. The difference is clear in the rough comparison of Kephala and Phournoi presented in Chapter 5, while similar differences are implied in the description of the Kythnian sites (Bassiakos and Philaniotou in press). Unfortunately even approximate quantitative data are not at present available for Kythnos so a more systematic comparison of volumes is not possible.

In terms of location, the slag heaps show very similar features, which were also mentioned earlier in this thesis. Specifically, the pattern that prevails from the metal production sites on Kythnos, as well as Ayios Sostis on Siphnos and Chrysokamino on Crete, shows that the slag heaps are usually found on windswept promontories, in most cases coastal. A very similar setting was noted for the three slag heaps on Seriphos. The most obvious explanation for the selection of these locations is the manipulation of the naturally occurring strong winds to aid smelting, although the issue requires further investigation in order to understand exactly how these were used in each case (see also section 5.5.5). Easy access to the sea in order to facilitate transportation of raw materials and/or products is also likely to have prompted the selection of coastal locations.

### *7.2.1.2 Distance of slag heaps from mining sites*

The slag heaps are found within a metalliferous area of the Cyclades. Kythnos, Siphnos and Seriphos all bear the necessary ore mineralisations. The question that needs to be addressed here is to what extent one can associate the smelting sites with particular mining sites on each island and decide how much proximity to resources influenced the selection of the particular smelting locations.

Siphnos is the only island where a thorough archaeomining investigation has been undertaken. At the site of Ayios Sostis the association of the slags with the ore source appears straightforward, as the scatter of metallurgical remains is identified next to the dated mine (Wagner and Weisgerber 1985), without excluding the possibility that ore from this mine was additionally transported elsewhere for smelting.

In their recent survey on Kythnos, Bassiakos and Philaniotou (in press) identified copper mineralisations at a small distance (500-1000 m) from almost every heap. Evidence for mining is, however, scarce with the exception of Aspra Kellia and Petra (see section 2.4.4). This absence does not contradict the possibility that the smelting sites were indeed using ores brought from these nearby sources. Several factors may inhibit the identification of evidence for ancient mining in this case, particularly as open air mining is assumed, including more recent works and the hardness of the mineral-bearing quartz rock that would not retain tool marks (Bassiakos and Philaniotou in press). Stone tools, a common find on mining sites, were very scarce here, but the authors note that sources of appropriate hard volcanic rocks are not found on Kythnos. As a result, tools may have been valued and would not have been discarded (Bassiakos and Philaniotou in press). Interestingly, the only securely dated EBA open air copper mine on the island, that of Cape Tzoulis, lacks any evidence for smelting in its vicinity, suggesting that ore from this mine may have been shipped or carried elsewhere for processing (Hadjianastasiou 1998).

On Seriphos, the geological reconnaissance (Chapter 4) showed that copper mineralisations can be found in many parts of the island. Surprisingly, the three slag heaps discussed in this thesis are all situated within the northern schist unit (Figure

4.1), which is, with a few exceptions, comparatively metal-poor. A limited copper mineralisation was, however, found close to the slag heap of Kephala (section 4.4.1), indicating that the source may have actually been located close to the smelting site, but further exploration will be necessary to address this question. Copper mineralisations have not been identified so far close to Phournoi or Avessalos. The absence may, however, be a result of the small scale of these occurrences on the Cycladic islands and the early state of research on Seriphos. In short, the association of the smelting sites on Seriphos with a specific ore source in their vicinity cannot be deduced at present, and it is acknowledged that the issue requires substantial further investigation in the future. It should also be noted that slag heaps are not presently known on the much less researched south-western part of the island, which is particularly rich in secondary iron deposits and accompanying smaller copper mineralisations (see Kalavatsena and Koutalas in Chapter 4). The area presents an interesting case for further archaeometallurgical survey, although the effects of extensive modern mining on the surrounding landscape are certainly going to be a limiting factor.

Overall, although there are in many cases indications that the selection of smelting sites may have been influenced to some extent by the presence of a nearby ore source, additional or sole transportation of ores, whether from the same island or beyond, cannot be excluded. It is, for example, tempting to suggest that the Seriphos slag heaps, located on the northern, comparatively metal-poor, part of the island, resulted from processing ores brought from the neighbouring metal-bearing western and southern Kythnos. Ultimately, resolving such micro-patterns for transportation of raw materials between the islands would have to entail a thorough field and analytical investigation, while the extent to which these efforts will be fruitful is uncertain given the potential geochemical similarities.

#### *7.2.1.3 Association of slag heaps with settlements*

One of the most puzzling aspects in the interpretation of these slag heaps is that at present there is no adjacent settlement that can be directly shown to have been involved in the associated activities. This situation is not uncommon also in other metal-producing areas of the Old World, largely impeding a substantiated consideration of the social organisation of these early industries (e.g. Hauptmann and Weisgerber 1992: 63; Ottaway 2001: 91; White and Pigott 1996: 153, 158; but see Shennan 1998, 1999 for an exception).

At present the Cycladic smelting sites are therefore considered to be isolated from contemporaneous settlements (e.g. Bassiakos and Philaniotou in press; Broodbank 2000a: 294). This observation is true to the extent that no habitation remains have been identified in the immediate vicinity of the smelting sites on any of the three islands, with the exception of south-eastern Kythnos, which is discussed separately below. Archaeological investigations on all three islands, and particularly on Seriphos, have, however, been very limited. At least one EBA settlement is known on each island, usually at some distance from the smelting sites (Hadjianastasiou 1998: 260; Philaniotou 2004; Tsountas 1899: 74-8), but none have been excavated and their association with metallurgy is uncertain. In addition, in the absence of intensive surface surveys, the settlement pattern in the broader area of the smelting sites remains unclear. Another peculiarity in the case of the Cyclades stems from the fact that it is an island environment, which influences the perception of proximity, making communications between adjacent islands easier than those between different parts of the same island. As a result, associated permanent settlements for the smelters (assuming such existed) could in fact be located beyond the geographical limits of the specific island.

South-eastern Kythnos presents an interesting exception to this pattern. Bassiakos and Philaniotou (in press) report that several slag scatters have been observed here together with evidence testifying to EBA habitation (see section 2.4.4). A preliminary surface investigation was only, however, carried out on the site of Lefkes. The authors noted that, contrary to the slag heaps of northern Kythnos, the slags here are very dispersed and metallurgical ceramics are absent. These differences are intriguing and urge for a more systematic study of Lefkes and a comparison with the other smelting sites known on the island. Is there evidence for a permanent settlement on Lefkes and if so, what role, if any, did it play in the organisation of the metallurgical activities in this part of the Cyclades? How do the metallurgical activities on Lefkes compare with those on other EBA Cycladic settlements (see for example Chapter 6 and below)?

### *7.2.2 Aspects of technology*

The EBA copper slag heaps identified on the Cyclades and the broader southern Aegean show several technological similarities, but also differences between them that may prove important in assessing the level of overall organisation of metal production in this region. First, it should be repeated that only copper smelting is attested on all the sites studied so far. A previous beneficiation step or a subsequent slag crushing step may also have been practised in-situ at least in some cases, but there is no concrete evidence (e.g. melting crucibles or moulds) for melting or casting of objects.

Contrary to metallic artefacts, which follow particular types that signify a certain period or culture, and can therefore be grouped stylistically (e.g. Branigan 1974; Renfrew 1967), the composition and microstructure of production remains is determined by several parameters (e.g. available raw materials, necessary physico-chemical conditions), and observed similarities or differences will not necessarily reflect meaningful cultural patterns (although see, for example, Hauptmann (2000) for a characteristic shift in the nature of copper ores exploited between Chalcolithic and EBA Feinan). Still, even metal production activities may encompass several features, characteristic of a particular regional or chronological technology (see for example Craddock 2001), and a few examples are given below.

#### *7.2.2.1 The furnaces*

The absence of excavation on the metal production sites of Kythnos and Seriphos presents a seriously limiting factor in their study, particularly with regards to reconstructing the furnaces used. Nevertheless, several interesting observations emerge already by looking at the evidence presented so far from these and other EBA Aegean metallurgical sites.

An intriguing and apparently distinctively southern Aegean metallurgical find are the perforated furnace fragments. Examples were found on Kephala and Avessalos on Seriphos, while these are also known from Sideri and Paliopyrgos-Aspra Spitia on Kythnos (Bassiakos and Philaniotou in press), Chrysokamino on Crete (Betancourt *et al.* 1999), Kephala on Kea (Coleman 1977: 4 and Plate 66), and Raphina on Attica (Theocharis 1952: 131). Apart from the finds from Kephala on Kea, which are dated on the basis of context to the FN, and the Avessalos material, which still awaits dating, the perforated ceramics from the other sites are all dated directly (by TL of the finds themselves) or indirectly (on the basis of associated pottery) broadly to the EBA.[7.1]

The identification of these ceramic finds on several EBA Aegean smelting sites points to a particular local technology (see also Bassiakos and Philaniotou in press; Craddock 2001: 160-1). Equally interesting is, however, the apparent absence of these finds from other contemporaneous copper slag heaps (e.g. Phournoi on Seriphos, Skouries on Kythnos). Additionally, it should be noted that these finds, although similar, often show considerable differences that may indicate different use in each case. Bassiakos and Philaniotou (in press) have compared the ceramics from Kythnos and Chrysokamino and noted three differences between the finds from the two areas: the thickness of the specimens (c. 4 cm for Kythnos and c. 1.5 cm for Chrysokamino), the direction of the holes (the holes on the Kythnos fragments slope inwards, while the ones from Chrysokamino do not), the suggested reconstructed shape (truncated cone for Kythnos, cylindrical for Chrysokamino). Another associated difference is that on Paliopyrgos-Aspra Spitia a fragment of a clay nozzle was found among the heap suggesting the use of blow pipes (Bassiakos and Philaniotou in press), while fragments of bellows were recovered from Chrysokamino (Betancourt *et al.* 1999). A somewhat different use of the perforated furnaces has therefore been suggested in the preliminary reconstructions offered for the two areas on the basis of these observations. On Kythnos the finds are regarded as the remains of a free-standing perforated cone placed above the hearth. Air supply would have been provided by the use of blow pipes inserted through the surrounding perforations (Bassiakos and Philaniotou in press). On Chrysokamino on the other hand, the perforated cylinder is viewed as a 'shaft furnace', where air was provided by the use of bellows attached to the bottom of the shaft via tuyères, while the perforations would have additionally allowed air inflow from natural drafts

---

[7.1] MBA pottery is also reported from Paliopyrgos-Aspra Spitia (Bassiakos and Philaniotou in press).

(Betancourt 2004; Betancourt *et al.* 1999: 354; Catapotis *et al.* 2004).[7.2] Hence, although a common underlying concept is implied by the presence of perforations, the two examples suggest certain distinctions in their function.

It is impossible at present to discuss any further the other Aegean examples known from Kea and Raphina as these have not been presented in any detail. In terms of the Seriphos finds, and particularly Kephala, which has been examined in more detail, two differences were noted already (see section 5.2.1). First, the fragments found so far usually do not bear traces of more than one hole, a phenomenon which may be due to erosion, as indicated by the identification of at least one specimen with two holes. Second, the fragments with traces of perforations are only a small percentage of the total of metallurgical ceramics observed on the site. This latter point requires further examination both systematically in the field, as well as through laboratory analyses in order to clarify whether there are indeed two 'types' of ceramics and if that is the case whether they may be associated with different uses or structures. The thickness of the finds from Kephala is comparable to the ones from Kythnos. The holes in some cases slant inwards, while in others they do not. At present the total number of perforated fragments from Kephala (and Avessalos) is comparably small and fragments of the rim or base of these structures, as found on Kythnos and Chrysokamino, have not been recognised on Seriphos. A reconstruction of the corresponding furnaces cannot therefore be offered at this stage, but the issue presents intense interest for further study and direct comparison with finds from other areas.

Apart from the ceramic furnace fragments, two types of structures attributed to furnaces have been identified among EBA Cycladic metallurgical sites. The first are the wide round structures at Skouries (see section 2.4.4), which appear to have surrounded a smaller furnace (Hadjianastasiou and MacGillivray 1988). The second is the rock-carved furnace identified at Kephala (see section 5.2.1.3). The two

---

[7.2] Reconstruction experiments based on the proposed Chrysokamino smelting model were carried out in autumn 2004 at N.C.S.R. Demokritos between M. Catapotis, O. Pryce, and Y. Bassiakos. These have not been published so far, but were presented in a recent international symposium, which the author attended, at Rethymno (Crete) entitled "Aegean Metallurgy in Bronze Age" (see corresponding abstract). Information on the as yet unpublished results from the analyses of the Chrysokamino material was also obtained during presentations at the symposium (Bassiakos *et al.* 2004; Catapotis *et al.* 2004).

examples are evidently different. Clearly, excavations at these sites are necessary in order to obtain a better picture of the furnace structure, and hence the technology associated with each site, but the two contrasting examples already suggest some variability, which will need to be addressed.

#### *7.2.2.2 Production of arsenical copper alloys*

The comparatively few tin-bronzes known from the EBA Cyclades are generally considered to be non-Aegean imports, at least as far as tin metal is concerned, since relevant sources are not known in this region (e.g. Stos-Gale *et al.* 1984). The more common arsenical copper alloys, however, are believed to be local products using locally available raw materials (see, however, discussion in sections 2.4.1 and 4.4.2 for uncertainties regarding sources of arsenical minerals). Several pathways can be followed in the production of arsenical copper alloys (see section 6.4.1.3). A closer look at the evidence for metal production in the Aegean indicates that little is known regarding the processes associated with arsenical copper alloys, while several different possibilities have been proposed so far.

The examination of slags from Kephala and Phournoi (Chapter 5), as well as five copper smelting sites on Kythnos (Bassiakos and Philaniotou in press), showed that the western Cycladic slag heaps appear to be associated mainly with the production of unalloyed copper. The only exception to this pattern stems from the analyses of four slags from Skouries on Kythnos that gave arsenic contents in the entrapped prills above 1% (Gale *et al.* 1985). At present these form an exception to a larger number of non-arsenical slags from this site (see section 2.4.4), which remains to be explained. Gale and Stos-Gale (1989a) have used this evidence to propose that arsenical copper production in the Cyclades could, to a large extent, have been 'accidental', which has since been taken for granted in associating alloyed objects to sources via lead isotope analyses (e.g. Gale and Stos-Gale 1989b). In essence they argued that accidental smelting of oxidised arsenical copper ores, which can easily be confused with other non-arsenical secondary copper ores, would soon lead to an appreciation of the advantageous properties of the alloys and smelters would have deliberately favoured the mixed minerals for production of the alloys (Gale and Stos-Gale 1989). Although this scheme is certainly plausible it is unclear whether the Skouries slags testify to such 'accidental' production (see also criticism in Merkel *et al.* 1994: 201-2). Unfortunately, details of the macroscopic and microscopic characteristics of these samples are not given. It is therefore impossible at this stage to compare further the two 'types' of slag from Skouries (arsenical and non-arsenical) and establish whether any further differences can be discerned between them or to identify any features (e.g. ore remains) within the arsenical slags that would point to a particular production mechanism. Alternative to the accidental production scenario suggested by Gale and Stos-Gale (1989a), the possibility that a further alloying step, or mixing of materials during smelting, was carried out at Skouries cannot be excluded *a priori.* Copper prills enriched in arsenic were also identified in two of the small slags from the large Avessalos slag heap (section 5.6.1). The study of Avessalos is, however, at a very preliminary stage and, given additionally the uncertainties surrounding its dating, the significance of these analyses cannot be ascertained at present.

Several other recent archaeometallurgical studies in the Aegean have brought forward more substantial evidence for arsenical copper production. The only Cycladic example comes from the examination of the Group 2 slags and metallurgical ceramics from Daskaleio-Kavos presented in this thesis (Chapter 6). Unfortunately, the evidence available so far does not provide any conclusive indications on the nature of the raw materials used, and hence a clear distinction between the different potential paths for arsenical copper production is not possible at present (see section 6.4.1.3).

Outside the Cyclades, two sites on the island of Crete are particularly informative in this respect. The first is the copper slag heap of Chrysokamino. Analyses of a large number of slags consistently detected arsenic and lower amounts of nickel in the prills (Bassiakos *et al.* 2004; Catapotis *et al.* 2004).[7.2] The two elements were not detected in any appreciable quantities in the copper ore samples found on the site, leading to the suggestion that an arsenic and nickel-rich mineral was deliberately added together with the copper ore to the smelting charge. Fragments of this alloying component have not, however, been recovered from the slag heap so far. Intentional alloying is also proposed for the site of Poros-Katsambas (Dimopoulou-Rethemiotaki 1993: 458; Doonan *et al.* 2004; Wilson *et al.* in press). Excavations of the EBA levels of this settlement (Early Minoan I-Early Minoan IIA period) brought to light remains associated mainly with secondary metalworking activities (alloying, casting).[7.3] Among them was found a fragment of a partially heated iron arsenide mineral (identified as loellingite $FeAs_2$). The identification of this specimen together with analyses of the slag layer found within the crucibles was used as evidence to suggest a deliberate alloying step at Poros-Katsambas that, contrary to the case of Chrysokamino, did not involve mixing of ores during smelting, but rather mixing of copper metal with the arsenic-rich mineral.

A similar alloying process (i.e. addition of arsenic-rich minerals to copper metal) is proposed by Papadimitriou (2001), who used a statistical analysis of published analytical data (data taken from Craddock 1976; Renfrew 1967) of Aegean EBA copper artefacts to investigate whether any particular compositional patterns could be discerned. A normal distribution is obtained by plotting the number of artefacts against the arsenic content with a maximum value around 3%. Papadimitriou (2001) attributes this pattern to deliberate alloying and notes that a certain control of the arsenic content is implied, which would only be possible if arsenic-rich minerals were added to copper metal, rather than smelting a mixture of copper and arsenic minerals. The small number of analytical data used, however, as well as the potential problems associated with some of the earlier analyses and the uncertainties often surrounding the contexts of the objects (see section 2.3) urge for a degree of caution in this case.

The examples presented above suggest at least three different potential methods for arsenical copper production in the EBA Aegean. Although such diversity is plausible, the associated case studies are still few in number and the evidence is not usually conclusive, so the issue still requires substantial further research. Returning to the western Cycladic slag heaps, however, the rarity of evidence for arsenical copper is intriguing, given on the one hand the apparent importance of this metal in EBA metallurgy and on the other hand the dominant role of these sites in copper production as suggested by their comparatively large scale. Several hypotheses can

---

[7.3] The analyses of the material from Poros-Katsambas have not been published so far. Information was obtained during a presentation given by Doonan *et al.* (2004) at the international symposium "Aegean Metallurgy in Bronze Age".

be envisaged to explain these compositional inconsistencies, but none can be proved at present. These include a separate step where the 'clean' copper was alloyed, possibly taking place elsewhere (as suggested for Poros-Katsambas), as well as the presence of further as yet unidentified slag heaps associated with arsenical copper production (south-western Seriphos forms a possible candidate given the identification of arsenical copper minerals, see section 4.4.1). The possibility that arsenical copper production was additionally taking place on the known smelting sites and that relevant remains were not recognised (with the exception of Skouries) cannot be excluded given the relatively small number of samples analysed, compared to the often extensive volume of the heaps. It appears unlikely, however, at least on Seriphos, where every effort was made to pursue a comprehensive surface sampling both in terms of the macroscopic characteristics of the slags and the area covered and still no indications for arsenical copper production were found. In closing this section it should be noted that on the basis of the present results and the uncertainties that still surround arsenical copper production in the EBA Cyclades the attribution of alloyed objects to the western Cycladic slag heaps using solely lead isotope analysis must be questioned.

#### *7.2.2.3 Other technological features*

The absence of charcoal in the slags from Kythnos and Chrysokamino and the scarcity of stone tools in mining and metal production sites in this region are two of the common characteristics that have been noted by other researchers (e.g. Bassiakos and Philaniotou in press; Philaniotou-Hadjianastasiou 2000). The absence of charcoal was also encountered in the slags on Seriphos. Apart from the obvious difficulties this generates in terms of dating the slag heaps, the nature of the fuel used remains uncertain. At present it is impossible to conclude whether the common absence of charcoal on these sites represents a regional technological idiosyncrasy (in terms of nature, quantity and/or size of fuel used) or whether it is the result of unfavourable preservation conditions.

Regarding the absence of stone tools, the explanation offered by Bassiakos and Philaniotou (in press) was given above. Contrary to Kythnos, Seriphos bears an extensive granite unit on its central/south-eastern part, which would form an excellent source for tool preparation. In this respect it is interesting to note that a comparatively large number of stone tools have been recovered from the site of Avessalos, while several more possible fragments were noted in the field. Stone tools were rare on Kephala and seem to be absent from Phournoi. Unfortunately, the problems still surrounding the dating of the Avessalos slag heap leave open the possibility that this may be due to chronological differences. It is, however, noteworthy that from the three smelting sites on Seriphos presented in this thesis, Avessalos is situated much closer to the granite unit. Could the abundance of tools on this site reflect easier availability of the necessary raw materials? A smaller dyke of igneous rock was also identified close to Kephala (see section 4.4.1) and interestingly the single stone tool recovered so far from the slag heap appears at least macroscopically to be associated with this occurrence.

## 7.3 Metallurgy at Daskaleio-Kavos and other EBA Cycladic settlements

The scarcity of excavated EBA Cycladic settlements unavoidably limits our understanding of metallurgical activities in such contexts (see also Doumas 1990b: 161). Still, small quantities of metallurgical remains have been recovered from a number of investigated EBA Cycladic settlements that, apart from Daskaleio-Kavos, include Kastri on Syros, Ayia Irini on Kea, Provatsa on Makronisos, and Avyssos on Paros (see section 2.4). Unfortunately, although the provenance of some of these finds has been sought via lead isotope analyses, technological studies have not been undertaken. As a result, the nature and technological details of the activities that produced these remains are unknown. Particularly with reference to copper, in the absence of appropriate examination it is unclear whether, for example, slag and crucible fragments are associated with smelting or working of the metal, or whether pure or alloyed copper was processed. A substantiated comparison of metallurgical activities on Daskaleio-Kavos with those from other contemporaneous settlements is therefore impossible at present. Despite these problems, a few thoughts are presented here, mainly stressing the important contributions that can be gained from the study of these finds.

The metallurgical remains from EBA Cycladic settlements are often attributed a secondary metalworking origin (e.g. Barber 1987: 112; Broodbank 2000a: 293-7), an assumption common in considerations of settlement metallurgy (Bachmann 1982b: 149). The examination of the material from Daskaleio-Kavos challenged this generalisation by bringing forward evidence for the practise of two copper-producing activities and some additional indications for lead-silver metallurgy, while it is possible that further sampling and analyses will add to this diversity. Are similar activities to be expected in the other settlements? It is argued here that several features of EBA Cycladic settlements may influence the nature and scale of metallurgical activities taking place in each case.

A first example is the size of the settlements and the extent to which they appear to be involved in inter-island interactions. Broodbank (1993, 2000a: 211-246) has identified at least four exceptionally large and rich sites to which he attributes a prominent role in the EBA Cyclades due to their nodal position within a wider inter-island communication system (see also section 2.2). These are Daskaleio-Kavos, Chalandriani-Kastri, Ayia Irini, and Grotta-Aplomata, while Marthari (in press) has also recently argued for Skarkos. Interestingly, remains of both copper and lead-silver processing have been reported from the first three sites. Only a small part of EBA Grotta-Aplomata has been excavated and the material has not been fully published, while the work on Skarkos is still on-going, so the apparent absence of evidence on these sites certainly does not constitute evidence for absence at present (for Grotta see also discussion in Broodbank 2000a: 219-220). The question that therefore arises is whether similar activities are taking place in all these settlements and how they compare with those on other smaller and possibly less widely connected sites. In this context it is intriguing that at least on the basis of the excavators' reports, only lead-silver debris (slag and litharge) were found at Provatsa on Makronisos (Lambert 1973; Spitaels 1982), while only copper slags were reported from Avyssos on Paros (Tsountas 1898). It is also noteworthy that a small copper mineralization is known on Paros (at a considerable distance from Avyssos however) and lead ores are known on Makronisos. Obviously this picture may change following informed examination of the recovered assemblages, but the example highlights potential distinctions that may reflect different attitudes to metallurgy.

This leads to another important parameter, namely the distance of settlements from exploited ore sources. Several apparently different cases can be envisaged already. The site of Lefkes combines evidence for habitation, ore sources in the immediate vicinity and remains of metallurgical activities. The settlement of Akrotiraki on Siphnos is located on a metal-rich island, but is not directly associated with a particular ore source. Metallurgical remains have not been reported from this site, but to date only the cemetery has been excavated (Tsountas 1899). Similarly unclear is the association between the settlements reported on Kythnos and Seriphos with the local resources (see section 7.2.1). The position of Ayia Irini between Lavrion and the western Cycladic metal-producing islands appears advantageous (Wilson 1987) compared to the other larger settlements highlighted by Broodbank (1993, 2000: 211-246), which seem to be situated in metal-poor areas. The extent to which the distance from ore sources influences the metallurgical activities remains to be investigated, but clearly the identification of metal production on Lefkes and Daskaleio-Kavos (assuming that the apparent absence of ore sources on Keros holds), for example, has different implications in each case.

The EBA is a period that sees several changes in the Cycladic communities, some of which undoubtedly influenced local metallurgy. Metallurgical remains from excavated settlements allow a clearer chronological resolution between the different sub-periods of the EBA than is likely to be possible with the slag heaps, while the other material finds recovered from the same contexts synthesize a cultural framework within which specific questions can be addressed. It is, for example, interesting to examine directly from the metallurgical remains whether the introduction of tin-bronze affected metallurgical activities on the site of Kastri, while the material from different strata of the Ayia Irini site allow one to view changes in metallurgy throughout the Bronze Age within a single site.

In short, it is proposed that the issue of metallurgical activities within settlements merits further in-depth study as several different parameters suggest that these cannot be assumed to be similar in all cases. Such results provide further insight into the settlements themselves, but also contribute to an assessment of the regional structure of metallurgy.

## 7.4 Metallurgy at Daskaleio-Kavos compared with the western Cycladic slag heaps

Comparing the evidence from the study of the Daskaleio-Kavos metallurgical remains, where primary production was also testified (Chapter 6), with that from the metal-producing sites of the western Cycladic islands, as these are understood from studies carried out to date, several differences are immediately apparent. The first and most evident is the context within which metallurgy was practised in each case. While, as was discussed above, in the western Cyclades, the identified sites appear to be used solely for metallurgical purposes, with no clear evidence at present for habitation or other functions in the near vicinity, metallurgy is only one of many other activities attested at Daskaleio-Kavos.

Secondly, the scale of metal production between the two cases appears to differ markedly, in one case represented by slag scatters or heaps, often covering substantial areas, and in the other case by a few handfuls of finds recovered so far. Admittedly, an accurate estimation of the scale of activities on Daskaleio-Kavos is not possible at this stage, since without excavation at south-central Kavos and Kavos North, we cannot assess how prevalent the activities were, or whether they were pursued at a comparable intensity throughout the use of the site. Still, in comparison to the western Cycladic smelting sites, the activities on Daskaleio-Kavos appear to correspond to a much smaller-scale production.

Thirdly, a striking feature of the metallurgy on Daskaleio-Kavos is the observed variability. Two apparently distinct copper smelting activities were identified, involving the use of different types of ore, while the presence of a single litharge specimen raises the possibility that lead/silver metallurgy was also taking place. In contrast, data available from the western Cycladic smelting sites generally testify to activities related to the production of just one type of metal (whether copper or lead/silver), with the possible exception of Ayios Sostis and Platy Gialos, where a limited number of copper slags were found among material associated mainly with lead/silver metallurgy (see section 2.4.3). Additionally, significant compositional differences in the slags from a single site have only been reported from the site of

Skouries (Bassiakos and Philaniotou in press; Gale *et al.* 1985; Stos-Gale 1989), and the source of these discrepancies remains at present unclear (see section 2.4.4).

A final difference relates to the proximity of the sites to the ore sources used. Even though the association of the slag heaps with a particular nearby source is not always clear, the sites are situated within a broader area that bears the associated minerals (see section 7.2.1.2). On Daskaleio-Kavos the variability observed in the metallurgical activities indicates that the inhabitants of the site had access to several ore sources. Are the identified remains associated with exploitation of two putative small copper (and possibly an additional argentiferous lead?) occurrences local to the island of Keros, or were these ores imported from elsewhere? Addressing the question of provenance of these raw materials will play a crucial role in clarifying the reasons that led to small-scale metal production on this site (i.e. proximity to the exploited resources or extensive involvement in exchange of goods?) as well as exploring the spatial organisation of Early Cycladic metallurgy, particularly with reference to the transport of materials.

### 7.5 Cycladic metallurgy in the context of the Aegean

This thesis has so far focused almost exclusively on the metallurgical evidence identified on the Cycladic islands, without expanding to the broader Aegean. This geographical restriction has been deliberate in order to allow for a more detailed consideration of the results and problems associated with archaeometallurgical research in this region. The Cyclades, however, do not exist in isolation during the EBA, instead the archaeological record points to extensive interaction, both within and beyond the island group, whose dynamics appear to change within the sub-periods of the EBA (Broodbank 2000a: 299-319). Metal is commonly considered one of the prime materials that both stimulated and was influenced from this interaction (e.g. Renfrew 1967, 1972). The results of lead isotope analysis have given ground to suggestions of the circulation of Cycladic metal beyond the island group (see references in section 2.5.2). Leaving aside discussions concerning the final products of metallurgy, of particular interest to this thesis is to what extent this interaction affected the metal production processes in terms of, for example, raw material export and import and sharing of technological know-how. Remains associated with metallurgical activities are found on several other neighbouring Aegean areas (see McGeehan-Liritzis 1996: 218-9, 372-3 and references within), but, with a few exceptions, appropriate technological studies have not been undertaken. At this stage it is worth reviewing some of the evidence presented so far from three neighbouring regions, namely south-eastern Attica, Crete and the northern Aegean islands, and examine the somewhat different ways they appear to be interacting with the Cyclades with reference to metal production.

### *7.5.1 South-eastern Attica*

The Cyclades border with south-eastern Attica to their northwest, where the extensive multimetallic deposit of Lavrion is found, whose exploitation certainly dates back at least to the EBA (see section 2.4.1). The similarities in the pottery repertoire and other aspects point to a strong association between this area and the site of Ayia Irini during the EBA (mainly Ayia Irini Periods II and III corresponding to the EBII period) forming a unit in terms of material culture that brings together elements from both the islands and the mainland and acts as a bridge between the two (Caskey 1972; Wilson 1987, 1999: 227-9). Analogous characteristics were noted on the site of Provatsa on the island of Makronisos, situated between Kea and south-eastern Attica (Spitaels 1982). The transition from the islands to the mainland at the northwest appears therefore smooth, indicating intense communications, facilitated by the short distances involved (Broodbank 2000a: 307-8). Unfortunately, the absence of archaeological investigations on the immediate neighbours of Kea to the south, copper-producing Kythnos and Seriphos, do not allow an assessment of the extent of this affiliation.

Apart from mining, prehistoric metallurgical activities involving copper and lead/silver have been reported from a number of sites in Attica (Kakavogianni *et al.* 2004; McGeehan-Liritzis 1996: 218-9, 372-3 and references within), while further excavations are bringing forward additional material as yet unpublished (Douni pers. comm.). Only a preliminary study of a small number of slags from the excavations at the site of Raphina has, however, been presented and these confirmed a copper smelting origin and suggested Lavrion as the source for the ores (Gale 2004). A technological association with Cycladic copper production was already noted above, namely the identification of perforated furnace fragments also at Raphina (Theocharis 1952: 131), although the lack of appropriate examination excludes any further comparisons at this stage.

On the basis of the evidence available so far from south-eastern Attica and the wealth of the Lavrion deposit it is reasonable to suspect intense metallurgical activity in this area during the EBA. The close interaction with the north-western islands implied by the archaeological evidence would certainly reflect on metallurgy, forming a broader metal-rich zone, involving both communication of technological knowledge and possibly some circulation of raw materials. Continuing archaeological and archaeometallurgical studies on both areas are, however, necessary in order to assess in more detail the nature of this relationship.

### *7.5.2 Crete*

The ties between northern Crete and the Cyclades are strong throughout most of the EBA, although the dynamics of this relationship appear to change between the different sub-periods (Broodbank 2000a: 299-319; Papadatos 2003; Wilson *et al.* in press), as is briefly summarised below. In the transitional Kampos phase (EBI-II), apart from the Cycladic imports identified in various parts of the northern coast of Crete, particularly significant is the identification of potential Cycladic colonies. The most well-known example is that of the impressive Ayia Photia cemetery, whose use appears to be restricted to this period (Broodbank 2000a: 301-9; Betancourt 2003; Davaras and Betancourt 2004; Day *et al.* 1998 and references within). Crete remains a destination for Cycladic traders during the early part of the EBII period (Keros-Syros culture) with Cycladic elements now penetrating beyond the coast as foreign objects within predominantly Minoan environments (Betancourt 2003; Broodbank 2000a: 306-7). The picture appears to change, however, in the later parts of the EBA, when, although the use of Cycladic raw materials such as obsidian and presumably metal continues, Cycladic objects and influences on Crete become extinct (Broodbank 2000a: 317-8; Wilson *et al.* in press). Broodbank (2000a: 317-8) suggests that this possibly indicates elimination of the intermediate Cycladic traders in favour of direct procurement of raw materials by Cretan expeditions.

Turning to metallurgy it should first be noted that although Crete possesses limited copper ores, lead isotope analysis results have suggested little, if any, exploitation of these local resources (Branigan 1982; Gale 1990; Gale and Stos-Gale 1986b; Gize and Droop 2004; McGeehan Liritzis 1996: 387; Stos-Gale 1993, 1998). The majority of copper on EBA Crete is attributed a Kythnian or Lavrion origin (Gale 1990; Stos-Gale 1993, 1998). Investigations of Cretan ore occurrences have, however, been very limited and the island is significantly under-represented in the lead isotope database (Gale and Stos-Gale 1986b). Even though the strong affiliations with the Cyclades during the EBA make the current lead isotope model highly probable, a degree of caution is urged in assuming *a priori* metal as an indicator for Cycladic contact (c.f. Broodbank 2000a: 299-319; Day *et al.* 1998).

Recent excavations at the site of Kephala-Petras at Siteia brought to light a small number of slags from a FN-EBI context, which preliminary analyses concluded resulted from small-scale copper smelting (Papadatos *et al.* 2004). The source of the ores used has not been sought so far. With the exception of these finds the majority of metallurgical material recovered from EBA settlements or cemeteries at the northern coast of Crete are crucibles and moulds that appear to correspond to secondary metalworking activities (see Evely 2000 and references within). Particularly noteworthy are the metallurgical remains from the site of Poros-Katsambas (Dimopoulou-Rethemiotaki 1993: 458; Doonan *et al.* 2004; Wilson *et al.* in press) mentioned earlier, which testify to deliberate production of arsenical copper using copper metal and iron arsenide minerals. On the basis of this evidence and with the exception of the site of Chrysokamino discussed below there does not appear to be significant primary production of copper on the island of Crete during most of the EBA. The majority of evidence indicates working of already smelted metal, which would agree with the notion that raw metal was imported from elsewhere for local processing (see also Broodbank 2000a: 299). Given the strong Cycladic element in some of the communities that brought forward evidence for metalworking (see for example Day *et al.* 1998 for Cycladic influence at Poros-

Katsambas and a crucible find at Ayia Photia; Wilson *et al.* in press), a Cycladic origin is not unlikely.

The only exception to this pattern is the copper smelting site of Chrysokamino on Crete (Bassiakos *et al.* 2004; Betancourt 2004; Betancourt *et al.* 1999; Catapotis *et al.* 2004). The site is attributed a FN to Early Minoan III (EMIII) date by the excavators, based on the pottery, but by far the majority of finds are of EMIII date (Betancourt *et al.* 1999: 354-8; Muhly 2004). In fact, only a few FN sherds, and only one sherd from each of the following periods EMI-IIA and EMIIB were recovered during excavations in the heap. Additionally, a cave with evidence for use between FN and EMIII is found in the proximity of the metallurgical site, while habitation during this time span is testified in the broader north-eastern Crete. It is therefore possible that the pre-EMIII pottery resulted from other activities in this area and is not directly related to the metallurgical site. At present analyses of slags from different depths of the heap have failed to recognise any consistent differences that would indicate any changes in the technology of metal production suggestive of a long period of use (Catapotis *et al.* 2004).[7.2] In any case, on the basis of the currently available evidence it is safe to suggest that the site was used primarily, if not exclusively, during the EMIII period (see also Muhly 2004: 287).

This coincides with a period, when, as was mentioned previously, significant changes appear to take place regarding trade with the Cyclades, which seems to cease in favour of possibly direct access of the Cretans to the Cycladic resources (Broodbank 2000a: 317-8). This observation may hold the key to interpreting the role of Chrysokamino, the only site known so far on Crete with evidence for comparatively larger scale metal production, situated within an area devoid of copper sources (Betancourt *et al.* 1999; Stos-Gale 1998: 721). Lead isotope analyses have suggested a Lavrion and Cycladic source for the copper ores used (Stos-Gale 1998), but recent suggestions for the deliberate production of arsenical copper using a mixture of copper and arsenic-rich minerals challenges the provenance studies carried out so far on the slag samples (Catapotis *et al.* 2004).[7.2] Further analyses on the discarded ore fragments found on the site will be necessary in order to address the question of provenance more safely. Apart from the source of the ores, however, Chrysokamino shows several more features that are clearly reminiscent of Cycladic smelting sites, both in its location and in the use of perforated furnaces. The differences noted in the perforated furnaces (see above) and the presence of bellows, not known so far on any of the Cycladic smelting sites, indicate a separate technology, adapting, however, 'Cycladic' elements. In light of the suggested shifts in the relationship between Crete and the Cyclades at the end of the EBA, could this effort to produce metal locally on a larger scale (using Cycladic technological influences and possibly raw materials) be a reflection of the growing independence of Cretan communities?

At this point it is important to note an idiosyncrasy of the Cretan metal industry during the later parts of the EBA and the ensuing MBA that also suggests Crete follows a separate path to the rest of the southern Aegean concerning the acquisition of metallurgical raw materials during these periods. Contrary to other areas including the Cyclades, where tin bronze appears in the later parts of the EBA and grows progressively more important in the ensuing MBA, analyses of Minoan copper artefacts have concluded that the use of this alloy on Crete is delayed, and appears to become important only during the LBA (Branigan 1974: 147-54; Mangou and Ioannou 1998).

### *7.5.3 North-eastern Aegean islands*

During the EBA impressive centres flourish on the north-eastern Aegean islands, the most famous being Poliochni on Lemnos (Bernabò-Brea 1964, 1976; Doumas and La Rosa 1997), Thermi on Lesbos (Lamb 1936), and Emporio on Chios (Hood 1982). The rich and varied metallic artefacts recovered from these sites, and particularly the first two, testify to an independent and comparatively advanced metal industry, which finds its closest parallels stylistically in Troy and north-western Anatolia (Branigan 1974; Doumas 1990c, 1994; Nakou 1997). Crucibles, moulds, and other finds indicate in situ metallurgy, probably involving mainly secondary metalworking. The provenance of copper-based artefacts from Poliochni (Pernicka *et al.* 1990) and Thermi (Begemann 1992; Stos-Gale 1992) presents a complicated picture, suggesting Anatolian and Aegean origins, but the exact sources are usually difficult to pinpoint. Evidence for the use of Cycladic copper is meagre, but a Siphnian origin is compatible with some of the lead and silver objects from Poliochni (Pernicka *et al.* 1990: 279). Overall, although there are indications for some interaction between the Cyclades and the north-eastern Aegean islands during the earlier parts of the EBA (see also Broodbank 2000a: 308), metallurgy in the two areas appears to develop largely separately.

This picture changes in the later parts of the EBII during the Kastri phase, which sees the introduction of tin-bronzes in the Cyclades. Lead isotope analyses of the tin-bronzes from Kastri on Syros gave similar signatures as some of the objects from the north-eastern Aegean islands (Stos-Gale *et al.* 1984; Stos-Gale 1992). The question of the origin of tin in the Aegean remains unanswered, but longer non-Aegean trade routes are generally favoured for its acquisition (see references in section 2.4.1). Nakou (1997) highlights the favourable position of the large sites in the north-eastern Aegean and their potential role as intermediaries in the supply of this new material.

Regarding the technology of metal production, at present there is no concrete evidence that suggests in-situ smelting at any of the above mentioned sites. A few slags have been reported at Poliochni (Blue Period), but their nature remains uncertain (Bernabò-Brea 1964: 591). Slags, albeit still unstudied, were also found at the site of Koukonisi on Lemnos (Boulotis 1997). Interestingly, slags and other finds that appear to be the products of smelting together with a mould were recovered from the site of Palamari on the island of Skyros, situated further to the west (Hadjipouliou 1997; Theochari and Parlama 1997: 351; Theochari *et al.* 1993). The material was found in the most windswept area at the edge of the settlement. Palamari shows several similarities with the contemporaneous site of Kastri on Syros and appears to have played an important role in the maritime connections operating at this time in the Aegean. Results of the examination of the metallurgical finds must, however, be awaited before any further comparisons can be drawn.

## 7.6 The organisation of metal production in the EBA Cyclades

The study of the organisation of a particular production industry ultimately seeks the level of specialisation involved and can potentially be studied archaeologically by assessing a number of variables within an appropriate theoretical framework (e.g. Costin 1991; Doonan 1999; White and Pigott 1996; Shennan 1999). Such attempts regarding early copper-production industries have, however, been extremely limited (Doonan 1999: 72-3; Ottaway 2001: 91; Shennan 1999: 356), whether owing to the limitations of the relevant evidence or the technological orientation of the corresponding research. In the Cyclades studies of metal production are still at a comparatively early stage and significant archaeological and archaeometallurgical work remains to be done. Still, some informative patterns can be drawn already.

On the basis of the evidence available so far, the majority of primary metal production in the EBA Cyclades was concentrated on the western comparatively metal-rich islands, namely Kythnos, Seriphos, and Siphnos. The identified sites testify to a pattern also attested by the EBA in other parts of the Old World (e.g. Hauptmann 2003; Hauptmann *et al.* 1988: 35), where smelting is not carried out within a domestic or settlement context, but rather in specialised sites in the vicinity of the metal resources. The study of the material from Daskaleio-Kavos confirmed that small-scale smelting was additionally, however, taking place within some of the contemporaneous settlements, indicating that larger-scale production systems should not necessarily be expected to eliminate smaller-scale household or settlement-based production (c.f. Dobres and Hoffman 1994: 241).

The smelting sites of the western Cyclades have not given any evidence associated with secondary metalworking activities, so it is safe to assume that the raw metal was transported to settlements for artefact manufacture (c.f. Barber 1987: 112; Broodbank 2000a: 293-7). Very few finds from EBA Cycladic settlements can, however, conclusively be attributed a secondary metalworking origin, which is largely due to the small number of settlements excavated as well as the limitations of research undertaken to date. Additionally, it is clear from the discussion above that Cycladic metal is likely to have travelled as a raw material beyond the limits of the island group.

What can be said, however, at present about the level of specialisation involved in this broader production system? In his recent model of the EBA Cyclades, Broodbank (2000a: 292-9) argues that it is unlikely that the ore sources and metal production sites of the western Cyclades were directly controlled by a particular community or group of people. Some level of indirect constraint of access to metal is certainly plausible given the uneven distribution of resources and the different involvement of Cycladic communities with maritime travel. The spatial distribution and some of the technological features of the slag heaps appear to agree with this proposal.

Contrary to suggestions that explicitly gave a central and comparatively more important role to the site of Skouries regarding copper metallurgy (Stos-Gale 1998), favouring a somewhat centralised production, the identification of several more EBA copper smelting sites both on Kythnos and on Seriphos testifies to widely dispersed production, possibly carried out by different groups of people (for a similar model regarding EBA copper production in Feinan see Weisgerber 2003: 84). Admittedly, some of these sites are larger in size than others, which may indicate larger-scale production or prolonged use.

The technological differences noted already between some of the slag heaps, particularly regarding the furnace structures (presence or absence of perforated furnaces and differences between them, circular structures of Skouries etc) can also be used to argue in favour of production by several independent groups. Obviously this issue requires substantial further research in order to assess more clearly the similarities and differences, potential chronological distinctions, or particular parameters that would necessitate the adoption of a specific furnace structure.

Ultimately, these observations lead to two main questions of crucial importance in understanding the organisation of metal production associated with the western Cycladic slag heaps. Who were the people doing these activities, and was the same group of people involved in all the stages from mining to transporting the smelted metal or is some degree of specialisation to be expected? At least two different models can be envisaged (Broodbank 2000a: 293-7). The first involves direct procurement by several individual non-local (to the island) and possibly also non-Cycladic communities. The second assumes the existence of local communities specialised to a certain degree in metal production, with the possible involvement of the larger maritime settlements in subsequent transportation and trade. A combination of both of the above strategies, as suggested for the obsidian exploitation on Melos is also plausible (Broodbank 2000a: 297-9). Extensive archaeological investigations on the metal-producing islands will be necessary in order to address this issue further. Additionally, useful information may be gained by detailed study of the pottery recovered from the slag heaps, in order to assess whether there is evidence for different Cycladic and external groups (c.f. White and Pigott 1996: 153-4).

Lead isotope analyses of Aegean metallic artefacts suggest that exploitation of Cycladic metal resources was confined mainly to the EBA, with Lavrion, Cypriot and other sources taking predominance in succeeding periods (see section 2.5.2). The limited pottery collected so far from the identified slag heaps and other dating methods applied largely support this observation (MBA pottery has only been reported from the slag heap of Paliopyrgos-Aspra Spitia, see Bassiakos and Philaniotou in press), although excavation and more systematic archaeological investigations of the slag heaps will be necessary in order to examine the extent to which Cycladic metal production ceases after the EBA. The prominence of Cycladic communities during the EBA and the important changes attested during this period provide a stimulating context for the study of this early production system, while the peculiarities associated with an island environment present an additional challenge.

# CHAPTER 8.

## Conclusions

The existence of an indigenous metallurgy in the EBA Cyclades had long been postulated based on earlier typological studies of metallic artefacts (e.g. Branigan 1974; Renfrew 1967). Subsequent archaeometallurgical work had proved that production of copper, lead, and silver was taking place on these islands during the EBA using local ore sources (e.g. Bassiakos and Philaniotou in press; Wagner and Weisgerber 1985). These discoveries sparked considerable research interest into the field of EBA Cycladic metallurgy in the last two decades, with a focus primarily on provenance issues, where the islands constituted a small part of a geographically wider research area (e.g. Gale and Stos-Gale 2002; Stos-Gale and Gale 2003). Aspects relevant to the technology and organisation of this early industry remained, however, under-explored. This thesis aimed to contribute to such issues concerning copper production in the EBA Cyclades using an analytical investigation of metallurgical remains from slag heaps on Seriphos and the site of Daskaleio-Kavos on Keros. The effort has been very fruitful leading to several conclusions, which are summarised in the following paragraphs.

The joint archaeometallurgical project undertaken between the Ephorate of Prehistoric and Classical Antiquities of the Cyclades and the Laboratory of Archaeometry N.C.S.R Demokritos established the importance of Seriphos in EBA Cycladic copper production. The slag heaps of Kephala and Phournoi were dated to the third millennium BC based on TL dating of furnace lining fragments from the two heaps and diagnostic pottery recovered from the latter, while there are indications that at least part of the Avessalos material is contemporaneous (Philaniotou 2004).

In the absence of excavation little can be said at present regarding the structure of the associated furnaces or the mechanisms used for the supply of air. Nevertheless, the position of these sites suggests some degree of manipulation of the naturally occurring strong winds, as noted for other EBA Cycladic smelting sites (e.g. Bassiakos and Philaniotou in press). In addition, two rock-carved furnaces were identified at Kephala, while particularly noteworthy on the same site and on Avessalos is the recognition of perforated furnace fragments, characteristic finds associated with southern Aegean EBA metallurgy.

Significant insight into the technology of copper production was allowed by the study of a substantial suite of samples from the sites of Kephala and Phournoi. Although a relatively comprehensive surface sampling methodology was followed, which included different types of material and areas, no significant analytical differences were discerned within each heap. The sites appear to have been used solely for copper smelting, possibly with some in-situ ore beneficiation and/or slag crushing; indications of secondary metalworking activities have not been recognised so far. The slags are of an essentially fayalitic composition with variable amounts of iron oxides, mainly magnetite. The product was unalloyed copper metal, in a few cases including minor amounts of arsenic and other base metals. The ores used appear to have included an iron-rich and a silica-rich component, making them largely self-fluxing. Particularly interesting concerning the nature of the ores was the identification of evidence for the incorporation of sulphidic copper-iron minerals, such as chalcopyrite, as raw materials in the smelting charge, possibly mixed with a mainly oxidic ore. In addition, for the first time small isolated matte fragments were identified on EBA smelting sites. The examination of partially reacted samples showed that these sulphides were probably not roasted prior to smelting. The estimated temperatures for smelting are in the range of 1100-1200°C, typical of early copper metallurgy, while the process appears to have been carried out under only moderately reducing conditions.

The slag heap of Avessalos presents a much more complicated picture, both because of its larger size and because several features indicate the site may have been used in different periods in antiquity. Only a preliminary study of four slags from this site was carried out for this thesis. The slags were found to be primarily iron and silica-rich, very much the same as above, while their copper smelting origin was confirmed. An interesting deviation was noted in the arsenic contents of the entrapped prills within slags collected from different contexts within the heap. The extent and significance of this observation, however, need to be evaluated by substantial further sampling and analyses.

The geological reconnaissance on Seriphos carried out as part of this thesis demonstrated the presence of copper minerals on the island. Five such occurrences were identified and sampled in various parts of the island (Kephala, Koutalas, Playia, Vounies, and Kalavatsena); while it is clear from a review of the relevant geological literature that several more exist accompanying the much more extensive iron deposits. Evidence for ancient exploitation of these occurrences was not found so far, but for this more systematic fieldwork will be necessary in the future given the inherent difficulties associated with such investigations. Among the five mineralisations presented in this thesis, two should be highlighted. The first is the one at Kephala, particularly significant due to its proximity to the homonymous slag heap. The second is the occurrence at Koutalas, where secondary arsenical copper minerals were found. This is the first substantiated report of arsenical copper minerals within a Cycladic archaeometallurgical study, and is interesting given the prominence of arsenical copper alloys in EBA Cycladic metallurgy and the claims for their 'accidental' production. Both occurrences merit substantial further exploration in order to clarify whether they were used as ore sources in ancient metal production.

The material from Daskaleio-Kavos represents metallurgical activities within a settlement context, an area that has received virtually no research from a technological point of view. The analyses proved that relatively small-scale primary copper production was taking place on the site, challenging previous models that proposed that only secondary metalworking activities were taking place within EBA Cycladic settlements (Barber 1987: 112; Broodbank 2000a: 293-7). Two groups of slags with different macroscopic, compositional and microstructural characteristics were identified. The first (Group 1) are mainly fayalitic with some magnetite and entrapped matte prills. The second are very rich in magnetite, iron silicates were identified only in some cases, while the entrapped prills are arsenical copper metal with lower amounts of other base metals, primarily lead. The two groups appear to have been the products of two different copper-producing processes, involving different types of ore and producing in one case unalloyed copper and in the other arsenical copper with minor amounts of other base metals, such as nickel, lead, and antimony. A single litharge fragment was also identified, showing that cupellation may also have been practised at Daskaleio-Kavos.

A consideration of the spatial distribution of the metallurgical remains across the site, largely facilitated by the systematic collection strategies followed during fieldwork, reached three main conclusions. First, indisputable evidence for the practise of metallurgical activities was not found in the special deposit area, supporting the different nature of this part of the site in agreement with other archaeological finds (Broodbank 2000b). Second, material associated with the two separate copper smelting processes was found mixed together and no spatial separation for the two activities could be discerned within or between Kavos and Kavos North. Third, although the number of metallurgical finds from Kavos and Kavos North are similar in terms of raw counts of material, consideration of the sampling intensities between the two areas suggested that the real density of material on the ground might be substantially higher in Kavos North in comparison to Kavos.

Although the study of EBA Cycladic metal production is still at a relatively early stage, several interesting patterns relevant to the organisation of this early industry emerge by considering the results from Seriphos and Daskaleio-Kavos in the context of previous relevant studies in this region. The majority of copper production in the EBA Cyclades appears to have taken place on ‘specialised’, non-domestic production sites, at present conclusively identified on both Kythnos and Seriphos, while there are additionally preliminary indications for possible similar sites on Siphnos and Kea (see section 2.4). Kythnos and Seriphos are situated in a comparatively metal-rich part of the Cyclades, suggesting proximity of the smelting sites to ore sources, without excluding some inter-island transportation of raw materials. The dispersed spatial distribution of these EBA slag heaps, together with some potential technological differences noted between them, are more consistent with a largely uncentralised production, although a comprehensive evaluation of the level of specialisation involved in these activities will require substantially more archaeological and archaeometallurgical work. In addition to this model for relatively large-scale metal production, the evidence from Daskaleio-Kavos showed that smaller-scale smelting activities were also undertaken at least in some of the EBA Cycladic settlements. These exhibit different characteristics to the western Cycladic slag heaps in terms of context, scale, variability, and proximity to ore sources.

On the basis of the present evidence an important metal production industry existed in the Cyclades during the EBA, while lead isotope analyses and archaeometallurgical work carried out to date suggest that in the following periods this largely subsides and metal is imported from elsewhere. The pinnacle of metal production in this region coincides with a period of prominence for the islands, placing additional archaeological significance on this research field. This thesis has demonstrated the value of small-scale, site-directed archaeometallurgical studies in unravelling the technological details of this early metallurgy and ultimately building a comprehensive picture of its organisation.

# REFERENCES

Angelopoulou, A., 2003. I «Omada Kastriou» kai to Korfari ton Amygdalion (Panormos) Naxou, in A. Vlachopoulos and K. Birtacha (eds.) *Argonautis, Timitikos Tomos gia ton Kathigiti Christo G. Douma*, 159-189. Athens: Kathimerini A. E.

*Annual Report of the Managing Committee of the British School at Athens, 1986-7.*

Atkinson, T. D., Bosanquet, R. C., Edgar, C. C., Evans, A. J., Hogarth, D. G., Mackenzie, D., Smith, C., and Welch, F. B., 1904. *Excavations at Phylakopi in Melos*. Macmillan: London.

Baboula, E., 2000. 'Buried' metal in Late Minoan inheritance customs, in C. F. E. Pare (ed.), *Metals Make the World Go Round: The Supply and Circulation of Metals in Bronze Age Europe*, 56-69. Oxford: Oxbow Books.

Bachmann, H.-G., 1980. Early copper smelting techniques in Sinai and Negev as deduced from slag investigations, in P. T. Craddock (ed.), *Scientific Studies in Early Mining and Extractive Metallurgy* (British Museum Occasional Paper No. 48), 103-134. London: The British Museum.

Bachmann, H.-G., 1982a. *The Identification of Slags from Archaeological Sites.* London: Institute of Archaeology.

Bachmann, H.-G., 1982b. Copper smelting slags from Cyprus: review and classification of analytical data, in J. D. Muhly, R. Maddin, and K. Karageorghis (eds.), *Early Metallurgy in Cyprus 4000-500B.C.*, 143-52. Nicosia: Pierides Foundation.

Barber, R. L. N., 1983. The definition of the Middle Cycladic period, *American Journal of Archaeology*, **87**, 76-81.

Barber, R. L. N., 1984. The pottery at Phylakopi, First City, phase ii (I-ii), in J. A. MacGillivray and R. L. N. Barber (eds.), *The Prehistoric Cyclades: Contributions to a Workshop on Cycladic Chronology*, 88-94. Edinburgh: Department of Classical Archaeology, University of Edinburgh.

Barber, R. L. N., 1987. *The Cyclades in the Bronze Age*. London: Duckworth.

Barber, R. L. N. and MacGillivray, J. A., 1980. The Early Cycladic period: matters of definition and terminology, *American Journal of Archaeology*, **84**, 141-157.

Bartelheim, M., Eckstein, K., Huijsmans, M., Krauß, R., and Pernicka, E., 2003. Chalcolithic metal extraction in Brixlegg, Austria, in *Archaeometallurgy in Europe, vol. 1*, 441-447. Milan: Associazione Italiana di Metallurgia.

Bassiakos, Y., Kilikoglou, V., Vassilaki-Grimani, M., Grimanis, A. P., 1990. Provenance studies of Theran Lead, in D. A. Hardy, J. Keller, V. P. Galanopoulos, N. C. Fleming, and T. H. Druitt (eds.), *Thera and the Aegean World III, vol. 2*, 337-345. London: The Thera Foundation.

Bassiakos, Y. and Doumas, C., 1998. The island of Keros and it enigmatic role in the Aegean E.B.A.: A geoarchaeological approach, in *Argyritis Gi*, 55-64. Athens: Ethniko Metsoveio Polytechneion.

Bassiakos, Y., Chlouveraki, S., and Betancourt, P. P., 2004. Further questioning on the Early Minoan copper production as derived from the study of Chrysokamino smelting site, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 9.

Bassiakos, Y. and Philaniotou, O., in press. Early copper production on Kythnos: material and analytical reconstruction of metallurgical processes, in P. M. Day (ed.), *Metallurgy in the Early Bronze Age Aegean: New Evidence for Production and Consumption* (Sheffield Studies in Aegean Archaeology 6). Oxford: Oxbow.

Baxter, M. J., Beardah, C. C., and Westwood, S., 2000. Sample size and related issues in the analysis of lead isotope data, *Journal of Archaeological Science*, **27**, 973-980.

Baxter, M. J. and Gale, N. H., 1998. Testing for Multivariate Normality via Univariate Tests: A case Study Using Lead Isotope Ratio Data, *Journal of Applied Statistics*, **25**, 671-683.

Bayley, J. and Eckstein, K., 1997. Silver refining-production, recycling, assaying, in A. Sinclair, E. Slater, and J. Gowlett (eds.), *Archaeological Sciences 1995*, 107-111. Oxford: Oxbow Books.

Bent, J. T., 1884. Researches among the Cyclades, *The Journal of Hellenic Studies*, **5**, 42-59.

Bent, J. T., 1885. On the gold and silver mines of Siphnos, *The Journal of Hellenic Studies*, **6**, 195-198.

Begemann, F., Schmitt-Strecker, S., and Pernicka, E., 1992. The metal finds from Thermi III-IV: A chemical and lead-isotope study, *Studia Troica*, **2**, 219-239.

Begemann, F., Kallas, K., Schmitt-Strecker, S., Pernicka, E., 1999. Tracing ancient tin via isotope analyses, in A. Hauptmann, E. Pernicka, Th. Rehren, Ü. Yalçin (eds.), *The Beginnings of Metallurgy* (Der Anschnitt, Beiheft 9), 277-284. Bochum: Deutsches Bergbau-Museum.

Bernabò-Brea, L., 1964. *Poliochni: Città Preistorica Nell' Isola di Lemnos* (vol. 1). Rome: L' 'Erma' di Bretschneider.

Bernabò-Brea, L., 1976. *Poliochni: Città Preistorica Nell' Isola di Lemnos* (vol. 2). Rome: L' 'Erma' di Bretschneider.

Betancourt, P. P., 2003. The impact of Cycladic settlers on Early Minoan Crete, *Mediterranean Archaeology and Archaeometry*, **3**, 3-12.

Betancourt, P. P., 2004. The copper smelting workshop at Chrysokamino: reconstructing the smelting process, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 11.

Betancourt, P. P., Muhly, J. D., Farrand, W. R., Sterans, C., Onyshkevych, L., Hafford, W. B., and Evely, D., 1999. Research and excavation at Chrysokamino, Crete, 1995-1998, *Hesperia*, **68**, 344-370.

Bossert, E. M., 1967. Kastri auf Syros: Vorbericht über eine Untersuchung der prähistorischen Siedlung, *Archaiologikon Deltion (Meletai)*, **22A**, 53-76.

Boulotis, C., 1997. Koukonisi Lemnou. Tessera chronia anaskafikis erevnas: theseis kai ypotheseis, in G. Doumas and V. La Rosa (eds.), *I Poliochni kai i Proimi Epochi tou Chalkou sto Voreio Aigaio*, 634-648. Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Bourgarit, D., Mille, B., Prange, M., Ambert, P., and Hauptmann, A., 2003. Chalcolithic fahlore smelting at Cabrières: reconstruction of smelting processes by archaeometallurgical finds, in *Archaeometallurgy in Europe, vol. 1*, 431-440. Milan: Associazione Italiana di Metallurgia.

Bowman, R., Friedman, A. M., Lerner, J., and Milsted, J., 1975. A statistical study of the impurity in copper ores and their relationship to ore types, *Archaeometry*, **17**, 157-164.

Branigan, K., 1967. Early Bronze Age daggers of Crete, *The Annual of the British School at Athens*, **62**, 211-239.

Branigan, K., 1968. *Copper and Bronze Working in Early Bronze Age Crete* (Studies in Mediterranean Archaeology, 14). Lund: Paul Åström.

Branigan, K., 1974. *Aegean Metalwork of the Early and Middle Bronze Ages.* Oxford: Clarendon Press.

Branigan, K., 1977. Metal objects and metal technology of the Cycladic culture, in J. Thimme (ed.), *Art and Culture of the Cyclades*, 117-122. Karlsruhe: C. F. Müller.

Branigan, K., 1982. Minoan metallurgy and Cypriot copper, in in J. D. Muhly, R. Maddin, and K. Karageorghis (eds.), *Early Metallurgy in Cyprus 4000-500B.C.*, 203-11. Nicosia: Pierides Foundation.

Broodbank, C. 1989. The longboat and society in the Cyclades in the Keros-Syros culture, *American Journal of Archaeology*, **93**, 319-337.

Broodbank, C. 1993. Ulysses without sails: trade, distance, knowledge and power in the early Cyclades, *World Archaeology*, **24**, 315-331.

Broodbank, C., 1999. Colonization and configuration in the insular Neolithic of the Aegean, in P. Halstead (ed.), *Neolithic Society in Greece* (Sheffield Studies in Aegean Archaeology, 2), 15-41. Sheffield: Sheffield Academic Press.

Broodbank, C., 2000a. *An Island Archaeology of the Early Cyclades.* Cambridge: Cambridge University Press.

Broodbank, C., 2000b. Perspectives on an Early Bronze Age island centre: an analysis of pottery from Daskaleio-Kavos (Keros) in the Cyclades, *Oxford Journal of Archaeology*, **19**, 323-342.

Budd, P. and Ottaway, B. S., 1991. The properties of arsenical copper alloys: implications for the development of eneolithic metallurgy, in P. Budd, B. Chapman, C. Jackson, R. Janaway, and B. Ottaway (eds.), *Archaeological Sciences 1989*, 132-142. Oxford: Oxbow Books.

Budd, P., Gale, D., Pollard, R. G., Thomas, R. G., and Williams, P. A., 1992. The early development of metallurgy in the British Isles, *Antiquity*, **66**, 677-686.

Budd, P., Pollard, A. M., Scaife, B., and Thomas, R. G., 1995. Oxhide ingots, recycling and the Mediterranean metals trade, *Journal of Mediterranean Archaeology*, **8**, 1-32.

Caley, E. R., 1949. On the prehistoric use of arsenical copper in the Aegean region, *Hesperia Supplement*, **8**, 60-63.

Caskey, J. L., 1971. Investigations in Keos: Part I: Excavations and explorations, 1966-1970, *Hesperia*, **40**, 359-396.

Caskey, J. L., 1972. Investigations in Keos: Part II: A conspectus of the pottery, *Hesperia*, **41**, 357-401.

Caskey, M., Mendoni, L., Papastamataki, A., and Beloyannis, N., 1988. Metals in Keos: a first approach, in P. G. Marinos and G. C. Koukis (eds.), *The Engineering Geology of Ancient Works, Monuments and Historical Sites,* 1739-1745. Rotterdam: Baltema.

Catapotis, M., Pryce, O., Bassiakos, Y., 2004. Prehistoric copper smelting at Chrysokamino: archaeological analysis and experimental reconstruction, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 13.

Charles, J. A., 1967. Early arsenical bronzes-A metallurgical view, *American Journal of Archaeology*, **71**, 21-26.

Charles, J. A., 1980. The coming of copper and copper-base alloys and iron: a metallurgical sequence, in T. A. Wertime and J. D. Muhly (eds.), *The Coming of the Age of Iron*, 151-181. New Haven: Yale University Press.

Cherry, J. F., 1990. The first colonization of the Mediterranean island: a review of recent research, *Journal of Mediterranean Archaeology*, **3**, 145-221.

Cherry, J. F., Davis, J. L., and Mantzourani, E., 1991. *Landscape Archaeology as Long-Term History, Northern Keos in the Cycladic Islands from Earliest Settlement until Modern Times*. Los Angeles: Institute of Archaeology, University of California.

Cherry, J. F. and Knapp, A. B., 1991. Quantitative provenance studies and Bronze Age trade in the Mediterranean: some preliminary reflections, in N. H. Gale (ed.), *Bronze Age Trade in the Mediterranean*, 92-119. Jonsered: Paul Åströms Förlag.

Ciliberto, E. and Spoto, G., 2000. *Modern Analytical Methods in Art and Archaeology*. New York: Wiley-Interscience.

Coleman, J. E., 1977. *Keos I: Kephala. A Late Neolithic Settlement and Cemetery.* Princeton: American School of Classical Studies.

Conophagos, C. I., 1980. *To Archaio Lavrio kai i Elliniki Techniki Paragogis tou Argyrou*. Athens: Ekdotiki Ellados A. E.

Constantinou, G., 1982. Geological features and ancient exploitation of the cupriferous sulphide ore bodies of Cyprus, in J. D. Muhly, R. Maddin, and K. Karageorghis (eds.), *Early Metallurgy in Cyprus 4000-500B.C.*, 13-24. Nicosia: Pierides Foundation.

Costin, C. L., 1991. Craft specialisation: Issues in defining, documenting, and explaining the organisation of production, in M. Schiffer (ed.), *Archaeological Methods and Theory*, **3**, 1-56. Tucson: University of Arizona Press.

Craddock, P. T., 1976. The composition of the copper alloys used by the Greek, Etruscan and Roman civilisations, Part 1: The Greeks before the Archaic period, *Journal of Archaeological Science*, **3**, 93-113.

Craddock, P. T., 1995. *Early Metal Mining and Production*. Edinburgh: Edinburgh University Press.

Craddock, P. T., 2001. From hearth to furnace: evidences for the earliest metal smelting technologies in the Eastern Mediterranean, *Paléorient*, **26**, 151-65.

Craddock, P. T., Freestone, I. C., Gale, N. H., Meeks, N. D., Rothenberg, B., and Tite, M. S., 1985. The investigation of a small heap of silver smelting debris from Rio Tinto, Huelva, Spain, in P. T. Craddock and M. J. Hughes (eds.), *Furnaces and Smelting Technology in Antiquity* (British Museum Occasional Paper No. 48), 199-217. London: The British Museum.

Craddock, P. T. and Meeks, N. D., 1987. Iron in ancient copper, *Archaeometry*, **29**, 187-204.

Craddock, P. T., La Niece, S., and Hook, D. R., 2003. Evidences for the production, trading and refining of copper in the Gulf of Oman during the third millennium BC, in Th. Stöllner, G. Körlin, G. Steffens, and J. Cierny (eds.), *Man and Mining* (Der Anschnitt, Beiheft 16), 103-112. Bochum: Deutsches Bergbau Museum.

Craig, J. R. and Vaughan, D. J., 1981. *Ore Microscopy and Ore Petrography*. New York: John Wiley & Sons.

Cummer, W. W. and Schofield, E., 1984. *Keos III, Ayia Irini: House A*. Mainz on Rhine: Verlag Philipp von Zabern.

Davaras, C. and Betancourt, P. P., 2004. *Hagia Photia Cemetery I: The Tomb Groups and Architecture* (Prehistory Monographs 14). Pennsylvania: INSTAP Academic Press.

Davi, E., 1998. Emfanisi galinitou sto kristallosxistodes tis nisou Keas, in L. G. Mendoni and A. J. Mazarakis Ainian (eds.), *Kea-Kythnos: History and Archaeology*, 713-716. Athens: Research Centre for Greek and Roman Antiquity- National Hellenic Research Foundation.

Davies, O., 1932. Bronze Age mining round the Aegean, *Nature*, **130**, 985-7.

Davies, O., 1935. *Roman Mines in Europe*. Oxford: Clarendon Press.

Davis, J. L., 1992. Review of Aegean prehistory I: The islands of the Aegean, *American Journal of Archaeology*, **96**, 699-756.

Davis, J. L., Tzonou-Herbst, I., and Wolpert, A. D., 2001. Addendum:1992-1999, in T. Cullen (ed.), *A Review of Aegean Prehistory* (American Journal of Archaeology Supplement 1), 77-94. Boston: Archaeological Institute of America.

Day, P. M., Wilson, D. E., and Kiriatzi, E., 1998. Pots, labels and people: burying ethnicity in the cemetery at Aghia Photia, Siteias, in K. Branigan (ed.), *Cemetery and Society in the Aegean Bronze Age* (Sheffield Studies in Aegean Archaeology 1), 133-49. Sheffield: Sheffield Academic Press.

Demoule, J.-P. and Perlès, C., 1993. The Greek Neolithic: A new review, *Journal of World Archaeology*, **7**, 355-416.

Dimopoulou-Rethemiotaki, N., 1993. Poros-Katsambas, *Archaiologikon Deltion (Chronika)*, **48B**, 450-9.

Dimou, E. and Oikonomou, G., 1997. Oryktologiki-oryktoxhimiki systasi ton archaion skorion apo diafores theseis tou Elladikou chorou, in *Ancient Greek Technology*, 313-23. Thessaloniki: Etaireia Makedonikon Spoudon.

Dimou, E., Perdikatsis, V., Economou, G., and Televadou, Chr., 2001. Mineralogical study of ancient slags from the island of Andros, Cyclades, in Y. Bassiakos, E. Aloupi, and Y. Facorellis (eds.), *Archaeometry Issues in Greek Prehistory and Antiquity*, 645-658. Athens: Hellenic Society of Archaeometry, Society of Messenian Archaeological Studies.

Dobres, M.-A. and Hoffman, C. R., 1994. Social agency and prehistoric technology, *Journal of Archaeological Method and Theory*, **1**, 211-258.

Doonan, R. C. P., 1999. Copper production in the Eastern Alps during the Bronze Age: Technological change and the unintended consequences of social reorganization, in S. M. M. Young, A. M. Pollard, P. Budd, and R. A. Ixer (eds.), *Metals in Antiquity* (BAR International Series No 792), 72-7. Oxford: Archaeopress.

Doonan, R. C. P., Day, P. M., and Dimopoulou, N., 2004. Mixing traditions and practice: composite materials in early third millennium Crete, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 16.

Doumas, C. G., 1963. Seriphos, *Archaiologikon Deltion (Chronika)*, **18B**, 285.

Doumas, C.G., 1964. Archaiotites kai mnimeia ton Kykladon, *Archaiologikon Deltion (Chronica)*, **19B**, 409-12.

Doumas, C. G., 1972. Notes on Cycladic Architecture, *Archäologischer Anzeiger*, **87**, 151-179.

Doumas, C. G., 1977. *Early Bronze Age Burial Habits in the Cyclades.* Göteborg: Paul Åströms Förlag.

Doumas, C. G., 1988. EBA in the Cyclades: continuity or discontinuity?, in E. B. French and K. A. Wardle (eds.), *Problems in Greek Prehistory*, 21-29. Bristol: Bristol Classical Press.

Doumas, C. G., 1990a. Death, in L. Marangou (ed.), *Cycladic Culture: Naxos in the 3rd millennium BC*, 93-5. Athens: Nicholas P. Goulandris Foundation.

Doumas, C. G., 1990b. Metallurgy, in L. Marangou (ed.), *Cycladic Culture: Naxos in the 3rd millennium BC*, 161-4. Athens: Nicholas P. Goulandris Foundation.

Doumas, C. G., 1990c. Ta nisia kai I proimi metallourgia sto Aigaio, in *Idryma N. P. Goulandri, Mouseio Kykladikis Technis, Dialexeis 1986-1989*, 111-6. Athens: Nicholas P. Goulandris Foundation-Museum of Cycladic Art.

Doumas, C. G., 1994. I pyrotechnologia sti Lemno tis Proimis Epochis tou Chalkou, *Archaiologia*, **50**, 28-30.

Doumas, C. G. and La Rosa, V., 1997. *I Poliochni kai i Proimi Epochi tou Chalkou sto Voreio Aigaio.* Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Einaudi, M. T., Meinert, L. D., and Newberry, R. J., 1981. Skarn deposits, *Economic Geology*, 75th Anniversary Volume, 317-91.

Evans, J. D. and Renfrew, A. C., 1968. *Excavations at Saliagos near Antiparos.* London: British School at Athens.

Evans, R. T. and Tylecote, R. F., 1967. Some vitrified products of non-metallurgical significance, *Bulletin of the Historical Metallurgy Group*, **1**, 22-23.

Evely, R. D. G., 2000. *Minoan Crafts: Tools and Techniques*. Jonsered: Åströms.

Fiedler, K. G., 1841. *Reise durch alle Theile des Königreiches Griechenland.* Leipzig.

Fitton, J. L., 1984. *Cycladica: Studies in Memory of N. P. Goulandris*. London: British Museum Publications.

Fitton, J. L., 1989. Esse quam videri: A reconsideration of the Kythnos hoard of early Cycladic tools, *American Journal of Archaeology*, **93**, 31-9.

Freestone, I. C., 1989. Refractory materials and their procurement, in A. Hauptmann, E. Pernicka, and G. A. Wagner (eds.), *Old World Archaeometallurgy* (Der Anschnitt, Beiheft 7), 155-162. Bochum: Deutsches Bergbau-Museum.

Freestone, I. C. and Tite, M. S., 1986. Refractories in the ancient and preindustrial world, in W. D. Kingery (ed.), *High-technology ceramics: past present and future*, 35-63. Westerville: The American Ceramic Society.

Friedrich, W. L. and Doumas, C. G., 1990. Was there local access to certain ores/ minerals for the Theran people before the Minoan eruption? An Addendum, in D. A. Hardy, C. G. Doumas, J. A. Sakellarakis, and P. M. Warren (eds.), *Thera and the Aegean World III, vol 1*, 502-503. London: The Thera Foundation.

Galanos, F., 1962. *Seriphos, Part 1*. Athens.

Gale, N. H., 1978. Lead isotopes and Aegean metallurgy, in C. Doumas (ed.), *Thera and the Aegean World I*, 529-545. London: Thera and the Aegean World.

Gale, N. H., 1980. Some aspects of lead and silver mining in the Aegean, in C. Doumas (ed.), *Thera and the Aegean World II*, 161-195. London: Thera and the Aegean World.

Gale, N. H., 1990. The provenance of metals for Early Bronze Age Crete-local or Cycladic, *Proceedings of the 6th Cretological Conference*, vol. A1. Chania: Philological Society “Chrysostomos”.

Gale, N. H., 1998. The role of Kea in metal production and trade in the Late Bronze Age, in L. G. Mendoni and A. J. Mazarakis Ainian (eds.), *Kea-Kythnos: History and Archaeology*, 737-758. Athens: Research Centre for Greek and Roman Antiquity-National Hellenic Research Foundation.

Gale, N. H., 2001. Archaeology, Science-Based Archaeology and the Mediterranean Bronze Age Metals Trade: A Contribution to the Debate, *European Journal of Archaeology*, **4**, 113-130.

Gale, N. H., 2003. Disciplinary fault lines: science and archaeology-another view, *Mediterranean Archaeology and Archaeometry*, **3**, 55-62.

Gale, N. H., 2004. Early Helladic metallurgy at Raphina, Attica, and the role of Lavrion, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 19.

Gale, N. H. and Stos-Gale, Z. A., 1981a. Cycladic lead and silver metallurgy, *The Annual of the British School at Athens*, **76**, 169-224.

Gale, N. H. and Stos-Gale, Z. A., 1981b. Lead and silver in the ancient Aegean, *Scientific American*, **244**, (6), 142-52.

Gale, N. H. and Stos-Gale, Z. A., 1982. Bronze Age copper sources in the Mediterranean: a new approach, *Science*, **216**, 11-19.

Gale, N. H. and Stos-Gale, Z. A., 1984. Cycladic metallurgy, in J. A. MacGillivray and R. L. N. Barber (eds.), *The Prehistoric Cyclades*, 255-276. Edinburgh: Department of Classical Archaeology.

Gale, N. H. and Stos-Gale, Z. A., 1986a. Anatolian and Cycladic metal sources, *PACT Journal of the European Study Group on Physical, Chemical and Mathematical Techniques Applied to Archaeology*, **15**, 14-30.

Gale, N.H. and Stos-Gale, Z. A., 1986b. Oxhide copper ingots in Crete and Cyprus and the Bronze Age metals trade, *The Annual of the British School at Athens*, **81**, 81-100.

Gale, N.H. and Stos-Gale, Z. A., 1989a. Some aspects of early Cycladic copper metallurgy, in C. Domergue (ed.), *Mineria y Metallurgia en las Antiguas Civilizaciones Mediterraneas y Europeas,* 21-37. Madrid.

Gale, N. H. and Stos-Gale, Z. A., 1989b. Bronze Age archaeometallurgy of the Mediterranean: The impact of Lead Isotope studies, in R. O. Allen (ed.), *Archaeological Chemistry IV*, 159-198. Washington DC: American Chemical Society.

Gale, N. H. and Stos-Gale, Z. A., 1992a. Lead isotope studies in the Aegean (The British Academy Project), in A. M. Pollard (ed.), *New Developments in Archaeological Science*, 63-108. Oxford: OUP.

Gale, N. H. and Stos-Gale, Z. A., 1992b. Evaluating lead isotope data: comments I, *Archaeometry*, **34**, 311-317.

Gale, N. H. and Stos-Gale, Z. A., 1995. Comments on 'Oxhide ingots, recycling, and the Mediterranean metals trade', *Journal of Mediterranean Archaeology*, **8**, 33-41.

Gale, N. H. and Stos-Gale, Z. A., 1996. Lead isotope methodology: the possible fractionation of lead isotope compositions during metallurgical processes, in Ş. Demirci, A.M. Özer, and G. D. Summers (eds.), *Archaeometry '94: The Proceedings of the 29th International Symposium on Archaeometry*, 287-299. Ankara: Tübitak.

Gale, N. H. and Stos-Gale, Z. A., 2000. Lead isotope analyses applied to provenance Studies, in E. Ciliberto and G. Spoto (eds.), *Modern Analytical Methods in Art and Archaeology,* 503-584. New York: Wiley-Interscience.

Gale, N. H. and Stos-Gale, Z. A., 2002. Archaeometallurgical research in the Aegean, in M. Bartelheim, E. Pernicka, R. Krause (eds.), *The Beginnings of Metallurgy in the Old World*, 277-302. Rahden/Westf.: Leidorf.

Gale, N. H. and Stos-Gale, Z. A., in press. Changing patterns in metallurgy, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Gale, N. H., Gentner, W., and Wagner, G. A., 1980. Mineralogical and geographical silver sources of Archaic silver coinage in D. M. Metcalf and W. A. Oddy (eds.), *Metallurgy in Numismatics vol. 1*, 3-49. London: The Royal Numismatic Society.

Gale, N. H., Stos-Gale, Z. A., and Davis, J. L., 1984. The provenance of lead used at Ayia Irini, Keos, *Hesperia*, **53**, 389-406.

Gale, N. H., Papastamataki, A., Stos-Gale, Z. A., and Leonis, K., 1985. Copper sources and copper metallurgy in the Aegean Bronze Age, in P. T. Craddock and M. J. Hughes (eds.), *Furnaces and Smelting Technology in Antiquity* (British Museum Occasional Paper No. 48), 81-101. London: The British Museum.

Georgiou, H. S., 1986. *Keos VI. Ayia Irini: Specialized domestic and industrial pottery*. Mainz on Rhine: Verlag Philipp von Zabern.

Getz-Preziosi, P., 1982. The Keros hoard, in D. Metzler and B. Otto (eds.), *Antidoron: Festscrift für Jürgen Thimme*, 37-44. Karlsruhe: C. F. Müller.

Gill, D. W. J. and Chippindale, C., 1993. Consequences of esteem for Cycladic figures, *American Journal of Archaeology*, **97**, 601-659.

Gize, A. P. and Droop, G., 2004. Bronze Age copper and iron resources on Crete, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 22.

Gournellos, Th., Georgiou, Ch., and Papadopoulos, Z., 1986. Geologikes kai geomorphologikes paratiriseis sto nisi tis Seriphou, *Bulletin of the Geological Society of Greece*, **18**, 83-9.

Gropengiesser, H., 1986. Siphnos, Kap Agios Sostis: Keramische prähistorische Zeugnisse aus dem Gruben- und Hüttenrevier I (Tafeln 1-10, Beilagen 1-2), *Mitteilungen des Deutschen Archäologischen Insituts (Athenische Abteilung)*, **101**, 1-39.

Gropengiesser, H., 1987. Siphnos, Kap Agios Sostis: Keramische prähistorische Zeugnisse aus dem Gruben- und Hüttenrevier II (Tafeln 1-4), *Mitteilungen des Deutschen Archäologischen Insituts (Athenische Abteilung)*, **102**, 1-54.

Hadjianastasiou, O., 1988. A Late Neolithic settlement at Grotta, Naxos, in E. B. French and K. A. Wardle (eds.), *Problems in Greek Prehistory*, 11-20. Bristol: Bristol Classical Press.

Hadjianastasiou, O., 1998. Simeioseis apo tin Kythno, in L. G. Mendoni and A. J. Mazarakis Ainian (eds.), *Kea-Kythnos: History and Archaeology*, 259-273. Athens: Research Centre for Greek and Roman Antiquity- National Hellenic Research Foundation.

Hadjianastasiou, O. and MacGillivray, S., 1988. An Early Bronze Age smelting site on the Aegean island of Kythnos; Part Two: The archaeological evidence, in J. E. Jones (ed.), *Aspects of Ancient Mining and Metallurgy*, 31-4. Bangor: Classical Association, Bangor and North Wales Branch.

Hadjipouliou, E., 1997. Exeidikeumenes drastiriotites sto Palamari tis Skyrou sto telos tis tritis chilietias, in C. G. Doumas and V. La Rosa (eds.), *I Poliochni kai i Proimi Epochi tou Chalkou sto Voreio Aigaio*, 357-361. Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Hadji-Vallianou, D., 1975. Keros, *Archaiologikon Deltion (Chronika)*, **30B**, 327.

Hansen, M. and Anderko, K., 1958. *Constitution of Binary Alloys*. New York: McGraw-Hill Book Company Inc.

Hauptmann, A., 1989. The earliest periods of copper metallurgy in Feinan, Jordan, in A. Hauptmann, E. Pernicka, and G. A. Wagner (eds.), *Old World Archaeometallurgy* (Der Anschnitt, Beiheft 7), 119-135. Bochum: Deutsches Bergbau-Museum.

Hauptmann, A. 2000. *Zur frühen Metallurgie des Kupfers in Fenan/ Jordanien* (Der Anschnitt, Beiheft 11). Bochum: Deutsches Bergbau-Museum.

Hauptmann, A., 2003. Developments in copper metallurgy during the fourth and third millenia BC at Feinan, Jordan, in , P. T. Craddock and J. Lang (eds.), *Mining and Metal Production Through the Ages*, 90-100. London: The British Museum Press.

Hauptmann, A., Weisgerber, G., and Bachmann, H.-G., 1988. Early copper metallurgy in Oman, in R. Maddin (ed.), *The Beginning of the Use of Metals and Alloys*, 34-51. Massachussetts: MIT Press.

Hauptmann, A. and Weisgerber, G., 1992. Periods of ore exploitation and metal production in the area of Feinan, Wadi 'Arabah, Jordan, *Studies in the History and Archaeology of Jordan*, **4**, 61-66.

Hauptmann, A., Rehren, Th., Scmitt-Strecker, S., 2003. Early Bronze Age copper metallurgy at Shahr-i Sokhta (Iran), reconsidered, in Th. Stöllner, G. Körlin, G. Steffens, and J. Cierny (eds.), *Man and Mining* (Der Anschnitt, Beiheft 16), 197-213. Bochum: Deutsches Bergbau Museum.

Haustein, M., Roewer, G., Krbetschek, M. R., and Pernicka, E., 2003. Dating archaeometallurgical slags using thermoluminescence, *Archaeometry*, **45**, 519-530.

Healy, J. F., 1978. *Mining and Metallurgy in the Greek and Roman World.* London: Thames and Hudson.

Hess, K., Hauptmann, A., Wright, H., and Whallon, R., 1998. Evidence for fourth millenium BC silver production at Fatmalı-Kalecik, East Anatolia, in Th. Rehren, A. Hauptmann, and J. D. Muhly (eds.), *Metallurgica Antiqua* (Der Anschnitt, Beiheft 8), 57-67. Bochum: Deutsches Bergbau-Museum.

Hood, S., 1982. *Excavations in Chios 1938-1955: Prehistoric Emporio and Ayio Gala* (vol. 2). Athens: The British School of Archaeology at Athens, Thames and Hudson.

Hook, D. R., Freestone, I. C., Meeks, N. D., Craddock, P. T., and Onorato, A. M., 1991. The early production of copper-alloys in south-east Spain, in E. Pernicka and G. A. Wagner (eds.), *Archaeometry '90*, 65-76. Basel: Birkhäuser Verlag.

Ixer, R. A. and Pattrick, R. A., 2003. Copper-arsenic ores and Bronze Age mining and metallurgy with special reference to the British Isles, in P. T. Craddock and J. Lang (eds.), *Mining and Metal Production Through the Ages*, 9-20. London: The British Museum Press.

Jovanovic, B., 1980. Primary copper mining and the production of copper, in P. T. Craddock (ed.), *Scientific Studies in Early Mining and Extractive Metallurgy* (British Museum Occasional Paper No. 20), 31-40. London: The British Museum.

Juleff, G., 1996. An ancient wind-powered iron smelting technology in Sri Lanka, *Nature*, **379**, 60-63.

Junghans, S., Sangmeister, E., Schröder, M., 1968. *Kupfer und Bronze in der frühen Metallzeit Europas.* Berlin: Gebr. Mann Verlag.

Kakavogianni, O., Douni, K., and Nezeri, F., 2004. Silver metallurgical findings dated from the end of the Final Neolithic period until the Middle Bronze Age at the area of Mesogeia, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 25.

Karantzali, E., 1996. *Le Bronze Ancien dans les Cyclades et en Crète; Les Relations Entre les Deux Régions; Influence de la Grèce Continentale.* Oxford: Tempus Reparatum.

Kassianidou, V., Rothenberg, B., and Andrews, P., 1995. Silver production in the Tartessian period; the evidence from Monte Romero, *ARX*, **1**, 17-34.

Katsa, L., 1997. Copper alloys and Cycladic metallurgy during the Bronze Age, in *Ancient Greek Technology*, 73-84. Thessaloniki: Etaireia Makedonikon Spoudon.

Keesman, I., 1993. Naturwissenschaftliche Untersuchungen zur antiken Kupfer- und Silberverhüttung in Südwestspanien, in H. Steuer and U. Zimmermann (eds.), *Montanarchäologie in Europa*, 105-122. Sigmaringen: Jan Thorbecke Verlag.

Knapp, A. B., 2000. Archaeology, science-based archaeology and the Mediterranean Bronze Age metals trade, *European Journal of Archaeology*, **3**, 31-56.

Knapp, A. B., 2002. Disciplinary fault lines: science and social archaeology, *Mediterranean Archaeology and Archaeometry*, **2**, 37-44.

Kongoli, F. and Yazawa, A., 2001. Liquidus surface of $FeO$-$Fe_2O_3$-$SiO_2$-$CaO$ slag containing $Al_2O_3$, $MgO$, and $Cu_2O$ at intermediate oxygen partial pressures, *Metallurgical and Material Transactions*, **32B**, 583-92.

Kontoleon, N. M., 1949. Anaskaphi en Naxo, *Praktika tis en Athinais Archaiologikis Etaireias*, 112-22.

Kordellas, A., 1902. *O Metalleutikos Ploutos kai ai Alykai tis Ellados ypo Geologikin, Statistikin kai Istorikin Apopsin Exetazomena.* Athens: Sakellariou.

Koucky, F. L. and Steinberg, A., 1982. The ancient slags of Cyprus, in J. D. Muhly, R. Maddin, and V. Karageorghis (eds.), *Early Metallurgy in Cyprus, 4000-500B.C.*, 117-141. Nicosia: Pierides Foundation.

Kresten, P. 1986. Melting point and viscosities of ancient slags: A discussion, *Journal of the Historical Metallurgy Society*, **20**, 43-45.

Kresten, P. and Hjärthner-Holdar, E., 2001. Analyses of the Swedish ancient iron reference slag W-25:R, *Historical Metallurgy*, **35**, 48-51.

Ktenas, K. A., 1917. *Erevnai peri tis Metallogeneias tis ND. Aigiidos.* Athens: Oryktologiko kai Petrografiko Ergastirio Ethnikou Panepistimiou.

Lamb, W., 1936. *Excavations at Thermi in Lesbos.* Cambridge: Cambridge University Press.

Lambert, N., 1973. Vestiges préhistoriques dans l'île de Macronisos, *Athens Annals of Archaeology*, **6**, 1-12.

Lechtman, H., 1991. The production of copper-arsenic alloys in the Central Andes: highland ores and coastal smelters?, *Journal of Field Archaeology*, **18**, 43-76.

Lechtman, H., 1996. Arsenic bronze: dirty copper or chosen alloy? A view from the Americas, *Journal of Field Archaeology*, **23**, 477-514.

Lechtman, H. and Klein, S., 1999. The production of copper-arsenic alloys (arsenic bronze) by cosmelting: modern experiment, ancient practice, *Journal of Archaeological Science*, **26**, 497-526.

Leese, M. N., 1992. Comments...II, *Archaeometry*, **34**, 318-322.

MacGillivray, J. A., 1980. Mount Kynthos in Delos: the Early Cycladic settlement, *Bulletin de Correspondance Hellénique*, **104**, 3-45.

MacGillivray, J. A., 1983. On the relative chronologies of Early Cycladic IIIA and Early Helladic III, *American Journal of Archaeology*, **87**, 81-83.

MacGillivray, J. A., 1984. The relative chronology of Early Cycladic III, in J. A. MacGillivray and R. L. N. Barber (eds.), *The Prehistoric Cyclades: Contributions to a Workshop on Cycladic Chronology*, 70-77. Edinburgh: Department of Classical Archaeology, University of Edinburgh.

MacGillivray, J. A. and Barber, R. L. N., 1984. *The Prehistoric Cyclades: Contributions to a Workshop on Cycladic Chronology*. Edinburgh: Department of Classical Archaeology, University of Edinburgh.

Mangou, H. and Ioannou, P. V., 1997. On the chemical composition of prehistoric Greek copper-based artefacts from the Aegean region, *The Annual of the British School at Athens*, **92**, 60-72.

Mangou, H., and Ioannou, P. V., 1998. On the chemical composition of prehistoric copper-based artefacts from Crete, *The Annual of the British School at Athens*, **93**, 91-102.

Maniatis, Y. and Tite, M. S., 1981. Technological examination of Neolithic-Bronze Age pottery from central and southeast Europe and from the Near East, *Journal of Archaeological Science*, **8**, 59-76.

Manning, S. W., 1995. *The Absolute Chronology of the Aegean Early Bronze Age*. Sheffield: Sheffield Academic Press.

Marinos, G. 1951. Geologia kai metallogeneia tis nisou Serifou, *The mineral wealth of Greece*, **1**, 95-127.

Marthari, M., 1990. Skarkos: Enas protokykladikos oikismos stin Io, in *Idryma N. P. Goulandri, Mouseio Kykladikis Technis, Dialexeis 1986-1989*, 97-100. Athens: Nicholas P. Goulandris Foundation-Museum of Cycladic Art.

Marthari, M., 1997. Apo ton Skarko stin Poliochni: paratiriseis gia tin koinoniko-oikonomiki anaptyxi ton oikismon tis Proiimis Epochis tou Chalkou stis Kyklades kai ta nisia tou voreioanatolikou Aigaiou, in C. G. Doumas and V. La Rosa (eds.), *I Poliochni kai I Proimi Epochi tou Chalkou sto Voreio Aigaio*, 362-82. Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Marthari, M., 1998. *Syros Chalandriani Kastri: Apo tin Erevna kai tin Prostasia stin Anadeixi tou Archaiologikou Chorou-Syros Chalandriani Kastri: From the Investigation and Protection to the Presentation of the Archaeological Site*. Athens: Ministry of the Aegean.

Marthari, M., 2001. Altering information from the past: illegal excavations in Greece and the case of the Early Bronze Age Cyclades, in N. Brodie, J. Doole, and A. C. Renfrew (eds.), *Trade in Illicit Antiquities: the Destruction* *of the World's Archaeological Heritage*, 161-172. Cambridge: McDonald Institute for Archaeological Research.

Marthari, M., in press. Aspects of pottery circulation in the Cyclades during the early EBII: Fine and semi-fine imported ceramic wares at Skarkos, Ios, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Mass, J., Wypyski, M., and Stone, R. E., 2002. Malkata and Lisht glassmaking technologies: towards a specific link between second millennium BC metallurgists and glassmakers, *Archaeometry*, **44**, 67-82.

Mass, J. and Stone, R. E., 2003. Reply, *Archaeometry*, **45**, 191-198.

Matthäus, H., 1985. Sifnos im Altertum, in G.A. Wagner and G. Weisgerber (eds.), *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3), 17-58. Bochum: Deutsches Bergbau-Museum.

Maxwell, V., 2002. Metalworking at Ftelia, in A. Sampson (ed.) *The Neolithic Settlement at Ftelia, Mykonos*, 147-9. Rhodes: University of the Aegean.

McGeehan-Liritzis, V., 1983. The relationship between metalwork, copper sources and the evidence for settlement in the Greek Late Neolithic and Early Bronze Age, *Oxford Journal of Archaeology*, **2**, 147-180.

McGeehan-Liritzis, V., 1996. *The Role and Development of Metallurgy in the Late Neolithic and Early Bronze Age of Greece*. Jonsered: Paul Åströms Förlag.

Mendoni, L. and Beloyannis, N., 1993. Metalleutikes kai metallourgikes drastiriotites stin archaia Kea, *Archaiognosia*, 7, 91-104.

Merkel, J. F., Shimada, I., Swann, C. P., and Doonan, R., 1994. Pre-Hispanic copper alloy production at Batán Grande, Peru: Interpretation of the analytical data for ore samples, in D. A. Scott and P. Meyers (eds.), *Archaeometry of Pre-*

*Columbian Sites and Artifacts*, 199-228. Los Angeles: The Getty Conservation Institute.

Michael, C.T., Zacharias, N., Dimotikali, D., Maniatis, Y. 1997. A new technique for measuring the natural dose in TL dating and its application in the dating of a mortar containing ceramic grains, *Ancient TL*, **15**, 36-42.

Michael, C.T., and Zacharias, N., 2000. A new technique for thick-source alpha counting determination of U and Th, *Nuclear Instruments and Methods*, **439**, 167-177.

Michailidou, A., 1995. Investigating metal technology in a settlement. The case of Akrotiri at Thera, *Archaiognosia*, **8**, 165-80.

Moesta, H. and Schlick, G., 1989. The furnace of Mitterberg: An oxidising Bronze Age copper process, *Bulletin of the Metals Museum*, **14**, 5-16.

Morton, G. R. and Wingrove, J., 1969. Constitution of bloomery slags: Part I: Roman, *Journal of the Iron and Steel Industry*, **207**, 1555-1564.

Mountjoy, P. A., 1995. Thorikos Mine No.3: The Mycenean pottery, *The Annual of the British School at Athens*, **90**, 195-227.

Muhly, J. D., 1985a. Beyond typology: Aegean metallurgy in its historical context, in N. C. Wilkie and W. D. E. Coulson (eds.), *Contributions to Aegean Archaeology: Studies in Honour of William A. McDonald*, 109-141. Minnesota: Center for Ancient Studies, University of Minnesota.

Muhly, J. D., 1985b. Sources of tin and the beginnings of bronze metallurgy, *American Journal of Archaeology*, **89**, 275-291.

Muhly, J. D., 1995. Lead isotope analysis and the archaeologist, *Journal of Mediterranean Archaeology*, **8**, 54-58.

Muhly, J. D., 2004. Chrysokamino and the beginnings of metal technology on Crete and in the Aegean, in L. P. Day, M. S. Mook, and J. D. Muhly (eds.), *Crete Beyond the Palaces*, 283-9. Philadelphia: INSTAP Academic Press.

Mussche, H., 1998. *Thorikos: A Mining Town in Ancient Attica*. Gent: Belgian Archaeological School in Greece.

Nakou, G., 1995. The cutting edge: A new look at early Aegean metallurgy, *Journal of Mediterranean Archaeology*, **8**, 1-32.

Nakou, G., 1997. The role of Poliochni and the North Aegean in the development of Aegean metallurgy, in C. G. Doumas and V. La Rosa (eds.), *I Poliochni kai i Proimi Epochi tou Chalkou sto Voreio Aigaio*, 634-648. Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Northover, J. P., 1989. Properties and use of arsenic-copper alloys, in A. Hauptmann, E. Pernicka, and G. A. Wagner (eds.), *Old World Archaeometallurgy* (Der Anschnitt, Beiheft 7), 111-118. Bochum: Deutsches Bergbau-Museum.

Nowell, G., Clayton, R., Gale, N. H., and Stos-Gale, Z. A., 2002. Sources of tin-is isotopic evidence likely to help?, in M. Bartelheim, E. Pernicka, R. Krause (eds.), *The Beginnings of Metallurgy in the Old World*, 291-302. Rahden/Westf.: Leidorf.

Ottaway, B. S., 2001. Innovation, production and specialization in early prehistoric copper metallurgy, *European Journal of Archaeology*, **4**, 87-112.

Overbeck, J. C., 1989. *Keos VII. Ayia Irini Period IV: The Stratigraphy and the Find Deposits*. Mainz on Rhine: Philipp von Zabern.

Papadatos, Y., 2003. "Ena palimpsisto, loipon…", in A. Vlachopoulos and K. Birtacha (eds.) *Argonautis, Timitikos Tomos gia ton Kathigiti Christo G. Douma*, 277-91. Athens: Kathimerini A. E.

Papadatos, G., Tsipopoulou, M., Bassiakos, Y., and Catapotis, M., 2004. The beginning of metallurgy in Crete: new evidence from the FN-EMI settlement at Kephala Petras, Siteia, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 36.

Papadimitriou, G. D., 2001. I exelixi ton kramaton ton chalkon ston Elladiko choro mechri to telos tis Geometrikis Epochis: kramatikes prosmixeis kai technologiki exelixi, in Y. Bassiakos, E. Aloupi, and Y. Facorellis (eds.), *Archaeometry Issues in Greek Prehistory and Antiquity*, 587-608. Athens: Hellenic Society of Archaeometry, Society of Messenian Archaeological Studies.

Papadimitriou, G. D. and Kordatos, I., 2001. Metallourgiki meleti archaion lithargyron apo tin periochi tou Lauriou, in Y. Bassiakos, E. Aloupi, and Y. Facorellis (eds.), *Archaeometry Issues in Greek Prehistory and Antiquity*, 679-695. Athens: Hellenic Society of Archaeometry, Society of Messenian Archaeological Studies.

Papadimitriou, G. D. and Fragiskos, A. Z., 2003. The study of ancient copper slags from Seriphos, *Book of Abstracts of the 4th Symposium on Archaeometry of the Hellenic Society for Archaeometry*, 139.

Papastamataki, A., 1998. Metallourgikes drastiriotites stin Kea kata tin arxaiotita: Neotera stoixeia, in L. G. Mendoni and A. J. Mazarakis Ainian (eds.), *Kea-Kythnos: History and Archaeology*, 759-766. Athens: Research Centre for Greek and Roman Antiquity- National Hellenic Research Foundation.

Papastavrou, S. E. and Zographos, Ch., 1979. *Ekthesi ton mexri tora apotelesmaton* *tis koitasmatologikis ereunas sti niso Serifo*, Unpublished report. Athens: IGME.

Papathanassopoulos, G. A., 1961-2. Kykladika Naxou, *Archaiologikon Deltion (Meletai)*, **17A**, 104-51.

Pare, C. F. E., 2000. Bronze and the Bronze Age, in C. F. E. Pare (ed.), *Metals Make the World Go Round: The Supply and Circulation of Metals in Bronze Age Europe*, 1-38. Oxford: Oxbow Books.

Perdikatsis, V. and Papastavrou, S., 1993. Non-metamict allanite from Serifos island, Cyclades (Greece), *Bulletin of the Geological Society of Greece*, **28**, (2), 13-21.

Perlès, C., 1987. *Les Industries Lithiques Taillées de Franchthi (Argolide, Grèce). I. Présentation Générale et Industries Paléolithiques* (Excavations at Franchthi Cave, Greece, Fascicle 3). Bloomington: Indiana University Press.

Perlès, C., 1990. *Les Industries Lithiques Taillées de Franchthi (Argolide, Grèce). II. Les Industries du Mésolithique et du Néolithique Initial* (Excavations at Franchthi Cave, Greece, Fascicle 5). Bloomington: Indiana University Press.

Pernicka, E., 1987. Erzlagerstätten in der Ägäis und ihre Ausbeutung im Altertum, *Jahrbuch des Römisch-Germanischen Zentralmuseums*, **34**, 607-714.

Pernicka, E., 1992. Comments...III, *Archaeometry*, **34**, 322-326.

Pernicka, E., 1993. Comments...III, *Archaeometry*, **35**, 259-262.

Pernicka, E., Wagner, G. A., Assimenos, K., Doumas, C., Begemann, F., and Todt, W., 1983. An analytical study of prehistoric lead and silver objects from the Aegean, in A. Aspinall and S. E. Warren (eds.), *Proceedings of the 22nd Symposium on Archaeometry*, 292-302. Bradford: University of Bradoford.

Pernicka, E., Lutz, C., Bachmann, H. –G., Wagner, G. A., Elitzsch, C, and Klein, E., 1985. Alte Blei-Silber-Verhüttung auf Sifnos, in G.A. Wagner and G. Weisgerber (eds.), *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3), 185-199. Bochum: Deutsches Bergbau-Museum.

Pernicka, E. and Wagner, G. A., 1985. Alte Goldgruben auf Sifnos, in G.A. Wagner and G. Weisgerber (eds.), *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3), 174-184. Bochum: Deutsches Bergbau-Museum.

Pernicka, E., Begemann, F., Schmitt-Strecker, S., and Grimanis, A., 1990. On the composition and provenance of metal artefacts from Poliochni on Lemnos, *Oxford Journal of Archaeology*, **9**, 263-297.

Pernicka, E., Rehren, Th., Schmitt-Strecker, S., 1998. Late Uruk silver production by cupellation at Habuba Kabira, Syria, in Th. Rehren, A. Hauptmann, and J. D. Muhly (eds.), *Metallurgica Antiqua* (Der Anschnitt, Beiheft 8), 123-134. Bochum: Deutsches Bergbau-Museum.

Philaniotou, O., 2004. Early copper production in the Aegean: the case of Seriphos, in *Aegean Metallurgy in Bronze Age, Book of Abstracts of an International Symposium held at the University of Crete between 19-21 November 2004*, 41.

Philaniotou-Hadjianastasiou, O., 2000. H Siphnos kata tin proimi epochi tou chalcou: i simvoli ton metallon, *Proceedings of the First Siphnian Symposium, Siphnos, 25-8 June 1998,* 201-218.

Pigott, V. C., 1999. Reconstructing the copper production process as practised among prehistoric mining/ metallurgical communities in the Khao Wong Prachan Valley of central Thailand, in S. M. M. Young, A. M. Pollard, P. Budd, and R. A. Ixer (eds.), *Metals in Antiquity*, 10-21. Oxford: Archaeopress.

Pigott, V. C., Weiss, A. D., and Natapintu, S., 1997. The archaeology of copper production: Excavations in the Khao Wong Prachan Valley, Central Thailand, in R. Ciarla and F. Rispoli (eds.), *South-East Asian Archaeology 1992*, 119-157. Rome: Instituto Italiano Per L'Africa e L'Oriente.

Pollard, A. M., Thomas, R. G., Williams, P. A., 1991. Some experiments concerning the smelting of arsenical copper, in P. Budd, B. Chapman, C. Jackson, R. Janaway, and B. Ottaway (eds.), *Archaeological Sciences 1989*, 169-74. Oxford: Oxbow Books.

Ramdohr, R., 1980. *The Ore Minerals and Their Intergrowths*. Frankfurt: Pergamon Press.

Rapp, G., 1999. Copper, tin, and arsenic sources in the Aegean Bronze Age, in P. P. Betancourt, V. Karageorghis, R. Laffineur, and W.-D. Niemeir, *Meletemata III*, 699-704. Liège: Université de Liège.

Reedy, C. L. and Reedy, T. J., 1988. Lead isotope analysis for provenance studies in the Aegean region: a re-evaluation, in E. V. Sayre, P. B. Vandiver, J. Druzik, and C. Stevenson (eds.), *Materials Issues in Art and Archaeology*, 65-70. Pittsburgh: Materials Research Society.

Reedy, T. J. and Reedy, C. L., 1991. Statistical analysis of lead isotope data in provenance studies, in P. B. Vandiver, J. Druzik, and G. S. Wheeler (eds.) *Materials Issues in Art and Archaeology II*, 39-48. Pittsburgh: Materials Research Society.

Reedy, T. J. and Reedy, C. L., 1992. Comments...IV, *Archaeometry*, **34**, 327-329.

Rehren, Th., 2003. Comments on J. L. Mass, M. T. Wypyski, and R. E. Stone, 'Malkata and Lisht glassmaking technologies: towards a specific link between second millennium BC metallurgists and glassmakers, Archaeometry, 44 (1) (2002), 67-82, and reply, *Archaeometry*, **45**, 185-198.

Rehren, Th., Hess, K., and Philip, G., 1996. Auriferous silver in western Asia: Ore or alloy?, *Historical Metallurgy*, **30**, 1-10.

Rehren, Th., Hess, K., and Philip, G., 1997. Fourth millennium BC copper metallurgy in northern Jordan: the evidence from Tell esh-Shuna, in H. G. K. Gebel, Z. Kafafi, and G. O. Rollefson (eds.), *The Prehistory of Jordan, II. Perspectives from 1997*, 625-640. Berlin: ex oriente.

Rehren, Th. And Kraus, 1999. Cupel and crucible: the refining of debased silver in the Colonia Ulpia Traiana, Xanten, *Journal of Roman Archaeology*, **12**, 263-272.

Rehren, Th., Vanhove, D., Mussche, H., and Oikonomakou, M., 1999. Litharge from Laurion: a medical and metallurgical commodity from South Attica, *L'antiquité Classique*, **68**, 299-308.

Renfrew, A. C., 1967. Cycladic metallurgy and the Aegean Early Bronze Age, *American Journal of Archaeology*, **71**, 1-20.

Renfrew, A. C., 1972. *The Emergence of Civilisation*. London: Methuen & Co.

Renfrew, A. C., 1978. Varna and the social context of early metallurgy, *Antiquity*, **52**, 199-203.

Renfrew, A. C., 1984a. From Pelos to Syros: Kapros grave D and the Kampos Group, in J. A. MacGillivray and R. L. N. Barber (eds.), *The Prehistoric Cyclades: Contributions to a Workshop on Cycladic Chronology*, 41-54. Edinburgh: Department of Classical Archaeology.

Renfrew, A. C., 1984b. Speculations on the use of Early Cycladic sculpture, in J. L. Fitton (ed.), *Cycladica: Studies in Memory of N. P. Goulandris*, 24-30. London: British Museum Publications.

Renfrew, A. C., 1986. Varna and the emergence of wealth in prehistoric Europe, in A. Appadurai (ed.), *The Social Life of Things: Commodities in Cultural Perspective*, 141-8. Cambridge: Cambridge University Press.

Renfrew, A. C., 1991. *The Cycladic Spirit: Masterpieces from the Nicholas P. Goulandris Foundation*. London: Thames and Hudson.

Renfrew, A. C. and Wagstaff, M., 1982. *An Island Polity. The Archaeology of Exploitation in Melos*. Cambridge: Cambridge University Press.

Rohl, B. and Needham, S., 1998. *The Circulation of Metal in the British Bronze Age: The Application of Lead Isotope Analysis*. London: The British Museum.

Rostoker, W., Pigott, V. C., and Dvorak, J. R., 1989. Direct reduction to copper metal by oxide-sulfide mineral interaction, *Archaeomaterials*, **3**, 69-87.

Rostoker, W. and Dvorak, J. R., 1991. Some experiments with co-smelting to copper alloys, *Archaeomaterials*, **5**, 5-20.

Rothenberg, B., 1988. *The Egyptian Mining Temple at Timna*. London: IAMS.

Rothenberg, B., 1999a. Archaeometallurgical researches in the southern Arabah 1050-1990. Part 1: Late pottery Neolithic to Early Bronze IV, *Palestine Exploration Quarterly*, **131**, 68-89.

Rothenberg, B., 1999b. Archaeometallurgical researches in the southern Arabah 1050-1990. Part 2: Egyptian New Kingdom (Ramesside) to Early Islam, *Palestine Exploration Quarterly*, **131**, 149-75.

Rutter, J. B., 1979. *Ceramic Change in the Aegean Early Bronze Age (The Kastri Group, Lefkandi I, and Lerna IV: A Theory Concerning the Origin of Early Helladic III Ceramics)* (UCLA Institute of Archaeology Occasional Paper 5). Los Angeles: UCLA Institute of Archaeology.

Rutter, J. B., 1983. Some observations on the Cyclades in the later third and early second millennia, *American Journal of Archaeology*, **87**, 69-76.

Rutter, J. B., 1984. The Early Cycladic III gap, in J. A. MacGillivray and R. L. N. Barber, (eds.), *The Prehistoric Cyclades: Contributions to a Workshop on Cycladic Chronology*, 95-107. Edinburgh: Department of Classical Archaeology, University of Edinburgh.

Salemink, J., 1980. On the geology and petrology of Seriphos island, (Cyclades, Greece), *Annales Géologiques des Pays Helléniques*, **30,** 342-365.

Salemink, J., 1985. *Skarn and ore formation at Seriphos, Greece as a consequence of granodiorite intrusion*. Alblasserdam: Offsetdrukkerij Kanters B.V.

Sampson, A., 2002. *The Neolithic Settlement at Ftelia, Mykonos*. Rhodes: University of the Aegean, Department of Mediterranean Studies.

Sampson, A., in press. I architektoniki sto neolithiko oikismo tis Ftelias Mykonou, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Sampson, A., Koslowski, J. K., Kaszanowska, M., and Giannouli, B., 2002. The Mesolithic settlement at Maroulas, Kythnos, *Mediterranean Archaeology and Archaeometry*, **2**, 45-67.

Sayre, E. V., Yener, K. A., Joel, E. C., and Barnes, I. L., 1992a. Statistical evaluation of the presently accumulated lead isotope data from Anatolia and surrounding regions, *Archaeometry*, **34**, 73-105.

Sayre, E. V., Yener, K. A., and Joel, E. C., 1992b. Reply, *Archaeometry*, **34**, 330-336.

Schneider, G., 1989. Investigation of crucibles and moulds from bronze foundries in

Olympia and Athens and determination of provenance of bronze statues, in Y. Maniatis (ed.), *Archaeometry*, 305-10. Amsterdam: Elsevier Science Publishers B. V..

Schofield, E., 1990. Evidence for household industries on Thera and Kea, in D. A. Hardy, C. G. Doumas, J. A. Sakellarakis, and P. M.Warren (eds.), *Thera and the Aegean World, III, vol. 1*, 201-211. London: The Thera Foundation.

Schreiner, M., Heimann, R. B., and Pernicka, E., 2003. Mineralogical and Geochemical Investigations into Prehistoric Smelting Slags From Tepe Sialk/ Central Iran, in *Archaeometallurgy in Europe, vol. 1*, 487-496. Milan: Associazione Italiana di Metallurgia.

Schwedt, A., Mommsen, H., and Zacharias, N., 2004. Post-depositional elemental alterations in pottery: Neutron Activation Analysis of surface samples, *Archaeometry*, **46**, 85–101.

Scott, V. D., Love, G., and Reed, S. J. B., 1995. *Quantitative Electron-Probe Microanalysis*. New York: Ellis Horwood.

Shennan, S. J., 1998. Producing copper in the eastern Alps during the second millennium BC, in A. B. Knapp, V. C. Pigott, and E. W. Herbert (eds.), *Social Approaches to an Industrial Past: The Archaeology and Anthropology of Mining*, 191-204. London: Routledge.

Shennan, S. J., 1999. Cost, benefit and value in the organisation of early European copper production, *Antiquity*, **73**, 352-63.

Sherratt, S., 2000. *Catalogue of Cycladic Antiquities in the Ashmolean Museum, The Captive Spirit, vol. 1. Text.* Oxford: Oxford University Press.

Shimada, I. and Merkel, J. F., 1991. Copper-alloy metallurgy in ancient Peru, *Scientific American*, 62-8.

Shortland, A. J., 2003. Comments II, *Archaeometry*, **45**, 190-1.

Shugar, A. N., 2000. *Archaeometallurgical Investigation of the Chalcolithic site of Abu Matar, Israel: A Reassessment of Technology and its Implications for the Ghassulian Culture*. Unpublished PhD Thesis. Institute of Archaeology, University College London.

Slater, E. A. and McKenzie, A., 1980. Late Bronze Age Aegean metallurgy in the light of the Thera analyses, in C. Doumas (ed.), *Thera and the Aegean World II*, 197-215. London: Thera and the Aegean World.

Sotirakopoulou, P., 1986. Early Cycladic pottery from Akrotiri, *Annual of the British School at Athens*, **81**, 297-312.

Sotirakopoulou, P. 1990. The earliest history of Akrotiri: the Late Neolithic and Early Bronze Age phases, in D. A. Hardy and A. C. Renfrew (eds.), *Thera and the Aegean World III, vol. 3. Chronology*, 41-47. London: Thera Foundation.

Sotirakopoulou, P., 1993. The chronology of the 'Kastri Group' reconsidered, *Annual of the British School at Athens*, **88**, 5-20.

Sotirakopoulou, P., in press(a). Akrotiri, Thera: The Late Neolithic and Early Bronze Age phases in the light of the recent excavations at the site, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Sotirakopoulou, P., in press(b). Kavos-Daskaleio, Keros: The pottery from the investigations of the 1960's, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Spitaels, P., 1982. Provatsa on Makronissos, *Athens Annals of Archaeology*, **15**, 155-158.

Spitaels, P., 1984. The Early Helladic Period in Mine No. 3, in H. F. Mussche, J. Bingen, J. Servais, and P. Spitaels (eds.), *Thorikos VIII 1972/1976*, 151-174. Gent: Comité des Fouilles Belges en Grèce.

Stos-Gale, Z. A., 1989. Cycladic copper metallurgy, in A. Hauptmann, E. Pernicka, and G. A. Wagner (eds.), *Old World Archaeometallurgy* (Der Anschnitt, Beiheft 7), 279-291. Bochum: Deutsches Bergbau-Museum.

Stos-Gale, Z. A., 1992. The origin of metal objects from the Early Bronze Age site of Thermi on the island of Lesbos, *Oxford Journal of Archaeology*, **11**, 155-177.

Stos-Gale, Z. A., 1993. The origin of metal used for making weapons in Early and Middle Minoan Crete, in C. Scarre and F. Healy (eds.), *Trade and Exchange in Prehistoric Europe*, 115-129. Oxford: Oxbow Books.

Stos-Gale, Z. A., 1998. The role of Kythnos and other Cycladic islands in the origins of Early Minoan metallurgy, in L. G. Mendoni and A. J. Mazarakis Ainian (eds.), *Kea-Kythnos: History and Archaeology*, 717-735. Athens: Research Centre for Greek and Roman Antiquity National Research Foundation.

Stos-Gale, Z. A., 2000. An overview of lead isotope data for provenance studies and the trade in metals in the Bronze Age Mediterranean, in C. F. E. Pare (ed.), *Metals Make the World Go Round: The Supply and Circulation of Metals in Bronze Age Europe*, 56-69. Oxford: Oxbow Books.

Stos-Gale, Z. A. and Gale, N. H., 1982. The sources of Mycenaean silver and lead, *Journal of Field Archaeology*, **9**, 467-485.

Stos-Gale, Z. A., Gale, N. H., and Gilmore, G. R., 1984. Early Bronze Age Trojan metal sources and Anatolians in the Cyclades, *Oxford Journal of Archaeology*, **3**, (3), 23-43.

Stos-Gale, Z. A., Gale, N. H., and Papastamataki, A., 1988. An Early Bronze Age smelting site on the Aegean island of Kythnos, in J. E. Jones (ed.), *Aspects of Ancient Mining and Metallurgy*, 23-30. Bangor: Classical Association, Bangor and North Wales Branch.

Stos-Gale, Z. A. and Gale, N. H., 1990. The role of Thera in the Bronze Age trade in metals, in D. A. Hardy, C. G. Doumas, J. A. Sakellarakis, and P. M. Warren (eds.), *Thera and the Aegean World III, vol.1*, 72-92. London: The Thera Foundation.

Stos-Gale, Z. A. and Macdonald, C. F., 1991. Sources of metals and trade in the Bronze Age Aegean, in N. H. Gale (ed.), *Bronze Age Trade in the Mediterranean*, 249-288. Jonsered: Paul Åströms Förlag.

Stos-Gale, Z. A., Gale, N. H., and Annetts, N., 1996. Lead isotope data from the isotrace laboratory, Oxford: Archaeometry data base 3, Ores from the Aegean, Part 1, *Archaeometry*, **38**, 381-390.

Stos-Gale, Z. A. and Gale, N. H., 2003. Lead isotopic and other isotopic research in the Aegean, in K. P. Foster and R. Laffineur (eds.), *Metron: Measuring the Aegean Bronze Age* (Aegaeum 24), 83-101. Liège and Austin: Université de Liège and University of Texas at Austin.

Televadou, C. A., in press. Strophilas-A Neolithic settlement on Andros, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Theochari, M. D., Parlama, L. Hadjipouliou, E., 1993. Kerameiki tis Proimis Chalkokratias III apo to Palamari tis Skyrou, in C. Zerner, P. Zerner, and J. Winder (eds.), *Wace and Blegen: Pottery as evidence for trade in the Aegean Bronze Age 1939-1989*, 187-193. Amsterdam: J. C. Gieben.

Theochari, M. D., Parlama, L., 1997. Palamari Skyrou: I ochiromeni poli tis Proimis Chalkokratias, in C. G. Doumas and V. La Rosa (eds.), *I Poliochni kai i*

*Proimi Epochi tou Chalkou sto Voreio Aigaio*, 344-356. Athens: Panepistimio Athinon, Tomeas Archaiologias kai Istorias tis Technis/ Scuola Archeologica di Atene.

Theocharis, D. R., 1951. Anaskaphi en Araphini, *Praktika tis en Athinais Archaiologikis Etaireias*, 77-92.

Theocharis, D. R., 1952. Anaskaphi en Araphini, *Praktika tis en Athinais Archaiologikis Etaireias*, 129-151.

Theocharis, D. R., 1953. Anaskaphi en Araphini, *Praktika tis en Athinais Archaiologikis Etaireias*, 105-118.

Theocharis, D. R., 1954. Anaskaphi en Araphini, *Praktika tis en Athinais Archaiologikis Etaireias*, 104-113.

Theocharis, D. R., 1955. Anaskaphi en Araphini, *Praktika tis en Athinais Archaiologikis Etaireias*, 109-117.

Tite, M. S., 1972. *Methods of Physical Examination in Archaeology*. London: Seminar Press.

Tite, M. S., Maniatis, Y., Meeks, N. D., Bimson, M., Hughes, M. J., and Leppard, S. C., 1982. Technological studies of ancient ceramics from the Near East, Aegean, and Southeast Europe, in T. A. Wertime and S. F. Wertime (eds.), *Early Pyrotechnology: The Evolution of the First Fire-Using Industries*, 61-71. Washington D. C.: Smithsonian Institution Press.

Tite, M. S., Freestone, I. C., Meeks, N. D., and Craddock, P. T., 1985. The examination of refractory ceramics from metal-production and metalworking sites, in P. Phillips (ed.), *The Archaeologist and the Laboratory*, 50-7. London: Council for British Archaeology.

Tite, M. S., Hughes, M. J., Freestone, I. C., Meeks, N. D., and Bimson, M., 1990. Technological characterisation of refractory ceramics from Timna, in B. Rothenberg (ed.), *The Ancient Metallurgy of Copper*, 158-75. London: IAMS.

Tsountas, C., 1898. Kykladika, *Archaiologiki Ephimeris,* **1898**, 137-212.

Tsountas, C., 1899. Kykladika II, *Archaiologiki Ephimeris*, **1899**, 73-134.

Tylecote, R. F., 1982. Metallurgical crucibles and crucible slags, in J. S. Olin and A. D. Franklin (eds.), *Archaeological ceramics*, 231-243.Washington D. C.: Smithsonian Institution Press.

Tylecote, R. F., Ghaznavi, H. A., and Boydell, P. J., 1977. Partitioning of trace elements between ores, fluxes, slags and metals during the smelting of copper, *Journal of Archaeological Science*, **4**, 305-333.

Varlas, I., 1998. *Seriphos: To Agnosto Nisi Enos Megalou Pontoporou.* Athens.

Vavelidis, M., Bassiakos, Y., Begemann, F., Patriarcheas, K., Pernicka, E., Schmitt-Strecker, S., Wagner, G. A., 1985. Geologie und Erzvorkommen, in G.A. Wagner and G. Weisgerber (eds.), *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3), 59-80. Bochum: Deutsches Bergbau-Museum.

Veldhuijzen, H. A., 2003. 'Slag_Fun'-A new tool for archaeometallurgy: Development of an analytical (P)ED-XRF method for iron-rich materials, *Papers from the Institute of Archaeology*, **14**, 102-118.

Wagner, G. A., Gentner, W., Gropengiesser, H., and Gale, N. H., 1980. Early Bronze Age lead-silver mining and metallurgy in the Aegean: The ancient workings on Siphnos, in P. T. Craddock (ed.), *Scientific Studies in Early Mining and Extractive Metallurgy* (British Museum Occasional Paper No. 20), 63-86. London: The British Museum.

Wagner, G. A. and Weisgerber, G., 1985. *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3). Bochum: Deutsches Bergbau-Museum.

Warren, P., 1976. Review of 'Aegean Metalwork of the Early and Middle Bronze Age', *The Antiquaries Journal*, **56**, 93-95.

Warren, P. and Hankey, V., 1989. *Aegean Bronze Age Chronology*. Bristol: Bristol Classical Press.

Watrous, L. V., 1994. Review of Aegean Prehistory III: Crete from earliest Prehistory through the Protopalatial Period, *American Journal of Archaeology*, **98**, 695-753.

Watt, I. M., 1997. *The Principles and Practise of Electron Microscopy*. Cambridge: Cambridge University Press.

Weisgerber, G., 1985. Bemerkungen zur prähistorischen und antiken Bergbautechnik, in G.A. Wagner and G. Weisgerber (eds.), *Silber, Blei und Gold auf Sifnos* (Der Anschnitt, Beiheft 3), 86-112. Bochum: Deutsches Bergbau-Museum.

Weisgerber, G., 2003. Spatial organisation of mining and smelting in Feinan, Jordan: mining archaeology beyond the history of technology, in P. T. Craddock and J. Lang (eds.), *Mining and Metal Production Through the Ages*, 76-89. London: The British Museum Press.

White, J. C. and Pigott, V. C., 1996. From community craft to regional specialization: intensification of copper production in pre-state Thailand, in B. Wailes (ed.), *Craft Specialization and Social Evolution: in Memory of V. Gordon Childe*, 151-75. Philadelphia: The University Museum of Archaeology and Anthropology University of Pennsylvania.

Whitelaw, T., 2000. Settlement instability and landscape degradation in the southern Aegean in the third millennium BC, in P. Halstead and C. Frederick (eds.), *Landscape and Land Use in Postglacial Greece* (Sheffield Studies in Aegean Archaeology, 3), 135-161. Sheffield: Sheffield Academic Press.

Whitelaw, T., 2003. Investigating site diversity in the Early Bronze Age Aegean, *Archaeology International 2002/2003, Annual Publication of the Institute of Archaeology, University College London*, 29-32.

Wilson, D. E., 1987. Kea and East Attike in Early Bronze II: Beyond pottery typology, in J. M. Fossey (ed.), *Syneisfora McGill I, Papers in Greek Archaeology and History in Memory of Colin D. Gordon*, 35-49. Amsterdam: J. C. Gieben.

Wilson, D. E., 1999. *Keos IX. Ayia Irini: Periods I-III. The Neolithic and Early Bronze Age Settlements*. Mainz am Rhein: Verlag Philipp von Zabern.

Wilson, D. E., Day, P. M., and Dimopoulou, N., in press. The gateway of Poros-Katsambas: Trade and exchange between north-central Crete and the Cyclades in EBI-II, paper delivered to the conference 'Orizon: A Colloquium on the Prehistory of the Cyclades' (2004).

Wingrove, J., 1970. Identification of iron oxides, *Journal of the Iron and Steel Institute*, **208**, 258-264.

Wintle, A.G., 1997. Luminescence dating. Laboratory procedures and protocols, *Rad. Meas.*, **27**, 769-817.

Yazawa, A., 1980. Distribution of various elements between copper, matte and slag, *Erzmetall*, **33**, 377-382.

Yener, K. A., 2000. *The Domestication of Metals*. Leiden: Brill.

Zacharias, N., Buxeda i Garrigós, J., Mommsen, H., Schwedt, A., Kilikoglou, V., 2005. Implications of burial alterations on luminescence dating of archaeological ceramics, *Journal of Archaeological Science*, **32**, 49-57.

Zacharias, N., Michael, C. T., Philaniotou-Hadjianastasiou, O., Hein, A., and Bassiakos, Y., forthcoming. Fine-grain TL dating of archaeometallurgical furnace walls, *Journal of Cultural Heritage* (submitted).

Zachos, K., 1951.Geomagnitiki erevna sti niso Seripho, *The mineral wealth of Greece*, **1**, 129-152.

Zachos, K, L. 1990. The Neolithic period in Naxos, in L. Marangou (ed.), *Cycladic Culture: Naxos in the 3rd Millennium BC*, 29-38. Athens: N. P. Goulandris Foundation Museum of Cycladic Art.

Zachos, K. L., 1996a. The Zas Cave, in G. A. Papathanassopoulos (ed.), *Neolithic Culture in Greece*, 88-89. Athens: N. P. Goulandris Foundation.

Zachos, K. L., 1996b. Metallurgy, in G. A. Papathanassopoulos (ed.), *Neolithic Culture in Greece*, 140-143. Athens: N. P. Goulandris Foundation.

Zachos, K. L., 1999. Zas cave on Naxos and the role of caves in the Aegean Late Neolithic, in P. Halstead (ed.), *Neolithic Society in Greece*, 153-163. Sheffield: Sheffield Academic Press.

Zachos, K. L. and Douzougli, A., 1999. Aegean metallurgy: How early and how independent?, in P. P. Betancourt, V. Karageoris, R. Laffineur, and W.-D. Niemeier (eds), *Meletemata III*, Liège: Université de Liège.

Zapheiropoulou, P., 1967. Archaiotites kai mnimeia Samou kai Kykladon: Keros, *Archaiologikon Deltion (Chronica)*, **22B**, 466.

Zapheiropoulou, P., 1968. Kyklades: anaskaphikai erevnai-periodeiai: Keros, *Archaiologikon Deltion (Chronica)*, **23B**, 381.

Zapheiropoulou, P., 1975. Ostraka ek Kerou, *Athens Annuals of Archaeology*, **8**, 79-85.

Zwicker, U., Greiner, H., Hofmann, K.-H., and Reithinger, M., 1985. Smelting, refining and alloying of copper and copper alloys in crucible furnaces during prehistoric up to Roman times, in P. T. Craddock and M. J. Hughes (eds.), *Furnaces and Smelting Technology in Antiquity* (British Museum Occasional Paper No. 48), 103-115. London: The British Museum.

# APPENDIX 1.

## Analyses of Certified Reference Materials on the x-ray fluorescence spectrometer, the scanning electron microscope, and the electron microprobe used in this thesis

A set of Certified Reference Materials (CRMs) were selected from a collection available at the Wolfson Laboratories of the Institute of Archaeology (UCL) to test the performance of the instruments used. The specific materials were selected to represent the range of elements and compositions encountered in the metallurgical remains examined. Unavoidably, the selection of specific materials was largely dependant on availability. Table A1.1 gives the list of CRMs used in this study, their nature and the instrument on which they were analysed. The samples used can be divided into two types: silica-rich (first seven samples in Table A1.1) and iron-rich materials, representing the two major components present in the analysed slags, with varying amounts of the other gangue oxides.

The samples were prepared for analysis as described in section 3.6 for each instrument (pellets for XRF and mounted sections for SEM and EPMA), with two exceptions. All the iron-rich materials in the reference collection are only available as powders and could not be analysed as polished sections on the electron microscopes. In order to examine the performance of the EDS-SEM against iron-rich materials, very important in the analyses of slag phases, a small amount of two of these powders (ECRM676-1 and FER4) was pressed on to a pellet and mounted on an aluminium stub. The basalt standards (BIR-1, BCR-2, and BHVO-2) were available both as powders and as fused glasses and both pellets and mounted sections could be prepared.

Tables A1.2, A1.3, and A1.4 give the results of analyses of CRMs on the three different instruments used together with the certified analysis for each specimen. Two CRMs were run consistently with every set of analyses on the EDS-SEM and the WDS-EPMA. The corresponding results were produced over a period of approximately two years. Three CRMs were run with every set of unknowns on the (P)ED-XRF. The data presented were accumulated over a period of approximately four months.

The reference material Swedish Slag W-25:R has been analysed by a number of independent laboratories using a range of instruments and the results are presented fully by Kresten and Hjärthner-Holdar (2001). The values used for comparison in the following tables are the mean values reported. The authors note that significant differences were reported between laboratories for elements such as chromium, cobalt, nickel, copper, and zinc, which may be attributed to partial heterogeneity of the reference material with respect to these components. The mean values given for these elements are reported in Tables A1.4a and A1.4b followed by an asterisk (*) to highlight potential problems.

***Table A1.1** Certified Reference Materials (CRMs) used in this thesis, their description, and the instruments on which they were analysed.*

| **CRM name** | **Description** | **Instrument** |
|---|---|---|
| **BIR-1** | Basalt Icelandic | EPMA |
| **BCR-2** | Basalt Col. River | EPMA, SEM, XRF |
| **BHVO-2** | Basalt Hawaian Volcanic | EPMA, SEM |
| **Glass A** | Glass (Corning) | EPMA |
| **Glass B** | Glass (Corning) | EPMA |
| **Glass C** | Glass (Corning) | EPMA |
| **Glass D** | Glass (Corning) | EPMA |
| **ECRM676-1** | Iron ore sinter | SEM |
| **ECRM681-1** | Iron ore | XRF |
| **FER-2** | Iron ore | XRF |
| **FER-4** | Iron ore | SEM |
| **Swedish Slag W-25:R** | Ancient iron slag | XRF |

***Table A1.2** Analyses of CRMs on the EDS-SEM JEOL JSM-35CF (weight %). Sample names followed by (A) are averages of all the analyses, (AN) are averages normalised to the sum of the certified analysis, and rows in bold correspond to the certified analysis accompanying each specimen (b.d.l.: below detection limit, n.r.: not reported). Highlighted values should be read as elements instead of oxides.*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FER4 | b.d.l. | 1.21 | 1.86 | 43.3 | b.d.l. | 0.27 | 0.34 | 2.45 | b.d.l. | b.d.l. | 0.37 | 0.23 | 28.4 | 78.4 |
| FER4 | b.d.l. | 1.26 | 1.70 | 42.1 | b.d.l. | 0.25 | 0.31 | 3.03 | b.d.l. | b.d.l. | 0.66 | 0.31 | 27.6 | 77.2 |
| FER4 | b.d.l. | 1.19 | 1.30 | 44.7 | b.d.l. | 0.38 | 0.17 | 3.05 | b.d.l. | b.d.l. | 0.55 | 0.19 | 27.3 | 78.8 |
| FER4 | b.d.l. | 1.32 | 1.48 | 39.7 | b.d.l. | 0.41 | 0.16 | 2.16 | b.d.l. | b.d.l. | 0.27 | 0.16 | 34.1 | 79.7 |
| FER4(A) | b.d.l. | 1.25 | 1.59 | 42.4 | b.d.l. | 0.33 | 0.25 | 2.67 | b.d.l. | b.d.l. | 0.46 | 0.22 | 29.3 | 78.5 |
| FER4(AN) | b.d.l. | 1.52 | 1.94 | 52.0 | b.d.l. | 0.40 | 0.30 | 3.27 | b.d.l. | b.d.l. | 0.57 | 0.27 | 35.9 | 96.2 |
| **FER4** | **0.05** | **1.41** | **1.70** | **50.1** | **0.13** | **0.11** | **0.29** | **2.23** | **0.07** | **n.r.** | **n.r.** | **0.19** | **40.0** | **96.2** |
| | | | | | | | | | | | | | | |
| ECRM676-1 | b.d.l. | 1.23 | 5.41 | 13.7 | 1.36 | 0.41 | 0.52 | 19.0 | 0.28 | 0.17 | b.d.l. | 0.88 | 46.8 | 88.5 |
| ECRM676-1 | b.d.l. | 1.24 | 5.39 | 13.8 | 1.43 | 0.41 | 0.57 | 19.6 | 0.28 | 0.13 | b.d.l. | 0.92 | 46.2 | 88.7 |
| ECRM676-1 | b.d.l. | 1.21 | 5.37 | 14.1 | 1.43 | 0.36 | 0.48 | 19.7 | 0.27 | 0.14 | b.d.l. | 0.87 | 46.4 | 89.1 |
| ECRM676-1 | b.d.l. | 1.26 | 5.28 | 13.3 | 1.39 | 0.45 | 0.51 | 18.9 | 0.22 | 0.15 | b.d.l. | 0.91 | 47.3 | 88.3 |
| ECRM676-1 | b.d.l. | 1.03 | 4.81 | 12.2 | 1.34 | 0.41 | 0.52 | 18.4 | 0.17 | 0.17 | b.d.l. | 0.86 | 44.9 | 83.8 |
| ECRM676-1 | b.d.l. | 1.12 | 4.94 | 13.4 | 1.21 | 0.33 | 0.52 | 17.5 | 0.22 | 0.14 | b.d.l. | 0.89 | 44.7 | 83.8 |
| ECRM676-1 | b.d.l. | 1.02 | 5.21 | 11.9 | 1.42 | 0.30 | 0.45 | 17.7 | 0.20 | 0.19 | b.d.l. | 0.85 | 45.2 | 83.4 |
| ECRM676-1 | b.d.l. | 1.05 | 4.53 | 11.6 | 1.20 | 0.37 | 0.41 | 18.9 | 0.23 | 0.16 | b.d.l. | 0.94 | 44.2 | 82.5 |
| ECRM676-1(A) | b.d.l. | 1.15 | 5.12 | 13.0 | 1.35 | 0.38 | 0.50 | 18.7 | 0.23 | 0.16 | b.d.l. | 0.89 | 45.7 | 86.0 |
| ECRM676-1(AN) | b.d.l. | 1.34 | 5.98 | 15.2 | 1.57 | 0.44 | 0.58 | 21.8 | 0.27 | 0.18 | b.d.l. | 1.04 | 53.4 | 100 |
| **ECRM676-1** | **0.13** | **1.92** | **6.42** | **13.7** | **1.35** | **0.30** | **0.52** | **17.9** | **0.32** | **0.12** | **n.r.** | **1.08** | **56.8** | **100** |

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | |
| BHVO-2 | 2.30 | 5.75 | 10.9 | 42.7 | b.d.l. | b.d.l. | 0.47 | 10.6 | 2.55 | b.d.l. | b.d.l. | b.d.l. | 11.5 | 86.8 |
| BHVO-2 | 2.34 | 5.73 | 10.7 | 41.7 | b.d.l. | b.d.l. | 0.37 | 10.4 | 2.58 | b.d.l. | b.d.l. | b.d.l. | 11.2 | 85.1 |
| BHVO-2 | 2.43 | 5.96 | 11.2 | 43.6 | b.d.l. | b.d.l. | 0.42 | 10.6 | 2.67 | b.d.l. | b.d.l. | 0.18 | 11.4 | 88.5 |
| BHVO-2 | 2.41 | 5.95 | 11.1 | 43.3 | b.d.l. | b.d.l. | 0.37 | 10.7 | 2.57 | b.d.l. | b.d.l. | 0.15 | 11.4 | 88.0 |
| BHVO-2 | 1.70 | 5.79 | 11.1 | 43.7 | b.d.l. | b.d.l. | 0.39 | 10.9 | 2.68 | b.d.l. | 0.15 | 0.10 | 11.8 | 88.3 |
| BHVO-2 | 1.66 | 5.88 | 11.2 | 44.0 | b.d.l. | b.d.l. | 0.42 | 11.0 | 2.68 | b.d.l. | 0.17 | 0.14 | 11.9 | 89.1 |
| BHVO-2 | 1.75 | 5.74 | 11.0 | 43.1 | b.d.l. | b.d.l. | 0.36 | 10.6 | 2.52 | b.d.l. | 0.24 | 0.17 | 11.4 | 86.9 |
| BHVO-2 | 1.72 | 5.69 | 11.0 | 42.9 | b.d.l. | b.d.l. | 0.35 | 10.5 | 2.58 | b.d.l. | 0.26 | 0.12 | 11.4 | 86.5 |
| BHVO-2 | 1.78 | 5.62 | 10.7 | 41.9 | b.d.l. | b.d.l. | 0.38 | 10.4 | 2.51 | b.d.l. | 0.27 | 0.14 | 11.1 | 84.8 |
| BHVO-2 | 1.64 | 5.68 | 10.9 | 42.6 | b.d.l. | b.d.l. | 0.44 | 10.7 | 2.54 | b.d.l. | 0.15 | 0.15 | 11.4 | 86.2 |
| BHVO-2 | 1.62 | 5.59 | 10.8 | 42.8 | b.d.l. | b.d.l. | 0.41 | 10.9 | 2.57 | b.d.l. | 0.16 | 0.09 | 11.7 | 86.6 |
| BHVO-2 | 1.89 | 5.55 | 10.9 | 43.4 | b.d.l. | b.d.l. | 0.50 | 10.9 | 2.61 | b.d.l. | b.d.l. | b.d.l. | 11.5 | 87.4 |
| BHVO-2 | 1.65 | 5.46 | 10.6 | 41.8 | b.d.l. | b.d.l. | 0.35 | 10.5 | 2.53 | b.d.l. | b.d.l. | 0.11 | 11.3 | 84.4 |
| BHVO-2 | 2.47 | 5.97 | 11.1 | 43.5 | b.d.l. | b.d.l. | 0.44 | 11.0 | 2.62 | b.d.l. | b.d.l. | 0.16 | 11.8 | 89.1 |
| BHVO-2 | 2.70 | 6.39 | 11.6 | 45.4 | b.d.l. | b.d.l. | 0.52 | 11.3 | 2.63 | b.d.l. | b.d.l. | b.d.l. | 12.0 | 92.6 |
| BHVO-2 | 2.62 | 6.26 | 11.6 | 45.2 | b.d.l. | b.d.l. | 0.48 | 11.2 | 2.67 | b.d.l. | b.d.l. | 0.18 | 12.0 | 92.2 |
| BHVO-2 | 2.21 | 5.79 | 11.0 | 43.5 | b.d.l. | b.d.l. | 0.45 | 11.0 | 2.72 | b.d.l. | b.d.l. | b.d.l. | 12.0 | 88.8 |
| BHVO-2 | 2.19 | 5.77 | 10.9 | 43.5 | b.d.l. | b.d.l. | 0.45 | 10.8 | 2.70 | b.d.l. | b.d.l. | 0.14 | 11.7 | 88.2 |
| BHVO-2 | 2.29 | 6.00 | 11.3 | 44.7 | b.d.l. | b.d.l. | 0.48 | 11.1 | 2.67 | b.d.l. | b.d.l. | 0.22 | 11.9 | 90.9 |
| BHVO-2 | 2.26 | 6.08 | 11.3 | 45.0 | b.d.l. | b.d.l. | 0.44 | 11.2 | 2.68 | b.d.l. | b.d.l. | b.d.l. | 12.0 | 90.9 |
| BHVO-2 | 2.50 | 6.04 | 11.3 | 44.4 | b.d.l. | b.d.l. | 0.45 | 10.8 | 2.57 | b.d.l. | b.d.l. | 0.17 | 11.6 | 89.8 |
| BHVO-2 | 2.55 | 6.01 | 11.2 | 43.9 | b.d.l. | b.d.l. | 0.44 | 10.8 | 2.53 | b.d.l. | b.d.l. | 0.11 | 11.5 | 89.0 |
| BHVO-2 | 2.40 | 6.00 | 11.1 | 43.4 | b.d.l. | b.d.l. | 0.43 | 10.7 | 2.60 | b.d.l. | b.d.l. | 0.15 | 11.4 | 88.3 |
| BHVO-2 | 2.23 | 6.00 | 11.4 | 44.9 | b.d.l. | b.d.l. | 0.47 | 10.9 | 2.65 | b.d.l. | b.d.l. | 0.18 | 11.6 | 90.4 |
| BHVO-2 | 2.19 | 5.98 | 11.3 | 44.8 | b.d.l. | b.d.l. | 0.45 | 10.9 | 2.66 | b.d.l. | b.d.l. | b.d.l. | 11.9 | 90.2 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BHVO-2 | 2.18 | 5.67 | 11.0 | 43.7 | b.d.l. | b.d.l. | 0.46 | 10.6 | 2.57 | b.d.l. | b.d.l. | b.d.l. | 11.5 | 87.7 |
| BHVO-2 | 2.21 | 5.83 | 11.1 | 44.0 | b.d.l. | b.d.l. | 0.43 | 10.7 | 2.51 | b.d.l. | b.d.l. | b.d.l. | 11.4 | 88.2 |
| BHVO-2(A) | 2.14 | 5.86 | 11.1 | 43.6 | b.d.l. | b.d.l. | 0.43 | 10.8 | 2.61 | b.d.l. |  |  | 11.6 | 88.3 |
| BHVO-2(AN) | 2.43 | 6.65 | 12.6 | 49.5 | b.d.l. | b.d.l. | 0.49 | 12.3 | 2.96 | b.d.l. |  |  | 13.2 | 100 |
| **BHVO-2** | **2.22** | **7.23** | **13.5** | **49.9** | **0.27** | **n.r.** | **0.52** | **11.4** | **2.73** | **0.03** | **0.03** | **0.13** | **12.3** | **100** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| BCR-2 | 2.92 | 2.87 | 10.6 | 45.2 | b.d.l. | b.d.l. | 1.47 | 6.47 | 2.16 | b.d.l. | b.d.l. | 0.12 | 12.4 | 84.2 |
| BCR-2 | 3.08 | 2.98 | 11.3 | 47.8 | b.d.l. | b.d.l. | 1.67 | 6.78 | 2.14 | b.d.l. | b.d.l. | 0.24 | 13.0 | 89.0 |
| BCR-2 | 3.18 | 3.06 | 11.4 | 48.5 | b.d.l. | b.d.l. | 1.72 | 6.87 | 2.24 | b.d.l. | b.d.l. | 0.18 | 13.3 | 90.5 |
| BCR-2 | 3.19 | 3.05 | 11.3 | 48.4 | b.d.l. | b.d.l. | 1.69 | 6.90 | 2.29 | b.d.l. | b.d.l. | 0.29 | 13.5 | 90.7 |
| BCR-2 | 3.24 | 3.15 | 11.6 | 49.5 | b.d.l. | b.d.l. | 1.71 | 7.09 | 2.36 | b.d.l. | b.d.l. | 0.20 | 13.9 | 92.7 |
| BCR-2 | 2.28 | 2.81 | 11.1 | 47.2 | b.d.l. | b.d.l. | 1.51 | 6.56 | 2.21 | b.d.l. | 0.20 | 0.17 | 13.0 | 87.0 |
| BCR-2 | 2.25 | 2.79 | 11.0 | 46.7 | b.d.l. | 0.41 | 1.56 | 6.57 | 2.17 | b.d.l. | 0.16 | 0.13 | 12.9 | 86.6 |
| BCR-2 | 2.16 | 2.76 | 10.9 | 46.4 | b.d.l. | 0.42 | 1.53 | 6.49 | 2.13 | b.d.l. | 0.17 | 0.18 | 12.6 | 85.8 |
| BCR-2 | 2.16 | 2.73 | 11.0 | 47.2 | b.d.l. | b.d.l. | 1.63 | 6.71 | 2.23 | b.d.l. | 0.12 | 0.13 | 13.3 | 87.1 |
| BCR-2(A) | 2.72 | 2.91 | 11.1 | 47.4 | b.d.l. |  | 1.61 | 6.72 | 2.21 | b.d.l. |  | 0.19 | 13.1 | 88.6 |
| BCR-2(AN) | 3.07 | 3.29 | 12.6 | 53.6 | b.d.l. |  | 1.82 | 7.59 | 2.50 | b.d.l. |  | 0.21 | 14.8 | 99.9 |
| **BCR-2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **n.r.** | **1.79** | **7.12** | **2.26** | **0.04** | **0.00** | **0.15** | **13.8** | **99.9** |

***Table A1.3*** *Analyses of CRMs on the WDS-EPMA JEOL SUPERPROBE JXA-8600 (weight %). Sample names followed by (A) are averages of all the analyses and rows in bold correspond to the certified analysis accompanying each specimen (b.d.l.: below detection limit, n.r.: not reported, n. a.: not analysed). Highlighted values should be read as elements instead of oxides.*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | NiO | CuO | $SnO_2$ | $Sb_2O_5$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BIR-1 | 1.94 | 9.71 | 16.0 | 47.3 | n.a. | b.d.l. | 13.5 | 0.96 | 0.17 | 10.2 | 0.01 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.9 |
| BIR-1 | 2.19 | 9.96 | 15.9 | 47.6 | n.a. | b.d.l. | 13.5 | 0.95 | 0.15 | 11.4 | 0.04 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 102 |
| BIR-1 | 1.82 | 9.67 | 15.1 | 45.4 | n.a. | b.d.l. | 13.7 | 0.87 | 0.16 | 11.3 | n.a. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98.1 |
| BIR-1 | 1.78 | 9.75 | 15.3 | 45.8 | n.a. | b.d.l. | 13.5 | 0.90 | 0.16 | 11.4 | n.a. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98.6 |
| BIR-1 | 1.88 | 9.88 | 15.2 | 46.2 | n.a. | b.d.l. | 13.7 | 0.89 | 0.19 | 11.5 | n.a. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.5 |
| BIR-1 | 1.75 | 9.58 | 16.0 | 48.1 | 0.03 | b.d.l. | 13.5 | 0.96 | 0.18 | 10.7 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BIR-1(A) | 1.87 | 9.73 | 15.7 | 46.9 | | b.d.l. | 13.6 | 0.93 | 0.17 | 11.0 | | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.9 |
| **BIR-1** | **1.82** | **9.70** | **15.5** | **48.0** | **0.02** | **0.03** | **13.3** | **0.96** | **0.18** | **11.3** | **0.02** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **101** |
| | | | | | | | | | | | | | | | | |
| BHVO-2 | 2.60 | 7.33 | 14.2 | 50.8 | n.a. | 0.43 | 11.8 | 2.76 | 0.14 | 10.6 | 0.03 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BHVO-2 | 2.27 | 7.01 | 13.9 | 50.2 | n.a. | 0.46 | 11.7 | 2.67 | 0.16 | 11.7 | 0.03 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| BHVO-2 | 2.29 | 7.30 | 13.9 | 51.2 | n.a. | 0.41 | 11.7 | 2.83 | 0.16 | 11.1 | 0.02 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BHVO-2 | 2.17 | 6.87 | 14.0 | 50.1 | 0.30 | 0.43 | 11.5 | 2.75 | 0.18 | 11.7 | 0.02 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| BHVO-2 | 2.24 | 7.12 | 14.1 | 50.5 | 0.29 | 0.48 | 11.6 | 2.76 | 0.19 | 11.6 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BHVO-2 | 2.17 | 7.24 | 14.0 | 50.5 | 0.29 | 0.44 | 11.6 | 2.75 | 0.17 | 11.4 | 0.01 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BHVO-2 | 2.17 | 7.18 | 14.1 | 50.4 | 0.26 | 0.45 | 11.6 | 2.71 | 0.16 | 11.5 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BHVO-2(A) | 2.27 | 7.15 | 14.0 | 50.5 | 0.29 | 0.44 | 11.6 | 2.75 | 0.16 | 11.4 | | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| **BHVO-2** | **2.22** | **7.23** | **13.5** | **49.9** | **0.27** | **0.52** | **11.4** | **2.73** | **0.13** | **12.3** | **0.01** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **100** |
| | | | | | | | | | | | | | | | | |

|  | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | P$_2$O$_5$ | K$_2$O | CaO | TiO$_2$ | MnO | Fe$_2$O$_3$ | NiO | CuO | SnO$_2$ | Sb$_2$O$_5$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BCR-2 | 1.81 | 3.72 | 14.3 | 55.4 | n.a. | 1.62 | 7.47 | 2.21 | 0.18 | 13.2 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.9 |
| BCR-2 | 1.83 | 3.62 | 14.6 | 56.2 | n.a. | 1.42 | 7.42 | 2.32 | 0.17 | 13.7 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BCR-2 | 2.11 | 3.58 | 14.0 | 51.5 | n.a. | 1.57 | 7.31 | 2.12 | 0.19 | 14.3 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 96.7 |
| BCR-2 | 2.11 | 3.83 | 14.3 | 51.6 | n.a. | 1.62 | 7.43 | 2.26 | 0.13 | 15.2 | 0.03 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98.5 |
| BCR-2 | 2.07 | 3.54 | 14.5 | 55.4 | n.a. | 1.65 | 7.43 | 2.14 | 0.18 | 15.1 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 102 |
| BCR-2 | 2.03 | 3.75 | 13.8 | 55.2 | n.a. | 1.67 | 7.45 | 2.23 | 0.19 | 13.5 | 0.06 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99.9 |
| BCR-2 | 2.05 | 3.70 | 13.7 | 55.2 | n.a. | 1.59 | 7.43 | 2.23 | 0.20 | 14.0 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| BCR-2 | 1.67 | 3.64 | 13.6 | 54.7 | n.a. | 1.48 | 7.43 | 2.29 | 0.18 | 13.7 | 0.05 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98.7 |
| BCR-2 | 2.64 | 3.74 | 13.5 | 53.4 | n.a. | 1.69 | 7.59 | 2.20 | 0.15 | 14.0 | n.a. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 98.8 |
| BCR-2 | 3.08 | 3.55 | 14.0 | 55.4 | 0.40 | 1.69 | 7.30 | 2.31 | 0.20 | 13.0 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BCR-2 | 3.03 | 3.60 | 14.0 | 55.2 | 0.37 | 1.76 | 7.31 | 2.29 | 0.20 | 12.8 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BCR-2 | 3.16 | 3.57 | 14.1 | 55.2 | 0.45 | 1.75 | 7.26 | 2.27 | 0.18 | 13.3 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 101 |
| BCR-2(A) | 2.30 | 3.65 | 14.0 | 54.5 | 0.41 | 1.63 | 7.40 | 2.24 | 0.17 | 13.8 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| **BCR-2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **1.79** | **7.12** | **2.26** | **0.15** | **13.8** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **100** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| GlassA | 14.4 | 2.62 | 0.86 | 66.8 | 0.11 | 2.96 | 5.12 | 0.82 | 1.01 | 0.98 | b.d.l. | 1.05 | 0.19 | 1.61 | 0.11 | 98.5 |
| GlassA | 14.3 | 2.59 | 0.97 | 67.5 | 0.11 | 2.91 | 5.09 | 0.85 | 1.01 | 1.02 | 0.05 | 1.08 | 0.25 | 1.49 | 0.06 | 99.2 |
| GlassA | 14.4 | 2.60 | 0.95 | 66.7 | 0.08 | 2.85 | 5.02 | 0.78 | 1.00 | 1.05 | 0.01 | 1.15 | 0.20 | 1.57 | 0.01 | 98.3 |
| GlassA(A) | 14.4 | 2.60 | 0.93 | 67.0 | 0.10 | 2.91 | 5.08 | 0.82 | 1.01 | 1.02 |  | 1.09 | 0.21 | 1.56 | 0.06 | 98.6 |
| **GlassA** | **14.3** | **2.66** | **1.00** | **67.0** | **0.13** | **2.87** | **5.03** | **0.79** | **1.00** | **1.09** | **0.00** | **1.17** | **0.19** | **1.75** | **0.12** | **99.9** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| GlassB | 17.2 | 1.01 | 4.30 | 62.4 | 0.77 | 1.04 | 8.90 | 0.09 | 0.19 | 0.36 | 0.09 | 2.41 | 0.02 | 0.33 | 0.45 | 99.5 |
| **GlassB** | **17.0** | **1.03** | **4.36** | **62.3** | **0.82** | **1.00** | **8.56** | **0.09** | **0.25** | **0.34** | **0.10** | **2.66** | **0.04** | **0.46** | **0.61** | **99.8** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| GlassC | 1.03 | 2.64 | 0.87 | 34.7 | 0.11 | 3.17 | 5.48 | 1.25 | b.d.l. | 0.23 | 0.08 | 1.12 | 0.18 | b.d.l. | 36.7 | 87.6 |
| **GlassC** | **1.07** | **2.76** | **0.87** | **36.2** | **0.14** | **2.84** | **5.07** | **0.79** | **0.00** | **0.34** | **0.00** | **1.13** | **0.19** | **0.03** | **36.7** | **88.1** |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | NiO | CuO | $SnO_2$ | $Sb_2O_5$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| GlassD | 1.33 | 3.86 | 5.23 | 54.7 | 4.20 | 11.7 | 15.2 | 0.41 | 0.57 | 0.49 | b.d.l. | 0.31 | 0.07 | 0.69 | 0.20 | 98.9 |
| GlassD | 1.36 | 3.83 | 5.29 | 55.4 | 4.24 | 11.9 | 15.4 | 0.41 | 0.49 | 0.53 | b.d.l. | 0.29 | 0.06 | 0.69 | 0.25 | 100 |
| GlassD(A) | 1.35 | 3.85 | 5.26 | 55.1 | 4.22 | 11.8 | 15.3 | 0.41 | 0.53 | 0.51 | b.d.l. | 0.30 | 0.06 | 0.69 | 0.22 | 99.5 |
| **GlassD** | **1.20** | **3.94** | **5.30** | **55.5** | **3.93** | **11.3** | **14.8** | **0.38** | **0.55** | **0.52** | **0.00** | **0.38** | **0.10** | **0.97** | **0.48** | **99.9** |

***Table A1.4a*** *Analyses of CRMs using the Cu_Slag method on the (P)ED-XRF Spectro X-Lab Pro2000 (major and minor elements in weight %). Sample names followed by (A) are averages of all the analyses, (AN) are averages normalised to the sum of the certified analysis, and rows in bold correspond to the certified analysis accompanying each specimen (n.r.: not reported). Highlighted values should be read as elements instead of oxides, values followed with an asterisk are elements noted as potentially problematic (see above).*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$P_2O_5$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **$V_2O_5$** | **$Cr_2O_3$** | **MnO** | **$Fe_2O_3$** | **Sum** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BCR-2 | 2.63 | 2.22 | 14.9 | 51.6 | 0.25 | 0.01 | 1.81 | 6.67 | 2.16 | 0.07 | 0.00 | 0.17 | 13.2 | 95.7 |
| BCR-2 | 3.01 | 2.17 | 15.0 | 52.0 | 0.24 | 0.01 | 1.83 | 6.68 | 2.17 | 0.06 | 0.00 | 0.17 | 13.2 | 96.6 |
| BCR-2 | 2.77 | 2.13 | 14.8 | 51.5 | 0.23 | 0.01 | 1.80 | 6.62 | 2.15 | 0.07 | 0.00 | 0.17 | 13.1 | 95.3 |
| BCR-2 | 2.79 | 2.20 | 14.8 | 51.9 | 0.26 | 0.01 | 1.83 | 6.66 | 2.18 | 0.07 | 0.00 | 0.18 | 13.2 | 96.1 |
| BCR-2 | 2.84 | 2.14 | 15.0 | 51.7 | 0.25 | 0.02 | 1.82 | 6.65 | 2.17 | 0.07 | 0.00 | 0.17 | 13.2 | 96.0 |
| BCR-2 | 3.05 | 2.21 | 15.0 | 52.0 | 0.21 | 0.02 | 1.83 | 6.69 | 2.19 | 0.07 | 0.00 | 0.17 | 13.2 | 96.6 |
| BCR-2 | 2.94 | 2.22 | 15.0 | 52.2 | 0.25 | 0.01 | 1.83 | 6.67 | 2.19 | 0.07 | 0.00 | 0.18 | 13.3 | 96.8 |
| BCR-2 | 2.89 | 2.21 | 15.0 | 52.4 | 0.24 | 0.01 | 1.84 | 6.71 | 2.20 | 0.07 | 0.00 | 0.18 | 13.3 | 97.0 |
| BCR-2 | 2.95 | 2.13 | 14.9 | 52.0 | 0.23 | 0.02 | 1.83 | 6.67 | 2.17 | 0.07 | 0.00 | 0.18 | 13.2 | 96.4 |
| BCR-2 | 2.94 | 2.24 | 14.8 | 51.8 | 0.23 | 0.03 | 1.82 | 6.65 | 2.16 | 0.06 | 0.00 | 0.17 | 13.3 | 96.1 |
| BCR-2 | 2.54 | 2.21 | 15.0 | 52.0 | 0.24 | 0.03 | 1.83 | 6.70 | 2.17 | 0.07 | 0.00 | 0.17 | 13.2 | 96.2 |
| BCR-2 | 2.53 | 2.14 | 14.6 | 51.2 | 0.26 | 0.03 | 1.80 | 6.60 | 2.15 | 0.07 | 0.00 | 0.17 | 13.1 | 94.6 |
| BCR-2 | 2.94 | 2.17 | 14.8 | 51.8 | 0.21 | 0.01 | 1.83 | 6.67 | 2.17 | 0.07 | 0.00 | 0.18 | 13.4 | 96.2 |
| BCR-2 | 2.87 | 2.20 | 14.8 | 51.5 | 0.23 | 0.01 | 1.82 | 6.66 | 2.15 | 0.07 | 0.00 | 0.17 | 13.3 | 95.8 |
| BCR-2 | 2.78 | 2.18 | 14.9 | 51.6 | 0.23 | 0.01 | 1.82 | 6.66 | 2.16 | 0.07 | 0.00 | 0.17 | 13.3 | 95.8 |
| BCR-2(A) | 2.83 | 2.18 | 14.9 | 51.8 | 0.24 | 0.02 | 1.82 | 6.66 | 2.17 | 0.07 | 0.00 | 0.17 | 13.2 | 96.1 |
| BCR-2(AN) | 2.94 | 2.27 | 15.5 | 53.9 | 0.25 | 0.02 | 1.89 | 6.92 | 2.25 | 0.07 | 0.00 | 0.18 | 13.7 | 99.9 |
| **BCR-2** | **3.16** | **3.59** | **13.5** | **54.1** | **0.35** | **n.r.** | **1.79** | **7.12** | **2.26** | **0.04** | **0.00** | **0.15** | **13.8** | **99.9** |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| ECRM681-1 | 0.38 | 1.16 | 11.3 | 16.6 | 1.90 | 0.08 | 0.52 | 3.57 | 0.45 | 0.14 | 0.06 | 0.27 | 45.8 | 82.3 |
| ECRM681-1 | 0.20 | 1.12 | 11.4 | 16.4 | 1.89 | 0.08 | 0.52 | 3.55 | 0.45 | 0.14 | 0.06 | 0.27 | 45.6 | 81.8 |
| ECRM681-1 | 0.41 | 1.15 | 11.2 | 16.4 | 1.85 | 0.08 | 0.51 | 3.54 | 0.44 | 0.14 | 0.06 | 0.27 | 45.3 | 81.4 |
| ECRM681-1 | 0.19 | 1.13 | 12.1 | 16.8 | 1.93 | 0.09 | 0.52 | 3.57 | 0.46 | 0.14 | 0.07 | 0.27 | 45.8 | 83.0 |
| ECRM681-1 | 0.32 | 1.13 | 12.1 | 16.8 | 1.96 | 0.10 | 0.53 | 3.58 | 0.46 | 0.14 | 0.07 | 0.27 | 45.6 | 83.0 |
| ECRM681-1 | 0.27 | 1.04 | 12.0 | 16.6 | 1.94 | 0.10 | 0.52 | 3.56 | 0.46 | 0.14 | 0.07 | 0.27 | 45.3 | 82.2 |
| ECRM681-1 | 0.38 | 1.13 | 12.0 | 16.7 | 1.93 | 0.09 | 0.52 | 3.54 | 0.45 | 0.14 | 0.07 | 0.27 | 45.3 | 82.5 |
| ECRM681-1 | 0.29 | 1.15 | 12.0 | 16.7 | 1.93 | 0.09 | 0.52 | 3.53 | 0.46 | 0.14 | 0.07 | 0.27 | 45.3 | 82.4 |
| ECRM681-1 | 0.41 | 1.13 | 11.8 | 16.4 | 1.90 | 0.10 | 0.51 | 3.50 | 0.45 | 0.14 | 0.07 | 0.27 | 45.0 | 81.7 |
| ECRM681-1 | 0.18 | 1.13 | 12.1 | 16.7 | 1.92 | 0.09 | 0.52 | 3.54 | 0.46 | 0.15 | 0.07 | 0.27 | 45.3 | 82.3 |
| ECRM681-1 | 0.39 | 1.11 | 12.1 | 16.6 | 1.93 | 0.10 | 0.52 | 3.54 | 0.46 | 0.15 | 0.07 | 0.27 | 45.1 | 82.3 |
| ECRM681-1 | 0.15 | 1.15 | 12.1 | 16.8 | 1.94 | 0.09 | 0.52 | 3.56 | 0.46 | 0.15 | 0.07 | 0.27 | 45.3 | 82.5 |
| ECRM681-1 | 0.26 | 1.14 | 11.8 | 16.3 | 1.85 | 0.10 | 0.51 | 3.53 | 0.45 | 0.14 | 0.07 | 0.27 | 45.8 | 82.2 |
| ECRM681-1 | 0.17 | 1.11 | 11.6 | 16.5 | 1.87 | 0.10 | 0.51 | 3.55 | 0.46 | 0.14 | 0.07 | 0.27 | 45.9 | 82.2 |
| ECRM681-1 | 0.30 | 1.18 | 11.7 | 16.2 | 1.84 | 0.09 | 0.51 | 3.52 | 0.45 | 0.14 | 0.07 | 0.27 | 45.4 | 81.6 |
| ECRM681-1(A) | 0.29 | 1.13 | 11.8 | 16.5 | 1.90 | 0.09 | 0.52 | 3.55 | 0.45 | 0.14 | 0.07 | 0.27 | 45.5 | 82.2 |
| ECRM681-1(AN) | 0.30 | 1.17 | 12.3 | 17.1 | 1.97 | 0.10 | 0.54 | 3.67 | 0.47 | 0.15 | 0.07 | 0.28 | 47.1 | 85.2 |
| **ECRM681-1** | **0.09** | **1.48** | **10.6** | **17.8** | **2.02** | **0.26** | **0.59** | **3.92** | **0.48** | **0.14** | **0.06** | **0.28** | **47.5** | **85.2** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| FER-2 | 0.44 | 2.53 | 5.54 | 51.6 | 0.29 | 0.15 | 1.56 | 2.18 | 0.18 | 0.00 | 0.01 | 0.12 | 36.1 | 101 |
| FER-2 | 0.35 | 2.44 | 5.40 | 51.6 | 0.28 | 0.15 | 1.55 | 2.19 | 0.18 | 0.00 | 0.01 | 0.12 | 36.1 | 100 |
| FER-2 | 0.65 | 2.64 | 5.66 | 51.8 | 0.29 | 0.15 | 1.56 | 2.19 | 0.18 | 0.00 | 0.01 | 0.12 | 36.2 | 101 |
| FER-2 | 0.30 | 2.59 | 6.24 | 52.5 | 0.29 | 0.15 | 1.60 | 2.22 | 0.19 | 0.00 | 0.01 | 0.13 | 36.6 | 103 |
| FER-2 | 0.20 | 2.49 | 6.26 | 52.3 | 0.31 | 0.15 | 1.59 | 2.20 | 0.19 | 0.00 | 0.01 | 0.13 | 36.3 | 102 |
| FER-2 | 0.26 | 2.54 | 6.27 | 52.4 | 0.29 | 0.16 | 1.59 | 2.22 | 0.18 | 0.00 | 0.01 | 0.13 | 36.6 | 103 |

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$P_2O_5$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **$V_2O_5$** | **$Cr_2O_3$** | **MnO** | **$Fe_2O_3$** | **Sum** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FER-2 | 0.38 | 2.60 | 6.27 | 52.5 | 0.31 | 0.15 | 1.60 | 2.22 | 0.19 | 0.00 | 0.01 | 0.13 | 36.3 | 103 |
| FER-2 | 0.19 | 2.50 | 6.25 | 52.7 | 0.32 | 0.15 | 1.59 | 2.22 | 0.19 | 0.00 | 0.01 | 0.13 | 36.3 | 103 |
| FER-2 | 0.13 | 2.54 | 6.21 | 52.7 | 0.30 | 0.15 | 1.58 | 2.21 | 0.19 | 0.00 | 0.01 | 0.13 | 36.3 | 102 |
| FER-2 | 0.22 | 2.65 | 6.17 | 52.1 | 0.29 | 0.15 | 1.58 | 2.20 | 0.18 | 0.00 | 0.01 | 0.13 | 36.3 | 102 |
| FER-2 | 0.25 | 2.52 | 6.21 | 52.6 | 0.30 | 0.15 | 1.60 | 2.23 | 0.19 | 0.00 | 0.01 | 0.13 | 36.6 | 103 |
| FER-2 | 0.22 | 2.62 | 6.17 | 52.1 | 0.28 | 0.15 | 1.58 | 2.20 | 0.18 | 0.00 | 0.01 | 0.13 | 36.4 | 102 |
| FER-2 | 0.27 | 2.60 | 5.95 | 51.5 | 0.29 | 0.16 | 1.55 | 2.18 | 0.18 | 0.00 | 0.01 | 0.13 | 35.8 | 101 |
| FER-2 | 0.80 | 2.63 | 5.97 | 51.1 | 0.27 | 0.16 | 1.55 | 2.17 | 0.18 | 0.00 | 0.01 | 0.12 | 35.7 | 101 |
| FER-2 | 0.31 | 2.50 | 6.00 | 51.3 | 0.29 | 0.16 | 1.55 | 2.18 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 100 |
| FER-2 | 0.64 | 2.70 | 6.08 | 51.5 | 0.27 | 0.16 | 1.57 | 2.18 | 0.18 | 0.00 | 0.01 | 0.13 | 36.0 | 101 |
| FER-2 | 0.66 | 2.52 | 6.10 | 51.5 | 0.27 | 0.15 | 1.56 | 2.19 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| FER-2 | 0.32 | 2.51 | 5.98 | 51.8 | 0.29 | 0.15 | 1.57 | 2.19 | 0.18 | 0.00 | 0.01 | 0.12 | 35.7 | 101 |
| FER-2 | 0.38 | 2.56 | 6.02 | 51.3 | 0.28 | 0.16 | 1.55 | 2.17 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| FER-2 | 0.72 | 2.66 | 5.91 | 51.1 | 0.27 | 0.16 | 1.56 | 2.17 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| FER-2 | 0.68 | 2.68 | 6.05 | 51.5 | 0.27 | 0.16 | 1.56 | 2.18 | 0.18 | 0.00 | 0.01 | 0.13 | 35.9 | 101 |
| FER-2 | 0.36 | 2.46 | 6.10 | 51.6 | 0.28 | 0.16 | 1.56 | 2.18 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| FER-2 | 0.53 | 2.51 | 6.14 | 51.6 | 0.25 | 0.15 | 1.56 | 2.17 | 0.18 | 0.00 | 0.01 | 0.12 | 35.7 | 101 |
| FER-2 | 0.43 | 2.40 | 6.01 | 51.7 | 0.41 | 0.17 | 1.58 | 2.18 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| FER-2(A) | 0.40 | 2.56 | 6.04 | 51.9 | 0.29 | 0.15 | 1.57 | 2.19 | 0.18 | 0.00 | 0.01 | 0.13 | 36.1 | 101 |
| FER-2(AN) | 0.40 | 2.53 | 5.99 | 51.4 | 0.29 | 0.15 | 1.56 | 2.17 | 0.18 | 0.00 | 0.01 | 0.12 | 35.8 | 101 |
| **FER-2** | **0.41** | **2.10** | **5.16** | **49.2** | **0.27** | **0.17** | **1.33** | **2.17** | **0.18** | **n.r.** | **n.r.** | **0.12** | **39.4** | **101** |
| | | | | | | | | | | | | | | |
| Slag W-25:R | 1.09 | 0.18 | 7.20 | 23.2 | 0.14 | 0.09 | 1.06 | 1.42 | 0.34 | 0.03 | 0.01 | 2.89 | 66.0 | 104 |
| Slag W-25:R | 1.19 | 0.28 | 7.14 | 23.2 | 0.15 | 0.09 | 1.05 | 1.38 | 0.34 | 0.03 | 0.01 | 2.88 | 66.0 | 104 |
| Slag W-25:R | 0.87 | 0.14 | 7.44 | 22.4 | 0.14 | 0.09 | 1.03 | 1.37 | 0.33 | 0.03 | 0.02 | 2.67 | 64.7 | 101 |
| Slag W-25:R | 1.22 | 0.18 | 7.54 | 22.5 | 0.12 | 0.09 | 1.03 | 1.36 | 0.33 | 0.03 | 0.01 | 2.69 | 64.9 | 102 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Slag W-25:R | 1.08 | 0.12 | 7.43 | 22.5 | 0.12 | 0.09 | 1.03 | 1.35 | 0.33 | 0.03 | 0.01 | 2.67 | 64.5 | 101 |
| Slag W-25:R | 0.85 | 0.16 | 7.07 | 21.3 | 0.12 | 0.08 | 1.00 | 1.33 | 0.32 | 0.03 | 0.01 | 2.54 | 63.7 | 98.5 |
| Slag W-25:R | 0.88 | 0.26 | 7.25 | 21.8 | 0.13 | 0.08 | 1.02 | 1.34 | 0.33 | 0.03 | 0.01 | 2.58 | 63.9 | 99.6 |
| Slag W-25:R | 0.78 | 0.18 | 7.14 | 21.4 | 0.12 | 0.08 | 1.00 | 1.44 | 0.32 | 0.03 | 0.01 | 2.55 | 63.5 | 98.6 |
| Slag W-25:R | 0.78 | 0.16 | 7.26 | 21.7 | 0.11 | 0.10 | 1.00 | 1.32 | 0.32 | 0.03 | 0.01 | 2.55 | 63.5 | 98.8 |
| Slag W-25:R | 0.91 | 0.00 | 6.32 | 20.9 | 0.19 | 0.12 | 1.03 | 1.50 | 0.33 | 0.04 | 0.01 | 2.97 | 63.1 | 97.4 |
| Slag W-25:R | 0.91 | 0.00 | 6.30 | 20.8 | 0.17 | 0.10 | 1.03 | 1.53 | 0.33 | 0.04 | 0.01 | 2.98 | 63.6 | 97.8 |
| Slag W-25:R | 0.90 | 0.27 | 7.21 | 23.6 | 0.15 | 0.09 | 1.07 | 1.43 | 0.34 | 0.03 | 0.01 | 2.91 | 66.5 | 105 |
| Slag W-25:R | 0.77 | 0.24 | 7.09 | 23.0 | 0.14 | 0.09 | 1.05 | 1.37 | 0.34 | 0.03 | 0.01 | 2.85 | 65.6 | 103 |
| Slag W-25:R | 1.11 | 0.15 | 7.42 | 22.4 | 0.13 | 0.08 | 1.03 | 1.36 | 0.33 | 0.03 | 0.01 | 2.67 | 64.6 | 101 |
| Slag W-25:R | 0.93 | 0.20 | 7.42 | 22.1 | 0.13 | 0.09 | 1.02 | 1.34 | 0.33 | 0.03 | 0.01 | 2.64 | 64.4 | 101 |
| Slag W-25:R | 0.71 | 0.17 | 7.58 | 22.8 | 0.13 | 0.09 | 1.03 | 1.36 | 0.34 | 0.03 | 0.01 | 2.69 | 65.2 | 102 |
| Slag W-25:R | 0.71 | 0.14 | 6.95 | 21.2 | 0.13 | 0.08 | 0.99 | 1.39 | 0.32 | 0.03 | 0.01 | 2.52 | 63.2 | 97.7 |
| Slag W-25:R | 0.72 | 0.19 | 7.00 | 21.5 | 0.13 | 0.09 | 1.00 | 1.33 | 0.32 | 0.03 | 0.01 | 2.54 | 63.4 | 98.2 |
| Slag W-25:R | 0.90 | 0.13 | 7.18 | 21.6 | 0.12 | 0.08 | 1.00 | 1.48 | 0.32 | 0.03 | 0.01 | 2.57 | 63.9 | 99.3 |
| Slag W-25:R | 0.98 | 0.18 | 7.25 | 21.8 | 0.13 | 0.10 | 1.01 | 1.33 | 0.32 | 0.03 | 0.01 | 2.56 | 63.7 | 99.4 |
| Slag W-25:R | 1.04 | 0.19 | 6.35 | 20.8 | 0.18 | 0.13 | 1.04 | 1.48 | 0.33 | 0.04 | 0.01 | 2.95 | 63.2 | 97.7 |
| Slag W-25:R | 1.15 | 0.00 | 6.37 | 20.9 | 0.17 | 0.10 | 1.04 | 1.50 | 0.33 | 0.04 | 0.01 | 2.98 | 64.0 | 98.6 |
| Slag W-25:R | 0.97 | 0.14 | 7.53 | 22.7 | 0.13 | 0.09 | 1.03 | 1.37 | 0.34 | 0.03 | 0.01 | 2.71 | 65.4 | 102 |
| Slag W-25:R | 0.91 | 0.19 | 7.49 | 22.7 | 0.13 | 0.09 | 1.04 | 1.36 | 0.34 | 0.03 | 0.01 | 2.69 | 65.2 | 102 |
| Slag W-25:R | 1.01 | 0.24 | 7.63 | 22.9 | 0.13 | 0.09 | 1.04 | 1.38 | 0.34 | 0.03 | 0.01 | 2.71 | 65.6 | 103 |
| Slag W-25:R | 0.79 | 0.20 | 6.99 | 21.3 | 0.13 | 0.08 | 1.01 | 1.40 | 0.32 | 0.03 | 0.01 | 2.54 | 63.4 | 98.1 |
| Slag W-25:R | 0.74 | 0.21 | 7.07 | 21.5 | 0.12 | 0.08 | 1.01 | 1.33 | 0.32 | 0.03 | 0.01 | 2.55 | 63.5 | 98.5 |
| Slag W-25:R | 0.93 | 0.19 | 7.12 | 21.3 | 0.13 | 0.09 | 0.99 | 1.45 | 0.32 | 0.03 | 0.01 | 2.53 | 63.0 | 98.0 |
| Slag W-25:R | 0.94 | 0.27 | 7.44 | 22.4 | 0.12 | 0.10 | 1.04 | 1.36 | 0.33 | 0.03 | 0.01 | 2.62 | 64.8 | 101 |
| Slag W-25:R | 1.30 | 0.00 | 6.40 | 20.9 | 0.18 | 0.12 | 1.03 | 1.47 | 0.33 | 0.04 | 0.01 | 2.98 | 62.8 | 97.5 |

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Slag W-25:R | 0.72 | 0.24 | 6.31 | 20.5 | 0.18 | 0.10 | 1.02 | 1.47 | 0.33 | 0.04 | 0.01 | 2.96 | 63.2 | 97.1 |
| Slag W-25:R | 1.04 | 0.22 | 7.20 | 23.2 | 0.13 | 0.09 | 1.07 | 1.40 | 0.34 | 0.03 | 0.01 | 2.91 | 67.2 | 105 |
| Slag W-25:R | 0.95 | 0.14 | 7.19 | 21.8 | 0.12 | 0.08 | 1.02 | 1.38 | 0.33 | 0.03 | 0.01 | 2.63 | 64.5 | 100 |
| Slag W-25:R | 1.08 | 0.19 | 7.21 | 23.5 | 0.13 | 0.08 | 1.08 | 1.41 | 0.35 | 0.03 | 0.01 | 2.93 | 67.2 | 105 |
| Slag W-25:R | 0.93 | 0.18 | 7.34 | 21.6 | 0.14 | 0.08 | 1.01 | 1.38 | 0.33 | 0.03 | 0.01 | 2.63 | 64.5 | 100 |
| Slag W-25:R | 0.80 | 0.26 | 7.23 | 23.4 | 0.15 | 0.09 | 1.08 | 1.41 | 0.35 | 0.03 | 0.01 | 2.91 | 67.1 | 105 |
| Slag W-25:R | 0.94 | 0.24 | 7.36 | 21.8 | 0.14 | 0.09 | 1.02 | 1.40 | 0.33 | 0.03 | 0.01 | 2.64 | 64.8 | 101 |
| Slag W-25:R(A) | 0.93 | 0.17 | 7.12 | 22.0 | 0.14 | 0.09 | 1.03 | 1.40 | 0.33 | 0.03 | 0.01 | 2.72 | 64.5 | 101 |
| Slag W-25:R(AN) | 0.95 | 0.18 | 7.25 | 22.4 | 0.14 | 0.09 | 1.05 | 1.42 | 0.34 | 0.03 | 0.01 | 2.78 | 65.7 | 102 |
| **Slag W-25:R** | **0.61** | **0.38** | **7.14** | **24.7** | **0.26** | **0.04** | **1.02** | **1.42** | **0.32** | **0.02** | **0.00** | **3.01** | **63.5** | **102** |

***Table A1.4b*** *Analyses of CRMs using the Cu_Slag method on the (P)ED-XRF Spectro X-Lab Pro2000 (trace elements in ppm). Sample names followed by (A) are averages of all the analyses and rows in bold correspond to the certified analysis accompanying each specimen (n.r.: not reported). Highlighted values should be read as elements instead of oxides, values followed with an asterisk are elements noted as potentially problematic (see above). Elements consistently detected below 5ppm are not presented.*

| | NiO | CuO | ZnO | Ga | $As_2O_3$ | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ba | La | Ce | Nd | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BCR-2 | 8 | 38 | 147 | 24 | 4 | 1 | 51 | 396 | 34 | 255 | 215 | 643 | 0 | 48 | 38 | 0 |
| BCR-2 | 11 | 38 | 149 | 22 | 5 | 0 | 52 | 400 | 34 | 242 | 215 | 647 | 20 | 52 | 0 | 0 |
| BCR-2 | 8 | 33 | 146 | 20 | 4 | 1 | 51 | 394 | 33 | 244 | 214 | 643 | 20 | 51 | 35 | 0 |
| BCR-2 | 11 | 29 | 154 | 20 | 4 | 1 | 50 | 400 | 35 | 229 | 219 | 642 | 19 | 50 | 0 | 0 |
| BCR-2 | 13 | 29 | 149 | 20 | 4 | 1 | 51 | 399 | 33 | 234 | 216 | 645 | 22 | 48 | 0 | 0 |
| BCR-2 | 10 | 32 | 152 | 22 | 4 | 1 | 50 | 399 | 35 | 257 | 203 | 634 | 0 | 45 | 51 | 0 |
| BCR-2 | 18 | 27 | 152 | 22 | 4 | 0 | 50 | 399 | 35 | 243 | 215 | 645 | 0 | 49 | 0 | 0 |
| BCR-2 | 14 | 31 | 151 | 21 | 5 | 1 | 51 | 398 | 35 | 244 | 211 | 639 | 0 | 35 | 0 | 0 |
| BCR-2 | 10 | 29 | 153 | 22 | 4 | 1 | 51 | 398 | 34 | 234 | 219 | 641 | 0 | 52 | 35 | 0 |
| BCR-2 | 13 | 30 | 147 | 21 | 4 | 1 | 51 | 403 | 35 | 257 | 211 | 632 | 0 | 39 | 32 | 2 |
| BCR-2 | 9 | 33 | 151 | 24 | 6 | 1 | 51 | 398 | 34 | 236 | 214 | 647 | 19 | 41 | 0 | 0 |
| BCR-2 | 15 | 31 | 147 | 24 | 5 | 1 | 50 | 396 | 34 | 252 | 210 | 634 | 0 | 56 | 32 | 0 |
| BCR-2 | 16 | 35 | 151 | 23 | 6 | 0 | 52 | 398 | 34 | 251 | 213 | 616 | 0 | 44 | 42 | 1 |
| BCR-2 | 14 | 27 | 143 | 20 | 5 | 1 | 51 | 395 | 35 | 250 | 205 | 606 | 23 | 50 | 0 | 0 |
| BCR-2 | 15 | 30 | 149 | 22 | 3 | 0 | 52 | 399 | 33 | 256 | 209 | 624 | 21 | 48 | 0 | 0 |
| BCR-2(A) | 12 | 31 | 149 | 22 | 4 | 1 | 51 | 398 | 34 | 246 | 213 | 636 | <23 | 47 | <51 | 0 |
| **BCR-2** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **300** | **n.r.** | **n.r.** | **n.r.** | **700** | **n.r.** | **n.r.** | **n.r.** | **n.r.** |
| | | | | | | | | | | | | | | | | |

|  | NiO | CuO | ZnO | Ga | $As_2O_3$ | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ba | La | Ce | Nd | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ECRM681-1 | 104 | 16 | 452 | 13 | 163 | 6 | 0 | 1140 | 103 | 287 | 0 | 130 | 145 | 335 | 112 | 0 |
| ECRM681-1 | 59 | 18 | 449 | 13 | 169 | 11 | 3 | 1143 | 104 | 285 | 0 | 118 | 123 | 316 | 138 | 3 |
| ECRM681-1 | 92 | 29 | 443 | 16 | 163 | 12 | 0 | 1119 | 102 | 283 | 0 | 121 | 133 | 328 | 72 | 4 |
| ECRM681-1 | 70 | 18 | 444 | 10 | 177 | 10 | 0 | 1119 | 102 | 281 | 0 | 114 | 134 | 318 | 94 | 5 |
| ECRM681-1 | 53 | 0 | 451 | 13 | 166 | 11 | 0 | 1110 | 102 | 295 | 0 | 126 | 144 | 329 | 90 | 2 |
| ECRM681-1 | 47 | 23 | 423 | 11 | 170 | 11 | 0 | 1105 | 98 | 302 | 0 | 120 | 129 | 311 | 115 | 0 |
| ECRM681-1 | 93 | 15 | 434 | 10 | 162 | 16 | 0 | 1107 | 100 | 284 | 0 | 131 | 138 | 318 | 48 | 3 |
| ECRM681-1 | 66 | 16 | 436 | 11 | 179 | 15 | 0 | 1106 | 100 | 285 | 0 | 112 | 136 | 329 | 87 | 0 |
| ECRM681-1 | 52 | 21 | 434 | 8 | 149 | 17 | 0 | 1099 | 101 | 301 | 0 | 117 | 126 | 314 | 73 | 3 |
| ECRM681-1 | 56 | 21 | 423 | 13 | 164 | 20 | 0 | 1106 | 101 | 289 | 0 | 132 | 136 | 326 | 59 | 2 |
| ECRM681-1 | 50 | 28 | 446 | 10 | 179 | 15 | 0 | 1105 | 98 | 274 | 0 | 135 | 152 | 333 | 69 | 4 |
| ECRM681-1 | 55 | 21 | 424 | 8 | 176 | 20 | 0 | 1101 | 101 | 300 | 0 | 130 | 169 | 362 | 156 | 2 |
| ECRM681-1 | 114 | 9 | 455 | 10 | 169 | 19 | 0 | 1129 | 103 | 283 | 0 | 118 | 126 | 314 | 52 | 5 |
| ECRM681-1 | 119 | 19 | 446 | 11 | 168 | 17 | 0 | 1126 | 101 | 307 | 0 | 121 | 143 | 317 | 97 | 4 |
| ECRM681-1 | 52 | 23 | 430 | 10 | 167 | 17 | 0 | 1114 | 101 | 272 | 0 | 127 | 121 | 292 | 47 | 4 |
| ECRM681-1(A) | 72 | 18 | 439 | 11 | 168 | 14 | 0 | 1115 | 101 | 289 | 0 | 123 | 137 | 323 | 87 | <5 |
| **ECRM681-1** | **200** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| FER-2 | 0 | 55 | 58 | 2 | 5 | 0 | 56 | 64 | 17 | 50 | 0 | 222 | 0 | 31 | 0 | 0 |
| FER-2 | 0 | 83 | 56 | 6 | 4 | 0 | 58 | 66 | 14 | 51 | 0 | 210 | 0 | 36 | 0 | 0 |
| FER-2 | 0 | 63 | 48 | 2 | 4 | 0 | 58 | 63 | 16 | 54 | 0 | 211 | 0 | 41 | 0 | 3 |
| FER-2 | 0 | 56 | 49 | 2 | 5 | 0 | 56 | 60 | 15 | 64 | 0 | 208 | 0 | 20 | 0 | 0 |
| FER-2 | 0 | 70 | 55 | 0 | 4 | 0 | 55 | 61 | 14 | 61 | 0 | 219 | 0 | 0 | 0 | 0 |
| FER-2 | 0 | 62 | 55 | 3 | 5 | 0 | 57 | 63 | 16 | 48 | 0 | 224 | 0 | 26 | 0 | 2 |
| FER-2 | 0 | 54 | 60 | 6 | 4 | 0 | 57 | 61 | 15 | 44 | 0 | 202 | 0 | 29 | 0 | 3 |
| FER-2 | 0 | 68 | 51 | 6 | 4 | 0 | 59 | 64 | 17 | 54 | 0 | 211 | 0 | 30 | 0 | 0 |

| | NiO | CuO | ZnO | Ga | $As_2O_3$ | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ba | La | Ce | Nd | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FER-2 | 0 | 56 | 53 | 0 | 5 | 0 | 54 | 62 | 14 | 44 | 0 | 205 | 0 | 24 | 0 | 2 |
| FER-2 | 0 | 88 | 62 | 5 | 5 | 0 | 57 | 62 | 14 | 62 | 0 | 215 | 0 | 28 | 0 | 3 |
| FER-2 | 0 | 57 | 52 | 0 | 4 | 0 | 56 | 63 | 16 | 56 | 0 | 217 | 0 | 32 | 0 | 2 |
| FER-2 | 0 | 67 | 56 | 5 | 3 | 0 | 56 | 60 | 14 | 51 | 0 | 212 | 0 | 32 | 0 | 2 |
| FER-2 | 0 | 55 | 51 | 0 | 5 | 0 | 55 | 61 | 17 | 68 | 0 | 205 | 0 | 26 | 0 | 5 |
| FER-2 | 0 | 76 | 50 | 6 | 6 | 0 | 56 | 61 | 14 | 48 | 0 | 209 | 0 | 27 | 0 | 2 |
| FER-2 | 0 | 71 | 51 | 6 | 4 | 0 | 58 | 63 | 16 | 58 | 0 | 205 | 0 | 24 | 0 | 2 |
| FER-2 | 0 | 72 | 52 | 6 | 4 | 0 | 58 | 62 | 14 | 57 | 0 | 209 | 0 | 25 | 0 | 3 |
| FER-2 | 0 | 70 | 48 | 5 | 4 | 0 | 57 | 61 | 16 | 56 | 0 | 211 | 0 | 28 | 0 | 1 |
| FER-2 | 0 | 63 | 52 | 3 | 5 | 0 | 56 | 60 | 17 | 63 | 0 | 216 | 0 | 0 | 0 | 0 |
| FER-2 | 0 | 80 | 55 | 5 | 4 | 0 | 54 | 62 | 15 | 46 | 0 | 210 | 0 | 26 | 0 | 1 |
| FER-2 | 0 | 83 | 54 | 7 | 6 | 0 | 58 | 66 | 24 | 45 | 0 | 208 | 0 | 45 | 0 | 0 |
| FER-2 | 0 | 64 | 54 | 3 | 6 | 0 | 56 | 63 | 17 | 46 | 0 | 209 | 0 | 25 | 0 | 0 |
| FER-2 | 0 | 76 | 50 | 5 | 6 | 0 | 58 | 61 | 15 | 58 | 0 | 201 | 0 | 0 | 0 | 3 |
| FER-2 | 0 | 75 | 56 | 2 | 6 | 0 | 56 | 59 | 13 | 48 | 2 | 213 | 0 | 29 | 0 | 0 |
| FER-2 | 0 | 70 | 54 | 3 | 5 | 0 | 57 | 60 | 15 | 53 | 0 | 215 | 0 | 25 | 0 | 2 |
| FER-2(A) | 0 | 68 | 53 | <7 | 5 | 0 | 57 | 62 | 16 | 54 | 0 | 211 | 0 | 25 | 0 | <5 |
| **FER-2** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **200** | **n.r.** | **n.r.** | **n.r.** | **n.r.** |
| | | | | | | | | | | | | | | | | |
| Slag W-25:R | 0 | 13 | 31 | 0 | 0 | 0 | 0 | 87 | 124 | 140 | 0 | 1009 | 72 | 317 | 106 | 5 |
| Slag W-25:R | 0 | 18 | 29 | 0 | 0 | 0 | 0 | 87 | 123 | 145 | 0 | 1014 | 108 | 331 | 12 | 6 |
| Slag W-25:R | 0 | 28 | 28 | 0 | 0 | 0 | 0 | 86 | 117 | 149 | 0 | 985 | 79 | 324 | 0 | 7 |
| Slag W-25:R | 0 | 21 | 31 | 5 | 0 | 0 | 0 | 85 | 117 | 133 | 0 | 993 | 93 | 312 | 0 | 8 |
| Slag W-25:R | 0 | 29 | 29 | 0 | 0 | 0 | 0 | 85 | 115 | 153 | 0 | 963 | 99 | 310 | 91 | 4 |
| Slag W-25:R | 0 | 44 | 30 | 5 | 0 | 0 | 0 | 87 | 121 | 144 | 0 | 986 | 108 | 320 | 0 | 6 |
| Slag W-25:R | 0 | 24 | 23 | 6 | 0 | 0 | 0 | 85 | 119 | 138 | 0 | 974 | 96 | 318 | 0 | 6 |

| | NiO | CuO | ZnO | Ga | $As_2O_3$ | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ba | La | Ce | Nd | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Slag W-25:R | 0 | 23 | 31 | 7 | 3 | 0 | 0 | 87 | 119 | 134 | 0 | 992 | 96 | 321 | 0 | 7 |
| Slag W-25:R | 0 | 16 | 23 | 0 | 0 | 0 | 0 | 84 | 118 | 166 | 0 | 988 | 101 | 300 | 95 | 4 |
| Slag W-25:R | 0 | 57 | 0 | 4 | 8 | 0 | 0 | 98 | 114 | 72 | 0 | 957 | 25 | 106 | 115 | 8 |
| Slag W-25:R | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 99 | 112 | 93 | 0 | 970 | 30 | 104 | 0 | 6 |
| Slag W-25:R | 0 | 13 | 33 | 7 | 1 | 0 | 0 | 88 | 120 | 142 | 0 | 966 | 84 | 326 | 135 | 6 |
| Slag W-25:R | 0 | 28 | 31 | 5 | 0 | 0 | 0 | 83 | 120 | 143 | 0 | 960 | 97 | 321 | 109 | 6 |
| Slag W-25:R | 0 | 21 | 23 | 8 | 0 | 0 | 0 | 83 | 119 | 131 | 0 | 955 | 95 | 305 | 119 | 3 |
| Slag W-25:R | 0 | 25 | 32 | 0 | 2 | 0 | 0 | 85 | 118 | 134 | 0 | 1009 | 91 | 310 | 41 | 5 |
| Slag W-25:R | 0 | 31 | 25 | 3 | 0 | 0 | 0 | 83 | 121 | 138 | 0 | 1006 | 93 | 310 | 49 | 5 |
| Slag W-25:R | 0 | 23 | 29 | 6 | 0 | 0 | 0 | 88 | 122 | 136 | 0 | 963 | 104 | 310 | 0 | 6 |
| Slag W-25:R | 0 | 15 | 18 | 0 | 0 | 0 | 0 | 88 | 121 | 154 | 0 | 954 | 108 | 323 | 119 | 7 |
| Slag W-25:R | 0 | 19 | 23 | 5 | 0 | 0 | 0 | 85 | 121 | 136 | 0 | 970 | 106 | 315 | 117 | 7 |
| Slag W-25:R | 0 | 25 | 27 | 9 | 0 | 0 | 12 | 87 | 119 | 149 | 0 | 974 | 101 | 330 | 73 | 0 |
| Slag W-25:R | 0 | 57 | 0 | 9 | 5 | 0 | 0 | 99 | 119 | 62 | 0 | 997 | 31 | 110 | 127 | 6 |
| Slag W-25:R | 0 | 20 | 0 | 9 | 0 | 0 | 0 | 95 | 115 | 67 | 0 | 981 | 37 | 104 | 0 | 6 |
| Slag W-25:R | 0 | 19 | 25 | 6 | 0 | 0 | 0 | 89 | 124 | 131 | 0 | 983 | 107 | 331 | 59 | 10 |
| Slag W-25:R | 0 | 21 | 25 | 3 | 3 | 0 | 0 | 88 | 120 | 137 | 0 | 962 | 96 | 321 | 143 | 7 |
| Slag W-25:R | 0 | 33 | 31 | 0 | 4 | 0 | 0 | 87 | 123 | 139 | 0 | 978 | 87 | 323 | 0 | 7 |
| Slag W-25:R | 0 | 0 | 29 | 0 | 0 | 0 | 0 | 87 | 121 | 143 | 0 | 1001 | 106 | 321 | 0 | 5 |
| Slag W-25:R | 0 | 24 | 28 | 0 | 0 | 0 | 0 | 87 | 122 | 151 | 0 | 984 | 112 | 341 | 131 | 5 |
| Slag W-25:R | 0 | 19 | 27 | 5 | 1 | 0 | 0 | 86 | 117 | 121 | 0 | 954 | 96 | 315 | 0 | 5 |
| Slag W-25:R | 0 | 0 | 24 | 4 | 0 | 0 | 0 | 88 | 124 | 132 | 0 | 954 | 94 | 308 | 77 | 6 |
| Slag W-25:R | 0 | 52 | 0 | 6 | 7 | 0 | 0 | 99 | 113 | 77 | 0 | 981 | 31 | 93 | 0 | 9 |
| Slag W-25:R | 0 | 12 | 32 | 4 | 0 | 0 | 0 | 97 | 114 | 69 | 0 | 970 | 28 | 101 | 0 | 8 |
| Slag W-25:R | 0 | 18 | 38 | 6 | 2 | 0 | 0 | 89 | 125 | 150 | 0 | 969 | 113 | 333 | 55 | 5 |
| Slag W-25:R | 33 | 25 | 33 | 4 | 0 | 0 | 0 | 83 | 117 | 140 | 0 | 980 | 113 | 336 | 105 | 6 |

|  | NiO | CuO | ZnO | Ga | $As_2O_3$ | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ba | La | Ce | Nd | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Slag W-25:R | 0 | 40 | 33 | 11 | 5 | 0 | 0 | 90 | 123 | 148 | 0 | 987 | 108 | 320 | 0 | 7 |
| Slag W-25:R | 56 | 23 | 37 | 7 | 5 | 4 | 0 | 83 | 123 | 154 | 0 | 1018 | 90 | 316 | 0 | 4 |
| Slag W-25:R | 0 | 37 | 23 | 3 | 0 | 0 | 0 | 90 | 124 | 154 | 0 | 970 | 91 | 317 | 131 | 5 |
| Slag W-25:R | 40 | 23 | 29 | 0 | 0 | 0 | 0 | 84 | 123 | 145 | 0 | 989 | 113 | 308 | 70 | 6 |
| Slag W-25:R(A) | <56 | 24 | <38 | <11 | <8 | 0 | 0 | 88 | 120 | 131 | 0 | 980 | 87 | 284 | <143 | 6 |
| **Slag W-25:R** | ***70** | ***29** | ***48** | **n.r.** | **n.r.** | **n.r.** | **n.r.** | **94** | **95** | **192** | **9** | **806** | **79** | **274** | **119** | **13** |

# APPENDIX 2.

## Tables of (P)ED-XRF analyses of mineral samples from Seriphos

*Table A2.1a (P)ED-XRF analyses of mineral samples from Seriphos (major and minor elements in weight %). Values not given here (empty boxes) are included in the trace element table (below). Values labelled with (av) are calculated averages of the three analyses above. Highlighted values should be read as elements instead of oxides. Low totals are due to the presence of carbonates and hydroxides typical in secondary ores.*

| | $Na_2O$ | MgO | $Al_2O3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | ZnO | $As_2O_3$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **RK1** | 0.29 | 8.01 | 2.71 | 28.7 | 0.12 | 0.14 | 0.01 | 0.02 | 0.54 | 0.06 | 0.02 | 0.00 | 0.05 | 21.4 | 24.2 | | 0.19 | | 86.4 |
| **RK1b** | 0.54 | 7.88 | 2.64 | 28.6 | 0.11 | 0.13 | 0.01 | 0.02 | 0.52 | 0.06 | 0.02 | 0.00 | 0.06 | 21.3 | 24.0 | | 0.19 | | 86.0 |
| **RK1c** | 0.66 | 7.79 | 2.66 | 28.5 | 0.12 | 0.13 | 0.01 | 0.01 | 0.53 | 0.06 | 0.02 | 0.00 | 0.06 | 21.3 | 24.0 | | 0.19 | | 86.0 |
| **RK1av** | 0.50 | 7.89 | 2.67 | 28.6 | 0.12 | 0.13 | 0.01 | 0.02 | 0.53 | 0.06 | 0.02 | 0.00 | 0.06 | 21.3 | 24.1 | | 0.19 | | 86.2 |
| **RK2** | 0.27 | 7.69 | 2.61 | 28.6 | 0.13 | 0.15 | 0.01 | 0.00 | 0.52 | 0.05 | 0.02 | 0.00 | 0.05 | 21.1 | 23.8 | | 0.19 | | 85.1 |
| **RK2b** | 0.17 | 7.77 | 2.63 | 28.5 | 0.11 | 0.13 | 0.01 | 0.01 | 0.50 | 0.05 | 0.02 | 0.00 | 0.06 | 21.0 | 23.3 | | 0.18 | | 84.4 |
| **RK2c** | 0.45 | 7.57 | 2.63 | 28.3 | 0.12 | 0.13 | 0.01 | 0.01 | 0.50 | 0.05 | 0.02 | 0.00 | 0.06 | 20.9 | 23.5 | | 0.19 | | 84.4 |
| **RK2av** | 0.30 | 7.68 | 2.62 | 28.5 | 0.12 | 0.14 | 0.01 | 0.01 | 0.51 | 0.05 | 0.02 | 0.00 | 0.06 | 21.0 | 23.5 | | 0.18 | | 84.6 |
| **KOUT1** | 0.54 | 14.4 | 1.90 | 13.4 | 0.51 | 0.00 | 0.07 | 0.23 | 11.5 | 0.07 | 0.02 | 0.00 | 0.54 | 1.24 | 22.2 | | 19.4 | | 86.0 |
| **KOUT1b** | 0.40 | 14.7 | 1.98 | 13.5 | 0.50 | 0.00 | 0.07 | 0.21 | 11.6 | 0.06 | 0.02 | 0.00 | 0.54 | 1.25 | 22.1 | | 19.3 | | 86.2 |

| | $Na_2O$ | MgO | $Al_2O3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | ZnO | $As_2O_3$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KOUT1c** | 0.36 | 14.7 | 1.99 | 13.8 | 0.51 | 0.00 | 0.07 | 0.23 | 11.8 | 0.07 | 0.01 | 0.00 | 0.53 | 1.26 | 22.4 | | 19.5 | | 87.1 |
| **KOUT1av** | 0.43 | 14.6 | 1.95 | 13.6 | 0.51 | 0.00 | 0.07 | 0.23 | 11.6 | 0.07 | 0.01 | 0.00 | 0.54 | 1.25 | 22.2 | | 19.4 | | 86.5 |
| **KOUT2** | 0.34 | 9.72 | 0.92 | 11.9 | 0.17 | 0.00 | 0.01 | 0.00 | 20.7 | 0.02 | 0.00 | 0.00 | 0.44 | 0.46 | 20.5 | | 10.9 | | 76.2 |
| **KOUT2b** | 0.22 | 9.93 | 0.91 | 12.3 | 0.18 | 0.00 | 0.01 | 0.00 | 21.3 | 0.00 | 0.00 | 0.00 | 0.45 | 0.46 | 20.9 | | 11.1 | | 77.7 |
| **KOUT2c** | 0.21 | 9.66 | 0.91 | 11.9 | 0.18 | 0.00 | 0.01 | 0.00 | 20.8 | 0.03 | 0.00 | 0.00 | 0.43 | 0.45 | 20.1 | | 10.9 | | 75.7 |
| **KOUT2av** | 0.26 | 9.77 | 0.91 | 12.0 | 0.17 | 0.00 | 0.01 | 0.00 | 20.9 | 0.02 | 0.00 | 0.00 | 0.44 | 0.45 | 20.5 | | 11.0 | | 76.5 |
| **KOUT3** | 0.37 | 0.83 | 4.25 | 11.6 | 0.01 | 1.49 | 0.04 | 0.08 | 3.12 | 0.20 | 0.00 | 0.00 | 0.05 | 30.1 | 23.8 | | 0.09 | | 76.1 |
| **KOUT3b** | 0.60 | 0.85 | 4.39 | 11.8 | 0.00 | 1.48 | 0.05 | 0.10 | 3.17 | 0.18 | 0.00 | 0.00 | 0.05 | 30.6 | 24.1 | | 0.09 | | 77.4 |
| **KOUT3c** | 0.18 | 0.93 | 4.37 | 11.8 | 0.01 | 1.50 | 0.05 | 0.10 | 3.17 | 0.20 | 0.00 | 0.00 | 0.05 | 30.5 | 24.0 | | 0.09 | | 76.9 |
| **KOUT3av** | 0.38 | 0.87 | 4.34 | 11.7 | 0.00 | 1.49 | 0.05 | 0.09 | 3.15 | 0.20 | 0.00 | 0.00 | 0.05 | 30.4 | 24.0 | | 0.09 | | 76.8 |
| **KOUT4** | 0.55 | 18.8 | 3.10 | 8.68 | 0.35 | 0.00 | 0.05 | 0.06 | 18.6 | 0.07 | 0.00 | 0.00 | 0.35 | 1.76 | 30.7 | | 32.1 | | 115 |
| **KOUT4b** | 0.46 | 17.3 | 2.51 | 2.23 | 0.27 | 0.00 | 0.04 | 0.08 | 16.4 | 0.06 | 0.00 | 0.00 | 0.29 | 1.51 | 26.2 | | 27.6 | | 94.9 |
| **KOUT4c** | 0.42 | 17.2 | 2.84 | 7.76 | 0.32 | 0.00 | 0.05 | 0.08 | 16.6 | 0.06 | 0.00 | 0.00 | 0.32 | 1.58 | 27.1 | | 28.0 | | 102 |
| **KOUT4av** | 0.48 | 17.8 | 2.81 | 6.22 | 0.31 | 0.00 | 0.05 | 0.07 | 17.2 | 0.06 | 0.00 | 0.00 | 0.32 | 1.62 | 28.0 | | 29.2 | | 104 |
| **KOUT5** | 0.29 | 15.7 | 1.54 | 1.04 | 0.55 | 0.00 | 0.02 | 0.06 | 16.6 | 0.04 | 0.02 | 0.00 | 0.86 | 0.98 | 26.2 | | 27.7 | | 91.6 |
| **KOUT5b** | 0.15 | 16.4 | 1.58 | 0.89 | 0.58 | 0.00 | 0.02 | 0.09 | 18.2 | 0.04 | 0.02 | 0.00 | 0.94 | 1.08 | 28.3 | | 30.9 | | 99.3 |
| **KOUT5c** | 0.46 | 15.3 | 1.45 | 0.93 | 0.54 | 0.00 | 0.02 | 0.08 | 16.4 | 0.03 | 0.00 | 0.00 | 0.85 | 0.98 | 25.9 | | 27.5 | | 90.4 |
| **KOUT5av** | 0.30 | 15.8 | 1.52 | 0.96 | 0.55 | 0.00 | 0.02 | 0.08 | 17.1 | 0.04 | 0.01 | 0.00 | 0.88 | 1.01 | 26.8 | | 28.7 | | 93.8 |
| **PL1** | 0.23 | 2.03 | 1.80 | 29.3 | 0.01 | 0.04 | 0.00 | 0.63 | 4.46 | 0.07 | 0.05 | 0.00 | 0.15 | 31.2 | 8.39 | | | | 78.4 |
| **PL1b** | 0.24 | 1.94 | 1.79 | 29.5 | 0.01 | 0.03 | 0.00 | 0.66 | 4.46 | 0.07 | 0.05 | 0.00 | 0.15 | 31.4 | 8.39 | | | | 78.7 |
| **PL1c** | 0.53 | 1.99 | 1.73 | 29.5 | 0.00 | 0.04 | 0.00 | 0.63 | 4.47 | 0.07 | 0.05 | 0.00 | 0.16 | 31.3 | 8.34 | | | | 78.8 |
| **PL1av** | 0.33 | 1.99 | 1.77 | 29.5 | 0.01 | 0.04 | 0.00 | 0.64 | 4.46 | 0.07 | 0.05 | 0.00 | 0.15 | 31.3 | 8.37 | | | | 78.6 |
| **PL2** | 1.24 | 0.00 | 0.00 | 0.00 | 0.00 | 27.8 | 0.02 | 0.00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.02 | 51.2 | 0.25 | | | | 80.5 |
| **PL2b** | 0.61 | 0.00 | 0.00 | 0.00 | 0.00 | 27.3 | 0.02 | 0.05 | 0.01 | 0.01 | 0.00 | 0.00 | 0.02 | 50.6 | 0.25 | | | | 78.9 |
| **PL2c** | 0.34 | 0.00 | 0.00 | 0.00 | 0.00 | 27.9 | 0.02 | 0.00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.02 | 51.4 | 0.25 | | | | 79.9 |

|  | $Na_2O$ | MgO | $Al_2O3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | ZnO | $As_2O_3$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PL2av** | 0.73 | 0.00 | 0.00 | 0.00 | 0.00 | 27.7 | 0.02 | 0.02 | 0.02 | 0.01 | 0.00 | 0.00 | 0.02 | 51.0 | 0.25 |  |  |  | 79.8 |
| **PL3** | 0.00 | 1.20 | 0.00 | 9.96 | 0.00 | 22.6 | 0.00 | 0.00 | 17.3 | 0.02 | 0.00 | 0.00 | 0.18 | 22.2 | 13.5 |  |  |  | 86.9 |
| **PL3b** | 0.00 | 1.42 | 0.00 | 9.91 | 0.00 | 22.4 | 0.00 | 0.00 | 17.2 | 0.01 | 0.00 | 0.00 | 0.18 | 22.2 | 13.5 |  |  |  | 86.7 |
| **PL3c** | 0.00 | 1.33 | 0.00 | 9.96 | 0.00 | 22.4 | 0.00 | 0.00 | 17.2 | 0.02 | 0.00 | 0.00 | 0.19 | 22.2 | 13.6 |  |  |  | 86.9 |
| **PL3av** | 0.00 | 1.32 | 0.00 | 9.94 | 0.00 | 22.5 | 0.00 | 0.00 | 17.2 | 0.02 | 0.00 | 0.00 | 0.18 | 22.2 | 13.5 |  |  |  | 86.9 |
| **VOUN1** | 0.45 | 4.04 | 4.18 | 23.3 | 0.05 | 0.08 | 0.02 | 0.02 | 1.82 | 0.03 | 0.00 | 0.00 | 1.50 | 0.82 | 39.1 |  |  |  | 75.5 |
| **VOUN1b** | 0.29 | 3.56 | 4.05 | 21.9 | 0.04 | 0.08 | 0.02 | 0.02 | 1.79 | 0.03 | 0.00 | 0.00 | 1.48 | 0.81 | 37.9 |  |  |  | 72.0 |
| **VOUN1c** | 0.35 | 3.93 | 4.16 | 23.6 | 0.05 | 0.08 | 0.02 | 0.00 | 1.85 | 0.03 | 0.00 | 0.00 | 1.51 | 0.83 | 39.4 |  |  |  | 75.8 |
| **VOUN1av** | 0.36 | 3.84 | 4.13 | 22.9 | 0.05 | 0.08 | 0.02 | 0.01 | 1.82 | 0.03 | 0.00 | 0.00 | 1.49 | 0.82 | 38.8 |  |  |  | 74.4 |
| **VOUN2** | 0.19 | 0.13 | 0.74 | 3.02 | 0.04 | 0.67 | 0.01 | 0.12 | 0.08 | 0.00 | 0.00 | 0.00 | 0.33 | 72.7 | 0.20 |  |  |  | 78.3 |
| **VOUN2b** | 0.00 | 0.17 | 0.74 | 3.04 | 0.04 | 0.66 | 0.01 | 0.12 | 0.08 | 0.02 | 0.00 | 0.00 | 0.33 | 72.9 | 0.20 |  |  |  | 78.3 |
| **VOUN2c** | 0.17 | 0.20 | 0.70 | 3.05 | 0.04 | 0.66 | 0.01 | 0.12 | 0.08 | 0.02 | 0.00 | 0.00 | 0.34 | 72.9 | 0.19 |  |  |  | 78.5 |
| **VOUN2av** | 0.12 | 0.17 | 0.72 | 3.04 | 0.04 | 0.66 | 0.01 | 0.12 | 0.08 | 0.02 | 0.00 | 0.00 | 0.33 | 72.8 | 0.20 |  |  |  | 78.4 |
| **VOUN3** | 0.00 | 23.0 | 1.06 | 59.7 | 0.01 | 0.02 | 0.00 | 0.00 | 2.35 | 0.04 | 0.00 | 0.00 | 0.30 | 2.27 | 1.50 |  |  |  | 90.2 |
| **VOUN3b** | 0.43 | 23.2 | 1.10 | 60.3 | 0.00 | 0.02 | 0.00 | 0.00 | 2.38 | 0.04 | 0.00 | 0.00 | 0.30 | 2.31 | 1.51 |  |  |  | 91.6 |
| **VOUN3c** | 0.33 | 23.1 | 1.09 | 59.4 | 0.00 | 0.02 | 0.00 | 0.00 | 2.34 | 0.04 | 0.00 | 0.00 | 0.31 | 2.28 | 1.49 |  |  |  | 90.4 |
| **VOUN3av** | 0.25 | 23.1 | 1.09 | 59.8 | 0.00 | 0.02 | 0.00 | 0.00 | 2.36 | 0.04 | 0.00 | 0.00 | 0.30 | 2.29 | 1.50 |  |  |  | 90.7 |
| **KAL1** | 0.47 | 1.07 | 2.48 | 26.7 | 0.00 | 3.88 | 0.46 | 0.06 | 1.38 | 0.00 | 0.00 | 0.00 | 0.53 | 5.91 | 34.7 |  |  |  | 77.6 |
| **KAL1b** | 0.37 | 1.09 | 2.57 | 27.4 | 0.00 | 3.94 | 0.47 | 0.07 | 1.39 | 0.01 | 0.00 | 0.00 | 0.52 | 5.75 | 34.8 |  |  |  | 78.4 |
| **KAL1c** | 0.60 | 1.09 | 2.56 | 26.7 | 0.00 | 3.84 | 0.47 | 0.05 | 1.41 | 0.02 | 0.00 | 0.00 | 0.53 | 5.85 | 34.5 |  |  |  | 77.6 |
| **KAL1av** | 0.48 | 1.08 | 2.54 | 26.9 | 0.00 | 3.89 | 0.47 | 0.06 | 1.40 | 0.01 | 0.00 | 0.00 | 0.53 | 5.83 | 34.7 |  |  |  | 77.9 |
| **KAL2** | 1.60 | 0.00 | 0.07 | 3.73 | 0.00 | 6.23 | 0.01 | 0.15 | 0.05 | 0.01 | 0.00 | 0.00 | 0.03 | 54.7 | 0.03 |  |  |  | 66.6 |
| **KAL2b** | 0.43 | 0.00 | 0.07 | 3.77 | 0.00 | 6.22 | 0.01 | 0.14 | 0.05 | 0.01 | 0.00 | 0.00 | 0.03 | 54.9 | 0.03 |  |  |  | 65.7 |
| **KAL2c** | 0.95 | 0.00 | 0.07 | 3.85 | 0.00 | 6.28 | 0.01 | 0.14 | 0.05 | 0.01 | 0.00 | 0.00 | 0.03 | 54.9 | 0.03 |  |  |  | 66.3 |
| **KAL2av** | 0.99 | 0.00 | 0.07 | 3.78 | 0.00 | 6.24 | 0.01 | 0.14 | 0.05 | 0.01 | 0.00 | 0.00 | 0.03 | 54.8 | 0.03 |  |  |  | 66.2 |

|  | $Na_2O$ | MgO | $Al_2O3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | ZnO | $As_2O_3$ | PbO | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KAL3** | 0.85 | 1.89 | 10.4 | 55.9 | 0.00 | 0.31 | 0.08 | 0.10 | 2.48 | 0.02 | 0.00 | 0.00 | 0.34 | 8.13 | 5.01 |  |  |  | 85.5 |
| **KAL3b** | 0.21 | 1.78 | 10.5 | 56.1 | 0.00 | 0.31 | 0.08 | 0.10 | 2.47 | 0.01 | 0.00 | 0.00 | 0.33 | 8.14 | 4.99 |  |  |  | 85.0 |
| **KAL3c** | 0.49 | 1.81 | 10.5 | 56.1 | 0.00 | 0.30 | 0.08 | 0.10 | 2.46 | 0.01 | 0.00 | 0.00 | 0.34 | 8.12 | 5.01 |  |  |  | 85.3 |
| **KAL3av** | 0.52 | 1.83 | 10.4 | 56.0 | 0.00 | 0.30 | 0.08 | 0.10 | 2.47 | 0.01 | 0.00 | 0.00 | 0.34 | 8.13 | 5.00 |  |  |  | 85.3 |
| **KAL4** | 0.90 | 0.91 | 0.62 | 25.8 | 0.00 | 1.20 | 0.89 | 0.16 | 1.67 | 0.01 | 0.00 | 0.00 | 0.11 | 23.2 | 30.1 |  |  |  | 85.6 |
| **KAL4b** | 0.93 | 0.93 | 0.59 | 25.5 | 0.00 | 1.19 | 0.88 | 0.17 | 1.66 | 0.00 | 0.01 | 0.00 | 0.11 | 23.1 | 29.9 |  |  |  | 84.9 |
| **KAL4c** | 0.71 | 0.87 | 0.64 | 25.9 | 0.00 | 1.23 | 0.90 | 0.15 | 1.68 | 0.01 | 0.00 | 0.00 | 0.11 | 22.9 | 30.0 |  |  |  | 85.0 |
| **KAL4av** | 0.85 | 0.90 | 0.62 | 25.7 | 0.00 | 1.21 | 0.89 | 0.16 | 1.67 | 0.01 | 0.00 | 0.00 | 0.11 | 23.1 | 30.0 |  |  |  | 85.2 |
| **KAL5** | 1.36 | 0.00 | 0.00 | 5.58 | 0.00 | 34.0 | 0.01 | 0.08 | 0.01 | 0.02 | 0.00 | 0.00 | 0.01 | 37.1 | 0.00 |  |  |  | 78.2 |
| **KAL5b** | 0.65 | 0.00 | 0.00 | 5.65 | 0.00 | 34.1 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 | 37.1 | 0.00 |  |  |  | 77.5 |
| **KAL5c** | 1.60 | 0.00 | 0.00 | 5.56 | 0.00 | 33.9 | 0.01 | 0.07 | 0.02 | 0.02 | 0.00 | 0.00 | 0.02 | 37.0 | 0.00 |  |  |  | 78.1 |
| **KAL5av** | 1.20 | 0.00 | 0.00 | 5.59 | 0.00 | 34.0 | 0.00 | 0.05 | 0.01 | 0.02 | 0.00 | 0.00 | 0.01 | 37.1 | 0.00 |  |  |  | 77.9 |
| **MOUT1** | 0.00 | 0.00 | 0.03 | 8.91 | 0.00 | 18.4 | 0.00 | 0.02 | 0.03 | 0.02 | 0.00 | 0.00 | 0.04 | 17.8 |  | 11.6 | 0.18 | 11.2 | 68.2 |
| **MOUT1b** | 0.00 | 0.00 | 0.02 | 9.12 | 0.00 | 18.8 | 0.00 | 0.02 | 0.03 | 0.02 | 0.00 | 0.00 | 0.04 | 18.2 |  | 11.7 | 0.20 | 11.4 | 69.5 |
| **MOUT1c** | 0.00 | 0.00 | 0.02 | 9.31 | 0.00 | 19.3 | 0.00 | 0.00 | 0.03 | 0.03 | 0.00 | 0.00 | 0.04 | 18.6 |  | 11.8 | 0.19 | 11.6 | 70.8 |
| **MOUT1av** | 0.00 | 0.00 | 0.02 | 9.11 | 0.00 | 18.8 | 0.00 | 0.01 | 0.03 | 0.02 | 0.00 | 0.00 | 0.04 | 18.2 |  | 11.7 | 0.19 | 11.4 | 69.5 |
| **MOUT2** | 1.31 | 0.00 | 0.00 | 0.00 | 0.00 | 38.3 | 0.01 | 0.05 | 0.00 | 0.03 | 0.00 | 0.00 | 0.02 | 40.3 |  | 0.02 | 0.06 | 0.06 | 80.1 |
| **MOU2b** | 1.98 | 0.00 | 0.00 | 0.00 | 0.00 | 38.2 | 0.00 | 0.06 | 0.01 | 0.03 | 0.00 | 0.00 | 0.02 | 40.4 |  | 0.02 | 0.07 | 0.07 | 80.9 |
| **MOUT2c** | 1.22 | 0.00 | 0.00 | 0.00 | 0.00 | 38.7 | 0.00 | 0.00 | 0.01 | 0.02 | 0.00 | 0.00 | 0.02 | 40.8 |  | 0.02 | 0.07 | 0.07 | 80.9 |
| **MOUT2av** | 1.50 | 0.00 | 0.00 | 0.00 | 0.00 | 38.4 | 0.01 | 0.03 | 0.01 | 0.02 | 0.00 | 0.00 | 0.02 | 40.5 |  | 0.02 | 0.07 | 0.07 | 80.6 |
| **MOUT3** | 0.00 | 0.00 | 0.00 | 0.85 | 0.00 | 11.3 | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 | 0.00 | 0.01 | 2.12 |  | 3.43 | 0.12 | 65.0 | 82.9 |
| **MOUT3b** | 0.00 | 0.00 | 0.00 | 0.86 | 0.00 | 11.4 | 0.00 | 0.00 | 0.03 | 0.02 | 0.00 | 0.00 | 0.01 | 2.07 |  | 3.39 | 0.12 | 63.8 | 81.7 |
| **MOUT3c** | 0.00 | 0.00 | 0.00 | 0.77 | 0.00 | 10.1 | 0.00 | 0.00 | 0.05 | 0.02 | 0.00 | 0.00 | 0.00 | 1.87 |  | 3.07 | 0.12 | 58.1 | 74.1 |
| **MOUT3av** | 0.00 | 0.00 | 0.00 | 0.83 | 0.00 | 11.0 | 0.00 | 0.00 | 0.03 | 0.02 | 0.00 | 0.00 | 0.01 | 2.02 |  | 3.30 | 0.12 | 62.3 | 79.6 |

*Table A2.1b (P)ED-XRF analyses of mineral samples from Seriphos (trace elements in ppm). Values not given here (empty boxes) are included in the table above. Values labelled with (av) are calculated averages of the three analyses above. Elements consistently detected below 5 ppm have not been included in this table.*

| | NiO | CuO | ZnO | Ga | $As_2O_3$ | Se | SrO | Y | $ZrO_2$ | Mo | Ag | CdO | Sb | I | Ba | La | Ce | Hf | $Ta_2O_5$ | Hg | Tl | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **RK1** | 307 | | 154 | 13 | | 70 | 5 | 17 | 19 | 0 | 10 | 2 | 3 | 0 | 16 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 40 | 0 |
| **RK1b** | 284 | | 142 | 14 | | 69 | 5 | 20 | 6 | 0 | 5 | 0 | 4 | 0 | 0 | 11 | 15 | 0 | 0 | 0 | 0 | 0 | 41 | 0 |
| **RK1c** | 279 | | 147 | 14 | | 72 | 7 | 17 | 9 | 0 | 4 | 0 | 0 | 0 | 0 | 11 | 13 | 0 | 0 | 0 | 0 | 0 | 34 | 0 |
| **RK1av** | 290 | | 148 | 14 | | 70 | 6 | 18 | 11 | 0 | 6 | 1 | 2 | 0 | <16 | 11 | 9 | 0 | 0 | 0 | 0 | 0 | 38 | 0 |
| **RK2** | 274 | | 113 | 16 | | 68 | 8 | 23 | 0 | 0 | 8 | 2 | 0 | 0 | 0 | 12 | 12 | 0 | 0 | 0 | 0 | 0 | 35 | 0 |
| **RK2b** | 296 | | 154 | 0 | | 69 | 5 | 18 | 19 | 0 | 4 | 0 | 0 | 0 | 9 | 11 | 0 | 0 | 0 | 0 | 0 | 0 | 19 | 0 |
| **RK2c** | 299 | | 150 | 14 | | 71 | 8 | 21 | 9 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 37 | 0 |
| **RK2av** | 290 | | 139 | <16 | | 69 | 7 | 20 | <19 | 0 | 5 | 1 | 0 | 0 | <9 | <12 | <12 | 0 | 0 | 0 | 0 | 0 | 30 | 0 |
| **KOUT1** | 976 | | 670 | 40 | | 0 | 78 | 317 | 0 | 0 | 20 | 3 | 3 | 41 | 175 | 32 | 18 | 0 | 0 | 268 | 0 | 0 | 0 | 21 |
| **KOUT1b** | 983 | | 672 | 47 | | 0 | 84 | 309 | 15 | 0 | 18 | 3 | 3 | 41 | 168 | 29 | 20 | 0 | 0 | 223 | 0 | 0 | 0 | 23 |
| **KOUT1c** | 1021 | | 663 | 40 | | 0 | 80 | 326 | 11 | 0 | 20 | 3 | 0 | 43 | 170 | 24 | 21 | 0 | 0 | 240 | 0 | 0 | 0 | 34 |
| **KOUT1av** | 993 | | 668 | 42 | | 0 | 80 | 317 | 9 | 0 | 19 | 3 | 2 | 41 | 171 | 28 | 20 | 0 | 0 | 244 | 0 | 0 | 0 | 26 |
| **KOUT2** | 152 | | 196 | 39 | | 0 | 78 | 66 | 0 | 0 | 3 | 0 | 0 | 17 | 155 | 172 | 112 | 0 | 0 | 122 | 0 | 0 | 0 | 0 |
| **KOUT2b** | 150 | | 184 | 30 | | 0 | 84 | 78 | 0 | 0 | 3 | 0 | 0 | 18 | 163 | 186 | 112 | 0 | 0 | 114 | 0 | 0 | 0 | 0 |
| **KOUT2c** | 146 | | 195 | 0 | | 0 | 76 | 73 | 0 | 0 | 1 | 0 | 0 | 21 | 171 | 191 | 126 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KOUT2av** | 149 | | 192 | <39 | | 0 | 79 | 72 | 0 | 0 | 2 | 0 | 0 | 19 | 163 | 183 | 116 | 0 | 0 | <122 | 0 | 0 | 0 | 0 |
| **KOUT3** | 91 | | 123 | 0 | | 0 | 76 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 24090 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KOUT3b** | 78 | | 100 | 0 | | 0 | 80 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 24550 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KOUT3c** | 81 | | 113 | 0 | | 0 | 75 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 24230 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KOUT3av** | 83 | | 112 | 0 | | 0 | 77 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 24290 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

|  | NiO | CuO | ZnO | Ga | $As_2O_3$ | Se | SrO | Y | $ZrO_2$ | Mo | Ag | CdO | Sb | I | Ba | La | Ce | Hf | $Ta_2O_5$ | Hg | Tl | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KOUT4** | 488 |  | 618 | 0 |  | 0 | 198 | 264 | 0 | 0 | 6 | 0 | 0 | 69 | 405 | 67 | 57 | 0 | 2480 | 468 | 0 | 0 | 0 | 0 |
| **KOUT4b** | 443 |  | 556 | 0 |  | 0 | 171 | 216 | 0 | 0 | 5 | 0 | 1 | 58 | 359 | 61 | 54 | 0 | 5320 | 0 | 0 | 0 | 0 | 0 |
| **KOUT4c** | 413 |  | 516 | 0 |  | 0 | 173 | 226 | 0 | 0 | 7 | 0 | 2 | 59 | 359 | 64 | 51 | 0 | 2010 | 406 | 0 | 0 | 0 | 0 |
| **KOUT4av** | 448 |  | 563 | 0 |  | 0 | 180 | 235 | 0 | 0 | 6 | 0 | 1 | 62 | 374 | 64 | 54 | 0 | 3270 | <468 | 0 | 0 | 0 | 0 |
| **KOUT5** | 502 |  | 597 | 0 |  | 0 | 166 | 263 | 0 | 0 | 10 | 1 | 2 | 63 | 194 | 54 | 81 | 0 | 3300 | 0 | 0 | 0 | 0 | 31 |
| **KOUT5b** | 531 |  | 673 | 0 |  | 0 | 176 | 304 | 0 | 0 | 8 | 0 | 0 | 73 | 213 | 60 | 93 | 0 | 11220 | 0 | 0 | 0 | 0 | 35 |
| **KOUT5c** | 490 |  | 550 | 0 |  | 0 | 161 | 264 | 0 | 0 | 6 | 0 | 0 | 57 | 174 | 45 | 81 | 0 | 4070 | 0 | 0 | 0 | 0 | 26 |
| **KOUT5av** | 508 |  | 607 | 0 |  | 0 | 168 | 277 | 0 | 0 | 8 | 0 | 1 | 64 | 194 | 53 | 85 | 0 | 6197 | 0 | 0 | 0 | 0 | 31 |
| **PL1** | 930 |  | 203 | 0 | 74 | 3 | 18 | 59 | 14 | 24 | 8 | 0 | 6 | 0 | 186 | 0 | 0 | 0 | 620 | 0 | 0 | 0 | 0 | 11 |
| **PL1b** | 913 |  | 210 | 0 | 74 | 0 | 21 | 59 | 0 | 22 | 7 | 0 | 5 | 0 | 187 | 0 | 0 | 0 | 880 | 0 | 0 | 0 | 0 | 9 |
| **PL1c** | 896 |  | 223 | 0 | 70 | 5 | 21 | 60 | 14 | 23 | 7 | 0 | 4 | 0 | 190 | 0 | 0 | 0 | 440 | 0 | 0 | 0 | 0 | 0 |
| **PL1av** | 913 |  | 212 | 0 | 73 | 3 | 20 | 59 | <14 | 23 | 7 | 0 | 5 | 0 | 188 | 0 | 0 | 0 | 647 | 0 | 0 | 0 | 0 | 6 |
| **PL2** | 409 |  | 0 | 7 | 7 | 14 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **PL2b** | 448 |  | 0 | 10 | 3 | 11 | 0 | 4 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **PL2c** | 419 |  | 0 | 5 | 2 | 12 | 0 | 0 | 0 | 5 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **PL2av** | 425 |  | 0 | 7 | 4 | 12 | 0 | 1 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **PL3** | 447 |  | 1373 | 0 | 0 | 0 | 34 | 0 | 0 | 0 | 44 | 4 | 1 | 0 | 0 | 0 | 0 | 500 | 1820 | 0 | 0 | 0 | 0 | 0 |
| **PL3b** | 453 |  | 1368 | 0 | 0 | 0 | 34 | 0 | 0 | 0 | 48 | 2 | 0 | 0 | 0 | 0 | 0 | 370 | 1070 | 0 | 0 | 0 | 0 | 0 |
| **PL3c** | 457 |  | 1348 | 0 | 0 | 0 | 35 | 0 | 0 | 0 | 49 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **PL3av** | 452 |  | 1363 | 0 | 0 | 0 | 34 | 0 | 0 | 0 | 47 | 3 | 0 | 0 | 0 | 0 | 0 | <500 | <1820 | 0 | 0 | 0 | 0 | 0 |
| **VOUN1** | 169 |  | 794 | 0 | 25 | 0 | 18 | 192 | 0 | 0 | 0 | 1 | 0 | 0 | 24 | 148 | 227 | 0 | 0 | 0 | 0 | 19 | 0 | 25 |
| **VOUN1b** | 157 |  | 740 | 0 | 0 | 0 | 20 | 184 | 0 | 0 | 0 | 0 | 0 | 3 | 20 | 136 | 218 | 0 | 0 | 0 | 0 | 0 | 0 | 16 |
| **VOUN1c** | 185 |  | 797 | 0 | 17 | 0 | 18 | 191 | 0 | 0 | 0 | 0 | 0 | 0 | 25 | 151 | 221 | 0 | 0 | 0 | 0 | 26 | 0 | 21 |
| **VOUN1av** | 170 |  | 777 | 0 | 14 | 0 | 19 | 189 | 0 | 0 | 0 | 0 | 0 | 1 | 23 | 145 | 222 | 0 | 0 | 0 | 0 | <26 | 0 | 20 |
| **VOUN2** | 0 |  | 310 | 7 | 867 | 0 | 0 | 11 | 0 | 26 | 0 | 1 | 2 | 8 | 36 | 0 | 11 | 0 | 0 | 0 | 0 | 0 | 0 | 13 |

| | NiO | CuO | ZnO | Ga | $As_2O_3$ | Se | SrO | Y | $ZrO_2$ | Mo | Ag | CdO | Sb | I | Ba | La | Ce | Hf | $Ta_2O_5$ | Hg | Tl | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **VOUN2b** | 0 | | 335 | 11 | 856 | 6 | 2 | 8 | 0 | 15 | 0 | 0 | 0 | 7 | 41 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **VOUN2c** | 0 | | 330 | 11 | 872 | 0 | 0 | 9 | 0 | 11 | 0 | 0 | 0 | 8 | 36 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| **VOUN2av** | 0 | | 325 | 10 | 865 | 2 | 1 | 9 | 0 | 17 | 0 | 0 | 1 | 8 | 38 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | <13 |
| **VOUN3** | 28 | | 139 | 4 | 14 | 0 | 6 | 53 | 9 | 2 | 0 | 0 | 3 | 0 | 0 | 42 | 24 | 0 | 0 | 0 | 0 | 10 | 0 | 0 |
| **VOUN3b** | 32 | | 133 | 2 | 12 | 0 | 6 | 55 | 6 | 0 | 0 | 0 | 2 | 0 | 0 | 42 | 31 | 0 | 0 | 0 | 0 | 10 | 0 | 0 |
| **VOUN3c** | 33 | | 133 | 4 | 13 | 1 | 6 | 54 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 40 | 23 | 0 | 0 | 0 | 0 | 11 | 0 | 0 |
| **VOUN3av** | 31 | | 135 | 3 | 13 | 0 | 6 | 54 | 7 | 1 | 0 | 0 | 2 | 0 | 0 | 41 | 26 | 0 | 0 | 0 | 0 | 10 | 0 | 0 |
| **KAL1** | 227 | | 124 | 0 | 16 | 0 | 2 | 21 | 0 | 0 | 0 | 1 | 15 | 0 | 118 | 0 | 28 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL1b** | 215 | | 128 | 0 | 17 | 0 | 3 | 18 | 0 | 0 | 0 | 0 | 14 | 3 | 124 | 0 | 28 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL1c** | 219 | | 126 | 0 | 25 | 0 | 2 | 17 | 0 | 0 | 0 | 0 | 14 | 0 | 131 | 0 | 38 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL1av** | 220 | | 126 | 0 | 19 | 0 | 2 | 19 | 0 | 0 | 0 | 0 | 14 | 1 | 124 | 0 | 32 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL2** | 0 | | 0 | 14 | 299 | 12 | 0 | 0 | 0 | 0 | 6 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL2b** | 0 | | 0 | 6 | 307 | 10 | 0 | 6 | 0 | 12 | 3 | 0 | 0 | 0 | 16 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL2c** | 0 | | 0 | 10 | 305 | 8 | 0 | 5 | 0 | 16 | 3 | 0 | 0 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL2av** | 0 | | 0 | 10 | 304 | 10 | 0 | 4 | 0 | 9 | 4 | 0 | 1 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL3** | 118 | | 37 | 8 | 20 | 0 | 7 | 6 | 0 | 0 | 0 | 0 | 26 | 0 | 154 | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 0 | 0 |
| **KAL3b** | 125 | | 46 | 0 | 15 | 0 | 6 | 6 | 0 | 0 | 0 | 0 | 24 | 0 | 139 | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 0 | 0 |
| **KAL3c** | 105 | | 43 | 7 | 20 | 0 | 7 | 6 | 0 | 0 | 0 | 0 | 26 | 0 | 153 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 2 | 0 |
| **KAL3av** | 116 | | 42 | 5 | 18 | 0 | 7 | 6 | 0 | 0 | 0 | 0 | 25 | 0 | 148 | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 1 | 0 |
| **KAL4** | 134 | | 1412 | 0 | 43 | 0 | 5 | 0 | 0 | 0 | 2 | 1 | 4 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 712 | 0 | 0 |
| **KAL4b** | 148 | | 1363 | 0 | 35 | 0 | 6 | 3 | 0 | 0 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 705 | 0 | 0 |
| **KAL4c** | 164 | | 1379 | 0 | 30 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 686 | 0 | 0 |
| **KAL4av** | 149 | | 1385 | 0 | 36 | 0 | 5 | 1 | 0 | 0 | 1 | 1 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 701 | 0 | 0 |
| **KAL5** | 0 | 59 | 37 | 0 | 93 | 67 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL5b** | 0 | 57 | 37 | 0 | 89 | 70 | 0 | 3 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

|  | NiO | CuO | ZnO | Ga | $As_2O_3$ | Se | SrO | Y | $ZrO_2$ | Mo | Ag | CdO | Sb | I | Ba | La | Ce | Hf | $Ta_2O_5$ | Hg | Tl | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KAL5c** | 0 | 43 | 30 | 0 | 91 | 69 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **KAL5av** | 0 | 53 | 35 | 0 | 91 | 69 | 0 | 3 | 2 | 0 | 0 | 0 | 0 | 0 | <13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **MOUT1** | 128 | 95 |  | 0 |  | 0 | 79 | 0 | 29 | 0 | 31 | 284 | 39 | 0 | 9 | 0 | 0 | 118 | 37 | 57 | 175 |  | 0 | 0 |
| **MOUT1b** | 135 | 147 |  | 0 |  | 0 | 92 | 0 | 14 | 0 | 29 | 312 | 37 | 0 | 12 | 0 | 0 | 101 | 0 | 38 | 190 |  | 0 | 0 |
| **MOUT1c** | 168 | 106 |  | 0 |  | 0 | 79 | 0 | 22 | 0 | 34 | 310 | 40 | 0 | 0 | 0 | 0 | 78 | 39 | 49 | 188 |  | 0 | 0 |
| **MOUT1av** | 144 | 116 |  | 0 |  | 0 | 83 | 0 | 21 | 0 | 31 | 302 | 39 | 0 | 7 | 0 | 0 | 99 | <39 | 48 | 184 |  | 0 | 0 |
| **MOUT2** | 0 | 0 |  | 7 |  | 0 | 0 | 7 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 |  | 0 | 0 |
| **MOU2b** | 0 | 0 |  | 0 |  | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 |  | 0 | 0 |
| **MOUT2c** | 0 | 0 |  | 10 |  | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 |  | 0 | 0 |
| **MOUT2av** | 0 | 0 |  | 6 |  | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 1 | 0 |  | 0 | 0 |
| **MOUT3** | 169 | 201 |  | 0 |  | 0 | 348 | 0 | 0 | 0 | 234 | 141 | 149 | 0 | 0 | 0 | 0 | 70 | 0 | 310 | 1060 |  | 0 | 0 |
| **MOUT3b** | 264 | 175 |  | 0 |  | 0 | 364 | 0 | 0 | 0 | 214 | 131 | 132 | 0 | 0 | 0 | 0 | 117 | 0 | 270 | 1380 |  | 0 | 0 |
| **MOUT3c** | 135 | 140 |  | 0 |  | 0 | 308 | 0 | 0 | 0 | 220 | 108 | 128 | 0 | 0 | 0 | 0 | 88 | 0 | 257 | 1200 |  | 0 | 0 |
| **MOUT3av** | 189 | 172 |  | 0 |  | 0 | 340 | 0 | 0 | 0 | 223 | 127 | 136 | 0 | 0 | 0 | 0 | 92 | 0 | 279 | 1213 |  | 0 | 0 |

# APPENDIX 3.

## Thermoluminescence (TL) dating of furnace wall fragments from Kephala and Phournoi

(with report prepared by Dr N. Zacharias)

### Catalogue of samples submitted for TL dating

| Name | Context | Width (cm) | Description |
|---|---|---|---|
| **KEF1A** | Kephala 1 | 4.5 | Red-orange outer surface with impressions of burnt-out organic materials, thin layer of dark-grey vitrified layer in inner surface (c. 1 mm), coarse inclusions mainly of schist and quartz, does not appear to bear attached slag |
| **KEF1C** | Kephala 1 | 3.5 | As above, vitrification layer c. 0.4 cm, thin layer of slag attached |
| **KEF2B** | Kephala 2 | 4.0 | General description as before, shows a single hole impression |
| **KEF2C** | Kephala 2 | 2.5 | General description as for KEF1A |
| **F1A** | Phournoi 1 | 2.5 | Red-orange outer surface with impressions of burnt-out organic materials, thin layer of dark-grey vitrified layer in inner surface (c. 0.3 cm), coarse inclusions mainly of schist and quartz, traces of attached slag |
| **F1D** | Phournoi 1 | 2.0 | Description as before, shows green staining in slag attached in inner surface |

### Report of Quartz TL Dating Methodology and Results for the Seriphos Archaeometallurgical Samples (courtesy of Dr N. Zacharias)

Following the standard mechanical and chemical treatment (Wintle 1997), pure quartz grains were isolated for the preparation of measurement aliquots. For the estimation of the archaeological dose (De) the additive dose model of the *foil technique* (Michael *et al.* 1997) was used. For the internal dose rate estimation neutron activation analysis and a PIPS alpha-counting (Michael and Zacharias 2000) were employed. The environmental dose was recorded *in situ* using a portable NaI scintillator calibrated against values provided with $Al_2O_3$ phosphors buried at various archaeological sites in Greece.

Initial TL measurements for checking the material suitability provided indications for highly varied TL signals, which should be attributed to the large sample thickness and the thermal treatment the specimens had undergone. In order to correct for these effects and after the removal of an external thickness of ca. 0.3-0.5 cm, the remaining assays were divided in layers following the visually observed colour variation. The TL response of every layer were examined by comparing the natural TL intensity with the signal of the same aliquot after applying repeated irradiation and measurement cycles with the same standard laboratory dose. The main observations from this procedure (Figure A3.1) can be summarised as follows:

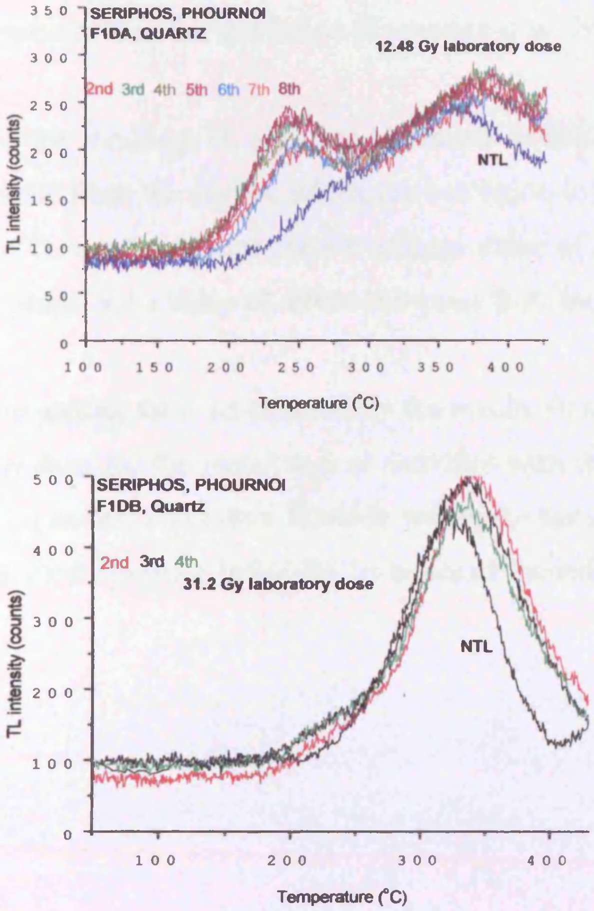


***Figure A3.1*** *Natural TL and repeated irradiation/ measurement signals from the two layers resulting from sample F1D (DA the outer, DB the inner layer).*

The TL sensitivity of the outer –to the firing process- layers is progressively increased up to a stable behaviour, while the signals from the innermost layers are slightly decreased. Also, the intensity of the natural TL read-out is reached by providing a laboratory dose of 12.48 Gy for the outer layers and three times higher dose (31.2 Gy) for the inner layers which indicates significant changes of sensitivity for the highly fired material.

Furthermore, chemical analysis of the samples using Neutron Activation Analysis provided the chemical patterns of the material. Of main interest for TL dating are the significantly lower values for the alkaline elements of K, Rb and Cs found for three out of the four innermost layers in comparison to the concentration values of the outer ones (Kef1aa/ Kef1ab, F1aa/F1ab, F1da/F1db). These lower values indicate that a leaching process (Schwedt *et al.* 2004) occurred some time during the burial period. The effect of K leaching on the luminescence (TL/OSL) dating has been explored recently and the relation between this effect and possible age overestimation is established (Zacharias *et al.* 2005).

All the resulting TL ages are presented in Table A3.1. Highlighted in bold are the results from the layers, which are not liable to any leaching effect. By considering the TL results of these layers a mean value of 4640±240 years B.P. is deduced for Kephala and a value of 4940±360 years B.P. for Phournoi.

Accounting for a 1σ-uncertainty the results from both sites indicate an Early Bronze Age date for the metallurgical activities with the site of Phournoi possibly pointing to an earlier event than Kephala within the same period. Age errors provided are the standard deviation using the 1σ errors of the individual ages.

***Table A3.1*** *Results of TL dating of metallurgical ceramics from Seriphos. In bold, the outer layers and layers which do not exhibit alteration (leaching) effects.*

| | **De**<br>(Gy) | **U, Th beta**<br>(mGy/a) | **K beta**<br>(mGy/a) | **Denv**<br>(mGy/a) | **total dose**<br>(mGy/a) | **AGE**<br>(ka, 1σ) |
|---|---|---|---|---|---|---|
| **KEPHALA 1** | | | | | | |
| **KEF1AA** | **13.09±0.92** | **0.89±0.05** | **1.43±0.07** | **0.67** | **2.99±0.27** | **4.38±0.50** |
| KEF1AB | 12.1±0.99 | 0.99±0.06 | 0.91±0.06 | 0.67 | 2.57±0.26 | 4.71±0.61 |
| **KEF1C** | **14.00±1.01** | **0.97±0.06** | **1.48±0.05** | **0.67** | **3.12±0.29** | **4.49±0.53** |
| **KEPHALA 2** | | | | | | |
| **KEF2BA** | **13.25±0.93** | **0.85±0.05** | **1.22±0.04** | **0.72** | **2.79±0.26** | **4.75±0.55** |
| **KEF2BB** | **13.59±0.95** | **0.86±0.06** | **1.19±0.04** | **0.72** | **2.78±0.27** | **4.89±0.59** |
| **KEF2C** | **13.85±0.90** | **0.84±0.04** | **1.40±0.06** | **0.72** | **2.96±0.29** | **4.68±0.55** |
| **PHOURNOI 1** | | | | | | |
| **F1AA** | **17.20±1.05** | **1.22±0.06** | **1.67±0.07** | **0.63** | **3.52±0.28** | **4.89±0.49** |
| F1BB | 15.80±1.11 | 1.27±0.07 | 1.19±0.04 | 0.63 | 3.09±0.27 | 5.12±0.57 |
| **F1DA** | **18.31±1.11** | **0.97±0.05** | **2.07±0.08** | **0.63** | **3.67±0.31** | **4.99±0.52** |
| FIDB | 18.14±1.07 | 0.91±0.05 | 1.85±0.08 | 0.63 | 3.39±0.29 | 5.35±0.56 |

# APPENDIX 4.

## Tables of results of the analyses of the metallurgical remains from Kephala and Phournoi

*Table A4.1 Catalogue of samples analysed from Kephala (D: dimensions, W: weight, S: slag, M: matte or weathered matte, O: Fe and/or Cu minerals, MC: copper metal fragment or prill).*

| Sample | Group | Type | D (cm) | W (g) | Description |
|---|---|---|---|---|---|
| **KEF1** | Kephala 1 | S | 1.5x1.5x1.5 | 8.2 | Small slag, shows flow texture on upper surface, non-porous |
| **KEF2** | Kephala 1 | S | 2.0x1.5x1.7 | 7.8 | Small slag, medium porosity, small inclusions of ceramic and stones, Fe-oxide and very little green staining |
| **KEF3** | Kephala 1 | S | 8.5x6.5x4.5 | 180.5 | Broken from large mass of slag, inclusions (1-3 mm) of schist and quartz, Fe-oxide staining and little green staining, porous (1-3 mm) |
| **KEF4** | Kephala 1 | S | 6.0x3.0x3.2 | 48.9 | Broken from large mass of slag, inclusions (1-3 mm) of schist and quartz, Fe-oxide staining and intense green staining on one side (internal), medium porosity (1-7 mm) |
| **KEF18** | Kephala 1 | S | 2.0x1.5x1.5 | 8.3 | Small slag, shows flow texture on upper surface, non-porous |
| **KEF23** | Kephala 1 | S | 5.2x5.5x7.8 | 840.0 | Large brown-black slag, shows intense crystallinity with elongated crystals stretching from one end to the other, little iron oxide staining, non-porous |
| **KEF24** | Kephala 1 | S | 7.8x7.5x4.5 | 330.0 | Large, black, with many inclusions mainly schist (up to c. 2 cm), shows flow texture and appears as if many inclusions were drawn during slag flow, green |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  |  |  |  |  | staining, little porosity, retains upper and lower surface, lower surface bears most inclusions |
| **KEF28** | Kephala 1 | M | 1.9x1.5x0.3 | 2.6 | One side covered in green staining with little Fe-oxide staining, from the side the sample is black and crystalline, bottom surface orange-brown from Fe-oxides and soil, non-magnetic |
| **KEF29** | Kephala 1 | O | 1.6x1.1x0.7 | 1.4 | Secondary iron and copper minerals, red-brown in colour with green colouration in parts, partly magnetic |
| **KEF30** | Kephala 1 | O | 1.3x1.0x0.5 | 0.5 | Secondary iron and copper minerals, red-brown in colour with green colouration in parts, partly magnetic, attached quartz and schist fragments |
| **KEF31** | Kephala 1 | S | 9.5x8.0x3.6 | 470.0 | Brown-black, top surface shows flow texture, bottom has 4 large schist fragments attached (7-24 mm) |
| **KEF32** | Kephala 1 | S | 2.5x1.5x1.3 | 11.1 | Small, black, Fe-oxide staining, intense green staining in some areas |
| **KEF33** | Kephala 1 | S | 4.7x2.7x0.9 | 22.5 | Small, black, shows flow texture on upper surface |
| **KEF34** | Kephala 1 | S | 3.4x3.1x2.5 | 36.0 | Black retains in large part lustrous surface and shows limited flow texture, may be two slags on top of each other, with lower showing more porosity and intense green staining on one side |
| **KEF35** | Kephala 1 | S | 4.8x3.2x2.3 | 65.9 | Black with many inclusions, medium porosity |
| **KEF36** | Kephala 1 | S | 3.2x2.1x3.0 | 25.0 | Black, shows flow texture on upper surface, lower surface non-porous followed by a layer with large pores (up to 1 cm), crystalline |
| **KEF41** | Kephala 1 | MC | 1.5x0.8x0.4 | 1.6 | Copper metal prill, completely covered externally in green corrosion layer |
| **KEF5** | Kephala 2 | S | 3.0x2.0x1.5 | 17.3 | Small slag, very little porosity (usually <1 mm), Fe-oxide staining |
| **KEF6** | Kephala 2 | S | 4.5x3.0x2.5 | 30.6 | Small slag, very little porosity (usually <1 mm), Fe-oxide staining, few small inclusions of stones (1-2 mm) |
| **KEF7** | Kephala 2 | S | 4.0x3.0x3.0 | 63.6 | Broken from a larger piece of slag that appeared to have been poured on the schist bedrock (the pieces had started fragmenting but remained in place), flow texture on upper surface, lower surface still retains schist, intense green and blue stringers on sides, non-porous |
| **KEF8** | Kephala 2 | S | 5.0x5.0x4.5 | 86.9 | Grey-brown-black, porous (usually ca 1-4 mm) slag, 30% of outer surface |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  |  |  |  |  | covered with yellow-brown layer (limonite/ soil?), few small inclusions of stones, one tiny green stain |
| **KEF9** | Kephala 2 | S | 6.0x3.5x0.7 | 53.9 | Brown-black slag, flat with circular upward 'lip' on one side, one surface shows intense crystallinity, the other appears to be the bottom surface from its texture |
| **KEF10** | Kephala 2 | S | 5.0x2.5x5.5 | 78.6 | Black slag, cut from larger piece, which was bowl-shaped and showed macroscopically intense crystallinity in its upper surface, non-porous |
| **KEF13** | Kephala 2 | S | 8.3x6.5x4.0 | 245.1 | Grey/black slag, Fe oxide and little Cu-oxide staining, little porosity (c. 1 mm), crystalline |
| **KEF14** | Kephala 2 | S | 6.0x6.0x3.0 | 236.8 | Grey/black slag, contains many inclusions of ceramic, quartz and schist (0.1-2.5 cm), crystalline, little porosity (usually <1 mm) |
| **KEF17** | Kephala 2 | S | 2.5x2.0x1.3 | 10.3 | Small slag, very little porosity (usually <1 mm), Fe-oxide staining |
| **KEF26** | Kephala 2 | S | 10x6.2x2.4 | 276.0 | Brown/ black, flow texture, crystalline, low porosity |
| **KEF27** | Kephala 2 | M | 1.8x1.3x0.6 | 2.6 | Roughly oval-shaped, green with little orange-brown staining (soil-Fe oxides?) |
| **KEF38** | Kephala 2 | S | 5.0x3.4x1.7 | 58.7 | Brown/black, upper surface shows flow texture, lower surface bears small inclusions mainly schist |
| **KEF39** | Kephala 2 | S | 3.6x3.7x2.5 | 29.6 | Grey/black, retains lustrous surface, flow texture, schist inclusions, green staining, low porosity |
| **KEF11** | Kephala 3 | S | 3.5x2.8x2.0 | 36.3 | Grey/black, very little porosity (1-2 mm) |
| **KEF12** | Kephala 3 | M | 2.8x1.5x1.0 | 4.1 | 90% of surface covered in green staining |
| **KEF15** | Kephala 3 | S | 5.0x3.0x2.5 | 48.3 | Grey/black, very little porosity (1-2 mm), little green staining |
| **KEF16** | Kephala 3 | S | 4.2x3.8x1.3 | 35.8 | Grey/black, very little porosity (1-2 mm), retains upper and lower surface and shows flow texture on upper one |
| **KEF40** | Kephala 3 | S | 3.0x3.0x1.5 | 25.0 | Grey/black, very little porosity (1-2 mm), two green prills on outer surface (c. 0.7 cm diameter) |
| **KEF25** | Furnace | S | 5.7x2.3x1.5 | 49.2 | Slag detached from rock-cut furnace, slag layer (1.3 cm thick) followed by schist leaf, which appears to have been thermally affected, and then thin layer of slag (2 mm) showing flow texture, brown-black colour, little green staining, practically non-porous |

***Table A4.2a*** *Results of (P)ED-XRF analyses on Kephala slag samples (major and minor elements in weight %). Analyses in bold are averages of three runs (a, b, c).*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$P_2O_5$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **$V_2O_5$** | **$Cr_2O_3$** | **MnO** | **$Fe_2O_3$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF1a** | 0.44 | 3.85 | 2.27 | 35.3 | 0.02 | 0.09 | 0.27 | 3.65 | 0.08 | 0.00 | 0.01 | 0.42 | 43.1 | 3.90 | 93.4 |
| **KEF1b** | 0.46 | 3.71 | 2.22 | 34.9 | 0.03 | 0.09 | 0.27 | 3.64 | 0.08 | 0.00 | 0.01 | 0.42 | 42.7 | 3.87 | 92.3 |
| **KEF1c** | 0.54 | 3.68 | 2.26 | 34.8 | 0.02 | 0.09 | 0.27 | 3.61 | 0.08 | 0.00 | 0.01 | 0.42 | 42.7 | 3.86 | 92.3 |
| **KEF1** | **0.48** | **3.74** | **2.25** | **35.0** | **0.02** | **0.09** | **0.27** | **3.63** | **0.08** | **0.00** | **0.01** | **0.42** | **42.8** | **3.88** | **92.7** |
| **KEF3a** | 0.62 | 3.12 | 1.92 | 33.3 | 0.00 | 0.00 | 0.21 | 7.62 | 0.03 | 0.00 | 0.01 | 0.17 | 50.6 | 0.74 | 98.3 |
| **KEF3b** | 0.46 | 3.05 | 1.92 | 33.6 | 0.00 | 0.00 | 0.21 | 7.63 | 0.03 | 0.00 | 0.01 | 0.17 | 50.6 | 0.73 | 98.3 |
| **KEF3c** | 0.57 | 3.16 | 1.97 | 33.4 | 0.00 | 0.00 | 0.21 | 7.67 | 0.02 | 0.00 | 0.01 | 0.17 | 51.0 | 0.74 | 98.9 |
| **KEF3** | **0.55** | **3.11** | **1.93** | **33.4** | **0.00** | **0.00** | **0.21** | **7.64** | **0.03** | **0.00** | **0.01** | **0.17** | **50.7** | **0.74** | **98.5** |
| **KEF4a** | 0.72 | 2.37 | 5.06 | 42.2 | 0.00 | 0.42 | 0.94 | 17.5 | 0.14 | 0.00 | 0.00 | 0.43 | 24.7 | 3.07 | 97.6 |
| **KEF4b** | 0.76 | 2.31 | 4.97 | 41.9 | 0.00 | 0.41 | 0.93 | 17.3 | 0.14 | 0.00 | 0.00 | 0.43 | 24.6 | 3.03 | 96.8 |
| **KEF4c** | 0.00 | 2.21 | 4.92 | 41.8 | 0.00 | 0.41 | 0.93 | 17.3 | 0.14 | 0.00 | 0.00 | 0.43 | 24.5 | 3.00 | 95.5 |
| **KEF4** | **0.49** | **2.30** | **4.98** | **42.0** | **0.00** | **0.41** | **0.94** | **17.3** | **0.14** | **0.00** | **0.00** | **0.43** | **24.6** | **3.03** | **96.6** |
| **KEF5a** | 0.76 | 2.16 | 5.34 | 26.1 | 0.01 | 0.49 | 0.76 | 2.20 | 0.23 | 0.00 | 0.01 | 0.16 | 57.4 | 2.76 | 98.4 |
| **KEF5b** | 0.83 | 2.19 | 5.26 | 26.2 | 0.01 | 0.49 | 0.77 | 2.21 | 0.22 | 0.00 | 0.01 | 0.17 | 57.7 | 2.80 | 98.9 |
| **KEF5c** | 0.52 | 2.08 | 5.20 | 26.2 | 0.01 | 0.49 | 0.75 | 2.21 | 0.22 | 0.00 | 0.01 | 0.17 | 57.3 | 2.78 | 97.9 |
| **KEF5** | **0.70** | **2.14** | **5.26** | **26.2** | **0.01** | **0.49** | **0.76** | **2.20** | **0.22** | **0.00** | **0.01** | **0.17** | **57.5** | **2.78** | **98.4** |
| **KEF6a** | 0.57 | 1.74 | 6.39 | 29.6 | 0.04 | 0.53 | 0.72 | 3.17 | 0.24 | 0.00 | 0.01 | 0.23 | 58.3 | 0.92 | 103 |
| **KEF6b** | 0.97 | 1.98 | 6.33 | 29.4 | 0.05 | 0.54 | 0.72 | 3.16 | 0.24 | 0.00 | 0.01 | 0.23 | 58.1 | 0.91 | 103 |
| **KEF6c** | 0.76 | 2.00 | 6.41 | 29.6 | 0.04 | 0.54 | 0.72 | 3.18 | 0.24 | 0.00 | 0.01 | 0.23 | 58.5 | 0.91 | 103 |
| **KEF6** | **0.77** | **1.91** | **6.38** | **29.5** | **0.04** | **0.54** | **0.72** | **3.17** | **0.24** | **0.00** | **0.01** | **0.23** | **58.3** | **0.91** | **103** |
| **KEF7a** | 0.50 | 7.67 | 4.00 | 31.6 | 0.00 | 0.10 | 0.32 | 8.16 | 0.09 | 0.00 | 0.00 | 0.23 | 45.1 | 1.13 | 98.8 |
| **KEF7b** | 0.42 | 7.57 | 4.00 | 31.3 | 0.00 | 0.10 | 0.32 | 8.09 | 0.08 | 0.00 | 0.00 | 0.23 | 45.0 | 1.13 | 98.2 |

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF7c** | 0.65 | 7.51 | 3.94 | 31.1 | 0.00 | 0.09 | 0.32 | 8.06 | 0.08 | 0.00 | 0.00 | 0.23 | 44.6 | 1.12 | 97.6 |
| **KEF7** | **0.52** | **7.59** | **3.98** | **31.3** | **0.00** | **0.10** | **0.32** | **8.10** | **0.09** | **0.00** | **0.00** | **0.23** | **44.9** | **1.13** | **98.2** |
| **KEF8a** | 0.98 | 1.13 | 6.61 | 30.7 | 0.14 | 0.71 | 0.83 | 1.96 | 0.26 | 0.00 | 0.01 | 0.23 | 58.7 | 0.73 | 103 |
| **KEF8b** | 1.05 | 1.12 | 6.61 | 30.3 | 0.16 | 0.70 | 0.81 | 1.94 | 0.26 | 0.00 | 0.01 | 0.22 | 58.2 | 0.73 | 102 |
| **KEF8c** | 0.88 | 0.99 | 6.55 | 30.1 | 0.17 | 0.69 | 0.80 | 1.94 | 0.26 | 0.00 | 0.01 | 0.22 | 57.7 | 0.73 | 101 |
| **KEF8** | **0.97** | **1.08** | **6.59** | **30.4** | **0.16** | **0.70** | **0.82** | **1.95** | **0.26** | **0.00** | **0.01** | **0.23** | **58.2** | **0.73** | **102** |
| **KEF9a** | 0.53 | 1.49 | 6.00 | 32.3 | 0.00 | 0.11 | 0.45 | 3.78 | 0.19 | 0.00 | 0.01 | 0.35 | 54.7 | 2.29 | 102 |
| **KEF9b** | 0.39 | 1.46 | 5.87 | 32.1 | 0.00 | 0.11 | 0.44 | 3.74 | 0.19 | 0.00 | 0.01 | 0.34 | 54.4 | 2.30 | 101 |
| **KEF9c** | 0.55 | 1.42 | 5.99 | 32.2 | 0.00 | 0.11 | 0.45 | 3.78 | 0.19 | 0.00 | 0.01 | 0.35 | 54.8 | 2.31 | 102 |
| **KEF9** | **0.49** | **1.46** | **5.96** | **32.2** | **0.00** | **0.11** | **0.45** | **3.76** | **0.19** | **0.00** | **0.01** | **0.34** | **54.6** | **2.30** | **102** |
| **KEF10a** | 0.67 | 7.94 | 4.65 | 39.3 | 0.00 | 0.00 | 0.22 | 16.9 | 0.07 | 0.00 | 0.00 | 0.22 | 29.7 | 0.98 | 101 |
| **KEF10b** | 0.52 | 7.97 | 4.67 | 39.2 | 0.00 | 0.00 | 0.22 | 16.8 | 0.07 | 0.00 | 0.00 | 0.22 | 29.5 | 0.97 | 100 |
| **KEF10c** | 0.38 | 8.07 | 4.64 | 39.4 | 0.00 | 0.00 | 0.22 | 17.0 | 0.07 | 0.00 | 0.00 | 0.23 | 29.8 | 0.97 | 101 |
| **KEF10** | **0.52** | **7.99** | **4.65** | **39.3** | **0.00** | **0.00** | **0.22** | **16.9** | **0.07** | **0.00** | **0.00** | **0.23** | **29.7** | **0.98** | **101** |
| **KEF11a** | 0.63 | 1.13 | 4.40 | 27.2 | 0.05 | 0.23 | 0.52 | 1.41 | 0.22 | 0.00 | 0.01 | 0.21 | 60.7 | 1.38 | 98.1 |
| **KEF11b** | 0.50 | 1.10 | 4.47 | 27.8 | 0.05 | 0.25 | 0.54 | 1.44 | 0.22 | 0.00 | 0.01 | 0.22 | 62.2 | 1.42 | 100 |
| **KEF11c** | 0.52 | 1.15 | 4.27 | 27.0 | 0.03 | 0.24 | 0.52 | 1.39 | 0.22 | 0.00 | 0.01 | 0.21 | 60.8 | 1.40 | 97.7 |
| **KEF11** | **0.55** | **1.12** | **4.38** | **27.3** | **0.04** | **0.24** | **0.53** | **1.41** | **0.22** | **0.00** | **0.01** | **0.21** | **61.2** | **1.40** | **98.7** |
| **KEF13a** | 0.44 | 2.47 | 4.44 | 29.1 | 0.00 | 1.70 | 0.41 | 6.51 | 0.20 | 0.00 | 0.01 | 0.33 | 47.9 | 1.24 | 94.7 |
| **KEF13b** | 0.48 | 2.53 | 4.51 | 28.9 | 0.00 | 1.70 | 0.41 | 6.46 | 0.20 | 0.00 | 0.01 | 0.33 | 47.6 | 1.24 | 94.4 |
| **KEF13c** | 0.59 | 2.56 | 4.39 | 28.9 | 0.01 | 1.70 | 0.41 | 6.47 | 0.20 | 0.00 | 0.01 | 0.33 | 47.8 | 1.25 | 94.6 |
| **KEF13** | **0.50** | **2.52** | **4.45** | **29.0** | **0.00** | **1.70** | **0.41** | **6.48** | **0.20** | **0.00** | **0.01** | **0.33** | **47.8** | **1.24** | **94.6** |
| **KEF14a** | 0.39 | 2.58 | 5.06 | 33.3 | 0.04 | 0.02 | 0.72 | 9.25 | 0.21 | 0.00 | 0.01 | 0.43 | 43.7 | 1.11 | 96.9 |
| **KEF14b** | 0.68 | 2.72 | 5.12 | 33.5 | 0.04 | 0.02 | 0.73 | 9.31 | 0.21 | 0.00 | 0.01 | 0.44 | 44.0 | 1.11 | 97.9 |
| **KEF14c** | 0.71 | 2.72 | 5.13 | 33.5 | 0.03 | 0.02 | 0.73 | 9.34 | 0.21 | 0.00 | 0.01 | 0.44 | 44.1 | 1.12 | 98.0 |
| **KEF14** | **0.59** | **2.67** | **5.10** | **33.4** | **0.04** | **0.02** | **0.73** | **9.30** | **0.21** | **0.00** | **0.01** | **0.44** | **43.9** | **1.11** | **97.6** |

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF15a** | 0.98 | 2.47 | 5.22 | 32.0 | 0.06 | 0.10 | 0.78 | 8.81 | 0.21 | 0.01 | 0.01 | 0.55 | 44.2 | 1.44 | 96.8 |
| **KEF15b** | 0.72 | 2.38 | 5.17 | 31.9 | 0.07 | 0.10 | 0.78 | 8.83 | 0.21 | 0.01 | 0.01 | 0.55 | 44.1 | 1.43 | 96.2 |
| **KEF15c** | 0.77 | 2.36 | 5.10 | 32.0 | 0.07 | 0.10 | 0.79 | 8.80 | 0.21 | 0.01 | 0.01 | 0.54 | 43.9 | 1.43 | 96.1 |
| **KEF15** | **0.82** | **2.40** | **5.16** | **32.0** | **0.06** | **0.10** | **0.78** | **8.81** | **0.21** | **0.01** | **0.01** | **0.55** | **44.1** | **1.43** | **96.4** |
| **KEF16a** | 0.65 | 0.52 | 2.94 | 28.9 | 0.01 | 0.31 | 0.59 | 4.30 | 0.09 | 0.01 | 0.01 | 0.28 | 59.4 | 1.84 | 99.8 |
| **KEF16b** | 0.51 | 0.47 | 2.98 | 29.0 | 0.01 | 0.30 | 0.58 | 4.27 | 0.09 | 0.01 | 0.01 | 0.28 | 59.1 | 1.83 | 99.4 |
| **KEF16c** | 0.54 | 0.43 | 2.96 | 28.7 | 0.01 | 0.30 | 0.57 | 4.24 | 0.09 | 0.01 | 0.01 | 0.28 | 59.1 | 1.80 | 99.0 |
| **KEF16** | **0.57** | **0.47** | **2.96** | **28.9** | **0.01** | **0.30** | **0.58** | **4.27** | **0.09** | **0.01** | **0.01** | **0.28** | **59.2** | **1.82** | **99.4** |
| **KEF23a** | 0.71 | 2.29 | 5.08 | 30.2 | 0.07 | 0.51 | 0.47 | 3.45 | 0.21 | 0.00 | 0.01 | 0.27 | 52.9 | 0.65 | 96.9 |
| **KEF23b** | 0.99 | 2.38 | 4.96 | 30.0 | 0.05 | 0.52 | 0.47 | 3.42 | 0.21 | 0.00 | 0.01 | 0.27 | 52.9 | 0.65 | 96.9 |
| **KEF23c** | 0.69 | 2.29 | 5.13 | 30.2 | 0.08 | 0.51 | 0.47 | 3.44 | 0.21 | 0.00 | 0.01 | 0.26 | 53.0 | 0.65 | 97.0 |
| **KEF23** | **0.80** | **2.32** | **5.06** | **30.2** | **0.06** | **0.51** | **0.47** | **3.44** | **0.21** | **0.00** | **0.01** | **0.27** | **53.0** | **0.65** | **96.9** |
| **KEF24a** | 0.65 | 4.45 | 2.28 | 40.8 | 0.00 | 0.00 | 0.27 | 8.32 | 0.07 | 0.00 | 0.00 | 0.30 | 40.4 | 1.90 | 99.4 |
| **KEF24b** | 0.58 | 4.35 | 2.33 | 40.8 | 0.00 | 0.00 | 0.27 | 8.31 | 0.07 | 0.00 | 0.00 | 0.30 | 40.3 | 1.89 | 99.2 |
| **KEF24c** | 0.50 | 4.41 | 2.36 | 40.5 | 0.00 | 0.00 | 0.26 | 8.31 | 0.07 | 0.00 | 0.00 | 0.30 | 40.3 | 1.91 | 99.0 |
| **KEF24** | **0.58** | **4.40** | **2.33** | **40.7** | **0.00** | **0.00** | **0.27** | **8.31** | **0.07** | **0.00** | **0.00** | **0.30** | **40.3** | **1.90** | **99.2** |
| **KEF25a** | 0.56 | 2.67 | 2.13 | 31.0 | 0.00 | 0.02 | 0.33 | 7.11 | 0.06 | 0.00 | 0.00 | 0.35 | 42.8 | 3.93 | 90.9 |
| **KEF25b** | 0.57 | 2.75 | 2.15 | 31.4 | 0.00 | 0.02 | 0.34 | 7.21 | 0.06 | 0.00 | 0.00 | 0.36 | 43.5 | 3.98 | 92.3 |
| **KEF25c** | 0.69 | 2.74 | 2.10 | 31.1 | 0.00 | 0.02 | 0.33 | 7.16 | 0.06 | 0.00 | 0.00 | 0.35 | 43.2 | 3.96 | 91.6 |
| **KEF25** | **0.61** | **2.72** | **2.12** | **31.1** | **0.00** | **0.02** | **0.33** | **7.16** | **0.06** | **0.00** | **0.00** | **0.35** | **43.2** | **3.96** | **91.6** |
| **KEF26a** | 0.64 | 2.16 | 3.90 | 33.3 | 0.00 | 0.07 | 0.63 | 3.47 | 0.11 | 0.00 | 0.01 | 0.31 | 52.3 | 1.87 | 98.8 |
| **KEF26b** | 0.65 | 2.06 | 3.84 | 32.9 | 0.00 | 0.07 | 0.62 | 3.42 | 0.11 | 0.00 | 0.01 | 0.31 | 51.4 | 1.84 | 97.2 |
| **KEF26c** | 0.59 | 2.07 | 3.87 | 32.7 | 0.00 | 0.07 | 0.62 | 3.44 | 0.11 | 0.00 | 0.01 | 0.31 | 51.6 | 1.84 | 97.2 |
| **KEF26** | **0.63** | **2.09** | **3.87** | **33.0** | **0.00** | **0.07** | **0.62** | **3.44** | **0.11** | **0.00** | **0.01** | **0.31** | **51.8** | **1.85** | **97.7** |
| **KEF31a** | 0.85 | 3.35 | 2.14 | 34.8 | 0.04 | 0.21 | 0.23 | 8.32 | 0.03 | 0.00 | 0.00 | 0.16 | 48.1 | 0.27 | 98.5 |
| **KEF31b** | 0.62 | 3.34 | 2.14 | 34.9 | 0.05 | 0.21 | 0.23 | 8.34 | 0.04 | 0.00 | 0.00 | 0.16 | 48.0 | 0.28 | 98.3 |

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF31c** | 0.57 | 3.43 | 2.10 | 34.7 | 0.05 | 0.21 | 0.23 | 8.26 | 0.04 | 0.00 | 0.00 | 0.16 | 47.8 | 0.28 | 97.8 |
| **KEF31** | **0.68** | **3.37** | **2.12** | **34.8** | **0.05** | **0.21** | **0.23** | **8.31** | **0.04** | **0.00** | **0.00** | **0.16** | **47.9** | **0.28** | **98.2** |
| **KEF32a** | 0.96 | 0.81 | 4.35 | 21.0 | 0.00 | 0.38 | 0.72 | 1.59 | 0.13 | 0.00 | 0.01 | 0.07 | 61.1 | 10.05 | 101 |
| **KEF32b** | 1.00 | 0.94 | 4.33 | 21.3 | 0.00 | 0.39 | 0.72 | 1.59 | 0.13 | 0.00 | 0.01 | 0.07 | 61.1 | 9.94 | 102 |
| **KEF32c** | 0.80 | 0.78 | 4.33 | 20.9 | 0.00 | 0.38 | 0.71 | 1.59 | 0.13 | 0.00 | 0.01 | 0.07 | 60.4 | 9.80 | 99.9 |
| **KEF32** | **0.92** | **0.84** | **4.34** | **21.1** | **0.00** | **0.38** | **0.72** | **1.59** | **0.13** | **0.00** | **0.01** | **0.07** | **60.9** | **9.93** | **101** |
| **KEF33a** | 0.51 | 2.84 | 0.69 | 29.6 | 0.00 | 0.00 | 0.12 | 5.92 | 0.00 | 0.00 | 0.00 | 0.16 | 61.0 | 1.05 | 102 |
| **KEF33b** | 0.38 | 2.70 | 0.69 | 29.0 | 0.00 | 0.00 | 0.12 | 5.83 | 0.00 | 0.00 | 0.00 | 0.16 | 60.2 | 1.02 | 100 |
| **KEF33c** | 0.46 | 2.76 | 0.71 | 29.5 | 0.00 | 0.00 | 0.12 | 5.87 | 0.00 | 0.00 | 0.00 | 0.16 | 60.3 | 1.02 | 101 |
| **KEF33** | **0.45** | **2.77** | **0.70** | **29.4** | **0.00** | **0.00** | **0.12** | **5.87** | **0.00** | **0.00** | **0.00** | **0.16** | **60.5** | **1.03** | **101** |
| **KEF34a** | 0.56 | 4.51 | 2.10 | 39.7 | 0.00 | 0.00 | 0.23 | 8.17 | 0.06 | 0.00 | 0.00 | 0.30 | 40.1 | 2.04 | 97.8 |
| **KEF34b** | 0.67 | 4.38 | 2.09 | 40.0 | 0.00 | 0.00 | 0.23 | 8.23 | 0.06 | 0.00 | 0.00 | 0.30 | 40.1 | 2.04 | 98.1 |
| **KEF34c** | 0.56 | 4.40 | 2.13 | 39.4 | 0.00 | 0.00 | 0.23 | 8.10 | 0.06 | 0.00 | 0.00 | 0.29 | 39.7 | 2.02 | 96.9 |
| **KEF34** | **0.60** | **4.43** | **2.11** | **39.7** | **0.00** | **0.00** | **0.23** | **8.17** | **0.06** | **0.00** | **0.00** | **0.30** | **40.0** | **2.03** | **97.6** |
| **KEF35a** | 0.63 | 2.49 | 4.24 | 34.7 | 0.01 | 0.01 | 0.51 | 6.44 | 0.13 | 0.00 | 0.01 | 0.26 | 46.0 | 1.45 | 96.9 |
| **KEF35b** | 0.63 | 2.51 | 4.29 | 34.5 | 0.01 | 0.00 | 0.51 | 6.40 | 0.13 | 0.00 | 0.01 | 0.25 | 45.7 | 1.45 | 96.4 |
| **KEF35c** | 0.65 | 2.51 | 4.34 | 34.8 | 0.00 | 0.01 | 0.52 | 6.47 | 0.13 | 0.00 | 0.01 | 0.26 | 45.8 | 1.43 | 96.9 |
| **KEF35** | **0.64** | **2.50** | **4.29** | **34.7** | **0.01** | **0.01** | **0.51** | **6.44** | **0.13** | **0.00** | **0.01** | **0.26** | **45.8** | **1.44** | **96.7** |
| **KEF36a** | 0.61 | 4.33 | 1.70 | 36.8 | 0.00 | 0.00 | 0.24 | 8.58 | 0.04 | 0.00 | 0.01 | 0.21 | 44.3 | 0.83 | 97.6 |
| **KEF36b** | 0.68 | 4.37 | 1.69 | 36.9 | 0.00 | 0.00 | 0.24 | 8.62 | 0.04 | 0.00 | 0.01 | 0.21 | 44.7 | 0.84 | 98.3 |
| **KEF36c** | 0.36 | 4.30 | 1.68 | 37.4 | 0.00 | 0.00 | 0.24 | 8.74 | 0.04 | 0.00 | 0.01 | 0.21 | 44.9 | 0.84 | 98.7 |
| **KEF36** | **0.55** | **4.33** | **1.69** | **37.0** | **0.00** | **0.00** | **0.24** | **8.65** | **0.04** | **0.00** | **0.01** | **0.21** | **44.6** | **0.84** | **98.2** |
| **KEF38a** | 0.74 | 2.58 | 4.21 | 34.9 | 0.01 | 0.00 | 0.52 | 6.52 | 0.13 | 0.00 | 0.01 | 0.26 | 46.1 | 1.44 | 97.4 |
| **KEF38b** | 0.74 | 2.38 | 4.27 | 34.8 | 0.00 | 0.00 | 0.52 | 6.49 | 0.13 | 0.00 | 0.01 | 0.26 | 45.8 | 1.44 | 96.9 |
| **KEF38c** | 0.64 | 2.45 | 4.14 | 34.7 | 0.00 | 0.00 | 0.52 | 6.46 | 0.13 | 0.00 | 0.01 | 0.26 | 45.6 | 1.42 | 96.4 |
| **KEF38** | **0.71** | **2.47** | **4.21** | **34.8** | **0.00** | **0.00** | **0.52** | **6.49** | **0.13** | **0.00** | **0.01** | **0.26** | **45.8** | **1.43** | **96.9** |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF39a** | 0.74 | 7.62 | 4.67 | 32.1 | 0.00 | 0.00 | 0.24 | 10.5 | 0.11 | 0.00 | 0.01 | 0.30 | 39.3 | 2.79 | 98.4 |
| **KEF39b** | 0.55 | 7.66 | 4.80 | 31.8 | 0.00 | 0.00 | 0.25 | 10.5 | 0.11 | 0.00 | 0.01 | 0.30 | 39.1 | 2.76 | 97.8 |
| **KEF39c** | 0.52 | 7.63 | 4.67 | 31.8 | 0.00 | 0.00 | 0.24 | 10.4 | 0.11 | 0.00 | 0.01 | 0.30 | 39.1 | 2.77 | 97.5 |
| **KEF39** | **0.60** | **7.64** | **4.71** | **31.9** | **0.00** | **0.00** | **0.24** | **10.5** | **0.11** | **0.00** | **0.01** | **0.30** | **39.2** | **2.77** | **97.9** |
| **KEF40a** | 0.47 | 0.72 | 2.18 | 24.4 | 0.01 | 0.28 | 0.16 | 0.81 | 0.34 | 0.01 | 0.01 | 0.16 | 68.1 | 4.92 | 103 |
| **KEF40b** | 0.40 | 0.72 | 2.14 | 24.2 | 0.00 | 0.28 | 0.16 | 0.81 | 0.33 | 0.01 | 0.01 | 0.16 | 67.5 | 4.86 | 102 |
| **KEF40c** | 0.41 | 0.71 | 2.24 | 24.1 | 0.01 | 0.28 | 0.16 | 0.81 | 0.33 | 0.01 | 0.01 | 0.16 | 67.3 | 4.81 | 101 |
| **KEF40** | **0.43** | **0.71** | **2.19** | **24.2** | **0.01** | **0.28** | **0.16** | **0.81** | **0.33** | **0.01** | **0.01** | **0.16** | **67.6** | **4.86** | **102** |

***Table A4.2b** Results of (P)ED-XRF analyses of slag samples from Kephala (trace elements in ppm). Analyses in bold are the averages of the three runs (a, b, c, ).*

| | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ag | $SnO_2$ | Sb | Ba | La | Ce | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF1a** | 103 | 102 | 72 | 0 | 23 | 15 | 22 | 0 | 0 | 1 | 11 | 642 | 0 | 0 | 0 | 0 | 3 |
| **KEF1b** | 120 | 111 | 76 | 0 | 25 | 18 | 20 | 0 | 0 | 1 | 12 | 655 | 0 | 0 | 0 | 0 | 4 |
| **KEF1c** | 138 | 97 | 75 | 0 | 21 | 15 | 17 | 0 | 0 | 2 | 12 | 648 | 0 | 0 | 0 | 0 | 4 |
| **KEF1** | **120** | **104** | **74** | **0** | **23** | **16** | **20** | **0** | **0** | **1** | **12** | **648** | **0** | **0** | **0** | **0** | **4** |
| **KEF3a** | 58 | 121 | 52 | 0 | 9 | 25 | 0 | 3 | 0 | 0 | 3 | 95 | 47 | 90 | 0 | 0 | 4 |
| **KEF3b** | 69 | 113 | 59 | 0 | 7 | 21 | 0 | 0 | 0 | 0 | 0 | 104 | 33 | 86 | 0 | 0 | 2 |
| **KEF3c** | 0 | 115 | 53 | 0 | 6 | 20 | 0 | 3 | 0 | 0 | 1 | 88 | 52 | 101 | 0 | 0 | 4 |
| **KEF3** | **42** | **116** | **55** | **0** | **7** | **22** | **0** | **2** | **0** | **0** | **1** | **95** | **44** | **92** | **0** | **0** | **3** |
| **KEF4a** | 42 | 461 | 270 | 17 | 99 | 14 | 59 | 0 | 7 | 0 | 0 | 228 | 0 | 26 | 0 | 0 | 0 |
| **KEF4b** | 33 | 457 | 275 | 17 | 96 | 16 | 53 | 0 | 6 | 0 | 2 | 220 | 0 | 22 | 0 | 0 | 0 |
| **KEF4c** | 34 | 465 | 270 | 16 | 96 | 15 | 45 | 0 | 7 | 0 | 2 | 235 | 0 | 0 | 0 | 0 | 0 |
| **KEF4** | **36** | **461** | **272** | **17** | **97** | **15** | **52** | **0** | **6** | **0** | **1** | **228** | **0** | **16** | **0** | **0** | **0** |
| **KEF5a** | 210 | 514 | 177 | 0 | 18 | 20 | 73 | 61 | 0 | 1 | 2 | 254 | 0 | 27 | 0 | 0 | 5 |
| **KEF5b** | 205 | 507 | 170 | 0 | 19 | 18 | 73 | 62 | 0 | 0 | 2 | 285 | 0 | 47 | 0 | 0 | 2 |
| **KEF5c** | 175 | 526 | 176 | 0 | 17 | 17 | 80 | 57 | 0 | 1 | 2 | 287 | 0 | 26 | 0 | 0 | 0 |
| **KEF5** | **197** | **516** | **174** | **0** | **18** | **18** | **76** | **60** | **0** | **1** | **2** | **275** | **0** | **34** | **0** | **0** | **3** |
| **KEF6a** | 55 | 509 | 21 | 0 | 37 | 20 | 66 | 49 | 0 | 0 | 3 | 323 | 0 | 28 | 113 | 0 | 2 |
| **KEF6b** | 48 | 485 | 28 | 0 | 36 | 20 | 59 | 50 | 0 | 0 | 0 | 333 | 0 | 34 | 110 | 0 | 3 |
| **KEF6c** | 0 | 492 | 17 | 0 | 35 | 20 | 70 | 49 | 0 | 0 | 3 | 312 | 0 | 22 | 127 | 0 | 3 |
| **KEF6** | **34** | **495** | **22** | **0** | **36** | **20** | **65** | **49** | **0** | **0** | **2** | **323** | **0** | **28** | **117** | **0** | **3** |
| **KEF7a** | 0 | 247 | 60 | 0 | 18 | 40 | 31 | 0 | 0 | 0 | 4 | 176 | 29 | 0 | 0 | 0 | 3 |
| **KEF7b** | 0 | 245 | 59 | 0 | 19 | 41 | 27 | 4 | 0 | 0 | 3 | 179 | 34 | 48 | 0 | 0 | 2 |

|  | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ag | $SnO_2$ | Sb | Ba | La | Ce | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF7c** | 0 | 244 | 41 | 0 | 16 | 39 | 24 | 6 | 0 | 0 | 4 | 180 | 27 | 38 | 0 | 0 | 0 |
| **KEF7** | **0** | **245** | **53** | **0** | **18** | **40** | **27** | **4** | **0** | **0** | **4** | **178** | **30** | **29** | **0** | **0** | **2** |
| **KEF8a** | 0 | 724 | 71 | 0 | 44 | 21 | 92 | 82 | 0 | 0 | 4 | 398 | 0 | 0 | 315 | 0 | 0 |
| **KEF8b** | 0 | 703 | 48 | 0 | 46 | 19 | 76 | 86 | 0 | 0 | 3 | 406 | 0 | 33 | 317 | 0 | 0 |
| **KEF8c** | 0 | 714 | 22 | 0 | 45 | 19 | 94 | 85 | 0 | 0 | 0 | 396 | 0 | 35 | 328 | 0 | 0 |
| **KEF8** | **0** | **714** | **47** | **0** | **45** | **20** | **87** | **84** | **0** | **0** | **3** | **400** | **0** | **22** | **320** | **0** | **0** |
| **KEF9a** | 42 | 574 | 76 | 0 | 6 | 18 | 78 | 165 | 4 | 0 | 3 | 56 | 0 | 23 | 0 | 0 | 6 |
| **KEF9b** | 82 | 547 | 76 | 0 | 4 | 17 | 66 | 178 | 2 | 0 | 0 | 57 | 0 | 38 | 0 | 0 | 4 |
| **KEF9c** | 64 | 555 | 81 | 0 | 6 | 19 | 70 | 172 | 1 | 0 | 2 | 49 | 0 | 24 | 0 | 0 | 3 |
| **KEF9** | **63** | **559** | **77** | **0** | **5** | **18** | **71** | **171** | **2** | **0** | **2** | **54** | **0** | **28** | **0** | **0** | **4** |
| **KEF10a** | 64 | 314 | 15 | 0 | 36 | 49 | 47 | 32 | 0 | 0 | 0 | 0 | 44 | 48 | 0 | 0 | 2 |
| **KEF10b** | 88 | 307 | 16 | 0 | 36 | 48 | 39 | 30 | 0 | 0 | 0 | 0 | 32 | 55 | 0 | 0 | 3 |
| **KEF10c** | 72 | 320 | 14 | 0 | 38 | 49 | 43 | 31 | 0 | 0 | 0 | 0 | 53 | 70 | 0 | 0 | 0 |
| **KEF10** | **75** | **314** | **15** | **0** | **37** | **49** | **43** | **31** | **0** | **0** | **0** | **0** | **43** | **58** | **0** | **0** | **2** |
| **KEF11a** | 0 | 503 | 25 | 0 | 21 | 14 | 108 | 41 | 0 | 0 | 0 | 31 | 0 | 35 | 0 | 0 | 4 |
| **KEF11b** | 148 | 520 | 41 | 0 | 20 | 14 | 108 | 46 | 0 | 0 | 0 | 39 | 0 | 33 | 0 | 0 | 4 |
| **KEF11c** | 92 | 507 | 23 | 0 | 20 | 14 | 91 | 50 | 0 | 0 | 0 | 30 | 0 | 29 | 0 | 0 | 3 |
| **KEF11** | **80** | **510** | **30** | **0** | **20** | **14** | **102** | **46** | **0** | **0** | **0** | **33** | **0** | **32** | **0** | **0** | **4** |
| **KEF13a** | 0 | 488 | 95 | 0 | 37 | 27 | 56 | 85 | 3 | 0 | 3 | 968 | 0 | 53 | 0 | 0 | 4 |
| **KEF13b** | 0 | 475 | 94 | 0 | 38 | 26 | 69 | 79 | 2 | 0 | 3 | 957 | 0 | 59 | 0 | 0 | 4 |
| **KEF13c** | 0 | 482 | 86 | 0 | 34 | 27 | 65 | 92 | 3 | 0 | 3 | 965 | 0 | 49 | 0 | 0 | 0 |
| **KEF13** | **0** | **481** | **92** | **0** | **36** | **27** | **63** | **85** | **2** | **0** | **3** | **963** | **0** | **54** | **0** | **0** | **3** |
| **KEF14a** | 83 | 745 | 163 | 0 | 93 | 21 | 71 | 39 | 0 | 0 | 5 | 526 | 0 | 28 | 658 | 0 | 5 |
| **KEF14b** | 76 | 724 | 118 | 0 | 94 | 22 | 61 | 39 | 0 | 0 | 6 | 544 | 0 | 31 | 645 | 0 | 0 |
| **KEF14c** | 76 | 751 | 172 | 0 | 91 | 23 | 67 | 37 | 0 | 0 | 6 | 543 | 0 | 27 | 651 | 0 | 5 |
| **KEF14** | **78** | **740** | **151** | **0** | **92** | **22** | **66** | **38** | **0** | **0** | **6** | **538** | **0** | **29** | **651** | **0** | **3** |

| | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ag | $SnO_2$ | Sb | Ba | La | Ce | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF15a** | 0 | 384 | 86 | 0 | 184 | 26 | 30 | 0 | 0 | 0 | 3 | 1319 | 0 | 26 | 412 | 0 | 3 |
| **KEF15b** | 0 | 379 | 78 | 0 | 183 | 25 | 53 | 0 | 0 | 0 | 4 | 1312 | 0 | 23 | 422 | 0 | 3 |
| **KEF15c** | 0 | 374 | 72 | 0 | 186 | 23 | 32 | 0 | 0 | 0 | 4 | 1302 | 0 | 0 | 417 | 0 | 2 |
| **KEF15** | **0** | **379** | **79** | **0** | **184** | **25** | **38** | **0** | **0** | **0** | **4** | **1311** | **0** | **16** | **417** | **0** | **3** |
| **KEF16a** | 0 | 528 | 196 | 0 | 65 | 28 | 33 | 8 | 0 | 0 | 6 | 598 | 0 | 0 | 278 | 0 | 5 |
| **KEF16b** | 0 | 544 | 192 | 0 | 64 | 31 | 20 | 4 | 0 | 0 | 7 | 572 | 0 | 0 | 288 | 64 | 3 |
| **KEF16c** | 0 | 505 | 203 | 0 | 64 | 31 | 26 | 8 | 0 | 0 | 6 | 578 | 0 | 0 | 251 | 53 | 0 |
| **KEF16** | **0** | **526** | **197** | **0** | **64** | **30** | **26** | **7** | **0** | **0** | **6** | **582** | **0** | **0** | **272** | **39** | **2** |
| **KEF23a** | 65 | 493 | 62 | 0 | 62 | 17 | 63 | 46 | 0 | 0 | 4 | 355 | 0 | 27 | 116 | 0 | 5 |
| **KEF23b** | 104 | 515 | 59 | 0 | 65 | 18 | 62 | 42 | 0 | 0 | 4 | 346 | 0 | 34 | 114 | 0 | 4 |
| **KEF23c** | 88 | 506 | 61 | 0 | 63 | 19 | 61 | 39 | 0 | 0 | 4 | 363 | 0 | 25 | 122 | 0 | 4 |
| **KEF23** | **86** | **505** | **60** | **0** | **63** | **18** | **62** | **42** | **0** | **0** | **4** | **355** | **0** | **28** | **117** | **0** | **4** |
| **KEF24a** | 250 | 1147 | 90 | 0 | 19 | 13 | 38 | 0 | 0 | 0 | 0 | 112 | 0 | 0 | 45 | 0 | 3 |
| **KEF24b** | 259 | 1142 | 57 | 0 | 20 | 13 | 39 | 0 | 0 | 0 | 4 | 113 | 0 | 0 | 39 | 0 | 2 |
| **KEF24c** | 285 | 1135 | 54 | 0 | 18 | 13 | 24 | 0 | 0 | 0 | 4 | 111 | 0 | 0 | 46 | 0 | 2 |
| **KEF24** | **265** | **1141** | **67** | **0** | **19** | **13** | **34** | **0** | **0** | **0** | **3** | **112** | **0** | **0** | **43** | **0** | **2** |
| **KEF25a** | 145 | 602 | 58 | 0 | 5 | 14 | 30 | 0 | 0 | 0 | 5 | 488 | 0 | 27 | 121 | 0 | 3 |
| **KEF25b** | 159 | 623 | 61 | 0 | 3 | 15 | 30 | 0 | 0 | 0 | 3 | 459 | 0 | 0 | 136 | 0 | 2 |
| **KEF25c** | 141 | 618 | 50 | 0 | 2 | 16 | 24 | 0 | 0 | 0 | 4 | 467 | 0 | 29 | 120 | 0 | 5 |
| **KEF25** | **148** | **614** | **56** | **0** | **3** | **15** | **28** | **0** | **0** | **0** | **4** | **471** | **0** | **19** | **126** | **0** | **3** |
| **KEF26a** | 0 | 346 | 200 | 0 | 35 | 20 | 29 | 0 | 0 | 0 | 2 | 80 | 0 | 22 | 0 | 0 | 3 |
| **KEF26b** | 0 | 338 | 199 | 0 | 36 | 19 | 41 | 0 | 0 | 0 | 2 | 79 | 0 | 32 | 0 | 0 | 0 |
| **KEF26c** | 0 | 326 | 190 | 0 | 37 | 18 | 30 | 0 | 0 | 0 | 3 | 90 | 0 | 29 | 0 | 0 | 3 |
| **KEF26** | **0** | **337** | **196** | **0** | **36** | **19** | **34** | **0** | **0** | **0** | **3** | **83** | **0** | **28** | **0** | **0** | **2** |
| **KEF31a** | 19 | 83 | 87 | 0 | 15 | 19 | 27 | 0 | 0 | 0 | 0 | 30 | 0 | 23 | 0 | 0 | 3 |
| **KEF31b** | 29 | 81 | 93 | 0 | 17 | 19 | 22 | 0 | 0 | 0 | 0 | 37 | 0 | 42 | 0 | 0 | 0 |

|  | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ag | $SnO_2$ | Sb | Ba | La | Ce | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF31c** | 29 | 80 | 93 | 0 | 17 | 19 | 33 | 0 | 0 | 0 | 0 | 28 | 0 | 40 | 0 | 0 | 3 |
| **KEF31** | **26** | **81** | **91** | **0** | **16** | **19** | **27** | **0** | **0** | **0** | **0** | **32** | **0** | **35** | **0** | **0** | **2** |
| **KEF32a** | 762 | 801 | 126 | 0 | 34 | 10 | 39 | 21 | 29 | 3 | 5 | 33 | 0 | 0 | 0 | 0 | 3 |
| **KEF32b** | 706 | 805 | 127 | 0 | 30 | 7 | 46 | 19 | 31 | 2 | 6 | 36 | 0 | 0 | 0 | 0 | 4 |
| **KEF32c** | 676 | 806 | 134 | 0 | 35 | 12 | 51 | 21 | 30 | 2 | 4 | 25 | 0 | 0 | 0 | 0 | 3 |
| **KEF32** | **715** | **804** | **129** | **0** | **33** | **10** | **45** | **21** | **30** | **2** | **5** | **31** | **0** | **0** | **0** | **0** | **3** |
| **KEF33a** | 0 | 89 | 52 | 0 | 0 | 22 | 0 | 11 | 0 | 0 | 0 | 0 | 66 | 122 | 0 | 0 | 2 |
| **KEF33b** | 0 | 84 | 48 | 0 | 0 | 22 | 0 | 6 | 0 | 0 | 0 | 0 | 67 | 128 | 0 | 0 | 3 |
| **KEF33c** | 0 | 86 | 50 | 0 | 0 | 24 | 0 | 2 | 0 | 0 | 0 | 0 | 56 | 113 | 0 | 0 | 3 |
| **KEF33** | **0** | **86** | **50** | **0** | **0** | **22** | **0** | **6** | **0** | **0** | **0** | **0** | **63** | **121** | **0** | **0** | **3** |
| **KEF34a** | 266 | 1145 | 105 | 0 | 19 | 12 | 24 | 0 | 0 | 0 | 4 | 109 | 0 | 0 | 32 | 0 | 4 |
| **KEF34b** | 261 | 1156 | 52 | 0 | 20 | 13 | 24 | 0 | 0 | 0 | 5 | 113 | 0 | 20 | 41 | 0 | 3 |
| **KEF34c** | 271 | 1120 | 60 | 0 | 18 | 12 | 24 | 0 | 0 | 0 | 4 | 113 | 0 | 24 | 35 | 0 | 2 |
| **KEF34** | **266** | **1140** | **72** | **0** | **19** | **13** | **24** | **0** | **0** | **0** | **4** | **112** | **0** | **15** | **36** | **0** | **3** |
| **KEF35a** | 173 | 297 | 353 | 0 | 53 | 40 | 48 | 0 | 0 | 0 | 7 | 238 | 11 | 35 | 0 | 62 | 0 |
| **KEF35b** | 138 | 301 | 358 | 0 | 53 | 39 | 44 | 0 | 0 | 0 | 6 | 242 | 11 | 57 | 0 | 60 | 0 |
| **KEF35c** | 125 | 307 | 349 | 0 | 53 | 39 | 49 | 0 | 0 | 0 | 6 | 236 | 1 | 49 | 0 | 57 | 0 |
| **KEF35** | **145** | **302** | **353** | **0** | **53** | **39** | **47** | **0** | **0** | **0** | **6** | **239** | **8** | **47** | **0** | **60** | **0** |
| **KEF36a** | 101 | 148 | 58 | 0 | 4 | 15 | 23 | 0 | 0 | 0 | 3 | 148 | 19 | 47 | 0 | 0 | 2 |
| **KEF36b** | 88 | 147 | 58 | 0 | 4 | 16 | 23 | 0 | 0 | 0 | 1 | 148 | 31 | 44 | 0 | 0 | 3 |
| **KEF36c** | 100 | 144 | 59 | 0 | 5 | 14 | 24 | 0 | 0 | 0 | 0 | 151 | 25 | 51 | 0 | 0 | 0 |
| **KEF36** | **96** | **146** | **58** | **0** | **4** | **15** | **23** | **0** | **0** | **0** | **1** | **149** | **25** | **47** | **0** | **0** | **2** |
| **KEF38a** | 158 | 300 | 355 | 0 | 53 | 41 | 38 | 0 | 0 | 0 | 5 | 227 | 14 | 0 | 0 | 55 | 2 |
| **KEF38b** | 132 | 297 | 363 | 0 | 54 | 41 | 37 | 0 | 0 | 0 | 5 | 234 | 7 | 50 | 0 | 78 | 3 |
| **KEF38c** | 90 | 300 | 348 | 0 | 50 | 39 | 42 | 0 | 0 | 0 | 6 | 237 | 12 | 40 | 0 | 49 | 3 |
| **KEF38** | **127** | **299** | **355** | **0** | **52** | **41** | **39** | **0** | **0** | **0** | **6** | **233** | **11** | **30** | **0** | **60** | **2** |

|  | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Mo | Ag | $SnO_2$ | Sb | Ba | La | Ce | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF39a** | 122 | 356 | 66 | 0 | 30 | 35 | 46 | 0 | 0 | 0 | 2 | 102 | 29 | 80 | 9 | 0 | 4 |
| **KEF39b** | 110 | 360 | 55 | 0 | 31 | 35 | 40 | 0 | 0 | 0 | 2 | 119 | 48 | 72 | 0 | 0 | 3 |
| **KEF39c** | 113 | 350 | 108 | 0 | 32 | 34 | 44 | 0 | 0 | 0 | 0 | 116 | 44 | 69 | 11 | 0 | 2 |
| **KEF39** | **115** | **355** | **76** | **0** | **31** | **35** | **43** | **0** | **0** | **0** | **1** | **112** | **40** | **73** | **7** | **0** | **3** |
| **KEF40a** | 297 | 1023 | 138 | 0 | 0 | 14 | 97 | 36 | 7 | 1 | 1 | 1770 | 0 | 0 | 0 | 0 | 3 |
| **KEF40b** | 298 | 1007 | 145 | 0 | 0 | 16 | 98 | 36 | 9 | 1 | 2 | 1742 | 0 | 0 | 0 | 0 | 0 |
| **KEF40c** | 258 | 989 | 152 | 0 | 0 | 13 | 100 | 23 | 7 | 0 | 3 | 1739 | 0 | 0 | 0 | 0 | 4 |
| **KEF40** | **284** | **1006** | **145** | **0** | **0** | **14** | **99** | **32** | **8** | **1** | **2** | **1750** | **0** | **0** | **0** | **0** | **2** |

***Table A4.3*** *Summary of the optical microscopy observations for the Kephala slags (IS: iron-silicates; M: magnetite; MA: magnetite aggregate, G: glass, W: wüstitite; CM: copper metal prills). The column labelled 'prills' describes whether the entrapped prills are mainly copper metal or matte or a mixture of both.*

| Sample | IS | M | MA | G | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|
| **KEF1** | + | + | | + | CM | | Cannot discern clearly fayalites from glass, glass appears to be very little |
| **KEF2** | + | + | + | + | Matte | Inclusion of vitrified ceramic on one edge | Matte often within or near magnetites |
| **KEF3** | + | + | | + | Matte | | Porous, one magnetite band with fayalites extending from either side |
| **KEF4** | + | | | + | Matte | | Pyroxenes of composition $(Fe, Mg)O.CaO.2SiO_2$ (EPMA), one large matte at the edge of the sample surrounds what appears to be a completely corroded prill |
| **KEF5** | + | + | | + | Matte | | Matte often within magnetite, medium porosity, phases smaller towards one edge |
| **KEF6** | + | + | | + | Matte | | Matte often within magnetite, medium-high porosity, phases get progressively smaller towards edge |
| **KEF7** | + | + | | + | Both | | Porous |
| **KEF8** | + | + | | + | Matte | 2-3 quartz inclusions | Many matte but small, sample heterogeneous with respect to size of phases, porous |
| **KEF9** | + | + | | + | Both | | Matte often surrounding Cu prills, phases get progressively smaller towards edge |
| **KEF10** | + | + | | + | Both | | Very large crystals of fayalite, little magnetite |
| **KEF11** | + | + | | + | Matte | | Numerous stringers |
| **KEF14** | + | + | | + | Matte | Small inclusions of vitrified ceramic and quartz on one edge | Porous, 2-3 fragmented magnetite bands, section heterogeneous with respect to size and distribution of phases |
| **KEF15** | + | + | | + | Matte | | Medium porosity |
| **KEF16** | + | + | | + | Matte | | Magnetite band and concentration of magnetites at the top edge of the sample. |

| Sample | IS | M | MA | G | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|
| **KEF17** | + | + |  | + | Matte |  | Low-medium porosity |
| **KEF18** | + | + | + | + | Matte |  | Porous |
| **KEF23** | + | + |  | + | Matte |  | Mainly elongated fayalites, which get progressively smaller/thinner from one side to the other |
| **KEF24** | + | + |  | + | Both |  | Compact fayalite crystals, very little glass, many small matte/ Cu prills |
| **KEF25** | + | + |  | + | CM |  | Magnetite low, compact crystals, low glass |
| **KEF26** | + | + |  | + | Matte |  | The section is traversed by a magnetite band, which is disrupted in some areas by a gap. The microstructure in the two slag sections is different, with much smaller phases appearing on the upper part of the sample. The texture is consistent with two flow events leading to one layer of slag superimposing another. |
| **KEF31** | + | + |  | + | Matte | 2-3 quartz inclusions at edge | Low-medium porosity, large circular pores surround quartz inclusions, magnetite less than in other samples |
| **KEF32** | + | + | + | + | CM | Thin vitrified ceramic on one edge | High concentration of magnetite and magnetite aggregates, which often include Cu prills. Sample is also rich in copper prills. |
| **KEF33** | + | + |  | + | Matte |  | Medium porosity |
| **KEF34** | + | + | + | + | Matte | Inclusions of vitrified ceramic | Very heterogeneous sample, compact phases, very little glass |
| **KEF35** | + | + | + | + | Both | On one edge ceramic | Porous |
| **KEF36** | + | + |  | + | Matte |  | Medium porosity, sample can be divided into two parts: one with larger phases and more magnetite and fragmentary magnetite bands |
| **KEF38** | + | + |  | + | Both |  | Matte often surround Cu prills, porous, phases smaller from one side to the other |
| **KEF39** | + | + |  | + | Matte |  | Porous |
| **KEF40** | + | + | + | + | Both |  | Copper prills often surrounded by matte and separate matte, one very large prill at the edge surrounded by matte and incorporating sulphide inclusions, relatively high concentration of magnetite, magnetite aggregates with matte, also one prill completely corroded and surrounded by matte |

***Table A4.4** Spot analyses on the WDS-EPMA of individual phases in slag samples from Kephala (weight %).*

Notes: *1. Iron oxide was calculated by the analytical software as $Fe_2O_3$ but was re-calculated for the following table depending on the valency expected for each phase. Analyses of the glass phase are, however, likely to incorporate iron of different valencies.*

*2. Fayalite is used to describe all the phases with a composition similar to compounds of the olivine group ($(Fe_xMg_{1-x})_2SiO_4$), but several of these with exceptionally high magnesium contents have compositions between fayalite and the mineral forsterite ($Mg_2SiO_4$).*

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF3a** | Fayalite | 0.0 | 13 | 0.0 | 32 | 0.0 | 0.0 | 0.9 | 0.0 | 0.2 | 54 |  | 0.1 | 99 |
| **KEF3b** | Fayalite | 0.0 | 14 | 0.0 | 32 | 0.0 | 0.0 | 0.7 | 0.0 | 0.2 | 52 |  | 0.0 | 98 |
| **KEF3c** | Fayalite | 0.0 | 7.2 | 0.0 | 31 | 0.1 | 0.0 | 1.3 | 0.0 | 0.2 | 60 |  | 0.1 | 99 |
| **KEF3d** | Magnetite | 0.0 | 0.8 | 0.8 | 0.4 | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 |  | 94 | 0.1 | 96 |
| **KEF3e** | Magnetite | 0.0 | 0.8 | 0.8 | 0.3 | 0.0 | 0.0 | 0.1 | 0.2 | 0.1 |  | 98 | 0.1 | 101 |
| **KEF3f** | Magnetite | 0.0 | 0.8 | 0.7 | 0.4 | 0.0 | 0.0 | 0.2 | 0.2 | 0.0 |  | 99 | 0.0 | 101 |
| **KEF3g** | Glass | 0.1 | 3.1 | 1.2 | 43 | 0.0 | 0.0 | 14 | 0.0 | 0.2 | 34 |  | 0.1 | 101 |
| **KEF3h** | Glass | 0.2 | 1.8 | 1.4 | 43 | 0.0 | 0.0 | 15 | 0.1 | 0.2 | 34 |  | 0.0 | 97 |
| **KEF4a** | Pyroxene | 0.1 | 7.4 | 2.8 | 47 | 0.0 | 0.0 | 23 | 0.1 | 0.3 | 16 |  | 0.1 | 96 |
| **KEF4b** | Pyroxene | 0.0 | 8.0 | 3.1 | 46 | 0.0 | 0.0 | 23 | 0.2 | 0.3 | 14 |  | 0.0 | 95 |
| **KEF4c** | Pyroxene | 0.0 | 6.6 | 3.2 | 46 | 0.0 | 0.0 | 23 | 0.1 | 0.3 | 17 |  | 0.0 | 96 |
| **KEF4d** | Glass | 0.2 | 0.4 | 7.5 | 44 | 0.2 | 0.6 | 19 | 0.3 | 0.5 | 22 |  | 0.1 | 94 |
| **KEF4e** | Glass | 0.8 | 0.4 | 11 | 37 | 1.3 | 2.7 | 11 | 0.3 | 0.4 | 31 |  | 0.1 | 96 |
| **KEF7a** | Fayalite | 0.0 | 6.9 | 0.1 | 29 | 0.0 | 0.0 | 0.3 | 0.0 | 0.2 | 57 |  | 0.0 | 94 |
| **KEF7b** | Fayalite | 0.0 | 1.3 | 0.1 | 28 | 0.0 | 0.0 | 0.6 | 0.0 | 0.2 | 63 |  | 0.1 | 93 |
| **KEF7c** | Magnetite | 0.0 | 0.6 | 10 | 0.5 | 0.0 | 0.0 | 0.0 | 1.5 | 0.0 |  | 82 | 0.1 | 95 |
| **KEF7d** | Magnetite | 0.0 | 0.4 | 9.2 | 0.4 | 0.0 | 0.0 | 0.0 | 1.4 | 0.0 |  | 82 | 0.1 | 93 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF7e** | Magnetite | 0.0 | 0.4 | 12 | 0.6 | 0.0 | 0.0 | 0.0 | 1.6 | 0.1 |  | 80 | 0.0 | 95 |
| **KEF7f** | Glass | 1.8 | 0.0 | 14 | 42 | 0.7 | 1.8 | 7.4 | 0.1 | 0.0 | 25 |  | 0.2 | 93 |
| **KEF8a** | Fayalite | 0.0 | 29 | 0.0 | 35 | 0.0 | 0.0 | 0.8 | 0.0 | 0.1 | 30 |  | 0.0 | 95 |
| **KEF8b** | Fayalite | 0.0 | 34 | 0.1 | 35 | 0.0 | 0.0 | 0.8 | 0.0 | 0.1 | 26 |  | 0.0 | 96 |
| **KEF8c** | Fayalite | 0.0 | 24 | 0.1 | 33 | 0.4 | 0.0 | 0.8 | 0.0 | 0.1 | 33 |  | 0.4 | 92 |
| **KEF8d** | Fayalite | 0.0 | 15 | 0.0 | 32 | 0.0 | 0.0 | 1.8 | 0.0 | 0.2 | 50 |  | 0.0 | 99 |
| **KEF8e** | Fayalite | 0.0 | 14 | 0.1 | 31 | 0.1 | 0.0 | 2.0 | 0.0 | 0.1 | 46 |  | 0.0 | 94 |
| **KEF8f** | Magnetite | 0.0 | 1.2 | 3.9 | 0.6 | 0.0 | 0.0 | 0.1 | 0.5 | 0.0 |  | 85 | 0.0 | 91 |
| **KEF8g** | Glass | 0.3 | 2.2 | 6.5 | 41 | 0.0 | 0.0 | 19 | 0.1 | 0.1 | 24 |  | 0.0 | 93 |
| **KEF9a** | Fayalite | 0.0 | 4.6 | 0.1 | 29 | 0.0 | 0.0 | 0.4 | 0.0 | 0.5 | 60 |  | 0.0 | 95 |
| **KEF9b** | Fayalite | 0.0 | 5.1 | 0.7 | 30 | 0.0 | 0.0 | 0.8 | 0.1 | 0.4 | 58 |  | 0.2 | 96 |
| **KEF9c** | Fayalite | 0.0 | 4.9 | 0.1 | 29 | 0.0 | 0.0 | 0.5 | 0.0 | 0.5 | 59 |  | 0.0 | 95 |
| **KEF9d** | Magnetite | 0.0 | 0.6 | 5.3 | 0.6 | 0.0 | 0.0 | 0.1 | 1.1 | 0.1 |  | 87 | 0.1 | 95 |
| **KEF9e** | Magnetite | 0.0 | 0.6 | 5.4 | 0.8 | 0.0 | 0.0 | 0.1 | 1.1 | 0.1 |  | 88 | 0.0 | 96 |
| **KEF9f** | Glass | 0.4 | 0.3 | 11 | 46 | 0.0 | 0.8 | 9.2 | 0.2 | 0.3 | 26 |  | 0.1 | 94 |
| **KEF9g** | Glass | 0.4 | 0.6 | 9.1 | 44 | 0.1 | 0.4 | 7.6 | 0.1 | 0.3 | 31 |  | 0.2 | 94 |
| **KEF9h** | Glass | 0.6 | 0.3 | 14 | 49 | 0.0 | 0.6 | 11 | 0.2 | 0.2 | 19 |  | 0.2 | 96 |
| **KEF10a** | Fayalite/ Kirschteinite | 0.0 | 2.4 | 0.0 | 29 | 0.0 | 0.0 | 15 | 0.0 | 0.5 | 49 |  | 0.0 | 97 |
| **KEF10b** | Fayalite | 0.0 | 14 | 0.0 | 32 | 0.0 | 0.0 | 2.7 | 0.0 | 0.5 | 47 |  | 0.0 | 96 |
| **KEF10c** | Fayalite | 0.1 | 1.2 | 0.1 | 29 | 0.0 | 0.0 | 7.6 | 0.0 | 0.5 | 57 |  | 0.0 | 95 |
| **KEF10d** | Pyroxene | 0.0 | 10 | 3.8 | 46 | 0.0 | 0.0 | 23 | 0.1 | 0.1 | 14 |  | 0.0 | 96 |
| **KEF10e** | Pyroxene | 0.1 | 2.3 | 5.7 | 42 | 0.0 | 0.0 | 22 | 0.1 | 0.2 | 25 |  | 0.1 | 97 |
| **KEF10f** | Pyroxene | 0.0 | 11 | 3.5 | 46 | 0.0 | 0.0 | 22 | 0.0 | 0.0 | 13 |  | 0.0 | 96 |
| **KEF11a** | Fayalite | 0.0 | 2.6 | 0.1 | 29 | 0.0 | 0.0 | 0.3 | 0.0 | 0.4 | 62 |  | 0.0 | 95 |
| **KEF11b** | Fayalite | 0.0 | 3.4 | 0.1 | 29 | 0.0 | 0.0 | 0.3 | 0.0 | 0.3 | 62 |  | 0.0 | 95 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KEF11c** | Glass | 2.8 | 0.0 | 18 | 46 | 0.2 | 2.6 | 13 | 0.5 | 0.1 | 13 | | 0.1 | 95 |
| **KEF11d** | Glass | 2.2 | 0.0 | 16 | 46 | 0.5 | 2.5 | 9.2 | 0.0 | 0.1 | 17 | | 0.0 | 93 |
| **KEF13a** | Fayalite | 0.0 | 11 | 0.0 | 32 | 0.0 | 0.0 | 0.9 | 0.0 | 0.5 | 55 | | 0.0 | 99 |
| **KEF13b** | Fayalite | 0.0 | 11 | 0.0 | 32 | 0.0 | 0.0 | 0.8 | 0.0 | 0.5 | 56 | | 0.0 | 100 |
| **KEF13c** | Magnetite | 0.0 | 0.3 | 3.6 | 0.5 | 0.0 | 0.0 | 0.2 | 1.6 | 0.1 | | 93 | 0.0 | 100 |
| **KEF13d** | Magnetite | 0.0 | 0.4 | 3.8 | 0.6 | 0.0 | 0.0 | 0.2 | 1.6 | 0.1 | | 91 | 0.0 | 97 |
| **KEF13e** | Glass | 0.1 | 1.1 | 6.2 | 42 | 0.0 | 0.0 | 18 | 0.3 | 0.3 | 29 | | 0.0 | 98 |
| **KEF13f** | Glass | 0.1 | 0.8 | 6.5 | 44 | 0.1 | 0.0 | 20 | 0.3 | 0.2 | 28 | | 0.0 | 99 |
| **KEF14a** | Fayalite | 0.0 | 9.1 | 0.0 | 31 | 0.0 | 0.0 | 1.7 | 0.0 | 0.6 | 57 | | 0.1 | 100 |
| **KEF14b** | Fayalite | 0.0 | 10 | 0.0 | 31 | 0.0 | 0.0 | 1.6 | 0.0 | 0.6 | 56 | | 0.1 | 99 |
| **KEF14c** | Magnetite | 0.0 | 0.9 | 3.2 | 0.5 | 0.0 | 0.0 | 0.1 | 1.1 | 0.1 | | 94 | 0.0 | 100 |
| **KEF14d** | Magnetite | 0.0 | 0.9 | 3.5 | 0.3 | 0.0 | 0.0 | 0.1 | 1.2 | 0.2 | | 92 | 0.0 | 98 |
| **KEF14e** | Glass | 0.4 | 1.1 | 7.6 | 42 | 0.0 | 0.2 | 20 | 0.4 | 0.1 | 26 | | 0.0 | 98 |
| **KEF14f** | Glass | 0.1 | 3.0 | 5.7 | 42 | 0.0 | 0.0 | 20 | 0.3 | 0.3 | 26 | | 0.0 | 98 |

***Table A4.5*** *WDS-EPMA point analyses of copper metal and matte prills entrapped in slags from the site of Kephala (weight %). Totals over 100% are mainly due to the simultaneous measurement of more than one phase in heterogeneous matte prills, while low totals were caused by the small size of some prills.*

*Notes: 1. Analysis KEF9E was done on the sulphidic rim surrounding the copper metal prill analysed in KEF9D.*

*2. The analyses of sample KEF40 are given in the text.*

| | S | Fe | Ni | Cu | As | Ag | Au | Pb | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **KEF1A** | 0.2 | 3.8 | 0.0 | 96 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF1B** | 0.2 | 4.9 | 0.0 | 95 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF1C** | 0.1 | 5.0 | 0.0 | 96 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF1D** | 0.0 | 5.4 | 0.0 | 95 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF1E** | 0.0 | 5.3 | 0.0 | 93 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 99 |
| **KEF1F** | 0.1 | 5.3 | 0.0 | 94 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF1G** | 0.0 | 3.8 | 0.0 | 97 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 101 |
| **KEF2A** | 24 | 3.8 | 0.1 | 77 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 105 |
| **KEF2B** | 24 | 2.8 | 0.1 | 76 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 103 |
| **KEF2C** | 23 | 5.4 | 0.0 | 76 | 0.4 | 0.0 | 0.0 | 0.6 | 0.0 | 105 |
| **KEF2D** | 23 | 5.4 | 0.1 | 74 | 0.2 | 0.0 | 0.0 | 0.3 | 0.0 | 103 |
| **KEF2E** | 24 | 5.2 | 0.1 | 74 | 0.2 | 0.0 | 0.0 | 0.8 | 0.0 | 105 |
| **KEF2F** | 24 | 1.6 | 0.0 | 77 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF3A** | 20 | 6.5 | 0.0 | 71 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 98 |
| **KEF3B** | 23 | 6.7 | 0.0 | 71 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 101 |
| **KEF3C** | 20 | 4.4 | 0.0 | 75 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF4A** | 29 | 12 | 0.0 | 61 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF4B** | 31 | 17 | 0.0 | 50 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 99 |
| **KEF4C** | 24 | 12 | 0.0 | 59 | 0.2 | 0.0 | 0.1 | 0.0 | 0.0 | 96 |
| **KEF4D** | 21 | 4.6 | 0.0 | 71 | 0.2 | 0.0 | 0.1 | 0.0 | 0.0 | 96 |
| **KEF4E** | 24 | 10 | 0.0 | 61 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 95 |
| **KEF4F** | 25 | 12 | 0.0 | 63 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 101 |
| **KEF5A** | 22 | 3.8 | 0.0 | 72 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 97 |
| **KEF5B** | 26 | 16 | 0.0 | 54 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 96 |
| **KEF5C** | 26 | 21 | 0.0 | 48 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 95 |
| **KEF5D** | 21 | 3.6 | 0.0 | 74 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 99 |
| **KEF6A** | 25 | 17 | 0.0 | 54 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 96 |
| **KEF6B** | 24 | 15 | 0.0 | 57 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 96 |
| **KEF6C** | 24 | 12 | 0.0 | 60 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF6D** | 19 | 9.4 | 0.2 | 72 | 0.0 | 0.0 | 0.3 | 0.0 | 0.1 | 101 |
| **KEF7A** | 0.1 | 3.9 | 0.0 | 95 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 99 |
| **KEF7B** | 19 | 5.8 | 0.0 | 68 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 93 |
| **KEF7C** | 0.1 | 3.7 | 0.0 | 94 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 98 |
| **KEF7D** | 0.1 | 4.0 | 0.0 | 94 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 98 |
| **KEF7E** | 0.1 | 3.5 | 0.0 | 96 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |

| | S | Fe | Ni | Cu | As | Ag | Au | Pb | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **KEF7F** | 0.0 | 4.6 | 0.0 | 95 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 100 |
| **KEF8A** | 37 | 22 | 0.1 | 40 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF8B** | 27 | 11 | 0.0 | 65 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 104 |
| **KEF8C** | 27 | 15 | 0.1 | 56 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF9A** | 20 | 0.3 | 0.0 | 77 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF9B** | 20 | 3.0 | 0.0 | 76 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |
| **KEF9C** | 0.1 | 2.9 | 0.0 | 98 | 0.3 | 0.1 | 0.0 | 0.0 | 0.1 | 101 |
| **KEF9D** | 0.0 | 2.6 | 0.0 | 98 | 0.6 | 0.1 | 0.0 | 0.0 | 0.1 | 101 |
| **KEF9E** | 20 | 3.1 | 0.0 | 76 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 99 |
| **KEF10A** | 0.1 | 0.9 | 0.0 | 98 | 0.2 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |
| **KEF10B** | 0.0 | 1.1 | 0.0 | 98 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |
| **KEF10C** | 23 | 8.4 | 0.0 | 65 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF10D** | 0.2 | 2.8 | 0.0 | 98 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 101 |
| **KEF11A** | 24 | 1.8 | 0.0 | 76 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF11B** | 24 | 4.3 | 0.0 | 73 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF11C** | 18 | 2.8 | 0.1 | 77 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 98 |
| **KEF11D** | 18 | 2.5 | 0.0 | 77 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF11E** | 18 | 3.5 | 0.0 | 76 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 98 |
| **KEF11F** | 25 | 0.3 | 0.0 | 78 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 103 |
| **KEF14A** | 19 | 3.3 | 0.0 | 74 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 96 |
| **KEF14B** | 20 | 0.7 | 0.0 | 76 | 0.2 | 0.0 | 0.0 | 0.1 | 0.0 | 97 |
| **KEF14C** | 26 | 2.0 | 0.0 | 75 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF14D** | 23 | 5.4 | 0.0 | 72 | 0.3 | 0.0 | 0.0 | 0.3 | 0.0 | 101 |
| **KEF14E** | 0.8 | 5.0 | 0.0 | 92 | 1.8 | 0.1 | 0.0 | 0.2 | 0.0 | 100 |
| **KEF23A** | 24 | 15 | 0.0 | 57 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF23B** | 21 | 11 | 0.0 | 65 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF23C** | 26 | 18 | 0.0 | 53 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF23D** | 26 | 19 | 0.0 | 52 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 97 |
| **KEF23E** | 20 | 4.7 | 0.1 | 73 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 98 |
| **KEF24A** | 0.1 | 3.9 | 0.0 | 94 | 0.2 | 0.0 | 0.2 | 0.0 | 0.2 | 98 |
| **KEF24B** | 0.2 | 3.8 | 0.0 | 94 | 0.2 | 0.0 | 0.0 | 0.0 | 0.1 | 98 |
| **KEF24C** | 0.1 | 3.9 | 0.0 | 93 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KEF25A** | 0.2 | 2.6 | 0.0 | 96 | 0.2 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |
| **KEF25B** | 0.1 | 2.3 | 0.0 | 98 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF25C** | 0.0 | 2.2 | 0.0 | 97 | 0.2 | 0.0 | 0.0 | 0.0 | 0.1 | 99 |
| **KEF25D** | 0.1 | 4.1 | 0.0 | 95 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF32A** | 0.1 | 2.3 | 0.0 | 99 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 102 |
| **KEF32B** | 0.0 | 1.2 | 0.0 | 99 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KEF32C** | 0.0 | 3.2 | 0.0 | 98 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 101 |
| **KEF32D** | 0.2 | 4.6 | 0.1 | 98 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 103 |
| **KEF32E** | 0.0 | 5.3 | 0.1 | 98 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 103 |
| **KEF32F** | 0.1 | 2.8 | 0.0 | 97 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |
| **KEF34A** | 26 | 19 | 0.0 | 50 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 94 |
| **KEF34B** | 20 | 4.4 | 0.0 | 74 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 98 |
| **KEF34C** | 21 | 5.1 | 0.0 | 72 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 98 |
| **KEF35A** | 0.0 | 3.5 | 0.0 | 95 | 0.5 | 0.1 | 0.0 | 0.0 | 0.9 | 100 |

|  | S | Fe | Ni | Cu | As | Ag | Au | Pb | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **KEF35B** | 0.1 | 3.2 | 0.0 | 93 | 1.5 | 0.0 | 0.0 | 0.0 | 0.6 | 98 |
| **KEF35C** | 19 | 0.5 | 0.0 | 74 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 93 |
| **KEF35D** | 0.0 | 3.2 | 0.0 | 93 | 1.8 | 0.0 | 0.0 | 0.0 | 0.4 | 99 |

*Table A4.6 Catalogue of samples analysed from Phournoi (D: dimensions, W: weight, S: slag, M: matte or weathered matte, O: Fe and/or Cu minerals (unreacted or partially reacted), MC: copper metal fragment or prill).*

| **Sample** | **Group** | **Type** | **D (cm)** | **W (g)** | **Description** |
|---|---|---|---|---|---|
| **FOU1** | Path | S | 5.0x3.0x2.5 | 117.0 | Black with intense orange staining in parts and very little green staining |
| **FOU2** | Path | S | 3.0x3.0x1.5 | 21.4 | Black, with intense orange staining in parts and little green staining, porous |
| **FOU3** | Path | S | 2.5x2.5x2.5 | 26.7 | Black, with little orange staining and some green staining in a pore, little porosity |
| **FOU4** | Path | S | 2.5x3.0x1.5 | 13.7 | Black, with little orange staining and little porosity |
| **FOU5** | Phournoi 3 | S | 3.0x3.5x2.0 | 22.1 | Black with Fe-oxide staining and very little green staining, little porosity, partly crystalline, small schist inclusions attached on one side |
| **FOU6** | Phournoi 3 | S | 3.0x3.0x2.0 | 32.6 | Black with yellow staining, which covers c. 25% of outer surface, very little green staining, little porosity (1-3 mm) |
| **FOU19** | Phournoi 3 | S | 5.0x3.0x2.5 | 37.7 | Black with iron oxide and green staining in parts, porous (1-5 mm), one schist inclusion (1.5x0.5 cm) |
| **FOU20** | Phournoi 3 | O | 3.5x2.0x1.0 | 8.4 | Surface covered c. 90% with green staining and little Fe-oxide staining in parts |
| **FOU26** | Phournoi 3 | S | 4.0x2.5x2.0 | 28.3 | Black, with Fe-oxide and green staining in parts, one side covered in yellow-red staining, on one side flow texture, other side shows increased porosity (c. 1 mm) |
| **FOU31** | Phournoi 3 | MC | Diam.: 0.5 |  | Completely covered with green corrosion layer |
| **FOU9** | Phournoi 1 | S | 4.0x4.0x2.5 | 47.0 | Black with little green staining, porous in parts (1-2 mm), at least two external green prills (1 mm and 5 mm) |
| **FOU10** | Phournoi 1 | S | 9.5x6.0x5.0 | 267.1 | Black, porous (1-2 mm), Fe and Cu oxide staining in parts |
| **FOU11** | Phournoi 1 | S | 5.5x3.5x3.0 | 121.3 | Black, crystalline, Fe-oxide and little green staining, small quartz inclusions |
| **FOU12** | Phournoi 1 | S | 3.5x3.0x1.5 | 21.4 | Black, widely covered in Fe-oxide staining, very little porosity |
| **FOU24** | Phournoi 1 | S | 8.0x5.5x3.0 | 210.0 | Black, little Fe and Cu oxide staining, practically non-porous, after sectioning a piece of ceramic was found attached on one side (red outer layer then black vitrified layer), interface with slag not distinct, the two appear to be interlocked, pieces of |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  |  |  |  |  | schist, quartz and tiny green inclusions in ceramic |
| **FOU27** | Phournoi 1 | S | 3.5x2.5x2.0 | 32.0 | Black, partly crystalline, Cu and Fe oxide staining, medium porosity, piece of quartz attached on one side |
| **FOU28** | Phournoi 1 | S | 6.0x3.52.5 | 85.5 | Black, retains upper and lower surface (h=2.5 cm), collapsed ropey texture on upper, few small pieces of calcite and quartz on bottom, limited Fe oxide staining |
| **FOU32** | Phournoi1 | MC | D: 0.3 cm |  | Completely covered with green corrosion layer |
| **FOU38** | Phournoi1 | O | 2.1x1.9x1.3 | 4.7 | 90% of surface covered in green staining with little Fe-oxide staining |
| **FOU39** | Phournoi1 | S | 2.5x2.0x1.8 | 2.8 | Piece of schist with green staining and slag |
| **FOU40** | Phournoi1 | O | 1.5x1.0x0.2 | 0.5 | Schist with green staining in parts |
| **FOU13** | Phournoi 2 | S | 7.0x6.0x3.0 | 238.1 | Black with little Fe-oxide staining, distinct upper and lower surfaces, upper shows flow texture, height 3 cm, little porosity mainly on upper surface |
| **FOU14** | Phournoi 2 | S | 3.5x1.5x1.0 | 8.0 | Black, green staining, inclusions, porous usually c. 1 mm |
| **FOU15** | Phournoi 2 | S | 5.5x3.0x1.5 | 149.6 | Black, green staining, porous often large c. 1 cm, 4-5 external green prills (1-2 mm) |
| **FOU16** | Phournoi 2 | S | 7.0x4.0x3.0 | 36.2 | Black with Fe-oxide staining in parts, minute green staining, not porous |
| **FOU21** | Phournoi 2 | S | 6.0x3.5x2.0 | 68.2 | Black with Fe-oxide staining, practically non-porous, one external green prill |
| **FOU22** | Phournoi 2 | S | 6.0x5.5x5.5 | 182.6 | Black, relatively porous, upon sectioning found large ceramic fragments close to the edge (with schist and quartz inclusions), slag shows increased porosity at interface with ceramic, red outer ceramic c. 2 cm, inner vitrified layer, clear interface between slag and ceramic, green copper inclusions in ceramic and slag |
| **FOU29** | Phournoi 2 | S | 4.0x3.0x2.0 | 25.0 | Black, porous, Cu and Fe oxide staining, one lump of ceramic (c. 1 cm) in one pore, tiny few quartz and calcite rocks attached |
| **FOU30** | Phournoi 2 | S | 4.0x2.0x1.5 | 17.0 | Black, medium porosity, little Fe oxide staining, 3 possible external green prills, fragments of quartz and calcite attached |
| **FOU7** | Phournoi 4 | S | 8.0x5.0x1.5 | 98.6 | Black, can distinguish upper and lower parts with upper part showing collapsed ropey texture, little porosity |
| **FOU8** | Phournoi 4 | S | 4.5x3.0x2.5 | 41.8 | Black-blue colour with brown staining in parts, little porosity, one green prill protruding on outer surface |
| **FOU17** | Phournoi 4 | S | 7.0x5.0x1.5 | 93.8 | Black, partly blue, little porosity (<1 mm-3 mm), very crystalline in parts |

| | | | | | |
|---|---|---|---|---|---|
| **FOU18** | Phournoi 4 | S | 5.0x4.0x3.0 | 49.2 | Black with Fe-oxide staining, porous (1-5 mm) |
| **FOU25** | Phournoi 4 | S | 2.5x2.0x1.0 | 12.3 | Black, not porous, on one side intense yellow and some green staining, one outer green prill |

***Table A4.7a** Results of (P)ED-XRF analyses on Phournoi slag samples (major and minor elements in weight %). Analyses in bold are averages of three runs (a, b, c).*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$P_2O_5$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **$V_2O_5$** | **$Cr_2O_3$** | **MnO** | **$Fe_2O_3$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU1a** | 0.46 | 0.61 | 3.98 | 31.0 | 0.00 | 0.05 | 0.39 | 1.62 | 0.12 | 0.01 | 0.01 | 0.80 | 52.7 | 2.54 | 91.7 |
| **FOU1b** | 0.66 | 0.54 | 4.12 | 31.2 | 0.00 | 0.05 | 0.40 | 1.64 | 0.13 | 0.01 | 0.01 | 0.81 | 52.8 | 2.53 | 94.9 |
| **FOU1c** | 0.32 | 0.53 | 4.05 | 31.4 | 0.00 | 0.05 | 0.40 | 1.64 | 0.13 | 0.01 | 0.01 | 0.81 | 53.2 | 2.57 | 95.1 |
| **FOU1** | **0.48** | **0.56** | **4.05** | **31.2** | **0.00** | **0.05** | **0.40** | **1.63** | **0.13** | **0.01** | **0.01** | **0.81** | **52.9** | **2.54** | **94.8** |
| **FOU2a** | 0.67 | 1.27 | 3.91 | 30.3 | 0.00 | 0.09 | 0.47 | 2.19 | 0.17 | 0.01 | 0.02 | 0.27 | 57.9 | 1.11 | 98.3 |
| **FOU2b** | 0.63 | 1.33 | 3.93 | 30.6 | 0.00 | 0.09 | 0.48 | 2.22 | 0.17 | 0.01 | 0.02 | 0.27 | 58.0 | 1.12 | 98.9 |
| **FOU2c** | 0.62 | 1.23 | 3.96 | 30.6 | 0.00 | 0.09 | 0.48 | 2.21 | 0.17 | 0.01 | 0.02 | 0.27 | 57.9 | 1.12 | 98.6 |
| **FOU2** | **0.64** | **1.27** | **3.93** | **30.5** | **0.00** | **0.09** | **0.48** | **2.20** | **0.17** | **0.01** | **0.02** | **0.27** | **57.9** | **1.12** | **98.6** |
| **FOU3a** | 1.25 | 1.99 | 8.46 | 27.0 | 0.09 | 0.96 | 1.31 | 2.75 | 0.30 | 0.01 | 0.04 | 0.56 | 55.7 | 2.66 | 103 |
| **FOU3b** | 1.27 | 2.13 | 8.66 | 27.5 | 0.10 | 0.99 | 1.33 | 2.82 | 0.31 | 0.01 | 0.04 | 0.57 | 56.8 | 2.74 | 105 |
| **FOU3c** | 1.04 | 1.81 | 8.48 | 27.1 | 0.09 | 0.96 | 1.31 | 2.77 | 0.31 | 0.01 | 0.04 | 0.56 | 56.3 | 2.73 | 103 |
| **FOU3** | **1.19** | **1.98** | **8.53** | **27.2** | **0.09** | **0.97** | **1.32** | **2.78** | **0.31** | **0.01** | **0.04** | **0.57** | **56.3** | **2.71** | **104** |
| **FOU4a** | 0.74 | 1.74 | 4.87 | 33.1 | 0.00 | 0.05 | 0.71 | 3.05 | 0.18 | 0.01 | 0.02 | 0.40 | 54.0 | 2.73 | 102 |
| **FOU4b** | 0.85 | 1.71 | 4.84 | 33.2 | 0.00 | 0.05 | 0.71 | 3.08 | 0.18 | 0.01 | 0.02 | 0.40 | 54.0 | 2.70 | 102 |
| **FOU4c** | 0.73 | 1.61 | 4.80 | 32.9 | 0.00 | 0.06 | 0.70 | 3.04 | 0.18 | 0.01 | 0.02 | 0.40 | 53.9 | 2.72 | 101 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU4** | **0.77** | **1.69** | **4.83** | **33.1** | **0.00** | **0.05** | **0.70** | **3.06** | **0.18** | **0.01** | **0.02** | **0.40** | **54.0** | **2.72** | **101** |
| **FOU5a** | 0.67 | 1.21 | 6.84 | 38.1 | 0.00 | 0.78 | 0.64 | 2.59 | 0.29 | 0.03 | 0.01 | 0.39 | 49.0 | 1.05 | 102 |
| **FOU5b** | 1.02 | 1.38 | 6.93 | 38.5 | 0.00 | 0.79 | 0.65 | 2.61 | 0.29 | 0.03 | 0.01 | 0.40 | 49.5 | 1.05 | 103 |
| **FOU5c** | 1.09 | 1.31 | 6.93 | 38.3 | 0.00 | 0.80 | 0.64 | 2.60 | 0.29 | 0.03 | 0.01 | 0.39 | 49.3 | 1.04 | 103 |
| **FOU5** | **0.93** | **1.30** | **6.90** | **38.3** | **0.00** | **0.79** | **0.64** | **2.60** | **0.29** | **0.03** | **0.01** | **0.40** | **49.3** | **1.05** | **102** |
| **FOU6a** | 0.47 | 2.35 | 8.34 | 49.0 | 0.00 | 0.50 | 1.29 | 5.84 | 0.29 | 0.01 | 0.02 | 0.21 | 30.4 | 0.41 | 99.2 |
| **FOU6b** | 0.47 | 2.35 | 8.22 | 48.9 | 0.00 | 0.50 | 1.29 | 5.96 | 0.28 | 0.01 | 0.02 | 0.21 | 30.5 | 0.41 | 99.1 |
| **FOU6c** | 0.92 | 2.46 | 8.34 | 48.7 | 0.00 | 0.49 | 1.28 | 5.94 | 0.28 | 0.01 | 0.02 | 0.21 | 30.3 | 0.41 | 99.3 |
| **FOU6** | **0.62** | **2.38** | **8.30** | **48.9** | **0.00** | **0.50** | **1.28** | **5.91** | **0.28** | **0.01** | **0.02** | **0.21** | **30.4** | **0.41** | **99.2** |
| **FOU7a** | 0.10 | 5.27 | 3.97 | 41.1 | 0.00 | 0.49 | 0.63 | 9.80 | 0.15 | 0.00 | 0.01 | 0.27 | 35.4 | 0.55 | 97.7 |
| **FOU7b** | 0.41 | 5.47 | 4.06 | 41.3 | 0.00 | 0.49 | 0.63 | 9.81 | 0.16 | 0.00 | 0.01 | 0.27 | 35.3 | 0.55 | 98.4 |
| **FOU7c** | 0.43 | 5.47 | 4.01 | 41.5 | 0.00 | 0.48 | 0.64 | 9.90 | 0.16 | 0.00 | 0.01 | 0.27 | 35.6 | 0.55 | 99.0 |
| **FOU7** | **0.31** | **5.40** | **4.01** | **41.3** | **0.00** | **0.49** | **0.64** | **9.83** | **0.16** | **0.00** | **0.01** | **0.27** | **35.4** | **0.55** | **98.4** |
| **FOU8a** | 1.11 | 2.64 | 5.72 | 27.5 | 0.02 | 0.53 | 0.92 | 3.92 | 0.28 | 0.01 | 0.02 | 0.32 | 54.3 | 1.97 | 99.2 |
| **FOU8b** | 0.97 | 2.65 | 5.71 | 27.2 | 0.02 | 0.51 | 0.91 | 3.90 | 0.28 | 0.01 | 0.02 | 0.32 | 53.8 | 1.94 | 98.2 |
| **FOU8c** | 1.26 | 2.79 | 5.68 | 27.3 | 0.03 | 0.52 | 0.92 | 3.93 | 0.28 | 0.01 | 0.02 | 0.32 | 54.4 | 1.96 | 99.4 |
| **FOU8** | **1.11** | **2.69** | **5.70** | **27.3** | **0.03** | **0.52** | **0.91** | **3.92** | **0.28** | **0.01** | **0.02** | **0.32** | **54.2** | **1.96** | **98.9** |
| **FOU9a** | 1.21 | 3.24 | 8.29 | 46.8 | 0.00 | 0.22 | 1.18 | 7.43 | 0.25 | 0.00 | 0.02 | 0.24 | 27.0 | 0.63 | 96.5 |
| **FOU9b** | 1.72 | 3.49 | 8.29 | 46.5 | 0.00 | 0.22 | 1.19 | 7.47 | 0.26 | 0.00 | 0.02 | 0.24 | 27.2 | 0.62 | 97.2 |
| **FOU9c** | 1.32 | 3.26 | 8.17 | 46.4 | 0.00 | 0.22 | 1.17 | 7.38 | 0.25 | 0.00 | 0.02 | 0.24 | 27.0 | 0.61 | 96.1 |
| **FOU9** | **1.42** | **3.33** | **8.25** | **46.6** | **0.00** | **0.22** | **1.18** | **7.43** | **0.26** | **0.00** | **0.02** | **0.24** | **27.1** | **0.62** | **96.6** |
| **FOU10a** | 0.65 | 4.06 | 3.29 | 33.9 | 0.04 | 0.80 | 0.32 | 4.01 | 0.09 | 0.00 | 0.01 | 0.24 | 45.2 | 0.92 | 93.5 |
| **FOU10b** | 0.65 | 3.97 | 3.26 | 33.7 | 0.02 | 0.80 | 0.32 | 4.04 | 0.09 | 0.00 | 0.01 | 0.24 | 45.0 | 0.91 | 93.0 |
| **FOU10c** | 0.57 | 3.97 | 3.18 | 33.1 | 0.03 | 0.79 | 0.32 | 3.97 | 0.09 | 0.00 | 0.01 | 0.23 | 44.3 | 0.89 | 91.5 |
| **FOU10** | **0.62** | **4.00** | **3.24** | **33.6** | **0.03** | **0.79** | **0.32** | **4.01** | **0.09** | **0.00** | **0.01** | **0.24** | **44.8** | **0.91** | **92.7** |
| **FOU11a** | 0.50 | 2.94 | 4.82 | 23.8 | 0.00 | 0.35 | 0.50 | 3.22 | 0.17 | 0.02 | 0.02 | 1.69 | 59.6 | 2.69 | 100 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU11b** | 0.82 | 2.93 | 4.88 | 24.1 | 0.00 | 0.36 | 0.50 | 3.27 | 0.17 | 0.02 | 0.02 | 1.71 | 60.4 | 2.69 | 102 |
| **FOU11c** | 0.65 | 2.90 | 4.80 | 23.5 | 0.00 | 0.34 | 0.49 | 3.20 | 0.17 | 0.02 | 0.02 | 1.69 | 59.1 | 2.63 | 99.5 |
| **FOU11** | **0.66** | **2.92** | **4.83** | **23.8** | **0.00** | **0.35** | **0.50** | **3.23** | **0.17** | **0.02** | **0.02** | **1.69** | **59.7** | **2.67** | **101** |
| **FOU12a** | 0.51 | 1.14 | 5.10 | 30.5 | 0.00 | 0.16 | 0.42 | 2.39 | 0.12 | 0.00 | 0.01 | 0.36 | 53.0 | 1.76 | 95.5 |
| **FOU12b** | 0.73 | 1.14 | 5.13 | 30.8 | 0.00 | 0.15 | 0.43 | 2.42 | 0.12 | 0.00 | 0.01 | 0.36 | 53.3 | 1.76 | 96.3 |
| **FOU12c** | 0.48 | 1.15 | 5.09 | 30.6 | 0.00 | 0.16 | 0.43 | 2.40 | 0.12 | 0.00 | 0.01 | 0.36 | 53.1 | 1.76 | 95.6 |
| **FOU12** | **0.57** | **1.14** | **5.11** | **30.6** | **0.00** | **0.16** | **0.43** | **2.40** | **0.12** | **0.00** | **0.01** | **0.36** | **53.1** | **1.76** | **95.8** |
| **FOU13a** | 0.52 | 10.0 | 6.52 | 39.1 | 0.00 | 0.01 | 0.70 | 6.83 | 0.17 | 0.00 | 0.01 | 0.23 | 27.5 | 1.30 | 92.9 |
| **FOU13b** | 0.41 | 10.3 | 6.52 | 39.6 | 0.00 | 0.01 | 0.71 | 6.87 | 0.17 | 0.00 | 0.01 | 0.23 | 27.7 | 1.29 | 93.8 |
| **FOU13c** | 0.44 | 10.1 | 6.49 | 39.5 | 0.00 | 0.01 | 0.71 | 6.91 | 0.17 | 0.00 | 0.01 | 0.23 | 27.7 | 1.31 | 93.6 |
| **FOU13** | **0.46** | **10.1** | **6.51** | **39.4** | **0.00** | **0.01** | **0.71** | **6.87** | **0.17** | **0.00** | **0.01** | **0.23** | **27.6** | **1.30** | **93.4** |
| **FOU14a** | 1.23 | 4.43 | 8.64 | 48.2 | 0.00 | 0.04 | 1.81 | 4.57 | 0.31 | 0.02 | 0.03 | 0.24 | 22.3 | 5.47 | 97.3 |
| **FOU14b** | 0.63 | 4.33 | 8.52 | 48.1 | 0.00 | 0.04 | 1.80 | 4.55 | 0.31 | 0.02 | 0.03 | 0.24 | 22.2 | 5.49 | 96.2 |
| **FOU14c** | 1.18 | 4.42 | 8.52 | 47.7 | 0.00 | 0.04 | 1.80 | 4.54 | 0.31 | 0.02 | 0.03 | 0.24 | 22.1 | 5.44 | 96.4 |
| **FOU14** | **1.01** | **4.39** | **8.56** | **48.0** | **0.00** | **0.04** | **1.80** | **4.55** | **0.31** | **0.02** | **0.03** | **0.24** | **22.2** | **5.47** | **96.6** |
| **FOU15a** | 0.88 | 2.85 | 5.56 | 35.8 | 0.00 | 0.26 | 0.71 | 2.51 | 0.20 | 0.02 | 0.01 | 0.98 | 47.5 | 2.99 | 100 |
| **FOU15b** | 0.80 | 2.79 | 5.70 | 36.1 | 0.00 | 0.27 | 0.73 | 2.56 | 0.21 | 0.02 | 0.01 | 1.00 | 47.7 | 2.95 | 101 |
| **FOU15c** | 1.04 | 2.86 | 5.51 | 36.1 | 0.00 | 0.27 | 0.72 | 2.56 | 0.21 | 0.02 | 0.01 | 1.00 | 47.5 | 2.94 | 101 |
| **FOU15** | **0.91** | **2.83** | **5.59** | **36.0** | **0.00** | **0.27** | **0.72** | **2.54** | **0.20** | **0.02** | **0.01** | **0.99** | **47.6** | **2.96** | **101** |
| **FOU16a** | 0.52 | 1.60 | 3.53 | 31.0 | 0.00 | 0.30 | 0.35 | 3.76 | 0.09 | 0.01 | 0.01 | 1.90 | 52.3 | 1.88 | 97.2 |
| **FOU16b** | 0.61 | 1.62 | 3.58 | 31.2 | 0.00 | 0.30 | 0.34 | 3.81 | 0.09 | 0.01 | 0.01 | 1.91 | 52.7 | 1.93 | 98.1 |
| **FOU16c** | 0.52 | 1.58 | 3.61 | 31.0 | 0.00 | 0.29 | 0.35 | 3.79 | 0.08 | 0.00 | 0.01 | 1.90 | 52.4 | 1.89 | 97.4 |
| **FOU16** | **0.55** | **1.60** | **3.57** | **31.1** | **0.00** | **0.30** | **0.35** | **3.79** | **0.09** | **0.01** | **0.01** | **1.90** | **52.4** | **1.90** | **97.6** |
| **FOU17a** | 0.82 | 4.14 | 3.27 | 39.8 | 0.00 | 0.44 | 0.38 | 6.80 | 0.09 | 0.00 | 0.01 | 0.30 | 39.2 | 1.61 | 96.8 |
| **FOU17b** | 0.73 | 4.19 | 3.24 | 39.9 | 0.01 | 0.45 | 0.38 | 6.78 | 0.09 | 0.00 | 0.01 | 0.30 | 39.2 | 1.61 | 97.0 |
| **FOU17c** | 0.91 | 4.04 | 3.25 | 39.7 | 0.00 | 0.44 | 0.38 | 6.76 | 0.09 | 0.00 | 0.01 | 0.29 | 39.2 | 1.60 | 96.6 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU17** | **0.82** | **4.12** | **3.25** | **39.8** | **0.00** | **0.44** | **0.38** | **6.78** | **0.09** | **0.00** | **0.01** | **0.30** | **39.2** | **1.61** | **96.8** |
| **FOU18a** | 1.13 | 2.17 | 7.32 | 35.5 | 0.00 | 0.32 | 0.84 | 2.18 | 0.19 | 0.00 | 0.01 | 0.26 | 47.8 | 1.31 | 99.0 |
| **FOU18b** | 1.25 | 2.24 | 7.35 | 35.7 | 0.00 | 0.31 | 0.85 | 2.21 | 0.19 | 0.01 | 0.01 | 0.26 | 48.0 | 1.29 | 99.7 |
| **FOU18c** | 1.09 | 2.11 | 7.46 | 35.7 | 0.00 | 0.32 | 0.85 | 2.22 | 0.19 | 0.00 | 0.01 | 0.26 | 48.2 | 1.30 | 99.8 |
| **FOU18** | **1.16** | **2.17** | **7.38** | **35.6** | **0.00** | **0.32** | **0.85** | **2.20** | **0.19** | **0.00** | **0.01** | **0.26** | **48.0** | **1.30** | **99.5** |
| **FOU19a** | 1.17 | 2.95 | 6.80 | 41.3 | 0.00 | 0.10 | 1.04 | 13.3 | 0.27 | 0.00 | 0.02 | 0.42 | 20.5 | 1.56 | 89.5 |
| **FOU19b** | 0.55 | 2.86 | 6.69 | 41.1 | 0.00 | 0.10 | 1.03 | 13.4 | 0.27 | 0.00 | 0.02 | 0.42 | 20.5 | 1.55 | 88.5 |
| **FOU19c** | 0.63 | 2.82 | 6.68 | 40.9 | 0.00 | 0.09 | 1.03 | 13.3 | 0.27 | 0.00 | 0.02 | 0.42 | 20.4 | 1.56 | 88.1 |
| **FOU19** | **0.78** | **2.88** | **6.72** | **41.1** | **0.00** | **0.10** | **1.03** | **13.3** | **0.27** | **0.00** | **0.02** | **0.42** | **20.5** | **1.56** | **88.7** |
| **FOU21a** | 0.67 | 1.41 | 3.72 | 31.5 | 0.00 | 0.11 | 0.35 | 3.91 | 0.08 | 0.01 | 0.01 | 1.93 | 51.0 | 1.81 | 96.5 |
| **FOU21b** | 0.39 | 1.53 | 3.67 | 31.7 | 0.00 | 0.11 | 0.36 | 3.91 | 0.08 | 0.01 | 0.01 | 1.92 | 51.1 | 1.82 | 96.6 |
| **FOU21c** | 0.54 | 1.55 | 3.66 | 31.9 | 0.00 | 0.11 | 0.36 | 3.92 | 0.08 | 0.00 | 0.01 | 1.93 | 51.3 | 1.81 | 97.2 |
| **FOU21** | **0.53** | **1.49** | **3.69** | **31.7** | **0.00** | **0.11** | **0.36** | **3.91** | **0.08** | **0.01** | **0.01** | **1.93** | **51.1** | **1.81** | **96.8** |
| **FOU22a** | 1.08 | 2.36 | 5.53 | 35.8 | 0.00 | 0.24 | 0.73 | 4.67 | 0.24 | 0.02 | 0.02 | 1.34 | 44.0 | 1.54 | 97.5 |
| **FOU22b** | 1.18 | 2.46 | 5.54 | 35.8 | 0.00 | 0.23 | 0.73 | 4.69 | 0.24 | 0.02 | 0.02 | 1.34 | 43.9 | 1.52 | 97.7 |
| **FOU22c** | 0.51 | 2.28 | 5.40 | 35.7 | 0.00 | 0.23 | 0.73 | 4.67 | 0.24 | 0.02 | 0.02 | 1.33 | 43.6 | 1.53 | 96.2 |
| **FOU22** | **0.92** | **2.37** | **5.49** | **35.7** | **0.00** | **0.23** | **0.73** | **4.68** | **0.24** | **0.02** | **0.02** | **1.34** | **43.8** | **1.53** | **97.1** |
| **FOU23a** | 0.31 | 3.39 | 6.53 | 46.1 | 0.00 | 0.22 | 1.14 | 7.42 | 0.24 | 0.00 | 0.01 | 0.32 | 28.8 | 1.09 | 95.6 |
| **FOU23b** | 0.55 | 3.39 | 6.49 | 46.1 | 0.00 | 0.21 | 1.13 | 7.39 | 0.23 | 0.00 | 0.01 | 0.32 | 28.9 | 1.10 | 95.8 |
| **FOU23c** | 0.82 | 3.54 | 6.60 | 46.3 | 0.00 | 0.22 | 1.14 | 7.47 | 0.24 | 0.00 | 0.01 | 0.32 | 29.1 | 1.10 | 96.8 |
| **FOU23** | **0.56** | **3.44** | **6.54** | **46.2** | **0.00** | **0.22** | **1.14** | **7.43** | **0.24** | **0.00** | **0.01** | **0.32** | **28.9** | **1.09** | **96.0** |
| **FOU24a** | 1.02 | 3.04 | 4.05 | 38.3 | 0.00 | 0.62 | 0.59 | 7.44 | 0.21 | 0.02 | 0.01 | 0.69 | 41.2 | 0.45 | 97.7 |
| **FOU24b** | 1.08 | 2.92 | 4.05 | 38.0 | 0.00 | 0.63 | 0.59 | 7.45 | 0.21 | 0.02 | 0.01 | 0.69 | 41.1 | 0.45 | 97.3 |
| **FOU24c** | 0.99 | 2.99 | 4.17 | 38.2 | 0.00 | 0.63 | 0.59 | 7.44 | 0.21 | 0.02 | 0.01 | 0.69 | 41.3 | 0.45 | 97.6 |
| **FOU24** | **1.03** | **2.99** | **4.09** | **38.2** | **0.00** | **0.63** | **0.59** | **7.44** | **0.21** | **0.02** | **0.01** | **0.69** | **41.2** | **0.45** | **97.5** |
| **FOU26a** | 1.03 | 2.19 | 7.48 | 45.2 | 0.00 | 0.66 | 1.18 | 5.11 | 0.26 | 0.01 | 0.01 | 0.24 | 33.4 | 0.88 | 97.6 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU26b** | 0.80 | 2.26 | 7.48 | 45.3 | 0.00 | 0.67 | 1.19 | 5.18 | 0.26 | 0.01 | 0.01 | 0.25 | 33.4 | 0.88 | 97.7 |
| **FOU26c** | 0.77 | 2.13 | 7.44 | 44.9 | 0.00 | 0.66 | 1.17 | 5.12 | 0.26 | 0.01 | 0.01 | 0.24 | 33.2 | 0.87 | 96.8 |
| **FOU26** | **0.87** | **2.19** | **7.47** | **45.1** | **0.00** | **0.66** | **1.18** | **5.14** | **0.26** | **0.01** | **0.01** | **0.25** | **33.3** | **0.88** | **97.4** |
| **FOU27a** | 0.80 | 2.32 | 3.77 | 29.9 | 0.00 | 0.18 | 0.32 | 5.17 | 0.15 | 0.02 | 0.01 | 0.39 | 53.8 | 1.78 | 98.6 |
| **FOU27b** | 0.30 | 2.25 | 3.70 | 29.8 | 0.00 | 0.18 | 0.32 | 5.15 | 0.15 | 0.02 | 0.01 | 0.39 | 53.6 | 1.78 | 97.6 |
| **FOU27c** | 0.47 | 2.24 | 3.79 | 30.1 | 0.00 | 0.19 | 0.32 | 5.21 | 0.15 | 0.02 | 0.01 | 0.39 | 54.3 | 1.80 | 99.0 |
| **FOU27** | **0.52** | **2.27** | **3.75** | **29.9** | **0.00** | **0.18** | **0.32** | **5.18** | **0.15** | **0.02** | **0.01** | **0.39** | **53.9** | **1.79** | **98.4** |
| **FOU28a** | 0.93 | 2.75 | 5.69 | 30.4 | 0.04 | 0.27 | 0.78 | 5.18 | 0.22 | 0.00 | 0.02 | 0.31 | 51.5 | 1.11 | 99.2 |
| **FOU28b** | 0.83 | 2.59 | 5.77 | 30.0 | 0.05 | 0.28 | 0.78 | 5.15 | 0.22 | 0.00 | 0.02 | 0.31 | 51.2 | 1.11 | 98.4 |
| **FOU28c** | 0.95 | 2.73 | 5.67 | 30.5 | 0.03 | 0.27 | 0.78 | 5.19 | 0.22 | 0.00 | 0.02 | 0.32 | 51.1 | 1.10 | 98.9 |
| **FOU28** | **0.90** | **2.69** | **5.71** | **30.3** | **0.04** | **0.27** | **0.78** | **5.17** | **0.22** | **0.00** | **0.02** | **0.31** | **51.3** | **1.11** | **98.8** |
| **FOU29a** | 1.23 | 2.25 | 8.37 | 35.4 | 0.00 | 0.26 | 1.21 | 3.81 | 0.31 | 0.02 | 0.02 | 0.41 | 45.0 | 1.47 | 99.8 |
| **FOU29b** | 1.25 | 2.20 | 8.36 | 35.0 | 0.00 | 0.26 | 1.20 | 3.81 | 0.30 | 0.02 | 0.02 | 0.41 | 44.9 | 1.48 | 99.3 |
| **FOU29c** | 1.12 | 2.41 | 8.37 | 35.5 | 0.02 | 0.27 | 1.20 | 3.81 | 0.31 | 0.02 | 0.02 | 0.42 | 45.0 | 1.47 | 99.9 |
| **FOU29** | **1.20** | **2.28** | **8.37** | **35.3** | **0.01** | **0.26** | **1.21** | **3.81** | **0.31** | **0.02** | **0.02** | **0.41** | **45.0** | **1.47** | **99.7** |
| **FOU30a** | 0.93 | 5.94 | 4.76 | 46.6 | 0.00 | 0.25 | 0.57 | 5.41 | 0.19 | 0.01 | 0.01 | 0.42 | 32.4 | 0.88 | 98.3 |
| **FOU30b** | 0.54 | 5.69 | 4.80 | 46.6 | 0.00 | 0.26 | 0.57 | 5.40 | 0.19 | 0.01 | 0.01 | 0.41 | 32.3 | 0.88 | 97.7 |
| **FOU30c** | 0.74 | 5.85 | 4.76 | 46.6 | 0.00 | 0.25 | 0.58 | 5.40 | 0.19 | 0.01 | 0.01 | 0.41 | 32.4 | 0.89 | 98.1 |
| **FOU30** | **0.74** | **5.82** | **4.77** | **46.6** | **0.00** | **0.25** | **0.57** | **5.40** | **0.19** | **0.01** | **0.01** | **0.41** | **32.4** | **0.88** | **98.1** |

*Table A4.7b Results of (P)ED-XRF analyses of slag samples from Phournoi (trace elements in ppm). Analyses in bold are the averages of the three runs (a, b, c).*

| | NiO | ZnO | Ga | $As_2O_3$ | Se | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ag | Sb | Ba | La | Ce | Nd | $Ta_2O_5$ | $WO_3$ | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU1a** | 0 | 553 | 7 | 64 | 0 | 13 | 0 | 51 | 59 | 36 | 0 | 1 | 1975 | 0 | 79 | 0 | 0 | 48 | 200 | 0 | 5 |
| **FOU1b** | 0 | 528 | 6 | 64 | 0 | 14 | 0 | 49 | 60 | 19 | 0 | 2 | 2019 | 0 | 55 | 0 | 0 | 45 | 215 | 0 | 4 |
| **FOU1c** | 0 | 565 | 6 | 56 | 0 | 13 | 0 | 53 | 62 | 34 | 0 | 0 | 2018 | 0 | 86 | 0 | 0 | 45 | 213 | 0 | 7 |
| **FOU1** | **0** | **549** | **6** | **61** | **0** | **13** | **0** | **51** | **60** | **30** | **0** | **1** | **2004** | **0** | **73** | **0** | **0** | **46** | **209** | **0** | **5** |
| **FOU2a** | 126 | 453 | 0 | 123 | 0 | 5 | 0 | 28 | 19 | 54 | 0 | 4 | 924 | 0 | 30 | 0 | 0 | 0 | 27 | 0 | 2 |
| **FOU2b** | 46 | 444 | 0 | 199 | 0 | 10 | 0 | 26 | 17 | 43 | 0 | 4 | 947 | 0 | 40 | 0 | 0 | 9 | 54 | 0 | 5 |
| **FOU2c** | 101 | 444 | 0 | 120 | 0 | 4 | 0 | 25 | 17 | 43 | 0 | 4 | 910 | 0 | 24 | 0 | 0 | 3 | 53 | 0 | 6 |
| **FOU2** | **91** | **447** | **0** | **147** | **0** | **6** | **0** | **26** | **18** | **47** | **0** | **4** | **927** | **0** | **31** | **0** | **0** | **4** | **44** | **0** | **4** |
| **FOU3a** | 0 | 294 | 0 | 19 | 0 | 0 | 0 | 104 | 34 | 76 | 3 | 1 | 323 | 40 | 52 | 0 | 0 | 0 | 0 | 0 | 3 |
| **FOU3b** | 0 | 306 | 7 | 23 | 31 | 0 | 0 | 102 | 36 | 83 | 3 | 2 | 343 | 31 | 45 | 0 | 0 | 0 | 0 | 0 | 2 |
| **FOU3c** | 0 | 305 | 4 | 16 | 21 | 0 | 0 | 97 | 36 | 85 | 3 | 0 | 324 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| **FOU3** | **0** | **302** | **4** | **19** | **17** | **0** | **0** | **101** | **35** | **81** | **3** | **1** | **330** | **23** | **32** | **0** | **0** | **0** | **0** | **0** | **3** |
| **FOU4a** | 247 | 343 | 0 | 58 | 0 | 11 | 0 | 51 | 24 | 55 | 0 | 4 | 589 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| **FOU4b** | 246 | 344 | 5 | 94 | 0 | 13 | 0 | 53 | 23 | 49 | 0 | 0 | 572 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| **FOU4c** | 314 | 337 | 5 | 98 | 0 | 13 | 0 | 52 | 24 | 53 | 0 | 3 | 567 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **FOU4** | **269** | **341** | **3** | **83** | **0** | **12** | **0** | **52** | **23** | **53** | **0** | **2** | **576** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **1** |
| **FOU5a** | 0 | 268 | 5 | 98 | 0 | 0 | 0 | 50 | 49 | 47 | 0 | 33 | 2538 | 0 | 55 | 98 | 0 | 0 | 0 | 0 | 6 |
| **FOU5b** | 0 | 279 | 9 | 181 | 0 | 0 | 0 | 48 | 47 | 47 | 0 | 31 | 2579 | 0 | 37 | 118 | 0 | 0 | 0 | 0 | 4 |
| **FOU5c** | 0 | 260 | 6 | 104 | 0 | 0 | 0 | 47 | 47 | 50 | 0 | 30 | 2534 | 0 | 29 | 74 | 0 | 0 | 0 | 0 | 5 |
| **FOU5** | **0** | **269** | **7** | **128** | **0** | **0** | **0** | **48** | **48** | **48** | **0** | **31** | **2550** | **0** | **40** | **97** | **0** | **0** | **0** | **0** | **5** |
| **FOU6a** | 0 | 166 | 0 | 97 | 0 | 0 | 34 | 107 | 18 | 70 | 0 | 3 | 309 | 0 | 22 | 0 | 0 | 17 | 0 | 0 | 2 |
| **FOU6b** | 0 | 168 | 0 | 98 | 0 | 0 | 34 | 104 | 19 | 71 | 0 | 0 | 313 | 0 | 0 | 0 | 3 | 16 | 0 | 0 | 2 |

|  | NiO | ZnO | Ga | $As_2O_3$ | Se | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ag | Sb | Ba | La | Ce | Nd | $Ta_2O_5$ | $WO_3$ | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU6c** | 0 | 167 | 0 | 96 | 0 | 0 | 33 | 105 | 18 | 60 | 0 | 3 | 311 | 0 | 20 | 0 | 2 | 15 | 0 | 0 | 0 |
| **FOU6** | **0** | **167** | **0** | **97** | **0** | **0** | **34** | **105** | **18** | **67** | **0** | **2** | **311** | **0** | **14** | **0** | **2** | **16** | **0** | **0** | **1** |
| **FOU7a** | 0 | 189 | 0 | 49 | 0 | 2 | 24 | 45 | 23 | 50 | 0 | 0 | 251 | 0 | 44 | 0 | 4 | 16 | 0 | 36 | 3 |
| **FOU7b** | 13 | 182 | 0 | 49 | 0 | 2 | 26 | 45 | 24 | 51 | 0 | 0 | 257 | 0 | 41 | 0 | 0 | 16 | 0 | 38 | 0 |
| **FOU7c** | 20 | 188 | 0 | 30 | 0 | 3 | 25 | 44 | 23 | 64 | 0 | 0 | 256 | 0 | 57 | 0 | 3 | 14 | 0 | 36 | 3 |
| **FOU7** | **11** | **186** | **0** | **42** | **0** | **2** | **25** | **45** | **23** | **55** | **0** | **0** | **254** | **0** | **47** | **0** | **2** | **15** | **0** | **37** | **2** |
| **FOU8a** | 93 | 142 | 5 | 13 | 0 | 4 | 0 | 131 | 14 | 61 | 0 | 0 | 529 | 0 | 0 | 0 | 0 | 99 | 0 | 0 | 3 |
| **FOU8b** | 59 | 145 | 8 | 15 | 0 | 0 | 0 | 129 | 13 | 68 | 0 | 0 | 516 | 0 | 42 | 0 | 0 | 99 | 0 | 0 | 4 |
| **FOU8c** | 143 | 148 | 3 | 13 | 0 | 0 | 0 | 133 | 14 | 71 | 0 | 0 | 531 | 0 | 33 | 0 | 0 | 98 | 0 | 0 | 3 |
| **FOU8** | **98** | **145** | **5** | **13** | **0** | **1** | **0** | **131** | **14** | **67** | **0** | **0** | **525** | **0** | **25** | **0** | **0** | **99** | **0** | **0** | **3** |
| **FOU9a** | 118 | 109 | 0 | 19 | 0 | 3 | 39 | 59 | 23 | 65 | 0 | 1 | 310 | 28 | 50 | 0 | 0 | 8 | 0 | 0 | 3 |
| **FOU9b** | 119 | 110 | 0 | 31 | 0 | 2 | 39 | 60 | 22 | 64 | 0 | 0 | 313 | 23 | 45 | 0 | 5 | 8 | 0 | 0 | 3 |
| **FOU9c** | 119 | 109 | 0 | 30 | 0 | 2 | 40 | 59 | 23 | 68 | 0 | 2 | 318 | 24 | 36 | 0 | 5 | 8 | 0 | 0 | 2 |
| **FOU9** | **119** | **109** | **0** | **27** | **0** | **2** | **39** | **59** | **22** | **66** | **0** | **1** | **314** | **25** | **44** | **0** | **3** | **8** | **0** | **0** | **3** |
| **FOU10a** | 0 | 115 | 4 | 27 | 8 | 0 | 0 | 35 | 20 | 30 | 0 | 4 | 271 | 0 | 0 | 0 | 0 | 10 | 0 | 0 | 7 |
| **FOU10b** | 0 | 114 | 5 | 52 | 8 | 2 | 0 | 32 | 20 | 27 | 0 | 4 | 274 | 0 | 0 | 0 | 0 | 10 | 0 | 0 | 3 |
| **FOU10c** | 0 | 114 | 3 | 28 | 0 | 2 | 0 | 35 | 23 | 34 | 0 | 3 | 271 | 0 | 0 | 0 | 0 | 11 | 0 | 0 | 0 |
| **FOU10** | **0** | **114** | **4** | **36** | **6** | **1** | **0** | **34** | **21** | **30** | **0** | **4** | **272** | **0** | **0** | **0** | **0** | **10** | **0** | **0** | **3** |
| **FOU11a** | 0 | 358 | 0 | 29 | 0 | 0 | 0 | 37 | 89 | 39 | 0 | 2 | 1805 | 67 | 127 | 0 | 0 | 0 | 0 | 0 | 7 |
| **FOU11b** | 0 | 367 | 0 | 56 | 0 | 0 | 0 | 38 | 90 | 35 | 0 | 3 | 1806 | 55 | 126 | 72 | 0 | 0 | 0 | 0 | 4 |
| **FOU11c** | 0 | 364 | 0 | 68 | 0 | 0 | 0 | 41 | 86 | 39 | 0 | 2 | 1786 | 50 | 114 | 101 | 0 | 0 | 0 | 0 | 6 |
| **FOU11** | **0** | **363** | **0** | **51** | **0** | **0** | **0** | **39** | **89** | **38** | **0** | **2** | **1799** | **57** | **122** | **58** | **0** | **0** | **0** | **0** | **5** |
| **FOU12a** | 82 | 560 | 4 | 273 | 0 | 6 | 0 | 26 | 42 | 44 | 2 | 10 | 720 | 0 | 0 | 0 | 0 | 0 | 187 | 0 | 6 |
| **FOU12b** | 67 | 544 | 6 | 279 | 0 | 5 | 0 | 26 | 43 | 37 | 0 | 11 | 725 | 0 | 0 | 0 | 0 | 0 | 193 | 0 | 0 |
| **FOU12c** | 34 | 566 | 0 | 274 | 0 | 6 | 0 | 25 | 39 | 52 | 1 | 10 | 747 | 0 | 0 | 0 | 0 | 0 | 183 | 0 | 3 |
| **FOU12** | **61** | **557** | **3** | **275** | **0** | **6** | **0** | **26** | **41** | **45** | **1** | **10** | **731** | **0** | **0** | **0** | **0** | **0** | **188** | **0** | **3** |

| | **NiO** | **ZnO** | **Ga** | **$As_2O_3$** | **Se** | **Br** | **$Rb_2O$** | **SrO** | **Y** | **$ZrO_2$** | **Ag** | **Sb** | **Ba** | **La** | **Ce** | **Nd** | **$Ta_2O_5$** | **$WO_3$** | **PbO** | **Bi** | **U** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU13a** | 55 | 268 | 0 | 31 | 0 | 1 | 16 | 50 | 66 | 66 | 0 | 0 | 112 | 51 | 69 | 0 | 0 | 0 | 0 | 0 | 3 |
| **FOU13b** | 60 | 255 | 0 | 37 | 0 | 0 | 16 | 51 | 65 | 63 | 0 | 0 | 109 | 57 | 63 | 0 | 0 | 0 | 0 | 0 | 0 |
| **FOU13c** | 51 | 270 | 0 | 33 | 0 | 1 | 16 | 50 | 66 | 59 | 0 | 0 | 104 | 33 | 55 | 0 | 0 | 0 | 0 | 0 | 2 |
| **FOU13** | **55** | **264** | **0** | **34** | **0** | **1** | **16** | **50** | **65** | **63** | **0** | **0** | **108** | **47** | **62** | **0** | **0** | **0** | **0** | **0** | **2** |
| **FOU14a** | 379 | 156 | 0 | 82 | 0 | 7 | 121 | 30 | 19 | 99 | 1 | 4 | 212 | 0 | 36 | 0 | 32 | 32 | 0 | 0 | 3 |
| **FOU14b** | 373 | 150 | 0 | 90 | 0 | 4 | 121 | 30 | 19 | 91 | 1 | 4 | 193 | 0 | 27 | 0 | 11 | 37 | 0 | 0 | 3 |
| **FOU14c** | 374 | 157 | 0 | 89 | 0 | 7 | 120 | 32 | 19 | 86 | 1 | 4 | 184 | 0 | 24 | 0 | 25 | 32 | 0 | 0 | 1 |
| **FOU14** | **375** | **154** | **0** | **87** | **0** | **6** | **121** | **31** | **19** | **92** | **1** | **4** | **196** | **0** | **29** | **0** | **23** | **34** | **0** | **0** | **2** |
| **FOU15a** | 185 | 397 | 0 | 112 | 0 | 11 | 0 | 49 | 85 | 32 | 0 | 5 | 1535 | 36 | 68 | 112 | 0 | 0 | 0 | 0 | 6 |
| **FOU15b** | 169 | 403 | 0 | 70 | 0 | 9 | 0 | 48 | 87 | 50 | 0 | 5 | 1544 | 52 | 67 | 63 | 20 | 0 | 0 | 0 | 5 |
| **FOU15c** | 171 | 400 | 0 | 78 | 0 | 12 | 0 | 48 | 87 | 38 | 0 | 4 | 1489 | 41 | 62 | 64 | 18 | 0 | 0 | 0 | 5 |
| **FOU15** | **175** | **400** | **0** | **87** | **0** | **10** | **0** | **48** | **86** | **40** | **0** | **5** | **1523** | **43** | **66** | **80** | **12** | **0** | **0** | **0** | **5** |
| **FOU16a** | 60 | 996 | 0 | 73 | 0 | 0 | 0 | 75 | 91 | 30 | 0 | 3 | 1124 | 57 | 91 | 72 | 0 | 0 | 0 | 0 | 9 |
| **FOU16b** | 66 | 998 | 0 | 77 | 0 | 0 | 0 | 74 | 93 | 15 | 0 | 0 | 1162 | 47 | 85 | 95 | 0 | 0 | 0 | 0 | 4 |
| **FOU16c** | 69 | 981 | 0 | 45 | 0 | 0 | 0 | 71 | 91 | 25 | 0 | 2 | 1113 | 54 | 98 | 62 | 0 | 0 | 0 | 0 | 3 |
| **FOU16** | **65** | **992** | **0** | **65** | **0** | **0** | **0** | **73** | **92** | **23** | **0** | **2** | **1133** | **52** | **91** | **76** | **0** | **0** | **0** | **0** | **6** |
| **FOU17a** | 0 | 130 | 4 | 42 | 24 | 9 | 0 | 52 | 24 | 20 | 0 | 3 | 135 | 32 | 49 | 0 | 0 | 8 | 0 | 0 | 2 |
| **FOU17b** | 12 | 125 | 3 | 21 | 15 | 9 | 0 | 52 | 23 | 39 | 0 | 3 | 138 | 33 | 66 | 0 | 0 | 10 | 0 | 0 | 2 |
| **FOU17c** | 22 | 131 | 5 | 42 | 19 | 7 | 0 | 54 | 25 | 36 | 0 | 0 | 127 | 0 | 44 | 0 | 0 | 8 | 0 | 0 | 4 |
| **FOU17** | **11** | **129** | **4** | **35** | **19** | **8** | **0** | **53** | **24** | **32** | **0** | **2** | **133** | **22** | **53** | **0** | **0** | **9** | **0** | **0** | **3** |
| **FOU18a** | 67 | 347 | 4 | 137 | 0 | 3 | 0 | 42 | 34 | 53 | 1 | 3 | 313 | 0 | 38 | 0 | 0 | 4 | 0 | 0 | 4 |
| **FOU18b** | 62 | 358 | 4 | 152 | 0 | 0 | 0 | 44 | 35 | 52 | 1 | 4 | 323 | 0 | 31 | 0 | 0 | 3 | 0 | 0 | 3 |
| **FOU18c** | 87 | 348 | 0 | 136 | 0 | 4 | 0 | 45 | 32 | 56 | 1 | 3 | 328 | 0 | 29 | 0 | 0 | 0 | 0 | 0 | 4 |
| **FOU18** | **72** | **351** | **3** | **142** | **0** | **2** | **0** | **44** | **34** | **54** | **1** | **3** | **321** | **0** | **33** | **0** | **0** | **2** | **0** | **0** | **4** |
| **FOU19a** | 107 | 134 | 0 | 147 | 0 | 4 | 28 | 115 | 16 | 67 | 0 | 0 | 223 | 0 | 22 | 0 | 6 | 0 | 0 | 0 | 2 |
| **FOU19b** | 91 | 136 | 0 | 149 | 0 | 3 | 27 | 118 | 17 | 61 | 0 | 0 | 229 | 0 | 32 | 0 | 6 | 0 | 0 | 0 | 1 |

|  | NiO | ZnO | Ga | $As_2O_3$ | Se | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ag | Sb | Ba | La | Ce | Nd | $Ta_2O_5$ | $WO_3$ | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU19c** | 91 | 135 | 0 | 147 | 0 | 3 | 28 | 116 | 17 | 62 | 0 | 0 | 234 | 0 | 19 | 0 | 0 | 0 | 0 | 0 | 0 |
| **FOU19** | **96** | **135** | **0** | **147** | **0** | **3** | **28** | **116** | **17** | **64** | **0** | **0** | **228** | **0** | **24** | **0** | **4** | **0** | **0** | **0** | **1** |
| **FOU21a** | 48 | 1015 | 0 | 73 | 0 | 4 | 0 | 76 | 97 | 34 | 0 | 0 | 1181 | 58 | 75 | 0 | 0 | 0 | 0 | 0 | 6 |
| **FOU21b** | 66 | 1026 | 0 | 69 | 0 | 4 | 0 | 75 | 95 | 16 | 0 | 3 | 1176 | 56 | 86 | 69 | 0 | 0 | 0 | 0 | 6 |
| **FOU21c** | 58 | 1048 | 0 | 69 | 0 | 4 | 0 | 74 | 97 | 23 | 0 | 1 | 1197 | 81 | 99 | 49 | 0 | 0 | 0 | 0 | 0 |
| **FOU21** | **57** | **1030** | **0** | **70** | **0** | **4** | **0** | **75** | **96** | **24** | **0** | **1** | **1185** | **65** | **87** | **39** | **0** | **0** | **0** | **0** | **4** |
| **FOU22a** | 80 | 706 | 5 | 117 | 0 | 4 | 0 | 108 | 67 | 37 | 0 | 2 | 2327 | 25 | 53 | 59 | 0 | 7 | 0 | 0 | 3 |
| **FOU22b** | 82 | 695 | 7 | 122 | 0 | 4 | 0 | 105 | 65 | 50 | 0 | 3 | 2350 | 28 | 58 | 0 | 0 | 6 | 0 | 0 | 3 |
| **FOU22c** | 83 | 706 | 6 | 115 | 0 | 5 | 0 | 109 | 63 | 42 | 0 | 2 | 2323 | 27 | 31 | 81 | 0 | 4 | 0 | 0 | 5 |
| **FOU22** | **82** | **702** | **6** | **118** | **0** | **4** | **0** | **107** | **65** | **43** | **0** | **2** | **2333** | **27** | **47** | **47** | **0** | **6** | **0** | **0** | **4** |
| **FOU23a** | 89 | 287 | 0 | 109 | 0 | 3 | 28 | 96 | 20 | 54 | 0 | 3 | 527 | 0 | 40 | 0 | 0 | 3 | 0 | 0 | 3 |
| **FOU23b** | 108 | 293 | 0 | 69 | 0 | 2 | 26 | 94 | 21 | 50 | 0 | 3 | 526 | 0 | 35 | 0 | 4 | 3 | 0 | 0 | 0 |
| **FOU23c** | 101 | 289 | 0 | 114 | 0 | 0 | 26 | 95 | 22 | 58 | 0 | 2 | 512 | 0 | 39 | 0 | 5 | 2 | 0 | 0 | 3 |
| **FOU23** | **99** | **290** | **0** | **97** | **0** | **2** | **27** | **95** | **21** | **54** | **0** | **3** | **522** | **0** | **38** | **0** | **3** | **3** | **0** | **0** | **2** |
| **FOU24a** | 0 | 380 | 5 | 130 | 0 | 0 | 0 | 75 | 32 | 36 | 0 | 5 | 2680 | 0 | 0 | 82 | 0 | 18 | 0 | 0 | 5 |
| **FOU24b** | 0 | 383 | 7 | 132 | 0 | 0 | 0 | 74 | 32 | 47 | 0 | 5 | 2707 | 0 | 29 | 79 | 0 | 16 | 0 | 0 | 4 |
| **FOU24c** | 0 | 384 | 5 | 128 | 0 | 0 | 0 | 76 | 32 | 36 | 0 | 6 | 2674 | 0 | 38 | 0 | 0 | 16 | 0 | 0 | 4 |
| **FOU24** | **0** | **382** | **6** | **130** | **0** | **0** | **0** | **75** | **32** | **40** | **0** | **5** | **2687** | **0** | **22** | **54** | **0** | **17** | **0** | **0** | **4** |
| **FOU26a** | 29 | 199 | 13 | 71 | 0 | 1 | 29 | 95 | 20 | 65 | 0 | 0 | 344 | 0 | 27 | 0 | 0 | 17 | 0 | 0 | 0 |
| **FOU26b** | 0 | 212 | 11 | 99 | 0 | 3 | 31 | 96 | 19 | 67 | 0 | 2 | 344 | 0 | 36 | 0 | 0 | 17 | 12 | 0 | 3 |
| **FOU26c** | 23 | 198 | 11 | 100 | 0 | 3 | 29 | 97 | 20 | 66 | 0 | 2 | 344 | 0 | 25 | 0 | 0 | 17 | 8 | 0 | 3 |
| **FOU26** | **17** | **203** | **12** | **90** | **0** | **2** | **30** | **96** | **20** | **66** | **0** | **1** | **344** | **0** | **29** | **0** | **0** | **17** | **7** | **0** | **2** |
| **FOU27a** | 0 | 168 | 0 | 46 | 0 | 6 | 0 | 29 | 33 | 33 | 0 | 0 | 2251 | 0 | 56 | 0 | 0 | 11 | 0 | 0 | 5 |
| **FOU27b** | 0 | 176 | 0 | 26 | 0 | 7 | 0 | 31 | 31 | 26 | 0 | 0 | 2245 | 0 | 56 | 0 | 0 | 16 | 0 | 0 | 0 |
| **FOU27c** | 0 | 177 | 0 | 60 | 0 | 7 | 0 | 30 | 33 | 31 | 0 | 0 | 2282 | 0 | 44 | 0 | 0 | 12 | 0 | 0 | 4 |
| **FOU27** | **0** | **173** | **0** | **44** | **0** | **6** | **0** | **30** | **32** | **30** | **0** | **0** | **2259** | **0** | **52** | **0** | **0** | **13** | **0** | **0** | **3** |

| | NiO | ZnO | Ga | $As_2O_3$ | Se | Br | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ag | Sb | Ba | La | Ce | Nd | $Ta_2O_5$ | $WO_3$ | PbO | Bi | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU28a** | 57 | 156 | 0 | 13 | 0 | 0 | 0 | 101 | 18 | 62 | 0 | 0 | 283 | 0 | 29 | 0 | 0 | 5 | 0 | 0 | 2 |
| **FOU28b** | 20 | 148 | 4 | 13 | 0 | 0 | 0 | 101 | 20 | 53 | 0 | 0 | 281 | 0 | 35 | 0 | 0 | 6 | 0 | 0 | 2 |
| **FOU28c** | 0 | 140 | 3 | 16 | 0 | 0 | 0 | 96 | 13 | 64 | 0 | 0 | 284 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 4 |
| **FOU28** | **26** | **148** | **2** | **14** | **0** | **0** | **0** | **99** | **17** | **59** | **0** | **0** | **283** | **0** | **22** | **0** | **0** | **5** | **0** | **0** | **3** |
| **FOU29a** | 76 | 410 | 8 | 109 | 16 | 0 | 18 | 108 | 30 | 74 | 0 | 6 | 1106 | 0 | 38 | 0 | 0 | 28 | 48 | 0 | 5 |
| **FOU29b** | 83 | 418 | 9 | 115 | 0 | 0 | 20 | 106 | 29 | 63 | 0 | 4 | 1093 | 0 | 26 | 0 | 0 | 26 | 37 | 0 | 3 |
| **FOU29c** | 56 | 412 | 9 | 102 | 13 | 0 | 21 | 107 | 28 | 66 | 0 | 6 | 1107 | 0 | 33 | 0 | 0 | 27 | 46 | 0 | 3 |
| **FOU29** | **72** | **413** | **9** | **109** | **10** | **0** | **20** | **107** | **29** | **67** | **0** | **5** | **1102** | **0** | **32** | **0** | **0** | **27** | **44** | **0** | **4** |
| **FOU30a** | 83 | 408 | 0 | 120 | 0 | 3 | 12 | 61 | 26 | 50 | 0 | 5 | 1066 | 0 | 0 | 0 | 0 | 4 | 67 | 0 | 0 |
| **FOU30b** | 81 | 409 | 8 | 117 | 0 | 3 | 10 | 61 | 25 | 56 | 0 | 4 | 1055 | 0 | 35 | 0 | 0 | 5 | 69 | 0 | 0 |
| **FOU30c** | 92 | 409 | 7 | 116 | 0 | 3 | 10 | 60 | 26 | 38 | 0 | 4 | 1101 | 0 | 26 | 0 | 0 | 4 | 67 | 0 | 0 |
| **FOU30** | **86** | **409** | **5** | **118** | **0** | **3** | **10** | **60** | **26** | **48** | **0** | **4** | **1074** | **0** | **20** | **0** | **0** | **4** | **67** | **0** | **0** |

*Table A4.8 Summary of the optical microscopy observations for the Phournoi slags (F/P: fayalite or pyroxene; M: magnetite; MA: magnetite aggregate, G: glass, W: wüstitite, CM: copper metal prills). The column labelled 'prills' describes whether the entrapped prills are mainly copper metal or matte or a mixture of both.*

| Sample | F/P | M | MA | G | W | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|---|
| **FOU1** | + | + |  | + |  | Matte |  | Medium porosity and several cracks, phases often corroded |
| **FOU2** | + | + |  | + |  | Matte |  | Medium porosity, heterogeneous distribution of phases, phases often corroded |
| **FOU3** | + | + | + | + | + | Matte |  | Matte frequently associated with magnetite and wüstite, wüstite also found as aggregates, little porosity |
| **FOU4** | + | + |  | + |  | Both |  | Matte often surround copper prills, phases are much smaller and more compact at the edge of the sample, little porosity |
| **FOU5** | + | + |  | + |  | Matte |  | Phases often corroded, low-medium porosity |
| **FOU6** | + |  |  | + |  | Matte | Quartz with Fe minerals | Glassy slag, quartz inclusions concentrated in one area of the sample, low-medium porosity |
| **FOU7** |  |  |  | + |  | Matte |  | Glassy, many cracks, medium porosity, many matte |
| **FOU8** | + | + | + | + |  | Matte |  | One magnetite band across sample, few small magnetite aggregates dissolving (with metallic phases) |
| **FOU9** | + | + |  | + |  | Matte | 1 quartz and 3 large partially reacted Cu-Fe sulphide minerals | Two large almost unreacted copper-iron sulphidic inclusions (one at edge). They have a cream-white colour and show many cracks. |
| **FOU10** | + |  |  | – |  | Matte | 2 quartz with Fe minerals | Porous |
| **FOU11** | + | + |  | + |  | Matte |  | Low porosity |
| **FOU12** | + | + | + | + |  | Matte |  | Few small magnetite aggregates dissolving, low porosity |

| Sample | F/P | M | MA | G | W | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|---|
| **FOU13** | + |  |  | + |  | Matte |  | Medium porosity, little magnetite only present at the edge of the sample |
| **FOU14** | + | + |  | + |  | Both | 1 quartz | Medium porosity, many small prills |
| **FOU15** | + | + |  | + |  | Both | 3 large partially reacted Cu-Fe sulphides | The inclusions have a cream-white colour and are surrounded by large round pores from the evaporation of sulphur dioxide. A thin magnetite band has formed around their edge. |
| **FOU16** | + | + |  | + |  | Matte |  | Low porosity |
| **FOU17** | + | + |  | + |  | Matte | 1 quartz | Porous, cracked |
| **FOU18** | + | + | + | + |  | Matte |  | Few small magnetite aggregates, 2-3 stringers, low porosity |
| **FOU19** |  | + |  | + |  | Matte | quartz | Very heterogeneous sample with quartz inclusions and large circular vesicles, slag glassy with magnetites and very few tiny matte only in one area |
| **FOU21** | + | + |  | + |  | Both |  | Cu prills tiny, while matte are larger |
| **FOU22** | + | + |  | + |  | Matte | One large ceramic fragment and several smaller ones | The ceramic fragment shows a red layer (with quartz and schist inclusions) and a vitrified layer with large circular vesicles and closely bound slag. Smaller vitrified clay inclusions are found within the centre of the slag matrix |
| **FOU24** | + | + |  | + |  | Matte | One large ceramic fragment | The ceramic fragment shows a red layer (with quartz and schist inclusions) and a vitrified layer with large circular vesicles and closely bound slag. |
| **FOU25** | + | + | + | + | + | Matte |  | Matte often associated with wüstite, wüstite also found as aggregates, low-medium porosity |
| **FOU26** | + | + |  | + |  | Matte | 2-3quartz with Fe minerals | Little-medium porosity |
| **FOU27** | + | + |  | + |  | Matte | quartz | Very heterogeneous in terms of size and distribution of phases |
| **FOU28** | + | + |  | + |  | Matte |  | Sample broke into two parts during sectioning at the edge of the two ‘ropes’ of slag. Upper and lower flow patterns examined separately, phases on lower one generally larger than in the top one, indicating that the former cooled more slowly, possibly quickly covered by the top |

| Sample | F/P | M | MA | G | W | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|---|
| **FOU29** | + | + |  | + |  | Matte |  | Medium porosity, one magnetite band |
| **FOU30** | + | + |  | + |  | Matte | 1 quartz | Medium porosity |

*Table A4.9 Spot analyses on the WDS-EPMA of individual phases in slag samples from Phournoi (weight %). See notes in Table A4.4.*

| Sample | Phase | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | $Fe_3O_4$ | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU1a** | Fayalite | 0.0 | 4.2 | 0.0 | 30 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 67 |  | 0.1 | 101 |
| **FOU1b** | Fayalite | 0.0 | 3.5 | 0.0 | 30 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 66 |  | 0.1 | 100 |
| **FOU1c** | Magnetite | 0.0 | 0.4 | 2.9 | 0.4 | 0.0 | 0.0 | 0.0 | 0.4 | 0.0 |  | 98 | 0.0 | 103 |
| **FOU1d** | Magnetite | 0.0 | 0.4 | 2.8 | 0.6 | 0.0 | 0.0 | 0.0 | 0.3 | 0.0 |  | 101 | 0.1 | 105 |
| **FOU1e** | Glass | 0.6 | 0.1 | 10 | 54 | 0.0 | 0.7 | 6.3 | 0.1 | 0.0 | 22 |  | 0.4 | 94 |
| **FOU1f** | Glass | 0.5 | 0.1 | 8.9 | 57 | 0.0 | 0.6 | 6.2 | 0.0 | 0.0 | 22 |  | 1.7 | 97 |
| **FOU2a** | Fayalite | 0.0 | 3.3 | 0.0 | 30 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 66 |  | 0.1 | 100 |
| **FOU2b** | Fayalite | 0.0 | 2.1 | 0.0 | 30 | 0.0 | 0.0 | 0.5 | 0.0 | 0.5 | 70 |  | 0.0 | 103 |
| **FOU2c** | Magnetite | 0.0 | 0.3 | 2.7 | 0.7 | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 |  | 100 | 0.0 | 104 |
| **FOU2d** | Magnetite | 0.0 | 0.4 | 3.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.7 | 0.1 |  | 101 | 0.0 | 105 |
| **FOU2e** | Glass | 0.7 | 0.1 | 8.0 | 50 | 0.1 | 1.1 | 14 | 0.1 | 0.2 | 26 |  | 0.1 | 100 |
| **FOU2f** | Glass | 0.8 | 0.1 | 8.5 | 51 | 0.1 | 1.3 | 12 | 0.1 | 0.0 | 25 |  | 0.0 | 99 |
| **FOU3a** | Fayalite | 0.0 | 7.0 | 0.1 | 30 | 0.0 | 0.0 | 1.1 | 0.0 | 1.3 | 62 |  | 0.1 | 102 |
| **FOU3b** | Fayalite | 0.0 | 7.8 | 0.2 | 31 | 0.0 | 0.0 | 1.0 | 0.0 | 1.4 | 60 |  | 0.0 | 101 |
| **FOU3c** | Fayalite | 0.0 | 7.6 | 0.1 | 30 | 0.0 | 0.0 | 1.1 | 0.0 | 1.3 | 60 |  | 0.0 | 101 |
| **FOU3d** | Wüstite? | 0.0 | 0.2 | 1.0 | 0.2 | 0.0 | 0.0 | 0.1 | 0.5 | 0.4 | 101 |  | 0.0 | 103 |
| **FOU3e** | Wüstite? | 0.0 | 0.4 | 0.9 | 2.1 | 0.0 | 0.0 | 0.1 | 0.2 | 0.4 | 98 |  | 0.1 | 103 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU3f** | Wüstite? | 0.0 | 0.4 | 0.5 | 0.5 | 0.0 | 0.0 | 0.0 | 0.2 | 0.3 | 100 | | 0.1 | 102 |
| **FOU3g** | Glass | 4.1 | 0.3 | 17 | 40 | 0.5 | 4.4 | 9.3 | 0.1 | 0.4 | 24 | | 0.3 | 100 |
| **FOU4a** | Fayalite | 0.0 | 7.1 | 0.0 | 31 | 0.0 | 0.0 | 0.3 | 0.0 | 0.8 | 64 | | 0.1 | 103 |
| **FOU4b** | Fayalite | 0.0 | 7.3 | 0.0 | 31 | 0.0 | 0.0 | 0.4 | 0.0 | 0.8 | 63 | | 0.1 | 102 |
| **FOU4c** | Magnetite | 0.0 | 0.6 | 3.2 | 0.4 | 0.0 | 0.0 | 0.0 | 0.6 | 0.2 | | 97 | 0.0 | 102 |
| **FOU4d** | Magnetite | 0.0 | 0.7 | 3.2 | 0.4 | 0.0 | 0.0 | 0.0 | 0.6 | 0.2 | | 96 | 0.1 | 102 |
| **FOU4e** | Glass | 1.4 | 0.3 | 8.0 | 49 | 0.0 | 1.2 | 7.1 | 0.1 | 0.3 | 28 | | 0.2 | 95 |
| **FOU4f** | Glass | 0.9 | 0.2 | 8.8 | 50 | 0.0 | 1.1 | 14 | 0.2 | 0.3 | 23 | | 0.2 | 99 |
| **FOU5a** | Fayalite | 0.0 | 4.2 | 0.0 | 30 | 0.0 | 0.0 | 0.2 | 0.0 | 0.7 | 66 | | 0.0 | 100 |
| **FOU5b** | Fayalite | 0.0 | 4.7 | 0.1 | 30 | 0.0 | 0.0 | 0.2 | 0.0 | 0.8 | 64 | | 0.0 | 100 |
| **FOU5c** | Fayalite | 0.0 | 3.9 | 0.0 | 30 | 0.0 | 0.0 | 0.2 | 0.0 | 0.7 | 65 | | 0.0 | 99 |
| **FOU5d** | Glass | 1.1 | 0.2 | 14 | 56 | 0.5 | 1.4 | 5.0 | 0.4 | 0.2 | 17 | | 0.2 | 97 |
| **FOU6a** | Fayalite | 0.0 | 8.0 | 0.0 | 30 | 0.0 | 0.0 | 0.8 | 0.1 | 0.5 | 61 | | 0.0 | 100 |
| **FOU6b** | Glass | 0.7 | 0.9 | 10 | 52 | 0.5 | 1.3 | 10 | 0.4 | 0.2 | 20 | | 0.1 | 96 |
| **FOU6c** | Glass | 0.7 | 0.6 | 10 | 53 | 0.6 | 1.0 | 13 | 0.4 | 0.2 | 17 | | 0.0 | 97 |
| **FOU7a** | Glass | 0.7 | 5.3 | 5.7 | 45 | 0.4 | 0.8 | 9.1 | 0.2 | 0.3 | 31 | | 0.1 | 99 |
| **FOU7b** | Glass | 0.7 | 4.9 | 6.9 | 47 | 0.3 | 1.2 | 8.6 | 0.2 | 0.3 | 28 | | 0.1 | 98 |
| **FOU7c** | Glass | 0.7 | 4.8 | 7.6 | 48 | 0.2 | 1.2 | 8.3 | 0.3 | 0.3 | 27 | | 0.1 | 99 |
| **FOU8a** | Fayalite | 0.1 | 9.1 | 0.0 | 31 | 0.0 | 0.0 | 0.9 | 0.0 | 0.6 | 61 | | 0.0 | 102 |
| **FOU8b** | Fayalite | 0.1 | 5.7 | 0.1 | 31 | 0.0 | 0.0 | 1.3 | 0.0 | 0.7 | 63 | | 0.0 | 101 |
| **FOU8c** | Magnetite | 0.0 | 0.8 | 12 | 0.3 | 0.0 | 0.0 | 0.0 | 2.3 | 0.1 | | 88 | 0.0 | 103 |
| **FOU8d** | Magnetite | 0.0 | 0.4 | 7.8 | 0.4 | 0.0 | 0.0 | 0.1 | 1.6 | 0.1 | | 94 | 0.0 | 104 |
| **FOU8e** | Glass | 0.8 | 0.2 | 15 | 46 | 0.3 | 1.3 | 5.2 | 0.1 | 0.1 | 22 | | 0.3 | 91 |
| **FOU9a** | Fayalite | 0.0 | 4.5 | 0.0 | 30 | 0.0 | 0.0 | 1.1 | 0.0 | 0.5 | 64 | | 0.1 | 100 |
| **FOU9b** | Fayalite | 0.0 | 4.9 | 0.0 | 30 | 0.0 | 0.0 | 1.1 | 0.0 | 0.5 | 63 | | 0.0 | 99 |
| **FOU9c** | Magnetite | 0.0 | 0.2 | 1.7 | 0.4 | 0.0 | 0.0 | 0.2 | 1.0 | 0.1 | | 97 | 0.0 | 101 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU9d** | Glass | 0.2 | 10 | 1.1 | 48 | 0.0 | 0.0 | 15 | 0.0 | 0.2 | 24 |  | 0.0 | 99 |
| **FOU10a** | Fayalite | 0.0 | 19 | 0.0 | 33 | 0.0 | 0.0 | 0.3 | 0.0 | 0.3 | 49 |  | 0.0 | 102 |
| **FOU11a** | Fayalite | 0.0 | 7.0 | 0.1 | 31 | 0.0 | 0.0 | 0.4 | 0.0 | 3.2 | 62 |  | 0.1 | 103 |
| **FOU11b** | Fayalite | 0.0 | 1.0 | 0.1 | 29 | 0.0 | 0.0 | 1.1 | 0.0 | 3.0 | 68 |  | 0.1 | 102 |
| **FOU11c** | Fayalite | 0.0 | 11 | 0.1 | 32 | 0.0 | 0.0 | 0.4 | 0.0 | 3.2 | 57 |  | 0.0 | 103 |
| **FOU11d** | Magnetite | 0.0 | 0.5 | 17 | 0.4 | 0.0 | 0.0 | 0.0 | 0.8 | 0.8 |  | 86 | 0.0 | 106 |
| **FOU11e** | Magnetite | 0.0 | 0.7 | 15 | 0.5 | 0.0 | 0.0 | 0.0 | 0.8 | 0.9 |  | 89 | 0.0 | 107 |
| **FOU11f** | Glass | 2.0 | 0.0 | 16 | 44 | 0.0 | 2.6 | 14 | 0.1 | 0.8 | 19 |  | 0.1 | 99 |
| **FOU12a** | Fayalite | 0.0 | 8.1 | 0.0 | 31 | 0.0 | 0.0 | 0.2 | 0.0 | 0.9 | 63 |  | 0.1 | 104 |
| **FOU12b** | Fayalite | 0.0 | 5.2 | 0.0 | 30 | 0.0 | 0.0 | 0.3 | 0.0 | 0.8 | 66 |  | 0.1 | 103 |
| **FOU12c** | Magnetite | 0.0 | 0.7 | 4.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.4 | 0.2 |  | 100 | 0.1 | 106 |
| **FOU12d** | Magnetite | 0.0 | 0.6 | 3.6 | 0.4 | 0.0 | 0.0 | 0.0 | 0.3 | 0.1 |  | 101 | 0.1 | 107 |
| **FOU12e** | Glass | 0.4 | 0.3 | 7.0 | 49 | 0.0 | 0.3 | 4.8 | 0.1 | 0.3 | 40 |  | 0.2 | 102 |
| **FOU12f** | Glass | 0.4 | 0.3 | 6.3 | 46 | 0.1 | 0.1 | 4.6 | 0.1 | 0.3 | 43 |  | 0.6 | 102 |
| **FOU13a** | Fay./Gl. | 0.0 | 33 | 0.1 | 35 | 0.0 | 0.0 | 0.4 | 0.0 | 0.3 | 28 |  | 0.1 | 97 |
| **FOU13b** | Fay./Gl. | 0.0 | 32 | 0.1 | 35 | 0.0 | 0.0 | 0.4 | 0.0 | 0.3 | 29 |  | 0.2 | 97 |
| **FOU13c** | Fay./Gl. | 0.0 | 27 | 0.1 | 34 | 0.0 | 0.0 | 0.6 | 0.0 | 0.3 | 36 |  | 0.1 | 98 |
| **FOU13d** | Glass | 0.6 | 3.2 | 9.7 | 50 | 0.0 | 1.0 | 15 | 0.3 | 0.1 | 16 |  | 0.1 | 95 |
| **FOU14a** | Fay./Gl. | 0.2 | 20 | 3.0 | 37 | 0.0 | 0.6 | 1.8 | 0.1 | 0.6 | 31 |  | 0.2 | 95 |
| **FOU14b** | Magnetite | 0.0 | 1.8 | 4.7 | 0.2 | 0.0 | 0.0 | 0.1 | 1.2 | 0.2 |  | 90 | 0.1 | 99 |
| **FOU14c** | Magnetite | 0.1 | 2.1 | 5.2 | 2.3 | 0.0 | 0.0 | 0.9 | 1.1 | 0.1 | 58 |  | 0.2 | 103 |
| **FOU15a** | Fayalite | 0.1 | 11 | 0.0 | 32 | 0.0 | 0.0 | 0.2 | 0.0 | 1.5 | 59 |  | 0.1 | 104 |
| **FOU15b** | Fayalite | 0.0 | 11 | 0.0 | 32 | 0.0 | 0.0 | 0.2 | 0.0 | 1.4 |  | 92 | 0.1 | 108 |
| **FOU15d** | Glass | 1.0 | 0.4 | 9.7 | 52 | 0.0 | 0.9 | 8.2 | 0.1 | 0.8 | 25 |  | 0.2 | 98 |
| **FOU15e** | Glass | 0.9 | 0.4 | 9.7 | 52 | 0.1 | 0.8 | 9.1 | 0.1 | 0.9 | 25 |  | 0.3 | 99 |
| **FOU16a** | Fayalite | 0.0 | 5.7 | 0.0 | 30 | 0.0 | 0.0 | 0.6 | 0.0 | 3.8 | 61 |  | 0.1 | 101 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FOU16b** | Fayalite | 0.1 | 5.6 | 0.1 | 30 | 0.0 | 0.0 | 0.6 | 0.0 | 4.3 | 64 |  | 0.1 | 105 |
| **FOU16c** | Glass | 0.8 | 0.4 | 6.4 | 46 | 0.0 | 0.6 | 8.6 | 0.0 | 2.1 | 35 |  | 0.2 | 100 |
| **FOU16d** | Glass | 0.7 | 0.8 | 5.1 | 46 | 0.0 | 0.6 | 4.8 | 0.0 | 3.1 | 42 |  | 0.4 | 103 |
| **FOU22a** | Fayalite | 0.0 | 10 | 0.0 | 30 | 0.0 | 0.0 | 0.5 | 0.0 | 2.2 | 55 |  | 0.0 | 97 |
| **FOU22b** | Fayalite | 0.0 | 11 | 0.0 | 30 | 0.0 | 0.0 | 0.5 | 0.0 | 2.0 | 54 |  | 0.1 | 98 |
| **FOU22c** | Fayalite | 0.0 | 10 | 0.0 | 30 | 0.0 | 0.0 | 0.4 | 0.0 | 2.0 | 52 |  | 0.1 | 96 |
| **FOU22d** | Glass | 0.9 | 0.5 | 11 | 48 | 0.3 | 1.5 | 13 | 0.4 | 0.8 | 18 |  | 0.2 | 95 |
| **FOU22e** | Glass | 0.9 | 0.4 | 10 | 48 | 0.9 | 1.2 | 12 | 0.2 | 0.9 | 21 |  | 0.2 | 97 |

***Table A4.10*** *WDS-EPMA point analyses of copper metal and matte prills entrapped in slags from the site of Phournoi (weight %). Totals over 100% are mainly due to the simultaneous measurement of more than one phase in heterogeneous matte prills, while low totals were caused by the small size of some prills.*

Note: *Analysis FOU4C was done on the sulphidic rim surrounding the copper metal prill analysed in FOU4D.*

| | S | Fe | Ni | Cu | As | Bi | Total |
|---|---|---|---|---|---|---|---|
| **FOU3A** | 20 | 2.3 | 0.0 | 75 | 0.0 | 0.1 | 98 |
| **FOU3B** | 21 | 3.1 | 0.0 | 74 | 0.0 | 0.0 | 98 |
| **FOU3C** | 19 | 3.9 | 0.0 | 77 | 0.0 | 0.0 | 100 |
| **FOU3D** | 20 | 1.6 | 0.0 | 77 | 0.0 | 0.0 | 99 |
| **FOU3E** | 20 | 0.6 | 0.0 | 78 | 0.0 | 0.1 | 99 |
| **FOU4A** | 0.1 | 0.1 | 0.2 | 100 | 0.1 | 0.1 | 100 |
| **FOU4B** | 0.0 | 4.0 | 0.0 | 97 | 0.0 | 0.0 | 101 |
| **FOU4C** | 19 | 0.7 | 0.0 | 79 | 0.0 | 0.0 | 98 |
| **FOU4D** | 0.0 | 0.4 | 0.3 | 99 | 0.6 | 0.0 | 100 |
| **FOU4E** | 0.0 | 3.1 | 0.0 | 98 | 0.0 | 0.0 | 101 |
| **FOU4F** | 0.3 | 2.3 | 0.1 | 98 | 0.1 | 0.0 | 101 |
| **FOU7A** | 25 | 14 | 0.0 | 59 | 0.1 | 0.7 | 98 |
| **FOU7B** | 27 | 17 | 0.0 | 51 | 0.0 | 0.0 | 96 |
| **FOU7C** | 21 | 2.1 | 0.0 | 74 | 0.0 | 0.0 | 97 |
| **FOU7D** | 27 | 16 | 0.0 | 54 | 0.0 | 0.0 | 96 |
| **FOU7E** | 23 | 11 | 0.0 | 63 | 0.0 | 0.1 | 98 |
| **FOU7F** | 27 | 16 | 0.0 | 52 | 0.0 | 0.7 | 96 |
| **FOU8A** | 21 | 1.6 | 0.0 | 76 | 0.0 | 0.0 | 98 |
| **FOU8B** | 22 | 5.5 | 0.0 | 70 | 0.0 | 0.0 | 97 |
| **FOU8C** | 21 | 3.4 | 0.0 | 73 | 0.0 | 0.1 | 97 |
| **FOU8D** | 21 | 2.1 | 0.0 | 75 | 0.0 | 0.0 | 97 |
| **FOU8E** | 21 | 0.7 | 0.0 | 76 | 0.3 | 0.0 | 98 |
| **FOU8F** | 21 | 6.4 | 0.0 | 72 | 0.2 | 0.0 | 99 |
| **FOU8G** | 21 | 3.0 | 0.0 | 74 | 0.0 | 0.0 | 98 |
| **FOU9A** | 26 | 1.9 | 0.0 | 72 | 0.0 | 0.0 | 100 |
| **FOU13A** | 19 | 1.7 | 0.0 | 77 | 0.0 | 0.0 | 98 |
| **FOU13B** | 21 | 2.5 | 0.0 | 74 | 0.0 | 0.0 | 98 |
| **FOU13C** | 20 | 0.8 | 0.0 | 77 | 0.0 | 0.1 | 98 |
| **FOU13D** | 19 | 2.4 | 0.0 | 77 | 0.1 | 0.1 | 98 |
| **FOU13E** | 25 | 1.9 | 0.0 | 70 | 0.1 | 0.0 | 98 |
| **FOU13F** | 21 | 1.9 | 0.0 | 75 | 0.1 | 0.0 | 98 |
| **FOU14A** | 0.0 | 0.8 | 0.0 | 99 | 0.0 | 0.0 | 100 |
| **FOU14B** | 0.0 | 2.3 | 0.0 | 97 | 0.3 | 0.0 | 100 |
| **FOU14C** | 0.0 | 1.6 | 0.0 | 94 | 0.6 | 0.0 | 96 |
| **FOU14D** | 19 | 2.3 | 0.0 | 77 | 0.0 | 0.0 | 98 |
| **FOU14E** | 19 | 3.3 | 0.0 | 76 | 0.0 | 0.0 | 98 |

|  | S | Fe | Ni | Cu | As | Bi | Total |
|---|---|---|---|---|---|---|---|
| **FOU14F** | 0.0 | 1.0 | 0.1 | 99 | 0.4 | 0.4 | 101 |
| **FOU14G** | 0.1 | 1.5 | 0.0 | 99 | 0.7 | 0.0 | 101 |
| **FOU14H** | 19 | 1.5 | 0.0 | 78 | 0.0 | 0.0 | 98 |
| **FOU15A** | 23 | 3.3 | 0.1 | 75 | 0.0 | 0.0 | 101 |
| **FOU15B** | 0.0 | 4.0 | 0.0 | 97 | 0.0 | 0.0 | 101 |
| **FOU15C** | 0.0 | 3.7 | 0.0 | 97 | 0.0 | 0.0 | 101 |
| **FOU16A** | 22 | 3.9 | 0.0 | 76 | 0.0 | 0.0 | 102 |
| **FOU16B** | 23 | 1.9 | 0.0 | 79 | 0.0 | 0.0 | 103 |
| **FOU16C** | 23 | 1.6 | 0.0 | 79 | 0.0 | 0.0 | 103 |
| **FOU17A** | 30 | 5.6 | 0.0 | 63 | 0.0 | 0.0 | 99 |
| **FOU18A** | 25 | 3.0 | 0.0 | 74 | 0.0 | 0.0 | 102 |
| **FOU18B** | 25 | 6.0 | 0.0 | 70 | 0.0 | 0.0 | 101 |
| **FOU21A** | 27 | 8.2 | 0.0 | 63 | 0.0 | 0.0 | 98 |
| **FOU22A** | 20 | 0.5 | 0.0 | 78 | 0.0 | 0.0 | 98 |
| **FOU22B** | 20 | 1.4 | 0.0 | 77 | 0.8 | 0.0 | 99 |
| **FOU22C** | 20 | 1.3 | 0.0 | 77 | 0.0 | 0.0 | 99 |
| **FOU22D** | 20 | 3.0 | 0.0 | 75 | 0.9 | 0.0 | 99 |
| **FOU22E** | 19 | 1.4 | 0.0 | 77 | 0.0 | 0.2 | 97 |
| **FOU22F** | 19 | 0.4 | 0.0 | 78 | 0.0 | 0.0 | 98 |
| **FOU22G** | 19 | 2.2 | 0.0 | 76 | 0.1 | 0.0 | 98 |
| **FOU24A** | 26 | 18 | 0.0 | 52 | 0.0 | 0.1 | 96 |
| **FOU24B** | 33 | 42 | 0.1 | 21 | 0.0 | 0.1 | 96 |
| **FOU24C** | 27 | 18 | 0.0 | 51 | 0.0 | 0.1 | 96 |
| **FOU24D** | 27 | 17 | 0.0 | 52 | 0.0 | 0.1 | 96 |
| **FOU25A** | 31 | 4.4 | 0.0 | 62 | 0.1 | 0.0 | 98 |
| **FOU25B** | 25 | 3.6 | 0.0 | 70 | 0.0 | 0.0 | 99 |
| **FOU25C** | 26 | 6.2 | 0.2 | 65 | 0.5 | 0.0 | 98 |
| **FOU25D** | 25 | 3.6 | 0.0 | 69 | 0.0 | 0.0 | 98 |
| **FOU26A** | 0.0 | 5.6 | 0.0 | 96 | 0.0 | 0.1 | 101 |
| **FOU26B** | 0.0 | 3.9 | 0.0 | 97 | 0.0 | 0.0 | 101 |
| **FOU28A** | 20 | 3.6 | 0.0 | 75 | 0.0 | 0.0 | 99 |
| **FOU28B** | 19 | 2.7 | 0.0 | 78 | 0.0 | 0.0 | 100 |
| **FOU28C** | 19 | 3.0 | 0.0 | 77 | 0.0 | 0.0 | 99 |
| **FOU28D** | 23 | 7.2 | 0.1 | 67 | 0.1 | 0.1 | 97 |
| **FOU28E** | 21 | 6.3 | 0.0 | 69 | 0.0 | 0.0 | 97 |
| **FOU28F** | 20 | 4.7 | 0.0 | 73 | 0.0 | 0.0 | 98 |
| **FOU28G** | 21 | 2.6 | 0.0 | 75 | 0.1 | 0.0 | 99 |
| **FOU28H** | 23 | 3.3 | 0.0 | 72 | 0.0 | 0.1 | 98 |
| **FOU38A** | 23 | 17 | 0.0 | 52 | 0.0 | 0.0 | 93 |
| **FOU38B** | 23 | 16 | 0.0 | 58 | 0.0 | 0.0 | 96 |
| **FOU38C** | 28 | 33 | 0.1 | 31 | 0.0 | 0.0 | 92 |
| **FOU38D** | 25 | 21 | 0.0 | 48 | 0.0 | 0.0 | 93 |
| **FOU38E** | 24 | 19 | 0.0 | 50 | 0.0 | 0.0 | 93 |
| **FOU39A** | 19 | 3.6 | 0.0 | 76 | 0.0 | 0.0 | 99 |
| **FOU39B** | 19 | 2.9 | 0.0 | 77 | 0.3 | 0.0 | 99 |
| **FOU39C** | 0.1 | 4.3 | 0.0 | 95 | 0.6 | 0.0 | 100 |

|  | S | Fe | Ni | Cu | As | Bi | Total |
|---|---|---|---|---|---|---|---|
| **FOU39D** | 0.1 | 3.4 | 0.0 | 95 | 0.0 | 0.0 | 99 |
| **FOU39E** | 18 | 3.0 | 0.0 | 77 | 0.0 | 0.0 | 98 |
| **FOU39F** | 18 | 3.4 | 0.0 | 77 | 0.2 | 0.1 | 98 |

# Appendix 5.

## Tables of results of the analyses of the metallurgical remains from Daskaleio-Kavos

*Table A5.1 Catalogue of metallurgical remains collected from Daskaleio-Kavos during the 1987 fieldwork project (U: unit, T: trench, C. No: catalogue number, D: dimensions, W: weight, S: slag, C-metallurgical ceramic, C/S-metallurgical ceramic with slag, ML- lead metal fragments, O: Fe minerals, MC: copper metal fragment or prill, n.a.: not analysed). Samples analysed in this thesis are given a number in the 'Sample' column. Weight measurements accompanied by c. or < are estimates.*

KAVOS

| Sample | U | T | C. No | Material | D (cm) | W (g) | Description |
|---|---|---|---|---|---|---|---|
| **n.a.** | 201 | | 123 | MC | 1.6x0.3x0.2 | 0.4 | long thin copper metal fragment, covered in green corrosion, in parts yellow-brown staining |
| **n.a.** | 202 | | | O | 2.5x2.3x1.4 | 7.9 | hematite/ limonite, partly covered by epigenetic calcareous layer |
| **n.a.** | 202 | | | O | 2.8x2.1x1.4 | 8.0 | hematite/ limonite, partly covered by epigenetic calcareous layer |
| **n.a.** | 203 | | | O | 3.9x2.4x1.2 | 15 | hematite crystalline, covered in yellow/orange staining, some quartz crystals attached |
| **n.a.** | 302 | | 737 | O | 3.0x2.9x1.5 | 9.0 | hematite, covered in yellow-orange staining, dense, relatively heavy |
| **n.a.** | 302 | | | O | 2.9x1.5x0.5 | c. 5 | hematite on limestone? |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **n.a.** | 319 | | 37 | Pb disc | 2.0x1.9x0.6 | 10 | circular/ oval lead object, covered in brown/ grey corrosion with white corrosion on one side, heavy, leaves traces of brown-red powder, thickness increases in towards centre to a maximum of 0.6cm (0.2cm on edges) |
| **n.a.** | 325 | | 660 | MC | 0.9x0.9x0.2 | 0.8 | circular droplet of copper metal, covered in green corrosion |
| **n.a.** | 330 | | 512a | MC | 1.0x0.8x0.1 | <5 | covered in green corrosion, shapeless |
| **n.a.** | 330 | | 512b | MC | 1.0x0.8x0.3 | 0.5 | covered in green corrosion, shapeless |
| **n.a.** | 330 | | 512b | MC | 0.2x0.2x0.1 | 0.04 | covered in green corrosion, shapeless |
| **n.a.** | 330 | | 512b | MC | 0.7x0.4x0.2 | 0.1 | covered in green corrosion, shapeless |
| **n.a.** | 330 | | 512b | MC | 0.5x0.4x0.2 | 0.1 | covered in green corrosion, shapeless |
| **KK14** | 333 | | 487 | MC | 1.5x1.1x0.9 | 4.1 | covered mainly in green corrosion, showing external small lumps |
| **n.a.** | 333 | | 487 | MC | 0.9x0.4x0.2 | 0.3 | thin fragment of copper metal covered mainly in green corrosion |
| **KK13** | 342 | | 481 | C/S | 1.9x1.5x1.0 | 1.9 | red/ orange clay with attached slag, slag bears tiny green prills |
| **n.a.** | 402 | | | O | 1.5x1.5x0.5 | c. 5 | hematite |
| **n.a.** | 403 | | | O | 4.1x3.1x1.7 | 25 | iron mineral in rock with quartz and mica crystals, some pores |
| **n.a.** | 404 | | | ML | 2.0x1.5x1.2 | c. 5 | lead metal fragment of nearly rectangular shape, covered externally by brown-red and white corrosion products |
| **n.a.** | 406 | | | O | 1.5x1.5x1.0 | c. 5 | hematite |
| **KK19** | 406 | | | litharge | 4.0x3.5x2.5 | 89 | dark red colour with patches of white, leaves behind a dark red powder, very heavy |
| **n.a.** | 408 | | 690 | O | 3.5x2.2x0.8 | 8.4 | hematite/ limonite, largely covered in yellow staining |
| **n.a.** | 408 | | 690 | O | 2.9x1.9x1.1 | 5.4 | hematite/ limonite, partly crystalline, heavy yellow staining |
| **KK20** | 409 | | | O | 5.3x4.3x2.8 | 49 | hematite, crystalline, covered in yellow-orange staining |
| **n.a.** | 409 | | | stone | 2.8x2.7x2.5 | 28 | limestone with traces of iron oxide staining |
| **KK1** | 434 | | | S | 2.0x2.0x1.2 | 12 | black, upper surface shows flow texture, partly retains original shiny surface, dense, magnetic |
| **n.a.** | 436 | | | MC | 0.4x0.3x0.1 | <5 | small shapeless fragment covered in green corrosion |
| **n.a.** | 437 | | 412 | MC | 0.9x0.8x0.4 | 0.3 | small shapeless fragment covered in green corrosion |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| **n.a.** | 437 |  | 412 | MC | 0.7x0.5x0.4 | 0.6 | small shapeless fragment covered in green corrosion |
| **n.a.** | 437 |  | 412 | MC | 0.5x0.4x0.3 | 0.2 | small shapeless fragment covered in green corrosion |
| **KK4** | 437 |  | 484 | C/S | 1.5x1.3x0.7 | 1.2 | one side orange-red ceramic and other side black slag, width of slag layer 2mm, relatively porous |
| **n.a.** | 439 |  |  | pebble | 1.0x0.2x0.1 | <5 | tiny, black with dark brown stains, moderately porous |
| **n.a.** | 443 |  |  | O | 1.4x0.9x0.8 | <5 | grey/ black with orange staining, relatively light |
| **n.a.** | 446 |  |  | stone? | 3.0x2.4x1.2 | c. 5 | looks like small black crystals cemented together in grey matrx, black crystals may be biotite? |
| **n.a.** | 501 |  |  | O | 3.0x2.5x1.5 | 20 | hematite, with quartz crystals and yellow staining |
| **n.a.** | 501 |  |  | O | 2.2x1.9x0.8 | c. 5 | hematite, with quartz crystals and yellow staining |
| **n.a.** | 501 |  |  | O | 1.5x1.3x0.8 | <5 | hematite |
| **n.a.** | 502 |  |  | O | 4.7x2.8x1.2 | 21 | hematite/ lemonite with a little quartz, partly crystalline |
| **n.a.** | 602 |  | 124 | Cu object | 9.0x0.2x0.2 | c. 5 | graver? well preserved, covered in green corrosion |
| **n.a.** | 631 |  |  | O | 2.5x1.6x1.3 | 6.1 | hematite, partly crystalline, external yellow limonitic staining |
| **KK9** | 631 |  |  | S on sherd | 2.7x2.3x1.2 | 7.6 | slag splashed over a medium mica quartz sherd, black slag with green staining and 3 green prills on surface |
| **n.a.** | 641 |  |  | O | 3.1x2.0x1.8 | 15 | hematite with some quartz grains |
| **n.a.** | 641 |  |  | pebble | 2.3x1.1x0.7 | c. 5 | black stone |
| **n.a.** | 641 |  |  | pebble | 2.2x1.8x1.4 | c. 5 | black stone |
| **n.a.** | 647 |  |  | O | 1.8x1.6x1.0 | 3.6 | hematite, grey black colour |
| **n.a.** | 647 |  |  | O | 2.4x1.8x1.1 | 4.6 | hematite, grey black colour, quartz fragments attached |
| **n.a.** | 650 |  | 490 | O | 1.9x1.5x0.7 | <5 | limonite/ hematite, covered in yellow/ orange staining, relatively light |
| **n.a.** | 664 |  |  | O | 4.1x3.0x2.2 | 10 | hematite, partly crystalline and partly covered externally with white calcareous layer |
| **KK12** | 669 |  | 602 | S | 2.7x2.1x1.6 | 15 | black slag with intense green copper and orange iron oxide staining |
| **n.a.** | 671 |  | 482 | MC | 1.5x1.0x0.7 | 1.3 | covered almost completely in green staining, slightly magnetic, black |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | colour in section with green staining in and around pores |
| **KK10** | 671 |  | 483 | S | 1.8x1.2x1.0 | 3.0 | black, weathered outer surface, moderately porous |
| **KK11** | 671 |  | 483 | S | 3.8x3.1x2.7 | 31 | black, weathered outer surface, moderately porous |
| **n.a.** | 671 |  | 584 | MC | 0.8x0.7x0.6 | 1.1 | rounded copper droplet covered in green corrosion |
| **KK5** | 671 |  | 586 | C | 2.5x2.2x0.7 | 3.5 | red colour, only on part of one side shows grey/ black colour but does not show intense vitrification, burnt out straw marks, quartz and other refractory inclusions (usually <1mm), partly covered by calcareous layer |
| **KK6** | 671 |  |  | C/S | 2.7x2.4x0.8 | 5.6 | red colour on outer side and grey/black moderately vitrified on the other side, burnt out straw marks, quartz and other refractory inclusions (usually <1mm) seen on outer surface, partly covered by calcareous layer, slag attached on inner surface is black in colour with limited green staining |
| **n.a.** | 671 |  | 583 | Cu object | 1.3x0.2x0.2 | <5 | four sided, possibly a nail/ rivet, good preservation, surface covered in green corrosion |
| **n.a.** | 671 |  |  | O | 1.6x1.2x0.9 | <5 | gossan |
| **n.a.** | 671 |  |  | O | 1.8x1.6x0.7 | c. 5 | gossan |
| **n.a.** | 672 |  |  | C | 3.6x2.0x2.0 | 7.2 | orange-red colour, grey-black only on one corner, burnt out straw marks and refractory inclusions seen (usually <1mm but some 2-3mm in length) |
| **KK18** | 677 |  |  | O | 2.2x1.6x1.4 | 4.2 | hematite/ goethite |
| **n.a.** | 711 |  |  | O | 1.7x1.2x0.7 | <5 | hematite/ limonite |
| **n.a.** | 711 |  |  | O | 2.9x2.4x1.1 | 10 | hematite partly crystalline and limonite |
| **KK15** | 729 |  | 594 | ML | 3.1x2.8x0.7 | 25 | amorphous lump of lead metal, partly corroded outer surface white on one side and brown-red on other |
| **KK8** | 729 |  |  | S on sherd | 3.0x2.1x0.6 | 5.1 | slag splashed over a red schist fabric coarseware shed with red/brown slip on one surface, some vitrification on sherd, black slag |
| **KK3** | 732 |  |  | S | 1.5x1.0x0.6 | 2.1 | black with yellow staining, 10 green prills on surface, very magnetic, |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | porous in section, green staining observed in and around pores in section |
| **n.a.** | 802 | VIII.2 | 255 | Pb object | 3.2x1.1x0.2 | c. 5 | lead strip, partly white corroded surface |
| **n.a.** | 808 | VIII.8 |  | O | 1.5x1.2x0.7 | <5 | hematite covered in yellow limonite staining |

KAVOS NORTH

| Sample | U | C. No | Material | D (cm) | W (g) | Description |
|---|---|---|---|---|---|---|
| **KKN1** | 906 | 605 | S | 2.6x2.5x1.2 | 14 | black, can distinguish upper and lower surfaces, upper surface shows in part flow texture, moderately porous, magnetic |
| **KKN2** | 906 | 606 | S | 1.5x1.0x0.7 | 2.4 | black, weathered outer surface, Fe oxide staining and three green prills observed on the surface, moderately porous, magnetic, upon sectioning observed increased porosity and green staining particularly in and around pores |
| **KKN3** | 908 | 607 | S | 1.8x1.0x0.8 | 2.3 | black with limited green staining and tiny green prills on surface, weathered outer surface in parts retaing original shine, moderately porous, very magnetic, upon sectioning observed limited green staining around pores |
| **n.a.** | 910 |  | C/S | 1.0x0.8x0.2 | <1 | metallurgical ceramic with possible marks of burnt-out organic material but no vitrification,in parts traces of green staining observed |
| **KKN4** | 912 | 517 | S | 3.0x2.4x1.4 | 18 | black, partly retains shiny surface, very little porosity, only slightly magnetic, observed increased porosity in section (pores usually <1mm) |
| **KKN5** | 914 | 608 | S | 1.5x1.0x1.0 | 2.0 | black, partly retains outer shiny surface, very little porosity, not magnetic |
| **KKN6** | 916 | 603 | MC | 1.0x1.4x0.5 | 3.0 | surface covered in green staining and limited Fe oxide staining, dense |
| **n.a.** | 916 | 604 | S | 0.7x0.5x0.2 | <5 | 90% of surface covered in green staining |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| **KKN7** | 917 | 592 | S | 1.0x1.2x1.0 | 2.7 | black, more than five small green prills on surface, porous, magnetic, upon cutting observed many Cu prills (usually <1mm but few larger), porosity and limited green corrosion in and around pores |
| **KKN8** | 919 | 519 | S | 3.7x2.0x1.2 | 14 | black, weathered outer surface, can distinguish upper and lower surfaces, moderately porous, not magnetic |
| **KKN12** | 919 | 518A | MC | 1.1x0.7x0.3 | 0.6 | covered in green corrosion |
| **n.a.** | 919 | 518A | MC | 0.7x0.6x0.4 | 0.4 | covered in green corrosion |
| **n.a.** | 919 | 518A | MC | 0.6x0.6x0.5 | 0.4 | covered in green corrosion |
| **n.a.** | 919 | 518A | MC | 0.3x0.2x0.1 | <0.1 | covered in green corrosion |
| **n.a.** | 919 | 518B | S | 0.5x0.3x0.1 | <5 | black slag with several green prills protruding on outer surface |
| **n.a.** | 921 | 609 | S | 2.2x1.5x1.2 | c. 5 | black, weathered outer surface, moderately porous |
| **n.a.** | 921 | 609 | S | 2.4x1.7x1.0 | c. 5 | black, weathered outer surface, moderately porous |
| **n.a.** | 921 | 609 | S | 2.0x1.6x1.4 | c. 5 | black, weathered outer surface, moderately porous |
| **KKN9** | 921 | 609 | S | 5.0x3.0x2.5 | 58 | black, weathered outer surface, moderately porous, non magnetic |
| **KKN10** | 921 | 609 | S | 3.5x2.5x2.5 | 35 | black, weathered outer surface, moderately porous, non magnetic |
| **KKN13** | 921 | 610 | ML | 2.0x1.2x0.7 | 8.7 | piece of lead covered in parts with white and brown corrosion |
| **KKN11** | 922 | 503 | C/S | 1.5x1.0x0.5 | 2.4 | black vitrified ceramic with slag, ceramic part could not be distinguished prior to analysis, four green prills on outer slag surface and green staining in and around porosity in section, quartz and one large schist inclusion (7mm length) in ceramic, ceramic part 1.5mm width |
| **n.a.** | 922 | 504 | C | 1.5x1.0x1.0 | <5 | orange-red ceramic and black vitrified layer, small quartz inclusions |
| **n.a.** | 922 | 504 | O | 1.9x1.1x0.5 | <5 | gossan |

## EXCAVATION

| Sample | U | T | C. No | Material | D (cm) | W (g) | Description |
|---|---|---|---|---|---|---|---|
| **n.a.** | 1002 | X | 374 | MC | 0.8x0.4x0.2 | <1 | covered in green corrosion, shapeless |
| **n.a.** | 1003 | X | 376 | MC | 0.3x0.3x0.1 | <1 | covered in green corrosion, shapeless |
| **KK16** | 1006 | x.6 | 670 | O | 2.9x1.9x1.4 | 9.2 | hematite/ goethite |
| **KK17** | 1006 | x.6 | 672 | MC | 1.7x0.8x0.2 | 0.6 | thin corroded copper metal |
| **n.a.** | 1101 | XI.1 | 671 | O | 2.8x2.1x1.4 | 7.4 | covered in yellow and red ochre |
| **n.a.** | 1306 | XIII.3 | 392 | Pb object | 3.2x2.7x0.7 | 35 | oval/ circular lead disk, white corroded surface, heavy, on one side shallow depression |
| **n.a.** | 1404 | XIV.4 | 530 | Pb object | 1.5x1.8x0.1 | <5 | lead sheet |

***Table A5.2a*** *Results of (P)ED-XRF analyses of Group 1 slag samples (major and minor elements in weight %). Analyses in bold are averages of three runs (a, b, c).*

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KKN1a | 0.61 | 4.09 | 1.97 | 35.1 | 0.00 | 0.35 | 12.7 | 0.05 | 0.19 | 41.4 | 0.68 | 97.1 |
| KKN1b | 0.14 | 3.77 | 1.87 | 34.9 | 0.00 | 0.34 | 12.7 | 0.05 | 0.19 | 41.2 | 0.69 | 95.8 |
| KKN1c | 0.58 | 4.02 | 1.89 | 34.8 | 0.00 | 0.34 | 12.6 | 0.05 | 0.19 | 41.0 | 0.67 | 96.1 |
| **KKN1** | **0.44** | **3.96** | **1.91** | **34.9** | **0.00** | **0.34** | **12.6** | **0.05** | **0.19** | **41.2** | **0.68** | **96.3** |
| KKN4a | 0.34 | 3.69 | 1.73 | 34.1 | 0.15 | 0.34 | 9.88 | 0.06 | 0.19 | 41.2 | 0.41 | 92.1 |
| KKN4b | 0.56 | 3.69 | 1.84 | 34.5 | 0.14 | 0.34 | 9.93 | 0.06 | 0.19 | 41.5 | 0.41 | 93.2 |
| KKN4c | 0.51 | 3.64 | 1.76 | 34.2 | 0.14 | 0.34 | 9.86 | 0.06 | 0.19 | 41.2 | 0.41 | 92.3 |
| **KKN4** | **0.47** | **3.67** | **1.78** | **34.3** | **0.14** | **0.34** | **9.89** | **0.06** | **0.19** | **41.3** | **0.41** | **92.6** |
| KKN8a | 0.51 | 4.67 | 1.29 | 36.5 | 0.00 | 0.15 | 10.3 | 0.01 | 0.21 | 35.4 | 0.31 | 89.3 |
| KKN8b | 0.58 | 4.68 | 1.26 | 36.3 | 0.00 | 0.15 | 10.3 | 0.01 | 0.21 | 35.6 | 0.32 | 89.5 |
| KKN8c | 0.79 | 4.48 | 1.27 | 36.3 | 0.00 | 0.14 | 10.3 | 0.01 | 0.21 | 35.3 | 0.32 | 89.1 |
| **KKN8** | **0.63** | **4.61** | **1.27** | **36.4** | **0.00** | **0.15** | **10.3** | **0.01** | **0.21** | **35.4** | **0.32** | **89.3** |
| KKN9a | 1.11 | 5.03 | 2.82 | 41.0 | 1.02 | 0.82 | 9.00 | 0.03 | 0.22 | 35.2 | 0.19 | 96.4 |
| KKN9b | 1.07 | 4.87 | 2.76 | 40.7 | 1.02 | 0.81 | 8.91 | 0.03 | 0.21 | 35.0 | 0.19 | 95.5 |
| KKN9c | 0.94 | 4.91 | 2.74 | 40.7 | 1.03 | 0.82 | 8.93 | 0.03 | 0.21 | 35.0 | 0.19 | 95.6 |
| **KKN9** | **1.04** | **4.94** | **2.77** | **40.8** | **1.02** | **0.82** | **8.94** | **0.03** | **0.21** | **35.1** | **0.19** | **95.8** |
| KKN10a | 0.55 | 3.75 | 2.13 | 36.2 | 0.30 | 0.26 | 9.84 | 0.03 | 0.18 | 42.2 | 0.47 | 95.9 |
| KKN10b | 0.66 | 3.74 | 2.04 | 35.7 | 0.29 | 0.25 | 9.70 | 0.03 | 0.18 | 41.7 | 0.46 | 94.8 |
| KKN10c | 0.53 | 3.68 | 2.11 | 35.8 | 0.29 | 0.26 | 9.89 | 0.03 | 0.18 | 42.1 | 0.47 | 95.4 |
| **KKN10** | **0.58** | **3.72** | **2.09** | **35.9** | **0.29** | **0.26** | **9.81** | **0.03** | **0.18** | **42.0** | **0.46** | **95.3** |
| KK1a | 0.76 | 3.39 | 2.24 | 30.5 | 0.11 | 0.47 | 16.3 | 0.08 | 0.22 | 38.2 | 0.64 | 92.9 |
| KK1b | 0.49 | 3.35 | 2.25 | 30.3 | 0.12 | 0.47 | 16.1 | 0.07 | 0.22 | 37.8 | 0.64 | 91.9 |

|  | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KK1c | 0.64 | 3.31 | 2.25 | 30.4 | 0.11 | 0.46 | 16.2 | 0.07 | 0.22 | 37.8 | 0.64 | 92.1 |
| **KK1** | **0.63** | **3.35** | **2.25** | **30.4** | **0.11** | **0.46** | **16.2** | **0.07** | **0.22** | **37.9** | **0.64** | **92.3** |

***Table A5.2b** Results of (P)ED-XRF analyses of Group 1 slag samples (trace elements in ppm). Analyses in bold are the averages of the three runs (a, b, c, ).*

|  | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ba | La | Ce | Nd | $WO_3$ | PbO | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KKN1a | 34 | 138 | 39 | 0 | 71 | 18 | 36 | 74 | 14 | 36 | 0 | 6 | 55 | 2 |
| KKN1b | 40 | 128 | 44 | 0 | 70 | 15 | 39 | 83 | 19 | 51 | 0 | 7 | 73 | 5 |
| KKN1c | 46 | 128 | 77 | 0 | 69 | 15 | 38 | 78 | 9 | 43 | 0 | 8 | 64 | 3 |
| **KKN1** | **40** | **131** | **53** | **0** | **70** | **16** | **38** | **78** | **14** | **43** | **0** | **7** | **64** | **3** |
| KKN4a | 9 | 170 | 48 | 0 | 51 | 16 | 40 | 35 | 4 | 31 | 13 | 9 | 0 | 5 |
| KKN4b | 5 | 171 | 52 | 0 | 51 | 18 | 41 | 27 | 9 | 33 | 7 | 8 | 0 | 2 |
| KKN4c | 0 | 178 | 51 | 0 | 51 | 18 | 32 | 31 | 20 | 42 | 40 | 10 | 0 | 5 |
| **KKN4** | **5** | **173** | **50** | **0** | **51** | **17** | **38** | **31** | **11** | **35** | **20** | **9** | **0** | **4** |
| KKN8a | 10 | 134 | 26 | 0 | 47 | 20 | 24 | 0 | 29 | 36 | 19 | 6 | 0 | 0 |
| KKN8b | 15 | 127 | 22 | 0 | 48 | 19 | 16 | 0 | 9 | 44 | 30 | 7 | 0 | 0 |
| KKN8c | 0 | 132 | 24 | 0 | 47 | 19 | 26 | 0 | 22 | 44 | 0 | 8 | 0 | 0 |
| **KKN8** | **8** | **131** | **24** | **0** | **47** | **19** | **22** | **0** | **20** | **42** | **16** | **7** | **0** | **0** |
| KKN9a | 0 | 147 | 42 | 14 | 93 | 26 | 29 | 58 | 0 | 32 | 0 | 11 | 0 | 4 |

|  | NiO | ZnO | $As_2O_3$ | $Rb_2O$ | SrO | Y | $ZrO_2$ | Ba | La | Ce | Nd | $WO_3$ | PbO | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KKN9b | 0 | 147 | 41 | 11 | 92 | 26 | 24 | 67 | 26 | 39 | 0 | 13 | 0 | 1 |
| KKN9c | 0 | 149 | 42 | 13 | 93 | 25 | 35 | 65 | 38 | 43 | 0 | 13 | 0 | 3 |
| **KKN9** | **0** | **147** | **42** | **13** | **93** | **25** | **29** | **63** | **21** | **38** | **0** | **12** | **0** | **3** |
| KKN10a | 0 | 155 | 45 | 0 | 50 | 20 | 42 | 65 | 0 | 36 | 0 | 12 | 0 | 3 |
| KKN10b | 0 | 159 | 44 | 0 | 49 | 19 | 27 | 74 | 0 | 0 | 0 | 12 | 0 | 2 |
| KKN10c | 0 | 153 | 44 | 0 | 46 | 17 | 26 | 69 | 0 | 38 | 0 | 11 | 0 | 4 |
| **KKN10** | **0** | **155** | **45** | **0** | **48** | **19** | **32** | **69** | **0** | **25** | **0** | **11** | **0** | **3** |
| KK1a | 35 | 147 | 27 | 0 | 136 | 15 | 42 | 123 | 23 | 69 | 0 | 8 | 0 | 3 |
| KK1b | 44 | 142 | 48 | 0 | 135 | 16 | 39 | 111 | 13 | 37 | 0 | 10 | 0 | 4 |
| KK1c | 30 | 143 | 30 | 0 | 137 | 18 | 34 | 120 | 17 | 34 | 0 | 9 | 0 | 3 |
| **KK1** | **36** | **144** | **35** | **0** | **136** | **17** | **38** | **118** | **18** | **47** | **0** | **9** | **0** | **3** |

***Table A5.3*** *Summary of the optical microscopy observations for the slags from Daskaleio-Kavos (IS: iron-silicates; M: magnetite; MA: magnetite aggregate, G: glass, W: wüstitite, D: delafossite, CM: copper metal prills). The column labelled 'prills' describes whether the entrapped prills are mainly copper metal or matte or a mixture of both.*

| Sample | IS | M | MA | W | D | G | Prills | Inclusions | Comments |
|---|---|---|---|---|---|---|---|---|---|
| **KKN1** | + | + | | | | + | Matte | | Several magnetite bands, fragmentary and in different directions |
| **KKN4** | + | + | | | | + | Matte | | Very small crystalline phases, many cracks |
| **KKN5** | + | + | | | | + | Matte | | Very small crystalline phases |
| **KKN8** | + | + | | | | + | Matte | | Many cracks |
| **KKN9** | + | + | | | | + | Matte | 1 quartz | Very few, small, and dispersed magnetite crystals, shows spinifex texture on one side |
| **KKN10** | + | + | | | | + | Matte | | Some large matte clearly showing different phases |
| **KK1** | + | + | | | | + | Matte | | Some large matte clearly showing different phases |
| **KK10** | + | + | | | | + | Matte | | Larger matte show different phases |
| **KK11** | + | + | | | | + | Matte | | One magnetite band |
| | | | | | | | | | |
| **KKN2** | + | + | + | + | | + | CM | quartz | Very heterogeneous section, concentration of wüstite crystals in one area, one large completely corroded copper prill at the edge |
| **KKN7** | | + | + | | | + | CM | quartz | Very rich in copper prills (some very large), one large completely corroded copper prill at the edge |
| **KK3** | | + | | | | + | CM | | Very heterogeneous section, porous, very rich in magnetite, copper salts deposited in pores, areas with concentrations of copper prills |
| **KK12** | + | + | + | | | + | Both | | Large magnetite aggregates with copper prills and matte |
| | | | | | | | | | |
| **KKN3** | | + | | | | + | CM | | Very rich in magnetite, copper salts fill pores |

***Table A5.4*** *Spot analyses on the EDS-SEM of individual phases in Group 1 slag samples (weight %). Results have been normalised to 100 %, measured totals are given in column labelled MT. See notes as for Table A4.4.*

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **MT** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN1a** | Fayalite | b.d.l. | 12 | b.d.l. | 31 | b.d.l. | 3.0 | b.d.l. | 0.3 | 53 |  | b.d.l. | 89 |
| **KKN1b** | Fayalite | b.d.l. | 8.3 | b.d.l. | 31 | b.d.l. | 3.8 | b.d.l. | 0.2 | 57 |  | b.d.l. | 89 |
| **KKN1c** | Magnetite | b.d.l. | 0.3 | 1.6 | 1.1 | b.d.l. | 0.5 | 0.5 | b.d.l. |  | 96 | b.d.l. | 92 |
| **KKN1d** | Magnetite | b.d.l. | 0.3 | 1.3 | 1.0 | b.d.l. | 0.4 | 0.4 | b.d.l. |  | 96 | b.d.l. | 91 |
| **KKN1e** | Glass | b.d.l. | 5.0 | 1.9 | 46 | b.d.l. | 23 | b.d.l. | b.d.l. | 24 |  | b.d.l. | 89 |
| **KKN1f** | Glass | b.d.l. | 4.1 | 2.0 | 46 | b.d.l. | 23 | b.d.l. | b.d.l. | 25 |  | b.d.l. | 87 |
| **KK1a** | Kirschteinite | b.d.l. | 5.7 | b.d.l. | 31 | b.d.l. | 22 | b.d.l. | 0.3 | 42 |  | b.d.l. | 88 |
| **KK1b** | Kirschteinite | b.d.l. | 4.8 | b.d.l. | 31 | b.d.l. | 22 | b.d.l. | 0.3 | 42 |  | b.d.l. | 87 |
| **KK1c** | Magnetite | b.d.l. | 1.0 | 2.1 | 0.4 | b.d.l. | 0.7 | 0.5 | b.d.l. |  | 95 | b.d.l. | 92 |
| **KK1d** | Magnetite | b.d.l. | 0.9 | 2.0 | 0.4 | b.d.l. | 0.5 | 0.5 | b.d.l. |  | 96 | b.d.l. | 91 |
| **KK1e** | Glass | b.d.l. | 2.1 | 4.9 | 41 | b.d.l. | 23 | 0.2 | b.d.l. | 29 |  | b.d.l. | 86 |
| **KK1f** | Glass | 1.5 | 1.3 | 6.4 | 42 | 0.8 | 21 | 0.2 | b.d.l. | 27 |  | b.d.l. | 86 |
| **KKN4a** | Fayalite | b.d.l. | 6.6 | b.d.l. | 31 | b.d.l. | 2.5 | b.d.l. | 0.3 | 59 |  | b.d.l. | 86 |
| **KKN4b** | Fayalite | b.d.l. | 9.0 | b.d.l. | 31 | b.d.l. | 2.1 | b.d.l. | 0.3 | 58 |  | b.d.l. | 88 |
| **KKN4c** | Magnetite | b.d.l. | b.d.l. | 1.2 | 1.6 | b.d.l. | 0.6 | 0.5 | b.d.l. |  | 96 | b.d.l. | 94 |
| **KKN4d** | Magnetite | b.d.l. | b.d.l. | 1.6 | 3.5 | b.d.l. | 1.0 | 0.7 | b.d.l. |  | 93 | b.d.l. | 92 |
| **KKN4e** | Glass | b.d.l. | 2.4 | 2.3 | 44 | b.d.l. | 21 | b.d.l. | b.d.l. | 30 |  | b.d.l. | 86 |
| **KKN4f** | Glass | b.d.l. | 1.8 | 2.5 | 43 | b.d.l. | 21 | b.d.l. | b.d.l. | 32 |  | b.d.l. | 88 |
| **KKN5a** | Fayalite | b.d.l. | 9.0 | b.d.l. | 31 | b.d.l. | 3.8 | b.d.l. | 0.3 | 56 |  | b.d.l. | 84 |
| **KKN5b** | Fayalite | b.d.l. | 4.7 | b.d.l. | 32 | b.d.l. | 7.0 | b.d.l. | 0.3 | 56 |  | b.d.l. | 89 |
| **KKN5c** | Fayalite | b.d.l. | 11 | b.d.l. | 31 | b.d.l. | 2.6 | b.d.l. | b.d.l. | 55 |  | b.d.l. | 89 |
| **KKN5d** | Glass | b.d.l. | 2.3 | 1.8 | 43 | b.d.l. | 21 | b.d.l. | b.d.l. | 32 |  | b.d.l. | 85 |

| **Sample** | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$K_2O$** | **CaO** | **$TiO_2$** | **MnO** | **FeO** | **$Fe_3O_4$** | **CuO** | **MT** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN5e** | Glass | b.d.l. | 2.1 | 2.2 | 43 | b.d.l. | 21 | 0.2 | b.d.l. | 32 |  | 0.3 | 85 |
| **KKN5f** | Glass | b.d.l. | 3.1 | 1.8 | 44 | b.d.l. | 22 | b.d.l. | b.d.l. | 29 |  | b.d.l. | 91 |
| **KKN9a** | Fayalite | b.d.l. | 13 | b.d.l. | 32 | b.d.l. | 0.9 | b.d.l. | b.d.l. | 54 |  | b.d.l. | 90 |
| **KKN9b** | Fayalite | b.d.l. | 11 | b.d.l. | 31 | b.d.l. | 1.4 | b.d.l. | b.d.l. | 56 |  | b.d.l. | 90 |
| **KKN9c** | Glass | b.d.l. | 2.7 | 2.9 | 49 | 0.8 | 17 | b.d.l. | b.d.l. | 27 |  | b.d.l. | 91 |
| **KKN9d** | Glass | b.d.l. | 6.9 | b.d.l. | 50 | b.d.l. | 14 | b.d.l. | 0.2 | 29 |  | b.d.l. | 88 |

***Table A5.5** EPMA spot analyses on matte prills in Group 1 slag samples (weight %). The prills were analysed for all the elements given in section 3.6.1.3 but elements consistently detected below 0.1% have not been included in this table. Low totals, where observed, are due to the small size of the prills. The exceptionally high Fe contents of analyses on sample KKN9 are probably due to partial measurement of surrounding slag matrix, as the prills in this sample were all very small.*

| | S | Fe | Cu | Total |
|---|---|---|---|---|
| **KKN1A** | 24 | 2.9 | 72 | 99 |
| **KKN1B** | 25 | 0.8 | 73 | 98 |
| **KKN1C** | 25 | 1.0 | 73 | 98 |
| **KKN1D** | 33 | 2.9 | 66 | 102 |
| **KKN4A** | 24 | 5.1 | 72 | 101 |
| **KKN4B** | 31 | 12 | 59 | 102 |
| **KKN5A** | 23 | 4.9 | 74 | 102 |
| **KKN5B** | 16 | 11 | 74 | 101 |
| **KKN5C** | 22 | 4.5 | 72 | 98 |
| **KKN5D** | 21 | 3.3 | 74 | 99 |
| **KKN5E** | 18 | 4.5 | 76 | 99 |
| **KKN8A** | 20 | 5.4 | 70 | 96 |
| **KKN8B** | 23 | 8.9 | 65 | 97 |
| **KKN8C** | 23 | 6.8 | 66 | 95 |
| **KKN9A** | 32 | 59 | 1.6 | 92 |
| **KKN9B** | 33 | 56 | 6.7 | 95 |
| **KKN9C** | 32 | 54 | 8.0 | 94 |
| **KKN10A** | 33 | 23 | 43 | 99 |
| **KKN10B** | 29 | 11 | 59 | 99 |
| **KKN10C** | 28 | 12 | 61 | 101 |
| **KKN10D** | 27 | 11 | 50 | 88 |
| **KKN10E** | 32 | 18 | 50 | 99 |
| **KK1A** | 27 | 7.2 | 65 | 98 |
| **KK1B** | 27 | 8.0 | 63 | 97 |
| **KK1C** | 25 | 3.3 | 70 | 99 |
| **KK1D** | 22 | 5.6 | 72 | 100 |
| **KK1E** | 22 | 2.2 | 75 | 99 |
| **KK1F** | 22 | 11 | 66 | 98 |
| **KK10A** | 35 | 18 | 45 | 98 |
| **KK11A** | 36 | 19 | 46 | 101 |
| **KK11B** | 27 | 15 | 54 | 97 |

***Table A5.6** Spot analyses on the EDS-SEM of individual phases in Group 2 slag samples (weight %). Results have been normalised to 100 %, measured totals are given in column labelled MT. See notes as for Table A4.4.*

| | | **Na2O** | **MgO** | **Al2O3** | **SiO2** | **K2O** | **CaO** | **TiO2** | **MnO** | **FeO** | **Fe3O4** | **NiO** | **CuO** | **As2O3** | **PbO** | **MT** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN2a** | Fayalite | b.d.l. | 9.0 | b.d.l. | 30 | b.d.l. | 2.7 | b.d.l. | 1.1 | 57 | | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 84 |
| **KKN2b** | Fayalite | b.d.l. | 6.6 | b.d.l. | 30 | b.d.l. | 1.5 | b.d.l. | 0.9 | 61 | | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 82 |
| **KKN2c** | Magnetite | b.d.l. | 2.4 | 2.8 | b.d.l. | b.d.l. | b.d.l. | 0.3 | 0.6 | | 94 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 87 |
| **KKN2d** | Magnetite | b.d.l. | 1.8 | 3.5 | 0.4 | b.d.l. | b.d.l. | 0.3 | 0.3 | | 92 | 1.2 | b.d.l. | b.d.l. | b.d.l. | 91 |
| **KKN2e** | Glass | 2.1 | 0.7 | 8.6 | 37 | 1.6 | 13 | 0.2 | 0.5 | 26 | | b.d.l. | b.d.l. | b.d.l. | 10 | 85 |
| **KKN2f** | Glass | 2.8 | 0.9 | 8.9 | 38 | 1.8 | 13 | b.d.l. | 0.5 | 23 | | b.d.l. | b.d.l. | b.d.l. | 11 | 89 |
| **KKN2g** | Glass | 2.9 | b.d.l. | 9.3 | 38 | 2.7 | 15 | b.d.l. | 0.4 | 28 | | b.d.l. | b.d.l. | b.d.l. | 3.3 | 89 |
| **KKN2h** | Glass | 2.8 | b.d.l. | 9.1 | 37 | 2.4 | 14 | b.d.l. | 0.4 | 31 | | b.d.l. | 0.3 | b.d.l. | 3.5 | 90 |
| **KKN7a** | Magnetite | b.d.l. | 0.6 | 2.8 | 0.3 | b.d.l. | b.d.l. | 0.2 | b.d.l. | | 94 | 1.2 | 0.5 | b.d.l. | b.d.l. | 94 |
| **KKN7b** | Magnetite | b.d.l. | 0.4 | 3.3 | 0.3 | b.d.l. | b.d.l. | 0.3 | b.d.l. | | 94 | 1.1 | 0.4 | b.d.l. | b.d.l. | 92 |
| **KKN7c** | Magnetite | b.d.l. | 0.7 | 2.8 | b.d.l. | b.d.l. | b.d.l. | 0.3 | b.d.l. | | 94 | 0.9 | 1.2 | b.d.l. | b.d.l. | 89 |
| **KKN7d** | Glass | 1.1 | 1.5 | 5.9 | 46 | 1.5 | 10 | b.d.l. | b.d.l. | 21 | | b.d.l. | 1.9 | b.d.l. | 11 | 80 |
| **KKN7e** | Glass | b.d.l. | 0.6 | 7.8 | 43 | 1.5 | 9.8 | 0.2 | b.d.l. | 16 | | b.d.l. | 4.5 | 3.7 | 12 | 84 |
| **KKN7f** | Glass | 1.5 | 1.6 | 5.2 | 45 | 1.5 | 9.9 | b.d.l. | b.d.l. | 29 | | b.d.l. | 0.8 | b.d.l. | 4.9 | 89 |
| **KKN7g** | Glass | 1.5 | 1.9 | 7.3 | 38 | 1.4 | 9.0 | 0.2 | b.d.l. | 33 | | b.d.l. | 0.3 | b.d.l. | 7.6 | 88 |
| **KKN7h** | Glass | b.d.l. | 2.6 | 7.9 | 43 | 1.6 | 13 | 0.3 | b.d.l. | 17 | | b.d.l. | 3.7 | b.d.l. | 11 | 83 |
| **KK3a** | Magnetite | b.d.l. | 1.8 | 1.2 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.7 | | 96 | b.d.l. | 0.4 | b.d.l. | b.d.l. | 94 |
| **KK3b** | Magnetite | b.d.l. | 1.4 | 1.0 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.6 | | 97 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 93 |
| **KK3c** | Glass | b.d.l. | | 7.7 | 72 | 0.5 | 2.8 | b.d.l. | b.d.l. | 4.2 | | b.d.l. | 3.0 | 3.6 | 5.9 | 74 |
| **KK3d** | Glass | 1.7 | b.d.l. | 6.3 | 65 | 1.2 | 2.2 | b.d.l. | 0.4 | 17 | | b.d.l. | 0.8 | 1.5 | 3.5 | 91 |
| **KK3e** | Glass | b.d.l. | 0.7 | 0.5 | 49 | b.d.l. | 1.9 | b.d.l. | 0.6 | 31 | | b.d.l. | 3.4 | 5.5 | 6.9 | 77 |
| **KK3f** | Glass | 5.2 | 1.0 | 9.7 | 45 | 1.7 | 6.3 | 0.3 | 0.3 | 15 | | b.d.l. | 1.0 | 0.4 | 14 | 79 |

|  |  | Na2O | MgO | Al2O3 | SiO2 | K2O | CaO | TiO2 | MnO | FeO | Fe3O4 | NiO | CuO | As2O3 | PbO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KK12a** | Fayalite | b.d.l. | 2.9 | b.d.l. | 28 | b.d.l. | 2.6 | b.d.l. | b.d.l. | 66 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 92 |
| **KK12b** | Fayalite | b.d.l. | 2.7 | b.d.l. | 28 | b.d.l. | 2.7 | b.d.l. | b.d.l. | 66 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 91 |
| **KK12c** | Magnetite | b.d.l. | b.d.l. | 4.2 | 0.5 | b.d.l. | b.d.l. | 0.4 | b.d.l. |  | 95 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KK12d** | Magnetite | b.d.l. | 0.3 | 5.0 | 0.4 | b.d.l. | b.d.l. | 0.3 | b.d.l. |  | 94 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 94 |
| **KK12e** | Glass | 1.0 | b.d.l. | 9.5 | 44 | 3.0 | 14 | b.d.l. | b.d.l. | 26 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 91 |
| **KK12f** | Glass | 0.9 | b.d.l. | 9.5 | 43 | 2.6 | 15 | b.d.l. | b.d.l. | 26 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 91 |
| **KK12g** | Glass | 1.7 | b.d.l. | 12 | 40 | 3.9 | 14 | b.d.l. | b.d.l. | 26 |  | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 90 |
| **KK12h** | Glass | 1.7 | b.d.l. | 11 | 38 | 3.0 | 14 | b.d.l. | b.d.l. | 28 |  | b.d.l. | 0.3 | b.d.l. | b.d.l. | 88 |

*Table A5.7 EPMA spot analysis of copper prills, matte (KK12B and F), and lead prills or lead-rich phases (highlighted) in Group 2 slag samples (weight %). Lead inclusions are very small and corresponding analyses usually include surrounding copper matrix. 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.*

*<u>Note</u>: 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.*

| | **S** | **Cl** | **Fe** | **Ni** | **Cu** | **As** | **Sn** | **Sb** | **Pb** | **Bi** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN2A** | 0.0 | 0.0 | 3.1 | 3.7 | 88 | 0.1 | 0.0 | 1.8 | 0.1 | n.a. | 97 |
| **KKN2B** | 0.0 | 0.0 | 1.0 | 2.0 | 90 | 0.5 | 0.0 | 2.2 | 0.1 | n.a. | 96 |
| **KKN2C** | 0.0 | 0.1 | 3.3 | 0.1 | 1.2 | 0.0 | 0.0 | 0.0 | 88 | n.a. | 92 |
| **KKN2D** | 0.0 | 0.0 | 0.0 | 0.9 | 90 | 2.3 | 0.0 | 0.4 | 2.6 | n.a. | 96 |
| **KKN2E** | 0.0 | 0.0 | 1.7 | 4.4 | 88 | 0.4 | 0.0 | 1.5 | 0.6 | n.a. | 96 |
| **KKN2F** | 0.0 | 0.2 | 1.4 | 0.1 | 1.1 | 0.0 | 0.0 | 0.0 | 89 | n.a. | 92 |
| **KKN2G** | 0.0 | 0.0 | 2.0 | 3.7 | 89 | 1.5 | 0.0 | 0.5 | 0.1 | n.a. | 97 |
| **KKN2H** | 0.0 | 0.0 | 0.4 | 2.3 | 96 | 0.0 | 0.0 | 0.3 | 0.6 | n.a. | 100 |
| **KKN2I** | 0.0 | 0.0 | 0.0 | 0.8 | 92 | 1.8 | 0.0 | 0.4 | 1.2 | 0.1 | 96 |
| **KKN7A** | 0.1 | 0.0 | 2.4 | 1.3 | 77 | 14 | 0.2 | 0.3 | 4.3 | n.a. | 100 |
| **KKN7B** | 0.0 | 0.0 | 0.2 | 1.0 | 74 | 8.8 | 0.1 | 0.2 | 18 | 0.6 | 102 |
| **KKN7C** | 0.0 | 0.0 | 2.1 | 0.1 | 91 | 5.6 | 0.0 | 0.1 | 0.0 | n.a. | 99 |
| **KKN7D** | 0.1 | 0.0 | 0.9 | 0.1 | 85 | 14 | 0.0 | 0.2 | 0.0 | n.a. | 100 |
| **KKN7E** | 0.0 | 0.0 | 0.6 | 0.5 | 43 | 8.4 | 0.0 | 0.1 | 37 | n.a. | 90 |
| **KKN7F** | 0.0 | 0.0 | 0.3 | 0.0 | 90 | 7.2 | 0.0 | 0.1 | 0.0 | n.a. | 97 |
| **KKN7G** | 0.0 | 0.0 | 0.0 | 0.0 | 93 | 5.3 | 0.0 | 0.0 | 0.0 | n.a. | 98 |
| **KKN7H** | 0.2 | 0.0 | 0.1 | 0.0 | 72 | 28 | 0.0 | 0.3 | 0.0 | n.a. | 101 |
| **KKN7I** | 0.0 | 0.0 | 0.0 | 0.0 | 94 | 4.3 | 0.0 | 0.0 | 0.0 | n.a. | 98 |
| **KKN7J** | 0.1 | 0.0 | 0.0 | 0.0 | 72 | 28 | 0.0 | 0.4 | 0.0 | n.a. | 100 |
| **KKN7K** | 0.0 | 0.0 | 3.0 | 0.0 | 87 | 7.9 | 0.0 | 0.0 | 0.3 | n.a. | 98 |
| **KKN7L** | 0.0 | 0.0 | 2.4 | 0.0 | 90 | 5.5 | 0.0 | 0.0 | 0.1 | n.a. | 98 |
| **KKN7M** | 0.0 | 0.0 | 0.2 | 0.4 | 92 | 6.7 | 0.1 | 0.1 | 0.1 | 0.0 | 100 |
| **KK3A** | 0.0 | 0.0 | 2.2 | 0.5 | 76 | 16 | 0.0 | 0.7 | 1.7 | 0.0 | 97 |
| **KK3B** | 0.0 | 0.1 | 2.4 | 0.2 | 28 | 0.6 | 0.0 | 0.0 | 73 | 0.0 | 104 |
| **KK3C** | 0.5 | 0.7 | 3.9 | 0.0 | 19 | 16 | 0.0 | 1.1 | 29 | 0.0 | 70 |
| **KK3D** | 0.0 | 2.1 | 7.3 | 0.0 | 13 | 19 | 1.8 | 0.3 | 21 | 0.0 | 65 |
| **KK3E** | 0.1 | 1.6 | 13 | 0.2 | 5.2 | 15 | 0.3 | 0.5 | 36 | 0.0 | 72 |
| **KK3F** | 0.0 | 1.8 | 6.9 | 0.1 | 15 | 21 | 1.0 | 0.4 | 20 | 0.0 | 67 |
| **KK3G** | 0.1 | 1.8 | 6.0 | 0.0 | 15 | 19 | 1.7 | 0.4 | 23 | 0.0 | 66 |
| **KK3H** | 0.0 | 1.7 | 15 | 0.0 | 5.8 | 14 | 0.0 | 0.3 | 33 | 0.0 | 69 |
| **KK3I** | 0.2 | 1.9 | 7.5 | 0.0 | 14 | 17 | 0.0 | 0.5 | 25 | 0.0 | 66 |
| **KK12A** | 0.0 | 0.0 | 2.8 | 1.4 | 94 | 1.8 | 0.0 | 0.0 | 0.0 | 0.1 | 100 |

|  | S | Cl | Fe | Ni | Cu | As | Sn | Sb | Pb | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **KK12B** | 21 | 0.1 | 7.3 | 0.0 | 68 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 96 |
| **KK12C** | 0.0 | 0.0 | 5.4 | 1.6 | 88 | 6.5 | 0.0 | 0.0 | 0.0 | 0.0 | 102 |
| **KK12D** | 0.0 | 0.0 | 2.1 | 1.3 | 90 | 6.6 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KK12E** | 0.4 | 0.0 | 6.7 | 0.5 | 71 | 21 | 0.0 | 0.1 | 0.2 | 0.1 | 100 |
| **KK12F** | 19 | 0.0 | 11 | 0.5 | 65 | 1.4 | 0.0 | 0.0 | 0.0 | 0.0 | 97 |
| **KK12G** | 0.0 | 0.0 | 3.6 | 1.6 | 91 | 4.7 | 0.0 | 0.0 | 0.0 | 0.0 | 101 |

***Table A5.8*** *Spot analyses on the EDS-SEM of individual phases in sample KKN3 (weight %). Results have been normalised to 100 %, measured totals are given in column labelled MT. See notes as for Table A4.4.*

| | | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | FeO | $Fe_3O_4$ | CuO | MT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN3a** | Delafossite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 50 | | | 50 | 101 |
| **KKN3b** | Delafossite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 51 | | | 49 | 99 |
| **KKN3c** | Delafossite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 51 | | | 49 | 103 |
| **KKN3d** | Magnetite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | | | 95 | 4.6 | 92 |
| **KKN3e** | Magnetite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | | | 90 | 10 | 95 |
| **KKN3f** | Glass | 5.3 | 1.3 | 40 | 0.0 | 1.2 | 0.0 | 0.0 | | 11 | | 40 | 82 |
| **KKN3g** | Glass | 4.1 | 0.9 | 39 | 0.0 | 1.3 | 0.0 | 0.0 | | 9.3 | | 46 | 65 |

***Table A5.9*** *EPMA spot analyses on sample KKN3 copper prills (weight %). High levels of iron probably result from simultaneous measurement of surrounding magnetite due to the small size of the prills.*

| | Fe | Ni | Cu | Pb | Bi | Total |
|---|---|---|---|---|---|---|
| **KKN3A** | 31 | 0.0 | 54 | 0.1 | 0.0 | 85 |
| **KKN3B** | 36 | 0.0 | 39 | 0.1 | 0.0 | 74 |
| **KKN3C** | 25 | 0.1 | 53 | 0.1 | 0.1 | 79 |

*Table A5.10 Summary of the optical microscopy observations for the metallurgical ceramics from Daskaleio-Kavos.*

| Sample | Description of Ceramic Layer | Description of Slag Layer |
|---|---|---|
| **KK4** | Inclusions of quartz and schist, very thin vitrification layer | Mainly magnetite in glass, some iron silicate crystals (melilite?), 1-2 magnetite aggregates, copper prills, thin elongated crystals close to the ceramic layer |
| **KK5** | Inclusions of quartz and schist | - |
| **KK6** | Inclusions of quartz and schist, calcite deposit at the edge of the sample, probably post-depositional | Very glassy, 1 quartz fragment, no prills observed, uncertain whether this is a proper slag layer |
| **KK13** | Inclusions of quartz and schist | Mainly magnetite in glassy matrix, many copper prills, thin elongated crystals in some parts, copper salts seen in pores and as stringers |
| **KKN11** | Only vitrified ceramic layer retained with intense round porosity, quartz inclusions | Very heterogeneous section, iron silicate crystals (melilite?), very rich in magnetite, glassy matrix, many copper prills |

*Table A5.11 Spot analyses on the EDS-SEM of individual phases in slag layer of metallurgical ceramic samples (weight %).*

| | Phase | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | NiO | CuO | ZnO | $As_2O_3$ | PbO | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KK4a** | Melilite? | b.d.l. | 1.5 | 9.7 | 25 | b.d.l. | 12 | 1.4 | b.d.l. | 45 | | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KK4b** | Melilite? | b.d.l. | 1.6 | 8.2 | 24 | 0.1 | 12 | 0.9 | b.d.l. | 47 | 0.3 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 94 |
| **KK4c** | Melilite? | b.d.l. | 1.7 | 9.2 | 25 | 0.2 | 12 | 1.5 | b.d.l. | 45 | 0.3 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KK4d** | Magnetite | b.d.l. | 0.6 | 0.7 | b.d.l. | b.d.l. | b.d.l. | 0.2 | b.d.l. | 98 | 0.6 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 100 |
| **KK4e** | Glass | 1.5 | b.d.l. | 7.6 | 32 | 3.0 | 6.1 | 0.2 | b.d.l. | 35 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 7.9 | 94 |
| **KK4f** | Glass | b.d.l. | 2.2 | 7.7 | 34 | b.d.l. | 19 | 0.5 | b.d.l. | 30 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 94 |
| **KK4g** | Glass | b.d.l. | 4.0 | 15.4 | 41 | 0.5 | 18 | 1.1 | b.d.l. | 8.4 | b.d.l. | 1.1 | b.d.l. | b.d.l. | b.d.l. | 90 |
| **KK13a** | Magnetite | b.d.l. | 2.7 | 4.3 | b.d.l. | b.d.l. | 0.1 | 0.3 | 1.9 | 75 | 4.1 | 2.6 | 2.2 | 1.4 | b.d.l. | 95 |
| **KK13b** | Magnetite | b.d.l. | 4.1 | 4.6 | 1.7 | b.d.l. | 0.4 | 0.4 | 1.9 | 71 | 2.6 | 4.1 | 2.2 | b.d.l. | b.d.l. | 93 |
| **KK13c** | Magnetite | b.d.l. | b.d.l. | 2.1 | b.d.l. | b.d.l. | 0.2 | b.d.l. | 1.4 | 82 | 4.3 | 0.6 | 2.6 | b.d.l. | b.d.l. | 94 |
| **KK13d** | Magnetite | b.d.l. | 1.6 | 0.6 | b.d.l. | b.d.l. | 0.2 | b.d.l. | 1.0 | 82 | 6.2 | 0.6 | 2.6 | b.d.l. | b.d.l. | 94 |
| **KK13e** | Glass | b.d.l. | 1.5 | 7.7 | 29 | 1.2 | 8.8 | b.d.l. | 1.1 | 5.5 | b.d.l. | 8.4 | 0.5 | 3.3 | 17 | 84 |
| **KK13f** | Glass | b.d.l. | 1.0 | 7.4 | 28 | 1.1 | 8.9 | b.d.l. | 0.9 | 6.2 | b.d.l. | 6.6 | b.d.l. | 4.5 | 16 | 80 |
| **KK13g** | Glass | 1.0 | 2.1 | 6.7 | 32 | 1.5 | 15 | b.d.l. | 1.4 | 10 | b.d.l. | 1.8 | 0.9 | 1.0 | 10 | 84 |
| **KKN11a** | Melilite? | b.d.l. | 8.0 | 6.1 | 40 | b.d.l. | 21 | 0.7 | b.d.l. | 12 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 88 |
| **KKN11b** | Melilite? | b.d.l. | 9.7 | 5.7 | 41 | b.d.l. | 21 | 0.8 | b.d.l. | 11 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 89 |
| **KKN11c** | Magnetite | b.d.l. | 1.6 | 2.0 | b.d.l. | b.d.l. | 0.4 | 0.4 | b.d.l. | 91 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 95 |
| **KKN11d** | Glass | 3.4 | 0.3 | 7.1 | 37 | 1.8 | 12 | 0.3 | b.d.l. | 8.6 | b.d.l. | 3.4 | b.d.l. | 1.9 | 9.5 | 85 |

***Table A5.12*** *EPMA spot analyses on copper prills and lead rich inclusions or prills (highlighted) in the slag attached to the metallurgical ceramics (weight %). Low totals on the lead prills may be due to the rapid oxidation of the metal surface, while totals above 100 % are due to the simultaneous measurement of two phases.*

| | **S** | **Cl** | **Fe** | **Ni** | **Cu** | **Ag** | **Sb** | **Pb** | **As** | **Bi** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN11A** | 0.0 | 0.0 | 2.8 | 0.0 | 90 | 0.5 | 0.0 | 0.0 | 4.9 | 0.1 | 98 |
| **KKN11B** | 0.0 | 0.0 | 2.3 | 0.0 | 95 | 0.0 | 0.0 | 0.0 | 0.8 | 0.0 | 98 |
| **KKN11C** | 0.0 | 0.0 | 1.4 | 0.0 | 96 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 98 |
| **KKN11D** | 0.0 | 0.0 | 0.5 | 0.0 | 94 | 0.0 | 0.1 | 0.1 | 4.4 | 0.1 | 99 |
| **KKN11E** | 0.0 | 0.0 | 3.0 | 0.0 | 92 | 0.0 | 0.0 | 0.0 | 4.9 | 0.0 | 100 |
| **KK4A** | 0.0 | 0.2 | 2.7 | 0.0 | 83 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 86 |
| **KK4B** | 0.0 | 0.1 | 6.7 | 0.1 | 0.8 | 0.0 | 0.0 | 69 | 0.0 | 0.0 | 76 |
| **KK4C** | 0.0 | 0.0 | 0.9 | 0.0 | 0.1 | 0.0 | 0.0 | 72 | 0.0 | 0.0 | 73 |
| **KK4D** | 0.0 | 0.0 | 3.2 | 4.0 | 87 | 0.0 | 0.0 | 3.8 | 0.0 | 0.0 | 98 |
| **KK4E** | 0.0 | 0.0 | 2.0 | 5.8 | 90 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 98 |
| **KK13A** | 0.0 | 0.0 | 1.2 | 0.1 | 91 | 0.1 | 0.1 | 0.0 | 8.7 | 0.0 | 101 |
| **KK13B** | 0.0 | 0.0 | 0.4 | 0.2 | 92 | 0.0 | 0.1 | 0.0 | 6.4 | 0.0 | 99 |
| **KK13C** | 0.1 | 0.0 | 0.5 | 0.1 | 77 | 0.0 | 0.6 | 0.0 | 16 | 0.0 | 94 |
| **KK13D** | 0.0 | 0.0 | 2.8 | 0.4 | 89 | 0.0 | 0.2 | 0.0 | 7.1 | 0.0 | 99 |
| **KK13E** | 0.0 | 0.0 | 0.3 | 1.1 | 73 | 0.0 | 0.4 | 16 | 17 | 0.3 | 108 |

*Table A5.13 EPMA spot analyses (weight %) on isolated metal prills or fragments and corresponding inclusions (highlighted).*

| | S | Fe | Ni | Cu | Zn | Ag | Sn | Sb | Pb | As | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KKN6A** | 0.0 | 0.0 | 0.4 | 100 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 101 |
| **KKN6B** | 0.0 | 0.0 | 0.0 | 1.3 | 0.0 | 0.0 | 0.0 | 0.0 | 97 | 0.0 | 0.2 | 98 |
| **KKN6C** | 0.0 | 0.0 | 0.5 | 99 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.1 | 100 |
| **KKN6D** | 0.0 | 0.0 | 0.5 | 99 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 | 100 |
| **KKN6E** | 0.0 | 0.0 | 0.4 | 99 | 0.0 | 0.1 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 100 |
| **KK14A** | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 90 | 0.0 | 7.9 | 99 |
| **KK14B** | 0.0 | 0.6 | 0.4 | 96 | 1.5 | 0.4 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 99 |
| **KK14C** | 0.0 | 0.5 | 0.5 | 96 | 0.9 | 0.5 | 0.0 | 0.2 | 0.0 | 0.3 | 0.0 | 98 |
| **KK14D** | 0.0 | 0.5 | 0.4 | 97 | 0.5 | 0.5 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 | 99 |
| **KK14E** | 0.0 | 0.6 | 0.5 | 95 | 1.4 | 0.4 | 0.0 | 0.2 | 0.1 | 0.4 | 0.0 | 99 |
| **KK17A** | 0.0 | 0.3 | 0.1 | 8.2 | 0.0 | 0.0 | 0.3 | 6.3 | 42 | 22 | 12 | 91 |
| **KK17B** | 0.0 | 0.0 | 0.3 | 8.2 | 0.0 | 0.0 | 0.2 | 4.9 | 33 | 21 | 20 | 88 |
| **KK17C** | 0.0 | 0.2 | 0.1 | 26 | 0.0 | 0.1 | 0.1 | 7.3 | 36 | 20 | 6.9 | 97 |
| **KK17D** | 0.0 | 0.0 | 0.1 | 98 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.3 | 0.0 | 99 |
| **KK17E** | 0.0 | 0.0 | 0.1 | 93 | 0.0 | 0.5 | 0.0 | 0.1 | 0.1 | 5.4 | 0.0 | 99 |
| **KK17F** | 0.0 | 0.0 | 0.1 | 99 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.3 | 0.1 | 99 |
| **KK17G** | 0.0 | 0.0 | 0.1 | 96 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 | 3.1 | 0.1 | 99 |
| **KK17H** | 0.0 | 0.0 | 0.0 | 8.8 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 95 | 104 |
| **KKN12A** | 0.0 | 0.0 | 0.2 | 99 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 99 |
| **KKN12B** | 0.0 | 0.0 | 0.1 | 99 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 100 |
| **KKN12C** | 0.0 | 0.0 | 0.2 | 99 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 99 |
| **KKN12D** | 7.3 | 0.1 | 0.0 | 82 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 90 |
| **KKN12E** | 19 | 0.0 | 0.0 | 81 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 100 |

***Table A5.14*** *Spot analyses on the EDS-SEM of individual phases in sample KK19 (weight %).*

| | **Phase** | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$K_2O$** | **CaO** | **$Fe_2O_3$** | **$Sb_2O_3$** | **PbO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **KK19a** | Litharge | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 93 | 93 |
| **KK19b** | Litharge | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 99 | 99 |
| **KK19c** | Cerussite | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 82 | 82 |
| **KK19d** | Crystals | 11 | b.d.l. | 29 | 44 | 9.3 | b.d.l. | 1.1 | b.d.l. | 1.2 | 95 |
| **KK19e** | Crystals | 10 | b.d.l. | 27 | 44 | 7.9 | 4.7 | 1.4 | b.d.l. | 1.6 | 97 |
| **KK19f** | Crystals | 1.3 | 3.0 | 9.3 | 2.5 | b.d.l. | 26 | 9.3 | 40 | 4.5 | 96 |
| **KK19g** | Crystals | 1.0 | 1.7 | 5.6 | 5.2 | b.d.l. | 27 | 16 | 32 | 9.0 | 97 |

***Table A5.15a*** *Results of (P)ED-XRF analyses of iron mineral samples (major and minor elements in weight %). Analyses in bold are averages of three runs (a, b, c).*

| | **$Na_2O$** | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **$SO_3$** | **$K_2O$** | **CaO** | **$Cr_2O_3$** | **MnO** | **$Fe_2O_3$** | **CuO** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KK16a | 0.17 | 0.39 | 0.99 | 7.49 | 0.07 | 0.04 | 0.65 | 0.01 | 0.03 | 80.1 | 1.30 | 91.2 |
| KK16b | 0.07 | 0.34 | 0.97 | 7.33 | 0.08 | 0.04 | 0.64 | 0.01 | 0.03 | 79.6 | 1.28 | 90.3 |
| KK16c | 0.23 | 0.30 | 0.97 | 7.43 | 0.08 | 0.04 | 0.65 | 0.01 | 0.03 | 79.9 | 1.27 | 90.9 |
| **KK16** | **0.16** | **0.35** | **0.97** | **7.42** | **0.08** | **0.04** | **0.65** | **0.01** | **0.03** | **79.8** | **1.28** | **90.8** |
| KK20a | 0.25 | 0.37 | 1.81 | 7.50 | 0.12 | 0.03 | 0.39 | 0.01 | 0.02 | 74.7 | 2.46 | 87.7 |
| KK20b | 0.14 | 0.35 | 1.80 | 7.58 | 0.13 | 0.03 | 0.39 | 0.01 | 0.02 | 74.6 | 2.45 | 87.5 |
| KK20c | 0.32 | 0.40 | 1.76 | 7.64 | 0.13 | 0.03 | 0.39 | 0.01 | 0.02 | 75.8 | 2.48 | 88.9 |
| **KK20** | **0.24** | **0.37** | **1.79** | **7.57** | **0.13** | **0.03** | **0.39** | **0.01** | **0.02** | **75.0** | **2.46** | **88.1** |

***Table A5.15b*** *Results of (P)ED-XRF analyses of iron mineral samples (trace elements in ppm). Analyses in bold are the averages of the three runs (a, b, c, ).*

| | **ZnO** | **$As_2O_3$** | **Se** | **Br** | **SrO** | **Y** | **$ZrO_2$** | **Mo** | **Sb** | **Ba** | **La** | **$WO_3$** | **U** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KK16a | 98 | 66 | 0 | 61 | 9 | 28 | 0 | 60 | 0 | 13 | 70 | 229 | 5 |
| KK16b | 87 | 63 | 0 | 55 | 7 | 20 | 0 | 62 | 2 | 8 | 68 | 238 | 4 |
| KK16c | 111 | 63 | 0 | 63 | 11 | 27 | 0 | 58 | 0 | 0 | 81 | 226 | 5 |
| **KK16** | **99** | **64** | **0** | **60** | **9** | **25** | **0** | **60** | **1** | **7** | **73** | **231** | **4** |
| KK20a | 85 | 79 | 60 | 11 | 0 | 85 | 17 | 472 | 11 | 0 | 281 | 64 | 6 |
| KK20b | 84 | 74 | 52 | 12 | 0 | 84 | 21 | 485 | 12 | 0 | 297 | 66 | 5 |
| KK20c | 66 | 69 | 43 | 13 | 0 | 80 | 0 | 479 | 12 | 0 | 311 | 68 | 0 |
| **KK20** | **78** | **74** | **52** | **12** | **0** | **83** | **13** | **479** | **12** | **0** | **296** | **66** | **4** |